ANALYTICAL CHEMISTRY

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Advisory Boards—Editor's Link with Readers

MEETING the needs of the reader is the prime responsibility of an editor. How the editor can tell when he is meeting these needs is no simple matter.

Increases or decreases in circulation give the editor some indications in this regard. Results of readership surveys and circulation promotion give him further clues. Acceptance of the publication by advertisers is another factor.

In the field of technical journals, the editor faces some unique situations. Compared to general circulation magazines, he is presenting a specialized type of information for a specific group of readers.

Even though journals cover specialized areas, such as those of the AMERICAN CHEMICAL SOCIETY, this field is still very comprehensive. The readers are engaged in a wide variety of activities in a large number of fields. Their interests and needs, therefore, are varied. The AMERICAN CHEMICAL SOCIETY, as a professional society, tries to gear its editorial operations to meet needs of the specialized and yet diverse group that make up the chemical profession.

One of the principal means used by the editorial staff of the ACS publications to keep a finger on the pulse of the readers is advisory boards.

Each of the journals has its own advisory board, members of which serve on a rotating basis. Each advisory board includes members who are representative of government, industry, academic institutions, and research institutions. They are engaged in research, development, production, management, teaching, and other activities in all parts of the country. In analytical chemistry, which involves both physical and chemical approaches, the board includes experts in these areas. These advisory boards meet regularly and study recent operations and discuss future plans, both immediate and long range.

In this period of growing specialization in every field of scientific endeavor, the problems of the editor become greater. With the help and advice of these boards, the editor can establish policies which reflect the reader's actual needs.

In the case of ANALYTICAL CHEMISTRY, the advisory board has long served a very valuable purpose. The most recent meeting, held in Washington late in October, was a good example. The entire headquarters editorial staff had an opportunity to meet with board members and exchange ideas.

Conversely, the board members had an opportunity to learn at first hand some of the problems encountered in getting out publications. The information they carry back to their professional associates, we know, benefits them and the editors.

The ANALYTICAL CHEMISTRY advisory board at present consists of 15 members, each of whom serves for three years. Under a rotation plan, five new members join the board each year, replacing five outgoing members (see page 19 A). This is a small enough group to work efficiently, and yet large enough to bring a representative viewpoint. The chairman and secretary of the Division of Analytical Chemistry are also invited to attend the advisory board meetings. This results in closer liaison between the editors and the division's activities and programs. The results, we believe, are of benefit to both the division and the publication.

Because the ANALYTICAL CHEMISTRY advisory board works quietly and without fanfare, the efforts and energy they expend in helping to make ANALYTICAL CHEMISTRY the best medium for analysts are often overlooked. We are happy to take this opportunity to thank them for their continuing efforts and interest.

Analysis of Industrial Wastes
Rapid Methods of Analysis
Analytical Problems in Biological Systems

Papers presented at the Ninth Annual Summer Symposium sponsored by the Division of Analytical Chemistry and *Analytical Chemistry*. Los Angeles, Calif., June 14 to 16, 1956

Coulometry

ERNEST H. SWIFT

Department of Chemistry, California Institute of Technology, Pasadena, Calif.

AS HAS been true of other fields, coulometry has collected a certain amount of nomenclature. Therefore, in consideration of those who may be resorting to the literature for the first time, an attempt to define certain of these terms will be made. With full cognizance that definitions are likely to be quite subjective in nature, it is proposed that coulometry include those electrolytic processes in which a determination of the quantity of a constituent is made by a measurement of the quantity of electricity—that is, the coulombs—required to react, directly or indirectly, with that constituent. Three terms in this definition should be emphasized: First, the process is electrolytic in nature. Secondly, a measurement must be made of the quantity of electricity involved. Thirdly, the constituent being determined can be involved directly or indirectly in an electrode reaction. As will be shown later, this third factor is of importance in the classification of coulometric processes.

Obviously, if an electrolytic process is to be used for the quantitative determination of a constituent, then one of the electrode reactions must be capable of yielding 100% current efficiency; and as many significant figures as are required can be used in writing the 100%. The work which was done in the latter part of the last century in connection with various types of coulometers, or voltammeters as they were then called, demonstrated that there were a considerable number of electrode reactions which could be made to proceed with 100% current efficiency. Although this work had as its primary objective the determination of the value of the faraday, the principles underlying coulometry were clearly established. For this reason, and in spite of the advances which have been made recently, we analytical chemists are entitled to a certain amount of humility arising from the fact that the analytical implications of this work were not exploited to a significant extent until after almost 40 years of this century had passed.

It is true that in 1917 Grower (*2*) estimated the thickness of a plating of tin on a copper wire by making the wire the anode in an electrolytic process and measuring the quantity of electricity required to dissolve the tin anodically. Here was a clear demonstration of the principles of coulometry. But, except for a few similar applications, over 20 years elapsed before this pioneering work was generally exploited. Then in 1942 Hickling (*3*) devised an electronic instrument which he called a potentiostat, whereby the potential applied to the working electrode could be controlled. By use of this device he demonstrated that 100% current efficiency could be obtained in the reduction of cupric copper to the metal at a platinum cathode and in the oxidation of iodide to iodine at a platinum anode. In 1945 Lingane made use of a mercury cathode for the determination of copper (*4*). He also used a silver anode at which the various halides were precipitated as the corresponding silver salts (*5*).

There are certain characteristic features of these procedures which are used as a means of classifying coulometric processes. First, in all cases the substance to be determined is involved in the half-cell reaction taking place at one of the electrodes—that is, the cupric copper is reduced at the cathode and the halide is either oxidized or precipitated at the anode. As a result such procedures have become known as primary or direct coulometric methods. In order to obtain 100% current efficiency in such primary processes, the potential applied to the working electrode must be controlled and, accordingly, such procedures are also designated as controlled potential processes. Choice as to which of the above terms is used is dictated by whether the predominant interest is in the external circuitry or in the reactions taking place within the electrolytic cell. The limits within which the potential control must be maintained will depend, first, upon the accuracy of the determination being made, and, secondly, upon the presence of other electrode reactive substances in the solution.

A chronological deviation of a few years has been made in order to present the above examples of primary processes, because in 1938 a series of seven articles, titled "Coulometric Analysis as a Precision Method," was published by Szebelledy and Somogyi (*7*), two Hungarian chemists. This title appears to have been the first use of the term coulometric analysis and, in the opinion of this author, these papers initiated the extensive developments in coulometry which have taken place in the past 10 years.

Rather than describe this work in general terms, a specific example can be used to illustrate the principles involved. These workers were interested in the determination of thiocyanate. They either knew or learned that the anodic oxidation of thiocyanate to cyanide and sulfate with 100% current efficiency is difficult, if not impossible, of attainment. However, it was known that thiocyanate could be quantitatively, stoichiometrically, and rapidly oxidized by bromine in acid solutions, and they knew or learned that bromide could be anodically oxidized to bromine in acid solutions with 100% current efficiency. Therefore, they added a relatively high concentration of a soluble bromide to an acid solution containing the thiocyanate, anodically produced bromine, and allowed this bromine to diffuse into the solution and to oxidize the thiocyanate. By working with relatively large samples of thiocyanate and by measuring the quantity of electricity involved by means of a chemical coulometer, they demonstrated that an accuracy of

within 1 p.p.t. could be attained. Szebelledy and Somogyi used chemical indicators for determining the end point of such titrations. Such a process as this has subsequently been termed a coulometric titration.

Two fundamental differences exist between such a process and those which have been described previously. First, in the previous ones, the substance being determined was directly involved in the electrode reaction; in this latter process an intermediate half-cell reaction is used to generate an active intermediate compound which then reacts with the substance being determined. For this reason such processes are called secondary or indirect coulometric methods. Secondly, for reasons which are discussed later, such processes can be caused to take place at a constant current value and in such cases are called constant current methods.

Each of these two types of processes has certain advantages and limitations. The primary process, when used with controlled potential, enables one to attain considerable specificity as to the half-cell reaction taking place. The reduction of one metal in the presence of another and the selective determination of various mixtures of the halides has been demonstrated by Lingane (*4*, *5*). The extent to which this fundamental property of the controlled potential method can be exploited to minimize preliminary separations will determine the ultimate analytical value of such methods. Also the commercial availability of reasonably priced potentiostats will be a factor in the development of such methods.

[1]In a controlled potential process the current decreases exponentially and approaches zero asymptotically. For this reason the time required for the process is fixed by the accuracy desired—essentially the ratio of the initial to the final concentration of the constituent being determined—and such a process is not adaptable to rapid determinations. In addition, since the current is varying continuously, an accurate measurement of the quantity of electricity involved has required the use of chemical coulometers. It is to be hoped that accurate electronic coulometers will be available in the future, because chemical coulometers do not lend themselves to ready use for operations on a micro scale.

The most fundamental limitation to the development of primary coulometric methods arises from the fact that an astonishing number of substances are not capable of being oxidized or reduced at conventional electrodes with 100% current efficiency. Systematic examination of a comprehensive list of half-cell reactions shows a surprising number that exhibit some degree of irreversibility. When the relative advantages of the secondary process are considered, it is apparent that, by taking advantage of those intermediate half-cell reactions which can be made to proceed with 100% current efficiency, the coulometric principle can be applied to many substances which are not reversibly oxidized or reduced at conventional electrodes. As a result much of the research work in the past 10 years has been directed toward studies of such intermediates. Among the oxidants which have been investigated are bromine, iodine, chlorine, hypobromite, ceric cerium, ferric iron, argentic silver, and manganic manganese. A partial list of the reductants includes cuprous copper in chloride and bromide solutions, ferrous iron, and titanous titanium. The possibility of coulometrically plating an excess of a metal, allowing the metal to react with an oxidant, and then stripping the excess by a reversal of polarity has been studied and has promise. Precipitants have included ferrocyanide and unipositive silver and mercury. Both acids and bases have been coulometrically generated.

The secondary process also allows a constant current to be maintained throughout the process, thus permitting the attainment of several desirable features. The first of these is rapidity; titrations of 100 seconds or less are conventional. Secondly, by control of the constancy of the current to within the desired accuracy of the titration, one can substitute for the chemical coulometer the constant current-time method of measuring the quantity of electricity involved in the titration. Finally, by reducing the current value, the times required for the titration of micro quantities of constituents can be extended to accurately measured intervals. As a result the titration of microgram quantities is readily made with accuracies as good as or better than those attained by the best volumetric methods with *milligram* quantities. Application of the secondary method of coulometric analysis to the field of quantitative microanalysis presents a fruitful field for further research and development.

Finally, because an electric current is so much more amenable to automatic control than is a stopcock or other mechanical device, coulometry offers obvious advantages in the ever developing field of automation. Methods and instruments for automatic control of titrations have already been developed, as have methods for obtaining a continuous record of the concentration of a constituent in solutions or in a gas phase.

Because of the interest of this conference in atmospheric constituents, it seems appropriate to describe briefly two examples of coulometric methods for obtaining a continuous analysis for two gaseous constituents.

The first of these instruments was developed initially to obtain a continuous record of the mustard gas concentration in the air (*6*). It has since been produced as a commercial instrument—the Titralog of Consolidated Electrodynamics Corp.—for obtaining a continuous record of reducing gases such as hydrogen sulfide or sulfur dioxide in the air. In the original instrument the air was drawn through a sulfuric acid solution containing a soluble bromide. A platinum sensing electrode coupled with a standard half-cell was used in conjunction with an amplifier to control a generating circuit. Bromine was produced at a platinum anode and hydrogen at a platinum cathode. With no mustard gas or other reducing constituent present in the incoming air, the sensing electrode controlled the generating current at a value which maintained a very low concentration of bromine in the electrolytic solution. When mustard gas was present in the air, it caused a decrease in the bromine concentration. The resultant change in potential of the sensing electrode caused the generating current to increase until the initial bromine concentration was restored. The generating current was sent through a recorder and a continuous record thus obtained.

The second instrument has been developed by Regener for obtaining a continuous record of the atmospheric ozone concentration. Only a preliminary model has been described (*1*). In his present instrument air is drawn at a known rate through a chamber in which a neutral solution of potassium iodide containing a known concentration of thiosulfate is also passing at a predetermined rate. The sensing system in the case consists of two similar platinum electrodes with a potential difference impressed across them. These electrodes control the current through the generating circuit, which produces iodine at the anode. With no ozone or other agents capable of oxidizing iodide in a neutral solution, in the influent air the sensing electrodes maintain the generating current at a value which will produce iodine just sufficient to oxidize the thiosulfate and produce a minimal iodine concentration in the solution passing from the reaction chamber. If ozone is present, it produces iodine and less current is required to maintain the minimal iodine concentration. In order to provide for the effect of other oxidants such as nitrogen dioxide, which could be present, Regener's latest instrument makes provision for dividing the influent air stream equally and passing the separate streams through identical absorbing and titrating systems. The air in one stream is heated to a temperature which will decompose ozone. Therefore, one titrating system measures ozone plus other oxidants, while the second system measures only the other oxidants. The difference between the values of the two generating currents is recorded as a measure of the ozone concentration.

Although the description of these two methods is brief, it

illustrates the flexibility with which the coulometric principle can be applied to such problems, and indicates the tremendous possibilities for future developments in this relatively new field of chemical analysis.

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Ninth Annual Summer Symposium—Analysis of Industrial Wastes

Spectrometric Investigations of Atmospheric Pollution

R. A. FRIEDEL

Central Experiment Station, Bureau of Mines, U. S. Department of the Interior, Bruceton, Pa.

Applications of spectrometry to studies of organic atmospheric pollutants are reviewed briefly. Recent work of this laboratory includes a mass spectral method for determining nitrogen dioxide and other components in complex mixtures, an infrared method for measuring specific hydrocarbons in coal-mine gases, and pyrolytic oxidation of aliphatic oxygenated compounds. Early results of a combination of methods had shown the presence of nitro- and possibly other nitrogen-oxygen groups in a Los Angeles air sample. More combinations of spectral methods and of spectral plus separations methods could be utilized in atmospheric pollution work. Suggestions for new approaches to studying atmospheric pollution include solvent extraction of organic constituents in the ice from freeze-out samples to reduce decomposition and other reactions, high-resolution infrared and mass spectrometry, and possibly magnetic resonance methods.

SPECTRAL investigations of atmospheric pollutants are being carried on at an increasing rate. The earliest such applications of mass spectra, described by Washburn (*34*), were followed by others (*7, 8, 16, 29, 35*). The principal information gained from investigation of metropolitan atmospheres has been the carbon number distribution of hydrocarbons in the air and an estimate of the total number of organic compounds present. The method does not permit discrimination between oxygenated compounds and hydrocarbons of the same molecular weight, nor between naphthenes and olefins. Mass spectrometry has also been used repeatedly to study automotive exhausts (*5, 7, 8, 18, 33*). Recently the mass spectrometer has been used for measurements of C^{12}/C^{13} ratios in atmospheric carbon dioxide (*9, 19*). These investigations hold promise for establishing the principal sources of carbonaceous materials in air.

Until recent years infrared analysis has been applied very little to air pollution studies (*10, 24, 26*). Hanst, Stephens, and coworkers are utilizing very long cells in infrared studies of synthetic smogs (*15*). Gates has investigated Los Angeles smog with the infrared portion of the solar spectrum (*12*). Twiss and coworkers have used infrared for investigating automobile exhausts (*32*).

Ultraviolet spectrometry has been used extensively for analysis of industrial plant atmospheres (*31*). The absorption sensitivity of most compounds in the ultraviolet region is not sufficient for widespread use in air pollution analysis. With a spectroradiometer, Stair has obtained maximum values for atmospheric ozone and nitrogen oxides (*30*). The absorption spectrum of ozone in the ultraviolet region has been used recently for the quantitative determination of ozone in the atmosphere (*22, 27*).

PROBLEMS RELATED TO AIR POLLUTION

Oxides of Nitrogen. A mass spectral method was developed for determining oxides of nitrogen (*11*) and other components in complex mixtures. The principal difficulty in determining oxides of nitrogen was the reactivity of nitrogen dioxide in the mass spectrometer. Prior conditioning of the instrument with nitrogen dioxide made analysis possible. Analyses of various mixtures are given in Table I. These blends were synthesized directly in the mass spectrometer at micron pressures, in order essentially to eliminate reaction among the components.

Sampling of gas from high-temperature exhaust systems containing water, oxides of nitrogen, and oxygen is difficult because of condensation of water, solution of nitrogen dioxide in water, reaction between nitric oxide and oxygen, formation of nitrogen trioxide, and other problems. These difficulties may be circumvented by collecting samples at micron rather than atmospheric pressure (*11*).

Although the sensitivity for nitrogen dioxide was no better than 0.5%, those for nitrogen dioxide and nitric oxide were of the order of 0.01%. Nitrogen dioxide is unstable in the mass spectrometer at pressures corresponding to 0.01%, but the nitric oxide from its decomposition is conveniently determinable. Although separate determinations of low percentages of nitric oxide and for nitrogen dioxide may not be accurate, their sum from the mass 30 peak is a reliable indication of total nitric oxide plus nitrogen dioxide.

Methane in Coal-Mine Air. Determination of methane in coal-mine air by infrared and mass spectrometry has been found feasible. The principal purpose of this analysis was provision of a specific test for traces of hydrocarbons found in coal-mine atmospheres, where the most plentiful hydrocarbon is methane. The customary Haldane gas analysis, although sufficiently accurate, is not specific enough. Mass spectrometry was applied with some success for determining less than 0.6 mole % methane, as shown in Table II by comparison with Haldane analyses. The mass spectral method requires only very small samples. The spectrum of methane is characteristic, but the chief atmospheric components (large percentages of nitrogen and oxygen, and small amounts of carbon dioxide and water) interfere with all the mass peaks of methane. These interferences can be corrected, as shown by the results in Table II; however, the presence of traces of methane in mine atmospheres is difficult to prove by mass spectra.

Table I. Mass Spectrometer Analyses of Synthetic Blends Containing Nitric Oxide and Nitrogen Dioxide

(Ionizing current, 10 μa. Synthetic blends prepared directly in mass spectrometer. Micron pressure measurements by micromanometer)

Blend		Mole %									
		He	NO_2	NO	N_2O	CO_2	CO	N_2	O_2	H_2O	H_2
1.	Anal.	..	5.3	3.9	..	13.1	13.1	16.2	4.3	44.1	..
	Syn.	..	5.1	4.0	..	13.2	13.3	16.3	4.3	43.8	..
2.	Anal.	..	9.4	10.1	12.1	12.4	12.0	25.2	6.7	..	12.1
	Syn.	..	10.2	9.6	12.0	12.0	12.1	25.4	6.8	..	11.9
3.	Anal.	..	11.0	11.1	14.1	13.5	14.1	28.6	7.6	..	..
	Syn.	..	11.6	11.2	13.6	13.6	13.7	28.7	7.6	..	..
4.	Anal.	97.4	0.65	0.44	..	0.54	0.56	0.41	..	..	..
	Syn.	97.1	0.75	0.54	..	0.54	0.54	0.54	..	..	..

The infrared method is preferred for the problem. Though the sample requirement is large, the method is very specific because of a group of fine-structure absorption bands in the region of 7.65 microns. A system of quantitative analysis has been based on the strongest of this group of bands. A 1-meter cell was used with the Perkin-Elmer Model 21 spectrometer.

The linear relationship between absorbance and concentration, on which infrared analysis of complex mixtures is based, does not apply to the 7.65-micron band of methane. Because of pressure broadening due to neighboring molecules, the absorbance of methane changes with the total pressure of the gas mixture. Several years ago McGovern found that the resulting analytical difficulties can be circumvented by merely using a high, constant total pressure for calibrating and determining methane in mixtures (*23*). Coggeshall (*6*), Lee (*20*), and Brady (*4*) have described the method for methane and other gases which show pressure broadening. The application of this method to mine gases is illustrated by the nonlinear calibration curve in Figure 1. Because most available samples are at pressures lower than 1 atm., air is added to attain a specific constant pressure, usually near 760 mm. of mercury; absorbances for the same partial pressures of methane are then equal. Infrared and mass spectrometric determinations of methane are compared in Table III. Infrared can also be used to detect other hydrocarbons, though sensitivities are generally lower. Values for total hydrocarbons can be obtained from absorption in the 3.5-micron CH absorption region (*17*).

Pyrolytic Oxidation of Aliphatic Oxygenated Compounds. Pyrolytic oxidation and decomposition of organic materials frequently cause disagreeable odors, particularly in enclosed places. Spectrometric investigations have been made on the products from reaction in a glass system of aliphatic oxygenated compounds, principally nonvolatile esters, under varying conditions of oxygen pressure, temperature, and reaction time. The extent of reaction increased directly with each of these variables. The volatile products from this degradation have mass spectra that are mixtures of peaks from hydrocarbons and oxygenated compounds. Only a few of the materials of higher molecular weight have been identified. Despite difficulties in identifying individual compounds, the mass spectrometric method has been useful in this problem. The extent of breakdown was measured by quantitative determination of the identifiable gases, such as carbon monoxide, carbon dioxide, and hydrogen, and water; and by determination of the unknown breakdown products as indicated by summation of mass spectral peaks. The latter technique was developed especially for air pollution. Characteristic curves for a typical set of experiments (Figure 2) indicate increased amounts of volatile products with higher temperature and longer reaction time. The analysis is essentially a micromethod; volatile products from the oxidation of 10 γ were quantitatively measurable.

The nonvolatile residues from these experiments have been investigated by infrared and ultraviolet spectrometry. Aqueous extracts of the residues afforded a means of concentrating the degradation products; the odoriferous constituents from the oxidation were found to be almost completely water-soluble. Ultraviolet analyses invariably showed a spectrum with a broad peak in the region of 2650 A. A rough measurement of the specific extinction coefficient, K, at 2650 A. gave a value of about 1.5, signifying either weak chromophoric groups or a very low concentration of strongly chromophoric groups. The ultraviolet spectrum of the basic solution of the residue shifted to considerably longer wave lengths and showed an appreciable increase in intensity. The spectral behavior of the aqueous residue was similar to that of phenol and basic solutions of phenol. However, the low K value and the wave length indicate that the chromophoric substance was not phenolic. Absorption was probably due to aliphatic substances containing acidic OH groups.

That the basic structure of the molecule had been oxidized appreciably was shown by the production of ketone, carboxyl, and hydroxyl groups; but no indication was found of drastic changes in skeletal structures.

Table II. Comparison of Haldane and Mass Spectrometric Determination of Methane in Synthetic Coal-Mine Gases

Sample	Methane, Mole %		Difference
	Haldane	Mass spectrometer	
1	0.52	0.47	−0.05
2	0.23	0.21	−0.02
3	0.44	0.44	0
4	0.27	0.25	−0.02
5	0.60	0.56	−0.04
6	0.14	0.12	−0.02

Table III. Mass Spectrometric and Infrared Determination of Methane in Synthetic Coal-Mine Gases

Methane, Mole %		
Mass spectrometer	Infrared	Difference
0.30	0.29	−0.01
0.36	0.34	−0.02

SUGGESTED APPLICATIONS IN ATMOSPHERIC POLLUTION

Combined Spectral Methods. The application of spectrometry to atmospheric pollution can be expanded in various directions. A combination of data from two spectrometric methods can often produce more information on a given problem than both methods used independently. In combination with chemical methods, spectrometric methods are always useful as scanning or screening techniques. Spectra serve both to detect the presence of certain functional groups and to prove the absence of others. Chemical reactions or separations can then be planned on the basis of the spectrometric examination.

A combination of infrared and mass spectral examinations of freeze-out samples may permit differentiation of saturated hydrocarbons and carbonyl compounds, and of olefins and naphthenes. The latter differentiation would be especially valuable for determining olefins in the hydrocarbons collected from polluted air. Direct evidence relating to Haagen-Smit's theory—reaction in the atmosphere of olefins with ozone and oxides of nitrogen (*14*)—would be the detection of an unexpectedly low ratio of olefins to other hydrocarbons in the atmosphere, and the presence of the expected oxygen and nitrogen compounds. The infrared data on carbonyls and olefins could then be combined with the mass spectral data to calculate concentrations of saturated hydrocarbons, naphthenes, and aromatics.

Investigation of freeze-out samples would not be easy by infrared, because samples must be larger than those required for mass spectra. This requirement might be met by utilizing large freeze-out traps and possibly by microspectroscopy for examining small samples from fractionations. Such samples from isothermal distillation might be frozen onto a minute surface (of the size required for microspectroscopy) for analysis in the frozen state, or, if sufficiently nonvolatile, in the liquid state after warming to room temperature.

Table IV is a summary of important points which are considered in this laboratory in choosing a spectral method or methods for a particular problem.

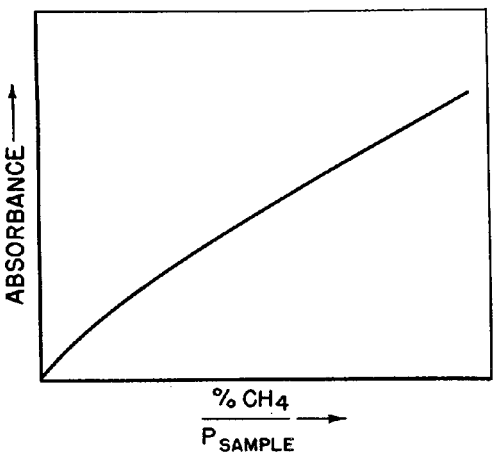


Figure 1. Calibration curve for infrared determination of methane in coal-mine gas

Nonlinearity due to pressure broadening. Air added to attain constant total pressure

Spectrometric methods should be applied more extensively as adjuncts to chemical analysis or chromatographic fractionation. Early infrared and ultraviolet investigations of neutral and acidic fractions of ether-soluble material, filtered out of Pasadena air in 1950, showed the presence of several functional groups. The neutral portion of this material contained long-chain hydrocarbons and ketones. The acidic portion was divided into carbon disulfide-soluble and carbon disulfide-insoluble portions. The carbon disulfide-soluble portions, according to infrared spectra, contained carboxyl and nitro groups. Other absorption bands indicated the possible presence of nitrate groups as well. The carbon disulfide-insoluble portion showed smaller amounts of carboxylic acids and larger amounts of nitro groups. Mass spectra of pyrolysis products of these extracts contained large peaks due to nitric oxide, confirming the presence of nitrogen-containing groups. Nitrosates of butadiene and of 1-hexene, prepared from olefins and nitrogen dioxide by Haagen-Smit, were examined by infrared. The nitrosate of 1-hexene contained a large number of nitrate groups [the experiments of Hanst with synthetic atmospheres have shown nitrate formation in mixtures containing 1-pentene and nitrogen dioxide (*15*)]. The nitrosate of butadiene, however, did not indicate the presence of nitrate groups, but nitro groups were found in high concentration.

Ultraviolet spectra were also employed in this problem. The lack of any intense absorption showed that the nitrogen dioxide groups found by infrared were not conjugated to any unsaturated system.

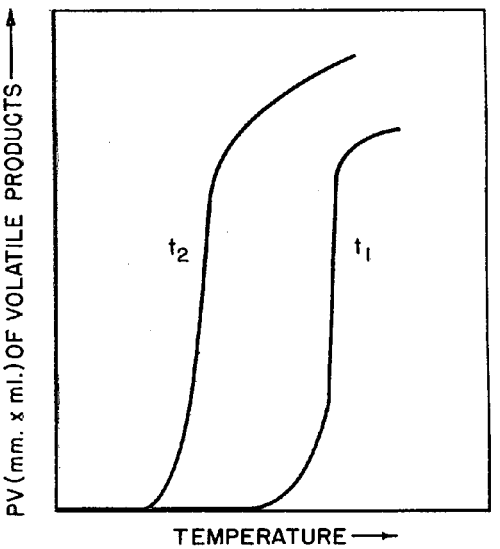


Figure 2. Effect of temperature and reaction time ($t_2 > t_1$) on pyrolytic oxidation of aliphatic oxygenated compound

In 1951 the Air Pollution Control laboratory carried out experiments on ether extracts of filtrates from Los Angeles air. The above findings of nitrogen-containing groups were not substantiated (*1*).

Low-Temperature Investigation. The aqueous portions, collected in freeze-out traps for mass-spectrometer analysis, have not been investigated extensively. Although it may be difficult to handle these very dilute samples, the aqueous portion should be investigated because it may contain such pollutants as hydroperoxides, nitrogen compounds, and perhaps unstable compounds or their reaction products. Components unstable at room temperature may decompose or react with water after freeze-out traps are warmed to room temperature.

A method for working with this material, suggested by Martin, consists of extracting frozen samples (below ice temperatures) with organic solvents (*25*). This approach should be successful if the organic materials are not bound within the ice crystals. After extraction, spectrometric and chemical investigations should also be carried out at low temperatures to reduce the chances of decomposition or reaction with water.

Table IV. Applicability of Spectral Methods

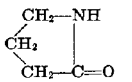
Instruments Available in Section	Substance	Solvents	Analytical Applications: General	Analytical Applications: Geometrical isomers
Mass spectrometers (Consolidated 21-103B and 21-103C)	Any element or compound (1) of sufficient vapor pressure, (2) stable at 10^{-6} mm.	Not usually needed. Sometimes needed for solids	Homologous series. Structural isomers. Type analyses. Aqueous solutions. Gases	Almost indistinguishable
Infrared spectrometers (Perkin-Elmer 21 and 112)	Any compound.[a] No monatomic elements	Often needed. All solvents have spectra which may interfere	Structural and geometrical isomers. Solids. Unstable substances. Functional groups	Readily distinguishable
Ultraviolet spectrophotometers (Cary 11 and Beckman DU)	Organic compounds containing C=O, C=C—C=C, phenyl ring, etc. Some inorganic compounds	Almost always needed. Some solvents may interfere	Aromatic compounds, particularly polynuclears	Sometimes distinguishable

[a] Homopolar diatomic molecules (H_2, N_2, O_2, Cl_2) have virtually no infrared absorption.

High-Resolution Infrared and Mass Spectrometry. Modifications of some spectrometric techniques may also be useful in atmospheric investigations. High-resolution infrared spectrometry, suggested by Gates (*12*), could be applied to analyses of CH groups. Up to now air pollution investigations have been limited to measurement of aliphatic CH's at 3.5 microns (*24, 32*). Increased resolving power makes possible determination of aromatic and unsaturated CH groups and of branched-chain groups (*17, 23*). Also, by means of high resolution, the difference between naphthenic CH and aliphatic CH in the 7-micron region might be utilized to differentiate between these two classes of hydrocarbons. The highest resolution in infrared is attained by means of gratings.

High-resolution mass spectrometry appears promising for investigating organic molecular structures. By this method, groups of nearly equal molecular weight can be differentiated. On an ordinary mass spectrometer, species of equal molecular weight are difficult to distinguish—for example, carbon monoxide, nitrogen, and ethylene, all have nominal molecular weights of 28. But with a mass spectrometer of high resolution, one can distinguish among these because of fractional differences in their molecular weights. This method has been described by Beynon, and one of his applications is shown in Table V (*3*). From the accurate determination of the mass of the molecule ion it is apparent that the method can be a powerful tool for ultimate analysis. The unknown, α-pyrrolidone, could have been identified by comparison of its complete spectrum with that of the pure compound. But Table V illustrates that the analysis was done by mass measurements alone, with only part of the spectrum. Thus the analytical applications of mass spectrometry can be greatly expanded. With such an instrument in air pollution work, hydrocarbons, oxygen- and nitrogen-containing compounds of the same mass can be differentiated on one instrument.

Table V. Application of High Resolution Mass Spectrometry to Structure Determination (*3*)

	Observed Partial Mass Spectrum	Possible Structures	Calculated Mass
Mass of unknown molecule ion	85.0794	$C_5H_{11}N^+$	85.1159
		$C_4H_7NO^+$	85.0794
		$C_3H_3NO_2^+$	85.0430
		$C_5H_7N_2^+$	85.0907
		$C_4H_5N_2O^+$	85.0543
		Fragment Structures	
Mass of fragment ions	56.0323	$C_2H_2NO^+$	56.0310
	56.0446	$C_3H_4O^+$	56.0436
	56.0670	$C_4H_8N^+$	56.0674
	42.0102	CNO^+	42.0109
	42.0287	$C_2H_2O^+$	42.0235
	42.0538	$C_3H_4N^+$	42.0473
	42.0592	$C_3H_6^+$	42.0599
Unknown is α-pyrrolidone.			

Magnetic Resonance Methods. The newer magnetic methods, nuclear magnetic resonance and electron paramagnetic resonance, appear to have possible applications in pollution investigations. Sample sizes required for both methods are low for ordinary purposes but still rather high for applications in air pollution. Electron paramagnetic resonance can be used to detect free radicals and other paramagnetic substances. Measurements of free radicals in the air would shed light on the questions involved in photochemical reactions in the atmosphere. Some preliminary paramagnetic resonance measurements have been carried out (*2, 36*). Measurements at low temperatures may be informative.

The other method, nuclear magnetic resonance, can yield information on the types of protons present in atmospheric pollutants. Gutowsky and others have demonstrated the applicability of the technique to such problems (*13*). The method is very sensitive to slight changes in the electronic shielding of the proton which depends on neighboring atoms. Thus functional groups in air-pollution samples might be determined, although samples may have to be obtained by extraction at low temperature to preserve unstable components. Such extraction can also be used to eliminate water which interferes with the application of this technique to protons. Nuclear magnetic resonance measurements for the differentiation of types of protons must nearly always be performed on liquids or gases.

Continuous Analysis of Total Organic Pollutants. Littman and Denton (*21*) have recently described a nondispersive infrared instrument which is capable of accurate determination of total organic components down to 0.1 p.p.m. Although the sensitivity differs over a considerable range for different compounds, the application of this instrument to the measurement of air pollution should be successful.

It should be possible to utilize the principles of mass spectrometry for the construction of a comparatively simple instrument for the measurement of total organic components in air. One possible apparatus would consist of a low resolution mass instru-

ment with provision for blocking all ions below 44. Thus all of the principal components of the atmosphere—nitrogen, oxygen, carbon dioxide, water, and argon—would not be recorded. Carbon monoxide, hydrogen sulfide, and nitric oxide would also be eliminated. All of the ions above mass 44 could be collected together and correlated with the total ionization above mass 44 from organic compounds. A disadvantage of this instrument would be the loss of the intense organic peak at mass 43. Another possible mass apparatus could utilize differences in ionization potential between organic compounds and the major components of air. Operation at an ionizing voltage below 12.2 volts would ionize all organic compounds except methane and would not ionize nitrogen, oxygen, carbon dioxide, water, argon, carbon monoxide, or sulfur dioxide. A disadvantage of such an instrument would be its low sensitivity.

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Automatic Apparatus for Determination of Nitric Oxide and Nitrogen Dioxide in the Atmosphere

M. D. THOMAS, J. A. MacLEOD, R. C. ROBBINS, R. C. GOETTELMAN, and R. W. ELDRIDGE
Stanford Research Institute, Menlo Park, Calif.
L. H. ROGERS
Air Pollution Foundation, Los Angeles, Calif.

Nitric oxide and nitrogen dioxide in the atmosphere can be determined continuously with automatic sampling and recording apparatus. Two special absorbers are employed for absorption of nitrogen dioxide in a modified Griess reagent followed by colorimetric recording. One absorber measures the nitrogen dioxide alone; the other measures nitrogen dioxide plus nitric oxide after the latter has been oxidized by ozone, permanganate, or chlorine dioxide. Concentration limits of the instrument range up to about 1 p.p.m., but they can be considerably extended or reduced. Standard error is about ±5%.

THE oxides of nitrogen, in the concentration range of parts per 10,000,000, play an important role in the photochemical reactions which are primarily responsible for Los Angeles smog (*5*). Nitrogen dioxide appears to be the principal acceptor of the radiant energy, and nitric oxide is involved in the chain reactions that follow. Nitrogen pentoxide or the equivalent nitric acid, both free and combined with organic radicals, is one of the products of the reactions. Aerosol samples collected in Los Angeles (*3*) contain about 10 times as much nitrate as similar samples collected in other cities. There is no evidence that nitrous oxide enters into either these reactions or the analytical procedures described later, even though it is probably present in appreciable amount.

Nitrogen dioxide is the logical member of this group to select for initial study. Its absorption in various reagents, though difficult, is practicable, and the highly specific and sensitive diazo reaction with one of the modified Griess reagents (*1*, *4*,

7, 9, 11) is available for its estimation. Jacobs (*7*) has reviewed the literature on this useful reagent. Nitric oxide is not significantly absorbed when aspirated through a solution that takes up nitrogen dioxide, but apparently passes through the system unchanged. Nitrogen pentoxide and nitric acid in comparable concentrations are also without effect on the Griess reagent, but excessive amounts change the red azo compound to a yellow color.

Nitric oxide is rapidly oxidized to nitrogen dioxide by ozone. The half-life of this reaction at 1 p.p.m. (*2*) is 1.8 seconds and at 0.1 p.p.m., 18 seconds. Further oxidation of nitrogen dioxide by ozone to the pentavalent state is much slower. The half-lives of the reactions at 1.0 and 0.1 p.p.m. are listed as 13 and 130 minutes, respectively. Evidently, ozone can be used as an oxidizing agent for nitric oxide if the concentration is controlled within comparatively narrow limits.

Other oxidizing agents for nitric oxide are being studied. Chlorine dioxide and acid permanganate solution are promising and are discussed below. Nitrogen pentoxide gave only 10 to 20% oxidation of nitric oxide in preliminary tests and further work does not seem justified. The pentoxide is largely converted into nitric acid by the moisture in the air sample.

Methods of analysis for the oxides of nitrogen are generally laborious. The sample is usually taken into an evacuated bottle where the oxides are absorbed in a basic solution or the Griess reagent. With agitation, nitrogen dioxide and nitrates can be absorbed in 15 minutes to 1 hour, and nitric oxide is absorbed about as quickly if peroxide is present. Oxidation of nitric oxide in the part per million range by oxygen is very slow. Results by the bottle method appear to be reliable if sufficient time is allowed for the absorption of nitric oxide. The lower oxides are determined colorimetrically by diazotization, total nitrogen and nitrate by phenoldisulfonic acid. Saltzman (*9*) developed an aspirating procedure for nitrogen dioxide which avoids much of the labor of the bottle method.

Shaw (*10*) determined nitric oxide in coke oven gas by adding air, allowing a residence time of 3 minutes, then absorbing the nitrogen dioxide in a solution containing 0.5% *m*-phenylenediamine and 2.5% acetic acid. The color is compared with that produced by known amounts of sodium nitrite. Use of a factor of 2 gives results comparable to those obtained for known nitric oxide–gas mixtures. Hollings (*6*) determines nitric oxide in coal gas by oxidizing with a solution containing 2.5% each of potassium permanganate and sulfuric acid, followed by absorption and colorimetric analysis in Griess reagent. A commercial instrument based on this method is available in England. The Rubicon Co. of Philadelphia also makes an analyzer for nitric oxide in coal gas based on oxidation by oxygen after standing in the presence of butadiene, followed by colorimetric analysis with Griess reagent. Stanford Research Institute was unable to make this instrument operate satisfactorily with atmospheric samples. In all these methods with coal gas, the nitrogen dioxide is removed before the nitric oxide treatment is applied. Commercial instruments for the oxides of nitrogen in air based on part of the work reported here have been made by the Borman Engineering Co. and by Harold Kruger Instruments, Inc., of Los Angeles.

INSTRUMENT

Figure 1 is a diagram and Figure 2, a photograph, of the apparatus in which nitrogen dioxide and nitric oxide plus nitrogen dioxide are determined continuously and automatically. Nitric oxide can then be found by difference.

The absorbing solution consists of 0.5% sulfanilic acid and 20 p.p.m. of *N*-(1-naphthyl)ethylenediamine dihydrochloride in 14% acetic acid. This formula is recommended by Saltzman (*9*), who tested various compounds suggested in the literature. It is drawn by means of two small glass metering pumps at a rate of 2.5 to 3.0 ml. per minute from a supply bottle, through the zero cell of the colorimeter, and allowed to drip on the top of a pair of absorber columns, where it contacts the air streams either concurrently or countercurrently. The liquid streams then pass by gravity, after a delay of about 8 minutes, through a pair of colorimeter cells, before uniting and flowing through a charcoal filter to a storage reservoir. The metering pumps consist of 2-ml. glass syringes operated by eccentrics on small 20-r.p.m. motors between two stainless steel ball check valves. Delivery is excellent. By turning the three-way stopcocks the liquid can be drawn from or returned to either supply bottle.

Simultaneously the air sample is split into two portions, one going directly to one absorber while the other passes through a 250-ml. ozonizing flask on the way to the other absorber. Zenith gear pumps (Zenith Products Co., West Newton, Mass.) are used to draw the gas samples. Their operation is very uniform. Only minor modifications of the system will be necessary if another oxidizing agent is selected instead of ozone.

Figure 3 is a wiring diagram of the analyzer. By a simple rearrangement of the connections, the nitrogen dioxide cell can be read against the nitrogen dioxide–nitric oxide cell to give nitric oxide directly.

GAS ABSORPTION

Nitrogen dioxide, like carbon dioxide (*12*), requires a contact time of several seconds with the absorbing solution for complete absorption. Evidently, slow chemical reactions such as hydration must precede the more rapid fixing reactions. This is indicated by the fact that absorption efficiency increases with increasing temperature. Good absorption can be obtained in an alkaline solution, using a fritted glass bubbler of medium porosity and butyl alcohol to induce frothing. Saltzman (*9*) found that his modification of the Griess diazotizing reagent was an excellent adsorbent for nitrogen dioxide under these conditions. No additive was needed to induce frothing. This type of absorber would give an average concentration over a definite period of time—for example, 10 minutes or longer—with intermittent measurement of the color.

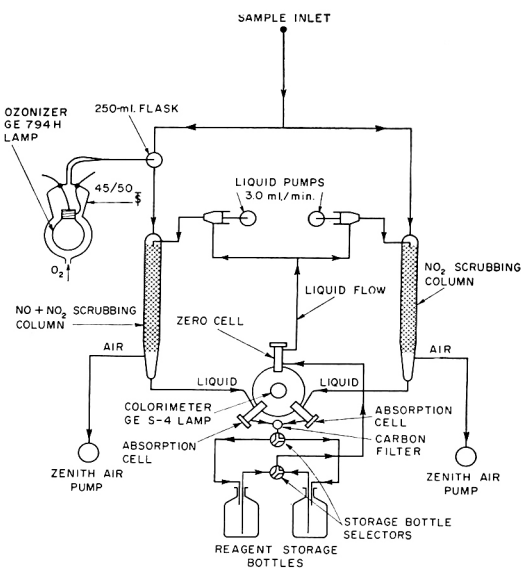

Figure 1. Gas and liquid flow systems in the nitrogen dioxide–nitric oxide analyzer

Quantitative absorption of the gas is also possible in continuously flowing gas and liquid streams. Three types of absorbers have been used. A glass tube of 3-mm. inside diameter, about 10 meters long and coiled into a 5-cm. diameter spiral, placed horizontally, is one of the best absorbers. Flow of gas and liquid are concurrent. Convenient volumes are about 250 ml. of gas and 2.5 ml. of liquid per minute. Suction of about 12 cm. of mercury is required to draw the fluids through the tube.

A second absorber is a 20-mm. glass tube, 60 cm. long, filled with $^3/_{32}$-inch glass helices and mounted vertically. A 15-mm. tube is too small. Gas and liquid flow is countercurrent, and resistance to flow is very small. Response to changing concentrations of the gas is fairly rapid, but definite channelling occur in the bed, which makes the washing out of the tube slower and more uncertain than with the other absorbers.

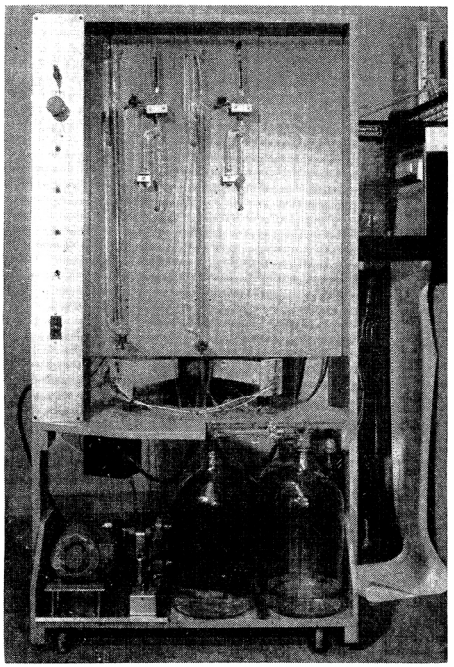

Figure 2. Nitrogen dioxide–nitric oxide analyzer

A third absorber appears to have fewer shortcomings than the others. It is the same size as the second, and has a Nichrome wire spiral mounted snugly between the inside surface of the larger tube and the outside surface of a concentric smaller tube. The wire consists of two pieces of No. 20 or 22 B. and S. gage, twisted together with a spacing of about 6 to 7 mm. between nodes, and wrapped in a seven-pitch spiral. Care is taken to select tubing of uniform bore or very slight uniform taper, so that the wire will engage both glass surfaces over its whole length. The 22-gage assembly offers considerably more resistance than the 20-gage, but both give nearly 100% absorption.

Colorimeter. Colorimetric determination of the red dye in the flowing solutions is accomplished in light absorption cells, of 15-cm. length and 15-ml. capacity, mounted in blocks of aluminum around a turret lamp housing. Cells of 10-cm. length would also be satisfactory. A green light of 5600 A. is provided, using a General Electric 4S lamp and three Corning filters, Nos. 3484, 4784, and 5120. One cell serves as a zero reference for the solution before it enters the absorbers. The other two receive the effluent from the absorbers after it passes through a 7-mm. tube of about 20-ml. capacity to give the solution time to develop its full color. Figure 4 shows the rate of color development, indicating 93% of full color in 5 minutes, 98% in 8 minutes, and 100% in 10 minutes. The difference in light transmission between the zero cell and each of the others is recorded on a two-point recorder.

The solution finally passes through a charcoal filter to a storage bottle. The charcoal removes the dye and also the coupling compound but does not significantly affect the sulfanilic acid or the acetic acid. Therefore, the solution can be re-used by adding another portion of coupling compound. With repeated use the solution develops a brown or green tinge, but this does not affect the calibration appreciably. The useful life of the solution has not been determined but it is at least 1 month.

Ozonizer. Ozone is supplied continuously by irradiating a stream of oxygen flowing at 10 ml. per minute with a 794H lamp and mixing the gas with the air sample for nitric oxide just before it enters the 250-ml. residence flask (Figure 1). The lamp is mounted in a 45/50 taper joint, the leads being sealed through the glass. If the lamp is operated at the minimum voltage that will keep it glowing, the output is sufficient to add 0.3 to 0.4 p.p.m. of ozone to the air sample of 240 ml. per minute. This concentration can readily be increased up to more than tenfold by raising the voltage.

A 250-ml. flask, providing a residence time of 1 minute, seems to be adequate. A larger flask sometimes gave a slightly higher value with the same gas mixture, or sometimes lower, depending presumably on the excess of ozone. A study was made of the oxidation of nitrogen dioxide by ozone. In carrying out these experiments the ozone stream was diverted intermittently through a potassium iodide–starch solution for ozone analysis. Later a stream of ozonated oxygen at 20 ml. per minute was divided into two equal portions by means of flowmeters, and one portion was analyzed while the other went into the residence flask.

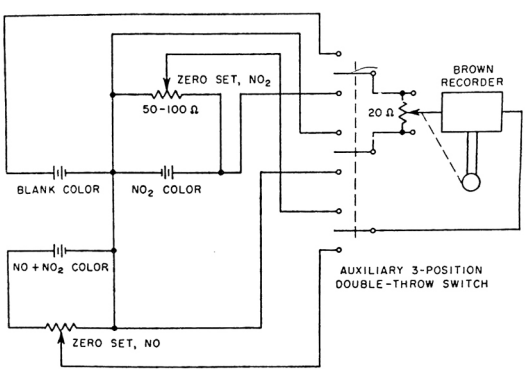

Figure 3. Schematic diagram of nitrogen dioxide–nitric oxide analyzer using two-point recorder and auxiliary switch

Figure 5 presents the values obtained for the oxidation of nitrogen dioxide due to excess ozone in the mixture. In those experiments in which nitric oxide was used, the value of the ozone added was reduced by the amount of nitric oxide. Though the data show appreciable variation, it is clear that the effect of ozone on nitrogen dioxide is a serious consideration. The analysis would be about 30% low due to 1 p.p.m. of ozone in excess of the nitric oxide present with a residence time of 2 minutes, and about 15% low with a residence time of 1 minute. Errors of more than 10% can be avoided only by keeping the ozone excess below 0.3 to 0.4 p.p.m. These data indicate that

the oxidation of nitrogen dioxide by ozone is considerably more rapid than would be suggested by a half-life of 13 minutes at 1 p.p.m. (2). In spite of many excellent features of ozone as an oxidizing agent for nitric oxide, the oxidation of nitrogen dioxide places definite limitations on its use. Possibly, in a situation like that in Los Angeles where the nitric oxide level seldom exceeds 0.5 p.p.m., it can be used satisfactorily if the peaks of the nitric oxide are sacrificed. Other oxidants need consideration.

Potassium Permanganate. Hollings (6) suggested the use of 2.5% potassium permanganate in 2.5% sulfuric acid as an oxidant for nitric oxide. This appears to be a promising reagent. When a simple bubbler was used with 20 ml. of the solution in parallel with an ozone oxidizer producing only a slight excess of ozone, the permanganate oxidation gave 90 to 97% of the recorder reading indicated by ozone oxidation. Nitric oxide concentration ranged from 0.24 to 0.70 p.p.m.

This lowering of the reading appears to be due primarily to solution and/or oxidation of the nitrogen dioxide in the permanganate bottle. In a careful comparison at 0.5 p.p.m. with nitric oxide alone and nitrogen dioxide alone, each gave 95% response as a result of the permanganate treatment, suggesting oxidation of nitrogen dioxide in both cases.

Chlorine Dioxide. Preliminary experiments with chlorine dioxide suggest that this compound may prove to be a satisfactory oxidant for nitric oxide. It is readily prepared by passing chlorine diluted with air through sodium chlorite. It oxidizes nitric oxide quantitatively when added in sufficient excess—ten- to 25-fold. Oxidation of nitrogen dioxide is much slower and probably will not present a serious problem. Table I presents data on these reactions.

In each analysis one sample was taken into the analyzer immediately; the other was delayed 1 minute in a 250-ml. flask. Less than 5 p.p.m. of chlorine dioxide gave incomplete oxidation. There appears to be a wide range of concentrations of chlorine dioxide above the 5-p.p.m. threshold which give the same recorder response for a given mixture of nitrogen oxides. In every case the delayed sample gave a lower result, indicating that oxidation of nitrogen dioxide was slow, because the reduction was only 2 to 12%. The three points in Figure 6 represented by crosses show these data in relation to the other results.

Table I. Oxidation of Nitric Oxide by Chlorine Dioxide

NO, P.P.M.	ClO_2, P.P.M.	Recorder Reading with Sampling Direct	Sampling Through 250-ml. flask	NO_2 Oxidized in Flask, %
0.33	3.8	65.5	61	12
0.33	5.0	69	65	11
0.48	3.4	67	66.5	3
0.48	4.9	73.5	70.5	8
0.49	6.0	77	75	6
0.48	7.4	76	73	7
0.48	9.4	76	74	6
0.48	13.2	75	73	6
0.69	4.8	85.5	85	2
0.69	6.0	86	85.5	2
0.69	8.2	86	85.5	2

CALIBRATION

Calibration of the instrument is done empirically with known mixtures of the oxides with air. A small blower is used, capable of moving 1000 to 3000 liters per minute. In Los Angeles the air was taken in through activated carbon filters. In Menlo Park outside air is generally of satisfactory purity and filtration is omitted. Air volume is measured with a calibrated 4-inch Biram anemometer. If the outlet pipe from the blower is constricted so that all the air goes through the instrument, it has been found empirically that the corrected velocity in feet per minute multiplied by 1.64 gives liters per minute. Similarly, the average velocity in an 8-inch pipe multiplied by 8.6 gives liters per minute.

The nitrogen dioxide is added to the intake of the blower from a small bubbler provided with stopcocks on the intake and outlet tubes. The stopcock plugs are held with rather strong springs. The vessel is filled about one third full with nitrogen dioxide, cooled in an ice bath, and aspirated with a slow stream of nitrogen. Then the stopcocks are closed and the vessel is weighed at room temperature as quickly as possible. It is returned to the ice bath for use. Nitrogen is aspirated at a definite rate controlled by an overflow through a water column and measured by a capillary flowmeter. After a known time, aspiration is stopped and the vessel is weighed again. The loss of weight (in milligrams per cubic meter of air through the blower × 0.54) gives parts per million of nitrogen dioxide.

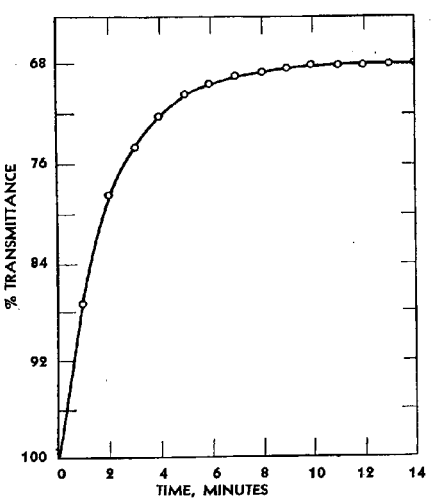

Figure 4. Effect of time on development of Griess-Saltzman color at 20° C.

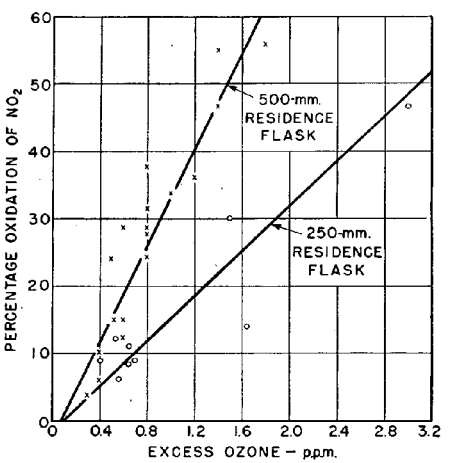

Figure 5. Oxidation of nitrogen dioxide with excess ozone

Nitric oxide is dispensed from a tank of compressed gas, through an Ascarite tube and a fine capillary flowmeter. It is then swept into the blower intake by a stream of nitrogen. Satisfactory precision can be obtained if the flowmeter delivers 1 ml. per minute with a head of 10 to 15 cm. Even after it is passed through the Ascarite, a few percent of nitrogen dioxide may be present in the gas. This is readily detected by a recorder response before the ozone is turned on. In earlier work the nitric oxide was displaced from a mercury pipet by adding mercury at a known rate. In this case the mercury removed the nitrogen dioxide chemically.

Data obtained for nitrogen dioxide and nitric oxide plus ozone, as well as for sodium nitrite solutions, are presented in Figure 6. Curves I and II represent calibrations with sodium nitrite calculated as nitrogen dioxide on May 8 and August 13 to 21, respectively. The displacement of the curve is small but definite. Slight changes in the optical system and some replacement of tubes in the recorder occurred during this time. Much larger and more inexplicable changes occurred in curves III, IV, and V, which represent the recorder responses to known concentrations of nitrogen dioxide (circles) and nitric oxide (squares).

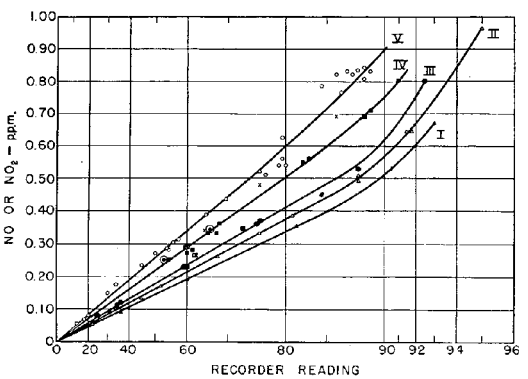

Figure 6. Calibration of nitrogen dioxide–nitric oxide analyzer

I. Sodium nitrite, May 8, 1956
II. Sodium nitrite, Aug. 8 to 21, 1956
III. ● Nitrogen dioxide and ■ nitric oxide after Aug. 13
IV. ⊙ Nitrogen dioxide and ■ nitric oxide, Aug. 2 to 13
V. ○ Nitrogen dioxide and □ nitric oxide, May 8 to Aug. 1
\+ Data obtained by oxidizing nitric oxide with chlorine dioxide

Curve V covers a period from May 8 to August 1. Most of the data were obtained with the columns containing glass helices, and only a few with the wire spirals. Toward the end of this period recorder operation was improved, but the last experimental results were not appreciably different from the others. It is unfortunate that a second calibration with sodium nitrite was not made during this period. Comparison of curves I and V indicates that the yield of nitrite from nitrogen dioxide is 57% instead of the 50% that is expected from a simple dismutation.

Curve IV covers the period from August 2 to 13. On August 2, two photocells were exchanged, and a slightly dirty light filter was cleaned. A definite displacement of the calibration curve occurred. The whole optical system, including one rather dirty filter, was cleaned on August 8, but this caused no change. The yield of nitrite from nitrogen dioxide, calculated from curves II and IV, is 75%. Curve III gives data after August 13. A zero flow cell was installed and a light shield was placed at the end of each absorption cell to confine the light to the center of the tube and avoid illuminating the walls. Again there was a displacement of the calibration curve, this time to a nitrite yield of 91%. *Sodium nitrite values on August 8, 13, 15, 16,* and 21 all fell on or very near curve II.

It is not clear why changes in the optical system should change the relations between the nitrogen dioxide and sodium nitrite curves. So far as is known, the absorption system was not changed except for the substitution of a nickel-chromium-iron-aluminum (Alloy K) wire for glass in the absorbers, near the end of the first period. Possibly the wire modified the reaction as its surface became cleaner and more active with continued use.

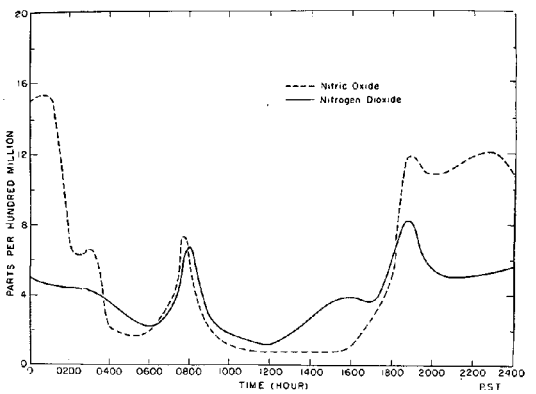

Figure 7. Sample record of nitric oxide from nitrogen dioxide recorder

Oct. 7, 1955, Pasadena, Calif.

In an attempt to clarify these relationships, the calibrations were repeated with and without the zero flow cell and the colorimeter light shields. Again the sodium nitrite response was affected only slightly by these changes. When the zero flow cells, the shields, and wire-packed absorbers were used, the nitrogen dioxide values fell on curve III, Figure 6, or even somewhat beyond it, indicating a close approach to 100% conversion to nitrous acid. On removal of the shields, there was a sharp drop in the nitrogen dioxide response amounting to 12 to 30% in different cells. Removal of the flow cell did not cause further change in these relationships. A new wire-packed absorber gave nitrogen dioxide values as low as 50 to 65% in initial tests. After continued use the response approached that of the older absorbers. Response of an absorber packed with glass helices varied from 78 to 100%. This was obviously due to channelling as indicated by the pink color of the helices, and the time required to wash out the dye after addition of nitrogen dioxide was stopped. Evidently the combined effects of variability in the absorbers and the influence of the colorimeter light shield serve to explain the shifting of the curves in Figure 6.

These circumstances point to the necessity for occasional calibration with nitric oxide or nitrogen dioxide. It must be emphasized that the calibration is empirical and that no reliance can be placed on calibration with sodium nitrite. Under conditions of steady use, however, the calibration remains quite constant. This is shown by the relatively small scatter of the points about the different curves in Figure 6. The data of curve V, which had the most dispersion, were analyzed statistically and the standard deviation of the points from the straight line

was found to be 5%. The 95% confidence level would therefore be about ±10%.

One erratic source of error is the collection of tiny bubbles of air along the upper surfaces of the inclined colorimeter tubes. These tubes should be examined occasionally and the bubbles removed.

Response Time. Response of the instrument is necessarily rather slow on account of the time required to permit full color development before the solution enters the colorimeter cell and the time to replace the solution in the cell. The former should be 8 to 10 minutes at room temperature. This reaction could be speeded up a great deal by heating the solution to 50° to 70° C., as suggested by Morriss and coworkers (*8*). However, for most purposes this delay would be relatively unimportant if a long tube of small bore were used, which would prevent appreciable turbulent mixing of the liquid column as it flowed to the colorimeter cell. The latter presents the principal difficulty, because a fairly large cell is necessary to attain the required sensitivity. Using a cell of 15-cm. length and 15-ml. capacity, at least 6 minutes would be needed to replace the solution completely at 2.5 ml. per minute. In practice, the displacement is 90% complete in 10 minutes after the initial recorder response to a change of gas concentration, and nearly 100% complete in 20 minutes. If more rapid response were needed, the cell could be reduced in length to 8 to 10 cm. without too much sacrifice of sensitivity. Possibly the diameter could also be reduced, which would reduce the mixing as well as the volume. Increased liquid flow could also be used.

INTERFERENCES

Several organic compounds were tested to see if they interfered with color development in Griess-Saltzman reagent. They were added to the reagent along with sodium nitrite and the resultant color was measured in a colorimeter. Quantities employed varied between 5 and 50 γ per ml. of organic compound with or without 0.015 γ per ml. of sodium nitrite. No significant differences in color development were noted as a result of addition of the following:

Aldehydes and ketones: Butyraldehyde, heptaldehyde, cyclohexanone
Peroxides: Primary, secondary, and tertiary butyl hydroperoxide, *n*-decyl hydroperoxide
Bases: Picolines, quinoline, isoquinoline, quinaldine

Some color destruction occurred upon the addition of the following:

Bases: Acridine
Aromatic nitroso compounds: *N*-*N*-dimethyl-*p*-nitrosoaniline, *p*-nitrosodiphenylaniline, *p*-nitrosophenol (sodium salt)

Slight color reinforcement occurred upon addition of nitrosopiperidine.

Three alkyl nitrites, ethyl, *n*-butyl, and isoamyl, were tested by introducing weighed amounts into the high volume stream of carbon-filtered air, in the same way as that employed with nitrogen dioxide. The bulb containing the liquid nitrite was maintained at constant temperature, the ethyl nitrite at 20° C., *n*-butyl nitrite at 30° C., and the isoamyl nitrite at 35° C. Nitrogen was bubbled through the bulb at a constant rate. The nitrite-air mixtures were then fed into the instrument. The data thus obtained (Table II) indicate that, if present in the atmosphere, alkyl nitrites will be recorded as nitrogen dioxide, but only for ethyl nitrite are the results quantitative.

Nitrous oxide was added to the mixture of nitrogen dioxide and ozone with and without a $2^1/_2$-minute residence time. There was no change in the nitrogen dioxide level, showing that nitrous oxide does not interfere with the analysis of nitrogen dioxide in the recorder.

When 5 p.p.m. of sulfur dioxide was added either to nitrogen dioxide alone or to a mixture of nitrogen dioxide and ozone, the analyses were not significantly affected.

RESULTS

Comparative Analyses. A program was instituted to compare the results of analyses of samples taken simultaneously and analyzed by various methods employed in three different laboratories. Table III gives the results of a series of analyses of mixtures with known concentrations of nitrogen dioxide.

If any nitric oxide were present in carbon-filtered air, it would react slowly in the bottles to give nitrogen dioxide. This reaction does not occur in the scrubber or recorder. Therefore, the evacuated bottle samples should yield high results whenever nitric oxide is present.

Table II. Analysis of Alkyl Nitrite–Air Mixtures

	NO_2 Concn., P.P.M.	
Compound	Calcd. concn.	NO_2 recorder
Ethyl nitrite	0.25	0.24
	0.16	0.15
	0.14	0.13
Butyl nitrite	0.14	0.08
	0.41	0.32
Amyl nitrite	0.07	0.04
	0.29	0.15

Table III. Comparative Analyses of Known Nitrogen Dioxide–Air Mixtures

		Laboratory A		Laboratory B	Laboratory C
Calcd., P.P.M.	NO_2 Recorder, P.P.M.	Scrubber, p.p.m.	500-ml. bottles	2-liter bottles	12-liter bottles
0.70	0.70	0.80	0.96	0.99	0.64
0.27	0.28	0.30	0.40	0.41	0.30
0.13	0.12	0.14	0.18	0.19	0.16
0.40	0.35	0.38	0.46	0.34	0.41
0.40	0.46	0.45	0.70	0.43	0.64
0.40[a]	0.35	0.35	0.44	0.35	0.43

[a] 0.40 p.p.m. NO_2 and 5 p.p.m. SO_2 added.

Sample Record. A sample record for nitric oxide and nitrogen dioxide for outside air in Pasadena on October 7, 1955, appears in Figure 7. It is interesting to note that both nitric oxide and nitrogen dioxide showed early morning maxima around 7 A.M., decreasing to a minimum during the day, and increasing again after 5 P.M. In Menlo Park, concentrations of nitric oxide up to 0.1 p.p.m. have frequently been observed at night or from 6 to 8 A.M., but not during the rest of the day. Nitrogen dioxide values have been consistently zero or very low. However, regular monitoring has not yet been carried out.

SUMMARY

With the apparatus described atmospheric nitrogen dioxide is determined by absorbing the gas in a modified Griess reagent recommended by Saltzman, containing 0.5% sulfanilic acid and 20 p.p.m. of *N*-(1-naphthyl)ethylenediamine dihydrochloride in 14% acetic acid. A continuous concurrent-flow absorber is employed with metered gas and liquid volumes in a ratio 80 to 1 up to 100 to 1. The red color produced by the action of nitrous acid on the reagents is measured in a 15-cm. cell of a recording colorimeter. The intensity of the color for a given amount of nitrogen dioxide is not stoichiometric, but depends on reactions that are not understood. Empirical calibration is, therefore,

essential. Nitric oxide is oxidized to nitrogen dioxide by ozone, permanganate, or chlorine dioxide, and determined along with preformed nitrogen dioxide in a duplicate absorber and colorimeter system. Nitric oxide can then be found by difference. The method is highly specific for compounds that can yield nitrite in solution. The only likely interfering substances are alkyl or other organic nitrites. Care must be taken to avoid oxidation of nitrogen peroxide by an excess of ozone. The other oxidants appear to be less critical in this respect.

Comparison with other methods gave satisfactory agreement on Los Angeles air samples to which known amounts of nitrogen dioxide were added.

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Ninth Annual Summer Symposium—Analysis of Industrial Wastes

Fixation of Sulfur Dioxide as Disulfitomercurate(II) and Subsequent Colorimetric Estimation

PHILIP W. WEST and G. C. GAEKE

Coates Chemical Laboratories, Louisiana State University, Baton Rouge, La.

Sulfur dioxide in the atmosphere is removed and concentrated by scrubbing through 0.1*M* sodium tetrachloromercurate(II). Stable, nonvolatile disulfitomercurate(II) is formed. The subsequent determination of the isolated sulfur dioxide is based on the red-violet color produced when *p*-rosaniline hydrochloride–hydrochloric acid mixture (0.04% dye–6% concentrated acid) and formaldehyde (0.2%) are added to the sampling solution. The absorption maximum is at 560 mμ and the color is temperature-independent and stable for several hours. The method is sensitive (0.005 to 0.2 p.p.m. with a 38.2-liter air sample scrubbed through 10.0 ml. of sampling solution) and should be useful in the absolute determination of sulfur dioxide in air pollution surveys. Nitrogen dioxide is the only common interference.

SULFUR dioxide is almost without question the most important of all air pollutants. It is an irritant gas that affects the upper respiratory tract, causing physical discomfort and even death. Four parts per million can readily be detected by odor; but as the nose becomes accustomed to it, the concentration necessary to produce a response increases. Eight to 12 p.p.m. will cause coughing and 20 p.p.m. will lead to eye irritation (*4*).

The toxicity of sulfur dioxide to man varies, apparently depending on the physical condition of the individual and on other factors. It has been considered a contributory cause of death in disasters such as those at London and Donora, Pa. The maximum allowable concentration is generally accepted as 10 p.p.m. However, sulfur dioxide may be toxic to vegetation in concentrations in the order of 2 or 3 p.p.m. and it is corrosive to metallic construction materials in concentrations of less than 1 p.p.m. Therefore, concentrations smaller than the stated maximum allowable concentration may be highly objectionable and, under some circumstances, even dangerous.

The occurrence of sulfur dioxide in air is general. This results from its uses in bleaching, fumigation, refrigeration, manufacture of sulfuric acid, etc. Of special significance is the release of this gas as a by-product in the burning of sulfur-containing coals and oils and in the smelting of many ores. It is also released during the manufacture of paper by the sulfite process and in such chemical operations as the synthesis of phenol.

In spite of its significance, methods for the determination of sulfur dioxide in air are generally not too satisfactory, especially if complex industrial atmospheres are to be analyzed. The methods used may be divided into two main groups: based on its reducing properties, or on its acidic character or the acidic nature of its oxidation product.

One of the methods used in early pollution surveys was that of the Selby Smelter Smoke Commission (*4*). A sample of the atmosphere was drawn into a partially evacuated 20-liter bottle containing a few milliliters of a standard solution of iodine. The sulfur dioxide in the sample was absorbed by the iodine when the bottle was shaken vigorously. The excess iodine was determined by thiosulfate titration. The main method in use today is based on a similar procedure, in which the air sample is scrubbed through a standard solution of iodine and potassium iodide; and the excess iodine is determined by titration with standard thiosulfate (*3*, *5*). Many variations of this method have been proposed. However, there are several disadvantages in the use of iodine as an absorber. During the collection of the sample some iodine may volatilize; other reducing agents present in the air, such as hydrogen sulfide, react with iodine, and some iodide is oxidized to iodine by the air bubbling through the solution or by oxidants that may be present in the atmosphere.

Hydrogen peroxide has also been suggested as an absorber for sulfur dioxide (*7*). The reaction produces sulfate and hydrogen ions, and several methods are available for the determination of

either of these ions. Again there are obviously a number of interferences, if a complex atmosphere is being sampled.

Aqueous solutions of alkali have also been used as absorbers. Nonvolatile sulfite ion is formed in this system and may be determined by several methods. Sulfite solutions, however, are unstable. The presence of alkali increases the instability, and when air is bubbled through such solutions, there is substantial loss due to increased contact with oxygen during the scrubbing operation.

The instability of sulfite solutions may be decreased by the addition of certain alcohols. Atkin (*1*) has used a solution containing 5% glycerol and 10% sodium hydroxide as a sulfur dioxide–absorbing solution and reports that oxidation is decreased. Urone and Boggs (*8*) have used a solution of 5% glycerol in 0.1*N* sodium hydroxide as the absorbing solution in their spectrophotometric determination of sulfur dioxide in air. These alcoholic alkali solutions have a tendency to froth and foam, because of their lowered surface tension, and, therefore, very low sampling rates must be used.

The sulfite content of these solutions is usually determined by a colorimetric procedure. The most common colorimetric reagent in use today is based on a sulfuric acid–bleached fuchsin reagent developed by Steigmann (*6*). Both Atkin and Urone and Boggs have modified this reagent for work on air pollution.

In the present investigation, an attempt has been made to find an absorbing system which is efficient and, equally important, which forms a stable compound. At the same time, it was thought that an improvement in the sulfuric acid–bleached fuchsin reagent could also be made. A simple, rapid and reliable procedure was needed, that would allow the preservation of field samples for later analysis in the laboratory.

Feigl (*2*) mentions that disulfitomercurate(II) ion, $[Hg(SO_3)_2]^{--}$, which is formed when sulfite is added to mercury(II) solutions, is very stable. In fact, even permanganate fails to oxidize the complex, except at a very slow rate. Complete information was not available, but this remarkable stability prompted further investigation, in the hope that an efficient method of isolation and determination of sulfur dioxide could be evolved.

EXPERIMENTAL

Reagents and Solutions. Sodium tetrachloromercurate(II), 0.1*M*. Reagent grade mercury(II) chloride (0.1 mole, 27.2 grams) and 0.2 mole (11.7 grams) of reagent grade sodium chloride are dissolved in water and diluted to 1 liter.

Hydrochloric acid–bleached *p*-rosaniline, 0.04%. Four milliliters of a 1% aqueous solution of *p*-rosaniline hydrochloride and 6 ml. of concentrated hydrochloric acid are mixed and diluted to 100 ml.

Formaldehyde, 0.2%. Five milliliters of 40% formaldehyde are diluted to 1000 ml. with distilled water.

Apparatus. Beckman Model DK-1 recording spectrophotometer.

Beckman Model B spectrophotometer.

Micro gas buret and gas dilution apparatus as described by Urone and Boggs (*8*).

Because complete information on the disulfitomercurate complex was not available, a thorough investigation was initiated into the use of solutions of mercury(II) salts as absorbers for sulfur dioxide. The compounds selected for the initial tests were mercury(II) chloride (a pseudo salt) and mercury(II) nitrate (a normal salt). It was found that with the chloride solution the complex is formed; but with nitrate, reduction to mercury(I) occurs. High concentrations of sulfur dioxide (in the order of 0.1% aqueous solutions) also tend to reduce small amounts of mercury(II) chloride. It is believed that the small concentration of free mercury(II) ion existing in the chloride solution accounts for the fact that complexation rather than reduction occurs. Because mercury(II) forms complexes easily with chloride, it was decided to determine the stability of the complex in solutions of various chloride strengths.

A series of solutions (10.0 ml.) was prepared which were 0.1*M* with respect to mercury(II) chloride and contained various amounts of sodium chloride. One hundred micrograms of sulfur dioxide as sodium bisulfite and 0.1 ml. of an approximately 1% potassium permanganate solution containing a small amount of sulfuric acid were added and mixed. The solutions were allowed to stand for 1 hour and the absorbance of the remaining permanganate was determined at 520 mμ (solutions containing only sulfur dioxide and permanganate were almost completely decolorized instantly).

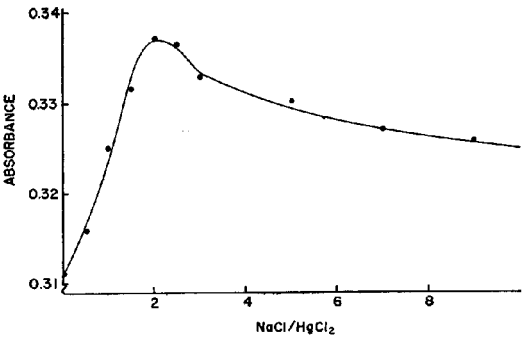

Figure 1. Effect of chloride concentration on stability of disulfitomercurate(II) complex

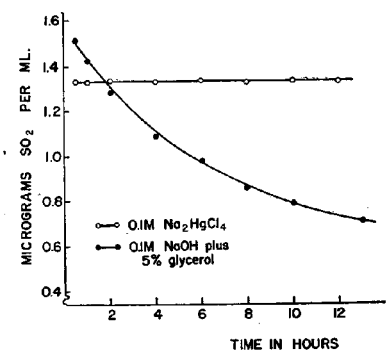

Figure 2. Rate of air oxidation of sulfur dioxide absorbed in sodium tetrachloromercurate(II) and in sodium hydroxide plus glycerol

The results of this experiment are shown in Figure 1, where absorbance is plotted against the molar ratio of sodium chloride to mercury(II) chloride. From this curve it can be seen that disulfitomercurate(II) ion is most stable in a solution corresponding to the composition of sodium tetrachloromercurate(II). Therefore, a 0.1*M* solution of sodium tetrachloromercurate(II) was chosen as the absorbing solution. The reaction involved in the absorption is thought to be an exchange reaction as shown by the equation

$$[HgCl_4]^{--} + 2SO_2 + 2H_2O \rightarrow [Hg(SO_3)_2]^{--} + 4Cl^- + 4H^+$$

The study of absorption efficiency was undertaken next.

Two scrubbers, each containing 10 ml. of 0.1*M* sodium tetrachloromercurate(II), were connected in series to the gas dilution apparatus. Air, containing various concentrations of sulfur dioxide, was passed through the scrubbers at different rates of flow. Fifty-liter samples were collected. The sample in the second scrubber was analyzed for sulfur dioxide.

From the data shown in Table I it can be seen that tetrachloromercurate(II) is a very efficient scrubber for sulfur dioxide even at high flow rates, as shown by the fact that no sulfur dioxide escapes the first scrubber.

The effect of air oxidation on the disulfitomercurate(II) complex was next studied. For comparison purposes, the effect of air oxidation on sulfites in 0.1*N* sodium hydroxide containing 5% glycerol was also determined. Between 250 and 300 γ of sulfur dioxide were absorbed in 200 ml. of the appropriate solution. A 10-ml. sample was withdrawn for analysis and then a slow current of air (about 2 liters per minute) was bubbled through the solutions. At various times, 10-ml. samples were withdrawn and analyzed. As can be seen from Figure 2, there was no oxidation of the disulfitomercurate(II) complex. This is important when large volumes of air containing small amounts of sulfur dioxide must be sampled.

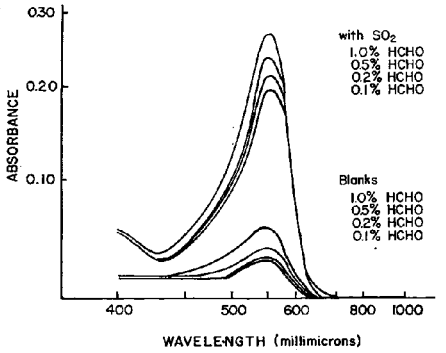

Figure 3. Influence of formaldehyde concentration on absorbance

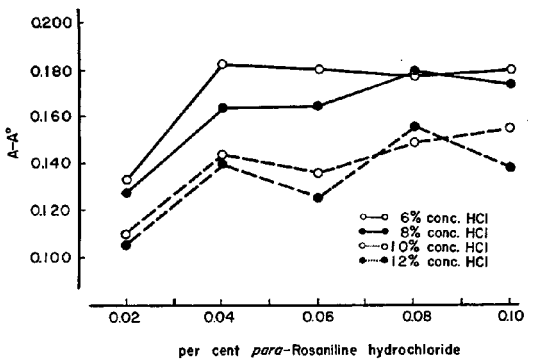

Figure 4. Sensitivities of various dye-acid mixtures

Investigation of the red-violet color, developed when fuchsin, sulfuric acid, and formaldehyde are mixed with alkali sulfite solutions (*8*), showed that the reaction also occurs with disulfitomercurate(II). As the reagent is difficult to prepare, is stable for only a few hours, and produces some color in the absence of sulfite, it seemed advisable to seek a more satisfactory color-producing agent. It was decided to use *p*-rosaniline hydrochloride as the dyestuff instead of basic fuchsin, which is an impure mixture of rosaniline and *p*-rosaniline hydrochlorides. It was found that hydrochloric acid will bleach *p*-rosaniline, giving solutions that are pale yellow to colorless. When this reagent and formaldehyde are added to solutions containing sulfite or disulfitomercurate(II), the characteristic red-violet color is produced.

Table I. Efficiency of Absorption in Sodium Tetrachloromercurate(II)

Concn. of SO_2, P.P.M.	Rate of Flow, Liters/Min.	SO_2 in Second Scrubber, γ
5	2	0.0
	5	0.0
	10	0.0
	15	0.0
10	10	0.0
	15	0.0

To determine the optimum conditions of dye, acid, and aldehyde concentration, a series of solutions was prepared. The dye-acid solutions covered the range from 0.02 to 0.1% *p*-rosaniline hydrochloride and 6 to 12% concentrated hydrochloric acid, while the aldehyde solutions ranged from 0.1 to 1% formaldehyde. It was found that for any given dye-acid solution the absorbance of the test solution (containing 5 γ of sulfur dioxide) and the blank increased with formaldehyde concentration (Figure 3). The absorbance maximum is at 560 mμ. The dye-acid concentrations in these solutions were 0.04% dye and 6% acid. All curves were obtained with a Beckman Model DK-1 recording spectrophotometer.

After all of the curves for the various solutions had been plotted, the sensitivities were calculated (absorbance of sample minus absorbance of blank) and plotted against dye concentration. These data for 0.2% formaldehyde are shown graphically in Figure 4. The reagent containing 0.04% dye and 6% acid with the addition of 0.2% formaldehyde was found to give the greatest sensitivity with the least blank correction (blanks are approximately 0.02 absorbance unit). In all cases, 1 ml. of dye-acid and 1 ml. of formaldehyde solution were added to 10 ml. of 0.1*M* sodium tetrachloromercurate(II) containing 5 γ of sulfur dioxide. Color development was found to be reasonably rapid, being complete in about 20 minutes and stable for 2 to 3 hours.

Table II. Effect of Temperature on Color Development

(Time, 30 minutes)

SO_2 Concn., γ/10 Ml.	Temperature, ° C. 11	15	20	22	26	30
	Absorbancies					
0.5	0.015	0.017	0.015	0.016	0.016	0.014
1.0	0.041	0.038	0.040	0.037	0.041	0.036
2.0	0.082	0.078	0.079	0.081	0.082	0.078
4.0	0.144	0.148	0.145	0.145	0.146	0.144
6.0	0.216	0.219	0.215	0.219	0.218	0.217
8.0	0.280	0.282	0.280	0.280	0.281	0.278
10.0	0.343	0.342	0.340	0.342	0.341	0.339

The effect of temperature was determined by taking solutions containing various amounts of sulfur dioxide, adding the color-developing reagents, and thermostating for 30 minutes. At the end of the standing time the absorbance was read at 560 mμ. The results are shown in Table II.

The reagent described has been found to be about 20% more sensitive than the sulfuric acid–bleached fuchsin reagent under

the same conditions. The system obeys Beer's law up to approximately 25 γ of sulfur dioxide per 10 ml. Nitrogen dioxide interferes if present in concentrations above 2 p.p.m. Higher levels decrease the color intensity and nitrogen dioxide concentrations over 8 p.p.m. prevent color development completely. The only other common interference, usually associated with the reagent, is sulfide. In the presence of the mercury-absorbing solution, this ion precipitates and may be removed by filtration or centrifugation. Sulfur trioxide, chlorine, ammonia, and halogen acids do not interfere.

RECOMMENDED PROCEDURE FOR DETERMINATION OF SULFUR DIOXIDE IN THE ATMOSPHERE

Collect 38.2 liters (1.35 cubic feet) of sample in 10.0 ml. of sodium tetrachloromercurate(II) solution in a small fritted bubbler. The sampling rate may be as high as 0.2 cu. foot per minute with no loss due to decreased efficiency of absorption. To the 10.0-ml. sample add 1.0 ml. of acidic *p*-rosaniline solution and 1.0 ml. of formaldehyde solution. Treat a blank of 10 ml. of sodium tetrachloromercurate(II) in the same manner. Allow to stand 20 to 30 minutes for full color development. Determine the absorbancy of the test solution compared to the blank at 560 mμ. Read the concentration of sulfur dioxide from a standard curve prepared by using standard solutions of sodium bisulfite in sodium tetrachloromercurate(II). If the sample size is 38.2 liters, then each microgram of sulfur dioxide represents 0.01 p.p.m. of sulfur dioxide in the air.

Nitrogen dioxide is the only interference with this method, and it can be tolerated in concentrations up to 2 p.p.m. (if sulfides are present, the precipitate formed must be removed by filtration or centrifugation). Samples may be collected in the field and analyzed at any later time with no loss of sulfur dioxide due to either oxidation of volatilization.

SUMMARY

A procedure for the fixation of sulfur dioxide is based on the formation of stable, nonvolatile disulfitomercurate(II) ion. The determination is based on the red-violet color developed when sulfur dioxide or disulfitomercurate(II), *p*-rosaniline, hydrochloric acid, and formaldehyde are mixed. The method is sensitive, reproducible, and accurate.

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Recent Trends in the Analysis of Industrial Wastes

W. ALLAN MOORE and M. B. ETTINGER

Robert A. Taft Sanitary Engineering Center, Cincinnati, Ohio

Surface waters are becoming progressively scarcer, and their use for disposing of liquid industrial waste should be continually re-examined. Intelligent control of waste discharge must be based on analytical methodology, which does not appear to be keeping pace with the problem that confronts it. Requirements for discharge of wastes to surface waters will become increasingly critical.

ESTIMATES based on "population equivalents" (*28*) rate industrial wastes as responsible for more than twice as much stream pollution as municipal sewage discharges. It has been further estimated that between 1950 and 1975 population will increase by about one third and industrial production will double. Estimates by chemical industry (*17*) of future expansion make these statements on industrial growth seem highly conservative. Production increase will obviously be accompanied by increasing use of water.

The future growth of water use is likely to occur in a framework of shrinking availability of surface water. The existing water shortages in the arid areas of the country are well understood. Supplementary irrigation in humid areas is increasing rapidly. This consumption of water occurs during dry summer periods, when most streams have their lowest flow of the year, and it has been estimated (*31*) that it can use the entire flow of many streams, even if only a small fraction of 1% of the land in a watershed is irrigated.

Municipal use of water is increasing faster than population. Thus, the average urban dweller uses 150 gallons of water today, whereas 30 years ago he used only 20 gallons (*11*). Recreational use of water is harder to assess, but both increased leisure time and increased income are causing the public to demand more water resources for recreation.

Requirements for discharge of wastes to surface waters will, of necessity, become increasingly critical. Analytical means of gaging the suitability of wastes for discharge must be developed further as implements for protecting an increasingly critical public interest in water quality, without unduly hampering industrial activity.

INSTRUMENTATION

The analytical work in progress does not appear to be adequate in relation to the expanded and critical waste control problem which it must eventually meet. Perhaps the most hopeful sign is the awakening interest in instrumentation as a means of recording waste properties or stream quality. Along with others, the Sanitary Engineering Center (*14*) is working toward the development of a machine for continuously indicating and recording dissolved oxygen in surface water. Kieselbach (*13*) of Du Pont has reported on an apparatus for continuous recording

of organic concentration in waste water. This instrument is expensive, but is a significant step in development.

The means for recording pH, conductivity, oxidation-reduction potential, and color are available for use in controlling industrial wastes or stream quality.

NEW PARAMETERS

New industrial developments will cause new parameters of pollution to appear. For instance, the color and ligneous materials associated with paper mill wastes have generally been of less concern than the organic portion of the waste, which is subject to rapid biological destruction with concurrent depletion of oxygen in receiving streams. However, lignin sulfates now find commercial use as dispersing agents, and are used to prevent coagulation of both solids and liquids (*26*). It would be reasonable to assume that the same material in a surface water might interfere with its coagulation in water treatment processes. It may be readily predicted that tests for tannins and lignins (*1*) will find increasing use and will undergo further laboratory refinement.

BIOASSAY TECHNIQUE

One important area of waste analysis cannot possibly be adequately covered by the chemist: the development of a basis for predicting the effects of a waste on the survival and growth of fishes and other aquatic life. Chemical limits on the permissible quantities of fish toxicants may be suggested, but they are not completely satisfactory. For instance, Doudoroff and Katz (*5*) cite one study in which, under a given set of test conditions, fishes survived 8 p.p.m. of zinc alone and 0.2 p.p.m. of copper alone but were killed by a combination of 1 p.p.m. of zinc and 0.025 p.p.m. of copper. A really sound estimate of the effect of industrial discharge on fish populations requires complicated procedures (*4*). The routine bioassay (*6*) for evaluating the acute toxicity of industrial wastes to fishes may be expected to come into more common use.

TOXICOLOGICAL EXAMINATION OF WASTE

Responsible manufacturers do not market a product for either internal use or dermal application by man without exhaustive studies of its toxicological characteristics and continued close quality control. But surface waters at present serving millions of people are continuously dosed with industrial wastes containing undetermined amounts of unknown chemicals of undetermined toxicity.

In the field of atomic energy there is record of sustained examination of wastes to preclude the entry of harmful amounts of toxic materials into natural water courses. Industry, in entering the radiation application field, has scrupulously followed the pattern of operation established by the Government (*29*) in the days of the Manhattan Project. Close and sustained observation and control of the toxic content of wastes may be expected to grow.

The concern felt by a state compact group over the problem of possible toxicity associated with industrial waste pollution was expressed by Cleary (*3*) as follows:

> What toxic effects to man and animals may result from continued consumption of water contaminated with industrial wastes? Or from end products of organic decomposition? Or from treatment of certain raw water supplies by chemical means?
>
> These are questions that cannot be ignored by those concerned with water quality. These questions have special meaning to the Ohio River Valley Water Sanitation Commission, dealing as it must with the establishment of industrial waste control procedures.

At present the authors are aware of only one case where organic chemical waste discharges are continuously examined for acute and chronic toxicity to mammals. However, in the next 20 years, there is bound to be an increasingly close scrutiny of the toxicity to humans of industrial wastes discharged to surface waters that are subsequently used as domestic water supplies. The toxicological examination of wastes and the analytical methodology to accompany it are not well defined but may soon be a matter of major concern.

RE-EXAMINATION OF TRADITIONAL PROCEDURES

The analytical procedures now used to measure industrial wastes are largely nonspecific tests drawn from the traditional techniques first devised for use in sewage disposal practice, assessment of stream pollution by sewage, and operation and control of water purification processes. Perhaps the procedures which have undergone the greatest recent re-evaluation are the biochemical oxygen demand test (most frequently 5-day B.O.D.), oxygen consumed, chemical oxygen demand, if preferred, and threshold odor.

An overwhelming mass of evidence has demonstrated that the real B.O.D. of an industrial waste frequently cannot be satisfactorily measured unless an effective seed is developed (*7, 10, 19, 27*). The increasing awareness of the difficulty of developing seeds has led to an increasing interest in long-term B.O.D. techniques. Examples of this trend are the "two-jug technique" (*24*) and the technique described by Mills and Stack (*20*), who recommended long-term B.O.D. studies using acclimated seeds as the preferred method for making a realistic measurement of the B.O.D. of industrial wastes.

Two procedures for determining the 5-day B.O.D. (*1*) (with the choice of method left to the analyst) which differ in manipulative detail, do not necessarily give identical results and may lead to differing views on equitable sewer rental charges for industrial wastes. This situation has been described in some detail (*8*) and is now under consideration by ASTM Committee D-19. It appears that B.O.D. may be redefined as "the amount of dissolved oxygen used both biologically and chemically under specified conditions."

Oxygen consumed (O.C.) or chemical oxygen demand (C.O.D.) has resumed its status as a measure of waste quality rather than a poor basis for estimating B.O.D. This usage of the oxygen-consumed test has been advocated periodically by the authors and their colleagues (*8, 9, 21*), and appears to be widely accepted by those concerned with industrial wastes. C.O.D. sometimes shows close correlation with B.O.D., and has been found in at least one case to be a satisfactory basis for operation of a waste disposal plant (*12*).

The expanded use of the oxygen-consumed test may be attributed to improved and extended technique (*22, 23*). Problems in the measurement of oxygen consumed in the presence of large amounts of chloride are in the joint presence of chloride and nitrogenous material are being examined in the Sanitary Engineering Center laboratories, and are also the subject of research in England, where these difficulties first had close scrutiny (*30*).

In commenting on the standard procedure adaptable to industrial wastes, the present situation with regard to nitrogen determinations deserves mention. The Kjehldahl digestion should be markedly improved as the result of studies by McKenzie and Wallace (*16*), and the nesslerization technique (*1*) appears to give good results. The nitrate procedures for sewage and industrial wastes, after being standard for years, have been allotted "tentative" status (*1*) in recognition of the difficulty of obtaining reproducible results with the available methods.

The possible effect of industrial effluents on the taste and odor of drinking water has received increased scrutiny. Drinking water is almost invariably chlorinated (*8*), so that the organoleptic properties of chlorinated dilutions of waste are the properties to be measured, and the variability of the sensory percep-

tion of observers should also be taken into account in rating taste or odor by the threshold technique.

SEARCH FOR INCREASING SPECIFICITY AND SENSITIVITY

There is a current trend toward sharpening the specificity of the identification of waste components, where technique can be devised and the existing situation demands such revision. In the Sanitary Engineering Center, for instance, Rosen and Burttschell have applied four different techniques—ultraviolet absorption, infrared absorption, x-ray diffraction of derivatives, and color reaction—to produce very firm evidence of ground water pollution by specific chemicals also present in an industrial lagoon. Sallee (*25*) gives evidence of this trend; a high degree of specificity for alkyl benzene sulfonates is sought and the desired sensitivity obtained by preliminary concentration through the use of carbon. For studies of the persistence of motor oil hydrocarbons, Ludzack and Whitfield (*15*) devised more definitive procedures for "oil" than any previously used.

The carbon absorption technique (*2, 18*) has in some cases enormously increased both the sensitivity and the specificity of analysis by making it possible for the analyst to work conveniently with a 5000-gallon sample of water, or with up to a 100-gallon sample of industrial waste. This technique has been used at the Sanitary Engineering Center by Rosen and coworkers to detect and later identify part per billion quantities of insecticides. It is expected that both sensitive and specific general-purpose procedures for the commoner chlorinated insecticides will develop.

There will be a growing need for more specific information on the actual chemical composition of industrial wastes, and of the chemical identity of specific harmful pollutants in streams. An increasing trend for more specific and more sensitive procedures may be confidently predicted, both to supplant and to supplement the traditional procedures such as B.O.D., C.O.D., and odor.

SUMMARY

During the next 20 years, surface water resources will become progressively scarcer. Their use as a means of disposal of liquid industrial waste discharges will be subject to continued reexamination in the interests of the total economy. There may be progressive restriction on the quality and quantity of liquid waste discharges. Intelligent control must be based on analytical methodology, which does not appear to be developing as fast as the control problem with which it is confronted. Present trends or future needs in the use of techniques for the analysis of industrial wastes are:

Instrumentation to measure and record waste quality

Increasing use of bioassay procedures to control the suitability of water for fish

Increasing need and pressure for examination of wastes for material toxic to man

Development of new parameters of pollution for changing patterns of water use and changing nature of waste discharges

Further modification of the traditional analytical procedures borrowed from the field of sewage disposal and water plant operation to adapt them to better use in the examination of industrial wastes

Increasingly specific waste analysis to pinpoint problems in waste control and to serve as the basis for research on waste properties and their effects in streams.

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Determination of Trace Amounts of Alkyl Benzenesulfonates in Water

Subcommittee on Analytical Methods, Technical Advisory Committee, Association of American Soap and Glycerine Producers, Inc.

E. M. SALLEE, Procter & Gamble Co.
J. D. FAIRING, Monsanto Chemical Co.
R. W. HESS, National Aniline Division, Allied Chemical & Dye Corp.
RALPH HOUSE, California Research Corp.
P. M. MAXWELL, Lever Brothers Co.
F. W. MELPOLDER, Atlantic Refining Co.
F. M. MIDDLETON, U. S. Public Health Service
JOHN ROSS, Colgate-Palmolive Co.
W. C. WOELFEL, Continental Oil Co.
P. J. WEAVER, Chairman, Procter & Gamble Co.

An analytical subcommittee of the Technical Advisory Committee of the Association of American Soap and Glycerine Producers, Inc., has cooperatively developed a specific, quantitative infrared procedure for the determination of trace concentrations of alkyl benzenesulfonate in raw and treated water supplies. Such a method is needed because of the lack of specificity in procedures currently used in analyzing most household synthetic detergents. The method involves concentration of alkyl benzenesulfonate through adsorption on activated carbon, desorption, removal of interfering materials through several purification steps, and final quantitative estimation with infrared spectrophotometry.

THE rapid rise in the use of synthetic detergents for washing and cleaning operations has caused some concern over the fate of these materials in waste waters. The surface-active agents in the large bulk of these detergents are anionic sulfates and sulfonates; the alkyl benzenesulfonates (ABS), with by far the largest share of production and a greater stability in solution, are of primary interest. Accurate analytical methods are essential to assessing the effect of this compound in the water and sewage treatment field. Methods currently available lack sufficient specificity to serve this purpose.

Colorimetric methods based on methylene blue have long been used, but often give erroneous results due to interference by many organic and inorganic materials, most of which are naturally occurring substances. In the absence of a check method, it has not been possible to determine the accuracy of these widely used procedures, and, consequently, misinterpretations of data have appeared in the literature. Such errors can be particularly serious at the fractional part per million concentrations of alkyl benzenesulfonates found in river waters.

Methylene blue is a water-soluble heterocyclic amine dye, which forms a slightly ionized salt with anionic detergents. The salt is soluble in organic solvents and can be extracted from the aqueous phase.

Early procedures were carried out by addition of methylene blue to an acidic aqueous solution of the sample and then extraction of the colored salt with chloroform. The amount of dye found in the organic phase was taken to be equivalent to the amount of detergent present. Though satisfactory for determination of detergents in distilled water, the methods could not be satisfactorily applied to samples of interest in water treatment.

Some of the proved interferences can be predicted on the basis of chemical properties. Organic sulfates, sulfonates, carboxylates, phosphates, and phenols, which complex methylene blue, and inorganic cyanates, chlorides, nitrates, and thiocyanates, which form ion pairs with methylene blue, are among the positive interferences. Organic materials (especially amines), which compete with the methylene blue in the reaction, cause low results. Positive errors are much more common than negative when anionic detergents are determined in natural water.

In the past few years, an extensive literature has been built in attempts to circumvent these interferences. Evans (*5*) proposed extraction of the complex at two different acidities and extrapolation to a third to reduce interference in sewage samples. While some interferences were prevented, others remained. Results were reproducible to about ±0.3 p.p.m.

In an attempt to remove inorganic interferences, Degens, Evans, Kommer, and Winsor (*3*) used water washing of the chloroform extract. Thiocyanate concentrations higher than 5 p.p.m. were removed by precipitation or destroyed by oxidation. This procedure still gave an apparent 0.2 p.p.m. anionic detergent when applied to a 2% solution of urine.

Longwell and Maniece (*6*) proposed extraction of the methylene blue complex from alkaline solution. In this way, they avoided negative interferences due to nitrogeneous material and positive interferences due to inorganic ions. Other interference, probably organic anions, has been shown to remain.

All the methylene blue methods are subject to error. Though special conditions may prevent or reduce a particular interference, in general, any substance that complexes with methylene blue to form a salt soluble in organic solvent will give high results. Any substance that competes with methylene blue to complex with alkyl benzenesulfonate will give low results. All methods based on similar chemistry can be expected to show similar interferences.

Some workers have recommended substitution of other amine dyes for methylene blue. The most recent are Moore and Kolbeson (*7*), who use methyl green and extract with benzene. Though the effects of different interferences may vary slightly, they are not prevented by this method.

A logical extension of the colorimetric determination is a titration in a two-phase system using the colored dye as indicator. Similar procedures were published almost simultaneously by Epton (*4*) and by Barr, Oliver, and Stubbings (*1*).

The essentials of these methods are a suitable water-soluble dye, a cationic surface-active agent for titrant, and an organic liquid to form the second phase. The dye is added to the aqueous solution of the sample, and the colored dye–alkyl benzenesulfonate complex is extracted into the organic phase. The cationic agent is used as titrant and combines more strongly with the alkyl benzenesulfonate than does the dye. Thus, the end point is indicated by a shift of color from the organic to the aqueous phase.

In more recent publications, both basic (amino) and acidic (sulfonic) dyes have been recommended. Surface-active quaternary ammonium and pyridinium salts are suitable as titrants. Both chlorinated compounds and hydrocarbons have been recom-

mended as solvents. The methods are most applicable for concentrations of 100 to 1000 p.p.m. Results are questionable between 10 and 100 p.p.m. and of little value at lower concentrations. Because the chemistry involved is the same, the titrimetric method is subject to the same interferences as the colorimetric.

In samples as complex as surface waters, it is evident that unequivocal results can be obtained only if the alkyl benzenesulfonate can be separated from interferences. Previous work has shown that prevention of interference by one type of interfering material does not suffice for others. Therefore, several different separation steps are necessary to remove the various types of interference. Many samples also require concentration.

CURRENT STUDIES

Early in 1954, analytical chemists from Atlantic Refining, California Research Corp., Continental Oil, Monsanto Chemical, National Aniline, and Procter & Gamble met to discuss the development of a specific, accurate method for the determination of ABS-type surface-active agents in water and sewage. Later, representatives of Colgate-Palmolive, Lever Brothers, and the U. S. Public Health Service joined the group, which was formalized as a subcommittee of the Association of American Soap and Glycerine Producers' Technical Advisory Committee.

It was clear from the outset that colorimetric methods, as outlined above, would not suffice to determine the true concentration of alkyl benzenesulfonate present in any given water sample. Infrared spectrophotometry offered the best hope for unequivocal identification and quantitative determination at the concentrations of interest.

It was also early realized that a standard reference would be necessary. Pure alkyl benzenesulfonate is hygroscopic and unsuited for this purpose. Commercially available package detergents vary widely in composition of surface-active material, and are subject to unannounced formula changes. Therefore, a quantity of typical commercial alkyl benzene was obtained from each of four manufacturers, composited, sulfonated, and analyzed in several laboratories by conventional methods. The standard material is a dry powder containing sodium sulfate and 62.4% alkyl benzenesulfonate. This material was used in the collaborative work, and is available for use as a reference standard for preparing infrared calibration curves.

The decision to point for an infrared procedure for the determination of alkyl benzenesulfonate in water supplies brought up several new problems, which would not normally be faced in a short colorimetric method. Probably the most important of these is the need to concentrate the alkyl benzenesulfonate from dilute solutions, so that sufficient is present to make the infrared determination. Also, because alkyl benzenesulfonate is not soluble in the organic solvents used for quantitative infrared work, possible complexing agents which would overcome that problem had to be investigated. Other problems, such as the removal of materials which would obscure the infrared spectrum, and other purification steps, were investigated as they came up.

Early efforts in this work were independent, with different organizations working on different aspects of the problem. After the proper developmental stage had been reached, the various individual efforts were combined into a single procedure. Thus, the final method is a cooperative achievement, and credit can be given only to the group as a whole.

Concentration of Sample. To achieve the necessary concentration, evaporation was considered, but this would be slow and would concentrate all other materials present at the same rate as the alkyl benzenesulfonate.

On the other hand, selective adsorption followed by elution would both concentrate and partially purify the sample. Activated carbon is a promising adsorbent for accomplishing the purpose. Absolute requirements are quantitative adsorption of alkyl benzenesulfonate from the sample and reproducible recovery by elution from the carbon.

Various carbons were evaluated in distilled water. The methylene blue colorimetric procedure was used to check completeness of adsorption and recovery. In a distilled water–alkyl benzenesulfonate system, this method is accurate.

Nuchar C-190 (West Virginia Pulp and Paper Co.) was used by Braus, Middleton, and Walton (*2*) for recovering organic materials from water. Unground Nuchar C-190, screened to "on 30 mesh," is much easier to handle during adsorption and desorption. It has nearly the capacity of the pulverized material, and has been used to concentrate synthetic detergents for qualitative infrared examination (*3*).

From trials with a number of solvents and conditions, it was found that a batchwise extraction of the carbon, with mixed solvent and alkali, gave the most complete recovery. A 1 to 1 mixture of methanol and benzene which is 0.04*N* in potassium hydroxide extracts 85% of the adsorbed alkyl benzenesulfonate in an hour and an additional extraction for 2 hours removes 50 to 75% of the remainder. This was established by tagging alkyl benzenesulfonate with sulfur-35 and running tests with 10 and 1 p.p.m. solutions.

Table I. Completeness of Adsorption and Desorption Using Activated Carbon

(Figures are in terms of % of ABS in original sample)

Sample	Original ABS Concn., P.P.M.	Adsorption of ABS in Filtrate, %	Recovery, %		Residual on Carbon, %	Total ABS Accounted %
			1st extr.	2nd extr.		
1	10	0.14	88	4.4	3.6	96.1
2	10	0.32	93	3.6	3.9	100.8
3	1	0.39	86	6.1	3.9	96.4
4	1	0.21	88	6.5	3.9	98.6

The data are summarized in Table I. One gram of carbon was shaken with 100 ml. of solution and filtered.

Adsorption is 99.6% complete at both 10 and 1 p.p.m. concentrations. This indicates a distribution between carbon and solution of about 250 to 1. Recovery by desorption was more than 95% in all four cases.

To check a still lower concentration of alkyl benzenesulfonate, and also check results using a carbon column, 20 liters of 0.1 p.p.m. radioactive alkyl benzenesulfonate were passed through a column containing 100 grams of the granular Nuchar C-190. The entire effluent from the column was evaporated to dryness and counted. The residual concentration in the water after adsorption was shown to be 0.1 p.p.b. (99.9% adsorbed). Thus, when passed through a column, the solution is quickly depleted and quantitative adsorption results. Also, recovery by the two extractions of the carbon was again more than 95% complete.

Some collaborators, in testing the carbon adsorption-desorption step by adding known amounts of alkyl benzenesulfonate to samples, have reported as low as 70 to 85% absolute recovery. Calibration curves set up in each laboratory correct for this.

Isolation and Infrared Determination. Concentration by the carbon adsorption-desorption technique yields sufficient alkyl benzenesulfonate for an infrared measurement, but materials that would interfere must first be removed. Treatment with hydrochloric acid hydrolyzes organic sulfates, phosphates, and other similar interferences. Petroleum ether extraction removes the organic fragments from the hydrolysis, hydrocarbons, alcohols, sterols, and other materials more soluble in organic solvents than in aqueous alkali.

Final isolation is best accomplished by extraction into chloroform of an alkyl benzenesulfonate-amine complex. This serves to remove inorganic salts and water-soluble organic material, and converts the alkyl benzenesulfonate to a form suitable for

infrared determination. As the quantitative measurement is made in the 9.5- to 10-micron region and the entire 2- to 15-micron spectrum is used qualitatively, an aliphatic amine is preferable. The 1-methylheptylamine was the most effective of the many tested, and has been adopted in the recommended procedure.

The amount of complex present, when dissolved in either carbon tetrachloride or carbon disulfide, can be determined by measuring absorption at the peaks near 9.6 and 9.9 microns. Good qualitative identification is obtained by use of a smear.

Typical infrared spectra are shown in Figure 1. The distinctive features are the sulfonate absorption at 8 to 8.5 and 9.58 microns, and the substituted benzene ring absorptions at 8.77, 9.90, and 12.04 microns. The triplet at 7.16, 7.27, and 7.34 is characteristic of certain polypropylene side chains.

Figure 2 is a composite photograph showing original and final sample size, the carbon column, an infrared spectrophotometer, and a typical infrared curve.

Cooperative Testing. The infrared procedure has been used in the cooperating laboratories to analyze water samples from the Ohio River below Cincinnati.

Alkyl benzenesulfonate is readily adsorbed on many types of solid material, such as the clay-type silt often suspended in river waters. In fact, on many such samples, the solids contain a much higher concentration than the solution itself. Whether or not this is a factor of importance in the analysis of specific water samples depends on the total amount of solids actually present. Though in most cases the alkyl benzenesulfonate in true solution may be of greater interest, the removal of solids from the several hundred gallons of river water required in this case for a cooperative test of a new analytical procedure was not practical. Consequently, the results reported are the total present in the Ohio River.

Samples were collected by passing the water through carbon columns from a manifold connected to a gasoline-driven pump (see Figure 3). Effluent from the columns was measured to determine sample size. Seven different laboratories analyzed the sample taken Nov. 22, 1955. Results are summarized in Table II.

Calibration curves were prepared in each laboratory by using the entire procedure on alkyl benzenesulfonate in distilled water. Choice of spectral solvent is left to the individual laboratory. Both carbon disulfide and carbon tetrachloride have been used on each peak. With the exception of two unexplained, low results, the values found are in excellent agreement.

In addition to this cooperative sample, a number of the laboratories individually checked the method by determining recovery of alkyl benzenesulfonate added to local river waters. When corrected for the amount already present, at least 95% was accounted for in all cases.

The cooperating organizations also investigated the applicability of a colorimetric conclusion to the infrared procedure. This seemed logical, as the concentration and purification steps in the procedure essentially isolate the alkyl benzenesulfonate from interferences. The sulfonate-amine complex can easily be broken by boiling with aqueous alkali. After the amine had been boiled off, and suitable dilutions made, colorimetric results checked well with the infrared values.

At present, the work of the committee is directed toward finding a referee method suitable for determining alkyl benzenesulfonate in sewage. Preliminary results are promising, but no cooperative samples have yet been analyzed. Another real need is for a short, accurate method suitable for use in water treatment plants.

SUMMARY

The infrared method presented is lengthy, and it is possible that few laboratories engaged in routine water analyses will have the necessary equipment. It does, however, for the first time, permit accurate specific determination of alkyl benzenesulfonate in water. For these reasons, the method will find its

Table II. Ohio River Cooperative Sample

(P.p.m. ABS by infrared method)

Laboratory	Gallons of Sample	Wave Length, μ 9.6 ABS Content, P.P.M.	9.9 ABS Content, P.P.M.
A	34.0	..	0.08
B	37.0	0.15	0.13
C	27.0	0.13	0.15
D	28.5	0.14	0.13
E	56.5	0.06	0.10
F	41.0	0.14	0.15
G	35.0	0.10	0.11

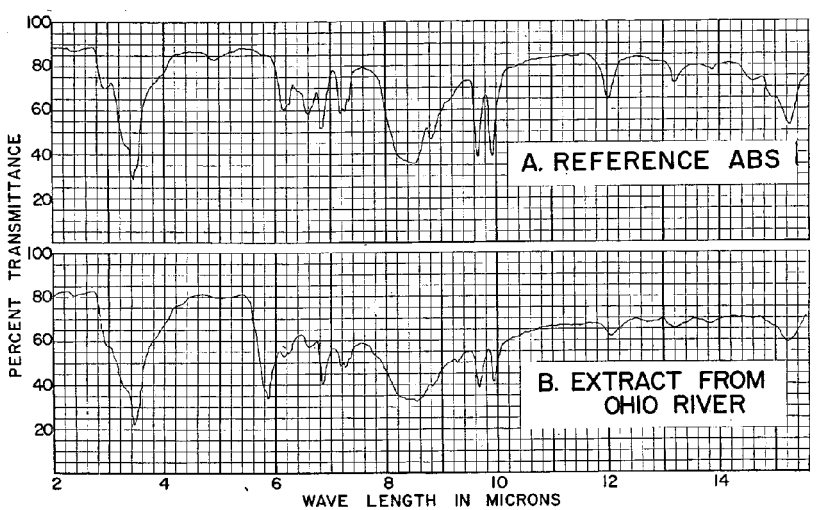

Figure 1. Infrared spectra of alkyl benzenesulfonate–methylheptylamine complex

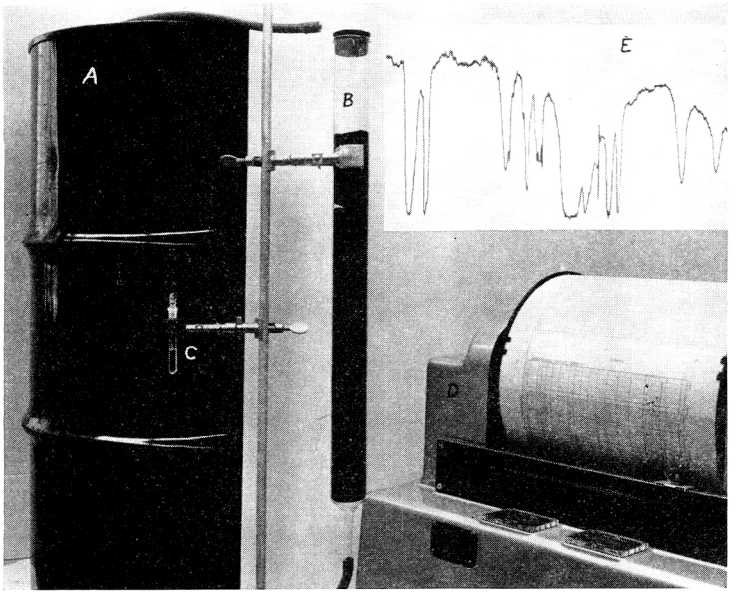

Figure 2. Infrared determination of alkyl benzenesulfonate

A. 50-gallon drum of river water
B. Carbon adsorption column
C. Final sample for infrared measurement
D. Spectrophotometer
E. Typical spectrum

greatest use in running referee analyses and checking the accuracy of proposed short methods.

The steps in the method and the principles behind each can be summarized as follows:

1. Adsorption of ABS on activated carbon (Nuchar C-190). This concentrates the ABS and separates it from many interferences. The technique quantitatively collects the ABS from concentrations as low as a few parts per billion.

2. Desorption from the carbon with alkaline benzene-methanol. At least 95% of the ABS can be recovered in this manner.

3. Acid hydrolysis. This destroys interferences such as organic sulfates, phosphates, and other hydrolyzable substances.

4. Petroleum ether wash. Hydrocarbons, alcohols, and sterols are among the materials removed by petroleum ether extraction from alkaline solution.

5. Amine extraction. The ABS is quantitatively extracted in chloroform as a complex of 1-methylheptylamine, and, thus, is separated from inorganic salts and water-soluble organic material.

6. Infrared determination. Infrared examination after evaporation of the chloroform shows nearly pure ABS-amine complex remaining. A carbon tetrachloride or carbon disulfide solution of this residue can be used for quantitative determination by measuring the absorption at 9.6 and 9.9 microns.

INFRARED METHOD

Most samples studied have contained both solid and liquid phases and the alkyl benzenesulfonate has been highly concentrated on the solids. For accurate analyses, therefore, it is essential that the solids be representatively sampled or excluded.

Special Reagents. Nuchar C-190, unground (obtainable from Industrial Chemical Sales Division, West Virginia Pulp & Paper Co., 230 Park Ave., New York 17, N. Y.). On 30-mesh (U. S. screen), 100%. Impurities in carbon 0.01 maximum.

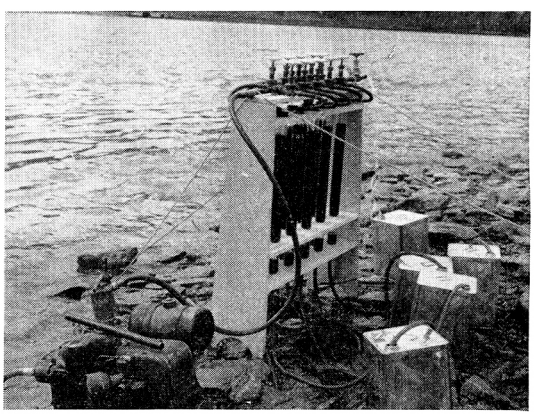

Figure 3. Collection of cooperative samples

Test for Impurities in Carbon. Extract 100 grams of carbon by boiling 1 hour in 500 ml. of thiophene-free benzene plus 500 ml. of methanol. Filter carbon, wash with 100 ml. of methanol, add washings to remainder of solvent mixture, evaporate to dryness on steam bath, and weigh. The residue consists of soluble organic impurities, and should be less than 10 mg. total (not including any residue from solvent).

The solution for extracting carbon is made up of 500 ml. of thiophene-free benzene, 420 ml. of methanol, and 80 ml. of approximately 0.5*N* alcoholic potassium hydroxide.

1-Methylheptylamine, Eastman No. 2439.

The solution for extracting alkyl benzenesulfonate is 400 mg. (20 drops) of 1-methylheptylamine in 400 ml. of chloroform. Prepare fresh daily.

Buffer solution. Dissolve 6.8 grams of potassium dihydrogen phosphate in 1 liter of water. Adjust to pH 6.8 to 6.9 with 25% sodium hydroxide.

Standard ABS for calibration (obtainable from the Association of American Soap & Glycerine Producers, Inc., 295 Madison Ave., New York 17, N. Y.).

Special Equipment. Carbon adsorption tube. Glass column about 2 × 24 inches containing 100 grams of carbon. Stainless steel or brass screens of about 30 mesh divide the carbon into sections of (from the top), 20, 30, 40, and 10 grams (see Figure 4).

Volumetric flasks, 2-ml. or 5-ml.

Glassware must be free of contamination. A thorough rinse with 1 to 1 hydrochloric acid must be used to remove adsorbed ABS.

pH meter.

Büchner funnel, 500-ml., medium porosity, sintered glass.

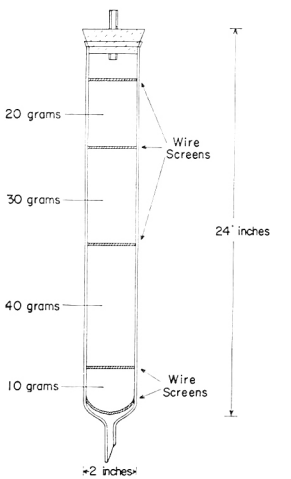

Figure 4. Carbon adsorption tube

Calibration Curve. Place 25 mg. of standard ABS in a 5-gallon glass vessel and dilute with about 4 gallons of distilled water. Mix thoroughly and, using Tygon tubing, siphon the entire solution through the carbon column. Determine the ABS on the carbon as described in the procedure. Repeat with 20, 15, 10, 5, and 0 mg. of ABS. Make two calibration curves by plotting the milligrams of ABS added as the abscissa and the absorbances of the maxima at 9.6 and 9.9 microns as the ordinate. The baseline technique is best used in determining the absorbance of the maxima.

Procedure. Estimate the concentration of ABS present in the sample. Calculate the volume of sample required to supply 10 to 25 mg. of ABS. If 2 liters or less, measure about 10 grams of granular carbon (Nuchar C-190) into a 2-liter glass-stoppered graduated cylinder, add the sample, and shake well for 2 minutes. Filter on a medium-porosity, sintered-glass Büchner funnel. If more than 2 liters of sample is required, pass through the column of the carbon at the rate of 10 gallons or less per hour.

Transfer the carbon from the Büchner funnel or column (treating the sections separately) to porcelain evaporating dishes and dry at 105° to 110° C. Brush the dried carbon from each dish into separate 2-liter bottles or flasks with standard-taper necks and add 1 liter of 1 to 1 benzene-alcohol which is 0.04*N* in potassium hydroxide. Add boiling chips and reflux under an air condenser for 1 hour. Filter with a vacuum through a medium-porosity sintered-glass Büchner funnel, draw off all liquid, release the vacuum, and add 100 ml. of methanol. Stir with a glass rod and draw off the wash with a vacuum. Wash a second time with another 100-ml. portion of methanol. Return the carbon to the flask, add solvent as before, and reflux for 1 hour.

While making this second extraction, evaporate the solvent from the first extract and washes. Carry out this evaporation in a 2-liter beaker on a steam bath. A gentle stream of nitrogen or air on the surface will hasten the evaporation.

Filter off the second extract and wash the carbon as before. Add the extract and washes to the beaker containing the first extract. Discard the carbon. Evaporate sufficiently to combine in one beaker the extracts from the 20-, 30-, and 40-gram sections of the column. Treat the extracts of the 10-gram section separately throughout the entire procedure. After the solvent has been removed, take up the residue in 50 ml. of warm water. Transfer to a 250-ml. standard-taper Erlenmeyer flask. Rinse the beaker with 30 ml. of concentrated hydrochloric acid and add slowly to the flask (carbon dioxide is evolved). Rinse the beaker with 50 ml. of water and combine with other washings in the flask. Reflux under an air condenser for 1 hour.

Remove the condenser and continue boiling until the volume is reduced to 20 to 30 ml., transfer to a steam bath, and evaporate to near dryness (a jet of air directed on the surface of the liquid will greatly aid evaporation). Take the solids up in 100 ml. of water and neutralize with a 5% sodium hydroxide solution to a pH of 8 to 9. Extract once with 50 ml. of petroleum ether (up to 70% ethanol may be added, if necessary, to break emulsions). Wash the petroleum ether twice with 25-ml. portions of water, discard the petroleum ether layer, and add the washes to the aqueous solution. Boil off the alcohol, if it was added.

Cool and transfer quantitatively to a 250-ml. separatory funnel. Neutralize by adding dilute sulfuric acid until just acid to litmus. Add 50 ml. of buffer solution and 2 drops of 1-methylheptylamine and shake vigorously. Add 50 ml. of 1-methylheptylamine–chloroform solution and 25 ml. of chloroform. Shake for 3 minutes and allow the phases to separate. If an emulsion forms, draw off the lower (chloroform) phase including any emulsion, and filter through a plug of glass wool wet with chloroform (using suction if necessary) into a 250-ml. separatory funnel. Draw off the chloroform phase into a 400-ml. beaker, and return any aqueous solution to the first separatory funnel. Wash the glass wool plug with 10 ml. of chloroform and add to the chloroform extract.

Make an additional extraction with 50 ml. of 1-methylheptylamine–chloroform solution and 25 ml. of chloroform. Shake 2 minutes and separate the phases as above, if necessary. Extract a third time with 5 ml. of the amine solution and 45 ml. of chloroform, and a fourth time with 50 ml. of chloroform. Evaporate the combined chloroform extracts on a steam bath. With 10 ml. of chloroform, quantitatively transfer the residue to a 50-ml. beaker using three 5-ml. portions of chloroform as rinses. Evaporate to dryness and continue heating on the steam bath for 30 minutes to remove excess amine. Take up the residue in about 1 ml. of carbon disulfide or carbon tetrachloride and filter through a plug of glass wool in a funnel stem (2-mm. bore) into a 2-ml. or 5-ml. volumetric flask. Dilute to volume through the filter with several rinsings from the beaker.

Transfer a portion of the sample to an infrared cell without further dilution. Run the infrared absorption curve from 9.0 to 10.5 microns against a solvent blank. Measure the absorbance of the 9.6- and 9.9-micron peaks, using base lines from 9.5 to 9.8 and 9.8 to 10.1 microns. From appropriate calibration curves, calculate the concentration of ABS in the original sample. Report the values based on each wave length separately.

Evaporate a 0.5- to 1.0-ml. portion of the ABS solution on a sodium chloride flat. Record the absorption spectrum from 2 to 15 microns for positive qualitative identification of ABS.

The carbon adsorption should be used on all samples, because it separates the ABS from many of the materials present and reduces emulsion difficulties.

From 10 to 50 ml. of water may be lost through a 60 × 1 cm. air condenser during acid hydrolysis. This loss, while not affecting the hydrolysis, reduces the amount of water that needs to be boiled off after removal of the condenser.

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Spectrophotometric Determination of Alkyl Benzenesulfonate Detergents in Surface Water and Sewage

JOHN D. FAIRING and FRANK R. SHORT

Central Research Department, Monsanto Chemical Co., Dayton 7, Ohio

A method for the determination of alkyl benzenesulfonates in surface water and sewage is based upon the isolation of the alkyl benzenesulfonate from interfering materials by solvent extractions of its 1-methylheptylamine salt, and measurement of the isolated benzenesulfonate by an improved methylene blue method. The procedure will measure less than 1 p.p.b. in water and 50 p.p.b. or less in sewage. It is not subject to any known interference from materials likely to be present in surface water or sewage.

A NEED arose for a method for the determination of alkyl benzenesulfonate detergents (ABS) in surface water and sewage which would be accurate, sensitive, reasonably rapid, and capable of general application (*11*). Therefore, this work was undertaken as a part of the collaborative project of the Association of American Soap and Glycerine Producers, Inc. Although the method (*30*) presented on behalf of the association does not favor use of colorimetric methods based on methylene blue, the authors have found that their procedure will measure less than 1 p.p.b. of alkyl benzenesulfonate in water and 50 p.p.b. or less in sewage and is not subject to any known interference from materials likely to be present in surface water or sewage. It is offered for this reason and because it can be used in laboratories which do not have the equipment needed for the infrared procedures.

The generic term alkyl benzenesulfonate, as used in this paper, refers to dodecyl benzenesulfonate and its closely related homologs, unless otherwise noted.

Numerous analytical methods have been proposed for the determination of alkyl benzenesulfonate, the more important of which may be grouped into four classes: (I) colorimetric; (II) volumetric, based upon the titration of alkyl benzenesulfonate with a cationic surface active agent (*1, 7, 8, 18*); (III) ultraviolet (*27*); and (IV) infrared (*17, 28–30*). The colorimetric methods are based upon the formation of the alkyl benzenesulfonate salt of a cationic dye, the extraction of this salt from the sample with an immiscible organic solvent, and the colorimetric determination of the extracted material (*24*). Several cationic dyes have been proposed (*16, 23, 24, 33*), but only methylene blue has found wide acceptance (*6, 9, 13, 15, 19*).

These dye methods have the decided advantage of speed and simplicity, and are the only methods possessing sufficient sensitivity to enable the low concentrations of alkyl benzenesulfonate usually encountered in surface waters to be determined accurately in a sample of reasonable size. They are, or can be made, highly accurate when their use is limited to the determination of alkyl benzenesulfonate in distilled water. However, when they are used with surface water or sewage samples, several sources of error are encountered. In general, all dye methods are subject to the same errors, although their relative magnitudes vary somewhat with the dye and the technique used.

The most serious error is caused by positive interferences—that is, materials other than alkyl benzenesulfonate which form extractable salts with the dye and give rise to high values. Table I shows some of the apparent alkyl benzenesulfonate values obtained by a direct methylene blue analysis of samples known to contain no alkyl benzenesulfonate. While many other positive interferences are known, both organic and inorganic, those shown were chosen as being representative of what might be found in practice. Unless otherwise noted, all methylene blue determinations reported in this paper were made by the improved method described at the end of the procedure.

Significant errors are also introduced by negative interferences, such as proteins and some organic and inorganic cations, which tie up the benzenesulfonate by the formation of complexes or salts (*4, 20, 21, 34*) in such a way that it will not react with methylene blue. As a result, low values are obtained. In Table II are shown some of the recoveries obtained by a direct methylene blue analysis when known amounts of alkyl benzenesulfonate were added to various materials.

Other sources of error also exist, such as the formation of stable emulsions during the extraction, which make the quantitative recovery of the alkyl benzenesulfonate–dye complex difficult or impossible; or the formation of precipitates that adsorb the alkyl benzenesulfonate or its salt.

If the alkyl benzenesulfonate is isolated quantitatively from such interfering materials, then a dye method can be applied without error. Several approaches to the problem were made. Chromatography, using acid alumina as an adsorbent and ammoniacal methanol as an eluent, offered one solution, but, although some promising results were obtained, the rather critical and time-consuming elution technique made it necessary to abandon this approach. Carbon has been reported as an adsorbent for alkyl benzenesulfonate (*12, 28, 30*), but under conditions giving quantitative desorption, the benzenesulfonate is not separated from all interfering materials.

Alkyl benzenesulfonate can be extracted from hydrochloric acid solutions with chloroform (*5*) or ether (*14*), and the present

Table I. Apparent Alkyl Benzenesulfonate Content of ABS-Free Samples

(Positive interferences)

Sample	Apparent ABS Found, P.P.M.	
	Direct methylene blue determinations	Double extraction method
Urine 1	7.1	None
Urine 2	21.1	None
Urine 3	6.3	...
Urine 4	17.1	...
Aqueous extract of straw 1	5.6	None
Aqueous extract of straw 2	0.9	None
Aqueous extract of manure	1.5	...
Aqueous extract of leaves	0.5	...
Aqueous extract of rotted wood	0.4	...
Sulfite waste liquor	14.7	None
Sodium lauryl sulfate, 7.56 p.p.m.	9.3	None
Igepon T-73, 10 p.p.m. (sodium-*N*-methyl-*N*-oleoyl taurate)	6.4	None
Aerosol OT, 10 p.p.m.	7.4	None
Sulfonated castor oil, 30 p.p.m.	6.2	None
Sodium lauryl ether sulfate, 30 p.p.m.	9.8	None
Cholesteryl sulfate, 12 p.p.m.	7.3	None

authors found that it can be extracted from 3.6*N* sulfuric acid with chloroform. In all these cases, however, the protein interference is increased, because reduction of the pH increases the anionic detergent binding power of proteins (*4*).

Sulfonic acids form salts with amines (*2, 3, 25, 26, 35*), and Marron and Schifferli (*22*) have shown that the *p*-toluidine salt of alkyl benzenesulfonate can be extracted from an aqueous solution with carbon tetrachloride. However, it was found that this extraction did not overcome the effect of negative interferences. While aromatic amines have been used in almost all of the published work on sulfonic acids, Smith and Page (*32*) used long-chain tertiary aliphatic amines (such as methyldioctylamine) for the extraction of strong acids from aqueous solutions.

The problem was to find an amine and a solvent that would permit the quantitative extraction of alkyl benzenesulfonate in the presence of negative interferences, and, at the same time, isolate the alkyl benzenesulfonate from positive interferences. Several amine-solvent combinations were found which would accomplish one of these tasks, but none that would do both satisfactorily. Therefore, two amine-solvent combinations were used in the procedure: the first to remove the alkyl benzenesulfonate from negative interferences, the second to isolate it from positive interferences. Consequently, this method has been termed the double extraction procedure. Of the amines tested, 1-methylheptylamine proved to be the best for both extractions.

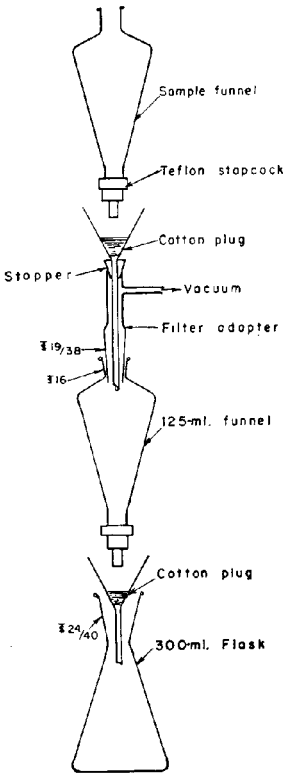

Figure 1. Apparatus used for extraction when emulsions form in sample

Table II. Recovery of Added Alkyl Benzenesulfonate by Direct Methylene Blue Determinations

(Negative interferences)

Sample	ABS, P.P.M. Apparent original content	Added	Total found	Added ABS Recovered, P.P.M.	Recovery of Added ABS, %
Surface water, 1	0.861	1.132	1.913	1.052	92.9
Surface water, 11	0.0	2.0	1.5	1.5	75
Raw sewage, 2	5.24	4.81	9.40	4.16	86.5
Aqueous extract of straw 1	5.6	9.6	12.1	6.5	68
Urine 1	7.1	21.8	25.8	18.7	86
Aqueous extract of manure	1.5	5.0	5.5	4.0	80
Aqueous extract of rotted wood	0.4	5.0	4.9	4.5	90
Albumin solution, 40 p.p.m.	0.00	1.00	0.70	0.70	70
Albumin solution, 10 p.p.m.	0.00	1.00	0.88	0.88	88
Gelatin solution, 23 p.p.m.	0.00	1.20	1.00	1.00	83

APPARATUS

Glass-stoppered separatory funnels, 125 ml. and larger, with Teflon stopcocks. All must be Desicoted. Separatory funnels used for the methylene blue determination must be kept separate from the others, and may have glass instead of Teflon stopcocks.

Filter adapter (Figure 1), fabricated from a standard-taper 19/38 male joint, 9-cm. over-all length, with a 3.5-cm. length of 7-mm. tubing sealed to it 2 cm. from the top.

All-glass wash bottles for solvents.

REAGENTS

Amine-chloroform solution. Mix 0.10 to 0.15 ml. of 1-methylheptylamine in 100 ml. of reagent grade chloroform. Make fresh daily.

Amine-hexane solution. Mix 0.10 to 0.15 ml. of 1-methylheptylamine in 100 ml. of commercial grade *n*-hexane. Make fresh daily.

Ammoniacal methanol. Concentrated ammonium hydroxide, 1% in redistilled methanol. Make fresh daily.

Buffer, pH 7.5. Dissolve 27.2 grams of potassium dihydrogen phosphate in 800 ml. of water, adjust to pH 7.5 with 25% sodium hydroxide, and make up to 1 liter with water. Add 10 ml. of chloroform as a preservative.

Buffer, pH 4.8. Dissolve 105 grams of citric acid monohydrate and 15 grams of sodium hydroxide in 800 ml. of water, adjust to pH 4.8 with 25% sodium hydroxide, and make up to 1 liter with water. Add a 2- to 5-mm. layer of hexane as a preservative.

Methylene blue solution. Dissolve 0.25 gram of methylene blue in 100 ml. of water, heat on a steam bath for 30 minutes, make up to 250 ml. with water, and filter into a brown glass bottle.

Desicote, green label, from Beckman Instruments, Inc., or Fisher Scientific Co.

PROCEDURE

Amine-Chloroform Extraction. Place in a separatory funnel of the smallest suitable size a well-mixed sample of not over 150 ml. of sewage or 1.5 liters of water containing 5 to 200 γ of alkyl benzenesulfonate; the optimum is 50 to 100 γ. (If desired, water samples up to 10 liters or more in volume may be made alkaline, about pH 9, with sodium hydroxide, boiled down to between 50 and 200 ml., transferred to the separatory funnel, and neutralized with sulfuric acid.) Dilute with water to 70 ml. or more. Add 5 ml. of pH 7.5 buffer plus 1 ml. for every 100 ml. of solution. Extract for 2 minutes with 25 ml. of amine-chloroform solution, plus 25 ml. of chloroform if the aqueous volume is greater than 250 ml. Swirl or stir to break the emulsion, and filter the chloroform extract through a chloroform-wetted cotton pledget into a 300-ml. Erlenmeyer flask with a 24/40 ground joint. If persistent emulsions form, filter through chloroform-wetted cotton into a 125-ml. separatory funnel, using the apparatus shown in Figure 1. Apply suction, if required, by means of a rubber bulb attached to the side arm of the filter adapter. Drain the chloroform from the lower funnel into the flask. Return any aqueous phase to the original funnel. Rinse the solution in the funnel twice with 15- to 20-ml. portions of chloroform without shaking, and filter into the flask.

Repeat the extraction and rinsing. Add to the flask 35 ml. of water, 3 drops of pH 7.5 buffer, and glass boiling beads. Attach a short (110 × 18 mm.) air condenser, boil off most of the chloroform, and then remove from the heat. Repeat the extraction and rinsing of the sample two additional times and collect the

extracts in the flask. Replace the condenser and boil off most of the chloroform. Rinse the condenser and flask walls with 5 to 10 ml. of chloroform, then heat until all the chloroform has evaporated and the aqueous solution has boiled 1 minute or more. Remove the air condenser, rinse it into the flask with 10 to 15 ml. of water, add 5 drops of 25% sodium hydroxide, cover the flask with a Short and Good special cover glass (*31*), and boil until the volume has been reduced to 15 to 20 ml. Add water if necessary to enable boiling for at least 5 minutes.

Acid Hydrolysis. Rinse the cover glass into the flask with 5 ml. of water, add 5 ml. of hydrochloric acid, and attach a long (500 × 8 mm.) air condenser. Reflux for 1 hour, keeping the condensate below the middle of the condenser. Cool and rinse the condenser with 15 ml. of 1% sodium hydroxide, draining it into the flask. Remove the air condenser and rinse it into a 600-ml. beaker with 15 to 20 ml. of ammoniacal methanol. Add 1 ml. of 1% sodium hydroxide to the beaker and reserve for later use.

Amine-Hexane Extraction. Add 1 drop of 1% phenolphthalein solution to the flask, make alkaline by dropwise addition of 25% sodium hydroxide, cool, acidify with 10% sulfuric acid, then make just alkaline with 1% sodium hydroxide. Transfer the solution to a 125-ml. separatory funnel containing 3 to 4 drops of 1% sulfuric acid, and rinse in with water to a total volume of 60 to 75 ml. Adjust to pH 4 to 6 (indicator paper) with 1% sulfuric acid or sodium hydroxide, add 2 ml. of pH 4.8 buffer, and extract for 2 minutes with 25 ml. of amine-hexane solution. Drain the aqueous phase into a second 125-ml. separatory funnel and the hexane into a Desicoted 150-ml. beaker. Rinse the funnel into the beaker with 15 to 20 ml. of hexane. Extract the aqueous phase with 25 ml. of hexane, draw off the aqueous phase into the first funnel and the hexane into the beaker, rinsing in as before.

Decant the hexane from the 150-ml. beaker into the 600-ml. beaker into which the condenser was rinsed, taking care not to transfer any aqueous droplets. Rinse the 150-ml. beaker twice with 10- to 15-ml. portions of hexane and decant the hexane into the large beaker. Rinse the 150-ml. beaker into the first separatory funnel with 5 ml. of water.

Repeat the extraction and rinsing of the solution in the separatory funnel two additional times, using 25 ml. of amine-hexane solution for the first and 25 ml. of hexane for the second extraction, and collect the extracts in the 150-ml. beaker previously used. After the last extraction discard the aqueous phase instead of collecting it in a separatory funnel. Decant the hexane from the 150- to the 600-ml. beaker and rinse with hexane as before. Shake out and discard any aqueous droplets in the small beaker. Rinse the 150-ml. beaker into one of the separatory funnels with 15 ml. of ammoniacal methanol, swirl for a few seconds to wash the sides, then drain into the large beaker. Rinse the separatory funnel with 10 ml. of ammoniacal methanol, then with 15 ml. of water. Repeat the above rinsing procedure using the other separatory funnel. Add all rinsings to the 600-ml. beaker. Finally, rinse the 150-ml. beaker into the large beaker with 15 ml. of water.

Stir the solution in the large beaker, add boiling beads, cover with a Speedyvap beaker cover (Fisher Scientific Co.), and boil off the hexane in a steam bath, then boil down to 20 to 30 ml. on a hot plate. Rinse cover and stirring rod into beaker with 20 to 30 ml. of water, cover again, and boil down to 25 to 40 ml. Cool to room temperature and determine alkyl benzenesulfonate by the following modified methylene blue method.

Methylene Blue Determination. Transfer the solution to a 125-ml. separatory funnel containing 2 ml. of 10% sulfuric acid, and rinse in with water to make a total volume of 85 ml. Add 1 ml. of methylene blue solution, swirl, and extract for 1 minute with 15 ml. of chloroform. Let stand for 1 minute, swirl, let stand for 2 minutes, and drain the chloroform into a second 125-ml. separatory funnel. Rinse the first funnel with 5 ml. of chloroform without shaking and drain the chloroform into the second funnel. Repeat the extraction two additional times. Add 55 ml. of 0.05% sulfuric acid to the second separatory funnel, shake 1 minute, let stand 1 minute, swirl, and let stand 2 minutes. Filter the chloroform through a plug of chloroform-wetted cotton into a 100-ml. Desicoted volumetric flask. Rinse the aqueous solution with 5 ml. of chloroform and filter the chloroform into the volumetric flask. Add 10 ml. of chloroform to the second separatory funnel, shake 30 seconds, let stand for 2 minutes, and filter the chloroform into the volumetric flask. Rinse the aqueous solution with 5 ml. of chloroform and filter the chloroform into the flask, then rinse the filter into the flask with 10 to 15 ml. of chloroform. Dilute the solution in the flask to volume with chloroform, mix well, transfer to a Desicoted spectrophotometer cell, and stopper. Do not rinse the cell with sample. After 5 to 20 minutes, measure the absorbance at 650 mμ, using chloroform as a reference solution. The solution may be stored in the volumetric flask or stoppered spectrophotometer cell for at least 2 hours before the absorbance measurement is made if it is kept in the dark.

Table III. Recovery of Added Alkyl Benzenesulfonate by Double Extraction Method

Sample	ABS, P.P.M. Original content	Added	Total found	Added ABS Recovered, P.P.M.	Recovery of Added ABS, %
Surface water					
1	0.654	1.132	1.781	1.127	99.6
2	0.077	0.197	0.272	0.195	99.0
3	1.06	1.972	3.024	1.964	99.6
4	0.064	0.050	0.114	0.050	100.0
5	0.76	0.986	1.742	0.982	99.6
6	0.00472	0.00962	0.01428	0.00956	99.4
				Av.	99.5 ± 0.2
				Std. dev.	±0.3
Raw sewage					
1	3.83	6.61	10.47	6.64	100.5
2	4.22	4.81	9.00	4.78	99.4
3	2.94	9.46	12.30	9.36	98.9
4	6.77	2.85	9.60	2.83	99.3
Sewage effluent	3.24	2.86	6.11	2.87	100.3
				Av.	99.7 ± 0.6
				Std. dev.	±0.7
Urine 1	0.00	21.8	21.7	21.7	99.5
Mixture 1[a]	0.00	10.88	10.82	10.82	99.5
Mixture 2[a]	0.00	9.72	9.64	9.64	99.2
All samples, av.					99.6 ± 0.3
Std. dev.					±0.5

[a] Table IV lists composition.

Table IV. Composition of Mixtures Tested for Interference with Double Extraction Method

Substance	Concentration, P.P.M. Mixture 1	Mixture 2
SO_4^{--}	500	300
SO_3^{--}	200	50
S^{--}	100	10
NO_3^-	500	200
NO_2^-	200	50
Cl^-	856	1150
Br^-	50	10
F^-	5	2
I^-	20	5
HCO_3^-	500	300
PO_4^{---}	9500	9500
Ca^{++}	100	50
Fe^{+++}	100	25
Mg^{++}	100	25
NH_4^+	100	50
Na^+	2100	1432
K^+	3900	3900
Soap	100	10
Nonionic detergent	20	10
Sodium lauryl sulfate	20	10
Albumin	50	10
Aqueous extract of straw	5000[a]	1000[a]
Sodium tripolyphosphate	100	10
Urine	20000	5000

[a] Calculated on dry weight of straw used.

Table V. Comparison of Alkyl Benzenesulfonate Values Obtained by Double Extraction and Infrared Determinations

Sample	ABS Found, P.P.M. Double extraction	Infrared	Infrared, % of Double Extraction Value
Surface water 9	1.19	1.20[a]	100.8
Surface water 10	0.148	0.144[b]	97.3
Raw sewage 5	11.07	11.0[a]	99.4
Raw sewage 6	12.00	11.9[c]	99.2
		Av., all samples	99.2

[a] Double extraction used to isolate ABS.
[b] Carbon adsorption, KOH-MeOH-C_6H_6 desorption, etc., used to isolate ABS.
[c] Carbon adsorption, NH_4OH-MeOH-C_6H_6 desorption, etc., used to isolate ABS.

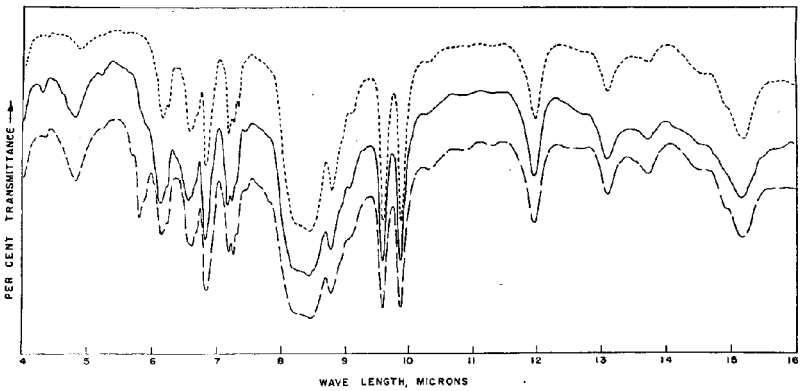

Figure 2. Infrared absorption spectra of 1-methylheptylamine salts of alkyl benzenesulfonate

• • • • • Standard tetrapropylbenzenesulfonic acid
———— ABS isolated from surface water 9 by double extraction procedure; sufficiently large sample taken for infrared determination
— — — ABS isolated from raw sewage 5 by double extraction procedure; sufficiently large sample taken for infrared determination

Subtract the absorbance of the blank (obtained by analyzing a sample of distilled water by the complete double extraction procedure described above) from that of the sample to obtain the net absorbance. From a standard curve convert net absorbance to weight of alkyl benzenesulfonate.

Standard Curve. Prepare the standard curve by analyzing known amounts of alkyl benzenesulfonate from 0 to 300 γ by the methylene blue method described above. Plot the net absorbance obtained against the weight of alkyl benzenesulfonate (*18*). Beer's law is obeyed.

DISCUSSION

This method, designed to attain the highest possible accuracy, requires about 3 hours for one sample and 30 minutes for each additional sample, the exact time depending upon the skill of the analyst and the physical setup available. Although the technique is not difficult, it requires some practice before satisfactory results are obtained, and, until the analyst has become familiar with the method, erratic blanks and recoveries may be expected.

The method recovers all of the alkyl benzenesulfonate in a sample and no correction factor is to be applied. It is essential that each chemist test the method by analyzing known amounts of the material in distilled water. The results should be at least 98% of those obtained by a direct methylene blue analysis of the same amounts of alkyl benzenesulfonate. If this recovery is not obtained, either the reagents or the techniques are at fault, and the trouble must be eliminated before proceeding with the analysis of any sample. The recovery must be checked with every lot of hexane and of 1-methylheptylamine; if it is low, reject the reagent.

A distilled water blank must also be carried through the entire procedure by each chemist, and should be equivalent to less than 8 γ of alkyl benzenesulfonate. Higher blanks indicate either impure reagents (most probably methanol or hexane) or improper preparation of the glassware. This blank must be redetermined for every lot of methanol and hexane. Methanol producing a high blank can be purified by distilling in all-glass apparatus, but hexane yielding a blank in excess of 8 γ is unfit for use.

None of the reagents or solvents may be stored in polyethylene ware.

All Desicoted glassware must be cleaned after applying Desicote by rinsing with 0.2% alkyl benzenesulfonate solution, then washing as described below before being used the first time. It must be re-Desicoted after every 50 to 75 analyses.

Glassware should be cleaned after use by washing with hot water, methanol, hot water, distilled water and acetone, and then drying. Contact between strong acids and the glassware used for the methylene blue determination may cause a 20-fold increase in the adsorption of the alkyl benzenesulfonate–dye salt on the walls of the apparatus. Alkalies will remove Desicote; consequently, care must be taken when transfering alkaline solutions into Desicoted apparatus. It is for this reason that the neutralization of the sample after acid hydrolysis is performed as indicated. As there is danger of loss of the benzenesulfonate by adsorption from acid solution onto glass, all transfers must be made in neutral or slightly alkaline media.

A value of 100 γ of alkyl benzenesulfonate has been stated to be the optimum for an analysis. This is based upon the use of a spectrophotometer and sample cell that yield an absorbance between 0.4 and 0.6 with 100 γ of alkyl benzenesulfonate. Should the instrument and cell being used yield significantly different figures, adjust the sample size for an optimum amount of alkyl benzenesulfonate that gives an absorbance of 0.5.

The use of a spectrophotometer (as contrasted with a filter colorimeter) is highly recommended, and is essential for achieving the highest accuracy. The absorption peak of the alkyl benzenesulfonate–methylene blue salt in chloroform is very sharp, and the narrow band width of a spectrophotometer is required to achieve high sensitivity. Because of this sharp absorption peak it is important to use a constant slit width. For example, with the same sample cell, the absorbance of a chloroform solution of the methylene blue salt of alkyl benzenesulfonate, when measured with a filter photometer using a 650-mμ filter, was only 49.6% of that obtained with a Beckman Model B spectrophotometer at 650 mμ and a slit width of 0.33 mm.

The methylene blue salt of alkyl benzenesulfonate purified by the double extraction method is stable in normal room light for over 2 hours, and in the dark for at least 100 hours.

Alkyl benzenesulfonate in surface water and sewage is subject to bacteriological degradation (*10*); therefore, samples should be analyzed within a few hours of collection. The addition of 0.2 to 0.4% by volume of chloroform and refrigeration at 4° to 10° C. will permit storage of samples for at least 2 weeks without loss of the benzenesulfonate.

Alkyl benzenesulfonate is adsorbed on any suspended solids or sediment present to such an extent that, generally, its concentration on the solids will be much greater than that in the

Table VI. Effect of Sample Size and Concentration

Ml. of Surface Water 1	Concentration or Dilution before Extraction	ABS Found, P.P.M.
85	None	0.654
85	Diluted to 850 ml.	0.654
850	None	0.650
850	Evaporated to 85 ml.	0.654

solids-free sample. It is essential, therefore, that the sample be well mixed and that the solids be representatively included in the portion taken for analysis if a true value is to be obtained. For example, of the 4.22 p.p.m. of alkyl benzenesulfonate found in a sample of raw sewage, 26.8% was adsorbed on the solids. This corresponds to a concentration of 4708 p.p.m. based upon the dry weight of the centrifuged solids.

The validity of the double extraction method has been proved in six ways: (1) by the complete recovery of alkyl benzenesulfonate added to various surface water and sewage samples and to a variety of substances known to interfere with the methylene blue determination; (2) by the elimination of the methylene blue interference caused by materials likely to be present in natural samples; (3) by the infrared characterization and measurement of the alkyl benzenesulfonate isolated from surface water and from sewage by the double extraction technique; (4) by the agreement obtained between the double extraction method and independent infrared determinations; (5) by the failure to recover additional quantities of alkyl benzenesulfonate from surface water or sewage samples by extended treatments; and (6) by the study of the precision of the method and the effect of variables upon the results obtained.

Table III shows the results of the analysis of several samples of surface water, sewage, and other materials before and after adding known amounts of alkyl benzenesulfonate between 40 and 100 γ. Mixtures 1 and 2, whose compositions are given in Table IV, caused no significant interference, either positive or negative. All double extraction values reported herein were calculated from a calibration curve prepared by direct methylene blue determinations of standard alkyl benzenesulfonate solutions (*18*), and no correction factors were used or needed.

The comparison of the results obtained by direct methylene blue determinations and by double extraction analyses of alkyl benzenesulfonate-free materials as listed in Table I demonstrates the ability of the method to eliminate positive methylene blue interferences. The method is specific for alkyl benzenesulfonates rather than for total anionic surfactants.

All water and sewage samples investigated contained alkyl benzenesulfonate and it was desirable to prove that these initial concentrations found by the double extraction method were true values and not due to the failure of the method to separate the alkyl benzenesulfonate from materials that would interfere with the final methylene blue determination.

Confirmation that these initial values were correct was obtained by infrared measurements of the alkyl benzenesulfonate found in samples of surface water and of raw sewage. Table V gives the result obtained by the double extraction method and by infrared measurements. Three different methods were used in obtaining the infrared figures. Surface water 9 and raw sewage 5 were analyzed by applying the technique of the double extraction procedure to a large volume of sample and measuring the isolated alkyl benzenesulfonate by the infrared absorption of its 1-methylheptylamine salt in carbon disulfide at 9.6 and 9.9 microns. Film spectra of these samples and of the 1-methylheptylamine salt of tetrapropylbenzenesulfonic acid are shown in Figure 2. The excellent agreement between the spectra at the characteristic wave lengths of 8.8, 9.6, 9.9, and 12.0 microns confirms the identification of the isolated material as alkyl benzenesulfonate.

Surface water 10 was analyzed by the infrared method developed by the cooperating laboratories of the Association of American Soap and Glycerine Producers, Inc. (*30*). Raw sewage 6 was analyzed by a modification of this infrared method. The alkyl benzenesulfonate was adsorbed from the sewage onto carbon, then quantitatively eluted from the carbon at room temperature with a 1% solution of ammonium hydroxide in a mixture of equal parts of methanol and benzene. The eluted material was hydrolyzed by refluxing with hydrochloric acid, and the alkyl benzenesulfonate isolated from the hydrolyzate by extraction with a chloroform solution of 1-methylheptylamine. Measurement was made of the infrared absorption of a solution of the 1-methylheptylamine salt of the isolated benzenesulfonate in carbon disulfide.

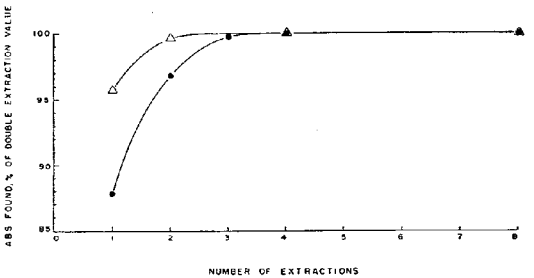

Figure 3. Efficiency of amine-chloroform extractions

● Surface water 1
△ Raw sewage 2

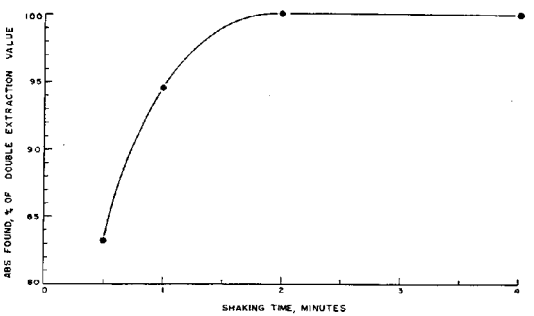

Figure 4. Effect of shaking time on recovery of alkyl benzenesulfonate by four amine-chloroform extractions

By using a desorbing solvent containing ammonium hydroxide, quantitative recovery of the alkyl benzenesulfonate from the carbon is obtained, and the desorption can be carried out without the use of heat, thus reducing the amount of extraneous matter extracted with the alkyl benzenesulfonate.

The infrared measurements proved that the material isolated from surface water and sewage by the double extraction method is actually alkyl benzenesulfonate, while the addition-recovery experiments indicate that the method recovers all of the alkyl benzenesulfonate in the sample. As further proof of this latter point, attempts were made to extract additional alkyl benzenesulfonate from several samples of surface water and sewage by such means as boiling the sample in alkaline solution, boiling the

Table VII. Comparison of Alkyl Benzenesulfonate Values Obtained by Various Treatments of Water and Sewage Samples

Treatment Prior to Methylene Blue Determination	Surface Water 1			Raw Sewage 2		
	ABS Found		Recovery of 1.132 p.p.m. ABS added to sample, %	ABS Found		Recovery of 4.81 p.p.m. ABS added to sample, %
	P.p.m.	% of double extraction value		P.p.m.	% of double extraction value	
None (direct methylene blue)	0.861	131.7	92.9	5.24	124.2	86.5
Amine-$CHCl_3$ extraction	0.809	123.7	100.0	5.38	127.5	100.0
Acid hydrolysis	0.986	150.8	86.5	5.12	121.3	79.0
Amine-hexane extraction	0.616	94.2	88.5	4.60	109.0	82.7
Amine-$CHCl_3$ extraction, acid hydrolysis	0.859	131.3	100.0	5.02	119.0	99.8
Acid hydrolysis, amine-$CHCl_3$ extraction	0.833	127.4	99.4	4.86	115.2	99.0
Amine-hexane extraction, acid hydrolysis	0.602	92.0	89.4	3.88	91.9	83.6
Acid hydrolysis, amine-hexane extraction	0.522	79.8	72.6	3.54	83.9	73.6
Amine-$CHCl_3$ extraction, amine-hexane extraction	0.732	111.9	99.7	4.98	118.0	99.8
Amine-hexane extraction, amine-$CHCl_3$ extraction	0.612	93.6	87.7	4.66	110.4	81.9
Amine-$CHCl_3$ extraction, acid hydrolysis, amine-hexane extraction (double extraction)	0.654	100.0	99.6	4.22	100.0	99.4

sample with alkaline methanol, and extracting the solids with hot ammonium hydroxide in methanol, and with a hot chloroform solution of 1-methylheptylamine. In all cases, no additional alkyl benzenesulfonate could be found.

The sum of the values obtained by the double extraction method applied to the supernatant of centrifuged surface water and sewage samples and to the ammoniacal methanol extract of the isolated solids has been found to be equal to the results obtained by a double extraction analysis of the unseparated sample. Furthermore, a constant value was obtained when both the sample volume and concentration were varied independently, as shown in Table VI. Therefore, it is believed that the double extraction procedure accurately determines the true alkyl benzenesulfonate content of surface water and sewage.

Replicate determinations made by the same or different chemists on eight water and sewage samples containing from 40 to 110 γ of alkyl benzenesulfonate had a standard deviation of ± 0.3 γ. For sewage the standard deviation was ± 22 p.p.b. and for surface water, ± 0.4 p.p.b.

Table VII shows the effect of various treatments on the removal of interferences and on the recovery of alkyl benzenesulfonate from water and sewage. Only the combination of an amine-chloroform extraction, acid hydrolysis, and amine-hexane extraction, in that order, removes all positive interferences and quantitatively recovers the alkyl benzenesulfonate. From the data shown and from other experiments, it has been demonstrated that any change from the specified arrangement of the three steps introduces errors.

In the double extraction method the negative interferences are eliminated by extracting the sample at pH 7.5 with a chloroform solution of 1-methylheptylamine. The amine salt of alkyl benzenesulfonate is extracted together with some, but not all, of the positive interferences. This extraction is somewhat selective, but it is not known with certainty just where the dividing line lies between extractable and non-extractable materials. Alkyl benzenesulfonates with a chain length of C_{10} or longer and alkyl sulfates of C_{12} and longer are extracted, while inorganic ions and *p*-toluenesulfonic acid are not. In Figure 3 the efficiency of the amine-chloroform extraction is shown. Although over 99% of the alkyl benzenesulfonate was recovered from surface water 1 by three amine-chloroform extractions, and from raw sewage 2 by two extractions, other water and sewage samples have required the four extractions specified in order to obtain 99% recovery. In Figure 3, as in the following ones, each point on the curve was arrived at independently using the double extraction procedure as described except for the variable under consideration. The values obtained are plotted as the percentage of the alkyl benzenesulfonate found by the complete double extraction procedure.

Table VIII. Effect on Direct Methylene Blue Determination of Washing Chloroform Extract

Sample	Apparent ABS Found, P.P.M.		
	0.05% H_2SO_4 wash	Water wash	No wash
Surface water 1	0.86	0.91	1.02
Raw sewage 2	5.24	5.72	6.38
Urine 2	21.1	25.0	...
Urine 3	6.3	7.6	35.5
Urine 4	17.1	19.9	49.8
Aqueous extract of straw 1	5.6	6.1	7.8
NO_3^-, 67 p.p.m.	0.00	0.00	0.33
NO_3^-, 200 p.p.m.	0.00	0.00	0.96
CNS^-, 20 p.p.m.	0.00	0.10	2.21

The effect of varying the shaking time during the amine-chloroform extraction is illustrated in Figure 4, which shows that the 2-minute period specified is as short as practicable.

The extracted alkyl sulfates, together with some of the other positive interferences, are destroyed by hydrolysis with hydrochloric acid. Figure 5 shows that refluxing for 1 hour is required to destroy all hydrolyzable interferences. Increasing the strength of the hydrochloric acid to three times the specified value caused no further reduction in the alkyl benzenesulfonate value.

The alkyl benzenesulfonate is extracted at pH 4.8 from the remaining positive interferences with a hexane solution of 1-methylheptylamine. Hexane acts as a highly selective solvent and probably does not remove alkyl benzenesulfonates with a chain length shorter than C_8. Here again, the critical chain length is not known with certainty.

The alkyl benzenesulfonate–amine salt is readily adsorbed from a hexane solution onto almost any surface; therefore, care must be taken during the hexane extraction step. The extract should not come into contact with anything other than the specified glassware, and under no conditions may it be filtered. Even with Desicoted glassware some adsorption will occur, and an ammoniacal methanol wash is required to obtain complete recovery.

The efficiency of the amine-hexane extraction is demonstrated in Figure 6. Curve *A* indicates the total amount of alkyl benzenesulfonate removed by the amine-hexane extraction and by the ammoniacal methanol rinse of the glassware, while the amount of alkyl benzenesulfonate in the amine-hexane extract alone is shown by curve *B* and in the ammoniacal methanol rinse by curve *C*. Each point was measured independently; note that the sums of the values of curves *B* and *C* equal those of curve *A*.

Alternate amine-hexane and hexane extractions are necessary to prevent the pH of the aqueous solution from rising to a point where the extraction becomes inefficient.

The isolated alkyl benzenesulfonate is determined spectrophotometrically by an improved methylene blue method that permits the attainment of the high accuracy of which the double extraction method is capable. This modified methylene blue method differs from those in general use by employing Desicoted glassware throughout and by using a 0.05% sulfuric acid wash of the chloroform extract of the alkyl benzenesulfonate–dye salt (*13*).

Desicoting greatly reduces the adsorption of the alkyl benzenesulfonate–methylene blue salt on the surfaces of the glassware. A 100-ml. un-Desicoted volumetric flask adsorbs the equivalent of 4 to 14 γ of the benzenesulfonate from 100 ml. of a chloroform solution containing the methylene blue salt of 100 γ of alkyl benzenesulfonate. The exact amount adsorbed is variable and depends upon the previous treatment and method of washing of the glassware. A similar flask after Desicoting adsorbs less than 0.4 γ of alkyl benzenesulfonate. This reduction in adsorption results in a higher precision in the determinations. Replicate methylene blue determinations of 100 γ of alkyl benzenesulfonate in distilled water using un-Desicoted glassware gave an average deviation of ± 3.9 γ and a standard deviation of ± 5.2 γ, while with Desicoted glassware both the average and standard deviations were ± 0.1 γ.

The 0.05% sulfuric acid wash of the chloroform extract of the alkyl benzenesulfonate–methylene blue salt reduces the effect of interferences. Table VIII illustrates this effect. Although the double extraction method removes all known interferences before the methylene blue determination is made, the use of the acid wash reduces the magnitude of the blank and acts as a safeguard against any residual amount of interference.

In Table IX the results obtained by the double extraction method and by direct methylene blue determinations are compared, and the magnitude of the errors in the latter method is indicated.

The two extractions, together with the acid hydrolysis, isolate all of the alkyl benzenesulfonate from positive and negative

Table IX. Comparison of Alkyl Benzenesulfonate Values Obtained by Double Extraction and Direct Methylene Blue Methods

Sample	Double Extraction, P.P.M. ABS	Direct Methylene Blue Determinations, Apparent ABS P.p.m.	Error, %
Surface water			
1	0.654	0.861	31.7
2	0.077	0.09	16.9
3	1.06	1.31	23.6
4	0.064	0.08	25.0
5	0.76	0.89	17.1
6	0.00472	0.0082	73.7
7	1.40	1.79	27.9
8	0.77	0.92	19.5
9	1.19	1.49	25.2
10	0.148	0.20	35.1
Raw sewage			
1	3.83	4.42	15.4
2	4.22	5.24	24.2
3	2.94	3.96	34.7
4	6.77	8.87	31.0
5	11.07	13.2	19.2
6	12.00	13.4	11.7
7	5.33	6.54	22.7
8	2.93	3.60	22.9
Sewage effluent	3.24	4.07	25.6
		Av.[a]	23.9±5.1

[a] Surface water 6 omitted.

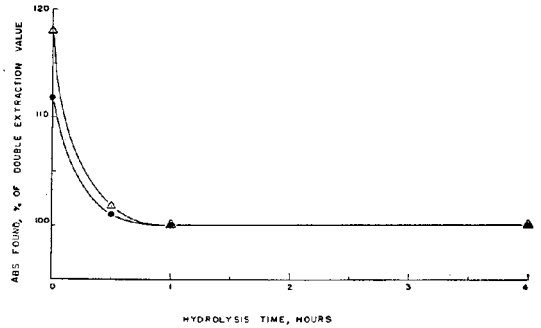

Figure 5. Effect of acid hydrolysis time on destruction of interferences

● Surface water 1
△ Raw sewage 2

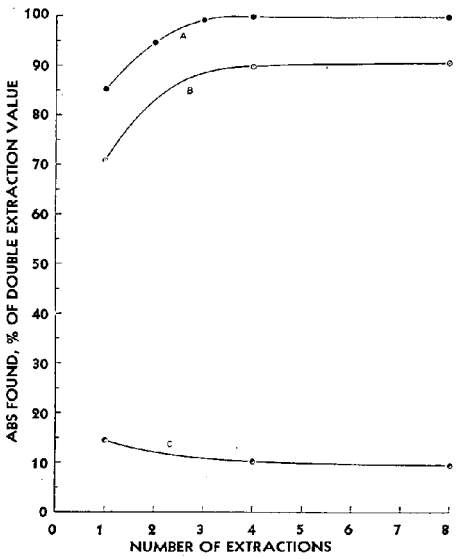

Figure 6. Efficiency of amine-hexane extractions

A. Total ABS in hexane extract and ammoniacal methanol rinse
B. ABS in hexane extract
C. ABS in ammoniacal methanol rinse

methylene blue interferences likely to be encountered in surface water and sewage, as well as from inorganic ions; but they do not isolate it from all other noninterfering materials. Fatty acids, nonionic detergents, and materials extractable by chloroform at pH 7.5 and by hexane at pH 4.8 will accompany the alkyl benzenesulfonate. Although such materials cause no error in this method, the possibility of their presence must be recognized if an attempt is made to use the extraction technique for other purposes.

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Direct Spectrophotometric Determination of Small Amounts of Chloride

PHILIP W. WEST and HANS COLL

Coates Chemical Laboratories, Louisiana State University, Baton Rouge, La.

There has long been a great need for a direct spectrophotometric method for the determination of small amounts of chloride. Such a procedure is now proposed, based on the use of iron(III) perchlorate. Chloro complexes of iron(III) exhibit an intense absorption band in the vicinity of 340 mμ and lend themselves to quantitative measurement. The proposed procedure is accurate and relatively free from interferences. Large amounts of sulfate tend to interfere. However, the method can be used in the presence of the other halides and practically all other common ions.

FOR some time it has been known that iron(III) is not yellow, as popularly believed, but instead is essentially colorless. The yellow color attributed to iron(III) is actually due (*3*) to chloro or hydroxo complexes of iron. The light-absorption properties of the chloro complexes suggested the possibility of using chloride-free iron as a reagent for the colorimetric estimation of chloride and the present report summarizes the results of an investigation undertaken to ascertain the validity of a direct spectrophotometric procedure based on such an approach.

Although iron(III) chloro complexes absorb radiant energy in the visible portion of the spectrum, the greatest absorption is in the ultraviolet. It was found that the intensity of the absorption band exhibited by the complex around 350 mμ depends largely on the amount of acid present. For reasons of sensitivity it was, therefore, desirable to maintain an acid concentration as high as possible and work in the ultraviolet rather than in the visible portion of the spectrum.

Among the strong acids available, perchloric acid appeared to be most suitable, for several reasons. The iron perchlorate complexes (*1*, *5*) have a low stability and they absorb little energy in the spectral range suitable for the determination of chloride.

Under the conditions employed in these studies, no decomposition of perchloric acid was evidenced at any time. No reduction to chloride was ever observed nor were there any indications of other interfering or hazardous reactions. The procedures involved may be considered as perfectly safe (*4*).

A spectrophotometric procedure for the determination of iron, presumably as the tetrachloroferrate(III) complex, has been reported by Desesa and Rogers (*2*). Their procedure requires a high concentration of hydrochloric acid and allows determination of iron in concentrations of the order of 10 mg. per liter.

APPARATUS AND REAGENTS

A Beckman Model DU spectrophotometer with matched 1-cm. silica cells was used for most of the studies; a tungsten lamp served as the light source. It was established that a Model B spectrophotometer and Corex cells are likewise suitable for this work. Absorption spectra were recorded by means of a Beckman Model DK-I recording spectrophotometer. A Machlett closed-system buret (10 ml.), connected with a large stock bottle by an all-glass conduit, was used for delivering exact volumes of perchloric acid. Drying tubes filled with anhydrous magnesium perchlorate protected the acid from moisture. The buret should have a close fitting glass stopcock to minimize leakage of perchloric acid. All stopcock lubricants studied were found to be attacked by the acid upon prolonged contact and therefore the fit of the plug is of considerable importance.

It was observed that the absorbancy of the iron chloro complex in perchloric acid stronger than 5*N* decreased when exposed to bright light. The solutions were, therefore, protected from light by coating the volumetric flasks with black paint almost up to the mark, and by covering the necks of the flasks with small bags of opaque paper. Low actinic glassware gave incomplete protection against bright light.

Iron(III) perchlorate solutions were prepared from reagent grade ferric perchlorate (nonyellow) as supplied by the G. F. Smith Chemical Co. Trace impurities of chloride present in the iron perchlorate were removed by treatment of the salt with small

portions of 70% perchloric acid and decantation of the acid. The salt is only sparingly soluble in the acid, but the chlorides are readily dissolved and removed. In preparing iron perchlorate solutions, an approximate amount of the purified salt was dissolved in water or in perchloric acid, and the solution was titrimetrically standardized by the potassium dichromate procedure. The solutions were then diluted to bring them to the desired strengths. Reagent grade perchloric acid (70 to 72 or 60%) supplied by Baker and Adamson and Mallinckrodt, respectively, was found to be of satisfactory purity. No detectable effects due to chloride present in the acid have been observed. The perchloric acid always seemed to be of a higher degree of purity than indicated by the manufacturer's assay (maximum limits of chloride impurity were given as 0.001%).

A standard chloride solution was prepared by dissolving 1.314 grams of dried sodium chloride and diluting to 1 liter with distilled water. This solution had a chloride-titer of 0.8000 mg. and was further diluted to yield solutions of appropriate chloride concentrations.

For evaluating the extent of interferences, solutions were prepared from reagent grade chemicals to contain known amounts of the ions listed in Table I. Solutions for anion interferences were prepared from sodium salts; those for cation interferences contained perchlorate or nitrate.

EXPERIMENTAL AND RESULTS

The effect of acid concentration on the absorbancy of solutions at a given concentration of chloride and ferric ion was studied.

Small volumes of iron and chloride solutions were transferred to 10-ml. flasks, and varying amounts of 70% perchloric acid were added. The flasks were filled to the mark, shaken, and allowed to cool. At higher concentrations of acid the solutions were protected from light as described above. A study of absorption spectra of various solutions differing in acid concentration disclosed a pronounced increase of absorbancy with acidity, accompanied by a shift of the absorption bands towards the red end of the spectrum. The absorption peaks shifted from 338 mμ (2.5*N* perchloric acid) to 348 mμ (8.5*N* perchloric acid). A series of measurements was then carried out at 350 mμ with solutions which contained 8 mg. per liter of chloride ion, 0.02 mole per liter of iron perchlorate, and perchloric acid concentrations varying from 2 to 10*N*. Blanks of appropriate iron and acid concentrations were prepared, and the absorbancies of all solutions were measured with respect to water. The absorbancies due to the presence of chloride ion were calculated by subtraction of the corresponding blank values (Figure 1).

The influence of iron concentration on the intensity of the absorption band was next studied. Two sets of measurements were carried out, one at 342 mμ, the other at 350 mμ (Figure 2). The first set contained 17.5 mg. of chloride per liter in 6*N* perchloric acid; the second contained 8.00 mg. of chloride per liter in 8*N* perchloric acid. The iron concentrations were varied from 0.001 to 0.1*M*. Curves indicating the increase of background absorption with increasing concentration of iron are included in Figure 2.

It is evident from Figure 1 that increasing the concentration of perchloric acid beyond 8.5*N* reduces the precision of the measurements because of the increase in background without a corresponding increase in net sensitivity. A practical limit is further set by the concentration of the commercially available perchloric acid (approximately 12*N*). As indicated by Figure 2, a high concentration of iron(III) seems to be desirable if the simultaneous increase of blank absorption with iron concentration is disregarded. If 70% perchloric acid is used, a limitation of iron(III) concentration is given by the decreased solubility of iron perchlorate in the more concentrated acid.

The stability, temperature dependency, and adherence to the Beer-Lambert law of the system were studied by preparing a reagent which contained 0.139 mole of ferric perchlorate in 1 liter

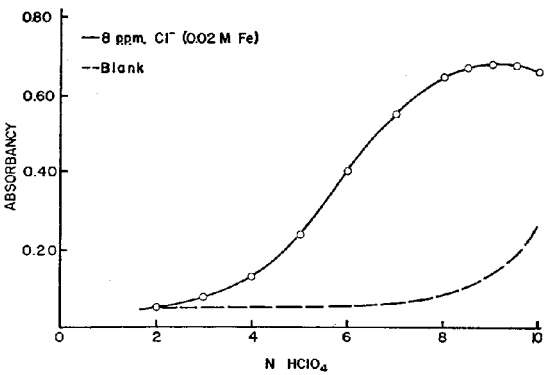

Figure 1. Influence of perchloric acid concentration on absorbancy at 350 mμ

Table I. Interferences

Species	Procedure 1 Interference	Procedure 1 Remarks[a]	Procedure 2 Interference	Procedure 2 Remarks[a]
Sulfate	Slight (+)	[200] (30)	Moderate (+)	[16] (4)
Nitrate	Negligible (+)	[30000]	Very slight (+)	[2500]
Acetate	None		Negligible (+)	[4000]
Thiocyanate		Decomposes	Heavy (+)	[2]
Bromide	Moderate (+)	[11]; can be corrected	Moderate (+)	[40]
Iodide	Slight (+)	[700]; precipitates above 200 mg./liter	Moderate (+)	[20] precipitates above 200 mg./liter
Fluoride	Negligible (−)	(400)	Slight (−)	(40)
Phosphate	Negligible (−)	(850)	Slight (+)	(20)
Mercury(II)	Heavy (−)	Must be absent	Heavy (−)	Must be absent
Chromium(III)	Negligible (+)	(200)	Negligible (+)	(>1000)
Cobalt(II)	Negligible (+)	(300)	Negligible (+)	(200)
Lead	Negligible (−)	(500)	Negligible (−)	(600)
Nickel	Negligible (+)	(600)	Negligible (+)	(300)
Manganese(II)	Negligible (+)	(1000)	None	
Aluminum	Negligible (−)	(>1000)	Negligible (−)	(200)
Copper(II)	Negligible (−)	(>1000)	Negligible (−)	(>1000)
Barium	None		None	
Calcium	None		None	
Sodium	None		None	
Potassium	Precipitates above 300 mg./liter		Precipitates above 400 mg./liter	

[a] Figures in brackets refer to mg./liter of interfering ion giving same absorbancy as 1 mg./liter of chloride. Figures in parenthesis refer to mg./liter of interfering ion causing a 3% error in the chloride value (these values were established at chloride levels of 5 and 8 mg./liter for Procedures 1 and 2, respectively).

of 11.8N perchloric acid. Transfer of 7.2 ml. of this reagent to a 10-ml. flask and dilution to the mark resulted in a solution 8.5N with respect to perchloric acid and 0.01M with respect to iron. Because of the hygroscopic properties of the perchloric acid, this reagent had to be kept under anhydrous conditions. The specified volume of the reagent was delivered from the Machlett buret into flasks protected from light, and aliquots of standard sodium chloride solution were added. After dilution to the mark with distilled water, the flasks were shaken and allowed to cool. The absorbancies of the solutions were measured at 353 mμ with respect to a blank which contained corresponding amounts of acid and iron. A linear relationship between absorbancy and chloride concentration was established.

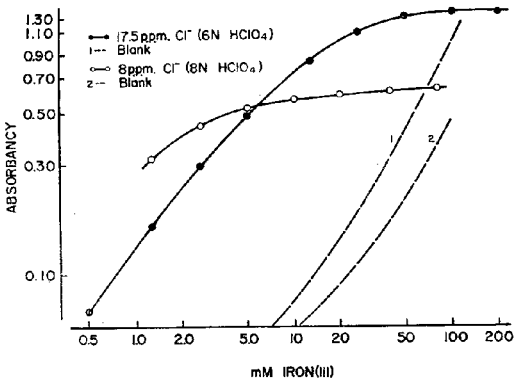

Figure 2. Influence of iron(III) concentration on absorbancies

Measured at 342 and 350 mμ for runs 1 and 2, respectively

The useful concentration range was found to be 1 to 12 mg. of chloride per liter (corresponding to absorbancies of 0.08 and 1.0 unit). Because only one fourth of the total volume is available for the chloride solution, these figures have to be quadrupled to represent the useful concentration range for an unknown solution. The blank exhibited an absorbancy of approximately 0.06 unit with respect to distilled water. The influence of temperature was determined to be 1.4% per degree centigrade for the blank with respect to water, and −0.02% per degree centigrade for the sample with respect to the blank.

The absorbancies of solutions protected from light were constant for 100 hours. Exposure to bright light in uncoated flasks after addition of chloride caused a rapid decrease of absorbancies. Subsequent storing in the dark slowly increased the absorbancies, although the original values were not again reached.

In order to test the reliability of the procedure, 21 solutions, each containing 5 mg. of chloride per liter, were measured with respect to blanks over a period of 1 week. The reagent as well as the volumetric equipment was the same in all experiments; corrections for changes in temperature were not applied. The values ranged from 0.428 to 0.449 absorbancy unit, the average being 0.440; the mean deviation was ±0.86%.

Interferences from a number of cations and anions were studied. Known amounts of potentially interfering ions were added to solutions containing 5 mg. of chloride per liter, and the difference from the theoretical value of absorbancy was calculated. In studies on certain cation interferences where a substantial amount of nitrate ion was added to the solutions, corrections were applied for the presence of this anion. The results are summarized in Table I (Procedure 1). Where positive deviations due to interaction of iron(III) and interfering ions, independent from chloride concentration, could be assumed, the extent of interference is expressed in terms of parts per million of interfering ions giving the same absorbancy as 1 p.p.m. of chloride. In other cases the extent of interferences is expressed as milligrams per liter of interfering ion causing an error of 3% at a given concentration of chloride ion. Consideration was also given to the presence of potassium ion, iron(III), and perchloric acid. Interferences arising from bromides and iodides were studied in special detail. The presence of bromide ion caused the appearance of an absorption band at 420 mμ, probably due to the formation of a bromo complex with iron (Figure 3). The ratio of absorbancies at 420 and 353 mμ, $A_{420}:A_{353}$, was found to be 3.6 and was reproducible. The same ratio for chloride absorption was calculated to be 0.082. Thus it is possible to correct for bromides present in solution, provided no interaction with the chloro complex takes place. Results obtained in this way are presented in Table II.

By an analogous procedure the effect of iodides was studied. Iodide ion when added to the perchloric acid reagent is oxidized to iodine. The resulting absorption spectrum is shown in curve 1 of Figure 3. When the iodide concentration exceeded 200 mg. per liter, crystals of iodine were precipitated. These were removed by extraction into carbon tetrachloride. The spectrum of the iodine remaining in the aqueous phase appears to be es-

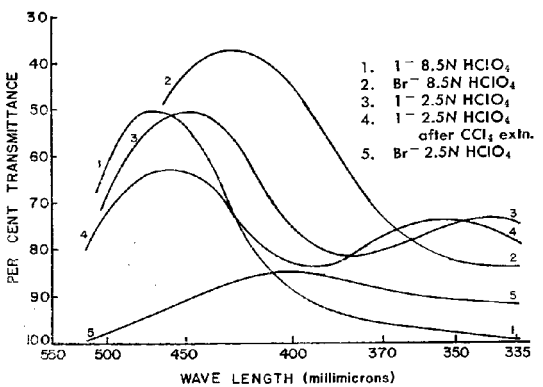

Figure 3. Absorption spectra due to bromides and iodides

Table II. Interferences from Bromide, Corrections

Concentration, Mg./Liter		Absorbancies		Absorbancies of Chloride at 353 mμ		Error,
Chloride	Bromide	353 mμ	420 mμ	Calcd.	Theor.	%
2.5	16	0.332	0.434	0.209	0.213	− 1.9
2.5	16	0.355	0.420	0.245	0.213	+15
2.5	40	0.504	1.095	0.207	0.213	− 2.8
2.5	40	0.498	1.11	0.195	0.213	− 8.5
5.0	8	0.475	0.220	0.426	0.427	− 0.2
5.0	16	0.541	0.438	0.432	0.427	+ 1.2
5.0	32	0.649	0.838	0.427	0.427	0.0
5.0	40	0.722	1.10	0.428	0.427	+ 0.5
5.0	40	0.710	1.10	0.416	0.427	− 2.6

Values obtained by correction formula, A_{353} (corrected) =

$$\frac{A_{353} \times 3.6 - A_{420}}{3.5}$$

Ratios of Absorbancies		
Chloride	$A_{420}/A_{353} = 0.082$	$A_{470}/A_{353} = 0.015$
Bromide	$A_{420}/A_{353} = 3.6$	$A_{470}/A_{353} = 2.3$
Iodide	$A_{420}/A_{353} = 4.5$	$A_{470}/A_{353} = 15$

sentially unaltered. It can be seen from Figure 3 that the absorbancy due to the presence of iodine drops to a low value around 353 mμ. Thus no extensive interference from iodides in a determination of chloride should be expected. A correction for iodides similar to the one applied for bromides is possible but is not considered necessary. Corrections for the presence of iodides and bromides simultaneously may be made by measuring the absorbancies of the solution at 353, 420, and 470 mμ. Constants expressing ratios of absorbanices at different wave lengths are included in Table II. The constants for iodide appeared to be less reproducible than those for bromide. The constants listed in Table II depend to a certain extent on the concentrations of iron(III) and perchloric acid present in solution.

In order to dispense with the necessity of storing the reagent under anhydrous conditions, an alternative procedure was investigated.

A reagent was prepared which contained 0.2 mole of iron(III) perchlorate in 1 liter of 5*N* perchloric acid. Acid of this or lower concentration does not exhibit hygroscopic properties. The large amount of iron was chosen to compensate for the decrease in sensitivity resulting from the use of lower acid concentrations. Five milliliters of this reagent—standardized with respect to acidity and iron concentration—were measured into 10-ml. flasks and the features of this procedure were studied by experiments analogous to the ones described for the first procedure.

The results may be summarized as follows: The plot of absorbancy against chloride concentration, measured at 348 mμ, is linear; the workable range for 1-cm. cells is 4 to 40 mg. of chloride per liter, corresponding to a concentration of 8 to 80 p.p.m. in the unknown solution to be analyzed. The absorbancy of the blank amounted to approximately 0.21 absorbancy unit. The temperature dependence was determined to be 3% per degree centigrade for the blank with respect to water, and 1.3% per degree centigrade for the sample with respect to the blank. A statistical study on 20 solutions of constant composition gave a spread from 0.387 to 0.424, averaging 0.401 with a mean deviation of ±1.9%. If the absorbancy values were corrected for temperature (30° C.), the spread was 0.404 to 0.416, averaging 0.408 with a mean deviation ±0.6%. The absorbancy readings for the blank as well as for the sample were practically constant with time. After 50 hours a decrease of approximately 3% was observed. No effect due to exposure to light could be detected.

The results of interference studies using the second procedure are listed in Table I (Procedure 2). The absorption bands arising from the presence of bromide and iodide (Figure 3) appeared to be shifted towards the ultraviolet compared with the ones obtained by the first procedure; the iodine spectrum exhibits a second band around 340 mμ. Extraction of precipitated iodine into carbon tetrachloride seems to have an effect on the spectrum of the aqueous phase (Figure 3, curves 3 and 4). No attempt was made to determine chloride in the presence of the other two halides, but it should be possible to apply a correction, as in the first procedure.

The preparation of the reagents, involving standardization of iron perchlorate solution and of perchloric acid, can be simplified for practical work by preparing reagents of approximate strength, for which an individual chloride calibration curve can be established. Perchloric acid can be assumed to be of the concentration stated by the manufacturer, and the appropriate amount of iron(III) perchlorate can be weighed on a triple-beam balance. After this salt has been treated in the manner outlined below, almost twice the amount corresponding to the formula weight of iron perchlorate has to be taken to give solutions of desired concentrations, because of the large quantities of water and perchloric acid absorbed on the crystals. Occasional checks by titration to establish the concentration of the ferric perchlorate solutions are recommended.

RECOMMENDED PROCEDURES

Procedure 1. Shake 20 to 30 grams of reagent grade iron(III) perchlorate with small portions of 70% perchloric acid in a glass-stoppered flask. Decant the acid and repeat this operation until the acid layer no longer appears yellow. Mount a coarse fritted-glass crucible of known weight on a suction flask, and transfer the purified iron perchlorate to the crucible. Press the crystals down with a glass rod flattened on one end, and remove the perchloric acid by suction. Then reweigh the crucible filled with iron perchlorate on a triple-beam balance; remove iron perchlorate from the crucible until approximately 8 grams are left. Then dissolve this quantity in a few milliliters of distilled water, and add 1 liter of 70% perchloric acid. Perchloric acid, like iron perchlorate, is extremely hygroscopic and should be exposed to air as little as possible.

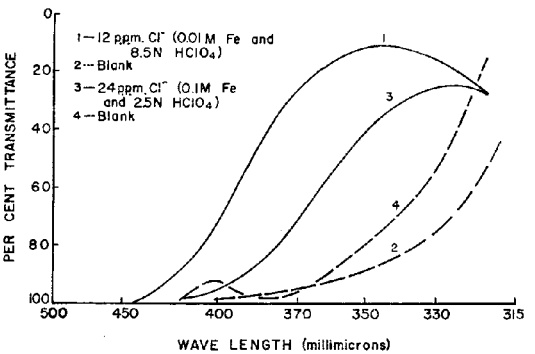

Figure 4. Absorption spectra of iron(III) chloro complexes and of corresponding blanks

Transfer the reagent to a container which is connected with a closed-system buret. The system is protected from moisture by means of magnesium perchlorate drying tubes. Deliver 7.4 ml. of the reagent accurately to 10-ml. volumetric flasks which have been protected from light by a black coating almost up to the mark. Transfer 2.5 ml. of the unknown solution, to contain not more than 50 p.p.m. of chloride, to the flasks, and bring the solutions to volume with distilled water. Shake the flasks to mix the solutions, and, after covering the necks of the flasks with a small bag of opaque paper, allow the solutions to cool. Measure the absorbancies of the solutions at 353 mμ with respect to a blank containing only reagent and distilled water. Determine the concentration of chloride by means of a calibration curve. Establish a new calibration curve every time a fresh reagent is prepared. If the reagent is to be kept over an extended period of time, occasional checks on the calibration curve are recommended.

Procedure 2. After purification of an appropriate amount of iron(III) perchlorate in the way described above, dissolve approximately 120 grams of the salt in a mixture of 540 ml. of 60% perchloric acid and 460 ml. of distilled water. The reagent may be stored in a glass container without protection from moist air. Transfer 4.9 ml. of this reagent to 10-ml. volumetric flasks, which need not be protected from light. Add 5 ml. of the unknown solution, to contain not more than 100 p.p.m. of chloride, and fill the flasks to the mark. Measure the absorbancies of the solutions at 348 mμ with respect to a blank. The temperature of the solutions should be recorded, but it can be assumed that the temperature difference between sample and blank is insignificant. After correcting the absorbancy readings to the temperature at which the calibration curve had been established, obtain the concentration of chloride from the curve. Apply the correction for temperature by adding to the absorbancy reading at temperature T the term $(T_0 - T) \times A_T \times 0.013$, where T_0 stands for the temperature at which the calibration curve was set up; A_T designates the absorbancy measured at temperature T.

DISCUSSION AND CONCLUSION

Procedures 1 and 2 present conditions for maximum sensitivity in a spectrophotometric determination of chloride by means

of iron(III). Other procedures which may employ a low concentration of perchloric acid and of iron(III) are conceivable.

It is evident from the experimental results that differences between the systems of complexes present in Procedures 1 and 2 must exist, as exemplified by the difference in temperature coefficients, the varying extent of interferences, and the instability of solutions obtained by Procedure 1 when exposed to light. Figure 4 shows the spectral bands of sample and blank in the two procedures. In determinations of chloride it was found desirable to measure absorbancies at slightly higher wave lengths than correspond to the peaks of the respective absorption bands, because of the increase in background and extent of interference from certain substances with decrease in wave length.

Because of higher background, appreciable temperature dependence, and more extensive interference from certain common ions, such as sulfate, Procedure 2 must be considered inferior to Procedure 1. Yet the advantages of Procedure 2—the fact that no protection from humidity is required and the insensitivity of the solutions towards light—should not be overlooked in practical work.

With the exception of mercury(II), a rather uncommon constituent, other ions do not seriously impair the applicability of Procedure 1. Bromides and iodides, which account for heaviest interferences in most classical methods for the determination of chloride, may be tolerated in this procedure. Corrections for bromides are required, if present in quantities above 30% of the chloride content. Iodides may be tolerated up to a 20-fold excess with respect to chloride, provided no precipitate of iodine is formed. Sulfate ion, up to a sixfold excess, does not interfere (corresponding to a positive error of up to +3%). In Procedure 2, on the other hand, interference from sulfate ion must be considered as serious, where sulfate present to the extent of 50% of the chloride concentration (by weight) causes a deviation of 3%. Larger quantities of sulfate must be removed by precipitation with barium perchlorate and subsequent centrifugation. Removal of sulfate ion by precipitation after iron perchlorate reagent has been added was found to be incomplete. Likewise, an error will be introduced if the unknown solution contains appreciable amounts of acid and iron(III) in addition to the quantities added as the iron perchlorate reagent. For a chloride concentration of 5 mg. per liter in Procedure 1 the error will amount to 3% if the iron(III) concentration is increased from 0.010 to 0.014*M*; the same effect is caused by an increase of perchloric acid concentration from 8.5 to 8.8*N*. In Procedure 2, at a chloride concentration of 8 mg. per liter, a 3% error is introduced by an increase of iron concentration from 0.100 to 0.102*M*, or by an increase of perchloric acid from 2.50 to 2.55*N*. These values represent a measure for the amounts of perchloric acid and iron(III) which may be tolerated in an unknown to be analyzed for chloride.

The main advantages of the methods described in this paper over other methods now in use for the determination of chloride lie in the simplicity of the procedures and their remarkable sensitivities. Generally speaking, only turbidimetric methods can be considered as more sensitive. Applications of this direct spectrophotometric method are anticipated in routine analysis of water, air, and certain physiological systems.

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Instrumentation for Rapid Spectrochemical Analysis

Optical and X-Ray Emission Monochromators and Polychromators

J. W. KEMP

Applied Research Laboratories, Glendale 8, Calif.

The success of direct-reading optical and x-ray emission techniques in providing high-speed analyses on a routine basis has led to the commercial availability of a variety of instruments for use in these fields. A review of these instruments and their capabilities should be of interest to those concerned with rapid routine analysis.

OPTICAL spectrographic analysis has been recognized as a high-speed, routine control method for 20 years. The additional time savings afforded by the application of direct-reading techniques to the optical method have been generally used for the past 10 years. The x-ray fluorescence technique is now going through its acceptance period as a routine control method.

Briefly, a sample brought to a sufficiently high temperature by appropriate means emits optical line spectra of the elements present. Analysis and measurement of these spectra then provide information on the elemental composition of the sample. Thus, the optical method is destructive, as it is necessary to consume at least a small sample to provide an analysis. However, the x-ray method is nondestructive. Here, the sample is irradiated with high intensity x-rays. This causes the sample to fluoresce in the x-ray region, this fluorescence consisting of the x-ray line spectra of the elements present in the sample. Analysis of these spectra also gives information on elemental composition.

Savings in both elapsed time and time per analysis are usually significant, and occasionally startling, with these techniques. In order to replace the older, slower methods by the new techniques, however, a sizable capital investment is required. Certain limitations on sensitivity and accuracy must also be recognized.

Because both optical and x-ray spectra are atomic phenomena, these limitations can be correlated with the periodic table of the elements. The optical technique can be used for all metals and metalloids, but requires special equipment for the nonmetals and gases. The x-ray technique has a different set of restrictions, being useful for all elements of atomic number greater than 19 without special equipment.

Two classes of instruments are used: parallel and sequential. The parallel instruments give simultaneous determinations of

several elements, and are thus faster, but less flexible, than the sequential types. The latter provide analyses, one at a time, in a programmed sequence (*3*).

COMPARISON OF OPTICAL AND X-RAY METHODS

The requirements of the first step, preparation of sample, are outlined in Table I. For the analysis of nonconducting materials, the x-ray technique generally offers considerable savings in time over the optical technique.

Table II summarizes the important features of the excitation of the two types of spectra. The radiation energy used in the optical technique generally originates in energy changes of the valence electrons of the atoms of the sample. The energy to bring about these changes is obtained from flames or electrical discharges. Only those elements with low excitation energy requirements (alkalies, alkaline earths) can be readily excited in a flame, while electrical discharges at reduced pressure are required to excite elements requiring high excitation energies (gases, halogens). The majority of the elements can be excited by arc or spark discharges in air, and these discharges are used for routine, high-speed analysis.

X-radiation is obtained from energy changes in the innermost shells of the atoms, generally the K and L shells. This requires excitation by a beam of high-voltage electrons in a vacuum, or by irradiation with a high-intensity x-ray beam. The latter technique is very much simpler in practice and allows any material to be used as a sample. Thus, for routine analysis, commercially available, high-intensity x-ray tubes are used as the primary excitation means. X-ray emitting isotopes have been suggested, but these are generally unsatisfactory for routine analysis, principally because of the very low intensities obtained.

Table I. Preparation of Sample

Sample Type	Optical Emission Requirements	X-Ray Emission Requirements
Solid metals	Surfacing usually required	
Metallic particles	Briquetting or putting into solution may be required	
Solid nonconductors	Grinding or putting into solution always necessary. Mixing and briquetting after grinding may be required	Surfacing may be required
Nonconducting particles	Mixing and briquetting may be required	Usually analyzed as is
Liquids	Often analyzed as is	

Table II. Excitation

Feature	Optical	X-Ray
Electron levels	Valence electrons	Innermost electrons (K & L shells)
Source of energy	Electrical discharge, usually in air	High intensity x-ray beam
Equipment	D.c. arcs A.c. arcs Intermittent triggered arcs Controlled a.c. and d.c. high voltage sparks	High voltage supply and x-ray tube
Quantity sampled	Usually less than few mg.	~100 mg.
Minimum sample	~1 mg.	Few mg.
Local analysis	Possible with special techniques	0.040 × 0.040 inch with reduced sensitivity

INSTRUMENTATION

Prism and grating spectrographs have been used for years for routine analysis. Direct readers generally use the same basic optical systems, with slits and multiplier phototubes substituted for the photographic film. In direct readers, however, the space requirements for slits, phototubes, etc., make the use of gratings almost mandatory.

X-ray dispersing instruments are not so well known. The only optical dispersing elements useful in the usual x-ray region are single crystals. Electronic dispersion, using proportional counters, has some application. For routine analysis, however, resolution is too low and circuits are complex. The large single crystals used as optical dispersing elements are usually lithium fluoride, sodium chloride, or quartz, and are used either flat or curved. Flat crystals are similar optically to flat gratings, requiring collimators. Curved crystals are optically similar to concave gratings, allowing focusing of the spectra without collimators.

In any direct-reading, multielement analytical system, there are two modes of operation: parallel and sequential. The parallel system determines several elements at once, and requires the use of polychromators. The sequential system determines one element at a time, requiring only a monochromator. Obviously,

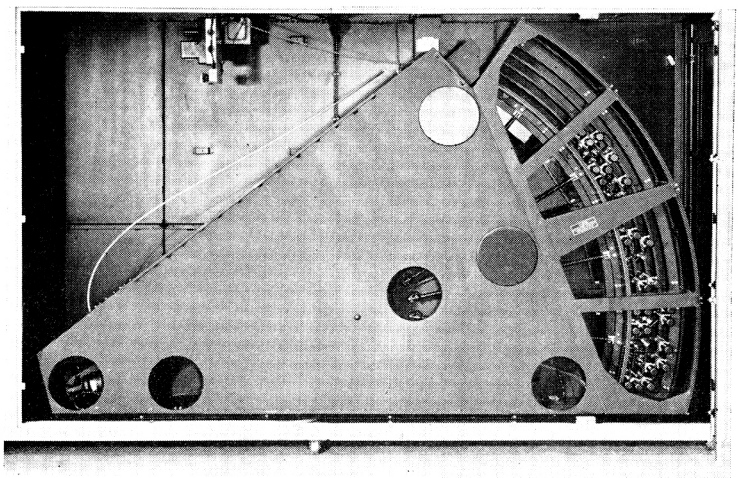

Figure 1. Optical assembly of ARL 2-meter production control Quantometer

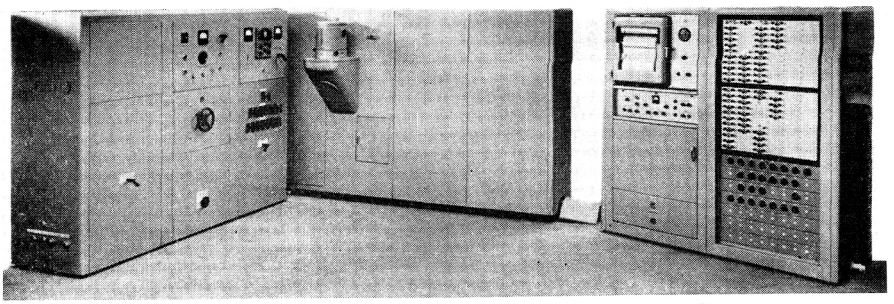

Figure 2. Complete ARL production control Quantometer, including source

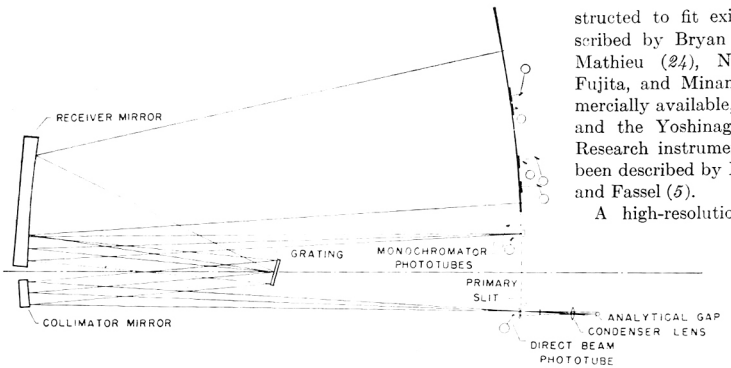

Figure 3. Optical system of ARL Quantograph

the parallel system is the fastest where several elements per sample are to be determined.

Parallel System Optical Instruments. Several instruments of this type have been described in the literature. These include the Applied Research Laboratories' Research Quantometer (*20*) and Production Control Quantometer (*2*), the Baird Associates–Atomic Instruments Direct Reader (*26*), and the Hilger Polychromators (*21*). Fisher Scientific Co. and Jarrell-Ash Co. also offer this type of instrument. Most of these instruments use concave gratings, and all of them are polychromators employing a single primary slit with a multiplicity of secondary slits, mirrors, or prisms, and multiplier phototubes. The differences are mainly in optical details and the recording electronics.

As an example of these polychromators, the optical assembly of the Applied Research Laboratories' Production Control Quantometer is shown in Figure 1. Radiation from the analytical gap enters the instrument at top center from the far side. It is deflected to the concave grating at lower left, and the dispersed spectra are received along the focal circle to the right by slits, mirrors, and phototubes. This particular Quantometer, using a 2-meter radius of curvature grating, can provide simultaneous measurement of as many as 68 lines. The complete instrument is shown in Figure 2, with its high-voltage excitation source to the left, and recording console to the right.

Sequential System Optical Instruments. A large number of instruments measure one line at a time, usually with provision for simultaneous measurement of an internal standard. Many of these are one-of-a-kind devices constructed to fit existing spectrographs. This type has been described by Bryan and Nahstoll (*6*), Bylund and Rudberg (*7*), Mathieu (*24*), Naish and Ramsden (*25*), and Yoshinaga, Fujita, and Minami (*28*). Two of these instruments are commercially available, the Mathieu instrument (Cie Radio-Cinéma) and the Yoshinaga instrument (Shimadzu Seisakusho, Ltd.) Research instruments using cathode-ray tube presentation have been described by Dieke and Crosswhite (*13, 14*) and by Brehm and Fassel (*5*).

A high-resolution monochromator designed for sequential analysis has been described by Fastie (*15*). A similar instrument, designed for either the sequential or parallel technique, as well as for use as a photographic instrument, is the Applied Research Laboratories' Quantograph (*12*). Figure 3 shows the optical layout of this instrument. The spectra excited at the analytical gap pass through the primary slit to the primary collimator to a flat grating and to the secondary collimator. When used in a sequential system, one element line at a time is brought to the monochromator slit by rotation of the grating. Alternatively, a number of slits and phototubes may be arranged along the focal circle to pick up a number of elements simultaneously in a parallel system. The complete unit is shown in Figure 4, with its attendant excitation source and recording console.

Sequential System X-Ray Instruments. Instruments of this type, using flat crystals as dispersing elements, include the fluorescence attachment for the General Electric XRD-5 diffraction instrument, and the various Norelco instruments (*4, 17*). The Applied Research Laboratories' x-ray scanning Quantometer (*23*) is a sequential instrument using curved and ground crystals. Its optical arrangement is shown in Figure 5. The motions re-

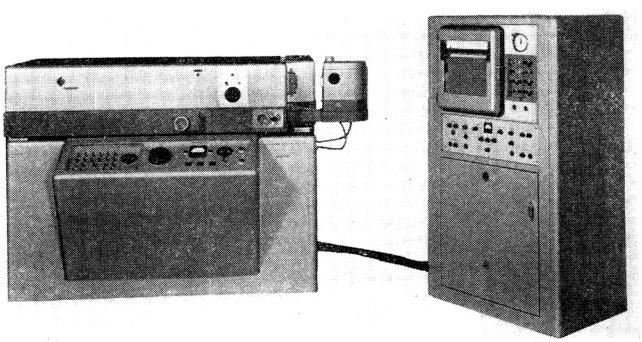

Figure 4. Complete ARL Quantograph, including source

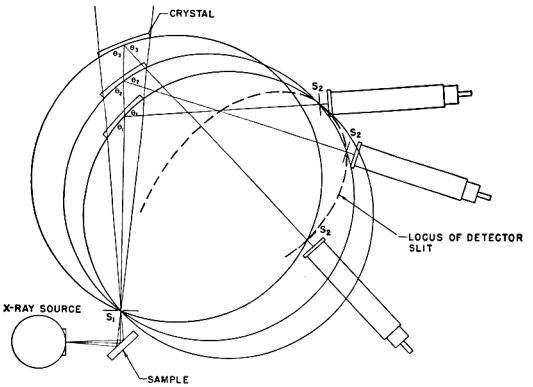

Figure 5. Optical system of cylindrical crystal x-ray monochromator

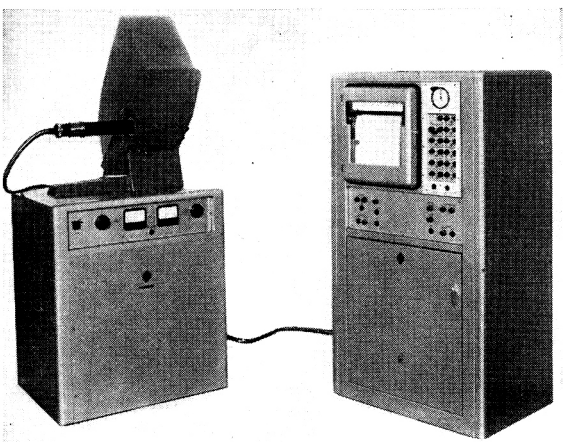

Figure 6. Complete ARL x-ray scanning Quantometer

quired to hold the secondary slit and crystal on the focal circle, while maintaining a fixed primary slit and sample position, are obtained with a single screw driving the appropriate linkage. The instrument is shown in Figure 6, mounted on top of its power supply with the recording console to the right. It contains two monochromators of the sort shown in Figure 5. One of these is provided with a crystal bent to an 8-inch radius and ground to a 4-inch radius, giving a focal circle of 4-inch radius. The other is bent to 22 inches and ground to 11 inches. Either monochromator can be aligned with the single primary slit, allowing efficient coverage of the useful x-ray wave length region.

Parallel System X-Ray Instruments. A one-of-a-kind instrument of this type has been described by Adler and Axelrod (*1*). Another instrument, using focusing crystals, is the Applied Research Laboratories' X-ray Industrial Quantometer (*22*), shown in Figure 7, mounted on its power supply. It consists of seven semifixed monochromators with the optics of Figure 5 mounted in a circle around the centrally located end-on x-ray tube and sample position. The XIQ provides the simultaneous determination of seven elements.

Recording. Optical spectrum lines are generally detected with multiplier phototubes. X-ray spectra may be detected with Geiger counters, proportional counters, or scintillators. Regardless of the detector used, the circuit of Figure 8 is used in all Applied Research Laboratories' direct readers. During integration, the detectors are connected to the integrating condensers, giving simultaneous charging of all condensers. At the end of the integration time (controlled by source intensity), the detectors are disconnected and the vibrating condenser electrometer amplifier is connected to the integrators one at a time. When a particular integrator is connected to the amplifier, the associated zero and sensitivity controls are also connected into the circuit. Thus, the voltages on the simultaneously charged integrators are read sequentially at the rate of one every two seconds, the results being traced on special chart paper by a Leeds & Northrup recorder. A digital voltmeter and electric typewriter combination is an alternative output system. An obvious future possibility of this system is closing the loop between the Quantometer output and the equipment manufacturing the samples.

Any of these instrumental analytical systems are sometimes complicated by complex relations between spectral intensity and concentration. In the simplest systems, the relation is linear, requiring only zero and sensitivity controls in the circuits to give direct concentrational output.

When the relation is nonlinear, special chart paper can be prepared to give direct concentrational output with L & N recording. The most complicated system is that in which the changes of concentration of some elements affect the spectral intensities of others. In other words, the intensity of the analyte is a function not only of its concentration, but also of concentrations of other elements present. The optical Quantometers contain circuits for correction of certain types of these functions, and special computers are under development for handling others. When the instrument cannot handle the more complex functions automatically, some computation time must be added to the total analysis time.

Other manufacturers of optical direct readers use circuits differing in detail from the circuit of Figure 8. Other types of x-ray equipment generally integrate through the use of conventional scaling circuits.

PRECISION AND ACCURACY

Precision of analysis of high concentrations is determined by all the factors in the analysis. With optical

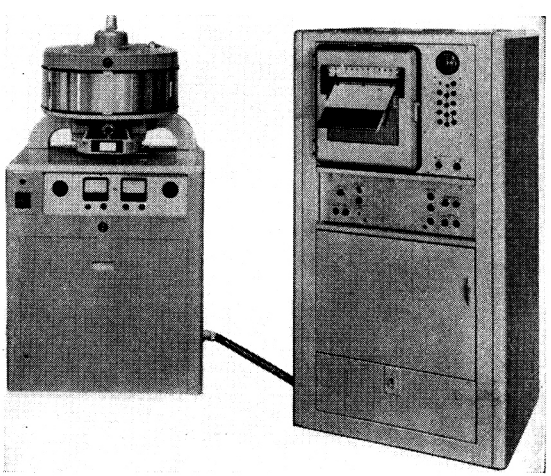

Figure 7. Complete ARL x-ray industrial Quantometer

direct readers, the precision is determined by excitation source characteristics and sample homogeneity. In metal analysis, concentrational coefficients of variation of 0.5 to 1.5% are obtained. For nonmetallics this may be 1 to 3% with the best techniques. With x-ray Quantometers, precision is determined by detector characteristics, giving coefficients of variation of 0.2 to 0.6% regardless of sample type. Precision at low concentrations is dependent on the sensitivity for the element in question.

Accuracy should approach precision in these systems, providing uniform samples are used and accurate standards have been used to calibrate the system. In some cases it is possible to standardize the instruments with synthetic samples.

SENSITIVITY

Because optical spectra originate in valence electron structures, the appearance and intensities of these spectra should bear some relation to the position of the elements in the periodic table. A summary of four semiquantitative systems is given in Table III. These data represent *limits of detectability* to order of magnitude only. Each author uses a different definition of sensitivity, etc. A study of Table III shows that highest sensitivity can be obtained for light alkalies and alkaline earths, but gases, halogens, and nometals are generally not detected with standard techniques. With special techniques, even these elements can be detected, and the limit of detectability can be reduced an order of magnitude or more on the metallic elements. Although these data were obtained by photographic techniques, similar results can be obtained with direct readers.

Table IV gives the order of magnitude of limits of detectability attainable with an Applied Research Laboratories' x-ray scanning Quantometer for three different modes of operation. The limits for continuous scanning are obtained at a scanning rate that will cover all elements of atomic number greater than 19 in 3 hours, or about 2.4 minutes per element. The concentration given rep-

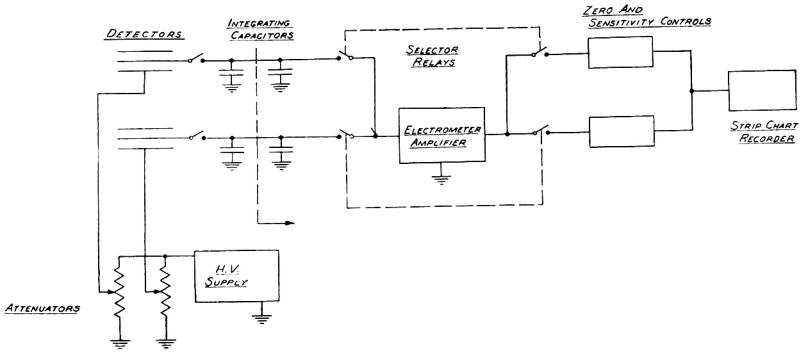

Figure 8. Schematic circuit diagram of ARL recording system

Table III. Optical Emission Sensitivities

Reference		(27)	(19)	(16)	(9)		(27)	(19)	(16)	(9)
Source		D.c. arc	D.c. arc	Cu spark	D.c. arc		D.c. arc	D.c. arc	Cu spark	D.c. arc
Matrix		Zn	C	HCl			Zn	C	HCl	
Sample		100 mg. powder	10 mg. powder	0.1 ml. sol.	Biologicals		100 mg. powder	10 mg. powder	0.1 ml. sol.	Biologicals
Z	Element	Parts per Million		Millimicrograms on Electrode		Z	Element	Parts per Million		Millimicrograms on Electrode
3	Li	10	1000	0.1		50	Sn	1	100		10
4	Be	1	1	0.1		51	Sb	10	100	1000	100
5	B	1	10	10		52	Te	10		100	
11	Na	1	1000	10	1000	55	Cs	10000		100	
12	Mg	1	1	1	10	56	Ba	100	1000	10	
13	Al	10	10	10	10	57	La	1000		10	
14	Si	1	10	10	100	58	Ce	100		100	
15	P	100	1000	1000	10000	59	Pr			10	
19	K	100	1000	10		60	Nd	10000		10	
20	Ca	10	1	10		62	Sm			10	
21	Sc			1		63	Eu			1	
22	Ti	10	10	10		64	Gd			10	
23	V	10	100	10		66	Dy			100	
24	Cr	1	10	10	100	67	Ho			10	
25	Mn	1	10	1	10	68	Er	100		100	
26	Fe	1	10	100	10	69	Tm			10	
27	Co	10	10	100		70	Yb			10	
28	Ni	1	10	10	100	71	Lu			100	
29	Cu	1	1		10	72	Hf			100	
30	Zn		100	100	1000	73	Ta	100	1000	100	
31	Ga	10	100	100		74	W	10	1000	100	
32	Ge	1	100			75	Re			100	
33	As	100	100	1000	1000	77	Ir	100		1000	
37	Rb	10000		10		78	Pt	10	10	1	
38	Sr	100	1000	100		79	Au	10	10	10	
39	Y	100		1		80	Hg	10	100	1000	100
40	Zr	10	10	10		81	Tl	100	1000	10	
41	Nb	10	1000	10		82	Pb	1	100	10	10
42	Mo	1	10	10		83	Bi	1	10	10	10
44	Ru		100			88	Ra			10	
45	Rh	10				90	Th	100		10	
46	Pd	100	10	100		91	Pa			100	
47	Ag	1	1		10	92	U	10000		100	
48	Cd	10	100	100	100	93	Np			100	
49	In	10	100	100		94	Pu			100	

Table IV. X-Ray Emission Limits of Detectability

(Standard deviation in parts per million at background)

Z	Element	Technique[a] 1	2	3	Z	Element	Technique 1	2	3	Z	Element	Technique 1	2	3
20	Ca	10,000	300	60	45	Rh	100	15	8	70	Yb	1,000	20	8
21	Sc	10,000	200	40	46	Pd	100	20	10	71	Lu	1,000	20	10
22	Ti	1,000	80	10	47	Ag	100	20	10	72	Hf	1,000	20	10
23	V	1,000	25	8	48	Cd	1,000	30	20	73	Ta	1,000	20	10
24	Cr	1,000	15	5	49	In	1,000	30	20	74	W	1,000	20	10
25	Mn	100	8	3	50	Sn	1,000	60	30	75	Re	1,000	30	10
26	Fe	100	6	3	51	Sb	1,000	60	40	76	Os	1,000	30	10
27	Co	100	6	3	52	Te	1,000	100	50	77	Ir	1,000	30	15
28	Ni	100	6	3	53	I	1,000	150	70	78	Pt	1,000	30	15
29	Cu	100	6	3	54	Xe	1,000	200	100	79	Au	1,000	30	15
30	Zn	100	6	3	55	Cs	10,000	400	200	80	Hg	1,000	30	15
31	Ga	100	8	3	56	Ba	10,000	200	50	81	Tl	1,000	30	15
32	Ge	100	8	3	57	La	10,000	80	30	82	Pb	1,000	40	20
33	As	100	8	3	58	Ce	10,000	60	20	83	Bi	1,000	40	20
34	Se	100	10	5	59	Pr	1,000	40	10	84	Po	1,000	40	20
35	Br	100	10	5	60	Nd	1,000	30	10	85	At	1,000	40	20
36	Kr	100	10	5	61	Pm	1,000	20	10	86	Rn	1,000	40	20
37	Rb	100	15	5	62	Sm	1,000	20	8	87	Fr	1,000	40	30
38	Sr	100	15	8	63	Eu	1,000	20	8	88	Ra	1,000	60	30
39	Y	100	6	3	64	Gd	1,000	20	8	89	Ac	1,000	60	30
40	Zr	100	6	3	65	Tb	1,000	20	8	90	Th	1,000	60	30
41	Nb	100	8	3	66	Dy	1,000	20	8	91	Pa	1,000	60	30
42	Mo	100	8	5	67	Ho	1,000	20	8	92	U	1,000	60	30
43	Tc	100	10	5	68	Er	1,000	20	8	93	Np	1,000	60	40
44	Ru	100	10	5	69	Tm	1,000	20	8					

[a] Techniques: 1. Continuous scanning. 2. 1-minute integration, high resolution. 3. 1-minute integration, low resolution.

Table V. Time Schedules

(20 elements per sample)

	Parallel	Sequential
Preparation, min.	0.5–18	0.5–18
Integration, min.	0.5– 1	7 –25
Readout, min.	1	1
Total, min.	2 –20	7.5–43
Time per element, min.	0.1– 1	0.4– 2

Reported Routine Times

Material	Elemental Analysis per Hour	Reference
Slag	30	Author's laboratory
Aluminum alloy	119	(*11*)
Aluminum alloy	550	(*10*)
Aluminum alloy	1500	(*8*)

resents that at which a line would be definitely visible above background. The limits given for 1-minute integration at high resolution (0.005 inch primary and secondary slits) are concentrations at which a coefficient of variation of 100% would be obtained. The low resolution limits are those obtained with slits adjusted for maximum sensitivity (usually 0.030-inch primary and secondary), rather than for maximum resolution and are given as the concentrations at the 100% coefficient of variation level. Again, special techniques can extend the x-ray method to lighter elements and can reduce the limits given here. These data can be considered representative of the capabilities of present day x-ray fluorescence instruments.

SPEED

Table V gives estimated time schedules for parallel and sequential direct-reader operation. The lower figures would apply to alloy analysis requiring a minimum of sample preparation. The higher figures would apply to nonmetallic analysis with an optical direct reader where considerable sample preparation may be required. The second part of the table gives results obtained on a routine basis with the Applied Research Laboratories' Quantometers, the original publications giving time in terms of analysis per shift, or per week. Such figures, then, include calibration time. With the latest direct readers, allowing 20 or 30 element determinations per sample, element analysis per hour can run over 1000.

The nature of the optical emission technique generally precludes its use as a continuous analysis system. The x-ray technique, however, is easily adaptable to continuous analysis. This characteristic has made possible the design of a variety of x-ray gaging instruments for use in tin and zinc plating thickness measurement, and continuous, single-element determinations in various types of plant streams (*18*).

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Flame Photometry

VILLIERS W. MELOCHE

Department of Chemistry, University of Wisconsin, Madison 6, Wis.

The term "flame photometry" is used here to designate that area of emission spectroscopy in which a solution of the sample is atomized into a flame, the wanted radiation is isolated by either a filter or monochromator, and the intensity of the isolated radiation is measured by photographic or electronic means. In some cases, the term "flame spectroscopy" is used to indicate methods that use the more discriminating monochromator or its equivalent. Miscellaneous methods include the use of multichannel detection or spark-in-flame excitation. A complete bibliography of flame photometry is not given. Only selected references that illustrate developments in the field are included.

RAPID development in emission spectroscopy occurred in the analysis of metals and alloys during the late thirties, and particularly during World War II. This was due in part to the urgency of the time. However, the manufacture of excellent spectrographs, and the fact that metals and alloys could be used as self-electrodes, multiplied the applications. Methods were developed for the spectrographic analysis of solid residues, soils and biological and mineral samples. Because excitation of solid, often nonconducting powders required special preparation before analysis, techniques were developed in which samples could be handled in the form of solutions. The most attractive and widely used of these methods are the Feldman porous hollow electrode (*20*), the Sloviter and Sitkin porous flat electrode (*54*), the Nachtrieb copper electrode (*22*), and the Pagliassotti and Porsche disk electrode (*43*). In these methods the sample is brought to the electrodes as a solution, a spark is usually used for excitation, and a spectrograph is used for dispersion and detection of wanted radiation. The sample must be volatilized into the analytical gap before dissociation and excitation can take place.

Flame photometry is also a solution method. In contrast to the above methods, the solution is atomized and the finely dispersed spray is introduced into a flame. Unlike the other methods, evaporation, dissociation, and excitation take place in the flame. Some evaporation takes place between the atomizer and the flame. There is no preliminary volatilization from electrodes.

EARLY METHODS

Although solutions had been used in flame spectroscopy by Bunsen and Kirchoff (*42*), it was not until Lundegardh (*36*) described his work that flame photometry was recognized as an important analytical tool. In Lundegardh's method the atomized sample passed into a condensing chamber and thence into the base of an acetylene-air burner. Radiation was dispersed and detected by means of a spectrograph. Lundegardh preferred the integration provided by the photographic emulsion. Others (*36, 45, 52*) in Europe and England used the flame photometric method and like Lundegardh atomized the sample solution through a condensing chamber into an air-acetylene burner. They used the spectrograph for isolation and detection of wanted radiation. Some (*36, 52*) used filters and electronic methods of detection. Some (*1*) used gases other than acetylene. Although Lundegardh mentioned the detection of nearly half the elements of the periodic system, determinations of sodium, potassium and the alkaline earths were most commonly reported.

Most of the combinations of equipment used in this country at the present time were used in Europe shortly after Lundegardh published his work on the analysis of plant residues from 1929 to 1934. Lundegardh even described the use of a photocell for the detection of radiation. Schuhknecht 1937 (*52*) described a simple filter photometer for the determination of potassium. Heyes in 1937 (*27*) used a filter photometer for the determination of chromium and manganese. He showed that the selection of the filter was important; some filters chosen to pass a given wave length also leaked light at adjacent wave lengths. With special filters from Zeiss, he was able to obtain excellent results. He demonstrated the absence of line interference by preparing spectrograms of chromium and manganese alongside of spectra from iron, vanadium, and other elements.

In the United States, Griggs, Johnstin, and Elledge (*26*) and Ells (*18*) used the Lundegardh method for the analysis of biological materials and soils. Cassen in 1940 (*8*) determined magnesium in body fluids and presented preliminary results on clinical material. However, the papers of Barnes (*3*) and Berry, Chappell, and Barnes (*4*) in 1945 and 1946 stimulated interest in the flame photometer in this country, probably because they used the more simple filter instruments. Barnes described a simple single-beam filter instrument which used a barrier-layer cell to detect the isolated radiation. Classical wet methods for sodium and potassium were long and tedious. The flame photometric method was short, simple, and accurate. Without question, research projects requiring many determinations of sodium and potassium were made feasible by the availability of this new short analytical method. Barnes and associates apparently recognized that filters would not isolate wanted radiation as effectively as would the spectrograph. They applied the filter photometer to the relatively simple spectra of sodium and potassium. Barnes used the low temperature flame produced by illuminating gas-air and Pyrofax-air mixtures. Berry, Chappell, and Barnes (*4*) devised a double-beam internal-standard filter photometer, using lithium as the internal standard.

INSTRUMENTS

After Barnes, Berry and others brought the flame photometric method to the attention of workers in this country, several instruments were made available by instrument makers. Of the instruments currently available, the Beckman DU with flame attachments, the Beckman B, and the Perkin Elmer 52 are spectrophotometers. The latter two cover a somewhat shorter wave length range than the Beckman DU. The Perkin Elmer 52 has a split-beam arrangement which permits the use of an internal standard. The Baird Associates instrument, the Barclay-Janke described by Fox (*21*), the North American Philips, the new Beckman, and the Coleman are filter instruments. The filter instruments are less expensive and prove adequate where the routine determination of sodium and potassium is of special interest. A large number of laboratories have a real need for filter instruments. For research laboratories and others which need a rapid analysis of a wider variety of elements, the instrument that approximates a spectrophotometer will be better suited. The extent to which filter instruments can be applied to a variety of elements is limited by the effective band pass of the filters as

well as freedom from leakage at wave lengths which should be absorbed.

ATOMIZERS AND BURNERS

Types of atomizers range from simple combinations of hypodermic needles to glass atomizers (Lundegardh, Baird Associates, Perkin-Elmer, and early Beckman), metal atomizers inserted in the base of the burner or in the center of the top of a Meker-type burner (Coleman, Weichselbaum-Varney), and types in which the atomizer is an integral part of the burner (attachments to the Beckman DU and Beckman B). The glass atomizers operate with a condensing chamber, which serves to condense the larger droplets of the dispersed solution. Some evaporation from the droplets takes place as the spray passes through the chamber. In some early models (Beckman) the chamber was heated. The metal atomizers, whether inserted in the burner or an integral part of the burner, operate without condensing chambers, projecting the dispersed solution directly into the flame. Alkemade (*1*) notes that the different systems vary in efficiency. When condensing chambers are used, as little as 4% of the solution atomized reaches the flame. However, it may not be assumed that where the solution is atomized directly into the flame, all of the sample produces radiation. In the case of the larger droplets, evaporation and excitation may not be complete. The particle may leave the flame without having contributed anything to total radiation.

Alkemade (*1*), Mavrodineanu and Boiteux (*42*), and Caton (*9*) have studied particle size distribution in the atomized sample solution. Effective particle size may be 10 microns or less. The different atomizers have a wide difference in consumption of solution per unit of time, differing from a fraction of 1 ml. to several milliliters per minute. Caton (*9*) showed that the presence of sucrose or glucose tended to slow evaporation and increase particle size. The addition of lower alcohols (isopropyl) tended to increase evaporation and decrease particle size. Vallee and Margoshes (*57*) showed that the presence of anions which formed stable compounds with the cations (calcium phosphate) caused interference because the particle was not dissociated during passage through the flame.

Differences in characteristics of the gas used necessitate changes in construction and operation of burners. To use different gases Alkemade provided interchangeable grids for his Meker-type burner. He gives the following data for two grids.

	Acetylene-Air	Propane or Ill. Gas-Air
Number of exit canals	71	19
Diameter of exit canals, mm.	0.8	2.0
Diameter of field containing exit canals, mm.	14	16

Alkemade reports the temperatures obtained with various gas mixtures: oxygen-acetylene 3100° C., air-acetylene 2200° C., oxygen-hydrogen 2700° C., and air with illuminating gas, propane, or butane about 1900° C. These values are not absolute, but differ with operating conditions.

FLAME TEMPERATURE EFFECTS

The temperature obtained in a flame is related to the intensity of radiation in a given case. In comparing the temperatures of oxyacetylene and oxyhydrogen flames and those of acetylene-air and hydrogen-air, it is noted that the presence of nitrogen tends to reduce the temperature of the flame. The advantage of the relatively low background of the hydrogen flame has been cited. Alkemade (*1*), Rothermel (*50*), and others noted that the high temperature of the acetylene flame may be a disadvantage in the determination of potassium in the presence of sodium. The increase of potassium intensity caused by the addition of sodium is due mainly to the repression of potassium ionization by the electrons produced by the ionized sodium; the proportion of potassium atoms and the atomic intensity are increased. Alkemade (*1*) noted that this effect should decrease with temperature. When he tried a propane-air flame, the effect of added sodium became smaller. He noted, further, that for the determination of calcium, only the acetylene flame appeared suitable.

In contrast, Margoshes and Vallee (*40*) favor the use of high temperature flames. They point out that "the inability of flames now available to excite more than just a few elements effectively enough to permit quantitative work in the parts per million range of concentration is one of the severe present limitations of flame photometry," and that "flames of higher temperatures will make possible the determination of many more elements at low concentrations." Their studies with a flame burning cyanogen and oxygen at 4850° K. show that many elements not excited by oxyhydrogen or oxyacetylene flames give strong emission lines in the cyanogen flame. Furthermore, they anticipate a lessening of interference from various anions as another advantage of the high temperature flame.

Mavrodineanu (*42*) and Alkemade (*1*) have reported temperatures at different distances above the cone of a flame, the highest temperature being closest to the cone. Most instruments provide for some integration of the radiation from a given area of the flame close to the cone and some intensify the radiation from the flame by means of a mirror mounted behind the flame. Mavrodineanu and Alkemade have commented on the characteristics of the flame. Alkemade (*1*) states that the design of the burner and the atomizer should be matched. The burner must provide good mixing, homogeneous speed, and direction of flow of the gas on leaving the top of the burner. The velocity of rise is also important.

INTERFERENCES

In general, some of the important interferences are (*24*):

Quenching, sensitization, reabsorption, and interference with combustion processes
Energy at other wave lengths than that selected for measurement reaching the photodetector
Direct interference, instances in which the line to be measured falls within a molecular emission band
Intense adjacent line emission, in which the emission interferes with the measurement of the analytical line
A general increase in flame background
Spray rate alteration

Alkemade (*1*, p. 105) lists factors and forms of spray interference, such as temperature of the solution, organic components, salts, acids; rate of liquid intake, atomization, evaporation; supply of spray and vapor to the flame; flame composition, flame temperature, flame content; spectral interference; and ionization-association interference. Caton (*9*) and others have examined the effect of viscosity, surface tension, and particle size.

It is difficult to examine and compare results reported in the literature. Most authors have been concerned with the development of a special application of the method, and have concentrated on finding stable conditions for a particular procedure. In most cases, they did not try to explain the interference, but merely to eliminate it. Some work was done with filter photometers and with spectrographs, with different atomizers and different types of burners. For example, Alkemade (*1*) and others reported the effect of sodium on potassium radiation and explained the effect of the basis of ionization of the sodium. To quote from Margoshes and Vallee (*39*):

Several workers have reported that one cation may affect the emission of light by another. Sodium and potassium have been variously reported to increase (*58*) and decrease (*4*) their respective emission and that of calcium (*21*, *53*). Bills and others (*5*) found that excess sodium led to either high or low results for potassium, depending on the potassium concentration. Others could find no effect of sodium on potassium when an instrument of adequate resolving power was employed (*31*).

The following articles illustrate the wide variety of applica-

tions of flame photometry and indicate specific interferences. West (*58*) used buffer solutions to eliminate interferences in the analysis of natural waters. He prepared a radiation buffer for sodium by saturating distilled water with potassium, calcium, and magnesium chlorides. He prepared a standard solution of sodium chloride in water. For the standard curve, he added the same amount of buffer solution to each standard as to the sample. He plotted radiation for a series of standards (concentration *vs.* transmittance), measured radiation for the prepared sample, and obtained the concentration from the working curve by interpolation.

Mosher and associates (*47*) used flame photometry to determine sodium and potassium in plasma and urine. Later Mosher determined calcium in brucite and magnesite (*47*). Fox also analyzed biological samples. Having used an internal standard, Fox made no attempt to control viscosity or surface tension (*21*). Conrad and Johnson (*14*) analyzed nonaqueous organic samples. They analyzed inhibited lubricating oils by dissolving weighed amounts of sample in 50–50 mixtures of benzene and isopropyl alcohol and atomizing the solution in the same manner as aqueous solutions. By excessive dilution of the sample, viscosity effects were eliminated. Blank corrections were critical but were made more certain by atomizing the organic solvent instead of water in determining the blank. Metal naphthenates were used as standards.

Baker and Johnson (*2*) studied the effect of perchlorate, phosphate, and sulfate on calcium emission. In the case of phosphate or sulfate interference, they indicated that the formation of pyro ions might account for the anomalies in calcium emission. Phosphate alone and sulfate alone lowered the emission for calcium, whereas perchlorate alone increased the calcium emission. Mixtures of perchlorate and phosphate or perchlorate and sulfate with calcium showed lower emission than calcium with perchlorate alone. When phosphate or sulfate were equivalent to or greater than perchlorate, calcium emission was the same as that of calcium and phosphate alone or calcium and sulfate alone. Margoshes and Vallee (*39*) used a multichannel flame spectrometer for the determination of five elements in one sample. They state that "extraneous cations produce heterochromatic background radiation and have no effect on the monochromatic radiation measured above the background. Certain anions are shown to reduce the emission intensity of alkaline earths." The interference of certain anions was attributed to the formation of compounds having high melting and boiling points. If some of the earlier workers had known the work on which the above statement was based and had used an instrument capable of isolating the monochromatic radiation of the element sought, they might have avoided some of the interferences they reported.

Another situation familiar to all analysts—the determination of a small concentration of one element in the presence of high concentrations of others—is illustrated by the determination of calcium in sea water, described by Chow and Thompson (*13*).

A Beckman DU spectrophotometer with photomultiplier attachment was used. Calcium emission was corrected for flame background and the results were calculated by the standard addition technique. In this case the added standard was calcium chloride. Twenty milliliters of sea water was diluted to 1 liter. A series of six portions of this solution, each containing 5 ml., was taken. To one portion, 5 ml. of distilled water was added. To each of the other five portions, 5 ml. of standard calcium chloride was added. The emission of the five standards and of the sample was graphed. The standards contained the calcium added plus that already in the sample. The sample contained only calcium present in the sea water. From these data it was possible to calculate the calcium content of the water.

Other papers describe the determination of less familiar elements. Diamond (*16*) describes the determination of strontium and alkalies in portland cement; McCoy determined lithium in portland cement; Gilliland (*25*) described the determination of alkalies in silicates, waters, and metals. Gilbert (*23*) has plotted the emission curves for the more common elements. The determination of nitrogen in organic compounds is unusual. Honma and Smith (*29*) describe the use of the cyanogen band at 3883 A. and the CH band at 3890 A. as internal standard. They plotted the log intensity ratios of these lines against log per cent concentration of nitrogen. Organic nitrogen can be determined in the presence of atmospheric nitrogen.

Alkalies and alkaline earths have been determined in cast iron (*32*) and magnesium in nickel (*35*).

Interferences of various types are recognized. Porter and Wyld (*49*) compare the effectiveness of the radiation buffer, the internal standard, and the direct injection burner as means of controlling interferences. It is of peculiar interest to users of flame photometry that Margoshes and Vallee (*39*) have emphasized the importance of reasonable resolution as well as a background correction in the elimination of interferences.

SPECIAL INSTRUMENTATION

King and Priestley (*30*) have reported a recording arrangement for flame photometry. Beckman has recently provided a recording attachment for the DU spectrometer. Boycks (*6*) has described special circuitry which permits the application of the Beckman DU spectrometer to the determination of sodium with a sensitivity of 1 part per billion. Not all instruments lend themselves to the determination of adjacent line background. The facility for scanning the spectrum provided by some recording attachments is helpful.

For higher levels of excitation the spark in flame has been used. Malmstadt (*38*) described one such application in the determination of vanadium and iron in titanium tetrachloride. Margoshes and Vallee (*40*) have described the use of a cyanogen-oxygen flame.

CONCLUSION

Only limited attempts have been made to extend the theoretical understanding of flame photometry. Isolated cases have been noted. The book by Mavrodineanu (*42*) and the printed thesis by Alkemade (*1*) are notable steps in this direction. Margoshes and Vallee have an excellent summary chapter on flame photometry in "Methods of Biochemical Analysis" (*40*). Mavrodineanu has published a complete bibliography on flame photometry (*41*). The dilution method, the buffering method, the internal standard method, the standard addition method, and the special line-background method have contributed to the control of interferences. The flame photometric method has made great progress in the number and variety of applications. It remains to be seen what will be done when more is known about the theoretical background for the method.

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Instrumental Methods of Gamma-Ray Spectrometry

R. E. CONNALLY

General Electric Co., Hanford Atomic Products Operation, Richland, Wash.

The gamma-ray spectrometer and its application to the rapid analysis of mixtures of gamma-emitting radioisotopes are discussed. The parameters of importance in the selection of the gamma-sensing unit are shown. The pulse height analysis systems commercially available for use in gamma-ray spectrometry are evaluated regarding their use as both qualitative and quantitative analytical instruments. The precision to be expected with each type of system is also discussed.

THE gamma scintillation spectrometer has found wide acceptance in the field of radiochemistry in the last 3 years. Its major advantages in the analysis of gamma-emitting radioisotopes are the speed, specificity, and simplicity of the method (*5*).

DISCUSSION

The gamma scintillation spectrometer is used to analyze the gamma spectra of radioisotopes in a manner similar to the analysis of the emission spectra of elements with the emission spectrograph. The sensing unit required for the detection of the emitted gamma radiation is the thalium-activated sodium iodide crystal.

A typical gamma spectrometer sensing element is shown in Figure 1. The gamma photons from the sample, penetrating the crystal, have a high probability of interacting with the crystal. This interaction results in the conversion of a single gamma photon, via a recoil electron, to a shower of light photons which are detected by one of several types of multiplier phototubes (such as the Dumont 6292 shown).

The current output from the multiplier phototube anode is directly proportional to the energy lost by the incident gamma photon. These current pulses are fed into an amplifier of sufficient gain to produce voltage output pulses in the amplitude range of 0 to 100 volts. The oscilloscope photograph in Figure 2,*b*, is a time exposure of the amplifier output pulses resulting from multiple cesium–barium-137 gamma interactions with the scintillation sensing element.

One method of analysis of the pulse spectra is by use of a single-channel pulse-height analyzer which plots the curve shown in Figure 2,*a*. The analyzer slowly scans the pulse distribution over a 0- to 100-volt range with an acceptance slit a few volts in width. Only those pulses falling within the acceptance slit are passed on to a rate meter and plotted.

For example, when the slit is at 75 volts, there are few pulses of this amplitude in the pulse spectrum, as shown on the photograph in Figure 2,*b*; thus, only a few pulses pass through the acceptance slit to the rate meter and recorder. As the slit sweeps on to the 65-volt region, there are a large number of pulses which are of proper amplitude to pass the acceptance slit and be recorded. As the acceptance slit completes its scan down to zero energy, the complete pulse height distribution is plotted. This same differential curve has been obtained by vertically scanning the face of the oscilloscope with a recording densitometer (*7*).

The curve of pulse height distribution, known as the differential scan, of a monoenergetic gamma emitter can be divided into two characteristic curves (Figure 2,a). The sharp symmetrical peak is the result of total absorption of the gamma energy by the NaI(Tl) crystal, and is normally referred to as the full-energy peak. The continuous curve below the full-energy peak is due to Compton interaction, wherein the gamma photon loses only

part of its energy to the crystal. The location of the full-energy peak on the pulse amplitude or gamma-energy axis is proportional to the gamma energy of the incident photon, and is the basis for the qualitative application of the gamma scintillation spectrometer. The area under the full-energy peak is related to the number of gamma photons interacting with the crystal, and is the basis for the quantitative application of the gamma scintillation spectrometer. The Compton continuum serves no useful purpose in full-energy peak analysis, and must be corrected for when a mixture of gamma emitters is analyzed.

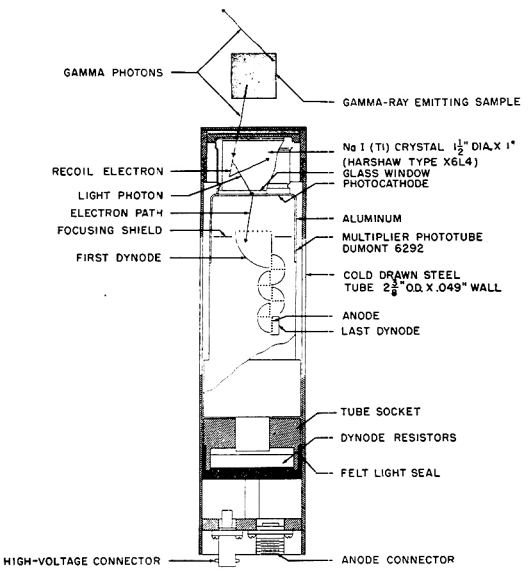

Figure 1. Diagram of gamma detector

Selection of Sensing Unit. As the area under the full-energy peak is the source of quantitative information and the Compton continuum is only a background which requires correction, it is desirable to increase the ratio of full-energy events to Compton events. This can be accomplished by increasing the size of the crystal, which increases the probability that a Compton-scattered gamma photon will lose all of its energy to the crystal by multiple interactions. Until recently the crystal $1^3/_4$ inches in diameter and 2 inches thick was the maximum practical size, because multiplier phototubes of larger diameter were not available. Today there are 3- and 5-inch multiplier phototubes available for this application. The 3 by 3-inch NaI(Tl) crystal operated with a 3-inch or 5-inch multiplier phototube is becoming a popular choice for the sensing element. With larger crystals the background increases at a greater rate than the signal. However, in most applications the improvement in full-energy peak to Compton ratio is worth the increase in background.

For quantitative applications it is desirable to have a calibration curve relating full-energy peak area to gamma activity. Such a curve can be obtained by using isotopes of known decay scheme. Each isotope is initially calibrated by absolute beta counting or other radiochemical methods, and then used to establish a point on the gamma detector efficiency curve. However, the number of possible calibration points is quite limited.

Lazer and coworkers have recently applied a more general technique wherein any gamma source emitting one or two major gamma rays can be used for calibration (*9*). R, the ratio of area under the full-energy peak to the area under the total spectrum, is determined in an experiment in which scattering is negligible. ϵ_t, the probability of interaction by the incident gamma photons for the geometry used in the experiment, is calculated. From these data the intrinsic peak efficiency is obtained as shown in Figure 3. The calibration curve does not include the geometry factor (solid angle), which must be taken into consideration when relating full-energy peak area to gamma activity. Berger and Doggett have calculated R, which they call photofraction (*3*). However their calculated values are somewhat higher than experimentally determined values.

The use of 3- and 4-inch crystals with re-entrant well can increase the counting signal to background ratio by a factor of 3 or 4. The presence of a well in the larger crystals has the effect of

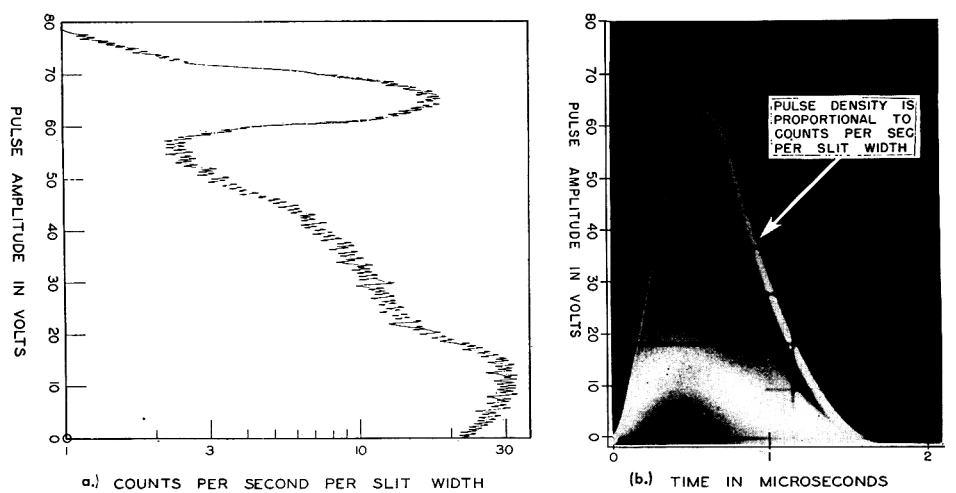

Figure 2. Two methods of pulse spectrum display for cesium-barium-137

***a.* (Left) differential** ***b.* (Right) oscilloscope pattern**

slightly decreasing resolution. The $4^3/_4$-inch crystal (Figure 3), in addition to having a well, was operated in anticoincidence with a guard crystal surrounding the detector crystal. Such an anticoincidence system substantially reduces the Compton continuum and background counting rate (*1*).

Preparation of Sample. For qualitative applications the reproducibility of the Compton continuum region is of negligible importance, and thus the size, phase, and location of the sample are not critical. Normally, the sample is placed close to the crystal on a sample support, as shown in Figure 4. If the gross counting rate exceeds 10^6 counts per minute (c.p.m.), the sample is simply moved to a position of reduced geometry. In the quantitative analysis of mixed gamma emitters, the absorption and forward scattering properties of the sample should be controlled so as to obtain a reproducible Compton continuum curve. For dry samples the weight is seldom of a sufficient magnitude to affect either the absorption or forward scatter properties. On the other hand, liquid samples are normally made up to a constant volume before spectrometer analysis in order to produce constant absorption and forward scatter properties.

Shielding. The background counting rate of a $1^3/_4$-inch diameter by 2-inch thick NaI(Tl) crystal due to cosmic and stray gamma radiation is in the order of 1000 to 2000 c.p.m. In most routine applications it is advisable to shield the system with 1 to 4 inches of lead. When minimum mass of shielding material is the major consideration, the shielding is located as close as possible to the crystal, as in Figure 4. However, when it is desired to keep the Compton continuum at a minimum, an analysis of the formula relating incident and scattered gamma photon energy to scattering angle, θ, for different Z materials brings one to the

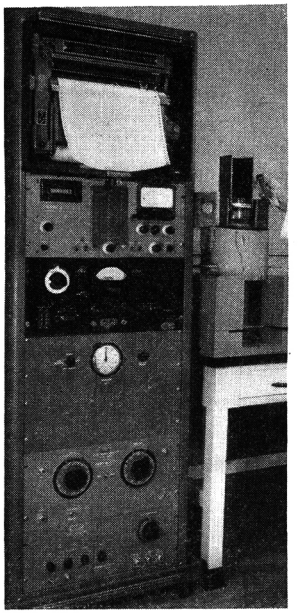

Figure 4. Gamma-ray spectrometer

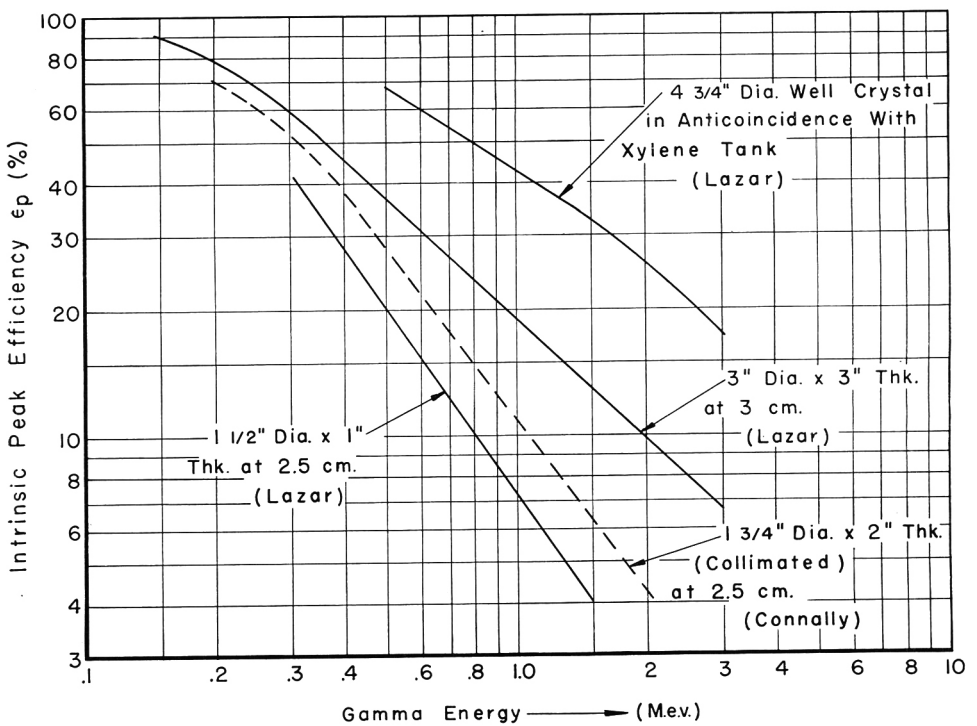

Figure 3. Peak efficiency *vs.* energy for sodium iodide crystals

$$\epsilon_p = R \times \epsilon_t \quad (9)$$

Where R = ratio of area under full-energy peak to area under total spectrum (experimental)
ϵ_t = probability of interaction by incident photon (theoretical)

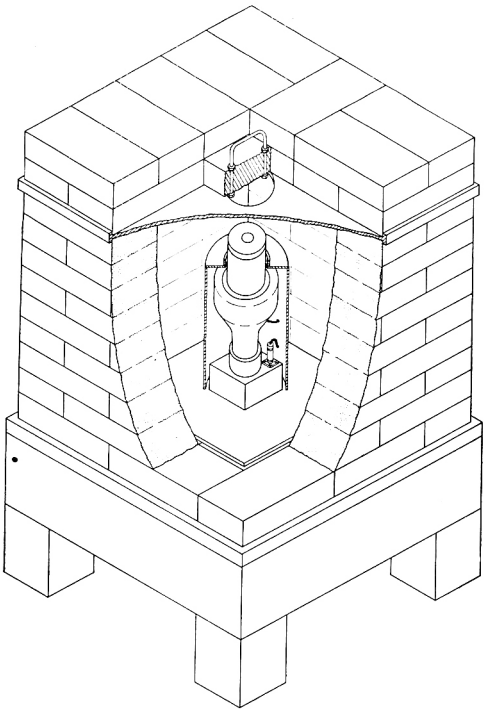

Figure 5. Typical low-Compton gamma detector system

following set of rules (*10*) to be used in designing a low-Compton system:

1. Maximize distance between crystal and shield.
2. Maximize Z (atomic number) of all scatterers. Photoelectric cross section varies as Z^2. Compton cross section varies as Z.
3. Maximize scattering angle between source, scatterer, and crystal.

$$E^1 = \frac{{}^1/_2 E}{{}^1/_2 + (1 - \cos\theta)E}$$

where E^1 = energy of scattered photon in m.e.v.
E = energy of incident photon in m.e.v.

4. Remove all unnecessary material from between source and crystal. Beta absorber, when required, should be of low Z material.

A typical solution to the low-Compton shielding problem results in a crystal, phototube, and light shield assembly of minimum mass low Z material. The shielding is usually 4 inches of lead or mercury located 5 inches or more from the crystal and enclosing the crystal and phototube on the sides and bottom. For low background work the shielding extends up and around the sample (Figure 5).

The gamma photons emitted from the sample generate characteristic x-rays in the high Z shield, resulting in a spurious x-ray peak in the gamma energy scan. This x-ray peak can be reduced by a factor of at least 100 by the use of a graded inner shield consisting of ${}^1/_{16}$ inch of cadmium or tin lined with 15 mils of copper (*2*).

Qualitative Analysis. The various gamma emitters are identified from the gamma scan by the location of their full-energy peaks on the energy axis, according to the curves shown in Figure 6. Where two full-energy peaks do not differ by sufficient magnitude to be resolved, or where a full-energy peak is hardly detect-

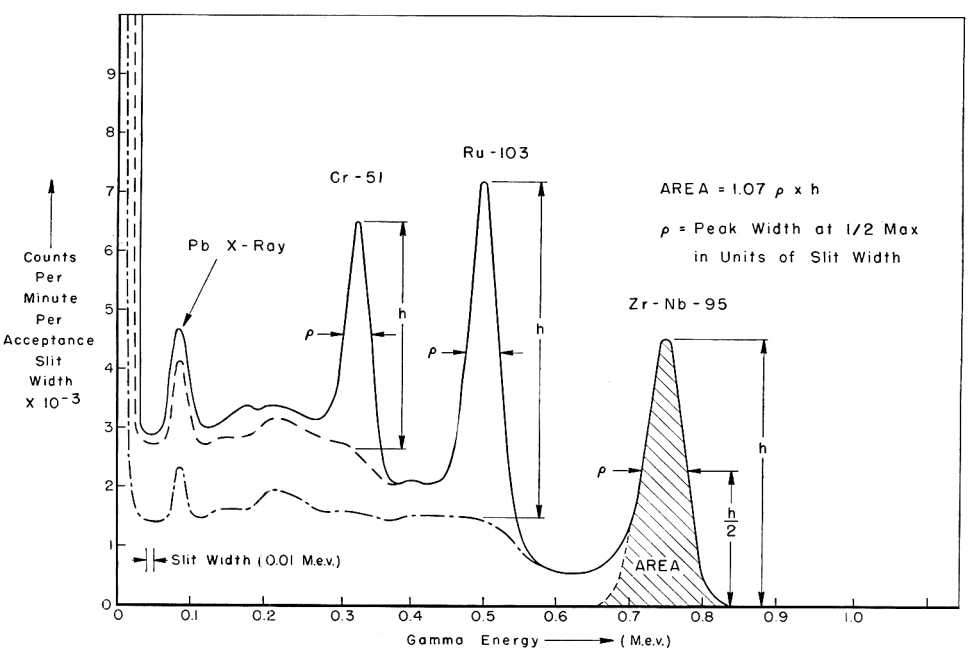

Figure 6. Typical three-component gamma spectrum

able above the Compton continuum of the more energetic gamma photons, preliminary chemical separations will be required.

Quantitative Analysis. The net area under each photopeak is directly proportional to the absolute gamma emission rate of the corresponding isotope. This is usually determined by taking the product of peak height, width at half maximum, and the normalizing factor, 1.07—based on the assumption that the full-energy peak is Gaussian (*5*).

For the analysis of mixed gamma-emitting radioisotopes, however, the characteristic lower energy curve of the most energetic full-energy peak must be drawn in from previously recorded standard curves detailing the Compton continuum region *vs.* principal full-energy peak area, as shown in Figure 6. By subtraction, the net height of the second most energetic gamma photon can be established and its width measured. The Compton continuum of the second full-energy peak is then drawn in and the area of the third peak can be evaluated, etc. (In a few cases a radioisotope may have a minor full-energy peak more energetic than its associated principal peak. This situation is normally solved by solution of simultaneous equations or by successive approximation.)

In the analysis of gamma photons in the energy range from 32 to 100 k.e.v., there appears to be an escape peak 28 k.e.v. below the full-energy peak. This is due to photoelectric interactions wherein the resulting iodine K x-ray escapes from the crystal. Above 1.5 m.e.v. the effect of pair production becomes apparent in the gamma scan. In addition to the full-energy peak, there are peaks in the scan at full-energy minus 0.51 m.e.v. and full-energy minus 1.02 m.e.v. Also a small peak occurs at 0.51 m.e.v. due to detection of an annihilation photon resulting from pair production in the shielding material (*2*).

It follows that the precision of measurement of each peak becomes less as successive Compton continuum corrections have to be made. In practice the five-component mixture is about the maximum which can be analyzed without the assistance of radioactive decay or chemical separation.

Finally, the full-energy peak yield curve, sample geometry, decay scheme data, half life, and atomic weight may be applied to carry the results to a weight basis. However, in many applications, such as in measuring the yield of a separation step, the gamma scan data can be retained on a total full-energy peak count basis.

A unique method of evaluating the full-energy peak without reference to Compton continuum is by graphically determining the point at which the characteristic width rho occurs, and by integrating the peak area above this point with a planimeter (*11*). This method is advantageous where very large Compton corrections must be made, but it must be limited to situations where the gross Compton continuum region is reasonably flat. The method requires recalibration if system resolution should change.

Pulse Analysis Systems. SINGLE-CHANNEL ANALYZERS. The typical block diagram of a single-channel gamma spectrometer is shown in Figure 7. The gamma detector, utilizing a 10-stage multiplier phototube, is capable of driving commercially available linear amplifiers via pulse cables 10 to 250 feet in length. This makes it possible to operate the gamma detector at remote locations where necessary (*4*). The regulated high voltage supply is usually a 1-ma., 500- to 1500-volt model with 0.01% line regulation and 0.1% stability per 24 hours.

The amplifier drives the pulse height analyzer, which has a discriminator level that can be adjusted continuously or stepwise in order to cover the pulse height spectrum of interest. The counting rate per acceptance slit width can be read on the scaler or recorded on the count rate meter–recorder system. When the discriminator level is driven continuously, the recording system usually consists of a linear count rate meter driving a strip chart recorder. The resulting curve is generally plotted automatically over a period of from 15 minutes to $2^1/_2$ hours, depending on sample counting rate and required precision. Another version of the same instrument is the single-channel stepping type, wherein the entire spectrum is analyzed in 1- or 2-volt steps. For low activity samples, more precise data can be obtained in a given sweep time. However, the analysis of data is usually more complex than with the continuous scanning type.

MULTIPEAK ANALYZERS. A useful multichannel analyzer for the analytical laboratory is the multipeak analyzer. With this instrument the boundary of each channel can be adjusted to encompass the full-energy peaks of the isotopes of interest (Figure 8). The total counts in each channel are stored on separate scalers and the Compton continuum can be subtracted by use of a Compton continuum table and an adding machine; graphical solution is not necessary. The data from such a system are adaptable to analog computation methods, in which the readout would be directly in units of full-energy peak counting rates corrected for Compton continuum interference.

The multipeak analyzer is most effective in the routine analysis of five or less known gamma peaks. When unknown gamma emitters must be searched for and identified, as in activation analysis (*13*), the five-peak analyzer is of little added value over the single-channel analyzer.

MULTICHANNEL ANALYZERS. The multichannel analyzers differ from the multipeak analyzers in that all channels are adjacent, but can be moved as a group to any region in the spectrum. Instruments with 20 channels are available, but must be moved five or six times to cover a 0.1- to 1-m.e.v. gamma energy spectrum with good resolution. To be used in qualitative analysis, 100 to 120 points must be plotted out in analog form for final analysis. Although it is more complex, the 20-channel analyzer has a real advantage over the single-channel type for short half life, low counting rate, and particle accelerator applications, as it can accumulate information 20 times as fast.

The multichannel analyzers of the 100- and 256-channel types all have provision for automatic analog readout. The resulting curve can be solved graphically to obtain qualitative data.

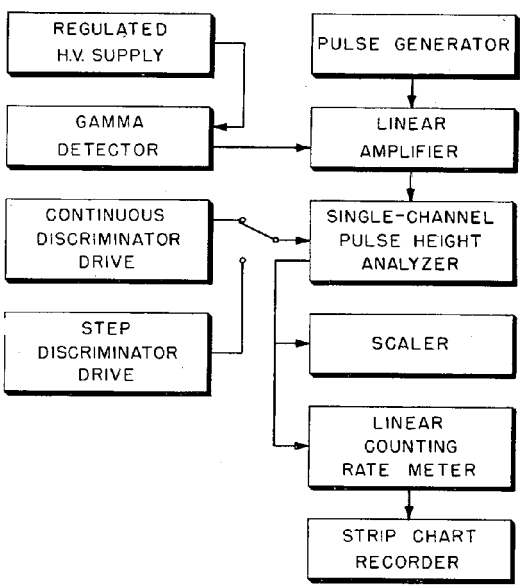

Figure 7. Block diagram of single-channel gamma scintillation spectrometer

Here again, the major advantage over the single-channel instrument is speed of analysis—that is, 1 to 5 minutes counting time compared to 30 to 150 minutes.

Precision. The precision of a gamma spectrometer system is less than might be calculated from the counting statistics alone. A drift in high voltage, multiplier phototube gain, amplifier gain, and channel level will all have their degrading effect on precision of multiple determinations over an 8-hour period. In general, the stability of a 0.1% per 24-hour high voltage supply is in the same order as that of the well-designed amplifier analyzer system, and the gain of the multiplier phototube (*12*).

The per cent standard deviation to be expected from the overall system for multiple determinations of the major constituent is shown in Table I.

The precision for minor constituents will vary from about 5% to undetectable, depending upon the number of successive Compton corrections and the relative magnitude of the constituents. The accuracy is seldom greater than within 5%, which is the accuracy to which most calibration curves of full-energy peak *vs.* gamma energy can be determined.

APPLICATIONS

Among the applications, the following can be mentioned. The determination of trace elements in semiconductor materials has been facilitated (*13*), and the analysis of mixed fission products has been simplified (*6*). Selected points in a spent nuclear fuel solvent extraction plant have been monitored for specific isotopes (*4*). A spectrometric method has been developed as a rapid means of determining neptunium-239, molybdenum-99, and cerium-141 in gross fission products (*11*). Radioisotopes shipped from Oak Ridge are checked for purity by use of a scintillation spectrometer (*8*). Localization of iodine-131 is greatly facilitated by elimination of the Compton scattering with a scintillation spectrometer. And finally, decay scheme studies and other nuclear data determinations have been facilitated by use of the gamma-ray spectrometer.

SUMMARY

In the analysis of radioisotope gamma spectra the sodium iodide crystal, activated with thalium, has gained prominence. The trend has been toward increasing crystal dimensions in order to yield more nearly pure line pulse spectra. This improvement is further increased by removing the shielding material from the immediate vicinity of the crystal. Radioisotope mixtures containing as many as five gamma-emitting isotopes can be determined qualitatively, and in many cases, quantitatively. The major constituent of a radioisotope mixture can readily be determined to a precision within 5% (standard deviation), and in special cases the precision has been improved to within 1%. The pulse analysis systems available for use in gamma-ray spectrometry vary from simple single-channel instruments to more complex 256-channel systems, designed for high data accumula-

Table I. Average Precision Obtainable with Several Types of Gamma Spectrometer Pulse Analysis Systems

Type of System	Precision Reported for Major Constituents, %	Literature Reference
Single channel, continuous sweep type with count rate meter	5	(*5*)
Single channel, step scanning with scaler	2	(*11*)
Multipeak with scalers	1	(*12*)
Multichannel	1	

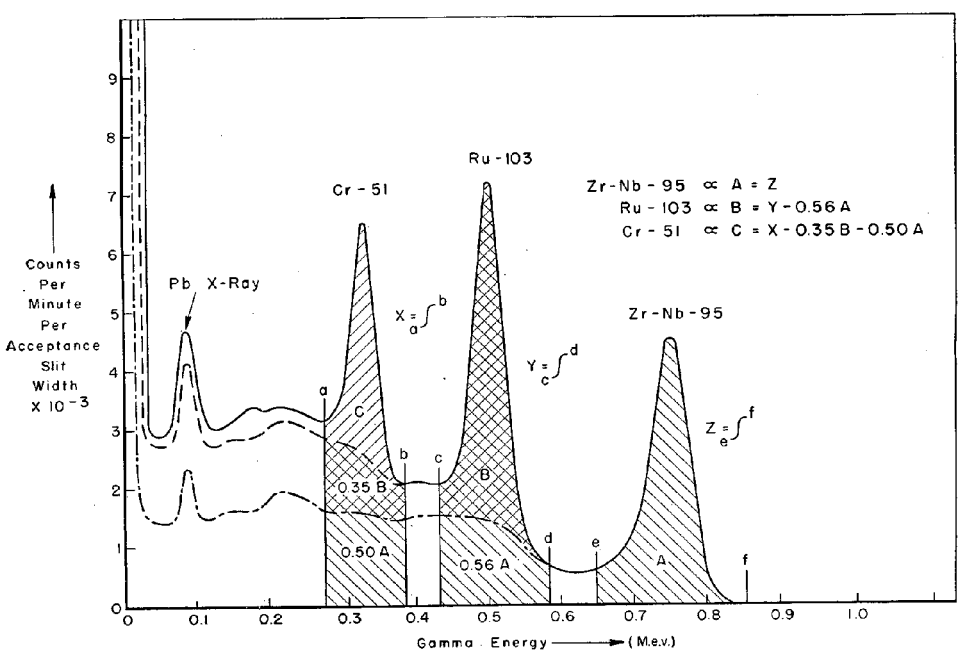

Figure 8. Typical three-peak analysis

tion rates. The application of the method continues to increase as complete gamma spectrometer systems are becoming commercially available and specific applications appear more frequently in the literature.

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Paper Chromatography in Steroid Determination

LESTER M. REINEKE

Research Laboratories, The Upjohn Co., Kalamazoo, Mich.

Paper chromatography has been applied to the identification and quantitative determination of steroids obtained from microbiological and chemical transformations. A clear indication of the probable structure is obtained by ultraviolet absorption, chemical tests, and mobility (as compared to various known steroids) in a variety of solvent systems of both the Bush and Zaffaroni types. A quantitative procedure using light absorption at 224 and 242 mμ has been developed for progesterone and 11α-hydroxyprogesterone. This procedure eliminates the necessity for running blanks and steroid standards with each determination.

THE technique of paper chromatography is discussed here, as applied to steroidal transformations induced microbiologically or chemically. The compounds considered are more polar than the sterols. In these laboratories, paper chromatography is used only for identification or determination of purity, but the information is also helpful in proof of structure.

When Zaffaroni, Burton, and Keutman (*31*) reported the formamide-benzene and propylene glycol–toluene systems, the first practical method of applying paper chromatography to steroids became available. [In this discussion, any solvent system (*1–4, 11, 15–17, 21, 23–25, 27, 28, 30*) using a paper impregnated with a high boiling polar solvent as the stationary phase and a nonpolar solvent saturated with the stationary phase as the mobile phase is referred to as the Zaffaroni type.] Later, Bush (*5*) used a series of systems in which the stationary phase, water and methanol, is preferentially adsorbed onto the paper from the vapor of both phases during equilibration. The mobile phase, consisting of various nonpolar solvents, is used for development. With the Bush systems, a slightly elevated temperature is usually desirable. [Any solvent system of similar nature (*6, 8, 14, 18, 19*) is referred to here as of the Bush type.] Various systems for paper chromatography of steroids, other than sterols (*5, 9, 13, 22, 26, 29*), have been published but, in general, they are one of the above two types.

COMPARISON OF DEVELOPMENT SYSTEMS

Much larger quantities of steroid can be applied to the Zaffaroni type of chromatogram than can satisfactorily be applied to the Bush type. The development time of the former is generally longer, but in the Zaffaroni type of system resolution of steroids having ultraviolet absorption can be conveniently followed by removing the strip from the chamber for ultraviolet scanning. The sheet may then be dipped through the mobile phase and the development continued. This is not possible with the Bush type of system.

In order to speed up and sharpen the resolution, it is a common practice, first reported by Zaffaroni (*28*), to reduce the amount of stationary phase by dipping the filter paper through the stationary phase diluted with a volatile solvent such as methanol. The diluent is then evaporated from the paper chromatogram before the development is started.

Two modifications of Zaffaroni's procedures (*28, 31*) have been made. (1) No wick is used to saturate the battery jar; the nonpolar solvents are sufficiently volatile to saturate the chamber rapidly. (2) Channeled sheets are not used, because they present greater manipulation problems, particularly when a sheet may be removed from the bath several times for observation. The slight sideways diffusion of the steroidal material is useful in the separation of a small quantity of material from a larger amount of a closely moving material. If confined to the narrow channel, the "edge effect" can obliterate the space between compounds of similar mobility.

The mobilities on these systems are expressed as a ratio to a standard steroid, R_S, because the solvent front has often moved off the chromatogram before sufficient resolution has been ob-

Table I. Zaffaroni-Type Solvent Systems[a]

System Symbol	Literature Reference	Phase		Dried at 37° C., Min.
		Mobile	Stationary	
CM	(*16*)	Methylcyclohexane	Carbitol[b]	..
CMF	..	Methylcyclohexane	Carbitol[c]	10
PT	(*31*)	Toluene	Propylene glycol	..
PTF	(*28*)	Toluene[d]	Propylene glycol[c]	10
K-1	(*11*)	Cyclohexane-benzene (1:1)	Propylene glycol[c]	10
FBF	(*28*)	Benzene	Formamide[c]	15
CFS	..	Skellysolve B[e]	Carbitol-formamide[f]	15

[a] Best grade of solvents commercially available is used. Only formamide is redistilled. Room temperature, 25° ± 2° C.
[b] Diethylene glycol monoethyl ether.
[c] Diluted with methanol (1:1). Methanol evaporates during indicated drying time.
[d] For materials such as 3-ketobisnor-4-cholenic acid, 2% glacial acetic acid can be added to reduce streakiness.
[e] Essentially a normal hexane, b.p. 60–70° C.
[f] Two parts of Carbitol-formamide (1:1) diluted with 1 part of methanol.

tained. An R_S difference of at least 5% is generally needed for positive differentiation—e.g., two materials with R_S values (as compared to 17α,21-dihydroxy-4-pregnene-3,11,20-trione) of 0.10 and 0.11, a 10% difference, could be easily separated from each other with a sufficient development period. With R_S values of 2.0 and 2.1 (5% difference), the separation is more difficult.

The Bush systems have an appreciably faster development time after equilibration. The resolution of the steroids is usually achieved with the advancing solvent front still on the paper. Hence, data can easily be expressed in terms of R_f (relative mobility of the material to the solvent front). However, if the solvent front has been allowed to move off the chromatogram, the R_f can easily be calculated by comparing the unknown to a control of known value. An R_f difference of as little as 0.02 is often sufficient for adequate resolution.

No one system does a perfect job; however, each system does a better job on one group of steroids than on another. For example, steroids such as 11α,17α,21-trihydroxy-4-pregnene-3,20-dione, 6β,17α,21-trihydroxy-4-pregnene-3,20-dione, and 11β, 17α,21-trihydroxy-4-pregnene-3,20-dione, which might require 10 days of development for adequate differentiation with the PTF system, may be differentiated in 3 hours of development time (after equilibration) with the Bush B-5 system. On the other hand, 6β,17β-dihydroxy-4-androsten-3-one and 14α,17β-dihydroxy-4-androsten-3-one, are not separated by the latter system, but differentiate nicely with the PTF system in 3 days. In practice, the results from several solvent systems are compared.

No matter what type of system is employed, the use of a slower system is indicated if a steroid is moving too rapidly. If the material is moving too slowly, time may be saved by running another aliquot from the sample on a faster system. No attempt is made to maintain exact values, as it has been found in these laboratories that mobility values can vary by ±10%. In addition, nonsteroidal materials in the fermentation extracts enhance or slow the mobility of the steroidal material. It is essential to run the sample and mixture of suitable controls side by side as well as mixed together, until sufficient experience has been obtained for a particular organism on a given substrate. There is, in general, an inverse relationship between the mobility and the expected polarity of the steroid.

To facilitate the resolutions of closely moving steroids, it has proved desirable to use at least one chamber, 36 inches high, for each of the major development systems. Very frequently, a resolution is achieved on a 34-inch chromatogram which was unsatisfactory on a conventional 21- or 23-inch chromatogram. Often, the longer sheet has made it possible to obtain a complete picture of a bioconversion from a single chromatogram instead of two.

Both Eaton and Dikeman No. 613 and Whatman No. 1 filter papers have been used. The former is preferred because it has superior wet strength when treated with Tollens reagent (*31*). Prewashing the filter paper is unnecessary for this work.

METHODS OF DETECTION

The ultraviolet absorption of the conjugated ketone in the A ring is the most useful identification test for the steroids encountered in this program. The scanner of Drake and associates (*7*) of these laboratories shows the materials as dark spots against a fluorescent background. By using a suitable photographic paper (Kodagraph Contact Standard) placed directly against the chromatogram, a full size photograph may be made as a permanent record and for convenient analysis of results. This leaves the paper available for color tests if desired.

For ketosteroids that do not have ultraviolet absorption, a spray reagent of 2,4-dinitrophenylhydrazine was developed. The solution is prepared by suspending 300 mg. of 2,4-dinitrophenylhydrazine (Eastman 1866) in 5 to 6 ml. of 3-A ethyl alcohol (U. S. Industrial Chemicals, Inc., SDA). Concentrated sulfuric acid (0.3 ml.) is added and the flask is heated on a steam bath until the reagent is in solution. It is then diluted to 200 ml. with 3-A ethyl alcohol. This reagent was independently developed in this laboratory in cooperation with B. J. Magerlein. Kochakian and Stidworthy (*11*) have developed a similar reagent using hydrochloric acid. 2,4-Dinitrophenylhydrazine has proved useful for the detection of ketones at C-3 or C-20, but does not react with those at C-11. Steroids with a conjugated ketone appear orange, while the other ketosteroids appear as yellow spots against a light yellow background. This test is sensitive to about 8 γ. The 20-ketone is less reactive than the 3-ketone, and a 3-keto-1,4-diene is still less reactive and in some cases is not detected at a level of 32 γ. This order of reactivity is in keeping with the findings from chemical syntheses.

When this reagent is followed with Tollens reagent, a more stable chromatogram is obtained. Steroids containing ketones now appear as yellow spots against a gray background. If the steroid has an α-ketol side chain as well as a 3-ketone, the spots are a dark yellow-gray. When no 3-ketone is available, the ketol side chain produces a dark gray to black spot against the lighter gray background. Apparently, a 21-hydroxyl or acetoxy group offers sufficient hindrance so that the 20-ketone will not react readily with the dinitrophenylhydrazine reagent.

Tollens reagent can be used by itself. Besides the cortical side chain, it has been found useful in detecting steroids such as 4β-bromo-17α-hydroxy-5β-pregnane-3,11,20-trione. A sensitivity of 1 γ is often obtained.

Kritchevsky and Kirk (*12*) developed a phosphomolybdic acid reagent which generally detects steroidal hydroxyl groups. The sheet is dipped in a 10% (w./v.) phosphomolybdic acid (Fisher A-237, Fisher Scientific Co.) in absolute methanol and then heated at 90° C. for 5 minutes. The spots appear bluish to black on a green background. Sixteen micrograms is generally necessary for detection. This method does not work well with sheets which have been treated with formamide as the stationary phase. Nor can this reagent be used satisfactorily on a sheet treated with the test reagents previously discussed. Because of its low sensitivity, it is used only when the other tests give poor detection.

Table II. Bush-Type Solvent Systems[a,b]

System	Composition
A	Skellysolve C,[c] methanol, water—5:4:1
B-1	Toluene, Skellysolve C, methanol, water—5:5:7:3
B-3	Benzene, Skellysolve C, methanol, water—333:667:800:200
B-5	Benzene, methanol, water—2:1:1

[a] See (*5*).
[b] Best grade commercial solvents; temperature of 34° ± 1° C. used for these systems.
[c] Essentially a saturated hydrocarbon fraction, b.p. 86–100° C.

MOBILITY RELATIONSHIPS

Several studies (*23*, *27*) on the relationship of mobility to chemical structure have been reported. A number of exceptions occur, not explicable from the author's experience. These reversals actually aid in making the probable identification more accurate. For example, 6β-hydroxy-4-pregnene-3,20-dione moves more slowly than 14α-hydroxy-4-pregnene-3,20-dione on all systems that have been tried, except the Bush A. On the CFS system, 5α-pregnane-3,11,20-trione moves faster than 5β-pregnane-3,11,20-trione. This is contrary to the usual experience that the 5α-steroids move more slowly. For example, a separation of 11α-hydroxy-5α-pregnane-3,20-dione from 11α-hydroxy-5β-pregnane-3,20-dione, the latter compound has the greater mobility—that is, is less polar. Both Savard (*23*) and Zaffaroni (*27*) have generalized that the 5α-configuration is the less polar, in contrast to the present author's findings.

The products of a microbiological conversion of a steroid can be very complex—e.g., a C_{21} steroid may have the side chain removed, the *D* ring altered, and a hydroxyl group added (*20*). A compilation of the mobilities of a number of steroids in several different development systems together with the method of detection is very useful in establishing the probable identification of the steroids in samples submitted for analysis. A common reference for the mobilities facilitates the identification of such varied products.

A study of Table III shows that the faster moving members of one series—for example, the C_{19} steroids—overlap with the slower members of another, the C_{21} steroids. This is typical of the results obtained.

A difference in reaction to a test is as useful as a different solvent system. For example, 17α,20β,21-trihydroxy-4-pregnen-3-one and 17α,21-dihydroxy-4-pregnene-3,11,20-trione are difficult to separate on the PTF system, but the latter compound gives a positive Tollens test. 17β-Hydroxy-4-androsten-3-one and 21-hydroxy-4-pregnene-3,20-dione have identical mobilities on the Bush B-3 system. Again, Tollens reagent would quickly show the difference.

Because it is generally desired that new steroids be isolated on a macro scale, characterization of an unknown by paper chromatography of derivatives obtained by micro techniques, a method used by Zaffaroni and Burton (*27, 28*) and others, is not attempted. Rather, a variety of solvent systems are relied upon to limit the number of steroid possibilities. As many as 10 or 15 steroids may move together when a single system is employed. When several systems are used, there are very few steroids which are not differentiated from each other if they are at least as polar as 11α-hydroxy-5β-pregnane-3,20-dione.

To help identify a steroid, physical and chemical properties are compared with those of as many steroids as possible. The characteristics compared are mobilities on several solvent systems, ultraviolet absorption, and functional groups as indicated by chemical reagents applied directly to the developed chromatogram. Table III gives this pertinent information for 121 steroids.

In this table the steroids are related to the solvent front or to the same standard steroid within a given development system. The values are obtained by direct comparison to key steroids for which average values from several determinations are used. To facilitate the location of a steroid, Table III is divided into the following sections.

A. Steroids of 19 carbon atoms in the basic molecule with a carbonyl group at position 17. 17β-Hydroxy-4-androsten-3-one is also included in this section for comparison purposes
B. Steroids of 19 carbons with a hydroxyl group in the 17β-position
C. Steroids of 18 carbon atoms (19-norsteroids)
D. Steroids of 21 carbon atoms, except those with an α-ketol or glycol side chain. For purposes of comparison with other monohydroxy-4-pregnene-3,20-dione steroids, 21-hydroxy-4-pregnene-3,20-dione is also included
E. Steroids of 21 carbon atoms with an α-ketol or glycol side chain

In each division, the compounds are listed in order of increasing number of functional groups. Carbon-carbon double bonds are not included in the number of functional groups. Within any category of total functional groups, the ones with the highest number of carbonyl groups are listed first; then they are listed by number of hydroxyl groups. The compounds with the α-orientation are listed first, with the 3α-hydroxyl group arbitrarily listed ahead of a 5α-hydrogen in a saturated steroid. When the functional groups are the same, listing is by decreasing degree of saturation.

SEMIQUANTITATIVE PROCEDURES

Visual Estimation. In working with conversion products formed by microorganisms, two assumptions are made: that the steroid is not destroyed by the organism, and that the steroid or its conversion product is completely extracted from the beer. Although these assumptions are often not true, the qualitative results obtained by comparing the spot with the amount of the control give significant information in plotting the steroid balance.

More precise quantitative and semiquantitative procedures using paper chromatography can readily be developed. Often a semiquantitative visual estimation is entirely satisfactory and can be obtained in considerably less time. Because such estimations at best will be $\pm 20\%$ of the amount present, the minor steroidal impurities are often estimated instead of the major transformation product. Levels of the suspected impurities comparable to that expected in the sample are used. For example, crystalline 11α-hydroxy-4-pregnene-3,20-dione estimated to contain 2% 4-pregnene-3,20-dione is run at levels of 200 and 400 γ along with levels of 4-, 8-, and 16-γ quantities of 4-pregnene-3,20-dione for visual comparison. If the material is fairly pure, it is assumed that the balance is the major steroidal component. For the impurities, the error may be $\pm$ 50%. However, if the impurity is present to the extent of only 1 or 2%, the range is still very acceptable. The actual significance of the sample should be kept in mind. When this technique was applied to large scale fermentation studies, using the CMF system, it was possible to give a good estimation of the residual 4-pregnene-3,20-dione within 2 hours of sampling.

Spectrophotometric Analysis. For more precise determination of a steroid having ultraviolet absorption, the material may be eluted from the developed chromatogram and estimated spectrophotometrically. It is necessary to correct the apparent absorption of the steroid for nonsteroidal material (blank) having ultraviolet end absorption, which is also eluted from the paper. Complete removal of this latter material from the chromatogram is very difficult. Compensation can be readily made for it, and the removal is not attempted.

Experimentation showed that the ultraviolet absorption curves of the eluate of a number of blank control strips were similar in shape, although they varied considerably in intensity, depending upon the size of the sample. Thus, the approach of Johnson, Struck, Scott, and Stafford (*10*) of this laboratory could be used for handling a component of varying ultraviolet absorption intensity but of constant shape in a two-component system. It reduces the quantity of the blank to a numerical ratio. This greatly simplifies the conventional algebraic handling of spectrometric data for a two-component system.

For the blank, a ratio was established of the absorbance at a point from the ultraviolet curve where the blank showed good absorption (224 mμ) and the absorbance at a point where the steroids being used had good absorption (242 mμ). The absorbance of a 1 mg. per ml. solution of the steroid at the same wave lengths was also determined. The calculation is done as indicated in the following formula:

$$\frac{R \times D_{242} - D_{224}}{R \times K_{242} - K_{224}} \times V \times P = \text{mg. in aliquots}$$

where

R = ratio of D_{224}/D_{242} mμ for the chromatogram blank
K = absorbance of a 1 mg. per ml. solution of steroid
V = volume of elution solvent
P = pipet correction when micropipets are used (100/95)
D = absorbance readings at 224 and 242 mμ for the sample

The determination of 11α-hydroxy-4-pregnene-3,20-dione and 4-pregnene-3,20-dione in a mixture will serve as an example.

A calibrated micropipet holding 0.01 ml. of solution containing 500 γ is applied as a single spot on a propylene glycol–impregnated sheet, and the paper strip is developed with toluene overnight. The chromatogram is removed from the developing chamber and dried at 105° C. for 2 hours. The area containing the steroid as seen on the scanner is outlined in pencil, and then cut from the developed chromatogram into a 250-ml. Erlenmeyer flask. Absolute methanol (50 ml.) is added and the flask is shaken on a rotary shaker for 2 hours. After the eluate is filtered through a coarse fritted funnel, an aliquot is read on a Beckman DU spectro-

Table III. Steroid Mobilities

Compound	Detection[a]	Development Systems: CM, R_S[b]	PT, R_S[c]	PTF, R_S[d]	K-1, R_S[c]	FBF, R_S[b]	Bush A, R_f[e]	Bush B-1, R_f[e]	Bush B-3, R_f[e]	Bush B-5, R_f[e]
A. C_{19} steroids										
5α-Androstane-3,17-dione	a	2.7	...[f]	...	...	...	0.76	...	...	..
4-Androstene-3,17-dione	b	1.65	...	...	5.3	...	0.5	0.89	0.78	..
1,4-Androstadiene-3,17-dione	c	1.0	...	...	...	...	0.27	...	0.78	..
4,9(11)-Androstadiene-3,17-dione	b	1.65	...	...	...	...	0.5	...	0.78	..
3β-Hydroxy-5-androsten-17-one	d	1.15	...	...	3.6	...	0.38	0.83	0.65	..
3β-Acetoxy-5-androsten-17-one	d	5.5	...	...	...	...	0.85	0.99	0.99	..
17β-Hydroxy-4-androsten-3-one	b	0.89	1.5	...	2.0	1.44	0.22	0.74	0.52	..
Testololactone	b	0.4	2.8	...	2.7	1.23	0.043	0.63	0.28	..
4-Androstene-3,6,17-trione	b	0.72	...	...	5.5	1.61	0.13	0.80	0.52	..
4-Androstene-3,11,17-trione	b	0.68	...	...	4.8	1.51	0.11	0.78	0.43	..
6β-Hydroxy-4-androstene-3,17-dione	b	..	1.0	8.4	0.89	0.74	...	0.43	0.19	0.90
11α-Hydroxy-4-androstene-3,17-dione	b	..	0.65	4.6	0.49	0.45	...	0.25	0.06	0.82
11β-Hydroxy-4-androstene-3,17-dione	b	..	1.50	...	1.4	1.0	...	0.53	0.26	..
14α-Hydroxy-4-androstene-3,17-dione	b	..	0.90	5.9	0.79	0.55	...	0.33	0.12	0.87
15α-Hydroxy-4-androstene-3,17-dione	b	..	...	4.0	0.40	0.41	...	0.22	..	0.82
B. C_{18} 17β-hydroxysteroids										
17β-Hydroxy-4-androsten-3-one	b	0.89	1.50	...	2.0	1.44	0.22	0.74	0.52	..
17β-Hydroxy-1,4-androstadien-3-one	c	0.60	1.0	...	1.35	1.24	0.11	0.69	0.34	..
17β-Acetoxy-4-androsten-3-one	b	3.5	...	...	...	...	0.83	...	..	..
17β-Propionoxy-4-androsten-3-one	b	4.25	...	...	...	...	0.85	...	..	..
17β-Cyclopentylpropionoxy-4-androsten-3-one	b	5.85	...	...	...	...	0.99	...	..	..
17α-Methyl-17β-hydroxy-4-androsten-3-one	b	1.15	1.80	...	3.1	1.66	0.33	0.82	0.64	..
17α-Ethinyl-17β-hydroxy-4-androsten-3-one	b	0.74[g]	1.80[g]	...	2.55[g]	1.55[g]	0.16[g]	0.74[g]	0.52[g]	..
5-Androstene-3β,17β-diol	d	..	0.38	2.9	0.57	...	...	0.62	..	..
17β-Hydroxy-4-androstene-3,11-dione	b	..	0.82	5.3	0.64	0.65	...	0.31	0.13	..
17α-Methyl-17β-hydroxy-4-androstene-3,11-dione	b	..	1.05	8.7	1.3	1.0	...	0.56	0.21	..
6β,17β-Dihydroxy-4-androsten-3-one	b	..	...	1.1	0.13	0.16	...	0.15	..	0.67
11α, 17β-Dihydroxy-4-androsten-3-one	b	0.16	0.074	0.61	0.065	0.09	...	0.07	..	0.47
17α-Methyl-11α,17β-dihydroxy-4-androsten-3-one	b	..	...	1.1	0.13	0.20	...	0.13	..	0.58
11β,17β-Dihydroxy-4-androsten-3-one	b	..	...	1.7	0.21	0.28	...	0.21	..	0.74
14α,17β-Dihydroxy-4-androsten-3-one	b	..	...	1.39	0.18	0.21	...	0.12	..	0.67
C. C_{18} steroids										
4-Estrene-3,17-dione	b	1.32	...	...	...	...	0.4	...	0.74	..
Estrone	d	0.66	1.3	...	1.6	1.42	0.14[g]	0.74	0.52	..
17β-Hydroxy-4-estren-3-one	b	0.78	1.3	...	1.86	1.32	0.14	0.68	0.43	..
Estradiol	d	..	...	1.7	0.40	0.68	...	0.47	0.21	..
11α-Hydroxy-4-estrene-3,17-dione	b	..	...	3.6	0.35	0.32	...	0.19	0.05	0.76
10ξ,17β-Dihydroxy-4-estren-3-one	b	..	...	1.2	...	...	...	0.11	..	0.66
11α,17β-Dihydroxy-4-estren-3-one	b	..	...	0.49	...	...	...	0.04	..	0.39
D. C_{21} steroids										
5α-Pregnane-3,20-dione	a	3.5	...	...	...	...	0.83	...	..	..
5β-Pregnane-3,20-dione	a	3.5	...	...	...	...	0.83	...	..	..
4-Pregnene-3,20-dione	b	2.7	...	...	6.0	...	0.76	0.95	0.96	..
1,4-Pregnadiene-3,20-dione	b	1.65	...	...	...	...	0.55	...	0.78	..
4,6-Pregnadiene-3,20-dione	b	2.7	...	...	...	...	0.68	...	0.96	..
4,9(11)-Pregnadiene-3,20-dione	b	2.7	...	...	...	...	0.68	...	0.96	..
4,16-Pregnadiene-3,20-dione	b	2.7	...	...	...	...	0.76	...	0.96	..
3α-Hydroxy-5β-pregnan-20-one	e	1.95	...	...	...	...	0.72	...	0.93	..
3β-Hydroxy-5α-pregnan-20-one	e	1.65	...	...	...	...	0.72	...	0.89	..
3β-Hydroxy-5-pregnen-20-one	d	1.65	...	...	...	...	0.64	...	0.78	..
3β-Hydroxy-5,16-pregnadien-20-one	d	1.65	...	...	...	...	0.61	...	0.78	..
5α-Pregnane-3,11,20-trione	a	1.25	...	...	...	...	0.42	0.89	0.78	..
5β-Pregnane-3,11,20-trione	a	1.25	...	...	...	...	0.42	0.89	0.78	..
4-Pregnene-3,11,20-trione	b	1.00	...	...	4.0	...	0.25	0.82	0.65	..
3α-Hydroxy-5β-pregnane-11,20-dione	a	0.79	1.6	...	2.1	...	0.14	...	0.43	..
3β-Hydroxy-5α-pregnane-11,20-dione	a	0.64	1.6	...	1.9	...	0.11	...	0.34	..
3β-Hydroxy-5β-pregnane-11,20-dione	a	0.79	1.6	...	2.1	...	0.16	...	0.43	..
11α-Hydroxy-5α-pregnane-3,20-dione	a	0.64	1.6	...	1.9	...	0.08	...	0.34	..
11α-Hydroxy-5β-pregnane-3,20-dione	a	0.79	1.6	...	2.1	...	0.12	...	0.43	..
11β-Hydroxy-5β-pregnane-3,20-dione	a	1.0	...	...	3.3	...	0.20	...	0.65	..
6β-Hydroxy-4-pregnene-3,20-dione	b	0.63	1.5	...	1.6	1.12	0.097	0.69	0.34	..
11α-Hydroxy-4-pregnene-3,20-dione	b	0.4	1.0	8.4	1.0	1.0	0.034	0.47	0.19	..
11α-Hydroxy-4,16-pregnadiene-3,20-dione	b	0.4	1.0	...	1.0	1.04	0.04	0.47	0.19	..
11α-Acetoxy-4-pregnene-3,20-dione	b	1.25	...	...	5.3	...	0.25	...	0.71	..
11β-Hydroxy-4-pregnene-3,20-dione	b	0.60	1.8	...	2.1	1.42	0.11	0.71	0.43	..
14α-Hydroxy-4-pregnene-3,20-dione	b	0.60	1.8	...	2.1	1.32	0.078	0.69	0.34	..

[a] Only preferred methods of detection are indicated.
a. 2,4-Dinitrophenylhydrazine reagent
b. Ultraviolet absorption and 2,4-dinitrophenylhydrazine reagent
c. Ultraviolet absorption
d. Phosphomolybdic acid reagent
e. 2,4-Dinitrophenylhydrazine and phosphomolybdic acid reagents
f. Ultraviolet absorption, 2,4-dinitrophenylhydrazine, and Tollens reagents
g. 2,4-Dinitrophenylhydrazine and Tollens reagents
h. Ultraviolet absorption and Tollens reagents
i. Tollens reagent

[b] Relative mobility to 4-pregnene-3,11,20-trione.
[c] Relative mobility to 11α-hydroxy-4-pregnene-3,20-dione.
[d] Relative mobility to 17α,21-dihydroxy-4-pregnene-3,11,20-trione.
[e] Relative mobility to solvent front.
[f] Dots indicates that mobility for R_f values has not been determined because of low polarity for the system, polarity too high for the system, or extreme streaking.
[g] Streaked on this system.

Table III. Steroid Mobilities (*Continued*)

Compound	Detection[a]	Development Systems: CM, Rs[b]	PT, Rs[c]	PTF, Rs[d]	K-1, Rs[c]	FBF, Rs[b]	Bush A, Rf[e]	Bush B-1, Rf[e]	Bush B-3, Rf[e]	Bush B-5, Rf[e]
15α-Hydroxy-4-pregnene-3,20-dione	b	0.37	1.0	6.8	0.77	0.82	0.017	0.40	0.13	..
15β-Hydroxy-4-pregnene-3,20-dione	b	0.4	1.1	...	1.2	1.0	0.036	0.49	0.20	..
16α-Hydroxy-4-pregnene-3,20-dione	b	0.4	0.8	6.8	0.92	0.74	0.024	0.43	0.15	..
17α-Hydroxy-4-pregnene-3,20-dione	b	0.78	1.8	...	2.55	1.51	0.16	0.78	0.52	..
21-Hydroxy-4-pregnene-3,20-dione	f	0.86	...	...	4.0	1.5	0.23	0.81	0.52	..
Methyl-3,11-diketo-4,17(20)-(*cis*)-pregnadien-21-oate	b	1.5	...	...	5.8	...	0.57	...	0.78	..
3α,11α-Dihydroxy-5β-pregnan-20-one	a	0.4	...	3.0	0.43	0.74	...	0.41	..	0.87
3β,11α-Dihydroxy-5α-pregnan-20-one	a	0.24	...	2.3	0.29	0.63	...	0.29	..	0.87
11β,21-Dihydroxy-4,17(20)-pregnadien-3-one	b	..	0.29	2.3	0.29	0.47	...	0.31	..	0.87
21-Acetoxy-11β-hydroxy-4,17(20)-pregnadien-3-one	b	1.15	...	...	4.8	...	0.5	...	0.78	..
6β-Hydroxy-4-pregnene-3,11,20-trione	b	..	0.91	...	0.57	0.58	...	0.28	..	..
17α-Hydroxy-5β-pregnane-3,11,20-trione	b	0.64	1.5	...	1.8	...	0.07	0.65	0.37	..
17α-Hydroxy-4-pregnene-3,11,20-trione	b	0.4	1.0	...	1.0	0.89	0.304	0.47	0.19	..
6β,11α-Dihydroxy-5β-pregnane-3,20-dione	a	..	...	1.0	...	0.067	...	0.05	..	0.47
3α,17α-Dihydroxy-5β-pregnane-11,20-dione	a	0.35	...	1.9	0.27	0.48	...	0.32	0.10	0.87
6β,11α-Dihydroxy-4-pregnene-3,20-dione	b	..	0.074	0.61	0.04	0.05	...	0.04	..	0.38
6β,17α-Dihydroxy-4-pregnene-3,20-dione	b	..	...	1.7	0.19	0.21	...	0.19	..	0.75
11α,17α-Dihydroxy-4-pregnene-3,20-dione	b	..	0.14	1.0	0.09	0.13	...	0.09	..	0.61
11β,17α-Dihydroxy-4-pregnene-3,20-dione	b	..	0.38	2.9	0.29	0.39	...	0.23	..	0.83
E. C_{21} 21-hydroxysteroids										
21-Hydroxy-4-pregnene-3,20-dione	f	0.86	...	...	4.0	1.5	0.23	0.81	0.52	..
21-Acetoxy-4-pregnene-3,20-dione	f	1.4	...	...	...	...	0.55	...	0.89	..
21-Acetoxy-4,16-pregnadiene-3,20-dione	f	1.15	...	...	...	...	0.50	...	0.89	..
21-Hydroxy-4-pregnene-3,11,20-trione	f	0.28	...	11.0	1.4	0.69	...	0.43	..	0.92
21-Acetoxy-4-pregnene-3,11,20-trione	f	0.47	...	...	4.7	1.6	...	0.75	0.43	..
6β,21-Dihydroxy-4-pregnene-3,20-dione	f	..	...	3.5	0.28	0.19	...	0.21	..	0.75
11α,21-Dihydroxy-4-pregnene-3,20-dione	f	..	0.23	1.7	0.16	0.13	...	0.10	..	0.61
11β,21-Dihydroxy-4-pregnene-3,20-dione	f	0.22	0.63	4.6	0.49	0.39	...	0.33	..	0.87
14α,21-Dihydroxy-4-pregnene-3,20-dione	f	0.17	0.42	3.5	0.36	0.25	...	0.21	..	0.77
15α,21-Dihydroxy-4-pregnene-3,20-dione	f	..	...	1.36	0.12	0.086	...	0.06	..	0.53
17α,21-Dihydroxy-4-pregnene-3,20-dione	f	0.28	0.42	3.5	0.36	0.35	...	0.33	..	0.87
17a-Hydroxymethyl-17aα-hydroxy-D-homo-4-androstene-3,17-dione (D-homo compound S)	b	..	0.71	6.4	0.33	0.35	...	0.30	..	0.87
21-Acetoxy-11β-hydroxy-4-pregnene-3,20-dione	f	0.4	2.6	...	2.1	1.36	...	0.71	0.38	..
21-Acetoxy-15α-hydroxy-4-pregnene-3,20-dione	f	..	0.92	...	0.73	0.79	...	0.34	0.10	..
21-Acetoxy-17α-hydroxy-4-pregnene-3,20-dione	f	0.49	1.8	...	1.7	1.5	...	0.73	0.43	..
17α,21-Dihydroxy-5β-pregnane-3,11,20-trione	g	0.21	...	1.5	0.11	0.11	...	0.21	..	0.75
17α,21-Dihydroxy-4-pregnene-3,11,20-trione	f	0.16	...	1.0	0.085	0.055	...	0.09	..	0.61
17α,21-Dihydroxy-1,4-pregnadiene-3,11,20-trione	f	..	...	0.66	...	...	...	...	...	0.57
21-Acetoxy-17α-hydroxy-5β-pregnane-3,11,20-trione	g	0.4	1.5[g]	9.5[g]	...	1.0	...	0.65[g]	0.28[g]	...
21-Acetoxy-17α-hydroxy-4-pregnene-3,11,20-trione	f	0.22	0.91[g]	6.0[g]	0.64[g]	0.65	...	0.44	0.15	0.95
21-Acetoxy-17α-hydroxy-1,4-pregnadiene-3,11,20-trione	h	..	...	4.4[g]	0.39[g]	0.56[g]	...	0.40	0.12	0.90
6β,17α,21-Trihydroxy-4-pregnene-3,20-dione	f	..	...	0.23	...	...	...	0.024	..	0.22[g]
11α,17α,21-Trihydroxy-4-pregnene-3,20-dione	f	..	...	0.12	0.01	0.01	...	0.013	..	0.12
11β,17α,21-Trihydroxy-4-pregnene-3,20-dione	f	..	...	0.44	0.033	0.029	...	0.04	..	0.37
11β,17α,21-Trihydroxy-1,4-pregnadiene-3,20-dione	h	..	...	0.27	...	0.018	...	0.025	..	0.27
21-Acetoxy-3α,17α-dihydroxy-5β-pregnane-11,20-dione	i	..	...	1.4	0.11	0.31	...	0.28	..	0.87
21-Acetoxy-3β,17α-dihydroxy-5α-pregnane-11,20-dione	i	..	...	1.1	0.08	0.23	...	0.21	..	0.87
21-Acetoxy-11β,17α-dihydroxy-4-pregnene-3,20-dione	f	0.17	...	2.9[g]	0.29[g]	0.39[g]	...	0.34[g]	0.09	0.9
21-Acetoxy-11β,17α-dihydroxy-1,4-pregnadiene-3,20-dione	h	..	...	1.3[g]	0.15[g]	0.25[g]	...	0.27[g]	0.07	0.82[g]
11β,17α,20α,21-Tetrahydroxy-4-pregnen-3-one	b	..	...	0.09	...	...	...	...	..	0.09
11β,17α,20β,21-Tetrahydroxy-4-pregnen-3-one	b	..	...	0.12	...	...	...	...	..	0.12
21-Acetoxy-11β,17α,20α-trihydroxy-4-pregnen-3-one	b	..	...	1.0	...	0.055	...	0.09	..	0.61
21-Acetoxy-4β-bromo-17α-hydroxy-5β-pregnane-3,11,20-trione	g	0.4	...	13.9[g]	...	1.42	...	0.71	0.39	..
2-Methyl-11β,17α,21-trihydroxy-4-pregnene-3,20-dione	f	..	...	0.86	...	0.09	...	0.10	..	0.69
21-Acetoxy-9α-fluoro-11β,17α-dihydroxy-4-pregnene-3,20-dione	f	..	...	1.4[g]	...	0.23	...	0.27[g]	..	0.9
2-Methyl-21-acetoxy-11β,17α-dihydroxy-4-pregnene-3,20-dione	f	..	...	6.1[g]	0.64	0.92	...	0.51	0.20	0.96
17α,21-Dihydroxy-5β-pregnane-3,11,20-trione-3,20-ethylene glycol diketal	a	0.5	...	...	1.7	1.26	...	0.60	0.37	..
17α,21-Dihydroxy-5-pregnene-3,11,20-trione-3,20-ethylene glycol diketal	a	0.36	...	...	1.4	1.0	...	0.47	0.23	0.91
11β,17α,21-Trihydroxy-5-pregnene-3,20-dione-3,20-ethylene glycol diketal	a	0.28	...	1.7	0.66	0.5	...	0.31	0.13	0.61
2-Methyl-9α-fluoro-11β,17α,21-trihydroxy-4-pregnene-3,20-dione	f	..	...	0.44	...	0.04	...	0.057	..	0.61
2-Methyl-21-acetoxy-9α-fluoro-11β,17α-dihydroxy-4-pregnene-3,20-dione	f	..	...	4.4[g]	0.49	0.56[g]	...	0.41[g]	0.15	0.95

[a] Only preferred methods of detection are indicated.
- a. 2,4-Dinitrophenylhydrazine reagent
- b. Ultraviolet absorption and 2,4-dinitrophenylhydrazine reagent
- c. Ultraviolet absorption
- d. Phosphomolybdic acid reagent
- e. 2,4-Dinitrophenylhydrazine and phosphomolybdic acid reagents
- f. Ultraviolet absorption, 2,4-dinitrophenylhydrazine, and Tollens reagents
- g. 2,4-Dinitrophenylhydrazine and Tollens reagents
- h. Ultraviolet absorption and Tollens reagents
- i. Tollens reagent

[b] Relative mobility to 4-pregnene-3,11,20-trione.
[c] Relative mobility to 11α-hydroxy-4-pregnene-3,20-dione.
[d] Relative mobility to 17α,21-dihydroxy-4-pregnene-3,11,20-trione.
[e] Relative mobility to solvent front.
[f] Dots indicates that mobility for R_f values has not been determined because of low polarity for the system, polarity too high for the system, or extreme streaking.
[g] Streaked on this system.

photometer at 224 and 242 mμ. The calculation (*10*) for 11 α-hydroxy-4-pregnene-3,20-dione is carried out as described in the above formula. Contact with rubber must be avoided at all stages after the paper strip has been developed.

The 4-pregnene-3,20-dione is determined in a similar fashion. As the amount of 4-pregnene-3,20-dione present as a contaminant in the 11α-hydroxy-4-pregnene-3,20-dione obtained by microbiological conversion is in the vicinity of 1%, it is necessary to streak 10 mg. of sample across a 3-inch space of a chromatogram prepared for the Carbitol-methylcyclohexane system. After overnight development, the papergram is dried and the area is cut out and eluted, filtered, and read.

In one study for evaluation of the accuracy of this method, four samples in the range of 90 to 95% 11α-hydroxy-4-pregnene-3,20-dione were assayed with six replicas of each analysis. The recovery averaged 100 ± 0.5% with no significant difference at the level of confidence of 19 out of 20 samples. For 4-pregnene-3,20-dione at the same level, two samples with six replicates each gave 99.7 ± 1.1%. These results are comparable to those obtained by infrared analyses.

When pure 4-pregnene-3,20-dione was applied to duplicate the amount present in an 11α-hydroxy-4-pregnene-3,20-dione sample containing 1 to 2% of 4-pregnene-3,20-dione as an impurity, the average recovery was 96.6 ± 2%, in two samples with six replicates each. It would be very difficult to work out an infrared analysis for 4-pregnene-3,20-dione present in crystalline 11α-hydroxy-4-pregnene-3,20-dione with this accuracy.

Table IV. Analyses of Crystalline 11α-Hydroxy-4-pregnene-3,20-dione

Blend	11α-Hydroxy-4-pregnene-3,20-dione	4-Pregnene-3,20-dione	Other (Visual)
1	95.8, 99.2 (92.3)[a] (98.7)[b]	2.0, 2.1 (1.73)[a] (2.29)[b]	1.0
2	100.6, 99.0	1.55, 1.34	1.4
3	99.2, 99.2	1.58, 1.62	1.8

[a] Percentage present in sample if lower extreme of 1.7 for blank ratio is used in formula for calculation.
[b] Percentage present if higher extreme of 2.9 for blank ratio is used.

Table IV shows typical results on three different blends of crystalline 11α-hydroxy-4-pregnene-3,20-dione. It is assumed that the ratio of D_{224}/D_{242} mμ for extraneous material elutable from the chromatogram by absolute methanol (blank correction) is a constant. The range of values determined on 66 samples was 1.7 to 2.9 with an average of 2.16. This is introducing an error into the determination, but it seems more logical to take an average value determined from a large number of samples of one lot of filter paper than to take a single sample from a fragment of the same lot (which is done with a single blank determination from the same strip). The need for a control is also eliminated because K for any given steroid is a constant.

Furthermore, the method is very flexible for any quantity of steroid from 50 γ to 10 or more mg. It can be applied to any steroid having ultraviolet absorption (with appropriate choice of wave lengths for reading the absorbance).

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Use and Abuse of pH Measurements

ISAAC FELDMAN

Division of Pharmacology, Department of Radiation Biology, School of Medicine and Dentistry, University of Rochester, Rochester, N. Y.

The development of the concept of pH from its invention by Sørenson in 1909 to the present-day National Bureau of Standards' pH scale is reviewed. The liquid junction potential problem involved in the use of the pH meter is discussed in detail. The magnitude of the error due to the junction potential depends upon the pH, ionic strength, nature of the solutes, nature of solvent, presence of colloids, temperature—in fact, anything that affects the mobilities of charged particles. Whether the junction potential error can be ignored depends upon the use to which the pH measurement is put. Some estimates from the literature as to the probable magnitude of this error are presented and discussed. Under certain relatively simple conditions an approximate relationship may be considered to exist between the pH meter reading and the hydrogen ion concentration. Under other conditions, the pH meter reading must be considered as simply a reproducible reference point having no theoretical significance. Under some conditions, the meter reading cannot even be considered as a reproducible reference point. These points are developed in detail.

THE original hydrogen ion exponent, pH, was invented by Sørenson (*34*) in 1909, for the sake of convenience in tabulating and discussing hydrogen ion concentrations. He defined it by the equation:

$$C_{H^+} = 10^{-p_H} \tag{1}$$

or

$$p_H = -\log_{10} C_{H^+} \tag{2}$$

In calculating p_H for a number of buffers, Sørenson made use of the then-current form of the Nernst equation,

$$\frac{E_x - E_o}{RT/F} = \log_e \frac{C_{H_o^+}}{C_{H_x^+}} \tag{3}$$

for the following cell:

$$\text{Pt; } H_2\text{, buffer} \,|\, \text{KCl salt bridge} \,|\, 0.1N \text{ calomel electrode} \tag{4}$$

where E_x and E_o are the electromotive forces, corrected for liquid junction potentials, for cells containing buffers having hydrogen ion concentrations $C_{H_x^+}$ and $C_{H_o^+}$, respectively, and a hydrogen pressure of 1 atm. When $C_{H_o^+}$ equals unity, this equation becomes

$$p_{H_x} = \frac{E_x - E_o}{2.3\ RT/F} \tag{5}$$

Sørenson determined E_0 by measuring the electromotive force for cells containing hydrochloric acid–sodium chloride mixtures. In calculating the hydrogen ion concentrations in these mixtures, he erroneously applied the Arrhenius belief that even strong electrolytes dissociate incompletely. In addition, at that time it was not known that the electromotive force of cells depends on activities rather than concentrations. Consequently, there is no direct relationship between Sørenson's p_H and the hydrogen ion activity or concentration.

ACTIVITY pH, OR paH

In 1924, Sørenson and Linderstrøm-Lang (*35*) made use of the concept of activity by defining a new pH term,

$$paH = -\log_{10} a_{H^+} \tag{6}$$

where a_{H^+} represents the hydrogen ion activity.

Although the introduction of *paH* represents a great advance in chemical thinking, much confusion is encountered in its interpretation. The chief difficulty is the impossibility of measuring the activity of a single ionic species without resorting to nonthermodynamic assumptions. Indeed, many assertions are made that single ion activities have no physical significance and are therefore meaningless.

Consider the cell,

$$\text{Pt; } H_2 \text{ (1 atm.), HCl, AgCl; Ag} \tag{7}$$

for which the electromotive force, E, is given by

$$E = E^0 - \frac{2.3\ RT}{F} \log_{10} a_{H^+} a_{Cl^-} \tag{8}$$

where E^0 is the electromotive force of the cell when the activity product, $a_{H^+}a_{Cl^-}$, is unity.

Combining Equations 6 and 8 gives

$$paH = \frac{E - E^0}{2.3\ RT/F} + \log_{10} a_{Cl^-} \tag{9}$$

It is obvious from Equation 8 that the electromotive force of cell 7 depends on the product of the individual ionic activities and that the contribution due to each ion individually cannot be evaluated. Conversely, for this type of cell the electromotive force can be used to determine only the product $(a_{H^+}a_{Cl^-})$, which by definition equals the square of the mean activity, $a_\pm$. Hence, Equation 9 is of no value in determining *paH* without some independent means of determining a_{Cl^-}.

Nor is it possible to determine individual ionic activities simply by separating the hydrogen ions to be measured from the chloride of the reference electrode as in cell 4. This device introduces a new source of trouble—namely, the liquid junction potentials at the ends of the salt bridge.

The liquid junction potential which exists at the boundary of two solutions differing in composition is due to a difference in the rates of diffusion of ions of opposite charge. Thus, when hydrochloric acid diffuses across a boundary, the hydrogen ions move much faster than the chloride ions and tend to produce a positive charge in the solution into which they diffuse. On the other hand, if sodium hydroxide is the migrating substance, the solution into which it migrates tends to become negatively charged, because the negative hydroxyl ions diffuse much faster than do sodium ions. Diffusing salts also produce junction potentials but not to as large an extent as do acids or bases, because hydrogen and hydroxyl ions have much greater mobilities than do other ions.

For cell 4, the electromotive force is given by,

$$E = (E^0 - E_j^0) + E_j - \frac{2.3\ RT}{F} \log_{10} a_{H_i^+} a_{Cl_i^-} \tag{10}$$

where E_j is the algebraic sum of the two liquid junction potentials at the ends of the salt bridge; E_j^0 is E_j for the hypothetical cell in which both $a_{H_b^+}$ and $a_{Cl_r^-}$ are unity; and the subscripts b and r indicate that $a_{H_b^+}$ refers to the hydrogen ion activity in the buffer solution whereas $a_{Cl_r^-}$ refers to the chloride ion activity in the calomel half cell.

Combining Equations 6 and 10 gives:

$$pa_{H_b} = \frac{E - (E^0 - E_j^0) - E_j}{2.3\ RT/F} + \log_{10} a_{Cl_r^-} \qquad (11)$$

It is impossible to determine any one of the terms, E_j, $a_{Cl_r^-}$, or $a_{H_b^+}$ without previously knowing two of these quantities.

THERMODYNAMIC pH, OR ptH

In an effort to get around this impasse it was advocated that pH be defined solely in terms of the most convenient method used for its determination—i.e., in terms of the electromotive force of a galvanic cell such as cell 4. Such a definition would be thermodynamically rigorous and therefore may be referred to as the thermodynamic pH, or ptH.

Bjerrum and Unmack (*9*) and Guggenheim and Schindler (*14*) proposed as the fundamental definition,

$$\text{ptH} = \frac{E - E^{0\prime} - E_j}{2.3\ RT/F} \qquad (12)$$

in which $E^{0\prime}$ is an experimentally determined constant. This is equivalent to setting $E^{0\prime}$ equal to $(E^0 - E_j^0 - \frac{2.3\ RT}{F} \log_{10} a_{Cl_r^-})$ of Equation 11. Thus, it would be recognized that, even though they are not rigorously determinable, E_j^0 and a_{Cl^-} may be considered as constants for a given cell at a given temperature. Hence, ptH would be a reproducible number dependent on the hydrogen ion activity if E_j could be obtained. They proposed that E_j be calculated by the Henderson equation (*21*). In addition to the fact that it would have to be performed for each pH measurement, such a calculation furnishes only a laboriously obtained approximation of questionable validity (*4*).

The present-day thermodynamic definition (*20*) of pH lumps the junction potential term, E_j, in with $E^{0\prime}$—i.e.,

$$\text{ptH} = \frac{E - E_{pH}^0}{2.3\ RT/F} \qquad (13)$$

where $E_{pH}^0 = E^{0\prime} + E_j = E^0 - E_j^0 + E_j - \frac{2.3\ RT}{F} \log_{10} a_{Cl_r^-}$

As Harned and Owen have stated (*20*), ". . .this equation completely defines a useful pH number, about which no confusion need arise unless an attempt is made to interpret it in terms of. . ." the hydrogen ion concentration. Unfortunately, however, the need does frequently arise when one wishes to know the hydrogen ion concentration. Hence, the pH cannot always be regarded simply as a variable which must be kept constant during a series of experiments. For this reason, beginning in 1928 with a suggestion by Cohn, Heyroth, and Menkin (*10*) as to a possible procedure, there have been several revisions of the pH scale in an attempt to equate, at least approximately, the hydrogen ion concentration with the thermodynamic ptH.

MacINNES pH

To the theoretical chemist it would be most pleasing if the thermodynamic hydrogen ion activity coefficient, f_t, in the formal expression

$$\text{ptH} = -\log_{10} a_H = -\log_{10} C_{H^+} f_t \qquad (14)$$

were equal to some type of mean activity coefficient, $f_\pm$. This attitude is understandable, as cell measurements provide only mean activity coefficients. For instance, the electromotive force and $f_\pm$ are accurately connected by Equation 15.

$$E = E^0 - \frac{2.3\ RT}{F} \log_{10} C_{HCl}^2 f_{H^+} f_{Cl^-} = E^0 - \frac{2.3\ RT}{F} \log_{10} C_{HCl}^2 f_\pm^2 \qquad (15)$$

This equation holds for cell 7 and also for cell 16,

Pt; H_2 (1 atm.), $HCl(C_1)$ | KCl salt bridge | $HCl(C_2)$, AgCl; Ag (16)

if the hydrochloric acid concentrations C_1 and C_2 are equal. When, however, $C_1 \neq C_2$ or the right half cell contains a chloride other than hydrochloric acid, $f_{H_1^+} f_{Cl_2^-} \neq f_\pm^2$. The failure to realize this latter inequality has probably led some chemists to the misconception that ptH equals $-\log_{10} a_{H^+} f_\pm$.

Undoubtedly, also many chemists hold the mistaken belief that MacInnes set up a pH scale in such a way that f_t and $f_\pm$ are synonymous. It is true that MacInnes, Belcher, and Shedlovsky (*27*, *29*), following Cohn's suggestion, used thermodynamic dissociation constants as a basis for their pH scale, but they did so in such a way that their ptH is only approximately equal to $pH_\pm$ or $-\log_{10} C_{H^+} f_\pm$.

MacInnes and associates found empirically that, for certain dilute buffer solutions in cell 4, the quantity E_{pH}^0 could be selected such that a plot of the left side of Equation 17 *vs.* the square root of the ionic strength, μ, was linear and gave an intercept equal to pK_t, the negative logarithm of the thermodynamic dissociation constant of the buffer acid, HX.

$$\frac{E - E_{pH}^0}{2.3\ RT/F} - \log_{10} \frac{C_{X^-}}{C_{HX}} = pK_t - S\sqrt{\mu} \qquad (17)$$

where S is an empirical constant, and C_{X^-} and C_{HX} are, respectively, the stoichiometric concentrations of buffer salt and acid corrected by the addition and subtraction, respectively, of the computed C_{H^+}.

This Equation 17 is similar in form to 18, the rearranged logarithmic form of the dissociation constant of a weak acid.

$$-\log_{10} C_{H^+} f_\pm - \log_{10} \frac{C_{X^-}}{C_{HX}} = pK_t + \log_{10} \frac{f_\pm}{f_u} \qquad (18)$$

where f_u is the activity coefficient of the undissociated weak acid. Hence, for their solutions of ionic strength ≤ 0.01, if $\text{ptH} = -\log_{10} C_{H^+} f_\pm$ the slope S of Equation 17 should equal the constant, A, of the Debye-Hückel equation, 19 and 20 (*11*, *20*):

$$\log_{10} f_i = \frac{-AZ_i^2\sqrt{\mu}}{1 + Ba_i\sqrt{\mu}} \qquad (19)$$

$$\log_{10} f_\pm = \frac{-AZ_+Z_-\sqrt{\mu}}{1 + Ba_i\sqrt{\mu}} \qquad (20)$$

where Z_i is the charge on any given ion, and Z_+ and Z_- are, respectively, the charges on the cation and anion of a binary electrolyte; A and B are constants dependent on the temperature and dielectric constant of the solvent; and a_i is an empirical constant related to the distance of closest possible approach between oppositely charged ions.

The S values obtained by MacInnes and associates for acetate and chloroacetate buffers were only 12% higher than those predicted by the Debye-Hückel theory. This discrepancy would imply a difference of less than 0.01 between ptH and $pH_\pm$ when $\mu \leq 0.01$. Hence, it might appear true that their method ". . .yields pH values which are not equal to $-\log_{10} C_{H^+} f_\pm$ but are probably as close as they can be adjusted to such equality using. . ." (*29*) the thermodynamic definition of pH. However, one must question their implication that their method ". . .will yield values of pH which are as useful as appears to be possible in the determination of ionization and other equilibrium constants," for in the ionic strength range of their solutions, 10^{-3} to 10^{-2}, the Debye-Hückel equation gives the same values for $\log_{10} f_\pm$ for a uni-univalent electrolyte as for the individual ionic activity coefficient term, $\log_{10} f_{H^+}$. That is, in the region, $\mu \leq 0.01$, where

the Debye-Hückel limiting law (numerators of Equations 19 and 20) is valid, $pH_{\pm}$ is equal to *pa*H. Their work, therefore, must not be interpreted as evidence for the validity of equating ptH with $pH_{\pm}$ at higher ionic strengths.

HITCHCOCK-TAYLOR pH

Hitchcock and Taylor (*22*) used an extended form of the Debye-Hückel equation,

$$\log_{10} f = -A'\sqrt{\mu} - B'\mu \qquad (21)$$

to set up a pH scale on the basis of E^0_{pH} values obtained over a higher ionic strength range, 0.01 to 0.1, than in the work of MacInnes and associates. Moreover, the former workers studied polyvalent electrolytes, such as the tartrate, citrate, and phosphate buffers, in addition to the uni-univalent buffers studied by the latter.

Replacing the last term of Equation 17 with the right side of Equation 21 and rearranging give Equation 22

$$E - kp\mathrm{K}_t - k\log_{10}\frac{C_{X^-}}{C_{HX}} - kA\sqrt{\mu} = E^0_{pH} + kB'\mu \qquad (22)$$

where $k = 2.3\ RT/F$.

Calculating A' from the Debye-Hückel theory, Hitchcock and Taylor plotted the left side of Equation 22 against the ionic strength. If such a plot were linear, the intercept would be E^0_{pH}. They obtained linear curves for the acetate and the glycollate buffers, but the phosphate and borate buffer plots showed curvature. The accuracy of the E^0_{pH} extrapolation for the latter buffers is therefore questionable, but to an extent of less than 0.2 mv., corresponding to only 0.003 pH unit.

The meaning of coefficient f in Equation 21, and therefore of the Hitchcock-Taylor pH scale, depends upon the means of obtaining A' and B'. B' is an empirical quantity, which may or may not be constant. Its value is a function of all the ions affecting E and its use therefore gives some sort of a mean activity coefficient nature to f in Equation 21. For the uni-univalent buffers, the value of A' would be equal to the Debye-Hückel constant, A, whether one attempted to compute $f_{\pm}$ or f_+. However, for the phosphate buffer, Hitchcock and Taylor set $A' = 3A$. This latter equality would be applicable if Equation 21 was used to express the individual-ion activity coefficient ratio in $\log_{10}(f_{HPO_4^=}/f_{H_2PO_4^-})$. Such a calculation would throw f_+, rather than $f_{\pm}$, into the E^0_{pH} term. At least for this particular buffer, it would seem then that their assigned pH is closer to *paH* than to $pH_{\pm}$, for the effect of the last term of Equation 21 becomes very small as μ approaches zero. Hitchcock and Taylor gave no data, other than their assigned pH, for the other polyvalent buffers which they studied.

NATIONAL BUREAU OF STANDARDS pH, OR pH_s

The pH scale established by the National Bureau of Standards workers, referred to as the pH_s scale, is based upon measurements on cells without liquid junction (*2–4, 6, 16–18*). The liquid junction problem will, of course, arise when the pH_s scale is used as the reference by other workers who employ cells containing liquid junctions.

The National Bureau of Standards method of assigning pH_s values consists of three steps (*2, 4*). First, for each of three or more portions of the buffer solution with different small concentrations of added soluble chloride

$$\mathrm{pwH} = \frac{E - E^0}{2.3\ RT/F} + \log_{10} C_{Cl^-} \qquad (23)$$

is determined by measuring the electromotive force of hydrogen-silver chloride cells without liquid junction. By combining Equations 8 and 23 it becomes evident that:

$$\mathrm{pwH} = -\log_{10} f_{H^+} f_{Cl^-} C_{H^+} \qquad (24)$$

Secondly, these pwH values are plotted against the molality of added chloride to give a straight line, the intercept of which corresponds to pwH when the buffer is infinitely dilute with respect to chloride (*16*). This intercept is designated as pwH^0. If $f^0_{Cl^-}$ represents the chloride activity coefficient in a solution of ionic strength equal to that of the buffer when infinitely dilute with respect to chloride, then for the buffer,

$$-\log_{10} f_{H^+} C_{H^+} = \mathrm{pwH}^0 + \log_{10} f^0_{Cl^-} \qquad (25)$$

Thirdly, the pH_s is finally defined as $(-\log_{10} f_{H^+} C_{H^+})$ in Equation 25 and is calculated from pwH^0 by introduction of a conventional, even though nonthermodynamic, scale of individual-ion activity coefficients.

Several reasonable definitions have been proposed for a conventional individual-ion activity coefficient. None of them may be rigorously tested for validity. In the words of Bates (*4*), "the choice should be based for the most part on convenience and reasonableness in the light of what is known from the theory of ionic solutions."

On the basis of electrical conductance data, MacInnes (*28*) concluded that it would be reasonable to assume (1) that the chloride activity in a solution of any univalent chloride is the same as in a solution of potassium chloride at the same total concentration and (2) that in the latter solution the potassium and chloride ions have the same activity. Combining these two "MacInnes assumptions" with the definition of the mean activity coefficient of hydrochloric acid, one might estimate hydrogen ion activity coefficients by:

$f_{H^+} = f^2_{HCl}/f_{Cl^-} = f^2_{HCl}/f_{KCl}$, where f_{HCl} and f_{KCl} refer to mean activity coefficients of hydrochloric acid and potassium chloride in the particular solution under study.

According to Guggenheim (*18*) the activity coefficient of an ion of a strong electrolyte, which dissociates into V_+ positive ions of charge Z_+ and V_- negative ions of charge Z_-, is given by:

$$\ln f_i = \frac{(V_+ + V_-)Z_i^2}{V_+Z_+^2 + V_-Z_-^2} \ln f_{\pm} \qquad (26)$$

By this convention, then, the ionic activity coefficients of a single binary electrolyte are equal to each other and also to the mean activity coefficient, $f_{\pm}$, of the electrolyte.

Strictly speaking, neither of these assumptions is readily applicable to a mixture of electrolytes, such as a buffer solution, in which the mean activity coefficients are not usually known. On the other hand, one may apply the Lewis and Randall hypothesis (*26*) that, "in dilute solutions the activity coefficient of any ion depends solely upon the total ionic strength of the solution." Of course, it is now known that this hypothesis may be used only for approximation purposes. For instance, in estimating activity coefficients in mixtures in which mean activity coefficients are unknown, it is frequently of value to employ as a first approximation the mean activity coefficient of a given substance in its pure solution having the same ionic strength as the mixture.

The terms "MacInnes assumptions" and "Guggenheim assumption" are therefore used hereinafter to describe the applied mathematical device only. Whether the mean activity coefficient of a given substance in its pure solution or in the given mixture is used will be evident from the following definitions: $f_{HCl\ (mixture)}$ refers to the mean activity coefficient of hydrochloric acid in the particular mixture indicated, whereas $f_{HCl(HCl)}$ refers to the mean activity coefficient of hydrochloric acid in pure hydrochloric acid solution having the same ionic strength as the mixture under study.

The pH_s values for the equimolal phosphate buffer, KH_2PO_4: $Na_2HPO_4 = 1:1$, have been calculated by Bates (*2*) as a function of ionic strength—i.e., molality of each phosphate × 4—using each of these three conventions. His results are shown in Figure 1. Using the Guggenheim assumption, $f^0_{Cl^-} = f_{HCl(HCl)}$, curve *G* resulted. Curves *D*3, *D*8, and *DL* were obtained by applying the Debye-Hückel equation using ($a_i = 3$) for curve

$D3$, (a_i = 8) for $D8$, and the limiting-law approximation ($f^0_{Cl^-}$ = $f_{H_2PO_4^-} = f^{1/4}_{HPO_4^-}$) for DL. Application of the MacInnes assumptions, using $f_{HCl(HCl)}$ and $f_{KCl(KCl)}$, by the present author gave curve M. The values assigned as the pH_s values are represented by the dots and were calculated by Bates from Equation 19 using a value of 4.4 as the a_i for chloride. The National Bureau of Standards (*4*) recommends using as a standard reference solution the mixture which is 0.025M with respect to each phosphate and which therefore has $\mu \cong 0.1$. The assigned pH, value is 6.86 ± 0.01 at 25°.

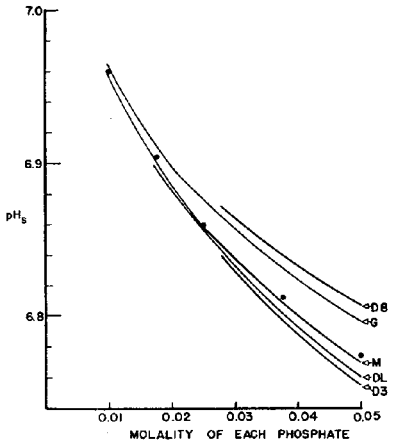

Figure 1. Relation of molality to pH of 1 to 1 phosphate buffers at 25° C.

Computed with various estimates of ionic activity coefficient (*2*, p. 657). See text for explanation of symbols

At $\mu \leq 0.1$ all three activity coefficient conventions (Guggenheim, MacInnes, and Debye-Hückel) furnish pH_s values which agree within ±0.01. The use of bromide or iodide cells (*5*) in place of chloride cells gave pH_s values within 0.015 unit of the National Bureau of Standards assigned values at $\mu \leq 0.1$. However, above μ = 0.1 the pH_s values depend significantly on the activity convention used. In Figure 1, however, even at μ = 0.2—i.e., 0.05 molal in each phosphate— the National Bureau of Standards pH_s differs by only 0.005 unit from that calculated using the MacInnes convention, but it is 0.02 unit lower than that obtained using the Guggenheim assumption. These differences result from the fact that the a_i used by the National Bureau of Standards to calculate $f^0_{Cl^-}$ is much closer to the a_i for potassium chloride, 4.1, than to the a_i for hydrochloric acid, ~6. It should be evident that, in interpreting pH values in terms of C_{H^+}, it is necessary to decide which activity convention is to be used.

Bates has plotted the pH_s values for the phthalate buffer as a function of molality (*2*). His graph is reproduced here as Figure 2. It is seen that even for 0.1 molar phthalate, application of the MacInnes and Guggenheim conventions gives pH_s values which differ from the National Bureau of Standards pH_s by only 0.002 and 0.01 unit, respectively. The National Bureau of Standards values, represented by dots, were obtained with the aid of the Hückel extension (*23*) of the Debye-Hückel equation:

$$\log_{10} f_i = \frac{-AZ_i^2\sqrt{C_i}}{1 + Ba_i\sqrt{C_i}} + \beta'' C_i \qquad (27)$$

using values of 3.76 and 0.01 for the parameters a_i and β'', respectively (*16*). The National Bureau of Standards (*4*) recommends as a standard either 0.05M or 0.05 molal potassium phthalate, both of which are assigned a pH_s of 4.01 ± 0.01 at 25° C.

Other National Bureau of Standards–recommended buffers and their assigned pH_s values can be found in Bates' book (*4*).

Correspondence from Beckman Instruments, Inc., Fisher Scientific Co., and Hartman-Leddon Co., has informed this author that the National Bureau of Standards standards are used by them as the basis for assigning pH numbers to their buffers.

PRACTICAL pH

For most of the pH measurements made by analytical or biological chemists, the glass electrode is employed as the indicator electrode and is connected by a potassium chloride salt bridge to a calomel reference electrode. Without going into the theory of the glass electrode, one may consider that it operates as a hydrogen ion electrode in that the surface potential of the glass, E_G, is equal to $(E^0 - \frac{RT}{F} \log_e a_{H^+})$; so that for the cell used in commercial pH meters,

Glass electrode ‖ standard buffer or test soln. | satd. KCl, Hg_2Cl_2; Hg (28)

the electromotive force is given by Equation 10.

When a pH meter is standardized with a standard buffer, actually a potentiometer circuit is adjusted so that it is in balance when the reading on the output meter equals the pH number assigned to the buffer. The standard buffer is then replaced with a test solution—i.e., the solution whose pH is desired—and the practical pH of the test solution is obtained, which is defined by

$$\text{Practical pH} = pH_s + \frac{E_t - E_s}{2.3\,RT/F} \qquad (29)$$

where E_t and E_s represent the electromotive force when test solution and buffer solution, respectively, are in the potentiometer circuit.

From the point of view of the magnitude of the practical pH measured for a system, the differences between the three modern

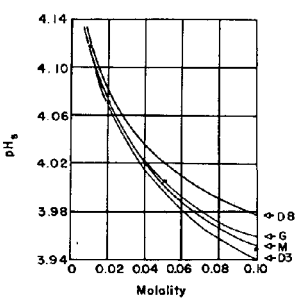

Figure 2. pH of potassium hydrogen phthalate at 25° C.

Computed with various estimates of ionic activity coefficient (*2*, p. 656). See text for explanation of symbols

pH scales (MacInnes, Hitchcock-Taylor, and National Bureau of Standards) hold almost no significance for a biological chemist. With one exception, the pH of standard buffers according to these three pH scales agree within the uncertainty of the National Bureau of Standards assigned values—i.e., within 0.01 from pH 3.5 to 9.2; 0.02 below pH 2.1; 0.03 near pH 13—and also within the limit of accuracy of commercial pH meters. The ex-

ception is the 0.1 *M* potassium tetroxalate buffer, which was assigned a pH value of 1.48 by Hitchcock and Taylor and 1.52 by the National Bureau of Standards investigators. The pH values assigned to standard buffers on the original Sørenson p_H scale are about 0.04 pH unit lower than on the three more modern scales.

An understanding of the various standardization scales, however, is essential for intelligent interpretation of the meaning of the practical pH. The interpretation is discussed in a later section of this paper.

LIQUID JUNCTION POTENTIAL ERRORS FOR AQUEOUS SOLUTIONS

From theoretical considerations (*20*), the junction potential across a boundary would be expected to be a function of pH, ionic strength, the nature of the diffusing ions, solvents, temperature, and, in fact, of anything which affects the mobility of an ion in solution.

Because the pH_s values assigned to standard buffers are based upon cells without liquid junction, the original standardization of the pH meter is subject to an error due to the junction potential term, $E_{js} - E^0_{js}$, subscript s referring to the fact that standard buffer is in the pH meter cell. This error is partially compensated by the junction potential term, $E_{jt} - E^0_{jt}$, which is involved when the test solution is placed in the cell of the meter.

Thus, because $E^0_{jt} = E^0_{js}$, the residual junction potential $E_{js} - E_{jt}$ inherent in the use of the pH meter, produces an error Δ_{pH}(= residual $E_j \times F/2.3\,RT$) in the determination of the practical pH. One cannot calculate the magnitude of this error accurately. However, an indication under certain conditions may be obtained.

Bates, Pinching, and Smith (*7*) determined the apparent pH, or pH_j, for a number of test solutions in the cell with liquid junction;

Pt; H_2, test soln. | satd. KCl | NBS phosphate buffer, H_2; Pt (30)

For each of the same test solutions they determined pH_s using hydrogen–silver chloride cells without liquid junction by the method already described. The difference, $pH_j - pH_s$, for each solution is equivalent to the Δ_{pH} which would prevail if the pH meter were employed for the pH measurement using the phosphate buffer as standard.

Their results may be summarized as follows: (1) $pH_j - pH_s$ did not exceed 0.02 unit for any of their 12 buffers having pH_s between 2.15 and 10.00; (2) $pH_j - pH_s$ reached a magnitude of 0.03 unit for four of the six buffers studied having $pH_s \leq 2.10$; and (3) $pH_j - pH_s$ exceeded 0.02 unit (0.05 at pH 12.62) for three out of the six buffers having $pH_s \geq 11$. No correlation between $pH_j - pH_s$ and μ can be drawn from their data. Hence the larger pH error below pH 2.1 and above pH 10 cannot be attributed to an ionic strength effect, but is probably a true pH effect.

Nevertheless, ionic strength has a real effect on Δ_{pH}. Its significance, however, depends on the accuracy required of the pH measurement. Some indication of its magnitude can be obtained from the electromotive force measurements of Harned (*19*) using cells I and II.

(I) Hg; Hg_2Cl_2, $HCl(m_o)$ + $MCl(m)$, H_2;
Pt-Pt; H_2, $HCl(m_o)$, Hg_2Cl_2; Hg

(II) Pt; H_2, $HCl(m_o)$ | KCl satd. | $HCl(m_o)$ + $MCl(m)$, H_2; Pt

For cell I, $E_I = \frac{RT}{F} \log_e \frac{(a_{H^+}a_{Cl^-})_s}{(a_{H^+}a_{Cl^-})_o}$, where subscripts s and o refer to the hydrochloric acid solutions with and without salt, respectively. For cell II, $E_{II} = \frac{RT}{F} \log_e \frac{(a_{H^+})_s}{(a_{H^+})_o} + E_j$. By employing known e.m.f. values for cells reversible to potassium and chloride ions and the MacInnes assumptions, Harned evaluated the ratio $(a_{Cl^-})_s/(a_{Cl^-})_o$. Inserting this ratio in E_I gave $E_o = \frac{RT}{F} \log_e \frac{(a_{H^+})_s}{(a_{H^+})_o}$, which when subtracted from E_{II} gave values for E_j in cell II. His results are plotted in Figure 3.

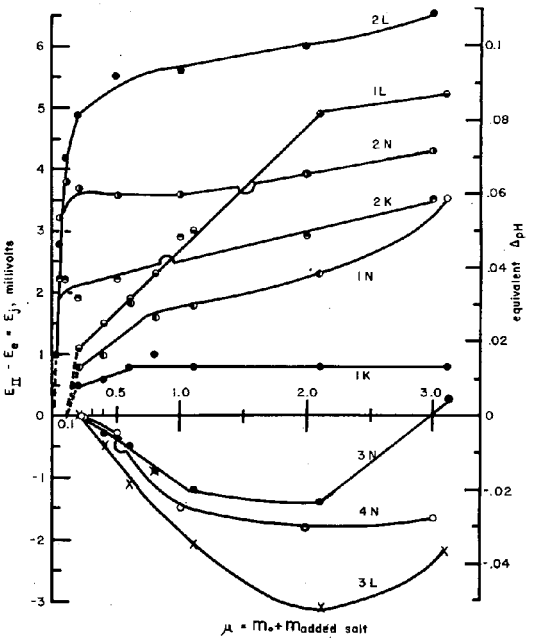

Figure 3. E_j estimated for cell II by Harned

1*K*. 0.1 molal HCl plus KCl
1*L*. 0.1 molal HCl plus LiCl
1*N*. 0.1 molal HCl plus NaCl
2*K*. 0.01 molal HCl plus KCl
2*L*. 0.01 molal HCl plus LiCl
2*N*. 0.01 molal HCl plus NaCl
3*L*. 0.1 molal NaOH plus LiCl
3*N*. 0.1 molal NaOH plus NaCl
4*N*. 0.01 molal NaOH plus NaCl

The pH equivalents of these data can be translated into Δ_{pH} values. For instance, if a pH meter were standardized with 0.01 molal hydrochloric acid, the practical pH measured for a solution 0.01 molal in hydrochloric acid and 0.09 molal in sodium chloride would be in error by 0.045 pH unit. For a solution 0.01 molal in hydrochloric acid and 2.0 molal in sodium chloride, this error would be 0.065 pH unit. However, if the meter were standardized originally with the (0.01 molal hydrochloric acid, 0.09 molal sodium chloride) solution, then Δ_{pH} for the (0.01 molal hydrochloric acid, 2.0 molal sodium chloride) solution would be reduced to 0.065 − 0.045 or only 0.020 pH unit. Such deductions from curves 2*K*, 2*N*, and 4*N* suggest that, if potassium chloride or sodium chloride is the predominant constituent in an aqueous solution having a pH between 2 and 12, the variation in Δ_{pH} due to ionic strength is less than 0.04 pH unit when the ionic strength is increased from 0.05 to 3!

The lithium chloride curves (1*L*, 2*L*, and 3*L*) consistently show greater values for $E_{II} - E_o$ than do the corresponding sodium and potassium chloride curves. This phenomenon is undoubtedly due to the fact that the mobility of the lithium ion differs

Table I. Approximate E_j at 25° C.

[From Milazzo (4, p 41; 32)]

Left Boundary Soln.	Right Boundary Soln. 0.1N KCl		Right Boundary Soln. 3.5N KCl	
	E_j, mv.	pH equivalent	E_j, mv.	pH equivalent
1N NaCl	−11.2	−0.19	−1.9	−0.03
0.1N NaCl	−6.4	−0.11	−0.2	−0.00
1N HCl	56.2	0.94	16.6	0.28
0.01N HCl	9.3	0.16	1.4	0.02
1N NaOH	−45	−0.75	−10.5	−0.18
0.1N NaOH	−18.9	−0.32	−2.1	−0.04

much more from that of the chloride ion than does the mobility of sodium or potassium ion.

The great effectiveness of the universal practice of using saturated potassium chloride rather than a lower concentration in the salt bridge to decrease Δ_{pH} is evident from a comparison of some of Milazzo's data (4, p. 41; 32) given in Table I. This table may also be used to emphasize an error in technique very frequently made. It is a fairly common practice to leave both electrodes soaking in distilled water when they are not in use. Such soaking, if prolonged, produces dilution of the salt bridge, which not only decreases the efficiency of the bridge in decreasing Δ_{pH} but may even change the E_j to such an extent that the potentiometer cannot be balanced with the standard buffer.

INTERPRETATION OF PRACTICAL pH MEASUREMENTS OF AQUEOUS SOLUTIONS

From the considerations of the previous section one might conclude that the practical pH measurements for aqueous solutions having pH between 2 and 12 and μ between 0.05 and 3 approach the limit of accuracy of the Beckman pH meter itself, providing that (1) the meter is standardized with a buffer whose pH and temperature are close to that of the test solution and whose ionic strength is between 0.05 and 3 and (2) neither the standard buffer nor the test solution is more than about 0.05 molal with respect to exceptionally slow-moving ions, such as the highly hydrated lithium ion or large organic ions.

A pH range limit must be imposed, however, because of the alkaline error characteristic of glass electrodes (8). It is well known that in basic solutions containing high concentrations of the cations of the alkali and alkaline earth series, especially the sodium and lithium ions, the pH response of glass electrodes is imperfect. For the Beckman general-purpose electrode at 25° C. a positive error in the response becomes noticeable at about pH 10.5 for solutions 0.01N in sodium ion. The pH at which this error is noticed decreases with increasing sodium ion concentration. At 3N sodium ion this error starts at about pH 8. For the Beckman Type E electrode at 25° the error begins at about pH 12 for solutions 0.1N in sodium ion. At 3N sodium ion, the error is significant at about pH 10.

Within the limitations imposed by Precautions (1) and (2) above and by the alkaline error of the glass electrode, the practical pH may be used, therefore, to reproduce the activity of the hydrogen ions in aqueous solutions to an accuracy equivalent to 0.04 pH unit, even up to an ionic strength of 3. Achieving this goal is sufficient for the great majority of experimenters who are primarily interested in the ability to reproduce, and to compare qualitatively, the hydrogen ion activity.

On the other hand, for some workers it is desirable to be able to calculate the actual hydrogen ion concentration from this convenient practical pH determination. Such a calculation requires that the hydrogen ion activity determined from the practical pH be given a fundamental meaning—i.e., practical $pH \cong -\log_{10} a_{H^+} = -\log_{10} C_{H^+} f_{H^+}$.

The proper method of choosing the f_{H^+} to be used in calculating C_{H^+} from the practical pH is debatable. Of necessity, an arbitrary convention must be employed. This convention should be consistent with the convention used in the original assignment of pH_s to the standard buffers.

In Figure 4 are presented values of $-\log_{10} f_{H^+}$ calculated by various proposed conventions. Because of the junction potential error, the uncertainty of the assigned pH_s of standard reference buffers, and the experimental error in the use of the pH meter, it is very unlikely that a measurement of the practical pH can be considered to be more accurate than within 0.02 unit for the simplest systems. Hence, it is evident from Figure 4 that it is immaterial which convention is used to estimate f_{H^+} at $\mu \leq 0.05$. However, as μ increases, the divergence of the curves increases.

Because the mobility of the hydrogen ion is five times the mobility of the chloride ion in aqueous solution, it seems justifiable to state that no individual-ion activity convention is reasonable that would allow $f_{H^+} < f_{Cl^-}$—that is, the Guggenheim assumption, $f_{H^+} = f_{HCl(HCl)}$, gives the absolute minimum value which need be considered for f_{H^+}. Thus, only the lower five curves in Figure 4 need be examined further.

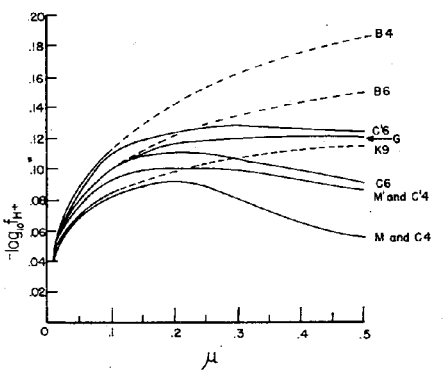

Figure 4. Variation of hydrogen ion activity coefficient with μ

G. $f_{H^+} = f_{HCl(HCl)}$ at given μ
B4, B6. D-H Equation 19 using a_i = 4 and 6 for H^+ ion, suggested by Bates for $\mu = 0.1$
K9. D-H equation using a_i = 9 for H^+ ion, suggested by Kielland for $\mu \leq 0.1$. For remaining curves, $f_{H^+} = f^2_{HCl}/f_{Cl^-}$ was used.
C4, C6, M. $f_{HCl} = f_{HCl(HCl)}$ at given μ
C'4, C'6, M'. $f_{HCl^-} = f_{HCl(0.1\ molal\ HCl\ +\ NaCl)}$
For curves *C* and *C'* f_{Cl^-} was obtained by the DH equation using a_i = 4 or 6; for curves *M* and *M'* $f_{Cl^-} = f_{KCl(KCl)}$ at given μ

Curve *M'* describes approximately the mean of the family of curves. Hence, f_{H^+} should be estimable with the least uncertainty by the method used to construct curve *M'*. That is, $f_{H^+} = f^2_{HCl(HCl\text{-}NaCl\ mixture)}/f_{KCl(KCl)}$. This convention embodies the definition, $f_{H^+} f^0_{Cl^-} = f^2_{HCl}$ at a given μ, and the MacInnes assumption, $f^0_{Cl^-} = f_{KCl(KCl)}$. Fortunately, this convention is as reasonable and convenient as any proposed, and more convenient than Debye-Hückel calculations. At this point, it is important to point out that, for a given $\mu \leq 0.5$, $\log_{10} f_{HCl}$ does not deviate by more than 0.015 unit from its value in a (0.01 molal hydrochloric acid plus sodium chloride) mixture when sodium chloride is replaced by hydrochloric acid or any of the following salts (20): LiCl, KCl, CsCl, LiBr, KBr, NaBr, $BaCl_2$, $SrCl_2$, $CeCl_3$, $AlCl_3$. The ionic strength at which it is no longer valid to estimate f_{H^+} depends, of course, on the degree of accuracy desired and the systems studied in a given investigation and therefore cannot be rigidly specified. However, the following values may be used as a guide in investigations not requiring great accuracy.

Table II

μ	$\Delta_{max.}$	Δf_{H^+}, %
0.05	0.007	1.5
0.1	0.011	2.6
0.2	0.016	3.5
0.3	0.020	4.5
0.4	0.032	7.1
0.5	0.035	7.7

In this table, $\Delta_{max.}$ is the maximum deviation of $\log_{10} f_{H^+}$ as given by curve M' from the value indicated by any of the lower five curves of Figure 4 at a given μ. Δf_{H^+} equals 100% times the ratio of the maximum deviation of f_{H^+} to the value of f_{H^+} indicated by curve M'.

MAGNITUDE OF APPROXIMATION IN pcH = PRACTICAL pH

In analytical chemistry and biochemistry courses and textbooks it is customary to recognize the existence of activity coefficients and then to ignore them blithely in pH calculations, under the assumption that the hydrogen ion concentration is approximately equal to the hydrogen ion activity. Thus, the practical pH is set equal to $-\log_{10} C_{H^+}$. The magnitude of the error in the determination of C_{H^+} from the practical pH, where a calculation is valid, is obtained easily from the activity coefficient of the hydrogen ion by: % error $= 100\% (1 - f_{H^+})/f_{H^+}$. At the μ of most interest in biological chemistry, 0.16, where f_{H^+} is ~0.8 at 25°, this error would amount to ~25%.

Large errors may also result from improper use of the Henderson-Hasselbach equation. For a buffer containing a weak acid, HX, and its salt, NaX, this equation is:

$$\mathrm{pH} = \mathrm{pK}' + \log_{10} \frac{C_X}{C_{HX}} \tag{31}$$

where K' is the apparent ionization constant of a weak acid, HX. The exact expression is:

$$\mathrm{pH} = \mathrm{pK}_t + \log_{10} \frac{C_X}{C_{HX}} + \log_{10} \frac{f_X}{f_{HX}} \tag{32}$$

Hence, if in applying the Henderson-Hasselbach equation the practical pH and the thermodynamic dissociation constant are used, an error equivalent to $\log_{10} \frac{f_X}{f_{HX}}$ is introduced. In the region of its validity, the Debye-Hückel equation may be used to estimate the magnitude of this error. From Equation 19,

$$\log_{10} \frac{f_X}{f_{HX}} = \log_{10} f_X - \log_{10} f_{HX} = \frac{-AZ_X^2\sqrt{\mu}}{1 + Ba_i\sqrt{\mu}} + \frac{AZ_{HX}^2\sqrt{\mu}}{1 + Ba_i\sqrt{\mu}} \tag{33}$$

For a simple buffer such as the acetate buffer, $\log_{10}(f_X/f_{HX})$, using Kielland's value (*25*) of $a_i = 4.5$, is calculated to be -0.12 at $\mu = 0.16$. For the more complicated phosphate buffer at the same ionic strength, using Kielland's a_i values (*25*) of 4 for HPO_4^{--} and 4.5 for $H_2PO_4^-$, the term $\log (f_{HPO_4^{--}}/f_{H_2PO_4^-})$ is estimated to be -0.48.

Thus for the acetate and phosphate buffers at $\mu = 0.16$, errors of approximately 0.1 and 0.5 pH unit, respectively, would result if the buffer pH were calculated from the Henderson-Hasselbach equation using thermodynamic pK values.

On the other hand, one cannot assume that pK values found in textbooks are always thermodynamic values. Frequently, it is the apparent ionization constant, K', as determined experimentally using the Henderson-Hasselbach equation, which is listed. This constant is neither the concentration constant K_c nor K_t, but is equal to $(K_t f_{HA}/f_A)$ or $(K_c f_{H^+})$. Obviously, if pK′ values are used, the Henderson-Hasselbach equation is the correct expression to employ.

It is very important to emphasize the fundamental fact that it is the ionic strength due to *all* the ionic constituents, rather than the buffer ions alone, which affects the activity coefficient of *each* constituent. Thus, the statement that "the $C_{H^+} \cong a_{H^+}$ when it is small" is obviously incorrect, although it is frequently implied even in the latest standard texts.

The ionic strength effect on buffer pH may be very strikingly illustrated by Table III, which lists the practical pH measured for solutions 0.05M in potassium acid phthalate and containing varying concentrations of potassium chloride. The previous considerations concerning liquid junction potentials make it evident that the decrease in pH is due mainly to changing activity coefficients with subsequent increased dissociation of the week acid.

Table III. Practical pH of 0.05M Potassium Hydrogen Phthalate plus Added Potassium Chloride at 25° C.

Added KCl, Molarity	Practical pH
0	4.00 (assigned)
0.10	3.92
0.50	3.73
1.0	3.63
1.5	3.62
2.0	3.57

COLLOIDS AND SUSPENSIONS

The existence of the "suspension effect" on the pH of clays, soils, and ion exchange resins has been known for some time. In general, the pH of suspensions and pastes appears to be lower than the pH of their supernatant liquids.

For instance, Jenny and associates (*24*) reported that a pH of 9.2 was obtained for a 10% potassium bentonite suspension, whereas a 1 to 1 potassium bentonite–water paste gave a pH of 5.8. They attributed the suspension effect to the liquid junction potential at the point of contact between the potassium chloride bridge and the suspension. As evidence, they presented the following results. For an ion exchange resin sediment in contact with its supernatant liquid, a pH of 6.0 was measured when both the glass and calomel electrodes were immersed in the supernatant, but a pH of 2.0 was indicated when the electrodes were immersed in the sediment. The e.m.f. equivalent of this pH difference, 240 mv., was obtained between two calomel electrodes when one was suspended in each phase, but when a glass electrode was suspended in each phase no potential difference existed between the two glass electrodes.

Although there is disagreement (*1, 12, 24, 31, 33*) as to whether the suspension effect is due to the liquid junction potential or is a true membrane potential at a Donnan system, there is no question that the effect exists and that, as a result, pH measurements on suspensions of highly charged particles are meaningless.

The effect is not significant, however, for solutions containing mobile colloidal ions or proteins of high equivalent weight because of the efficiency of the potassium chloride bridge. For instance, the author detected no difference between the pH of whole blood, the sedimented cells obtained on centrifugation, and the supernatant plasma. The meaning of the pH near cell surfaces or of dental plaques, however, may be questionable.

NONAQUEOUS SOLUTIONS

The junction potential between a nonaqueous solvent and an aqueous salt bridge is probably frequently large and variable, depending greatly on the nature of the solvent and on the percentage composition of the solvent if it is a mixture. For instance, Gutbezahl and Grunwald (*15*) estimated that E_j at the

junction (soln. in ethyl alcohol–water|satd. aqueous KCl) increases exponentially from 6.4 mv. (~0.1 pH unit) when the left boundary solvent is 35% ethyl alcohol to 139 mv. (~2.3 pH units) when it is 100% ethyl alcohol. They also concluded that the E_j values are relatively independent of the nature of the solute in the ethyl alcohol–water, but their calculations involved only solute concentrations for which the Debye-Hückel limiting law is valid—i.e., presumably $\mu \leq 0.01$. In fact, Van Uitert and Haas (*36*) showed that for the boundary (HCl-NaCl in dioxane-water| satd. aq. KCl) E_j increases, not only with the concentration of the organic compound, but also with the electrolyte concentration, reaching a value of about 70 mv. for 0.03 formal electrolyte in 82% dioxane.

Obviously, no fundamental meaning may be attributed to the practical pH of a nonaqueous solution which produces an unknown, but probably large, junction potential when in contact with saturated potassium chloride. Even when approximate junction potentials are known for nonaqueous solutions, they cannot be simply described by equations but only by a number of experimentally determined working curves (*36*). Hence, one may only rarely place even a qualitative interpretation on the difference between the practical pH values of two solutions having different solvents, or of two solutions whose solvent is a mixture of the same constituents but in different amounts. That is, with the present lack of data, one cannot even say whether a given pH for an acetone solution indicates a higher or a lower hydrogen ion activity than exists in an ether solution of the same pH, or in another acetone solution containing some water.

When the solvent composition is kept constant, however, it is probable (*15*, *36*) that with proper precautions E_j can be kept fairly constant [deviation about 2 mv. in ethyl alcohol solutions (*15*)]. Hence, the practical pH may be used as a reproducible property, interpretable qualitatively, for nonaqueous solutions *if the solvent composition is not varied*. Many analytical separations and determinations involve bringing the practical pH of a partially nonaqueous solution to a stipulated value. It is important, therefore, to emphasize the fact that a change in the solvent composition destroys the validity of considering a given pH as implying constant hydrogen activity.

In addition to the junction potential problem, there is another obstacle which must be overcome before useful relationships can be established between pH values of solutions having different solvents. The activity coefficient for a given solute varies greatly from solvent to solvent because of the effect of dielectric constant of the solvent. The Debye-Hückel equation is of only limited use in furnishing activity coefficients in nonaqueous solutions because of the inadequate knowledge of the ion-size parameter, a_i, in nonaqueous solutions. At low ionic strength, however, the Debye-Hückel limiting law can be employed to obtain activity coefficients, f_i^*, which are relative to a value of unity at infinite dilution of the solute in the given solvent. In order to connect the activity coefficients of a solute in two different solvents, the primary medium effect, f_m, must be determined. This coefficient measures the free energy of transfer of the solute from one solvent to another, so that f_i of a solute in a given solvent relative to a standard state in another solvent equals $f_i^* f_m$.

The primary medium effect can reach tremendous values. For instance, relative to an infinitely dilute aqueous solution as the standard state, f_m of hydrochloric acid at low concentrations increases from about 2 in 20% dioxane to about 200 in 82% dioxane (*20*). For an ethyl alcohol solution of hydrochloric acid, f_m of hydrochloric acid is about 300 relative to the water standard (*20*). Even more startling are the ionic f_m values estimated by Gutbezahl and Grunwald (*15*). They obtained 5×10^4 and 2×10^4 for hydrogen and ammonium ions, respectively, in ethyl alcohol relative to water as solvent but only 3.4 for the chloride ion in ethyl alcohol relative to the same standard state.

McKinney, Fugassi, and Warner (*30*) suggested that an acidity scale could be set up in any solvent by the same procedures used to establish the pH scale for aqueous solutions. Although an enormous amount of work must be performed before such scales will be useful, a significant start in this direction has been made by Gutbezahl and Grunwald (*15*) and by Bates (*4*).

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[END OF SYMPOSIUM]

Determination of Impurities in Silicon by Neutron Activation Analysis

ARTHUR KANT[1], J. PAUL CALI, and HARRIET D. THOMPSON

Air Research and Development Command, Air Force Cambridge Research Center, Bedford, Mass.

A method of determining trace elements in silicon in the concentration range of 10^{-2} to 10^{-8} p.p.m. by neutron activation analysis involves radiochemical separations, and the characterization and determination of the elements by their induced beta activities. The elements determined are: phosphorus, iron, copper, zinc, gallium, arsenic, silver, cadmium, indium, antimony, thallium, and bismuth. The method of treating phosphorus presents a special problem, because phosphorus-31 is formed in the neutron activation process.

THE development of silicon transistors is largely dependent on the production of ultra-high-purity silicon metal, because as little as 10^{12} to 10^{14} atoms of impurities per cc. can seriously affect transistor properties. For example, the resistivity of a bar of single-crystal silicon containing 10^{14} atoms of antimony per cc. is, at room temperature, approximately 52 ohm-cm. If the number of antimony atoms is increased to 5×10^{14}, the resistivity is decreased to 10.4 ohm-cm. Therefore, as little as 0.01 p.p.m. of donor- or acceptor-type impurity has a marked effect upon transistor properties. In like manner, other important electrical properties of transistors can be shown to vary markedly with very small amounts of impurity atoms.

In order to control the amounts of impurities in high-purity silicon, some means of control analysis must be available. In the concentrations with which this discussion is concerned, spectroscopic or colorimetric analyses are too insensitive, because the limits of detection for these methods are usually of the order of 1 p.p.m. The neutron radioactivation method (*11*) is used in this laboratory for the determination of trace impurities in silicon metal. Other methods may be employed for the determination of the individual elements considered herein, which would give a sensitivity as good as if not better than 1 p.p.m. However, it was the object of the authors to employ a single method which might be applied satisfactorily to a majority of the possible elements present in silicon. The neutron activation method was chosen for this reason. Historically, radioactivation was first used by Hevesy and Levi (*8*). The basic principles involved in this technique have been well set forth by Boyd (*1*). Many papers give general and specific information on the method (*2, 3, 6–10*).

Two methods of approach to the activation method are possible in determining the concentrations of the activated impurities in silicon. The first involves the techniques of gamma spectrometry and is well exemplified in the work of Morrison and Cosgrove (*15*). This technique has the advantage of speed, especially because no radiochemical separations must be performed, but it is useless where the activated impurity is a beta emitter. Intrinsically the method is not so sensitive as the second technique, as the sensitivity of any activation technique is eventually limited by the background count of the detector. In gamma counting the background rate is 20 to 50 times that of a beta detector; the gamma spectrometric method, in general, is therefore several times as insensitive as the beta method. Also contributing to the lesser sensitivity of the gamma spectrometric method is the fact that only 5 to 10% of the total available counting rate is recorded, as in this technique the usual procedure is to count on a specific gamma peak.

[1] Present address, Watertown Arsenal Laboratory, Watertown, Mass.

The second method of approach, the one utilized in this laboratory, involves the following steps:

1. Irradiation of silicon samples together with weighed amounts of the elements to be used as standards.
2. Dissolution of the irradiated sample together with microgram amounts of inactive isotopes of the elements to be determined and removal of silicon activity by fuming with nitric-hydrofluoric acid mixture.
3. Separation of the activated impurities by radiochemical techniques.
4. Measurement of the beta intensity of the separated activated impurity element.
5. Verification of the measured isotope by half life and energy determination.

The comparative method was used in determining the concentration of impurity elements. The silicon samples are placed in aluminum irradiation capsules together with small quartz needles containing weighed amounts of the oxides of the elements to be determined. The activity of the separated impurity element is compared to the activity of the standard and because the mass of the standard is known, the mass of the impurity element can be calculated. Utilizing this method, uncertainties in the values of the cross section, neutron flux, half life, and the detection coefficient of the counting setup are eliminated, as each parameter is identical in both the standard and the corresponding impurity element.

EXPERIMENTAL

Elements Determined. The following elements were chosen for determination: phosphorus, iron, copper, zinc, gallium, arsenic, silver, cadmium, indium, antimony, thallium, and bismuth.

The Group III and V elements are especially important, as they are added in known quantities to pure silicon metal, as either acceptor or donor elements, to produce transistor properties. Zinc is expected to be present, as a present-day process involves the zinc reduction of silicon tetrachloride to produce silicon metal. The remainder are important, in that they markedly affect the lifetime of transistors.

Nuclear Data. Samples of silicon were irradiated in the Brookhaven National Laboratory reactor. When a nucleus is subjected to a thermal neutron flux, the main nuclear process is the n, γ reaction. The target nuclei bombarded, together with the cross section for the n, γ reaction, the isotope produced, together with its half life, and the maximum energy of the emitted beta rays are given in Table I (*10, 16*). In addition to the activities listed, other radioisotopes of iron, copper, zinc, gallium, silver, cadmium, indium, antimony, and thallium are produced; however, they are eliminated from consideration because of the shortness of the

Table I. Nuclear Data for Elements Determined

Target Nucleus	Cross Section, Barns	Fraction Isotopic Abundance	Isotope formed by n,γ	$T_{1/2}$	Max. Energy of β^-, M.e.v.
P^{31}	0.23	1.0	P^{32}	14.3d	1.7
Fe^{58}	0.7	0.0033	Fe^{59}	47d	0.26; 0.46
Cu^{63}	3.9	0.69	Cu^{64}	12.9h	0.57
Zn^{68}	0.10	0.187	Zn^{69}	14h	0.90
Ga^{71}	3.4	0.398	Ga^{72}	14h	0.14; 3.15
As^{75}	4.2	1.0	As^{76}	27h	1.3; 2.5; 3.1
Ag^{109}	2.8	0.487	Ag^{110}	270d	0.09; 0.53
Cd^{114}	1.1	0.288	Cd^{115}	2.3d	0.6; 1.1
In^{115}	56	0.042	In^{114}	50d	2.05
Sb^{121}	6.8	0.572	Sb^{122}	2.8d	1.4; 1.9
Tl^{203}	8.0	0.295	Tl^{204}	2.7y	0.77
Bi^{209}	0.0017	1.0	Bi^{210}	5d	1.17

half life or their very low cross sections or because they have other types of decay than beta decay.

Samples. Gram quantities of silicon metal commercially available from E. I. du Pont de Nemours & Co., Wilmington, Del., were used. The silicon is Du Pont's densified material bearing the label "hyperpure silicon semiconductor grade." Two different lots, both spectroscopically pure, were analyzed—A and B. The oxides of the elements to be determined in the silicon samples were encapsulated in small quartz needles. The silicon samples were irradiated so that the standards and sample were subjected to the same neutron flux.

Irradiation Data. The samples and standards were irradiated for approximately 15 days in the Brookhaven National Laboratory reactor at a neutron flux of 3×10^{12} neutrons per sq. cm. per second. The principal nuclear reaction occurring under the conditions of irradiation is the n, γ reaction.

It is important to consider the n, γ reaction occurring with the overwhelming number of silicon atoms, as compared to the n, γ reaction on the smaller numbers of impurity atoms. The following occurs:

$$Si^{30} \xrightarrow{n,\gamma} Si^{31} \xrightarrow[2.6\ hr.]{\beta^-} P^{31}\ (stable)$$

The initial production of silicon activity in comparatively large amounts presents no serious problem: Its short half life causes the bulk of silicon-31 to decay to stable phosphorus before separation work begins; and most of the silicon is lost by evolution as silicon tetrafluoride during dissolution with hydrofluoric acid. Furthermore, silicon-31 activity is very effectively removed in the radio-chemical purification schemes.

In the determination of phosphorus the above reaction must be considered, as can be seen if the entire reaction is written, starting with silicon-30:

$$Si^{30} \xrightarrow{n,\gamma} Si^{31} \xrightarrow[2.6\ hr]{\beta^-} P^{31} \xrightarrow{n,\gamma} P^{32} \xrightarrow[14.3\ d]{\beta^-} S^{32}\ (stable)$$

From the above, it is evident that there will be two sources of phosphorus-32 activity: any impurity phosphorus-31 originally present in the silicon, and the above reaction. It is, therefore, necessary to compute the amount of phosphorus-32 formed by this latter reaction. In order to obtain the amount of phosphorus-32 as a function of the number of atoms of silicon-30, the neutron flux, and the time of irradiation, it is necessary to solve the following set of equations:

$$\frac{dN_1}{dt} = N_0\phi\sigma_1 - N_1\lambda_1 \quad (1)$$

$$\frac{dN_2}{dt} = N_1\lambda_1 - N_2\phi\sigma_2 \quad (2)$$

$$\frac{dN_3}{dt} = N_2\phi\sigma_2 - N_3\lambda_2 \quad (3)$$

where

N_0 = number of atoms of silicon-30 initially present
N_1 = number of atoms of silicon-31 formed by n, γ on silicon-30
N_2 = number of atoms of phosphorus-31 formed by decay of silicon-31
N_3 = number of atoms formed by n, γ on phosphorus-31
σ_1 = cross section for silicon-30 (n, γ) silicon-31 reaction, sq. cm.
σ_2 = cross section for phosphorus-31 (n, γ) phosphorus-32 reaction, sq. cm.
λ_1 = decay constant for silicon-31, sec.$^{-1}$
λ_2 = decay constant for phosphorus-32, sec.$^{-1}$
ϕ = thermal flux, neutrons per sq. cm. per second
t = time of irradiation, seconds

The value sought is $N_3\lambda_2$, which is the activity of phosphorus-32. The initial conditions for the solutions of Equations 1, 2, and 3 are $N_1 = 0$, $N_2 = 0$, and $N_3 = 0$ at $t = 0$ and the assumption that N_0 is essentially constant. The solution of Equation 1 subject to the initial conditions is:

$$N_1\lambda_1 = N_0\phi\sigma_1(1 - e^{-\lambda_1 t}) \quad (4)$$

If this value of $N_1\lambda_1$ is substituted in Equation 2, the result is:

$$\frac{dN_2}{dt} = N_0\phi\sigma_1(1 - e^{-\lambda_1 t}) - N_2\phi\sigma_2 \quad (5)$$

The solution of Equation 5 subject to the above stated conditions is:

$$N_2 = R\left[\frac{1}{\phi\sigma_2}(1 - e^{-\phi\sigma_2 t}) + \frac{1}{\phi\sigma_2 - \lambda_1}(e^{-\phi\sigma_2 t} - e^{-\lambda_1 t})\right] \quad (6)$$

where $R = N_0\phi\sigma_1$.

By substituting this value of N_2 in Equation 3 and solving, Equation 7 is obtained.

$$\frac{N_3\lambda_2}{R} = 1 - (1 - \phi\sigma_2\lambda_2 A + B)e^{-\lambda_2 t} - \phi\sigma_2\lambda_2 A e^{-\phi\sigma_2 t} + Be^{-\lambda_1 t} \quad (7)$$

where

$$A = \left(\frac{1}{\phi\sigma_2} - \frac{1}{\phi\sigma_2 - \lambda_1}\right)\left(\frac{1}{\lambda_2 - \phi\sigma_2}\right)$$

and

$$B = -\frac{\phi\sigma_2\lambda_2}{(\phi\sigma_2 - \lambda_1)(\lambda_2 - \lambda_1)}$$

Equation 7 is the general solution for Equation 3. However, several conditions are present for this system which simplify Equation 7:

$$t << \frac{1}{\phi\sigma_2};\ \frac{1}{\lambda_2} >> \frac{1}{\lambda_1} >> \frac{\phi\sigma_2}{\lambda_1\lambda_2},\ \text{and}\ t >> \frac{1}{\lambda_1}.$$

When simplified, Equation 7 reduces to:

$$\text{Activity of } P^{32} = N_3\lambda_2 = N_0\phi\sigma_1\left(\frac{\phi\sigma_2}{\lambda_2}\right)(\lambda_2 t + e^{-\lambda_2 t} - 1) \quad (8)$$

For the irradiation time used, the contribution of phosphorus-31 from silicon-30 is negligible if the phosphorus is initially present to an extent greater than 0.1 p.p.m. For phosphorus concentrations less than 0.1 p.p.m. the phosphorus as formed from silicon-30, according to Equation 8, must be subtracted from the total phosphorus-32 activity. In the latter case, the comparative method is not applicable, and absolute beta-counting techniques must be used.

In order to obtain the high sensitivity required, it is necessary to irradiate relatively large quantities of silicon. Because of the low neutron absorption cross section of silicon, it is possible to use relatively large amounts of silicon without appreciable neutron beam attenuation. Calculations indicate that as much as 10 grams of silicon will cause an inappreciable beam attenuation throughout the sample (of the order of 1%).

The amount of standard elements used was sufficiently small to cause no appreciable beam attenuation. In the case of indium, which has the largest neutron absorption cross section of any of the elements determined, the attenuation due to the indium standard is no more than 1%.

Treatment of Silicon Sample after Irradiation. After irradiation, the silicon samples are removed from the irradiation capsule. A 1- to 2-gram piece of silicon metal is placed in a platinum dish and the surface is completely etched in nitric acid–hydrofluoric acid to remove any surface contaminants which might possibly have been present and would now be activated. In the submicro concentration regions the introduction of surface impurities is an obvious and important source of anomalous results. The above method of etching obviates this source of error and only bulk impurities are then determined.

The sample is then transferred to another platinum dish and microgram amounts of carriers are added. Sample and carriers are then dissolved in a 50-50 mixture of concentrated nitric acid–hydrofluoric acid. Repeated fumings with hydrofluoric acid are carried out until all visible traces of silicon are removed. The residue—i.e., carriers—is then dissolved in a suitable medium,

usually hydrochloric acid, and the resulting solution is made up to volume in a volumetric flask. The platinum crucible is monitored at this point to make certain that all of the activities present are in solution and have been transferred. Suitable aliquots are then taken from the volumetric flask for the radiochemical separation and purification of the elements to be determined. It is at this point that known amounts of stable isotopic carriers are added, usually of the order of 10 mg. per determination. In order to ensure the isotopic exchange of the carrier and the activity, the carrier is added in its highest oxidation state, since in general the activity will also be in this state (having been fumed with concentrated nitric acid in the dissolution process). The solution is then warmed and allowed to stand for at least 15 minutes.

Chemical Procedures. The radiochemical procedures described below were designed with the following considerations.

The procedure for each element must, in its entirety, be specific—that is, the final precipitate must be entirely free of all possible contaminating or interfering radioactive species.

Because phosphorus-32 is formed from the irradiation of silicon-30, each radiochemical procedure must have a specific step for the removal of this interfering element.

Each procedure must effectively remove silicon-31 activity.

The procedures for gallium, copper, zinc, and arsenic must be fairly rapid, as these isotopes are relatively short-lived.

The following references were found useful in the preparation of these procedures (*12*, *17–20*, *22*).

GROUP SEPARATIONS

In order to simplify the radiochemical separations the following groupings were used:

Group A. Arsenic, Bismuth, and Gallium
Group B. Indium, Thallium, and Antimony
Group C. Silver, Cadmium, and Iron
Group D. Zinc and Copper
Group E. Phosphorus

The elements listed above are not separated as in a qualitative scheme. Rather, separations are made only within the groups. At no time is more than one group determined in a single aliquot of the solution to be analyzed. One aliquot is taken for the separation and determination of Group A, another aliquot for Group B, etc. All procedures start with the initial aliquot for that group.

Group A Separation. Arsenic, bismuth, and gallium are separated as follows: the arsenic as arsenic trisulfide; the gallium by extraction with ether. The bismuth remains in the original solution.

GALLIUM. The gallium is extracted from the ether with water, precipitated as the hydroxide, twice scavenged with arsenic trisulfide and bismuth trisulfide, scavenged with barium carbonate and ferric hydroxide, again extracted with ether using phosphorus as a holdback carrier, re-extracted with water and precipitated as gallium hydroxyquinolate, washed, dried, weighed, and mounted for counting.

ARSENIC. The arsenic trisulfide is dissolved in ammonia and scavenged with lanthanum hydroxide, precipitated as arsenic trisulfide using gallium, antimony, and phosphorus as holdback carriers, dissolved, distilled as arsenic trichloride, reduced to the metal, filtered, washed, dried, weighed, and mounted for counting as arsenic metal.

BISMUTH. The bismuth is precipitated several times as the hydroxide using arsenic, antimony, barium, strontium, and copper as holdback carriers, then precipitated as bismuth phosphate using arsenic, antimony, gallium, indium, and thallium as holdback carriers. The bismuth is then precipitated as bismuth trisulfide using strontium, indium, gallium, barium, and yttrium as holdback carriers, and finally precipitated as bismuth metal, filtered, washed, dried, weighed, and mounted for counting as the metal.

Group B Separation. The thallium, indium, and antimony are separated as follows: the thallium as thallous iodide; the antimony as antimony trisulfide (at pH 1); the indium as indium trisulfide (at pH 3 to 4).

THALLIUM. Thallium is extracted with isopropyl ether using phosphorus, bismuth, chromium, and yttrium as holdback carriers, scavenged with cupric sulfide, bismuth trisulfide, arsenic trisulfide, and antimony trisulfide, and scavenged with the hydroxides of indium, gallium, and iron. The thallium is then precipitated as thallous iodide with indium, gallium, and molybdenum as holdback carriers, and finally precipitated, filtered, washed, dried, weighed, and mounted for counting as thallous chromate.

INDIUM. The indium solution is scavenged several times with arsenic trisulfide, cupric sulfide, bismuth trisulfide, and antimony trisulfide, precipitated several times as indium trisulfide, extracted by 8-hydroxyquinoline in chloroform, and re-extracted into hydrochloric acid by boiling off the chloroform. The indium is then precipitated, filtered, washed, dried, weighed, and mounted for counting as indium quinolinate.

ANTIMONY. The antimony solution is scavenged with arsenic trisulfide, extracted with isopropyl ether, using phosphorus as a holdback carrier, extracted from the ether with 3*N* potassium hydroxide, and precipitated as antimony trisulfide. The antimony is distilled as antimony trichloride using tin as a holdback carrier, and finally precipitated, filtered, washed, dried, weighed, and mounted for counting as antimony metal.

Group C Separation. The silver and cadmium are separated as follows: The silver is precipitated as silver chloride; the cadmium is precipitated as cadmium sulfide in 0.3*N* acid. Iron in the supernatant solution is precipitated as ferric hydroxide.

SILVER. The silver is precipitated as silver chloride using phosphorus as a holdback carrier, scavenged with ferric hydroxide, precipitated, filtered, washed, dried, weighed, and mounted for counting as silver iodate.

CADMIUM. The cadmium is precipitated twice as cadmium sulfide, using phosphorus as a holdback carrier, scavenged with palladium sulfide, precipitated as cadmium sulfide, and twice scavenged with ferric hydroxide. The cadmium is finally precipitated, filtered, washed, dried, weighed, and mounted for counting as cadmium ammonium phosphate.

IRON. Ferric hydroxide is precipitated, washed, and dissolved in hydrochloric acid, and ferrous sulfide is precipitated in the presence of phosphorus as a holdback. The iron is extracted with ether; ferric hydroxide is reprecipitated and ignited to the oxide, then filtered, dried, weighed, and mounted for counting.

Group D Separation. The copper and zinc are separated as follows: the copper as cupric sulfide in 1*N* hydrochloric acid; the zinc as zinc sulfide at pH 7.

COPPER. The copper solution is scavenged twice with ferric phosphate and ferric hydroxide, precipitated as cuprous thiocyanate, reprecipitated as copper α-benzoinoxime, and finally precipitated, filtered, washed, dried, weighed, and mounted for counting as cuprous thiocyanate.

ZINC. The zinc is precipitated twice as zinc mercury thiocyanate, using phosphorus as a holdback carrier and oxalic acid as a complexing agent. The solution is scavenged with the excess mercury as mercuric sulfide; the zinc is precipitated as zinc sulfide, dissolved, scavenged twice with ferric hydroxide, and finally precipitated, washed, dried, weighed, and mounted for counting as zinc mercury thiocyanate.

Group E Separation. PHOSPHORUS. Yttrium, arsenic, and copper carriers are added to the phosphorus solution and arsenic and copper are precipitated with hydrogen sulfide. Magnesium ammonium phosphate is then precipitated, washed, dissolved in hydrochloric acid, and scavenged with arsenic, antimony, copper, and palladium, and magnesium ammonium phosphate is reprecipitated. This precipitate is dissolved and scavenged with lanthanum oxalate. Finally, magnesium ammonium phosphate is precipitated, washed, dried, weighed, mounted, and counted.

The standards are dissolved in suitable solvents and made to volume, and suitable aliquots are taken for determination of their radioactive content. In general, no radiochemical purification procedure is necessary. The standards are precipitated for mounting, using the same final precipitate as the unknown, and then the two are counted consecutively.

Instrumentation. The samples and standards are filtered on 1-inch circles of No. 42 Whatman paper. The paper containing the precipitate is placed on an aluminum planchet of the same diameter and approximately $^3/_8$ inch thick. A thin sheet of rubber hydrochloride (0.7 mg. per sq. cm.) is placed over the filter paper and an outer aluminum retaining ring is forced over the entire assembly. The sample is now ready for counting.

The samples and standards are counted using Tracerlab's auto-

matic sample changer (SC-6A) and TGC-2 Geiger tube (window 1.7 mg. per sq. cm.), and a Tracerlab SC-51 Autoscaler is used to record the counting rate. The time required for a predetermined number of counts is recorded on Tracerlab's Tracergraph SC-5D.

Counting rates are corrected for background and coincidence loss. In addition, a normalizing factor is used which corrects for variations in the day to day operation of the setup.

Atomic Instrument Multiscaler Model 1070 operated in conjunction with Tracerlab's shielded manual sample changer and a TGC-2 Geiger tube is used to determine the maximum beta energy. For this determination the Feather analysis is utilized (*5*).

RESULTS OF ANALYSES

Table II gives the results of the activation analysis on silicon samples A and B.

Table II. Results of Activation Analysis on Silicon

Element Determined	Isotope Measured	Measured $T_{1/2}$ Sample A	Measured $T_{1/2}$ Sample B	Analysis, P.P.M. Sample A	Analysis, P.P.M. Sample B
P	P^{32}	14d	14d	0.01	0.01 and 0.02
Fe	Fe^{59}		Long		0.1
Cu	Cu^{64}		12.5 hr.		0.002 and 0.006
Zn	Zn^{69}		14.6 hr.		0.007
Ga	Ga^{72}	NSA	NSA	0.0001[a]	0.0001[a]
As	As^{76}	26 hr.	27 hr.	0.00005	0.00002 and 0.00004
Ag	Ag^{110}		Long		0.001
Cd	Cd^{115}		NSA		0.0002
In	In^{114}	NSA	NSA	0.0003[a]	0.0003[a]
Sb	Sb^{122}	2.8d	2.8d	0.0001	0.0003
Tl	Tl^{204}	NSA	NSA	0.008[a]	0.008[a]
Bi	Bi^{210}	NSA	NSA	0.01[a]	0.01[a]

A blank indicates no analysis.
NSA. Not sufficient activity detected to be able to characterize half life.
Where two results are given, two separate analyses were performed.
[a] No activity found (see discussion of results). Background of detector was 20 counts per minute.

Discussion of Results. Spectrographic analyses of both lots detected no impurities whatsoever. This is in agreement with the activation analysis, as the impurities found by the latter method are in every case well below the limit of sensitivity for the spectrographic method.

In the determination of arsenic, phosphorus, and copper in sample B two results are given; two different chunks of silicon metal from the same lot number were analyzed. The differences are real and must be attributed to a certain degree of nonhomogeneity within the lot.

In the measurements of the half lives of the various isotopes, NSA (not sufficient activity) indicates that the activity for these samples was well below the background activity of the detector. The statistical variations in such cases preclude a determination of the half life with any degree of certainty. However, the half life found even in these cases was of the right order of magnitude.

One of the criteria for determining the purity of the final separated isotope was to have been the measurement of the maximum beta energy. Unfortunately, in order to accomplish this by means of a Feather analysis, several hundred counts per minute of activity were required. In only two cases was sufficient activity present for an energy determination. In sample B sufficient copper activity was found, and a Feather analysis gave an indicated maximum beta energy of 0.60 m.e.v. as against a reported (*10, 16*) energy of 0.57 m.e.v. Similarly for phosphorus, the measured beta energy was 1.8 m.e.v. as against a reported (*10, 16*) energy of 1.71 m.e.v. The Feather method is usually considered accurate within about 10% for uncomplicated cases.

Where no activity was found, the minimum amount detectable is reported in Table II. This represents the maximum amount of impurity that could possibly be present. The value is obtained from the equation:

$$A = N\sigma\phi(1 - e^{-\lambda t}) \quad (9)$$

where

A = disintegration rate of isotope formed, disintegrations per second
N = number of atoms of target nucleus
ϕ = thermal neutron flux, neutrons per sq. cm. per second
σ = activation capture cross section, sq. cm.
λ = decay constant of isotope formed, sec.$^{-1}$.
t = time of irradiation, seconds

The minimum detectable activity is taken as 1 disintegration per second.

RESULTS AND DISCUSSION

Discussion of Errors. The precision and accuracy of the activation method of analysis in the range from 1000 to 0.1 p.p.m. of trace impurities have been well established (*13, 14*). Duplicate determinations of indium in silicon dioxide were done comparing the activation method with the spectrographic method (Table III). Many of the errors involved in this method have been evaluated, and several of the possible sources of errors are discussed below.

1. Error Due to Incomplete Exchange of Activated Isotope and Inactive Isotopic Carrier. Many references (*4, 21*) show the steps that must be taken to obviate any difficulty on this account. The main source of error here exists when the carrier and the active species exist or can exist in different valence states. In every case where this could occur the chemistry is so designed that the carrier and active isotope are swept through all the oxidation states possible.

2. Error Existing by Loss of Activity during Dissolution. In the procedures described, the sample is dissolved in concentrated nitric acid–hydrofluoric acid in the presence of microgram amounts of carriers. The possibility of loss of activity during dissolution, either by the volatility of certain fluorides or through some other mechanism, exists. An experiment was designed and performed to evaluate this loss. A small piece of silicon to which was added a known amount of arsenic carrier was dissolved in the manner described in the dissolution procedure. After being treated several times with hydrofluoric acid, the residue was dissolved in concentrated hydrochloric acid and arsenic trisulfide precipitated. The loss of arsenic by the volatility of the fluorides was negligible. As arsenic trifluoride is the most volatile of any of the fluorides of the elements determined, it seems safe to assume that none of the other fluorides will be lost through volatility at this point in the procedure.

Table III. Comparison of Spectrographic and Activation Determination of Indium in Silicon

Sample No.	Theoretical,[a] P.P.M.	Spectrographic, P.P.M.	Activation, P.P.M.
1	1640	1640 ± 160	1565 ± 157
2	164	164 ± 16	147 ± 15
3	16	Faint line	15 ± 2
4	1.6	Not detected	3.9 ± 0.4[b]

[a] Prepared by doping silicon dioxide with weighed amounts of indium oxide.
[b] Value high by approximately 2 p.p.m., indicating indium impurity background in silicon dioxide base material of about this amount.

3. Errors of Reproducibility. In order to determine this error, a sample of silicon containing an unknown amount of phosphorus was irradiated as described above and six determinations of the activated phosphorus were performed (Table IV).

4. Error from Contaminating Activities. The radiochemical procedures described herein are specific enough so that errors from this source are small. In substantiation of this state-

Table IV. Reproducibility of Method for Phosphorus in Silicon

Sample No.	G. P/G. Si (× 10⁴)
1	8.28
2	7.75
3	7.87
4	7.80
5	7.72
6	7.93
Average	7.89
Standard error	2.40%

ment the following evidence is cited. In the determination of gallium, indium, thallium, and bismuth, no activity whatsoever was found in the final counting form (Table II). This is prima facie evidence that in these cases at least, no contaminating activity could have been present. In the case of phosphorus, iron, copper, zinc, silver, and antimony sufficient activity was found to be able to characterize the half life with a precision at least within 10%. Errors from this source are considered to be no more than 10% (standard error).

5. Errors Resulting from Statistical Variations in the Process. The standard error of a disintegration rate is given by $\sqrt{N}$, where N is the total number of events recorded. In all cases a sufficient number of counts was taken to give a standard error of no more than 10%. In cases of high activity the standard error was approximately 1%.

The over-all error of the method is estimated as approximately 50% for the absolute method and 10% for the comparative method.

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Amperometry with Two Platinum Electrodes with the Cuprous-Cupric Bromine-Bromide System

JAMES J. LINGANE and FRED C. ANSON

Department of Chemistry, Harvard University, Cambridge 38, Mass.

The behavior of the indicator current observed with two polarized indicator electrodes during coulometric titration with bromine or cuprous copper in acidic cupric bromide solutions has been critically examined. The interpretation of the indicator current, and the relation between the observed minimum current and the equilibrium constant of the reaction $2Cu^{++} + 7Br^- = 2CuBr_2^- + Br_3^-$, given by previous authors has been shown to be inadequate. Correct relations for this system have been derived; these lead to an apparent equilibrium constant more nearly in accord with the value deduced from the observed formal potentials of the half-reactions involved. However, because the bromine-bromide couple does not behave with the thermodynamic reversibility demanded by the correct treatment, the apparent equilibrium constant from the amperometric measurements is considerably larger than the true value. Two-electrode amperometry, although very useful as an empirical means of end point detection in titrations, is not appealing as a technique for measuring equilibrium constants.

AS ORIGINALLY demonstrated by Foulk and Bawden (*6*), the change in current between two platinum indicator electrodes subjected to a constant, small applied voltage can be used to recognize titration end points. During the past decade this technique has been applied very successfully (albeit empirically) for end point detection in divers types of coulometric titration, particularly by Swift and his collaborators. The principles and applications of the method are reviewed in the monographs of Lingane (*9*) and Delahay (*3*) and in articles by Duyckaerts (*4*), Bradbury (*1*), and Kolthoff (*7*).

Our interest here is with the application of amperometry with two polarized platinum electrodes to end point detection in the particular case of coulometric titration with bromine and cuprous copper as dual intermediates, as originally used by Buck and Swift (*2*) for slow bromination reactions. The titration cell is essentially as indicated in Figure 1. The electrolyte contains relatively large concentrations of bromide ion and cupric ion, and is acidified with sulfuric acid. By appropriate selection of the polarity of the generator electrode in the test solution bromine can be generated via anodic oxidation of bromide ion, or cuprous copper ($CuBr_2^-$) can be generated by cathodic reduction of cupric ion. Starting with either excess bromine or excess cu-

prous copper, and generating the other with strictly constant current, a plot of the resulting indicator current against generation time produces a V-shaped titration curve whose extrapolated point corresponds very closely to the equivalence point, as shown in Figure 2.

Farrington, Meier, and Swift (*5*) recognized that the magnitude of the minimum current not only depends on the geometrical characteristics of the indicator electrodes and cell, and the value of the constant voltage applied across the indicator electrodes, but is also a function of the equilibrium constant of the reaction

$$2Cu^{++} + 7Br^- = 2CuBr_2^- + Br_3^- \quad (1)$$

$$K = \frac{(CuBr_2^-)^2(Br_3^-)}{(Cu^{++})^2(Br^-)^7} \quad (2)$$

Farrington, Meier, and Swift derived a relation between the minimum current, the slopes of the two branches of the titration curve, and K, and used it to evaluate K. The average value which they obtained (1.4×10^{-16}) is about 100 times larger than the value deducible from the standard potentials (as quoted by Farrington, Meier, and Swift) for the half-reactions involved. This prompted the authors to examine more closely the derivation of Farrington and associates, and this study leads to the conclusion that certain of their basic assumptions are not valid under the experimental conditions which they employed.

The possible reactions at the indicator electrodes that can contribute to the observed indicator current are

$$Br_3^- + 2e = 3Br^- \quad \text{(cathode)} \quad (3)$$

$$Cu^{++} + 2Br^- + e = CuBr_2^- \quad \text{(cathode)} \quad (4)$$

and

$$3Br^- = Br_3^- + 2e \quad \text{(anode)} \quad (5)$$

$$CuBr_2^- = Cu^{++} + 2Br^- + e \quad \text{(anode)} \quad (6)$$

With excess bromine present, virtually all the current results from Reactions 3 and 5, and there is very little contribution from Reactions 4 and 6. Conversely, in the presence of excess cuprous copper, Reactions 4 and 6 so greatly predominate that Reactions 3 and 5 become insignificant. However, at the indicator current minimum all four reactions contribute to the observed current. That this is true is evident from the individual anodic and cathodic current-electrode potential curves shown in Figure 3.

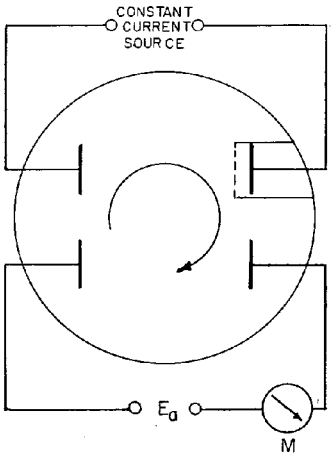

Figure 1. Cell for coulometric titration with amperometric end point detection by two polarized electrodes

All electrodes of bright platinum, lower pair indicator electrodes and upper generator electrodes. A constant small voltage E_a is maintained across the indicator electrodes and the indicator current is observed with microammeter M. The solution is stirred efficiently

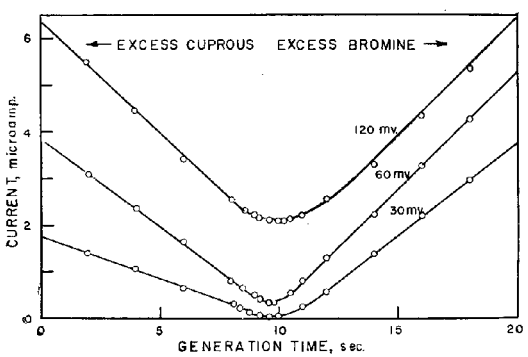

Figure 2. Amperometric titration curves with various voltages applied across indicator electrodes

Solution (volume 150 cc.) consisted of 1F sodium bromide, 0.067F cupric sulfate, and 0.33F sulfuric acid. Generator electrode area was 5 sq. cm. and constant generating current was 12.7 ma. Area of each indicator electrode was 3 sq. cm.

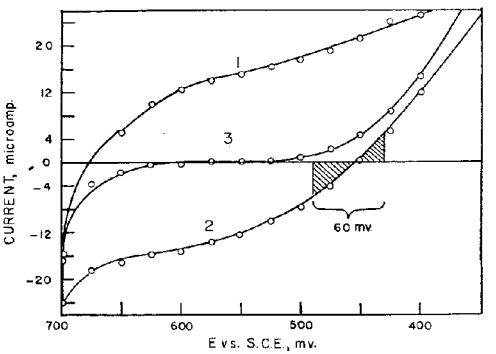

Figure 3. Individual cathodic and anodic current-electrode potential curves

1. Excess bromine
2. Excess cuprous copper
3. Solution adjusted to amperometric minimum current

Solution composition same as for experiments of Figure 2

The curves in Figure 3 were obtained with a single platinum indicator electrode (area 3 sq. cm.) in a solution containing 1F sodium bromide, 0.067F cupric sulfate, and 0.33F sulfuric acid. The potentials of the indicator electrode were measured against an external saturated calomel reference electrode. Curve 1 was obtained after generating a small excess of bromine, curve 2 in the presence of excess cuprous copper, and curve 3 after adjusting the solution composition by appropriate generation of bromine and cuprous copper until the minimum in the titration curve with two identical platinum electrodes (at 60 mv. applied) was precisely reached. For all three cases the final unlimited increase in cathodic current (upward) results from $Cu^{++} \rightarrow CuBr_2^-$, and the final unlimited increase in anodic current (at a potential above about 650 mv.) stems from $Br^- \rightarrow Br_3^-$.

Suppose, now, that two identical platinum electrodes are placed in the solution corresponding to curve 2 in Figure 3, and subjected to an applied e.m.f. of 60 mv. (the value used by Farrington and associates). The currents at the indicator cathode and indicator anode are equal, because each is simply the observed indicator current. Hence the potentials adopted by the indicator cathode and indicator anode are such as to correspond to equal cathodic and anodic currents as indicated by the shaded sections of curve 2. Because with excess cuprous copper (curve 2) the concentration of bromine (or tribromide ion) is vanishingly small, the cathodic current results practically entirely from reduction of cupric ion, even though the cathode potential corresponds to the limiting current region of bromine reduction. As the potential adopted by the anode (ca. 490 mv.) is well below the value at which oxidation of bromide ion is significant, the anodic current results almost entirely from oxidation of the cuprous bromide complex to cupric ion. An exactly similar interpretation applies to curve 1 (excess bromine), except that in this case the only significant reactions are reduction of bromine at the cathode and oxidation of bromide ion at the anode.

With excess cuprous copper (curve 2 in Figure 3) the potential adopted by the indicator anode is far below the limiting current section of the anodic curve. In other words, the observed indicator current is much smaller than the limiting anodic current corresponding to the extant concentration of cuprous copper in the solution. Similarly, with excess bromine (curve 1) the observed indicator current is much smaller than the limiting cathodic current for bromine reduction. In the "minimum solution" the potentials adopted by the cathode and anode are smaller than corresponds to the limiting cathodic and anodic currents, and in addition there are appreciable contributions to the current from reduction of cupric ion and oxidation of bromide ion. These latter contributions evidently will be greater the greater the voltage impressed across the indicator electrode pair, which is the chief reason the net minimum current increases with increasing applied voltage (see Figure 2).

The treatment of Farrington and associates rests on the assumption that at any stage of the titration the indicator current will be given by an equation of the form

$$i = k_1(\mathrm{CuBr_2^-}) + k_4(\mathrm{Br_3^-}) \tag{3}$$

where the concentrations are those in the body of the solution and k_1 and k_4 are assumed to be constants independent of solution composition. Farrington and associates evaluated k_1 and k_4 from the slopes of titration lines (like those in Figure 2) when the solution contained excess cuprous copper and excess bromine, respectively, and they assumed that the same values applied when the indicator current was minimal. They were led to this treatment by the supposition that the indicator current corresponds to the limiting current for the particular extant concentrations of cuprous copper and bromine at all stages of the titration. From the current-electrode potential curves in Figure 3, and the attendant discussion above, it is clear that these assumptions are not valid. In other words, Equation 3 is invalid with constant applied e.m.f. because the potentials adopted by the indicator electrodes correspond neither to the limiting sections of the current-potential curves, nor to any other fixed, relative point on the curves, as the concentrations of bromine and cuprous copper are varied. Because it rests on an invalid premise, the final equation given by Farrington and associates relating the minimum current, k_1, k_4, and the equilibrium constant of Reaction 2 (their Equation 6) cannot be correct, and it is understandable that the apparent value of K which they computed differs from the true value.

To obtain a correct relation between the indicator current at constant applied e.m.f. and concentrations of cuprous copper and bromine in the solution, one must take into account the fact that the concentrations of these reacting species at the surfaces of the indicator electrodes are not negligibly small (or zero) compared to their bulk concentrations. As the current is the same at both indicator electrodes, it is necessary to consider only the situation at one of the electrodes, say, the anode.

At any stage of the titration the reactions at the indicator anode are expressed by Equations 5 and 6, the total current being the sum of a contribution from the oxidation of cuprous copper and a contribution from the oxidation of bromide ion. Each of these contributions is proportional to a difference in concentration between the electrode surface and the body of the solution—viz.

$$i_{\mathrm{Cu}} = k_{\mathrm{Cu}}[(\mathrm{CuBr_2^-}) - (\mathrm{CuBr_2^-})_{an}] \tag{4}$$

$$i_{\mathrm{Br}} = k'_{\mathrm{Br}}[(\mathrm{Br^-}) - (\mathrm{Br^-})_{an}] \tag{5}$$

where (x) and $(x)_{an}$ represent concentrations in the solution and at the anode surface, respectively. Since a steady state is attained in which the rate of transfer of bromine (tribromide ion) away from the electrode balances the rate of transfer of bromide ion to the electrode, one can also write

$$i_{\mathrm{Br}} = k_{\mathrm{Br}}[(\mathrm{Br_3^-})_{an} - (\mathrm{Br_3^-})] \tag{6}$$

Hence the total indicator current is

$$i = k_{\mathrm{Cu}}[(\mathrm{CuBr_2^-}) - (\mathrm{CuBr_2^-})_{an}] + k_{\mathrm{Br}}[(\mathrm{Br_3^-})_{an} - (\mathrm{Br_3^-})] \tag{7}$$

If both reactions proceed reversibly, then

$$E_{an} - E = \frac{RT}{F} \ln \frac{(\mathrm{CuBr_2^-})}{(\mathrm{CuBr_2^-})_{an}} \tag{8}$$

$$E_{an} - E = \frac{RT}{2F} \ln \frac{(\mathrm{Br_3^-})_{an}}{(\mathrm{Br_3^-})} \tag{9}$$

where E_{an} is the actual working potential of the indicator anode and E is the potential of an unpolarized platinum indicator electrode in the solution, both measured against the same external reference electrode. The difference $E_{an} - E$, is the "polarization of the anode."

From these relations it follows that

$$(\mathrm{CuBr_2^-})^2(\mathrm{Br_3^-}) = (\mathrm{CuBr_2^-})^2_{an}(\mathrm{Br_3^-})_{an} \tag{10}$$

which is simply one way of stating that the relative proportions of Reactions 5 and 6 are such as to maintain equilibrium of Reaction 1, provided both reactions proceed reversibly.

From Equations 7, 8, and 9 the total indicator current is

$$i = k_{\mathrm{Cu}}(\mathrm{CuBr_2^-})\{1 - \exp[(E - E_{an})F/RT]\} + k_{\mathrm{Br}}(\mathrm{Br_3^-})\{\exp[(E_{an} - E)\,2F/RT] - 1\} \tag{11}$$

Comparison with Equation 3, assumed by Farrington and associates, shows that

$$k_1 = k_{\mathrm{Cu}}\{1 - \exp[(E - E_{an})\,F/RT]\} \tag{12}$$

$$k_4 = k_{\mathrm{Br}}\{\exp[(E_{an} - E)\,2F/RT] - 1\} \tag{13}$$

It is clear that k_1 and k_4 could be constants (for a constant voltage impressed across the indicator electrodes) only if the polarization of the anode, $E_{an} - E$, remained constant. Actually $E_{an} - E$ varies during the course of a titration as the concentrations of cuprous copper and bromine change. The exponential terms, and hence k_1 and k_4, do approach constant values with either a large excess of cuprous copper or a large excess of bromine. The data in Table I provide an idea of the magnitudes of these variations in a typical case. The exponential term, and hence k_1, varies almost twofold.

Because the values of k_1 and k_4 are different with excess cuprous copper, excess bromine, and at the indicator current minimum, the limiting values of k_1 and k_4 evaluated from the slopes of the two branches of the titration curve are not applicable to the minimum current when the titration is performed with constant voltage across the indicator electrodes.

Table I. Polarization of Indicator Anode in Typical Titration

(E_a = 60 mv., $CuSO_4$ = 0.067F, NaBr = 1.0F, H_2SO_4 = 0.33F, solution volume = 150 ml., generation current, i_g = 12.9 ma.)

Indicator Current, μa.	E_{an} vs. S.C.E., Mv.	E vs. S.C.E., Mv.	$E_{an} - E$, Mv.	$\left(1 - \exp\left\{\frac{E_{an} - E}{-RT/F}\right\}\right)$
3.5	548	505	43	0.81
1.4	572	529	43	0.81
0.87	590	545	45	0.83
0.54	614	579	35	0.75
0.67	628	607	21	0.57
0.79	631	611	20	0.54
0.96	640	622	18	0.50
2.2	648	633	15	0.44
6.2	661	646	15	0.44

If the titration is performed with $E_{an} - E$ held constant, by appropriate adjustment of the voltage applied across the indicator electrodes at each measurement point, k_1 and k_3 do become constants and Equation 3 becomes valid. In view of Equation 2,

$$(Br_3^-) = K(Cu^{++})^2 (Br^-)^7 (CuBr_2^-)^2 \quad (14)$$

which can be substituted into Equation 3 to express i as a function of $(CuBr_2^-)^2$,

$$i = k_1(CuBr_2^-) + \frac{k_4K(Cu^{++})^2(Br^-)^7}{(CuBr_2^-)^2} \quad (15)$$

As the concentrations of cupric and bromide ions are so very large that they are virtually constant, Equation 15 can be differentiated in respect to generation time, the differential di/dt equated to zero to correspond to the minimum current, i_m, and the following relation is obtained

$$K = \frac{4i_m^2}{27\, k_1^2\, k_4(Cu^{++})^2(Br^-)^7} \quad (16)$$

Figure 4 shows two typical titration curves obtained with the same solution. Curve 1 was obtained with $E_{an} - E$ held constant at 0.010 volt by appropriate adjustment of the applied voltage across the indicator electrodes at each point. Curve 2 was obtained with the applied voltage constant at 0.060 volt. The minimum current is only half as large with constant polarization as with constant applied voltage. The value of K derived from curve 2 by the method of Farrington and associates is 3.8×10^{-16}, which agrees with the values reported by them. From curve 1, the value of K is 0.76×10^{-16}. From six experiments like curve 1 with 0.067F cupric sulfate, 1F sodium bromide, and 0.33F sulfuric acid, values of K from 0.29 to 0.76×10^{-16} resulted, the average being $0.46\ (\pm 0.16) \times 10^{-16}$.

From potential measurements in solutions of the same composition as the solution used to obtain these data, and containing known concentrations of $CuBr_2^-$ and Br_3^-, the formal potential of the cupric-cuprous couple was found to be +0.301 volt *vs.* S.C.E., and that of the bromine-bromide couple to be +0.800 volt. From these formal potentials the values of K was computed to be 0.13×10^{-16} under the conditions of these experiments.

Although the value of K obtained by the present treatment (0.46×10^{-16}) agrees better with the value based on the formal potentials (0.13×10^{-16}) than the value (3.8×10^{-16}) by the technique of Farrington and associates, the discrepancy is larger than can be attributed to accidental error. The authors have found that the residual discrepancy results chiefly from the circumstance that the several electrode reactions do not proceed with the thermodynamic reversibility assumed by the foregoing treatment. Significant overpotentials are included in the observed potentials of the indicator electrodes, and consequently Equations 8 and 9 are not strictly obeyed.

That reduction of tribromide ion does not proceed reversibly at a platinum cathode is demonstrated by the current-cathode potential curves in Figure 5. For reversible reduction of tribromide ion according to Equation 3, in a solution containing such a large concentration of bromide ion that its concentration at the cathode surface is practically the same as in the body of the solution, the equation of the current-cathode potential curve is

$$E_c = E^\circ - 0.0296 \log k_{Br}(Br^-)^3 + 0.0296 \log (i_d - i) \quad (17)$$

In this equation k_{Br} is defined by Equation 6, E° is the standard potential of Reaction 3, and i_d is the limiting diffusion current. Because the concentration of bromide ion is so large that it is virtually constant, the second term in this equation is a constant. The dashed curves in Figure 5 correspond to Equation 17, using the observed value of i_d and the observed value of the cathode potential at zero current. The overpotential is decreased by cleaning the cathode with aqua regia just prior to use (curve 2), but is not entirely eliminated.

The curves in Figure 5, like all the data in this study, were obtained with stirred solutions.

The curves in Figure 5 are not a sufficient proof that the electrode reaction involves an overpotential—i.e., proceeds irrever-

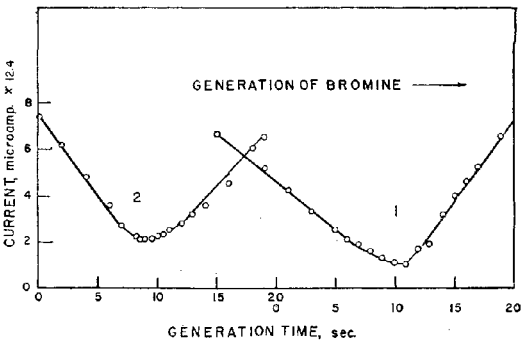

Figure 4. Amperometric titration curves

1. Polarization $E_{an} - E$ of indicator anode constant at 10 mv.
2. Total voltage applied across two indicator electrodes constant at 60 mv.

Solution composition same as in Figure 2

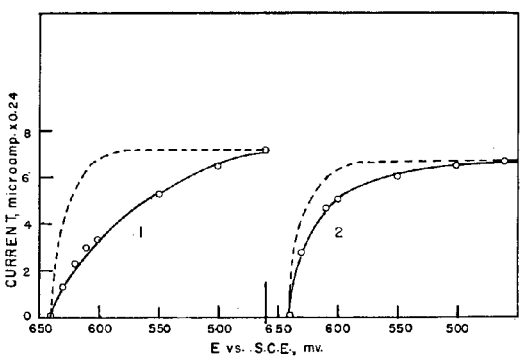

Figure 5. Current-cathode potential curves for bromine reduction at a platinum cathode

From solution containing ca. $2 \times 10^{-3}F$ bromine, 1F sodium bromide, and 0.33F sulfuric acid. Cathode area 3 sq. cm., solution stirred

1. With previously used cathode
2. After freshly cleaning cathode with aqua regia

sibly. The discrepancy could also result in whole or in part if transfer of tribromide ion to the cathode surface followed some relation different than that assumed by Equation 6. To test this possibility the authors studied current-cathode potential curves for the reduction of triiodide ion in solutions containing a large concentration of iodide ion. The iodine-iodide system is

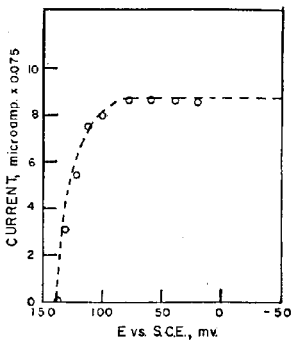

Figure 6. Current-cathode potential curves for reduction of ca $8 \times 10^{-6}F$ iodine

From solution containing $1F$ potassium iodide and $0.33F$ sulfuric acid, other conditions same as Figure 5
– – – – Predicted by Equation 17 for reversible reduction
O Experimental points

the exact analog of the bromine-bromide system, and the equation of the current-potential curve is identical in form with Equation 17. The dashed curve in Figure 6 is the theoretical curve for reversible reduction (Equation 17) and the points are the experimental observation for the iodine-iodide system. It is evident not only that the iodine-iodide couple behaves reversibly but also that the assumption involved in Equation 6 is valid under the conditions of these experiments—i.e., the current at any point is indeed proportional to the simple difference in concentration of the electroactive species between the solution and electrode surface. Kolthoff and Jordan (8) also concluded that the iodine-iodide couple is reversible. Consequently, the discrepant current-potential curves for the bromine-bromide system (Figure 5) do result from irreversible behavior.

The authors have also found that the oxidation of bromide ion at a platinum anode involves a significant overpotential of about the same magnitude as that observed for the reduction of bromine. On the other hand, anodic current-potential curves for the oxidation of the cuprous bromide complex correspond very closely with the curves expected for reversible oxidation, provided the platinum anode is freshly cleaned with aqua regia.

The effect of this irreversibility of the bromine-bromide couple is in the right direction to account for the discrepancy between the apparent value of K from the amperometric measurements and the value predicted from the formal potentials.

There is no question that amperometry with two polarized platinum electrodes is a very useful technique for the empirical detection of titration end points. However, the technique bristles with too many interpretative complexities to be attractive as a means of exactly measuring concentrations or evaluating thermodynamic constants. The drawbacks revealed by this study are inherent in the two-electrode amperometric system, and fundamentally stem from the simultaneous and unequal polarization of the two electrodes. The foregoing treatment demonstrates that correct concentration measurements with the two-electrode system can be obtained only when the electrode reactions proceed reversibly and if the degree of polarization of the electrodes is either measured or kept constant by appropriate readjustment of the total applied voltage at each measurement point.

These limitations do not pertain to amperometric measurements with a single polarized electrode in combination with an unpolarized auxiliary electrode. With the single electrode the electrode reaction need not be reversible, because the working potential is adjusted to correspond to the limiting current region of the current-potential curve, a condition which permits unambiguous and exact concentration determination. Furthermore, under this condition a constant condition of polarization is maintained by a constant applied voltage.

However, single-electrode amperometry is unsuited to the cupric bromide system, because with the equivalence point solution the cathodic current nearly exactly compensates the anodic current, so that the net current is too close to zero for practical measurement (see curve 3 in Figure 3).

ACKNOWLEDGMENT

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Coulometry with Quinquevalent Uranium

Determination of Ferric Ion

KENNETH W. EDWARDS and DAVID M. KERN

Dartmouth College, Hanover, N. H.

Quinquevalent uranium, the primary reduction product of uranyl ion in acid solutions, is a rapid and relatively powerful reducing agent, well suited for use in constant-current coulometry. Determinations of iron in amounts from 25 to 0.025 mg. were accurate within ±0.2%. The disproportionation of uranium(V) does not interfere above pH 1.5.

THE primary requirement for an internally generated reagent is that the process occur with 100% current efficiency. The main obstacle to achieving this in a reduction process is the drift of working electrode potential to values that permit the reduction of hydrogen ion. Thus it is improbable that any couple with potential much more reducing than zero volt *vs.* standard hydrogen electrode will find use in coulometric analysis. Couples whose potentials approach this limit are particularly useful, for the greater the reducing power, the more general the application. Of these, the most promising candidates are those which are reversible. For rapid electron interchange between couple and working electrode ensures obedience to the Nernst equation even at large current densities. If the reagent is then present in sufficient concentration to prevent exhaustion at the electrode surface, the potential can be expected to remain within 0.1 volt of E^0 for the couple, with no danger of hydrogen evolution.

These considerations suggested the investigation of quinquevalent uranium (UO_2^+) generated from uranyl solution, the standard potential of which, $E^0_{v,vi} = -0.06$ volt *vs.* S.H.E. (*4*), is equaled in reducing power only by titanium(III) (*7*) and iron(II) EDTA (*9*) among reagents investigated to date, and which shares with the latter the advantage that the usual platinum electrode may be used. The instability of uranium(V) with respect to disproportionation (*4*) and its rapid air oxidation have prevented its use as an ordinary volumetric reagent, but the peculiar advantages of internal generation, as fully exploited in this application, satisfactorily overcome both these difficulties.

The reversibility of the UO_2^{++}, UO_2^+ couple has been well established by studies of the first uranyl reduction wave at the dropping mercury electrode (*4*) in mildly acid solutions. The subsequent reduction to uranium(IV) and uranium(III) occurs only at potentials more than 0.5 volt more negative. Reduction at controlled potentials has accordingly been used successfully at both mercury (*4*) and platinum (*6*) surfaces to prepare quinquevalent uranium solutions.

In strongly acid solutions uranium(V) has only a brief existence, as its disproportionation rate into uranium(IV) and uranium(VI) is directly proportional to the hydrogen ion concentration (*4*). Under these conditions the product of uranyl reduction is essentially uranium(IV). If uranium(IV) were itself an effective reducing agent, the disproportionation would be no disadvantage. However, uranium(IV) does not compare well with uranium(V) in this respect. Its applications as a reducing agent in volumetric analysis are few, and even then elevated temperatures are necessary to obtain satisfactory end points (*1*).

The use of uranium(IV) as a reagent in coulometric analysis was recently described by Shults, Thomason, and Kelley (*10*), who used uranyl ion as the source. The essential difference between their technique and that described here is the high acidities (0.5*M* hydrogen ion) used by these authors, which favored uranium(V) disproportionation to uranium(IV). Thus under their conditions titration of ferric ion did not give satisfactory results even at 60° C., whereas in the present investigation excellent results have been obtained at room temperature over a thousandfold range of iron concentration using pH conditions (pH = ca. 2) retarding uranium(IV) formation.

APPARATUS AND REAGENTS

Electrical Apparatus. The constant current source was a General Radio Co. unit variable power supply Type 1204-B connected to a Sola constant voltage transformer. This current supply, in combination with resistors of suitable wattage varying from 6000 ohms to 1.5 megohms, gave currents constant usually to within ±0.1% at any desired value between 75 ma. and 20 μa. Because of drifting line voltage, it was sometimes necessary to average several current measurements made during a run in order to achieve the desired accuracy (±0.1%). Current was measured as potential drop across a General Radio Co. decade resistor Type 1432-J, with the aid of a Leeds & Northrop student-type potentiometer. Current addition was manually controlled. A double-pole double-throw relay switch activated a timer (Standard Electric Time Co. Type S-10) during periods of electrolysis. The rest of the time a dummy resistor replaced the cell in the circuit in order to maintain the flow of constant current.

Cells. Titrations of 1 mg. or more of iron were carried out in a glass H-cell. The 150-ml. cathode and 50-ml. anode compartments were separated by a glass frit 1.5 cm. in diameter, with an agar plug 0.5-inch long on the anode side. The cathode was a 20-sq. cm. platinum sheet. The cathode solution, about 100 ml. in volume, was kept free of oxygen by passage of prepurified nitrogen supplied by the Ohio Chemical and Surgical Equipment Co., a remarkably pure product requiring no further treatment for the removal of hydrogen or oxygen. (Some commercially available nitrogen, while free of oxygen, contains hydrogen which slowly reduces uranyl ion at platinum surfaces.) Carbon dioxide from a bottle of dry ice also proved a satisfactory deaerator. Oxygen formed at the platinum wire anode immersed in the 0.1*M* potassium sulfate anolyte did not infiltrate the cathode compartment for several hours; nitrogen bubbling of the anode compartment was dispensed with.

Magnetic stirring was provided. It was important to have the stirrer rotate without the least contact with the sides. The fine silica suspension resulting from the slow abrasion of the glass absorbed a significant amount of ferric ions in the more dilute runs. Plastic-coated stirrers tended to develop minute leaks in the circular end seams, with resulting contamination of the solution with iron from the magnet.

For microgram quantities of iron, a cell similar to the one described above but with one fifth the capacity was first used with fair success, the cathode area being reduced to 3 sq. cm. To avoid the danger presented by the glass frit, a second cell was devised in which the anode compartment was a narrow glass tube with an upturned capillary at the lower end, hermetically sealed at the upper end with a cement-coated cork bearing a silver wire. The tube was entirely filled with saturated potassium chloride and fitted into the stopper of the cathode compartment.

This silver–silver chloride anode proved entirely satisfactory with the small (less than 1 ma.) currents used. Diffusion of iron or silver chloride complex appeared to be negligible. Its behavior with larger currents was not investigated. The 25- and 5-γ runs were made in this cell in a total volume of 20 ml. The precision of the end point is limited by the extent of dilution rather than the absolute amount of unknown; smaller amounts of iron could probably be accurately determined if adequately stirred cells of smaller volume were designed. The dimensions of the cell used here were limited primarily by the size of commercially

available magnetic stirrers, as stirring with gas bubbles did not give sufficiently rapid mixing or steady indicator currents.

Reagents. Uranyl chloride and perchlorate solutions were prepared by fuming from Mallinckrodt analytical reagent uranyl nitrate hexahydrate. Because of the expense of this reagent, some effort was made to determine the minimum concentration compatible with 100% current efficiency. With the geometry and degree of stirring obtaining in this work, 0.02*M* uranyl ion was found adequate for current densities of 0.5 ma. per sq. cm. or less. For current densities of 2.5 ma. per sq. cm. this concentration failed to yield 100% current efficiency, but 0.1*M* uranyl ion proved satisfactory.

The 0.1*M* ferric chloride stock solution was prepared determinately from Mallinckrodt analytical reagent iron wire on the basis of the reported assay of 99.9%. Oxidation to the ferric state was carried out with hydrogen peroxide, the excess of which was destroyed by lengthy boiling. The final product was tested for ferrous ion with ferricyanide. This solution and those obtained from it by dilution were made weakly acid with hydrochloric acid to prevent hydrolysis.

The water used was doubly distilled, once from permanganate. All volumetric glassware was calibrated.

Table I. Titration of Iron(III) with Uranium(V)

Iron Taken, Mg.	Approx. Current, Ma.	Approx. Time, Sec.	% Error
27.73	50	1000	0, −0.4, −0.1, −0.1
2.942	10	550	+0.1, +0.2, −0.2, −0.3, −0.3
2.942[a]	10	550	−0.1, −0.2, 0, −0.1
2.859	10	550	+0.1, +0.1, 0, 0
1.118	3.5	530	−0.2, +0.3, +0.1, +0.1, 0, 0
0.2796	1	500	−0.2, −0.3, −0.1, −0.1
0.02813	0.27	175	0, −0.6, −0.2, 0, −0.1, +0.3
0.005575	0.05	190	+1.6, +0.8, −0.2, −0.7, +0.9

[a] 0.1*M* SO_4^{--}, pH 1.5.

PROCEDURE AND RESULTS

Determination of End Point. POTENTIOMETRIC. ΔE^0 for the uranium(V)-iron(III) reaction is 0.7 volt, although this value is effectively reduced by the partial hydrolysis of ferric ion and its complexation by chloride. The relatively large uranyl concentration, and the ferrous concentration which accumulates in the solution after a series of runs, also tend to diminish the break at the end point. Nevertheless the equilibrium remains extremely favorable. Curves of theoretical shape and precise end point were obtained with a platinum indicator electrode and a potassium chloride salt bridge connecting with an external calomel electrode. Results obtained in experiments on 2.5-mg. samples compared well with those appearing in Table I. But at least in these dilute solutions the potential behaved sluggishly, drifting for several minutes after each increment of current in the neighborhood of the end point; so a more convenient method was sought.

AMPEROMETRIC. In the method finally adopted, about 0.3 volt was applied across two platinum gauze electrodes of 0.5-sq. cm. area. The rather high voltage was dictated by the low sensitivity of the galvanometer (0.02 μa. per mm.). Theoretically it has been shown that low voltages (ca. 0.01 volt) give maximum end point precision (*2*). The current-time curves during the electrolysis had the V profile at the end point characteristic of the reaction between two reversible couples. The rate of decline just prior to the end point varied from solution to solution, probably depending on the equilibrium between the various iron(III) species. At times it was steep, at others almost horizontal during the last few seconds. The final rise corresponding to the presence of excess uranium(V) was always exceedingly abrupt, permitting dead-stop end points even with a 50-μa. generating current, without extrapolation. Probably because of the lag in mixing rather than in reaction, the last few 0.25- or 0.2-second increments were accompanied by an initial rise in the indicator current before it settled, usually within 20 seconds, to a lower value. The end point determination was a matter of about 3 minutes or less in most cases.

Optimum pH. The upper limit was fixed by the hydrolysis of ferric ion, the lower limit by the disproportionation of uranium(V). Successful runs were made at a pH as high as 2.6, but 3.25 was too basic. Iron recovery as determined by titration with EDTA has been reported incomplete at pH 3 (*3*)

Uranium(V) disproportionation obeys the rate law (*4*):

$$-d[U(V)]/dt = k(UO_2^{++})^2(a_{H^+})$$

$$k = \text{ca. } 70(\text{moles/liter})^{-1}\ \text{sec.}^{-1}.$$

A millimolar solution at pH 2 therefore has a half life of about 0.5 hour. Titration with uranium(V) will be successful only if the disproportionation rate is negligibly small compared with that of oxidation to uranium(VI). Disproportionation is favored not only by high acidities but also by anions such as oxalate (*5*). Chloride and perchlorate in dilute solution give comparable rates (*3*) and presumably exert no catalytic influence. The adverse effect of high acidity became evident at pH less than 1.5. Indicator currents were observed to reach equilibrium at an increasingly slow rate, and the rise beyond the end point grew less marked. At pH less than 1.0, excess uranium(V) did not give a constant indicator current as at lower acidities, but a gradually declining one. The slow attainment of equilibrium was presumably due to the presence of slow-reacting uranium(IV) in the solution, and the fading currents beyond the equivalence point to the disproportionation of uranium(V). At the 0.5*M* hydrogen ion concentration used by Shults, Thomason, and Kelley (*10*) these effects were so serious that end points could be recognized only with great difficulty and after long periods of waiting.

The recommended pH range is 2.5 to 1.5, although these figures do not represent the utmost limits. The effect of pH was observed during titrations of 3-mg. samples with 10-ma. currents. When very small currents are used, the lower limit of pH is considerably extended. The uranium(V) concentration is smaller under these conditions, and as disproportionation is second-order with respect to uranium(V), its rate will be greatly reduced with respect to the first-order reaction with ferric ion. The catalytic influence of other ions on the disproportionation rate also affect the limit (see also the effect of nitrate ion below).

Procedure. The generating current was chosen to give a titration time of about 500 seconds, a compromise between the precision and inconvenience afforded by a long run. Runs as short as 200 and as long as 1000 seconds were successfully made.

The generating solution was made up with appropriate quantities of uranyl chloride or perchlorate stock solution (see reagents) diluted to 100 or 20 ml., depending on the cell used. The mixture was brought to the desired pH (1.5 to 2.5) with hydrochloric acid. The solution was then deaerated for 15 minutes with nitrogen. The iron solution, appropriately diluted from the stock, was likewise deaerated with nitrogen that had been equilibrated by prior passage through a portion of the same solution. Deaeration was omitted when only small volumes of concentrated solution were to be added, as adequate oxygen removal would be effected during the electrolysis itself. [The reaction of uranium(V) with oxygen, though rapid, is much less so than with ferric ion. Titration of oxygen-containing solutions gives a succession of false end points owing to the sluggishness of the reaction.]

A blank run with a small quantity of iron present served to remove impurities and establish the nature of the end point. Thereafter a series of 0.5- or 5-ml. aliquots was analyzed in succession in the same solution, without apparent limit except the capacity of the cell. Nitrogen bubbling and indicator current measuring proceeded continuously throughout the run. The latter gave the clue to the approach of the end point. A half or a full second's current was added beyond the time of minimum indicator current as a precaution, and this amount was carried over to the next run.

RESULTS

Results are presented in Table I. The formula used in calculation was

Table II. Titration of Iron(III) with Uranium(V) in Presence of Nitrate

(Iron taken, 28.6 mg. I = 10 ma.)

pH	NO_3^-, M	% Error
2.0	0.1	+0.2, +0.2
	0.5	+0.6, +0.8
1.5	0.0	±0.0
	0.04	+1.1

$$\text{Mg. of Fe} = I(\text{ma.}) \times t(\text{seconds}) \times 55.84/96{,}493$$

In only the last run was the precise determination of the end point felt to be the major source of error. Further refinement of procedure and apparatus might reduce the small errors observed to even lower values.

Although there is evidence (*5*) that sulfate catalyzes uranium(V) disproportionation, the effect is not sufficient to interfere with the iron determination, as is evident from the third entry in Table I.

The effect of nitrate ion is shown in Table II for the electrolysis of 2.86 mg. of iron with a 10-ma. current.

Positive errors at high hydrogen and nitrate ion concentrations may be due either to direct cathodic reduction of nitrate, or to its reaction with generated uranium(V). It follows from these data that at pH 2, uranyl nitrate can be used directly as the source of uranium(V), *provided its concentration does not exceed about* 0.03M. At higher pH's more concentrated uranyl nitrate solutions could no doubt be used.

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Determination of Chloride in Titanium Sponge by the Rapid Potentiometric Method

H. V. MALMSTADT, E. R. FETT[1], and J. D. WINEFORDNER

Department of Chemistry and Chemical Engineering, University of Illinois, Urbana, Ill.

Two procedures are presented for the rapid, precise, and accurate determination of 0.001 to 0.5% chloride in titanium sponge, requiring only about 7 minutes per determination after dissolution of the sample. The chloride analysis involves a final measurement of the voltage difference between two silver–silver chloride electrodes in a concentration cell, one arm of which contains the unknown chloride solution and the other a standard chloride solution. Prior to the potentiometric measurement the unknown chloride solution must be prepared to prevent interferences from substances in the titanium samples. In one procedure the chloride is removed from an aliquot of a sulfuric acid solution of the titanium sample by a rapid distillation (about 5 minutes). In the other, the titanium sponge is dissolved in a measured quantity of either sulfuric or fluoboric-sulfuric acid mixture and prepared for the potentiometric measurement by selective oxidation with hydroxylamine sulfate.

THE quantitative determination of chloride in commercially produced titanium sponge is an important routine determination, and a rapid and accurate procedure is desirable. Several methods are used currently for the chloride determination, but most of them are time-consuming and some are rather inaccurate for the low concentrations of chloride which are usually present in titanium sponge.

The gravimetric (*6*) and colorimetric (*3*) chloride procedures give reliable results, but both methods involve a precipitation in which the precipitate must stand overnight. Some laboratories use titration procedures (*6*) which are more rapid than the gravimetric and colorimetric procedures but are not very reliable for samples containing less than 0.1% chloride.

The concentration of chloride in titanium sponge is usually in the range of 0.01 to 0.5%, and under the best conditions for dissolving the titanium samples, solutions containing about 20 mg. of titanium per ml. of solution are obtained. Therefore, the concentration of chloride in solution would usually be in about the range 6×10^{-5} to $3 \times 10^{-3}M$. An ideal method for determination of chloride in titanium sponge should make it possible to determine a low concentration of chloride rapidly and accurately in a very acid solution containing relatively large quantities of titanium and small quantities of iron, magnesium, manganese, vanadium, and other trace elements.

Blaedel, Lewis, and Thomas (*1*) have shown that high ionic strength renders turbidimetric, nephelometric, and direct titration procedures using adsorption indicators very unreliable. In addition, the direct visual color indicator titrations by the Mohr and mercurimetric methods do not have sufficient sensitivity, and the Volhard method is reliable for only relatively high percentage chloride samples (*6*).

Potentiometric titration of the chloride in the strong sulfuric acid and fluoboric-sulfuric acid mixture has not been too reliable, partly because of the erratic behavior of the silver indicator electrode in these solutions. Direct polarography and amperometric titration methods do not give good precision at the low chloride concentrations encountered in the titanium samples. Conductometric titration methods are useless because of the high ionic strength.

Ordinary potentiometric measurement of chloride concentration using a concentration cell generally involves consideration of and correction for liquid junction potential and ionic strength

[1] Present address, Union Oil Co., Fullerton, Calif.

effects, but Furman and Low (*4*, *5*) and more recently Blaedel, Lewis, and Thomas (*1*), have devised a simple differential method which eliminates errors from these two effects. The method was conceived primarily for measuring low chloride concentrations in solutions of high ionic strength, and is readily adaptable for routine analysis. The procedure consists of measuring the voltage of a silver–silver chloride electrode immersed in the unknown solution against an identical electrode immersed in a standard chloride solution. Both solutions must have practically identical composition, except for chloride concentration, which should contribute negligibly to ionic strength. From the voltage of the cell the unknown chloride concentration is easily determined.

Consideration of the characteristics of the acid titanium solutions containing low concentrations of chloride leads to two possibilities for utilizing the rapid potentiometric concentration cell method. One obvious general procedure is to remove, quantitatively, the chloride from the acid titanium solution and transfer it to a solution of known ionic strength which is free from possible interferences. Another general procedure is to dissolve each titanium sample in the same quantity of acid, treat the solutions so as to prevent interference from certain constituents likely to be present in titanium sponge, and measure the potential of the unknown solutions against a standard solution prepared in the same way.

The first general procedure can be carried out rapidly and accurately by dissolving the titanium sample in sulfuric acid, diluting to volume, rapidly distilling the chloride of an aliquot sample into a sulfuric acid solution of known concentration, and measuring the final unknown chloride solution in one arm of a concentration cell against a standard chloride–sulfuric acid solution in the other arm. The second procedure consists briefly of dissolving the titanium sample in a measured quantity of sulfuric or fluoboric-sulfuric acid mixture, diluting to volume, treating an aliquot of the solution with hydroxylamine sulfate to oxidize the titanium to titanium(IV), not oxidizing ferrous iron to ferric iron, and finally measuring in a concentration cell against a specially prepared standard.

Both procedures have been developed to provide rapid, precise, and accurate results. The total analysis time after dissolution of the sample is only about 5 to 7 minutes per sample by either procedure.

EQUIPMENT

The concentration cell used was similar to the one described by Blaedel and coworkers (*1*). The dimensions of the cell were chosen so that each arm had a capacity of about 15 ml. Therefore, 25 ml. of unknown chloride solution were sufficient to provide initial rinsing of the unknown arm prior to filling for a measurement. The cells were coated with Desciote, and one rinse was found to be sufficient.

The silver–silver chloride electrodes were prepared by the method of Brown (*2*). Square plate platinum electrodes, 4 sq. cm. in area, were used for most of this work, although wire electrodes, 2 cm. long and 1 mm. in diameter, were also satisfactory. The electrodes are stable for many months and last for hundreds of determinations.

A thermostat was used which controlled the solution temperature at 25° ± 0.1° C. An L and N type K potentiometer was used to make the voltage measurements of the cell, and a nomogram similar to the one described by Blaedel, Lewis, and Thomas (*1*) was used to convert the voltage readings to concentration values rapidly.

A simple distillation setup was used with which the chloride was removed quantitatively from the titanium sample. A 50-ml. distillation flask was used, and a condenser with a condensing tube 7-mm. in inner diameter, and 70 cm. long, surrounded by a water jacket, was attached to the side arm. A condensing tube with small diameter was used so that it could be easily rinsed down with a small volume of wash water. A 0° to 200° C. thermometer was inserted into the top of the distillation flask so that the tip was immersed in the solution. A glass tube adapter 7 mm. in inside diameter was made for the end of the condenser which fitted into the 25-ml. volumetric receiving flasks. The distillation flask was heated with a Meker burner.

DETERMINATION OF CHLORIDE IN TITANIUM SAMPLES BY DISTILLATION TECHNIQUE

Titanium sponge is often dissolved in sulfuric acid and the dissolved sample is diluted to be about 4*M* in sulfuric acid and to contain 20 mg. of sample per ml. of solution. Experiments were conducted, therefore, to determine the feasibility of rapidly and quantitatively removing the chloride from about a 4*M* sulfuric acid solution.

Preliminary Distillation Tests. Preliminary experiments showed that known amounts of chloride added to reagent grade 4*M* sulfuric acid could be rapidly and quantitatively distilled off and collected with a simple distillation setup as described above. A 25-ml. aliquot of 4*M* sulfuric acid containing a known quantity of chloride was added to the distillation flask, the tip of the condenser adapter was immersed in 2.50 ml. of 10.0*M* sulfuric acid contained in a 25-ml. volumetric receiving flask, and the chloride was distilled off by heating the distillation flask with a Meker burner until the solution temperature reached 130° to 140° C. The distillation was then stopped, the condenser was washed down with a fine jet of distilled water, and the distillate was diluted to volume with distilled water. After dilution to volume the chloride distillate was almost exactly 1*M* in sulfuric acid. A very small quantity of sulfuric acid was carried over from the distillation to the receiving flask during the distillation, but the quantity was not significant compared with the large known quantity of sulfuric acid added to the receiving flask to adjust the ionic strength.

The chloride concentration in the distillate was determined in the concentration cell as described below.

Dissolution of Titanium Sample. A solution containing about 10 ml. of concentrated sulfuric acid and 25 ml. of distilled water was used to dissolve each gram of titanium sample. Immediately after addition of the titanium sample to the cool sulfuric acid solution contained in an Erlenmeyer flask, a reflux condenser was connected to the top of the flask to prevent loss of any chloride during dissolution of the sample. The solution was heated gently on a hot plate until the sample was dissolved, usually about 4 hours. The solution was then cooled and quantitatively transferred to a 50-ml. volumetric flask and diluted to volume with distilled water.

Titanium samples larger than 1 gram are often used for analysis when the samples are nonhomogeneous, and proportionately larger quantities of acid solution and larger volumetric flasks are used, so that the final titanium concentration is the same regardless of sample size. In all cases, a 25-ml. aliquot of the final titanium solution, containing 0.500 gram of sample, is used for analysis.

Distillation of Chloride from Titanium Samples. The distillation of 25-ml. aliquots of titanium sponge solutions can be performed by the same basic procedure as for the sulfuric acid solutions, but the heating of the distillation flask must be carefully regulated, and the solution temperature raised to 150° C. to assure quantitative transfer of chloride. Local heating of the distillation flask must be eliminated to prevent severe bumping, and the solution must be heated so as to prevent condensation of solution in the neck of the flask. Most of the hydrochloric acid is distilled over near the end of the distillation, and condensate in the neck of the flask results in absorption of a considerable amount of hydrochloric acid. However, both of these difficulties can be readily prevented and a rapid distillation effected by adjusting a Meker burner as shown in Figure 1.

Several other methods of heating the distillation flask were attempted but none proved as simple, rapid, and effective as the Meker burner. No trouble was experienced with this distillation method of rapidly removing chloride from the titanium samples when the burner was adjusted as shown in Figure 1, and no attention was required except to turn off the flame when the solution temperature reached 150° C. The position and adjustment of the flame should approximate those shown in Figure 1. The 25-ml. volumetric receiving flask should contain 2.50 ml. of 10.0*M* sulfuric acid before the distillation is started.

Measurement of Chloride Concentration. After being diluted to the mark and thoroughly mixed in the 25-ml. volumetric receiving flask, the chloride distillate was 1.00*M* in sulfuric acid and ready to be transferred to the concentration cell. The unknown arm of the concentration cell was rinsed once with the distillate and then refilled. The chloride concentration was determined by measuring the voltage between the unknown solution and the chloride standard (a $1.000 \times 10^{-2}M$ sodium chloride, 1.00*M*

sulfuric acid solution). The measured voltage was converted to molar concentration using a nomogram (*1*), and then to percentage of chloride in the original titanium sample. The nomogram could, of course, be made to read directly in percentage of chloride.

Results. The method was first tested on a titanium sample which was analyzed by the gravimetric procedure (*6*) to give a result of 0.162% of chloride. The results of the distillation–concentration cell method are given in Table I. Each sample was an aliquot of a 20-gram sample of titanium dissolved in sulfuric acid solution as previously described. Prior to distillation, the iron content of aliquots 7 and 8 was increased from less than 0.1 to over 1% by adding ferrous ammonium sulfate, and the chloride results were not affected.

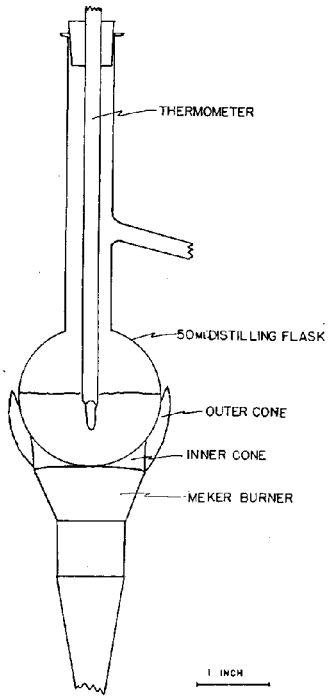

Figure 1. Flame adjustment and burner placement for rapid distillation of chloride

The method of standard addition was employed next as a means of testing the method. A 20-gram sample of titanium sponge containing only about 0.01% of chloride was dissolved as before. After accurately determining the small quantity of chloride originally present in the titanium sample, known amounts of chloride were added to aliquots of the titanium solution prior to distillation. The results are given in Table II.

When the concentration of chloride is very low (about 0.03% or less), the solubility of the electrode must be considered, and it is necessary to know the value of electrode solubility, *S*, which can be determined as described by Blaedel, Lewis, and Thomas (*1*). Also, the chloride content of the sulfuric acid solution used in dissolving a titanium solution should be determined and corrected for by applying a blank correction. The blank was found to be equivalent to less than 0.001% chloride in the titanium sample for all sulfuric acid solutions tested, and this quantity is generally insignificant for routine chloride determination of titanium sponge samples.

Five titanium sponge samples issued to the chloride panel of the Metallurgical Advisory Committee on Titanium were obtained from Watertown Arsenal. The nominal chloride values were available with which to compare the distillation results, but the arsenal samples were not checked by other standard chloride methods. The results in Table III illustrate the precision of the method for the arsenal samples.

DETERMINATION OF CHLORIDE WITHOUT SEPARATION FROM ORIGINAL TITANIUM SOLUTION

Although the total analysis time required for determination of chloride after dissolution of the sample is less than 7 minutes by the distillation method, the time involved in dissolution of the titanium sample with sulfuric acid is about 4 hours. The dissolution of the titanium sample can be decreased to about 30 minutes or less by using a sulfuric-fluoboric acid mixture, but such a solution is not suitable for the distillation method because of evolution of hydrofluoric acid at the temperature required to distill off hydrochloric acid quantitatively.

Consequently, a second basic method was investigated to enable chloride to be determined in the sulfuric-fluoboric acid solution of the titanium sponge. In this method, the dissolved sample is treated to prevent interferences and the solution is measured directly in the concentration cell.

Upon dissolving the sponge sample in sulfuric or a mixture of sulfuric-fluoboric acids, most of the titanium is in the trivalent state, and the strongly reducing solution destroys a silver chloride electrode surface almost immediately after contact. Therefore, it is necessary to oxidize the titanium to titanium(IV) before the

Table I. Precision of Chloride Distillation Method

Aliquot No.		Chloride Determined, %
1		0.164
2		0.159
3		0.163
4		0.162
5		0.165
6		0.162
7		0.164
8		0.162
	Av.	0.163
	Standard deviation	0.0018

Table II. Determination of Chloride in Titanium Samples Containing Known Quantities of Added Chloride

Chloride Added,[a] %	Chloride Found,[b] %
None (originally present in Ti sponge)	0.0108[c]
	0.0108[c]
	0.0099[c]
	0.0105[c]
0.025	0.026
	0.023
	0.027
	0.025
	0.024
0.050	0.050
	0.051
0.100	0.100
	0.099
0.200	0.199
	0.203
0.500	0.506
	0.495

[a] Added as NaCl to aliquots of same titanium solution.
[b] % chloride found is equal to total chloride determined minus chloride originally present in titanium sponge sample, except where no chloride was added.
[c] % chloride found in original titanium sample.

Table III. Determination of Chloride in Watertown Arsenal Titanium Samples by Distillation Method[a]

Sample	Nominal Concentration, % Chloride	Chloride Found, %
WA-46	0.09	0.108
		0.108
		0.108
WA-47[b]	0.18	0.203
		0.203
		0.203
WA-47[c]	0.18	0.182
		0.183
WA-48	0.05	0.0513
		0.0513
		0.0513
		0.0502
WA-64	0.19	0.190
		0.190
		0.190
WA-65	0.16	0.171
		0.171
		0.171
		0.171

[a] 5 grams of each sample were dissolved and several 25-ml. aliquots of each were individually distilled and concentration of the distillates was determined in the concentration cell.
[b] Results of this sample did not check closely with nominal value, so a second 5-gram sample, [c], was dissolved and chloride determined. Results indicate that sample was not very homogeneous.

solution can be transferred to the concentration cell. It is essential, however, that the iron, which is usually present in small but significant quantities in the titanium sponge, remain in the ferrous state, because ferric iron interferes with the method at concentrations greater than $10^{-4}M$ (*1*). In addition, a strong oxidizing agent could oxidize the chloride to free chlorine, which would be lost by volatilization. Hydroxylamine sulfate (Kodak, 99+%) fulfills the desired condition of selectively oxidizing the trivalent titanium and not the ferrous iron.

Dissolution of Titanium Sample. In the direct method for chloride determination it is necessary to dissolve all samples in the same way, so that all solutions have the same ionic strength. The method is applicable to either sulfuric or sulfuric-fluoboric acid solutions, but the latter was investigated most thoroughly because it dissolves the titanium much more rapidly than just the sulfuric acid solution.

A solution containing 8.0 ml. of concentrated sulfuric acid, 2.50 ml. of 48 to 50% fluoboric acid, and 25 ml. of distilled water was used to dissolve each gram of titanium sample. After addition of the titanium to the acid solution contained in an Erlenmeyer flask, a reflux condenser was immediately connected to the top of the flask, and the solution was heated gently on a hot plate until the sample was dissolved. One gram of hydroxylamine sulfate was then added to the dissolved sample and the solution was diluted to 125 ml. with distilled water. Proportionately larger quantities of acid, hydroxylamine sulfate, and increased dilution volumes were used for larger than 1-gram samples.

If the same titanium solution is to be used for determination of other elements, it might not be desirable either to make such a large dilution of the dissolved sample or to oxidize the entire sample with hydroxylamine sulfate. In this case, a dissolved 1-gram sample is quantitatively transferred to a 50-ml. volumetric flask and diluted to the mark with distilled water, so that the solution contains 20 mg. of sample per ml. A 10-ml. aliquot of this solution is then transferred to a 25-ml. volumetric flask, 0.2 gram of hydroxylamine sulfate is added, and after being shaken and cooled to room temperature, the solution is diluted to the mark with distilled water. This solution is used directly in the unknown arm of the concentration cell. The remainder of the more concentrated solution, containing 20 mg. of sample per ml., can be used for determination of other elements. The double quantitative dilution, whereby an intermediate solution of 20 mg. of sample per ml. and a final solution of 8 mg. of sample per ml. are prepared, is also convenient in the preparation of the standard solution as described below.

Experiments were tried using larger quantities of fluoboric acid to dissolve the titanium samples, and although the dissolution time was decreased by several minutes as compared with the above solution, two difficulties were experienced. The solutions with larger quantities of fluoboric acid hydrolyzed readily, and because the fluoboric acid contained significant quantities of chloride, the blank correction was increased appreciably.

Preparation of Standard Solution. It is essential to prepare a standard solution which has nearly the same ionic strength as the samples and has an accurately known quantity of chloride. The most straightforward way of preparing such a solution is to dissolve a titanium sample of known chloride concentration in exactly the same quantity of acid as for the samples. An amount of chloride is then added to give the desired chloride concentration and the solution is treated and diluted to volume as for the unknown samples.

This procedure is very satisfactory, but several considerations and precautions are necessary to ensure an accurately known standard. There are several sources of chloride in a titanium sponge sample used as a standard; the titanium sponge and the sulfuric and fluoboric acids all contain small quantities of chloride. Very pure titanium sponge is preferably chosen for preparing the standard; it will usually contain a few hundredths of a per cent of chloride. The quantity of sulfuric and fluoboric acids used to dissolve the titanium samples was found, respectively, to be equivalent to 0.0003 and 0.009% of chloride in the titanium sample for the particular batches of acid used in this work. No significant quantity of chloride was found in the hydroxylamine sulfate.

One method of accurately preparing a chloride standard is to determine individually the chloride in the titanium sponge and in the acid solution used to dissolve the sample, and then to add a known amount of chloride to give the desired total concentration of chloride. The chloride in the titanium can be determined by the previously described distillation method or by the standard gravimetric procedure (*6*). The chloride in the sulfuric-fluoboric acid solution can be determined by preparing two identical acid solutions except that to one is added a known quantity of chloride. The two solutions are poured in opposite arms of the concentration cell and the potential is measured. From the potential reading and known quantity of added chloride, the original concentration in the sulfuric-fluoboric acid solution can be readily calculated.

A more rapid method of preparing a chloride standard is to dissolve a large titanium sponge sample in sulfuric-fluoboric acid and to dilute to volume to give a solution containing 20 mg. of titanium sample per ml., and then to determine the total chloride in titanium sample and acid solution all at one time. This can be accomplished by the following method.

Two 10-ml. aliquots of the above solution are put into two 25-ml. volumetric flasks; 0.2 gram of hydroxylamine sulfate and a known quantity of chloride are added to each flask and the solutions are diluted to the mark with distilled water so as to contain 8 mg. of sample per ml. The known chloride added to one flask should be about ten times greater than added to the other flask. After shaking the flasks, the contents are poured into opposite arms of the concentration cell and the potential is measured on a potentiometer. The potential can be expressed in terms of chloride concentration by Equation 1,

$$E = 0.0591 \log_{10} \frac{k_1 + x}{k_2 + x} \qquad (1)$$

where x is the unknown chloride resulting from the chloride in the titanium and in the acid used to dissolve the sample, E is the measured potential of the cell, k_1 is the known added quantity of chloride to one aliquot of solution, and k_2 is the known added quantity of chloride added to the other aliquot of solution, and, for convenience, is ten times greater than k_1. It is assumed in making this calculation that the total chloride concentrations of both solutions are sufficiently great so that the solubility of the electrode is insignificant, which is the case when the total chloride concentration is greater than $0.25 \times 10^{-3}M$.

Equation 1 is rewritten to give Equation 2 for conveniently calculating x,

$$x = \frac{k_2 - k_1 10^{E/0.0591}}{10^{E/0.0591} - 1} \qquad (2)$$

After the value of x has been determined, a large measured volume of the same titanium solution, containing 20 mg. of sample per ml., is treated with sufficient hydroxylamine sulfate (1 gram per gram of titanium sample); and a known quantity of chloride is then added so that upon dilution to final volume (8 mg. of titanium sample per ml.) the total chloride concentration will be that chosen for the direct method standard ($0.500 \times 10^{-3}M$).

The above methods of preparing the standards are illustrated with the following experimental results: Chloride, k_1 (0.0100 mmole), was added to a 10-ml. aliquot of the sulfuric–fluoboric acid solution of titanium containing 20 mg. of sample per ml., 0.2 gram of hydroxylamine sulfate was added, and then diluted to volume in a 25-ml. volumetric flask. Then, 0.100 mmole of chloride, k_2, was added to the other 10-ml. aliquot and the above process was repeated. The two solutions were poured into opposite arms of the concentration cell and the potential, E, was measured and found to be 53.55 mv. The values of k_1, k_2, and E were substituted into Equation 2, and x was calculated to be 2.77×10^{-3} mmole per 25 ml. of solution.

The same measurement and calculation were performed for other pairs of the same titanium solution to which different amounts of chloride were added, and an average value of 2.75×10^{-3} mmole per 25 ml. of solution was determined for x.

This result compares favorably with that obtained by separately determining the chloride in the original titanium sample by the distillation method and the chloride in the acid solution by use of the concentration cell. The chloride in the same quantity of original titanium sample as used above was determined by the distillation method to be 2.23×10^{-3} mmole, and the chloride in an amount of acid, equivalent to that used above, to be 0.50×10^{-3} mmole, or a total of 2.73×10^{-3} mmole per 25 ml. of solution; which is nearly the same result obtained by the more rapid and single measurement method described above.

MEASUREMENT OF CHLORIDE CONCENTRATION IN TITANIUM SAMPLES

The dissolved, treated, and diluted titanium sample is placed in one arm of the concentration cell and the standard chloride solution in the opposite arm. The measured potential is converted to concentration with a suitable nomogram. A correction must be made for the quantity of chloride contained in the sulfuric-fluoboric acid solution used to dissolve the unknown sample. The chloride in the acid solutions used for this work was equivalent to 0.009% in the titanium sample. The chloride should be determined for each new lot of acid used for dissolving the unknown titanium samples.

Results. The method was tested for accuracy by preparing a sulfuric-fluoboric acid solution of a titanium sample for which the chloride concentration was accurately determined by the distillation method. Known quantities of chloride were then added to aliquots of this solution and, after proper oxidation and dilution, the solutions were measured in the concentration cell against the standard chloride solution. The results are given in Table IV.

The method was also tested by dissolving 5 grams of the WA samples in the sulfuric-fluoboric acid mixture; in general, the results agreed closely with those obtained by the distillation method. The precision and apparent accuracy of the method indicates that differences in the results of the WA samples by the distillation and direct methods are primarily the result of nonhomogeneity in the samples. The results for the WA samples by the direct method are given in Table V.

Table IV. Determination of Chloride by Direct Method in Titanium Samples Containing Known Added Quantities of Chloride

Chloride Added,[a] %	Chloride Found,[b] %
0.0071	0.0068
0.014	0.014
0.036	0.034
0.071	0.071
0.140	0.140
0.356	0.347
0.712	0.712

[a] Added as NaCl to titanium solution.
[b] % chloride found is equal to total chloride determined by voltage measurement minus chloride originally in titanium sample and in acid used to dissolve sample.

Table V. Determination of Chloride in Watertown Arsenal Titanium Samples by Direct Method

Sample	Nominal Concentration, % Chloride	Chloride Found,[a] %
WA-46	0.09	0.107
		0.107
		0.106
WA-47	0.18	0.183
		0.179
		0.179
WA-48	0.05	0.057
		0.058
		0.059
WA-64	0.19	0.199
		0.198
		0.199
WA-65	0.16	0.176
		0.171
		0.168

[a] % chloride found is equal to total chloride determined minus chloride present in acid used for dissolving sample.

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Indirect Determination of Free Titanium and of Oxygen in Titanium-Oxygen Alloys by Hydrogen Evolution Method

M. E. STRAUMANIS, C. H. CHENG, and A. W. SCHLECHTEN

Department of Metallurgy, University of Missouri School of Mines and Metallurgy, Rolla, Mo.

The amount of free titanium in titanium-oxygen alloys is calculated from the volume of hydrogen developed by the metal in hydrofluoric acid, if the sample is free from other hydrogen-developing metals. The oxygen is calculated on the basis of the lower volume of hydrogen developed in hydrofluoric acid because of the presence of oxygen in the alloys. Results on 11 samples agreed within 1% with results obtained by the method of Rahm (for total titanium present). Alloys containing up to 33.4% by weight of oxygen are amenable to analysis. One determination can be performed in about 1 hour.

FREE metallic titanium in titanium-oxygen alloys cannot be determined by a conventional method—e.g., that of Rahm (*4*)—but its amount can be computed from the volume of hydrogen developed by such an alloy in hydrofluoric acid.

This volume of hydrogen can also be used for the indirect determination of oxygen present in the alloys.

Although there are a few methods for the determination of oxygen in titanium (*1, 3, 8*), they are most effective if the amounts of oxygen are small. The method described below permits the determination of oxygen content of alloys up to the composition of Ti_2O_3. The method is simple, rapid, inexpensive, and sufficiently precise; however, it is limited to pure titanium-oxygen alloys containing no other common metals, carbides, or nitrides.

PRINCIPLE AND PROCEDURE

Pure titanium in a mechanical mixture of other substances can be determined by treating the mixture with hydrofluoric acid and measuring the volume of hydrogen developed according to the equation (*5, 6*):

$$Ti + 3HF \rightarrow TiF_3 + 1.5\ H_2 \qquad (1)$$

However, if the titanium contains oxygen in solid solution, the hydrogen volume will be as follows (*7*):

$$TiO_x + 3HF \rightarrow TiF_3 + xH_2O + (1.5 - x)\ H_2 \qquad (2)$$

If $x = 0$, hydrogen evolution occurs as shown by Equation 1; if $x = 1$ [as in TiO), only 0.5 mole of hydrogen is evolved; and if $x = 1.5$ (Ti_2O_3) the evolution of hydrogen gas is zero, and the Ti_2O_3 simply dissolves in hydrofluoric acid. Thus, free titanium or its equivalent can be calculated from the hydrogen volume collected, assuming that 1 ml. of hydrogen at standard conditions is equal to 1.425 mg. of titanium (Equation 1).

The oxygen content can be computed from the same volume of hydrogen as follows: According to Equation 1, 1 gram of titanium develops 702 ml. of hydrogen; 1 gram of alloy containing A grams of oxygen will evolve less hydrogen because of the weight of oxygen—702 $(1 - A)$ ml. of hydrogen per gram of alloy—and the oxygen will bind 1401 A ml. of hydrogen (Equation 2), as xH_2O are produced. The final volume, V, in milliliters, will then be:

$$702\ (1 - A) - 1401\ A = V$$

or oxygen in per cent by weight

$$A\% = 33.4 - 0.0475\ V \qquad (3)$$

If V is 702 ml., then $A = 0$, and the titanium is pure. However, if $V = 0$, the oxygen content is at least 33.4% by weight (upper limit of oxygen determination by the method), corresponding to the composition of Ti_2O_3.

The apparatus for dissolving the samples and collecting the hydrogen is shown in Figure 1.

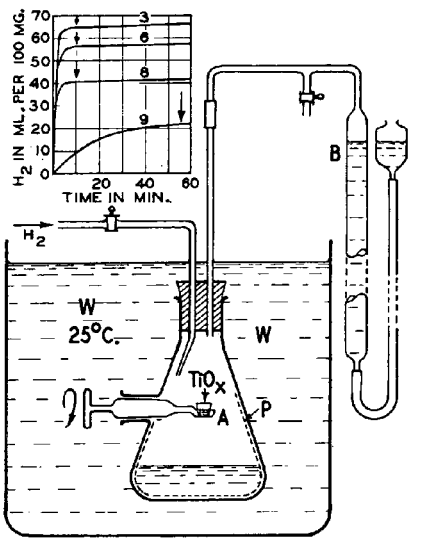

Figure 1. Apparatus for dissolving titanium-oxygen alloys in hydrofluoric acid and collecting hydrogen evolved

A. Spoon with TiO_x sample
B. Gas buret for hydrogen collection
P. Paraffin wax lining to prevent attack on glass
W. 25° ± 0.1° C. water thermostat
Inset. Hydrogen volume developed *vs.* time
Arrows indicate end of Reaction 2, numbers give alloys of composition listed in Table I.

Table I. Analysis of 11 TiO_x Samples by Hydrogen Evolution Method

[Concentration of HF ~ 3*N* (30 ml.) for alloys 1 to 8 and ~ 6*N* for 9 to 11]

Alloy No.	H_2 in Alloy, Ml./G.	Free Ti, Wt. %	Total Ti by Chem. Anal., Wt. %	O_2 by Eq. 3, Wt. %	Total Ti + O_2	Δ
1	697[a]	99.3	99.9[a]	0.2	100.1	+0.1
2	677	96.4	98.7	1.2	99.9	−0.1
3	666	94.8	98.3	1.7	100.0	±0.0
4	646	92.0	97.0	2.7	99.7	−0.3
5	619	88.1	96.7	4.0	100.7	+0.7
6	580	82.6	94.7	5.8	100.5	+0.5
7	542	77.2	92.7	7.7	100.4	+0.4
8	410	58.4	86.0	13.9	99.9	−0.1
9	225	32.3	76.4	22.7	99.1	−0.9
10	185	26.4	74.5	24.6	99.1	−0.9
11	5.6	0.8	66.1	33.1	99.2	−0.8

[a] Obtained by dissolving Ti produced by thermal decomposition of titanium iodide.

The sample in the form of a fine powder or filings (200 to 300 mg.) in a small platinum crucible (5 mm. in diameter), is placed on the polyethylene spoon, *A*, which is then introduced into a flask, and the whole is submerged in a water thermostat as shown in Figure 1. Pure hydrogen from a tank is flushed through the apparatus, in order to prevent the oxidation of titanium(III). The sample thrown into the acid by overturning spoon *A* dissolves, if it is fine enough and low in oxygen content, in ~3*N* acid in about 15 minutes; if it is high in oxygen, about 1 hour and 60 ml. of ~6*N* acid are required. After completion of Reaction 2, the end point of which is shown by arrows on the curves of Figure 1, hydrogen evolution continues at a very slow rate due to a secondary reaction (*7*):

$$TiF_3 + HF \rightarrow TiF_4 + 0.5H_2 \qquad (4)$$

which should not be taken into account.

RESULTS

Ten titanium-oxygen alloys were analyzed for free titanium and for their oxygen content (Equation 3), by the method described, and for their total titanium content by a method very similar to that of Rahm (*4*).

The alloys were prepared in a vacuum furnace by heating dry titanium powder (+65 mesh, 99.7% purity), supplied by the Belmont Smelting and Refining Works, Inc., with the calculated amount of titanium dioxide (99.9% pure) of the Fisher Scientific Co. (*2*).

The results summarized in Table I were obtained by the use of Equation 1 for free titanium and by Equation 3 for the oxygen content of the alloys.

The results agree within 1% with results obtained by the method of Rahm (*4*). Alloys 1 to 8, containing up to 13% by weight of oxygen, give better results than those with an oxygen content up to 33.4%. This is understandable, because with samples of higher oxygen content it is difficult to estimate the end of Reaction 2 (see inset of Figure 1). One oxygen determination can be finished in about 1 hour, if the necessary inexpensive equipment is available.

Limitations. Only pure titanium oxygen alloys which will completely dissolve in the acid are amenable to such analysis (Table I) with a precision within 1%; the maximum oxygen content that can be determined is just below 33.4% by weight; and oxygen cannot be accurately determined in mechanical mixtures of titanium and oxides higher than Ti_2O_3 by the method described (the errors will be larger than 1%), because Equation 3 is derived on the assumption that Ti_2O_3 is the highest oxide present. But free titanium can be determined in the mixtures.

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Determination of Titanium in Titanium Ores and Metal by Automatic Derivative Spectrophotometric Titration

HOWARD V. MALMSTADT and CHARLES B. ROBERTS

Chemistry Department, University of Illinois, Urbana, Ill.

To provide a relatively rapid and accurate method for determination of titanium in titanium ores, metal, and titanium dioxide, a procedure was developed utilizing the automatic derivative spectrophotometric end point detection system and electrolytic generation of the titrant at constant current. This provides a completely automatic titration method, which saves technician's time. After dissolution of the sample an aliquot of the solution is passed through a cadmium reductor and collected in a solution containing a known quantity of ferric iron. The titanium(III) reduces an equivalent amount of ferric iron and the excess ferric iron is automatically titrated with electrolytically generated titanous ion. The total elapsed time for the determination of titanium in rutile or ilmenite is about 40 minutes, including fluxing and dissolution of the sample. The precision and accuracy are within about 0.1%.

THE quantitative determination of titanium in ores and metal is an important analysis and several methods have been proposed. Papucci (*4*) reported good accuracy and a determination time of about 80 minutes using pertitanic acid in a differential colorimetric method. Thompson (*5*) reduced titanium(IV) to titanium(III) with a Jones reductor, after prereduction with zinc, and titrated with a standard solution of ferric iron.

A rapid and accurate titration procedure for the determination of iron in titanium materials (*2*) utilizes automatic derivative end point detection and electrolytic generation of the titrant at constant current (*1*, *2*). The basic titration procedure can be readily adapted for the quantitative determination of titanium.

The method consists of putting titanium material into solution by fluxing or acid dissolution, passing an aliquot of the solution through a cadmium reductor, and collecting the titanium(III) in a known quantity of ferric iron. The excess ferric iron is then automatically titrated using the derivative spectrophotometric titrator (*1*) and electrolytic generation of titanium(III) titrant. The method is precise, accurate, and relatively rapid. The total elapsed time for the determination of titanium in rutile or ilmenite is about 40 minutes, including fluxing and dissolution of the sample. Less than one half of the total elapsed time requires technician's time. The rest is used in the automatic titration and dissolving fluxed sample. Therefore, with a systematic arrangement it should be possible for one technician to run several ore samples simultaneously with little extra expenditure of time. The precision and accuracy are within about 0.1%.

Another aliquot of the sample can be run by the automatic titration procedure for the determination of iron (*2*) with a relative precision within about 0.1%.

Table I. Determination of Titanium in Pure Titanium Metal by Automatic Spectrophotometric Titration

Aliquot	Ti Taken, Mg.	Ti Found, Mg.	Error, Mg. Ti	Relative Error, %
1	81.52	81.42	−0.11	−0.13
2	81.52	81.58	+0.06	+0.07
3	81.52	81.54	+0.02	+0.02
4	81.52	81.44	−0.08	−0.10
5	81.52	81.47	−0.05	−0.06
6	81.52	81.33	−0.19	−0.23
Av.	81.52	81.46	0.08	0.10

Table II. Automatic Derivative Spectrophotometric Titration of 10-Ml. Aliquots of Commercial Titanium Sponge Each Containing 100.03 Mg. of Sample

Aliquot	Ti Found, Mg.	Titanium, %
1	99.36	99.33
2	99.35	99.32
3	99.33	99.30
4	99.15	99.12
Av.		99.27

Coefficient of variation = 0.10%

APPARATUS

Cadmium Reductor. Titanium(IV) is reduced to titanium(III) by means of a cadmium reductor. This is more efficient than an amalgamated zinc reductor, the evolution of hydrogen gas is less, and it reduces only a small amount of chromium when it is present. No blank correction is necessary. The flow rate through the reductor is sufficiently fast without the use of vacuum. The reductor column has a diameter of 1.9 cm. and is 27 cm. long. A glass wool plug is placed in the bottom of the column, which is then filled to a height of 24 cm. with cadmium shavings, made by turning a solid cadmium bar on a lathe and collecting the turnings. They should be made as small as possible, and any large pieces should be cut up with a shears. The cadmium turnings are attacked by sulfuric acid during the reduction process, and a small amount of turnings should be added about once a week to maintain the proper height in the column. When not in use, the reductor should be filled with distilled water.

Instrumentation. The spectrophotometric circuit and electrolysis apparatus are used in exactly the way described for the determination of iron(*2*).

REAGENTS

Standard ferric solution. For each determination approximately 1 gram of titanium(IV) must be in the 150 ml. of solution to give a current efficiency of 100%. As the amount of titanium in the sample aliquot is considerably less than this, the standard ferric solution is made up to contain this amount of titanium for each 50 ml. of ferric solution.

A stock solution of ferric chloride is made by accurately weighing approximately 25 grams of Mallinckrodt reagent grade iron wire and dissolving in a solution of 167 ml. of concentrated hydrochloric acid and 300 ml. of water; after the iron is dissolved, the solution is diluted to 1 liter with distilled water. This quantity serves for 200 to 400 titanium determinations, depending upon the amount of titanium in the samples being analyzed.

A titanium(IV) solution is prepared by dissolving 10 grams of Cramet high-purity titanium sponge in 250 ml. of water and 75 ml. of concentrated sulfuric acid, using a 500-ml. Erlenmeyer flask for dissolution. This is heated below the boiling point for 3 to 4 hours until the sponge is completely dissolved; the solution is cooled, and most of the titanous ion is oxidized by the addition, with stirring, of 6 grams of potassium permanganate. The oxidation is then completed by adding from a pipet a saturated solution of potassium permanganate until a slight excess is indicated by the pink permanganate color. The excess permanganate is destroyed by adding approximately 0.5 gram of sodium azide, and the solution is boiled for 7 minutes to destroy excess azide. After cooling, the solution is poured into a 500-ml. volumetric flask and the required amount of ferric chloride solution is added. Two strengths of iron solution were used in this work. One contained 1.25 grams of iron per 500 ml. of solution, and the other 0.62 gram of iron per 500 ml. of solution. The former is prepared by adding 50 ml. of the stock solution of ferric chloride to the titanium(IV) solution in the 500-ml. volumetric flask and diluting to volume; the latter is prepared in the same way, but 25 ml. of the stock ferric chloride solution are used.

For routine titanium determinations it is best to prepare a very large quantity of titanium–ferric chloride solution.

The ferric chloride solution (containing 20 mg. of titanium per ml.) is then standardized by titrating a 50-ml. portion. It is pipetted into the spectrophotometer cell, 16 to 17 ml. of concentrated sulfuric acid are added, and the solution is diluted with distilled water to a volume of about 150 ml.

The solution is boiled for 5 minutes, cooled to about 78°, and titrated like any iron sample by the automatic derivative spectrophotometric method (*1*, *2*). In this way the number of milligrams of ferric iron in 50 ml. of standard solution is determined and is used for all subsequent determinations of titanium.

All other reagents used in the analysis are the same as those used for the determination of iron (*1*, *2*).

PROCEDURE FOR DETERMINATION OF TITANIUM IN TITANIUM METAL

Size and Dissolution of Sample. A 1-gram sample of titanium sponge was added to a solution containing 25 ml. of water, 7.5 ml. of concentrated sulfuric acid, and 10 ml. of 48% fluoboric acid, and heated gently until dissolution was complete. This required about 15 minutes, after which the solution was cooled and made up to 100 ml. in a volumetric flask.

Pretitration Treatment. A 10-ml. aliquot was pipetted into the cadmium reductor and the stopcock was opened until the solution passed below the top level of the cadmium. The sulfuric acid which drained through the reductor was returned to the top of the reductor to prevent any loss of titanium and to prevent air from coming in contact with the cadmium.

The titanium aliquot was allowed to remain in contact with the cadmium for 2 to 3 minutes while 50 ml. of the standard ferric iron solution were pipetted into the titration cell. The reductor was then lowered until its tip dipped into the iron solution contained in the 180-ml. titration cell, the stopcock was completely opened, and the solution was stirred as titanous ion entered. The column was washed with 2*M* sulfuric acid and the stopcock was closed when the titration cell contained about 150 ml. of solution. Six to 7 ml. of concentrated sulfuric acid were added to the solution in the titration cell to bring to proper acid strength. The titration cell was removed after the tip of the reductor and glass stirring rod were washed from a wash bottle.

The solution was boiled for 5 minutes and cooled to about 78° C., and the excess ferric iron was determined by the automatic derivative spectrophotometric method.

Calculations. The per cent of titanium in the sample was calculated as follows:

$$\%\text{Ti} = \frac{\left\{\text{eq. Fe} - \frac{i(\text{amperes}) \times t(\text{seconds})}{96{,}494}\right\} \times 47.90 \times 100}{\text{Weight of sample (grams)}}$$

where eq. Fe = equivalents of iron in 50 ml. of standard ferric chloride solution.

EXPERIMENTAL RESULTS FOR THE DETERMINATION OF TITANIUM IN TITANIUM METAL

Table I shows the percentage of titanium found in 99.95% pure titanium (prepared by the iodide process), each determination being an aliquot of a 10-gram sample.

The same procedure was used for commercial titanium sponge with results as shown in Table II. Each determination is an aliquot of a 10-gram sample.

PROCEDURE FOR DETERMINATION OF TITANIUM IN TITANIUM DIOXIDE

The material used for this determination was National Bureau of Standards sample 154, which has a titanium dioxide assay of 98.7%. The dissolution was made in a manner similar to that recommended by the National Bureau of Standards (*6*).

Size and Dissolution of Sample. A 1-gram sample was placed in a 250-ml. Erlenmeyer flask with 10 grams of ammonium sulfate and 25 ml. of concentrated sulfuric acid. A short-stemmed glass funnel was placed in the neck of the flask and the contents were heated without boiling until all of the sample was dissolved. The solution was poured into 50 ml. of water with stirring, cooled, and made up to 100 ml. with 1*M* sulfuric acid.

Pretitration Treatment and Titration. The same procedure was used as for the determination of titanium in titanium metal.

EXPERIMENTAL RESULTS FOR DETERMINATION OF TITANIUM IN TITANIUM DIOXIDE

The results of this analysis are shown in Table III. Two different samples were used with determinations of aliquots from each.

Table III. Determination of Titanium Dioxide in National Bureau of Standards Sample 154 (98.7% TiO_2) by Automatic Derivative Spectrophotometric Titration

Sample No.	Aliquot No.	TiO_2 Found, %	Deviation, %
1	1	98.62	0.04
1	2	98.69	0.03
2	1	98.63	0.03
2	2	98.66	0.00
2	3	98.70	0.04
	Av.	98.66	0.03

Table IV. Determination of Titanium Dioxide in a Rutile Sample

Aliquot	TiO_2, %
1	88.21
2	88.46
3	88.47
4	88.46

Average TiO_2 in rutile = 88.40%
Coefficient of variation = 0.13%

PROCEDURE FOR DETERMINATION OF TITANIUM IN RUTILE AND ILMENITE

Rutile and ilmenite are not readily dissolved by the ammonium sulfate–sulfuric acid procedure as used for titanium dioxide. A fluxing procedure must be used, and in order to test its accuracy a sample of National Bureau of Standards sample 154 titanium dioxide was fluxed in a way similar to that used for the ores.

A 1-gram sample was placed in the bottom of a large platinum dish and covered with a mixture of 30 grams of potassium acid sulfate and 2 grams of $Na_2B_4O_7 \cdot 10H_2O$. The mixture was heated over a Meker burner until the titanium dioxide had completely fluxed. It was cooled, 75 ml. of 1*M* sulfuric acid were added, and the contents of the dish were stirred, while being heated gently, until all solid material had dissolved. This required 10 to 15 minutes. The solution was then poured into a dry 100-ml. volumetric flask, the platinum dish was rinsed with 1*M* sulfuric acid, and the solution was made up to volume by adding 1*M* sulfuric acid. Several aliquots gave about the same precision and accuracy as the results from the ammonium sulfate–sulfuric acid procedure shown in Table III. The procedure was then applied to rutile.

Size and Dissolution of Sample. The rutile was ground in a mortar to the fineness of flour. A 1-gram sample was accurately weighed and placed in the bottom of a large platinum dish, to which a mixture of 30 grams of potassium acid sulfate and 2 grams of $Na_2B_4O_7 \cdot 10H_2O$ were added. The dish was placed in an electric oven at approximately 1000° C. and fluxed for 4 minutes. The fluxed material was cooled, 150 ml. of 1*M* sulfuric acid were added, and the mixture was stirred while being heated gently until all solid material was dissolved. This required about 15 minutes.

Pretitration Treatment. The solution was cooled and made up to 200 ml. in a volumetric flask with 1*M* sulfuric acid.

A 20-ml. aliquot was placed in the cadmium reductor and the same procedure was followed as for the determination of titanium in titanium metal.

EXPERIMENTAL RESULTS FOR TITANIUM IN RUTILE AND ILMENITE

The results for several aliquots of a rutile sample are shown in Table IV.

The same procedure was applied to a sample of ilmenite to give a titanium dioxide content of 64.50%. Too few determinations were made to test its precision, but it appeared to be comparable to that of rutile.

PROCEDURE FOR DETERMINATION OF IRON IN RUTILE AND ILMENITE

The same solution of either rutile or ilmenite which was used to determine titanium may be used to determine the amount of iron in the ore. High-purity titanium was dissolved by the same method as previously described for the standard iron solution, and an iron blank was made by the automatic derivative spectrophotometric method to determine the weight of iron in 50 ml. of solution.

A 50-ml. aliquot of the rutile solution, or a 25-ml. aliquot of the ilmenite solution, was added to 50 ml. of the high-purity titanium solution, proper acidity being obtained by the addition of concentrated sulfuric acid; and the determination for total iron was made as previously described. The iron blank was subtracted from this to give the amount of iron in the aliquot of ore solution nd consequently in the sample. The rutile sample by this nethod contained 5.73% iron and the ilmenite sample 21.38% iron with a relative precision within about 0.1%. By this method both titanium and iron content for the ores can be determined from the same solution and with the same titration technique, within a total time of 1 hour or less.

DISCUSSION

When titanium sponge is dissolved in either sulfuric acid or a fluoboric–sulfuric acid mixture, approximately 95% of the titanium is in solution as titanium(III). The remaining 5% is titanium(IV), which is reduced when the solution is passed through the cadmium reductor. In order to test the efficiency of a single pass through the reductor, a sponge solution was completely oxidized to titanium(IV) before passing through the reductor. The results for per cent titanium were the same as those obtained when only 5% of the titanium was in the +4 oxidation state.

The higher acid strengths of the pipetted aliquots cause considerable error unless the pipets are calibrated for the solution which is being used, and because the solutions have a higher viscosity than water, drainage time should be at least 1 minute. By determining the density of a representative solution and weighing the amount delivered by each pipet, the volume delivered can be accurately determined. This value can then be used for all solutions of corresponding acid strength.

While the automatic spectrophotometric method is very convenient, because it requires no operator time after the titration has started, the end point may also be observed visually by noting the complete disappearance of methylene blue color, at which time the relays stopping electrolysis and the clock are manually terminated. This is of particular use with the ores, as titanium content is usually fairly closely known before the determination; thus the amount of ferric iron can be regulated so that the excess will be small and consequently the electrolysis time will be of the order of a minute or two. For laboratories which do not have a spectrophotometer and associated equipment, this could provide a simple method for determining titanium in ores. For samples containing large amounts of iron it has the disadvantage of requiring considerable operator time for the titration; automatic spectrophotometric detection makes this time available for the preparation of other samples.

INTERFERENCES

Elements commonly found in titanium ores and metal such as iron, magnesium, manganese, and chromium (less than 1%) do not interfere with the procedure. If titanium alloys are to be analyzed for titanium, elements such as molybdenum, tin, copper, or vanadium must be removed if they are present in significant quantities. Separation may be effected by using the mercury cathode (*5*) or by precipitating the sulfides of these metals (*3*).

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Flame Spectrophotometric Determination of Copper in Ferrous Alloys

JOHN A. DEAN and J. HAROLD LADY[1]

Department of Chemistry, University of Tennessee, Knoxville, Tenn.

Organic solvent extraction can be applied to the flame spectrophotometric determination of copper in ferrous alloys. Copper, in the form of the salicylaldoxime complex, is selectively extracted from the aqueous solution of the sample with either chloroform or *n*-amyl acetate. Citrate was employed to buffer the solution at pH 3 and mask the iron, thereby preventing its coextraction. The organic extract is aspirated directly into an oxyacetylene flame. This procedure circumvents interferences encountered when aspirating the bulk sample containing varying amounts of diverse elements and increases the spectral emission of the copper 324.7-mμ line tenfold as compared with an aqueous solution of copper. No interferences were found when the method was applied to a wide variety of ferrous alloys. Accurate measurements can be made on as little as 0.5 γ of copper per ml.

THE application of organic solvent extraction to flame spectrophotometry offers a number of advantages (*2*). Compared with an aqueous solution, the spectral emission of the element present in the organic extract is generally enhanced severalfold. A selective extraction avoids the introduction of high concentrations of diverse ions into the flame, thus eliminating errors that might arise due to their presence. Also minimized are variations of the physical properties of the aspirated solution, such as viscosity, droplet size, and volatility. The introduction of solutions containing high salt concentration into a flame produces considerable amounts of incandescence, apparently as a result of minute solid particle formation. Solvent extraction also affords a means for concentrating the test element. The authors have previously applied solvent extraction to the flame spectrophotometric determination of iron (*3*).

Copper exhibits two rather sensitive emission lines in the ultraviolet portion of the spectrum at 324.7 and 327.4 mμ. In addition, copper possesses a series of weak emission bands in the visible region (*11*). Lundegårdh (*9*) observed that the radiant power of copper was strongly dependent upon operating conditions, and that both lines were prone to suffer strong self-absorption.

Dean (*1*) has reported an extensive flame spectrophotometric study of copper and has developed methods for copper applicable to nonferrous alloys. However, interferences from unknown sources prevented the extension of the method to ferrous alloys. Prior to this, several investigators had employed the two emission lines mentioned to determine copper in biological materials (*7*) and other substances (*4*). Dean (*1*) found that the utility of the 324.7-mμ line was hindered by self-absorption, and, while not as serious in the case of the 327.4-mμ line, the latter line is about one half the radiant power of the former. It seemed desirable to develop a method for copper applicable to ferrous alloys and with sufficient sensitivity to facilitate the analysis of micro amounts of copper.

Feigl's general discussion on the behavior of *o*-hydroxyaldoximes (*5*) suggested the utilization of this class of reagents in an extraction process. Flagg and Furman (*6*) developed a gravimetric method for copper using salicylaldoxime. As the work reported here was being completed, Simonsen and Burnett (*10*) reported the spectrophotometric determination of copper as the salicylaldoxime following extraction with *n*-amyl acetate.

The copper complex of salicylaldoxime is soluble in chloroform, *n*-amyl acetate, and several other solvents, but most of these latter were undesirable for flame work because of the unsteady flames that resulted. Altogether, 12 solvents were studied (*8*). Most of this investigation was carried out using chloroform. Copper salicylaldoxime is more readily extracted by chloroform; on the other hand, *n*-amyl acetate solutions provide a greater enhancement of the spectral emission.

EXPERIMENTAL WORK

Apparatus. A Beckman Model DU spectrophotometer with Model 9220 flame attachment and photomultiplier unit was used. An integral atomizer-burner, supplied with the flame attachment, was used as the excitation source. Oxygen and acetylene were the gases used.

The wave length knob on the spectrophotometer was replaced by a 4 to 1 gear reduction knob to facilitate positioning of the wave length dial. The copper lines are sharp, arc emission lines. One must move slowly back and forth over the peak of each line to ascertain the maximum reading. It is inadvisable to set the instrument on the apparent peak found on one particular solution and make a series of readings.

The sensitivity knob on the spectrophotometer was replaced with a 10-turn dial to permit the sensitivity settings to be reproduced.

Gas flow meters were placed in the gas lines. They were calibrated using a wet test meter to measure the gas flow after it had passed through the burner. The calibration was done by placing a hose over the nozzle of the burner and connecting this to the wet test meter. The other burner openings were sealed off. The importance of controlling gas flows rather than gas pressures has been discussed (*2*, *8*).

Reagents. A standard solution of copper (1.00 ml. equivalent to 1.00 mg. of copper) was prepared by dissolving 3.942 grams of reagent grade copper sulfate pentahydrate in 1 liter of demineralized water. Less concentrated standards, having 1.00 ml. equivalent to 20, 40, 50, and 60 γ of copper, were prepared by appropriate dilution.

Solutions of salicylaldoxime in chloroform and *n*-amyl acetate, 1% (w./v.), were prepared by dissolving 10 grams of salicylaldoxime in the solvent and diluting to 1 liter.

A standard chloroform or *n*-amyl acetate solution of copper as copper salicylaldoxime, with 1.00 ml. equivalent to 25 γ of copper, was prepared by extracting 50 ml. of the standard aqueous solution of copper containing 50 γ per ml. at pH 3 with four 20-ml. portions of the chloroform or *n*-amyl acetate solution containing salicylaldoxime. The combined extracts were diluted to a final volume of 100 ml. with additional solvent previously saturated with water. Less concentrated standard solutions, 1.00 ml. equivalent to 1.0, 2.0, 3.0, 4.0, 5.0, and 6.0 γ of copper, were prepared by further dilution with the appropriate solution of salicylaldoxime, previously equilibrated with water.

An ammonium citrate solution, 1.77*M*, was prepared by dissolving 40 grams of reagent grade ammonium citrate in demineralized water and diluting to 100 ml.

Flame Spectrophotometer Settings. The instrument settings used to measure the copper emission were as follows:

Sensitivity control, turns from clockwise limit	4
Selector switch, position	0.1
Phototube resistor, megohms	22
Phototube, volts per dynode	60
Slit, mm.	0.030
Acetylene pressure, lb./sq. inch	5
Oxygen pressure, lb./sq. inch	10
Acetylene rate of flow, cu. feet/hour	4.32
Oxygen rate of flow, cu. feet/hour	7.28

Calibration Curve. A calibration curve for copper as the salicylaldoxime complex in chloroform (Figure 1) is obtained by meas-

[1] Present address, Westinghouse Research Laboratories, East Pittsburgh, Pa.

uring the radiant power observed from the standard solutions prepared as described in the section on reagents. Because of self-absorption, the curve bends considerably towards the concentration axis with copper concentrations exceeding 3.0 γ per ml. However, if the curve is replotted as emission *vs.* the logarithm of the copper concentration, the range of minimum relative error begins at about 2.0 γ of copper per ml., and is fairly constant to 6.0 γ per ml.

For *n*-amyl acetate solutions the radiant power is slightly larger for a given amount of copper. Both solutions are far superior to ordinary aqueous solutions.

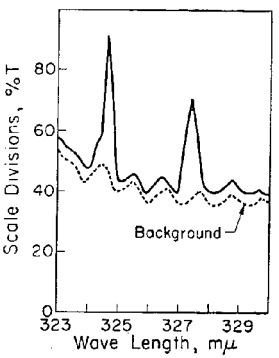

Figure 1. Flame emission spectrum for 5 γ of copper per ml.

Procedure. Weigh 0.5-gram samples into 250-ml. beakers. Dissolve in 30 ml. of 3*M* hydrochloric acid, adding small amounts of nitric acid, dropwise, to oxidize the iron. If carbon or tungsten is present, remove by filtration and wash the residue well with hot 1% hydrochloric acid. Dilute the sample to volume in a 100-ml. volumetric flask with demineralized water. Transfer aliquots containing 15 to 150 γ of copper into 50-ml. beakers. Add 1 ml. of 1.77*M* ammonium citrate solution for each 50 mg. of sample present in the aliquot.

Adjust the pH to 3.0 by the dropwise addition of 8*M* ammonium hydroxide. When the pH exceeds 2.5 the solution assumes a green color due to the formation of the iron citrate complex. Transfer the sample quantitatively to a separatory funnel. Extract with four successive 5-ml. portions of a 1% salicylaldoxime solution in chloroform or *n*-amyl acetate. Shake the sample at least 1 minute during each equilibration. Transfer the extracts to a 25-ml. volumetric flask and bring to volume with additional solvent. Aspirate the solutions and measure the radiant power of the flame background at 325.0 mμ and of the copper line at 324.7 mμ. Bracket the unknowns with standard solutions and determine the amount of copper present by interpolation.

Table I. Copper Analysis on Bureau of Standards Samples

Sample	Copper, % Certified Value	Copper, % Found
Cast iron, 5j	1.00	1.00 , 0.96
A.O.H. steel 35a	0.267	0.270, 0.268
Mo-W-Cr-V steel 132	0.149	0.153, 0.155
B.O.H. steel 152	0.127	0.126, 0.128
Cr-Ni(18-9) steel 101c	0.124	0.122, 0.124
A.O.H. steel 21d	0.107	0.096, 0.093
Cr-Ni steel 32d	0.096	0.099, 0.096
Cr-Ni-Mo steel 156	0.053	0.054, 0.053
Manganese steel 100a	0.050	0.051, 0.050 0.052, 0.052
Casting alloy 161 (64-Ni, 17-Cr, 15-Fe)	0.040	0.040, 0.037 0.036, 0.036
B.O.H. steel 14c	0.025	0.025, 0.025 0.024, 0.025
Lead-bearing steel 130	0.017	0.019, 0.019
Bessemer steel 22c	0.011	0.012, 0.012 0.009, 0.009

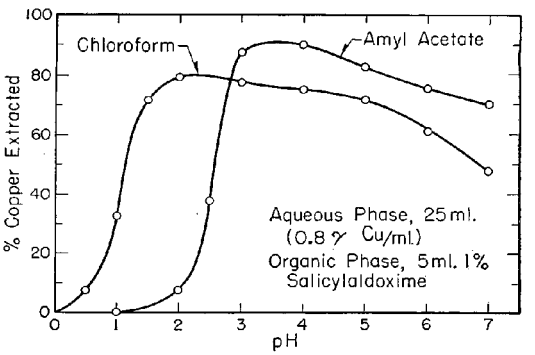

Figure 2. Extraction of copper as function of pH

RESULTS AND DISCUSSION

Table I summarizes the results obtained on National Bureau of Standards iron alloys. The results are in satisfactory agreement with the certificate values.

Flame Spectra of Copper. The emission spectra of copper salicylaldoxime from a chloroform solution and the flame background for chloroform alone are shown in Figure 2. Measurements were made only on the stronger copper line at 324.7 mμ, and the background was read at 325.0 mμ.

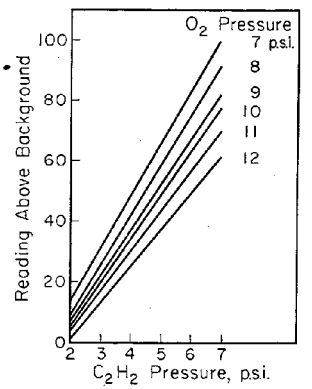

Figure 3. Emission of copper 324.7-mμ line as function of fuel and oxygen pressure

Nature of Copper Extraction. Copper was extracted from an aqueous solution with a 1% solution of salicylaldoxime in either chloroform or *n*-amyl acetate. Copper salicylaldoxime is insoluble in water; hence, the salicylaldoxime was dissolved in the organic phase rather than in the aqueous phase in order to prevent possible precipitation of the copper complex either in the aqueous phase or at the phase interface. By this procedure the copper

complex forms at the phase interface during the extraction step and passes directly into the organic phase.

The extraction of copper as a function of pH is shown in Figure 3. Copper is extracted at a lower pH with chloroform than with *n*-amyl acetate. Extraction with the latter solvent has been described by Simonsen and Burnett (*10*).

It was necessary to establish conditions for the extraction of copper from large quantities of iron without coextraction of the latter. Depending upon pH, ferric iron forms either an intense reddish-purple complex or a dark purple complex with salicylaldoxime. At pH 0.5 only a slight purple tinge is visible in the aqueous phase. As the pH is raised, the purple color increases in intensity, although remaining in the aqueous phase until pH 2 or greater, when the dark purple complex of iron salicylaldoxime passes almost entirely into the organic phase. Addition of citrate masked the formation of the iron complex. In the pH range from 2.5 to 3.0, iron forms a light green complex with citrate which exhibits no tendency to pass into the organic phase. On the other hand, copper is readily extracted at pH 3 in the presence of citrate. Four successive 1-minute equilibrations sufficed to remove copper completely. Iron could not be detected in the extract through its flame emission lines. The pH at which the copper complex is extracted is also a function of the salicylaldoxime concentration in the extracting solvent; therefore, the procedure should be followed exactly.

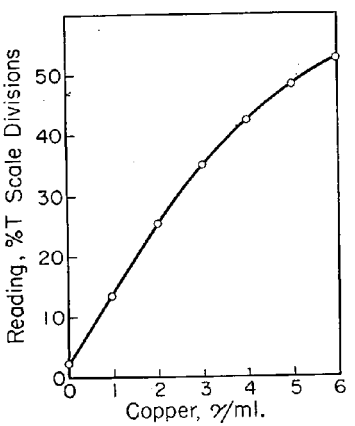

Figure 4. Standard calibration curve for copper in chloroform solutions

Fuel and Oxygen Pressures. The effect of varying fuel and oxygen pressures is shown in Figure 4. The emission of the copper 324.7-mμ line increases with decreasing oxygen pressure and increasing fuel pressure. Background varies similarly. Consequently, an intermediate value of fuel and oxygen pressures was chosen. One microgram of copper per milliliter gave an emission equivalent to 10 scale divisions (on the %T scale).

Some burners may exhibit a tendency to blowout when the organic solvent is removed. Reducing the oxygen pressure slightly will generally overcome this difficulty. Blowout is more frequent with chloroform solutions than with *n*-amyl acetate solutions.

Effect of Organic Solvents on Flame Emission. The heat of combustion of the organic solvent, compared with the cooling effect of water, is a significant factor in the consideration of the enhancement effect of organic solvents on the emission of metals in the flame. Also of importance is the aspiration rate of various solvents. The product of these two factors has been found to give hyperbolic curves when plotted against the observed emission (*2, 8*). Flame characteristics pertaining to the solvents employed in the study are summarized in Table II.

Table II. Flame Characteristics of Solvents

[Fuel and oxygen flow rates adjusted to maintain a stoichiometric flame (*8*). Copper concentration, 5 γ/ml.]

	n-Amyl Acetate	Chloroform	Water
Flame background, scale divisions	61.0	75.0	11.0
Height of inner cone, cm.	2.0	1.5	0.5
Flame width,[a] cm.	1.0	0.7	0.5
Flame height, cm.	9.5	4.5	6.0
Aspiration rate, ml./min.	1.09	1.18	0.77
Net emission above background	45.0	43.8	4.7

[a] At 2.0 cm. above the burner tip.

CONCLUSIONS

The extraction method is rapid and convenient for isolating copper from the bulk sample and interfering constituents. In addition, the use of an organic solvent gave as much as a tenfold increase in the radiant power compared with aqueous solutions. Consequently, accurate measurements can be made at copper concentrations as low as 0.5 γ per ml. The extraction also permits concentrating the copper in the organic phase if prior sample manipulations result in an excessively large volume of solution. When used in conjunction with flame spectrophotometry, the extraction method possesses a distinct advantage over colorimetric methods in that excess complexing agents and any other colored substances in the solution have no effect on the determination.

ACKNOWLEDGMENT

J. H. Lady is indebted to the Tennessee Eastman Co. for a fellowship under which this work was carried out.

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Flame Spectrophotometric Determination of Gallium in Copper-Gallium Alloys

VILLIERS W. MELOCHE and BENNY L. BECK

Department of Chemistry, University of Wisconsin, Madison 6, Wis.

The determination of gallium in copper-gallium alloys in two concentration ranges is described. Because copper enhances the emission at the 417.2-mμ gallium line, copper was added to the standard gallium solutions. One series of experiments allowed the determination of gallium in the range from 0 to 1% gallium to within 0.01%, with an average absolute deviation of 0.003%; the other series allowed determination in the range from 0 to 10% gallium to within 0.1% with an average absolute deviation of 0.1%. The effects of iron, aluminum, thallium, indium, and zinc upon the emission of gallium solutions at this wave length were also studied.

IN THE study of copper-gallium alloys, it was necessary to have a convenient and rather versatile method for the determination of gallium. The usual gravimetric method, in which the hydroxide is ignited to the oxide and weighed, did not satisfy these conditions. Indium has been determined by flame spectrophotometry (*4*); therefore, the application of this method to the determination of gallium was examined.

The spectrum of gallium has two usable lines: one at 417.2 mμ and the other at 403.3 mμ. The response at both wave lengths was examined. Although 417.2 mμ is a reversal line, it was used in preference to the 403.3-mμ line because of its greater intensity. The working curves and results presented below show that this is justifiable.

Although the alloys contained only copper and gallium, the effects of other elements likely to be present with gallium were also examined (*3*).

APPARATUS AND MATERIALS

The instrument used was a modified Beckman Model DU flame spectrophotometer with a Model 4300 photomultiplier attachment and a Model 4020 hydrogen burner. Modifications included a fine adjustment for the dark current control, a "bucking" circuit to balance the potential developed by the flame background, and an added 66-megohm load resistor. This load resistor was used only with gallium solutions in the 0- to 10-p.p.m. range.

A stock solution was prepared for each of the following elements: gallium, indium, thallium, iron, aluminum, zinc, and copper. The concentration of each of the solutions was 1000 p.p.m. with the exception of the copper, which was 4000 p.p.m. Solutions of gallium, indium, iron, and zinc were prepared by dissolving 1.000 gram of each metal in a minimum amount of hydrochloric acid and diluting to 1 liter with distilled water. For the copper solution, 4.000 grams of copper were dissolved in a minimum amount of nitric acid and diluted to 1 liter. Solutions of aluminum and thallium were prepared by dissolving 8.952 grams of aluminum(III) chloride hexahydrate and 1.303 grams of thallium(I) nitrate in distilled water and diluting each solution to 1 liter. All chemicals used were either of reagent grade or shown to be satisfactory through spectrographic analysis. Gallium was obtained from Fisher Scientific Co., Pittsburgh, Pa.

PROCEDURE

The radiation for a given concentration of gallium was about twice as intense at 417.2 mμ as it was at 403.3 mμ. Because fewer elements seemed to interfere at the former wave length (*1*), it was used throughout this study.

General. The instrument was allowed a warm-up period of about 1 hour, and the oxyhydrogen burner was allowed to burn for 10 minutes before any samples were run. The oxygen pressure, the hydrogen pressure and flow, and the wave length dial were adjusted to give maximum sensitivity for gallium at 417.2 mμ. Working curves were prepared in the three concentration ranges of 0 to 10 p.p.m., 0 to 100 p.p.m., and 0 to 1000 p.p.m. of gallium, using slit widths of 0.1, 0.04, and 0.01 mm., respectively. In preparing the working curves, the slit width was fixed at the values noted, and the sensitivity was adjusted so that each concentration range represented about 100 units on the transmission scale. Before any readings were taken, the bucking circuit was adjusted so that 0.0 p.p.m. of gallium represented about 3 units on the transmission scale. With this arrangement, it was always possible to check for drift in the instrument. The selector switch was in the 0.1 position at all times.

The curve for 0 to 1000 p.p.m. of gallium exhibited the most deviation from linearity, and is shown in Figure 1. The curve for the concentration range from 0 to 100 p.p.m. was more linear, and the curve for 0 to 10 p.p.m. was linear. In any case, the results for a given range were reproducible within experimental error.

Alloy Analysis. A 0.1-gram sample is convenient for analysis. The sample is dissolved in a minimum amount of nitric acid, and diluted to 100 ml. or 1 liter as noted below, depending upon the amount of gallium in the alloy.

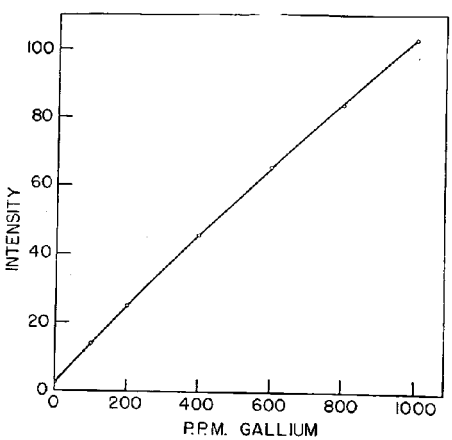

Figure 1. Relative intensity *vs.* concentration of gallium at 417.2 mμ

0 TO 1% RANGE. If a 0.1-gram sample is dissolved and diluted to 100 ml., the total concentration is 1000 p.p.m. of alloy. If 1% gallium is present, then the solution contains 10 p.p.m. of gallium. By using the 0 to 10 p.p.m. range on the flame spectrophotometer, each intensity unit corresponds to 0.1 p.p.m. or 0.01% gallium in the alloy. In such a system, the copper concentration varies between 990 and 1000 p.p.m.; therefore, 995 p.p.m. of copper were added to the standard gallium solutions.

0 TO 10% RANGE. If a 0.1-gram sample is dissolved and diluted to 1 liter, the total concentration is 100 p.p.m. of alloy. If 10% gallium is present, the solution again contains 10 p.p.m. of gallium. Through the same reasoning as above, each intensity unit equals 0.1 p.p.m. or 0.1% gallium in the alloy. Because the copper concentration varies from 90 to 100 p.p.m., 95 p.p.m. of copper were added to all gallium standard solutions.

Table I. Apparent Gallium Due to Various Concentrations of Pure Copper Solutions at Various Slit Widths

(Wave length = 417.2 mμ)

Cu Concn., P.P.M.	Slit Width, Mm. 0.02	0.04	0.06	0.08	0.10	0.12	0.14
	Apparent Gallium, P.P.M.						
100	0.0	0.0	0.8	0.9	1.0	1.1	1.3
250	1.1	1.3	1.7	2.0	2.6	2.4	2.8
500	1.3	1.8	2.9	3.8	4.7	5.0	5.6
750	2.6	2.9	4.0	5.3	6.8	7.0	8.1
1000	2.9	3.5	5.2	7.0	9.2	9.5	11.2
2000	4.8	7.5	10.4	14.3	18.6	19.2	22.3
3000	8.8	11.2	15.3	21.4	27.6	29.1	33.4
4000	12.1	15.0	19.8	28.5	36.4	38.3	44.0

INTERFERENCE STUDIES

Copper. Since the copper concentration was relatively high in the copper-gallium alloys, it was decided to first examine the effect of copper on the gallium radiation at 417.2 mμ. For this work, the slit was set at 0.04 mm. and the gallium concentration of 0 to 100 p.p.m. was used.

Two series of solutions were prepared by proper dilution of the stock solutions. The first series contained five solutions of 10 p.p.m. of gallium with 10, 50, 100, 250, and 500 p.p.m., respectively, of copper. A second series was identical except that it contained 50 p.p.m. of gallium.

As the concentration of copper increased, the intensity of radiation increased, giving a high apparent concentration of gallium. The apparent concentration of gallium in parts per million was determined by transferring the intensity reading obtained to parts per million of gallium via the working curve prepared for the 0 to 100 p.p.m. range. In the presence of 500 p.p.m. of copper, the apparent gallium concentration was about 2 units higher than that actually present. Inspection of the copper spectrum available in this laboratory showed continuous radiation at 417.2 mμ, and further examination of data showed the copper interference to be additive. Therefore, a second set of experiments was performed.

Eight solutions were prepared containing 100, 250, 500, 750, 1000, 2000, 3000, and 4000 p.p.m. of copper, respectively. These were examined in the gallium range from 0 to 100 p.p.m. at various slit widths at 417.2 mμ. The summary in Table I shows clearly that the copper interference increases with increasing concentration and slit width. Thus, it would be desirable to work at small slit widths. The effects were also examined at 403.3 mμ, and found to be more pronounced.

Because gallium could be determined accurately in the 0 to 10 p.p.m. range, and because at low gallium concentration the absolute amount of copper present would be smaller, it was decided to use this range for the determination, and to add copper to the standard solutions.

Other Metals. In addition to the effect of copper on the gallium radiation at 417.2 mμ, the effects of iron, aluminum, zinc, indium, and thallium were also studied. The same two series of solutions were prepared for each metal as for the preliminary copper interference study—i.e., five solutions containing 10 p.p.m. of gallium and 10, 50, 100, 250, and 500 p.p.m., respectively, of each metal and a similar set of five solutions containing 50 p.p.m. of gallium.

Of the five metals studied, iron showed the most interference. This is not surprising, as there is much iron radiation in this portion of the spectrum. A linear relationship was noted above 50 p.p.m. of iron between the concentration of iron present and the apparent concentration of gallium. The apparent concentration of gallium had risen to 24 and 65 p.p.m. in the 10- and 50-p.p.m. gallium series, respectively, in the presence of 500 p.p.m. of iron. Thallium exhibited no effect. Zinc decreased the intensity slightly. Aluminum and indium increased the intensity, giving an apparent part per million gallium reading one to two units higher than that actually present in the gallium solution in the presence of 500 p.p.m. of these two elements.

Variation of the acid strength of hydrochloric and nitric acids up to 0.5*N* showed no effect. The acid strength of all solutions was less than this value.

RESULTS

Solutions were prepared and tested in the 0 to 1% and in the 0 to 10% gallium range. Working curves were first prepared with 2, 4, 6, 8, and 10 p.p.m. of gallium containing the concentrations of copper given above. All solutions contained 0.04% Sterox SE (Monsanto Chemical Co.) which Boycks (2) found eliminated drift of spectrophotometer readings due to formation of small air bubbles in the capillary. Readings had to be made only to the nearest unit on the transmission scale of the instrument to obtain the results (Table II), and these readings could be reproduced with no deviation.

Table II. Application of Method to Gallium-Copper Alloys

Solution	P.P.M. in Solution Cu	Ga	% in Alloy Cu	Ga	Obsd. Ga, %	Absolute Error
			0 to 1% Range			
A	999.5	0.5	99.95	0.05	0.05	0.00
B	998.8	1.2	99.88	0.12	0.12	0.00
C	997.3	2.7	99.73	0.27	0.28	+0.01
D	996.1	3.9	99.61	0.39	0.39	0.00
E	994.7	5.3	99.47	0.53	0.53	0.00
F	993.2	6.8	99.32	0.68	0.67	−0.01
G	992.0	8.0	99.20	0.80	0.81	+0.01
H	991.0	8.9	99.10	0.89	0.89	0.00
J	990.5	9.5	99.05	0.95	0.95	0.00
			0 to 10% Range			
K	99.6	0.4	99.6	0.4	0.5	+0.1
L	98.7	1.3	98.7	1.3	1.4	+0.1
M	97.4	2.6	97.4	2.6	2.7	+0.1
N	96.0	4.0	96.0	4.0	4.0	0.0
P	94.6	5.4	94.6	5.4	5.4	0.0
Q	93.1	6.9	93.1	6.9	6.8	−0.1
R	91.9	8.1	91.9	8.1	8.0	−0.1
S	91.0	9.0	91.0	9.0	8.9	−0.1
T	90.3	9.7	90.3	9.7	9.6	−0.1

In the 0 to 1% range, the addition of 995 p.p.m. of copper to the standard gallium solutions gave excellent results with a maximum absolute error of only 0.01%. The trend of slight error observed in the 0 to 10% range can easily be explained. In solutions of low gallium concentration, the copper concentration was above the 95 p.p.m. in the standard solutions, giving a positive error, while in the high gallium concentrations, the copper concentration was below 95 p.p.m., giving a negative error. This effect was not noted in the 0 to 1% range because the percentage copper variation was smaller. Nevertheless, a maximum absolute error of only 0.1% was obtained.

ACKNOWLEDGMENT

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Photometric Titration of Cerium(III)

THOMAS L. MARPLE, E. P. PRZYBYLOWICZ, and DAVID N. HUME

Department of Chemistry and Laboratory for Nuclear Science, Massachusetts Institute of Technology, Cambridge 39, Mass.

A rapid and accurate method for the direct photometric titration of submilligram to decigram amounts of cerium(III), even in the presence of large amounts of cerium(IV), has been developed. The method is based on the oxidation of the cerium to the quadrivalent state with permanganate in a neutral pyrophosphate medium. Reducing agents such as mercury(II), vanadium(IV), arsenic(III), antimony(III), thallium(I), and iodide interfere, as do substances such as chromium(III) and fluoride, which form precipitates.

SMALL amounts of cerium(III), particularly in the presence of large amounts of cerium(IV), are not easily determined. Tomiček (*7*) showed potentiometric titration of macro quantities with ferricyanide solution to be feasible, and others (*6, 8*) have suggested oxidation in alkaline media. The solutions are highly susceptible to air oxidation, however, and the alkaline conditions result in precipitation of many metals. Goffart (*2*) has shown that the method of Lingane and Karplus (*4*) for the determination of manganese can be applied with slight modification to the titration of cerium. In it, the cerium is oxidized to the quadrivalent state in neutral sodium pyrophosphate medium by titration with standard permanganate. The visual end point is obscured by the color of the manganese(III) pyrophosphate complex which is produced and the potentiometric end point is unsatisfactory because of sluggishness in the vicinity of the equivalence point. Goffart suggested amperometric end point detection but the present authors have found considerable advantage to photometric detection of the end point, using the absorption of the excess permanganate at 525 mμ. The effects of potentially interfering substances, including large amounts of quadrivalent cerium, have been studied and optimum conditions for good precision and accuracy determined.

APPARATUS AND MATERIALS

Titrations were performed with the aid of a Beckman Model B spectrophotometer modified for photometric titrations as described by Goddu and Hume (*1*). A 150-ml. beaker and 5.000-ml. buret were used.

Chemicals were of reagent grade unless indicated to the contrary, and a good grade of distilled water was used throughout.

Stock tetrapotassium pyrophosphate reagent was prepared daily by dissolving 86 grams of the C.P. salt in 750 ml. of water and filtering through a Milipore (Lovell Chemical Co., Watertown, Mass.) filter. Unfiltered solutions contained sufficient suspended matter to give erratic absorbance readings when stirred in the titration cell. Approximately 0.02*M* potassium permanganate was prepared and stabilized by the usual procedure of boiling and filtering. Repeated standardizations against sodium oxalate showed no detectable change over a period of a month. The 0.02*M* solution, which is 0.1*N* against oxalate in acid medium, is 0.08*N* against cerium in the neutral pyrophosphate. For titration of very small amounts of cerium, the stock permanganate was diluted and the dilutions used within a few hours.

Cerous sulfate octahydrate was prepared from ceric sulfate by reduction with hydrogen peroxide in acid solution and boiling down to crystallization. Recrystallization once from 1*M* sulfuric acid yielded a satisfactory product. A stock cerium(III) solution was prepared in 1*M* sulfuric acid and standardized by oxidation with persulfate and silver catalyst, reduction with a measured excess of ferrous ammonium sulfate, and titration of the excess with standard ceric sulfate to a ferrous-phenanthroline visual end point. Dilutions of the standardized cerium(III) solutions were prepared for studies at several levels of cerium concentration.

PROCEDURE

To the titration beaker is added 75 ml. of the stock solution of tetrapotassium pyrophosphate. Unless the sample contains sufficient acid to bring the solution to between pH 5.5 and 7.0, sulfuric acid (1*M*) is added, approximately 10 ml. being required for neutral samples. The solution to be analyzed (1 to 10 ml.) is then added, the pH checked with universal indicator paper and adjusted with sulfuric acid or potassium hydroxide as necessary, and the cerium(III) titrated photometrically with standard permanganate solution at 525 mμ.

EFFECTS OF VARIABLES

The pyrophosphate medium serves three main functions: to keep the cerium and manganese, together with other metals which may be present, in solution as soluble pyrophosphate complexes; to diminish the oxidizing power of the cerous-ceric couple to the point where oxidation with permanganate is quantitative; and to stabilize the reduced manganese at a definite oxidation number. A fairly high concentration of pyrophosphate is desirable and it was found more practical to use the readily soluble tetrapotassium salt in place of saturated solutions of the sodium salt as previously suggested. The pH of the titration solution was found to be important but not extremely critical, as long as it fell within the range of 5.5 to 7.0. At higher pH values there is danger of basic salts precipitating out, and in more acid solutions, the stoichiometry of the reaction is altered, owing to incomplete stabilization of the reduced manganese at the trivalent state. Although it is clear that a manganese(III) pyrophosphate complex is formed, the formula in neutral media such as these has never been determined. The reaction, under titration conditions, is rapid and equilibrium is established immediately. No effect due to temperature was observed. From Goffart's data, one can estimate the formal oxidation potential of the ce-

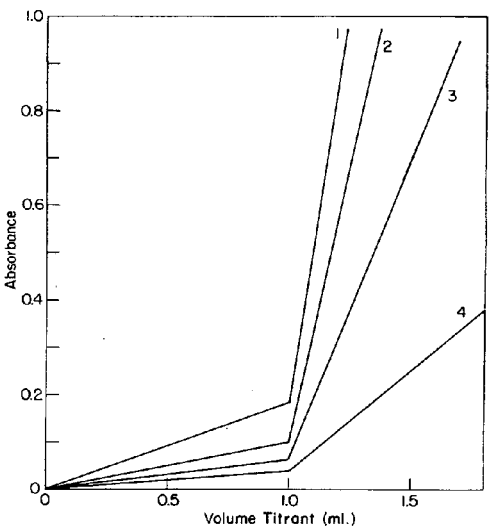

Figure 1. Titration curves of cerium(III) under conditions of procedure

Curves normalized to give end points of 1.000 ml. for ease of comparison

1. 0.0345*M*
2. 0.0172*M*
3. 0.00689*M*
4. 0.00345*M*

rous-ceric couple in pH 6.5 pyrophosphate medium to be about −0.65 volt *vs.* the standard hydrogen electrode and using Latimer's (*3*) sign convention.

The range of titrant concentration used in this study represents the most convenient working range for the path length given by a small beaker. At higher permanganate concentrations, the slope of the line of volume of titrant *vs.* absorbance is very steep (Figure 1); hence a smaller microburet must be used to add smaller volumes of titrant in order to plot this portion of the curve. The lower limit of titrant concentration is determined by the angle of intersection of the two straight lines determining the equivalence point (Figure 2). When this angle becomes very obtuse, the accuracy with which the equivalence point can be determined gets poorer. From these considerations it is evident that the permanganate concentration should be in the range of 0.04 to 0.002*M* for this titration.

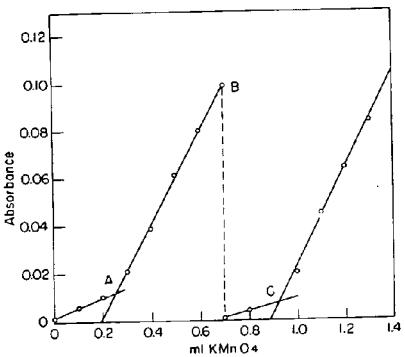

Figure 2. Titration of 0.675 mg. of cerium (III) added to 0.2344-gram sample of ceric ammonium nitrate after pretitration of oxidizable impurities to preliminary end point

A. Blank end point
B. Samples added
C. Final end point

It is apparent from the titration plot (Figure 1) that in addition to permanganate, another species is absorbing at 525 mμ. This is evidenced by the finite slope of the line prior to the equivalence point. The initial increase in absorbance was attributed to the formation of the pale violet pyrophosphate complex of manganese(III). This was verified by titrating a solution of manganese(II) under identical conditions wherein the initial slope increased fivefold.

EFFECT OF OTHER IONS

The effect of the presence of a number of potentially interfering substances was surveyed and the results are summarized in Table I. Various amounts of the substances under examination were added to samples containing known amounts (usually 12 to 16 mg.) of cerium(III) and the error in the titration was determined. As would be expected, strong reducing agents such as mercury(I), arsenic(III), antimony(III), thallium(I), vanadium(IV), and iodide vitiated the results by being preferentially or simultaneously oxidized by the permanganate. Surprisingly enough, the presence of neither tin(II) nor iron(II) constituted a serious difficulty. The rate of reaction of stannous ions with permanganate was found to be sufficiently slow to allow an excess permanganate end point to be measured if the points after the cerium equivalence point were taken quickly. Tin(II) does not react with cerium(IV) in neutral pyrophosphate. Prascodymium and neodymium do not react with permanganate under the conditions of the titration.

Table I. Effect of Various Substances on Cerium(III) Titration

Salt Added	Mg. Added	Ce(III), Mg. Taken	Found	Deviation
$Al(NO_3)_3 . 9H_2O$	200	11.84	11.87	+0.03
$Fe(NH_4)_2(SO_4)_2 . 6H_2O$	39	15.73	15.79	+0.06[a]
$FeNH_4(SO_4)_2 . 6H_2O$	200	11.84	11.92	+0.08
$Co(NO_3)_2 . 6H_2O$	156	15.73	15.75	+0.02
$Hg_2(NO_3) . H_2O$	210	15.73	Interferes	.. [b]
$MnSO_4 . H_2O$	17	15.73	15.93	+0.20[c]
$(NH_4)_6Mo_7O_{24} . 4H_2O$	200	11.84	11.84	+0.02
NH_4VO_3	200	11.84	11.86	+0.02
$VOSO_4 . 2H_2O$	200	11.84	Interferes	.. [b]
$Cr(NO_3)_3 . 9H_2O$	200	11.84	Interferes	.. [d]
$Na_2WO_4 . 2H_2O$	200	11.84	11.93	+0.09
$Th(NO_3)_4$	200	11.84	11.86	+0.02
As_2O_3	200	11.84	Interferes	.. [b]
Sb_2O_3	200	11.84	Interferes	.. [b]
KCl	200	11.84	11.91	+0.09
KBr	200	11.84	11.92	+0.08
KI	200	11.84	Interferes	.. [b,c]
KF	200	11.84	Interferes	.. [e]
$Ce(HSO_4)_4$	100	15.73	15.79	+0.06
	200	15.73	15.89	+0.16
	300	15.73	15.71	−0.02
	400	15.73	15.73	0.00
$Tl(C_2H_3O_2)$ $Ce(HSO_4)_4$	193 200	15.73	Interferes	.. [b]
$SnCl_2 . 2H_2O$ $Ce(HSO_4)_4$	285 200	15.73	15.79	+0.06
$Ni(NO_3)_2 . 6H_2O$ $Ce(HSO_4)_4$	750 200	15.73	15.78	+0.06
$CuCl_2 . 2H_2O$ $Ce(HSO_4)_4$	413 200	15.73	15.75	+0.02

[a] Without deliberate attempt to remove ferrous ion by aeration.
[b] Concurrent or prior oxidation of added constituent.
[c] Manganous ion oxidized before cerium but end point determinable. Error much larger if manganese–cerium ratio not unity. Determination not recommended in presence of manganese.
[d] Turbid mixture.
[e] Cerous fluoride precipitated.

Iron(II) was observed to react moderately rapidly and quantitatively with the oxygen of the air in neutral or alkaline pyrophosphate medium. When only a few milligrams of iron were present, usually no pretreatment was found necessary. Larger amounts required bubbling a stream of air through the sample prior to titration. Aeration in this manner was found to oxidize 25 mg. of ferrous ammonium sulfate in 5 minutes and 100 mg. in 15 minutes. The oxidation takes place readily regardless of whether the sample is first brought to pH 6.5 or allowed to remain at the initial alkaline pH of the pyrophosphate reagent. Fluoride interferes by forming insoluble cerium(III) fluoride. Chromium(III) was found to yield a turbid solution which could not be titrated accurately. Other substances which formed precipitates or suspensions in this medium likewise interfered.

The accurate potentiometric titration of the reduced form of a substance becomes increasingly difficult in the presence of larger and larger amounts of the oxidized form because of the nature of the titration curve. It was therefore of particular interest to establish whether traces of cerous-cerium could be determined in the presence of large amounts of ceric salts. The data in Table I showed no disturbance in the determination of 15-mg. amounts by the presence of as much as 400 mg. of ceric hydrogen sulfate. Experiments were then run in which 0.23- to 0.27-gram samples of reagent quality ceric ammonium nitrate (approximately the solubility limit) were titrated in neutral pyrophosphate medium to give a preliminary "blank" end point with 0.00716*N* permanganate. A known amount (3.000 ml.) of 0.225 mg. per ml. of cerium(III) solution was then added and the titration continued. Duplicate titrations gave values of 0.675 and 0.677, compared with the theoretical of 0.675 mg. of cerium, an average error of less than 2 parts per thousand with the ratio of cerium(IV) to

Table II. Precision and Accuracy of Cerium Determination

$KMnO_4$ M	Ce(III) Taken, Mg.	Ce(III) Found,[a] Mg.	Error, %	Standard Deviation Mg.	Standard Deviation %
0.03445	88.73	88.77	+0.045	0.21	0.24
0.01723	29.60	29.64	+0.13	0.13	0.44
0.00689	11.84	11.84	0.00	0.05	0.42
0.003445	5.921	5.926	+0.085	0.023	0.39

[a] Average of 10 determinations done in pairs on 5 different days.

cerium(III) about 100 to 1. The method can therefore be recommended for the determination of traces of cerium(III) in cerium(IV) salts soluble in neutral pyrophosphate.

PRECISION AND ACCURACY

In recognition of the fact that the agreement within a group of replicate samples all run at one time under identical conditions does not give a realistic estimate of the actual precision of an analytical method, an experiment was designed to determine the reproducibility of the method over a period of time and for different amounts of cerium. Samples of stock standard cerium(III) solutions at four levels of concentration were analyzed in duplicate each day for 5 successive days. The order of titration of the eight samples run on any given day was randomized to minimize bias from within-day trends. The levels of cerium concentration studied ranged from about 6 to 89 mg. per 85 ml. of solution, and for each level a permanganate solution about 25 times as concentrated as the cerium solution was used. The results, which are summarized in Table II, showed no significant differences in accuracy or precision between levels or between days. The over-all precision of the method under the conditions studied is best expressed by the coefficient of variation (standard deviation in per cent), which is 0.4%. Automatic performance of the titration using the apparatus of Marple and Hume (*5*) was found to be satisfactory.

ACKNOWLEDGMENT

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Differential Spectrophotometric Determination of Neodymium in Neodymium-Yttrium Mixtures

CHARLES V. BANKS, JOHN L. SPOONER, and JEROME W. O'LAUGHLIN

Institute for Atomic Research and Department of Chemistry, Iowa State College, Ames, Iowa

A differential spectrophotometric method for the determination of macro amounts of neodymium in neodymium-yttrium mixtures permits determination of neodymium in the presence of yttrium with errors in concentration of only 2 to 3 parts per thousand. A theoretical treatment is given of the corrections made necessary by differences in the lengths and absorbances of the cells.

BECAUSE the similar chemical properties of neodymium and yttrium make the analysis of mixtures of the two elements by classical methods extremely difficult, differences in physical properties are used whenever possible for the determination of these elements. Small amounts of neodymium have been determined in the presence of lanthanum, cerium, and praseodymium by spectrographic techniques (*2*). Larger amounts have been determined by spectrophotometric methods (*1, 5, 6, 8, 9*), which involve measuring the radiant energy absorbed by neodymium in dilute acid solutions at the wave length of one of its absorption bands. The absorption spectrum of neodymium has a series of very narrow bands in the visible region of the spectrum. Yttrium shows no absorption in this region of the spectrum and, therefore, does not interfere with the spectrophotometric determination of neodymium.

The extreme narrowness of the absorption bands of neodymium necessitates special techniques for making spectrophotometric measurements. Very small slit widths are necessary. Because of slight inaccuracies in setting the wave length dial, the region near the absorption peak must be scanned until the wave length is found at which maximum absorbance occurs. These difficulties, coupled with the low molar absorptivity of neodymium, make relative errors of about 1% in concentration about the lowest that can be expected by conventional spectrophotometric methods.

In connection with a careful determination of certain ion exchange constants, it became necessary to analyze a number of neodymium-yttrium oxide mixtures. A more accurate neodymium analysis was needed than could be obtained by the usual spectrophotometric methods.

Reilley and Crawford (*7*) recently reviewed the general principles of spectrophotometry and suggested two new methods. Their Method IV, which seemed theoretically capable of yielding the desired accuracies, involves setting the spectrophotometer to read 0 and 100 with two standard reference solutions of concentrations C_2 and C_1 in the light path. This method theoretically becomes more accurate as the difference between C_2 and C_1 becomes smaller. As the photometric error of a spectrophotometer is a minimum in reading an absorbance of 0.43, the best choice of concentrations for the reference solutions is such that the absorbance of $\frac{C_2 + C_1}{2}$ is approximately 0.43.

In the course of this work it was found necessary to make cell corrections. Several treatments of cell corrections in differential spectrophotometry appear in the literature (*3, 4*). These methods refer, however, to the technique in which a single reference solution is used to set the spectrophotometer at 100 and darkness is used to set the spectrophotometer at 0.

The present report is concerned with the application of Method IV of Reilley and Crawford (*7*) to the determination of neodymium in neodymium-yttrium mixtures. A method by which cell

corrections can be made when two reference standards are employed is presented.

APPARATUS

A Beckman Model DU spectrophotometer equipped with a photomultiplier attachment and a tungsten lamp was used. The lamp house was cooled and the cell compartment was thermostated at 25° C. The solutions were read in three matched, ground-glass-stoppered Corex cells 0.998 cm. long.

REAGENTS

Perchloric Acid, 10% Solution. A stock solution of 10% perchloric acid was prepared by diluting 715 ml. of reagent grade, 70 to 72% perchloric acid (Baker and Adamson) to 8 liters with distilled water.

Standard Neodymium Solutions. Neodymium oxide, Nd_2O_3 (Ames Laboratory stock, spectrographically free of other rare earths), was freed from small amounts of silica by evaporating to fumes of perchloric acid, diluting, and filtering. The neodymium was then precipitated with oxalic acid, filtered, and ignited to the oxide. It was stored in tightly capped bottles in a desiccator charged with anhydrous magnesium perchlorate. Samples of the oxide ranging from 0.7986 to 1.3559 grams were weighed into recalibrated 100-ml. volumetric flasks. Approximately 90 ml. of the stock 10% perchloric acid was added to each flask. Upon standing, the neodymium oxide dissolved, after which the contents of the flasks were diluted to volume with 10% perchloric acid. The molar concentrations of these standard solutions are shown in Table I.

Synthetic Neodymium-Yttrium Mixtures. These samples were prepared in exactly the same way as the standard neodymium solutions, except that various amounts of yttrium oxide, Y_2O_3 (Ames Laboratory stock, spectrographically free of other rare earths), were added at the same time as the neodymium oxide. The composition of these solutions is shown in Table II.

EXPERIMENTAL WORK

Spectrophotometric Measurement of Solutions. The cells were scrupulously cleaned by washing with a slurry of Dreft in water, thoroughly rinsed with water, and wiped dry with lint-free tissue. The optical faces were not touched or wiped during a series of readings. The two reference standards, C_1 and C_2, were placed in cells 1 and 2, respectively. The wave length was set at approximately 575 mμ and the slit width at 0.025 mm. The small slit width is made necessary by the narrowness of this absorption band of neodymium. The instrument was then balanced in the usual manner against solvent and darkness, and with one of the standards in the light path the wave length dial was carefully adjusted until the wave length of maximum absorbance was found.

The instrument was rebalanced at 100 and 0 with solutions of concentrations C_1 and C_2, respectively, in the light path, by repeated adjustments of the dark current and sensitivity controls on the Beckman Model DU spectrophotometer and the necessary adjustments on the photomultiplier attachment. Solution C_2 was then placed in cell 3 and the scale reading carefully determined. The same procedure was followed to obtain the scale reading for C_1 in cell 3. These readings are usually not 0 and 100, because of slight differences in the lengths and absorbances of the cells. If the instrument cannot be balanced with C_2 in cell 3, the position of the cells can be exchanged. This may happen, because the scale on the Beckman Model DU spectrophotometer covers only the range from 0 to 110. By rearranging the cells, however, it is always possible to obtain a scale reading for both C_1 and C_2 in one of the cells with the instrument balanced on C_1 and C_2 in the other two cells. Once this arrangement of the cells is found, it is used for all subsequent measurements.

The scale readings (R_M and R_N) were found for C_1 and C_2, respectively, when read in cell 3, after which the other standard solutions were read in cell 3. The instrument was rebalanced before every reading. R_M and R_N changed slowly with time. Because all cell corrections are based on these two measurements, they were redetermined frequently during a series of measurements. Table I shows how R_M and R_N changed during one series of measurements.

Cell Corrections. The fact that R_M and R_N are not constant, even during a series of measurements, makes the use of an empirical calibration curve unsatisfactory. The only reason that can be advanced for changes in R_M or R_N is a change in the absorbance of one or more cells. A change in cell length could hardly be postulated and the only two factors that are likely to affect R_M or R_N are differences in the lengths and absorbances of the cells, if any reflectance from cell walls is neglected or assumed to be constant.

It would be desirable to correct the observed scale reading for a sample to the value that would have been observed if there were no differences in the lengths or absorbances of the cells. If the correction could be expressed as a function of R_M and R_N, two measurements that could be made at the same time the sample was read, it would be of maximum usefulness. This would permit the construction of a standard calibration curve independent of changes in the absorbances of the cells which may occur while the measurements are made. One method of deriving a formula for making cell corrections is seen from the following considerations.

Reilley and Crawford (7) relate the observed scale reading in this method to the intensities of light I, I_1, and I_2 issuing from samples C, C_1, and C_2, respectively, by the relationship

$$I = \left[\frac{I_1 - I_2}{100}\right] R + I_2 \tag{1}$$

It is apparent that I is a linear function of R, if I_1 and I_2 are constant.

Reilley and Crawford (7) then assumed that

$$I = I_0 10^{-abc} \tag{2a}$$

$$I_1 = I_0 10^{-ab c_1} \tag{2b}$$

$$I_2 = I_0 10^{-ab c_2} \tag{2c}$$

This is justified only if all three solutions are read in the same cell or in three cells perfectly matched for length; in either case, it assumes the cells themselves absorb no light.

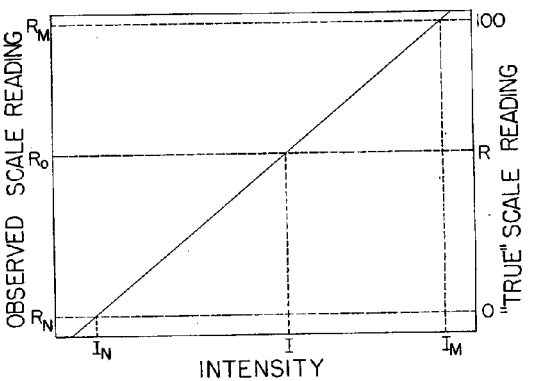

Figure 1. Relationships among I, R, and R_0

If reflectance from the cell walls is neglected, but it is assumed neither that the cells are of exactly the same length nor that they all have the same absorbance, it can be readily shown that

$$I = I_0 10^{-(abc + A)} \tag{3a}$$

$$I_1 = I_0 10^{-(ab_1c_1 + A_1)} \tag{3b}$$

$$I_2 = I_0 10^{-(ab_2c_2 + A_2)} \tag{3c}$$

where b, b_1, and b_2 are the lengths and A, A_1, and A_2 are the absorbances of the cells actually used.

If the relationships given by Equations 2a, 2b, and 2c are substituted in Equation 1, the following equation is obtained:

$$I_0 10^{-abc} = \left[\frac{I_0 10^{-abc_1} - I_0 10^{-abc_2}}{100}\right] R + I_0 10^{-abc_2} \quad (4)$$

When Equations 3a, 3b, and 3c, are substituted in Equation 1 we obtain:

$$I_0 10^{-(abc + A)} = \left[\frac{I_0 10^{-(ab_1c_1 + A_1)} - I_0 10^{-(ab_2c_2 + A_2)}}{100}\right] R_o + I_0 10^{-(ab_2c_2 + A_2)} \quad (5)$$

Figure 1 shows schematically the relationships among I, R, and R_o. I_M and I_N represent the light issuing from solutions C_1 and C_2, respectively, contained in cell 3 and corresponding to the observed scale readings, R_M and R_N. The expressions for I_M and I_N in terms of I_0 are seen to be

$$I_M = I_0 10^{-(abc_1 + A)} \quad (6)$$

and

$$I_N = I_0 10^{-(abc_2 + A)} \quad (7)$$

It is apparent from similar triangles in Figure 1 that

$$\frac{I - I_N}{I_M - I_N} = \frac{R - 0}{100 - 0} = \frac{R_o - R_N}{R_M - R_N} \quad (8)$$

which can be easily rearranged to give

$$R = 100\left[\frac{R_o - R_N}{R_M - R_N}\right] \quad (9)$$

Equation 9 can be used to calculate the "true" scale reading from the experimental quantities R_o, R_M, and R_N.

RESULTS

The results obtained when the series of standard neodymium solutions were read are given in Table I. R_M and R_N were remeasured after every three to five readings.

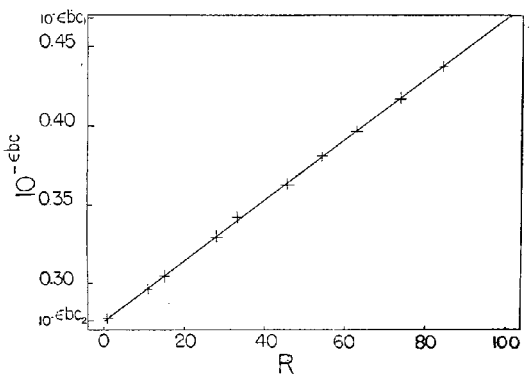

Figure 2. Plot of $10^{-\epsilon bc}$ as a function of R for standard neodymium solutions

Interpolated values of R_M or R_N were used in calculating R for samples read between measurements of R_M or R_N. Figure 2 is a plot of values of R for the series of neodymium samples as a function of $10^{-\epsilon bc}$. An average value of 6.95 ± 0.03 was used for the molar absorptivity, ϵ, of neodymium at its 575-mμ absorption band. This is an average value of nine independent determinations. The cell length was taken as 0.998 cm. The value for c, the molar concentration of neodymium, is taken from Table I.

Table I. Observed and Calculated Values of R

Solution	Nd Concn., M	R_o	R_M	R_N	R	$R_{calcd.}$
C_1	0.04750	...	..	..	100	100
1	0.05197	83.0	98.2	1.85	84.2	83.7
2	0.05478	72.85	98.2	1.85	73.6	73.2
3	0.05798	62.2	98.1	1.88	62.7	62.4
4	0.06037	54.0	98.1	1.85	54.2	54.7
5	0.06372	45.5	98.0	1.80	45.4	44.4
6	0.06719	33.6	97.4	1.70	33.5	34.4
7	0.06961	28.4	97.2	1.55	28.0	27.6
8	0.07447	16.2	97.0	1.55	15.1	14.9
9	0.07623	11.7	96.7	1.15	11.0	10.6
10	0.08018	1.8	96.5	0.90	0.9	1.1
C_2	0.08069	...	..	..	0	0

The mean deviation of the experimental points from the theoretical curve, a straight line defined by $R = 0$ at $10^{-\epsilon bc_2}$ and $R = 100$ at $10^{-\epsilon bc_1}$, in terms of R is ±0.48, which corresponds to a relative error in concentration of 0.26%.

The samples containing yttrium were read using two new reference solutions. This made construction of a new calibration curve necessary. As the calibration curve is a straight line for which $R = 0$ at $10^{-\epsilon bc_2}$ and $R = 100$ at $10^{-\epsilon bc_1}$, a new curve may be constructed immediately without reading additional standards. Table II shows the results obtained on known neodymium-yttrium mixtures, by using a calibration curve constructed in this manner.

It is apparent that yttrium does not interfere with the method and the use of a calculated calibration curve is justified.

RECOMMENDED PROCEDURE

Two reference standards are prepared as described, and a calibration curve is constructed. Samples of the neodymium-yttrium oxide mixtures are weighed into recalibrated flasks. The sizes of the samples are chosen such that the neodymium concentrations in the final solutions are between those of the two standards. If necessary, the approximate concentrations of neodymium are determined by conventional spectrophotometric methods. Approximately 90 ml. of the stock 10% perchloric acid is added to each flask and after dissolution is complete the contents of the flasks are diluted to volume with 10% perchloric acid.

The samples are then read on the spectrophotometer; the two standards are used to set the instrument at 0 and 100 as previously described. R_M and R_N are determined frequently, if a number of measurements are made. The scale reading, R_o, for the sample is corrected by use of Equation 9 and the concentration of neodymium is calculated from the calibration curve.

Table II. Determination of Neodymium in Known Neodymium-Yttrium Mixtures

Solution	Y_2O_3 Added, G.	Nd_2O_3 Added, G.	Nd_2O_3 Found, G.	% Error
11	0.5289	1.0113	1.0142	0.29
12	1.0455	1.0196	1.0203	0.07
13	1.9963	1.0030	1.0062	0.32

DISCUSSION

The proposed method permits the rapid and accurate determination of neodymium in neodymium-yttrium oxide mixtures. Difficult and time-consuming separations are avoided.

Errors associated with setting the wave length dial at the optimum position are minimized. Slight inaccuracies in setting the wave length dial affect the absorbances of the two reference solutions and the sample solution in a similar manner and the errors tend to cancel.

An error in setting the wave length dial, that would cause

approximately a 15% relative error in concentration by the usual spectrophotometric methods, would have comparatively little effect on the proposed method. It can be demonstrated that at observed R values of less than 10 or greater than 90, an apparent change of 15% in molar absorptivity would cause less than 0.2% relative error in concentration. The error would be greatest at R values around 50, but even in this region the relative error in concentration would be less than 0.5%.

The method can be used for very small samples. The sample solution can be prepared by weight and the only limiting factor would be the necessity of having a final volume great enough to fill a 1-cm. cell. If sample solutions are prepared by weight, it is necessary to determine the density of these sample solutions.

APPLICATIONS

The proposed method was used for the analysis of a large number of neodymium-yttrium oxide mixtures. The neodymium content of the samples varied from 10 to 80%.

Work on application of this method to other rare earth mixtures is being conducted. It should be generally applicable for the determination of larger amounts of many of the rare earths in rare earth mixtures, where a wave length can be chosen at which only the element being determined absorbs.

ACKNOWLEDGMENT

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Spectrophotometric Method for Simultaneous Determination of Nickel and Cobalt

R. D. WHEALY and S. O. COLGATE
West Texas State College, Canyon, Tex.

Aqueous solutions of nickelous and cobaltous nitrates react completely with excess diethylenetriamine to form solutions of colored complexes. Light absorption properties of these complexes permit the quantitative determination of both nickel and cobalt in the absence of interfering cations.

NICKEL nitrate reacts spontaneously with excess diethylenetriamine to form the violet complex $Ni[(C_2H_4NH_2)_2NH]_2(NO_3)_2$ (*1*). Aqueous solutions of this compound exhibit absorption maxima at 850 and 540 mμ (Figure 1). The absorption properties at each wave length closely follow Beer's law for initial nickelous ion concentrations of 0.01 to 0.06 gram-ion per liter. (Concentrations outside these limits were not studied.) The concentration of nickelous ions in solutions containing no interfering ions is readily obtained from absorption data at either of the two maximum wave lengths.

Solutions of cobaltous nitrate react with excess diethylenetriamine to form a yellow complex. The cobalt in this complex is apparently in the tripositive oxidation state. The cobaltous ion is easily oxidized by atmospheric oxygen. The reaction is hastened by bubbling air through the solution containing cobaltous ion and diethylenetriamine. The yellow complex has a single absorption maximum at 460 mμ (Figure 1). Behavior at this wave length is in good agreement with Beer's law for initial cobaltous ion concentrations of 0.001 to 0.006 gram-ion per liter. Thus, cobalt can be determined in solutions containing no interfering ions.

Figure 1 shows that nickel in solutions containing both nickel and cobalt ions can be determined by using the Beer's law graph for the nickel complex at 850 mμ. The total absorbance at 460 mμ (cobalt complex maximum) represents the combined absorbance of the nickel complex and the cobalt complex. If the concentration of the nickel complex at 850 mμ is known, the absorbance due to this species at 460 mμ can be calculated. This value is subtracted from the total absorbance at 460 mμ to obtain the absorbance at this wave length due to cobalt alone.

Fortunately, diethylenetriamine exhibits no appreciable absorbance at any of these absorption maxima. It can, therefore, be present in large excess to assure completeness of reaction.

MATERIALS AND APPARATUS

All absorption measurements were taken with a Beckman Model B spectrophotometer equipped with 1-cm. Corex cells.

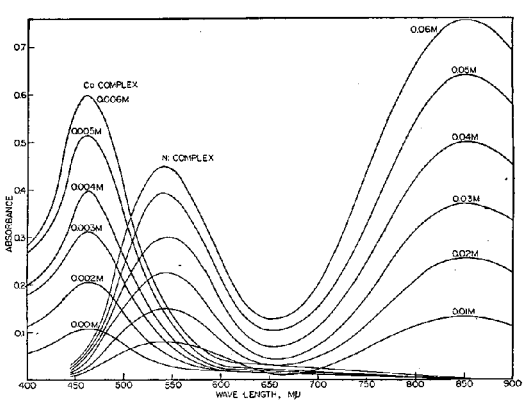

Figure 1. Absorption spectra of nickel nitrate and cobalt nitrate in presence of excess diethylenetriamine

The inorganic chemicals were Baker's analyzed reagent grade. The nickel nitrate contained 0.06% cobalt, and the cobalt nitrate contained 0.09% nickel. Solutions of these compounds were standardized gravimetrically.

The diethylenetriamine used was Eastman's technical grade.

PROCEDURE

Dissolve the sample, free from interfering impurities, in dilute nitric acid. Remove the excess acid by the dropwise addition of concentrated sodium hydroxide until a slight precipitate of combined hydroxides appears. Then add a drop or two of nitric acid, so that the resulting solution is again clear. Add approximately 2 ml. of diethylenetriamine for every 10 ml. of solution. Bubble air through the solution for 15 minutes to oxidize the cobalt. If there is a precipitate present, remove it by filtration. Wash the precipitate with small portions of water and dilute the filtrate to the smallest convenient volume. Check the absorbance of this solution at 460 and 850 mμ. If the concentration of either of the complexes is too high, dilute the solution volumetrically until the absorbance lies in the proper range.

Determine the concentration of nickel by reference to its standard graph at 850 mμ. Find the correction to be subtracted from the total absorbance at 460 mμ. Determine the concentration of cobalt by locating the corrected absorbance at 460 mμ on the standard graph for cobalt at this wave length.

RESULTS

Results of typical analyses by this method are given in Table I. The data illustrated in the first part are for solutions containing various concentrations of the metal ions. Deviations from the standard values, which were obtained by the volumetric dilution of gravimetrically standardized solutions, are not greater than ±5% for nickel or ±10% for cobalt.

The second part of Table I gives the results obtained when, after the addition of diethylenetriamine, the solutions were made 0.01*M* with respect to ferric iron. As is discussed below, the presence of this amount of iron has little affect on the accuracy of this method.

DISCUSSION

The compositions of the complex salts were determined in the following manner. With the concentration of nickelous nitrate held constant at 0.057*M*, the concentration of diethylenetriamine was varied from 0.01 to 0.2*M*. The stoichiometric point was reached when the concentration of diethylenetriamine was 0.115*M*, showing the violet complex to be empirically 2 parts of diethylenetriamine to 1 part of nickelous nitrate: $Ni[(C_2H_4NH_2)_2NH]_2(NO_3)_2$. Two distinct straight portions on the curve obtained indicated that nickel might easily be determined by spectrophotometric titration, in which the end point is located by intersection of the two straight portions of the curve.

With the concentration of cobaltous nitrate held constant at 0.005*M*, the end point occurred at a value of 0.005*M* for diethylenetriamine, indicating an empirical formula of $Co[(C_2H_4NH_2)_2NH](NO_3)_2$ for the yellow complex. Except for the necessity of oxidizing the cobaltous ion, it, too, could easily be determined by spectrophotometric titration. This cobalt complex has been previously prepared and discussed by Pure and Schwarzenbach (*2*).

Common cations which interfere with this method are copper, chromium, and manganese, which form, respectively, blue, purple, and yellow complexes with diethylenetriamine. Dilute solutions of these complexes absorb strongly in wave length regions of importance in this method.

Table I. Analysis of Nickel-Cobalt and Nickel-Cobalt-Iron Mixtures

	Concentration, Mole/Liter	
	Standard	Determined
Ni	0.0100	0.0095
Co	0.0010	0.0011
Ni	0.0100	0.0105
Co	0.0060	0.0061
Ni	0.0600	0.0595
Co	0.0010	0.0010
Ni	0.0300	0.0295
Co	0.0030	0.0031
Ni	0.0600	0.0600
Co	0.0060	0.0059
Solutions 0.01*M* in Ferric Iron		
Ni	0.0600	0.0595
Co	0.0010	0.0009
Ni	0.0300	0.0290
Co	0.0030	0.0029
Ni	0.0100	0.0095
Co	0.0060	0.0059

If iron is present in concentrations as high as 0.01*M*, it is precipitated in the basic medium as hydrous ferric oxide. The precipitate may be filtered off without greatly affecting the final results (Table I). Tin behaves similarly, forming a heavy white precipitate which may be removed by filtration. Aluminum, zinc, and lead, as well as large amounts of common anions, do not interfere.

The diethylenetriamine complexes of nickel and cobalt are stable in solutions whose temperatures range from 0° C. to their boiling points. The nickel complex is stable in solutions ranging in pH from 6 to 14. In stronger acid media the violet complex decomposes stepwise, first to the blue complex $Ni(C_2H_4NH_2)_2NH(NO_3)_2$, and then to nickelous ion. The cobalt complex is stable in solutions ranging in pH from 1 to 14.

Sodium peroxide reacts with the cobalt complex to produce a brown crystalline compound, whose composition has not yet been determined.

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Amperometric Titration of the Tetraphenylborate Ion

Method for Potassium

ARTHUR F. FINDEIS and THOMAS DE VRIES

Department of Chemistry, Purdue University, West Lafayette, Ind.

Potassium tetraphenylborate dissolved in acetonitrile-water mixtures can be titrated with an aqueous solution of silver nitrate with a high degree of precision. The method utilizes a dropping mercury electrode as an indicator with a mercury pool as a nonpolarized reference electrode at a potential of −0.1 volt *vs.* the pool. The procedure is suitable for between 1 and 20 mg. of potassium but could easily be extended to higher amounts. The precision and accuracy compare with other methods for potassium in this concentration range.

THE tetraphenylborate ion is unique in that it forms insoluble salts of potassium, rubidium, cesium, and ammonium ions in aqueous media (*9–11*). A large number of organic bases also form insoluble precipitates with this ion (*4*).

Previously a polarographic method using potassium tetraphenylborate in dimethylformamide had been developed for the determination of potassium (*2*). A titrimetric procedure for potassium was developed by Rüdorf and Zanier (*8*) based on the easy solubility of potassium tetraphenylborate in acetone-water mixtures and the insolubility of silver tetraphenylborate in both acetone and water. The equivalence point was detected by means of the adsorption indicator eosine. Recently Hahn (*5*) utilized potassium chromate as an indicator in a modified Mohr titration of the tetraphenylborate ion. Kemula and Kornacki (*6*) published an amperometric titration method for potassium, in which the excess of a standard solution of sodium tetraphenylborate was titrated in dilute acetic acid with thallous nitrate. A titration of potassium tetraphenylborate with perchloric acid in acetone and glacial acetic acid was utilized by Flaschka (*3*) for the determination of potassium, using crystal violet as the equivalence point indicator.

As potassium tetraphenylborate is soluble in a number of organic solvents, this work was initiated in order to study the feasibility of an argentimetric titration with an amperometric equivalence point. Dimethylformamide, methyl Carbitol [2-(2-methoxyethoxy)ethanol], and acetonitrile were utilized as solvents for the potassium tetraphenylborate. From the point of view of precision and accuracy, acetonitrile was found to be the better solvent for dissolution purposes. Because a large amount of water can be tolerated before potassium tetraphenylborate begins to precipitate from acetonitrile, the titrant silver nitrate was dissolved in water.

APPARATUS

A Sargent Model III manual polarograph was used to obtain the current-voltage curves as well as for the amperometric titrations. Corning marine barometer tubing which gave a drop time of 4.81 seconds, open circuit, was used for the dropping mercury electrode. All titrations were performed in a 100-ml. beaker with the dropping mercury electrode 7 mm. from the surface of the mercury pool. A calibrated microburet was used to measure the standard silver nitrate solutions. No degassing was necessary, as the titrations were performed at such a potential that dissolved oxygen did not interfere. No temperature control was necessary.

MATERIALS

Acetonitrile (Eastern Chemical Corp.), dimethylformamide (Du Pont), and methyl Carbitol, $CH_3OCH_2CH_2OCH_2CH_2OH$ (Carbide and Carbon Chemicals Co.), were used as obtained from stock. The standard silver nitrate solutions were prepared from weighed amount of reagent grade silver nitrate dissolved in water and diluted to the desired volume. Sodium tetraphenylborate (J. T. Baker Chemical Co.) was used without further purification. Potassium tetraphenylborate, after precipitation from a solution of potassium chloride acidified with dilute hydrochloric acid, was recrystallized twice from acetone, washed thoroughly with water, and dried at 110° C.

PROCEDURE

Weighed amounts of potassium tetraphenylborate were dissolved in 15 ml. of acetonitrile and enough water was added (5 to 8 ml.) so that the solution at the equivalence point contained 50 to 60% of acetonitrile by volume. Six milliliters of mercury was added to the 100-ml. beaker to serve as the nonpolarized anode and the titration was carried out at −0.10 volt *vs.* the mercury pool. During the addition of titrant the circuit to the galvanometer and cell was opened; otherwise the momentary excess of silver ion produced a galvanometer deflection of large magnitude. After the solution was stirred and allowed to stand for 15 to 30 seconds, the galvanometer was switched into the circuit and the diffusion current recorded. The equivalence point was determined by extrapolation of the current values to zero current. The same procedure was followed for the titrations performed with dimethylformamide or methyl Carbitol in the solvent system. The titrations in dimethylformamide were carried out at −0.20 volt: those in methyl Carbitol at −0.10 volt.

DISCUSSION

In order to obtain information about the potential to apply during the titration, current-voltage curves were obtained for potassium tetraphenylborate in acetonitrile-water mixtures

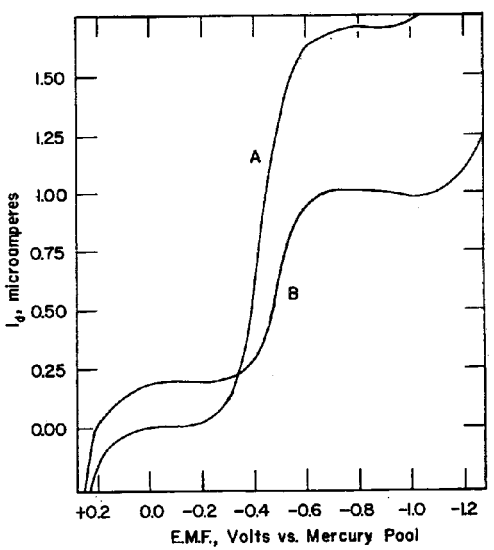

Figure 1. Polarograms for titration of tetraphenylborate ion with silver nitrate

A. Before titration
B. After addition of excess silver nitrate

both before the titration and after the addition of an excess of silver nitrate. Figure 1 shows the polarograms obtained for a 0.1853-gram (5.172×10^{-4} mole) sample of potassium tetraphenylborate dissolved in 15 ml. of acetonitrile and 5 ml. of water before addition of titrant (curve *A*) and after addition of 5.320 ml. of 0.1*M* silver nitrate, an excess of 0.148 ml. of titrant (curve *B*).

The increase of the diffusion current at −0.10 volt is due to the increase of the silver ion concentration. The wave at −0.8 volt for curve *A* is due to the reduction of oxygen, and the lowering of the wave height for curve *B* is probably due to the adsorption of the dissolved oxygen on the silver tetraphenylborate precipitate. This wave disappears when oxygen is removed from the solution. The shift in the half-wave potential can be explained by the fact that there is a change in potential at the mercury pool because tetraphenylborate ions have been replaced by nitrate ions.

From these polarograms it can be seen that the titration may be carried out at any potential between +0.1 and −0.2 volt *vs.* the mercury pool, at which the limiting current for the silver ion occurs, with no interference from the reduction of dissolved oxygen, which occurs at −0.5 volt. As a result, no degassing of the sample during the course of the titration was necessary. In this work the potential was set at −0.10 volt *vs.* the pool in order to be on the fully developed plateau of the silver ion.

Table I. Titrations of Potassium Tetraphenylborate Samples in Acetonitrile-Water Mixtures

K Taken, Mg.	$AgNO_3$ to Equivalence Point, Ml. Theoretical	Found	K Found, Mg.	Difference Mg.
	A. Titrations with 0.1*M* $AgNO_3$			
5.162	1.323	1.326	5.174	+0.012
5.205	1.334	1.329	5.185	−0.200
5.287	1.355	1.364	5.322	+0.033
5.443	1.395	1.398	5.454	+0.011
5.564	1.426	1.430	5.579	+0.015
5.650	1.448	1.448	5.650	0.000
12.58	3.223	3.240	12.64	+0.06
12.61	3.232	3.251	12.68	+0.07
12.85	3.293	3.278	12.79	−0.06
13.25	3.396	3.409	13.30	+0.05
13.50	3.461	3.475	13.56	+0.06
19.12	4.900	4.882	19.05	−0.07
19.41	4.974	4.954	19.33	−0.08
19.49	4.995	4.942	19.28	−0.21
19.74	5.059	5.001	19.51	−0.23
19.97	5.118	5.119	19.97	−0.00
20.18	5.172	5.138	20.05	−0.13
	B. Titrations with 0.03*M* $AgNO_3$			
1.170	1.000	0.988	1.168	−0.002
		1.000	1.170	0.000
		1.007	1.179	+0.009
		1.008	1.180	+0.010
		1.012	1.185	+0.015
2.341	2.000	2.001	2.342	+0.001
		2.001	2.342	+0.001
		2.004	2.345	+0.004
		2.010	2.353	+0.012
		2.012	2.355	+0.014

Titrations were also performed in dimethylformamide-water mixtures following the same type of procedure, but in both cases the precision and accuracy were not so good as titrations performed in the acetonitrile-water mixtures. In all titrations performed in these two solvent mixtures with water there was appreciable darkening of the precipitate due to the reduction of the silver ion to metallic silver, even when the titrations were performed in almost total darkness. It is assumed that either the titrant was reduced before the reaction of the silver ion with the tetraphenylborate ion or the precipitate was reduced after formation, liberating the tetraphenylborate ion which would react with more silver ion. The precipitate of silver tetraphenylborate formed with acetonitrile in the solvent system was white and flocculent and did not darken even after standing in daylight for 5 days in the presence of the mercury pool and an excess of silver nitrate. The reducing action of dimethylformamide-water mixtures has been reported (*7*) in regard to reduction of cupric ion to the cuprous state and so it is not unexpected that the solvent mixture would also reduce silver ion. Methyl Carbitol, no doubt, contains reducing impurities which cause the darkening of the precipitate.

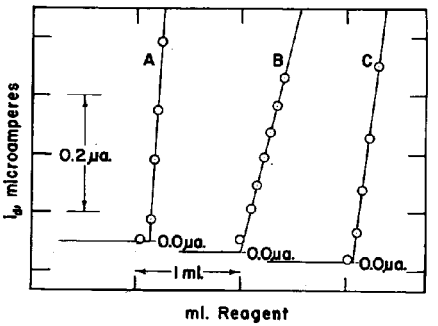

Figure 2. Titration of tetraphenylborate ion with silver nitrate

A. 0.1 *M* silver nitrate in acetonitrile-water
B. 0.03 *M* silver nitrate in acetonitrile-water
C. 0.1 *M* silver nitrate in dimethylformamide-water

Moreover, the literature (*1*) reports numerous cases of silver compounds forming stable complexes with nitriles, which may account for the inactivity of light toward the silver tetraphenyl borate precipitate in acetonitrile-water mixtures and also the lack of reaction of the silver ion with the mercury pool.

RESULTS

Data for titrations performed in acetonitrile-water mixtures are shown in Table I. The molarity of the solutions titrated was from $1 \times 10^{-3}M$ to $2 \times 10^{-2}M$. The results obtained in the laboratory indicated that the method would apply to higher concentrations. The greatest deviation observed was 1.3%; however, most of the samples titrated gave results within 0.6%. The concentration of the silver nitrate was varied from 0.03 to 0.1*M* with no significant d fference in the precision of the re-

Table II. Titrations of Potassium Tetraphenylborate in Dimethylformamide-Water Mixtures with 0.1*M* Silver Nitrate

K Taken, Mg.	$AgNO_3$ to Equivalence Point, Ml.	K Found, Mg.	Difference, Mg.
19.50	5.012	19.56	+0.06
19.52	5.090	19.86	+0.34
19.56	5.100	19.90	+0.34
19.57	5.044	19.68	+0.11
19.68	5.032	19.63	−0.05
20.84	5.370	20.95	+0.11
27.34	7.082	27.63	+0.29
27.44	6.972	27.20	−0.24
35.03	9.135	35.64	+0.61
35.06	8.845	34.51	−0.55
35.48	9.270	36.17	+0.69
35.53	9.118	35.57	+0.04

sults. The composition of the solvent may vary widely between 60 and 100% acetonitrile, so long as the potassium tetraphenylborate remains in solution. In previous methods which have been reported using nonaqueous solvents, the composition of the solvent had to be critically controlled (*8*) or be completely anhydrous (*3*).

Results for titrations in dimethylformamide-water mixtures at −0.20 volt are shown in Table II. These are not so precise as results obtained in acetonitrile-water mixtures. A large number of titrations were performed with 0.01*M* silver nitrate in dimethylformamide-water mixture, but the results were from 2 to 5% high. Methyl Carbitol in the solvent system yielded results for titrations with 0.1*M* silve nitrate from 1 to 3.5% high. These titrations were performed at −0.1 volt *vs.* the pool. Typical titration graphs are shown in Figure 2 for titrations in the acetonitrile-water and dimethylformamide-water system.

This method should also be applicable for the precise determination of equivalent weights of organic bases, in case they form tetraphenylborate precipitates soluble in acetonitrile.

ACKNOWLEDGMENT

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Theory of Countercurrent Distribution in Solvent Systems near a Critical Point

C. A. HOLLINGSWORTH and J. J. TABER
Department of Chemistry, University of Pittsburgh, Pittsburgh, Pa.

B. F. DAUBERT
Central Laboratories, General Foods Corp., Hoboken, N. J.

By the use of the theory of regular solutions, equations are obtained expressing the behavior of partition ratios near the critical temperatures of complete miscibility of two-component solvent systems and near the plait point of three-component, symmetric solvent systems. These results are used with a criterion of separation to predict the optimum conditions for separation by countercurrent distribution in these systems. The theory is then applied to experimentally determined partition ratios of some triglycerides to predict the amount of separation that can be obtained. The theory leads to the following conclusions: In systems to which the theory applies, the relative behavior of a pair of solutes can be characterized by a constant, γ, which is independent of the temperature or the third solvent component. Nearly optimum conditions for separation exist over a fairly wide range of temperature or solvent composition and far enough from the critical point so that extreme dependence on temperature or composition is not encountered.

WITH countercurrent distribution technique developed by Craig (*2*) using any given number of transfers, n, and any given ratio, r, of the two phases, the amount of separation obtained for two solutes depends upon the partition ratios (distribution coefficients) of the two solutes. It often happens that two solutes are difficult to separate because both the partition ratios (or their reciprocals) are very large, say, 50 or more. When possible in such cases automatic equipment is used, which makes hundreds, perhaps even thousands, of transfers practical (*3*). When such equipment is not available, the value of r may be adjusted, but large adjustments are usually not convenient. A withdrawal procedure may be used, but the possibilities here are limited. It may be possible to obtain the desired degree of separation by recycling, but when the equipment is not automatic this can be laborious and time-consuming. Sometimes the solvent system can be modified to improve the values of the partition ratios; there are various ways of doing this, and they depend upon the types of solutes and solvents that are involved.

Only one type of system is investigated here—one in which the solutes and solvents are nonelectrolytes and the solvent system possesses a critical temperature or a plait point within operating range. Both partition ratios (or both reciprocals) are lowered as the system moves toward a critical point. As the critical point is approached, both partition ratios approach unity, and separation is again poor. There is, therefore, an optimum condition for separation. In a two-component solvent system there is an optimum temperature, and in a three-component solvent system with a plait point there is an optimum composition (*6*), where optimum refers to that temperature, or composition, at which the degree of separation is a maximum for a given n and r. If the optimum conditions are not so close to the critical point that there is extreme dependence upon temperature or composition, it may be practical to carry out the distribution under these conditions.

It was the purpose of the work reported here to apply the theory of regular solutions to obtain theoretical expressions for these optimum conditions for separation and to apply them to experimentally determined partition ratios of some triglycerides in certain solvent systems.

PARTITION RATIOS NEAR A CRITICAL POINT

Two-Component Solvent Systems near Critical Temperature

Let x and y be the mole fractions of the two solvents, X and Y, and let w be the mole fraction of a solute, W. For a regular solution the Gibbs free energy of mixing is given by

$$G = axy + bxw + cyw + RT(x\ln x + y\ln y + w\ln w) \quad (1)$$

where a, b, and c are constants related to the interaction energy of the components. Meijering has shown (*8*) that when Equation 1 holds, and w is small, the distribution of W between two phases is given by

$$\frac{w_1}{w_2} = \left(\frac{x_1}{x_2}\right)^{(c-b)/a} \quad (2)$$

where x_1 and w_1 refer to the X-rich phase and x_2 and w_2 refer to the Y-rich phase. When w_1 and w_2 are small, x_1 and x_2 are the roots of the Van Laar equation

$$RT = a\frac{1-2x}{\ln\{(1-x)/x\}} \quad (3)$$

Since Equation 3 is symmetrical, its solutions can be expressed by

$$\left.\begin{aligned} x_1 &= \tfrac{1}{2}(1+\epsilon) \\ x_2 &= \tfrac{1}{2}(1-\epsilon) \end{aligned}\right\} \quad (4)$$

where $0 \leq \epsilon < 1$, and $\epsilon = 0$ at the critical temperature, $T_c = a/2R$. Equation 3 becomes by use of 4

$$RT = \frac{a\epsilon}{\ln\{(1+\epsilon)/(1-\epsilon)\}} \quad (5)$$

or

$$RT\ln\frac{x_1}{x_2} = a\epsilon \quad (6)$$

The logarithm in Equation 5 can be expanded as the power series

$$\ln\frac{1+\epsilon}{1-\epsilon} = 2\left(\epsilon + \frac{1}{3}\epsilon^3 + \frac{1}{5}\epsilon^5 + \dots\right) \quad (7)$$

which converges rapidly for all values of ϵ that are of interest here. The use of Equation 5 with Equation 7, neglecting powers of ϵ greater than the cube, leads to

$$\epsilon = \sqrt{3}\left(\frac{a}{2RT} - 1\right)^{1/2} \quad (8)$$

or

$$\epsilon = \sqrt{3}\left(\frac{T_c - T}{T}\right)^{1/2} \quad (9)$$

From Equations 2, 6, and 9 one obtains

$$\ln\zeta = k\theta^{1/2} \quad (10)$$

where

$$\zeta = \frac{w_1}{w_2} \quad (11)$$

$$k = \sqrt{3}(c-b)/RT_c^{3/2} \quad (12)$$

and

$$\theta = \left(\frac{T_c}{T}\right)^3(T_c - T) \quad (13)$$

For small values of θ/T_c, say, $\theta < 10$ when T_c is near room temperature, T_c/T can be taken as unity.

Partition ratios are usually defined by

$$K = \frac{c_1}{c_2} \quad (14)$$

where K is the partition ratio and c_1 and c_2 are the concentrations (grams per milliliter) of solute in the upper and lower layers, respectively. When w_1 and w_2 are small, and the compositions of the two phases are approximately equal, as they will be near the critical point, then

$$K \backsimeq \zeta \quad (15)$$

If there are two solutes, A and B, each satisfying Equation 10 for the same solvent system, then the following relationship exists between the partition ratios K_A and K_B:

$$K_B = K_A^{\gamma} \quad (16)$$

where

$$\gamma = k_B/k_A \quad (17)$$

and where k_A and k_B are the constants given by Equation 12 for the two solutes.

As the amount of separation of A and B that can be obtained by a given number of transfers in countercurrent distribution is a function of K_A and K_B, it follows from Equation 16 that the amount of separation that can be obtained at the optimum temperature is a function of γ alone. For regular solutions the minimum amount of information required to predict the separation as a function of the temperature, in the neighborhood of the critical temperature, is the value of the critical temperature and the values of the two partition ratios at one temperature not too far from the critical temperature.

In terms of the solubility parameters (*5*) of the solvents and the two solutes—i.e., δ_X, δ_Y, δ_A, and δ_B, respectively—the constant γ is given by

$$\gamma = \frac{(\delta_X - \delta_B)^2 - (\delta_Y - \delta_B)^2}{(\delta_X - \delta_A)^2 - (\delta_Y - \delta_A)^2} \quad (18)$$

or

$$\gamma = \frac{\delta_X + \delta_Y - 2\delta_B}{\delta_X + \delta_Y - 2\delta_A} \quad (19)$$

Thus from a knowledge of the solubility parameters one can, in principle, predict the amount of separation that can be obtained at the optimum temperature. However, in practice such a prediction is not very reliable unless the system satisfies closely the theory of regular solutions, and unless the solubility parameters are known accurately.

Three-Component, Symmetric Solvent Systems near Plait Point. The Gibbs free energy of mixing of a four-component regular solution is given by

$$G = axy + bxz + cyz + rxw + syw + tzw + RT(x\ln x + y\ln y + z\ln z + w\ln w) \quad (20)$$

where x, y, z, and w are the mole fractions of the components X, Y, Z, and W, and a, b, c, r, s, and t are constants. The chemical potential of solute w is given by

$$\mu_W = G + (1-w)\frac{\partial G}{\partial w} - \frac{x\partial G}{\partial x} - \frac{y\partial G}{\partial y} \quad (21)$$

which, with Equation 20, gives

$$\mu_W = rx + sy + tz - (axy + bxz + cyz + rxw + syw + tzw) + RT\ln w \quad (22)$$

When solute W is distributed between two phases, the condition for equilibrium gives for small values of w

$$RT\ln\frac{w_1}{w_2} + r(x_1 - x_2) + s(y_1 - y_2) + t(z_1 - z_2) = a(x_1y_1 - x_2y_2) + b(x_1z_1 - x_2z_2) + c(y_1z_1 - y_2z_2) \quad (23)$$

where x_1, y_1, etc., are the mole fractions in the first phase and x_2, y_2, etc., are the mole fractions in the second phase. The condition for equilibrium with respect to component Z gives, for the case $w \simeq 0$,

$$a(x_1y_1 - x_2y_2) + b(x_1z_1 - x_2z_2) + c(y_1z_1 - y_2z_2) = RT\ln(z_1/z_2) + b(x_1 - x_2) + c(y_1 - y_2) \quad (24)$$

From Equations 23 and 24 one obtains

$$RT\left(\ln\frac{w_1}{w_2} - \ln\frac{z_1}{z_2}\right) = (b - r)(x_1 - x_2) + (c - s)(y_1 - y_2) - t(x_1 - z_2) \quad (25)$$

Further treatment is greatly simplified by the assumption that $b = c$, and, therefore, the system is symmetric, so that

$$z_1 = z_2 = z;\ x_1 = y_2;\ x_2 = y_1 \quad (26)$$

In this case the tie lines are parallel to the $X - Y$ side of the triangular phase diagram, and this is a true first approximation for the type of system being considered here. For the symmetric system one has (*8*)

$$RT\ln\zeta = a(x_1 - x_2) \quad (27)$$

Use of Equations 25 and 26 gives

$$\zeta^p = x_1/x_2 \quad (28)$$

where

$$p = \frac{a}{s - r} \quad (29)$$

From Equations 26 and 28 and the approximations

$$\left.\begin{aligned} x_1 + y_1 + z &\cong 1 \\ x_2 + y_2 + z &\cong 1 \end{aligned}\right\} \quad (30)$$

one has after a little algebra

$$1 - z = \frac{RT}{a}\left(\frac{\zeta^p + 1}{\zeta^p - 1}\right)\ln\zeta^p \quad (31)$$

The plait point of a symmetric system is given by (*8*)

$$\left.\begin{aligned} z_c &= 1 - \frac{2RT}{a} \\ x_c &= y_c = \frac{RT}{a} \end{aligned}\right\} \quad (32)$$

where x_c, y_c, and z_c are the mole fractions at the plait point. Use of Equations 32 with 31 gives

$$z_c - z = \frac{RT}{a}\left(\frac{\zeta^p + 1}{\zeta^p - 1}\ln\zeta^p - 2\right) \quad (33)$$

If there are two solutes, W_A and W_B, in the same solvent system and w_A and w_B are both small, Equation 28 leads again to Equation 16, where in this case,

$$\gamma = p_A/p_B = \frac{s_B - r_B}{s_A - r_A} \quad (34)$$

and in terms of solubility parameters γ is again given by Equation 19.

It follows from these results that for a regular, symmetric, three-component system the minimum amount of information required to predict the separation as a function of the mole fraction z is the value of z_c and the values of the two partition ratios at two values of z not too far from z_c.

PREDICTION OF SEPARATION

Several criteria have been proposed for predicting the amount of separation that can be obtained by countercurrent distribution (*1, 2, 7, 9, 11*) when the partition ratios are known. Because of the assumptions involved, in most cases these criteria cannot be expected to give more than an approximate result. It happens that for the present purpose, although various criteria predict different amounts of separation, they, nevertheless, predict essentially the same optimum conditions for separation. For this reason only one criterion, a relatively simple one, is used here. This criterion is defined by

$$\tau = \left|\frac{K_B - K_A}{(K_B + 1)\sqrt{K_A} + (K_A + 1)\sqrt{K_B}}\right| \quad (35)$$

In terms of the symbols used by Nichols (*9*)

$$\tau = t_0/\sqrt{n} = 1/\sqrt{S} \quad (36)$$

and in terms of the "theta separation," θS, used by Weisiger (*11*)

$$\tau = \theta S/2\sqrt{n} \quad (37)$$

In Equation 36 t_0 is approximately the abscissa of the intersection of the two normal distribution curves when A and B are present in equal amounts; in Equation 37 θS is the distance between the peaks in units of the arithmetic mean of the two standard deviations. It can be shown, also, that τ has the following significance: When the distribution of mixture A and B is divided into two portions such that the percentage of A in one portion is equal to the percentage of B in the second portion, then $\sqrt{n}\,\tau\ (=t_0)$ is the abscissa corresponding to the point of division, and the percentage of the major component in either portion is $p(\sqrt{n}\tau)$, where

$$p(\sqrt{n}\tau) = 100\left[\frac{1}{2} + \phi(\sqrt{n}\tau)\right] \quad (38)$$

where $\phi(t)$ is the area between the peak of the normal curve and the abscissa, t.

Equation 35 has been given for the case in which $r = 1$—i.e., for the case in which the volumes of the upper and lower phases are equal. If $r \neq 1$, then K_A and K_B must be replaced by rK_A and rK_B in Equation 35. Only the case in which $r = 1$ is considered in detail here.

From $K_B = K_A^\gamma$ and with Equation 35 it is possible to calculate the values of K_A for which τ is a maximum for any given value of γ. These values of K_A are designated K_A^* and are shown as a function of γ in Figure 1 along with the corresponding maximum values, τ^* and $p^*(\sqrt{50}\,\tau)$. The values of K_A^* increase as γ decreases, and the limiting value of K_A^* as γ goes to unity is approximately 11.

PATHS TO THE CRITICAL POINT

For determining partition ratios as a function of a variable which is a measure of the distance from the critical point, several composition paths to the critical point can be used. The most convenient path for many purposes is that along which the

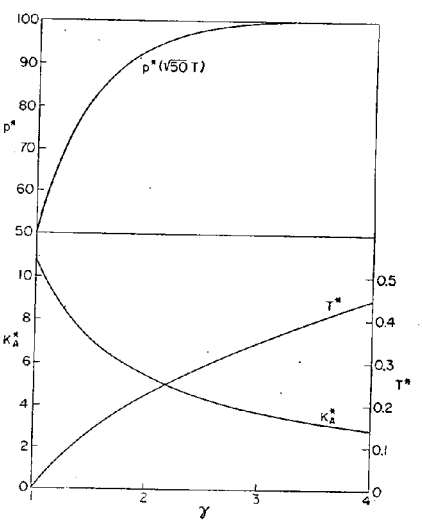

Figure 1. Optimum values as a function of γ

volumes of the two phases are kept equal to one another. To follow this path in the two-component solvent system, more of one of the two components will, in general, have to be added to keep the volume of the two phases equal to one another as the temperature is varied. Also, in the three-component solvent system more of one of the first two components must be added as the amount of the third component is varied. The use of the equal-volume path in the three-component solvent system has been discussed (*6*).

Equations 10, 16, and 33 are independent of the path to the critical point, but it may be more convenient to use volume per cent in place of mole fraction z in Equation 33 when the equal-volume path is used. The transformation equation is easily obtained as an approximation that holds near the plait point of a symmetric system. This equation is

$$\phi_c - \phi = \beta(z_c - z) \tag{39}$$

where ϕ is the volume per cent of Z in the total system, the total volume being taken as that before mixing, and where

$$\beta = \frac{V_z}{v_c}\left[1 - \frac{z_c}{2v_c}(2V_Z - V_X - V_Y)\right]$$

wherein V_X, V_Y, and V_Z are the molal volumes and where

$$v_c = z_c V_Z + x_c(V_X + V_Y)$$

x is the mole fraction of component X, and subscript c indicates the value at the plait point. Equation 33 becomes

$$\alpha = h\left(\frac{K_A p_A + 1}{K_A p_A - 1}\ln K_A p_A - 2\right) \tag{40}$$

where $\alpha = \phi_c - \phi$, and $h = \beta RT/a$.

EXPERIMENTAL

Triolein was prepared by the direct esterification of highly purified oleic acid and glycerol. The purified oleic acid was prepared from methyl esters obtained from olive oil and was subjected to repeated crystallizations and fractional distillations. Oleic acid obtained from the esters was molecularly distilled to give highly purified oleic acid. The triolein formed by esterification of the acid with glycerol was crystallized from acetone at a low temperature and molecularly distilled. The final product had an iodine value of 86.0 (theoretical 86.1) and a saponification equivalent of 295.2 (theoretical 294.9). Its melting point was 4.2–4.5° C.; the value 5.5° C. has been reported (*4*).

Tristearin was prepared from the completely hydrogenated triolein by crystallization from chloroform, from acetone-ethanol, and twice from acetone. It had an iodine value of 0.0 (theoretical 0.0) and a saponification equivalent of 296.5 (theoretical 297.1). Its melting point was 72–73.2° C.; the value 72–73.1° C. is given in the literature (*4*).

Tripalmitin was C. P. grade obtained from the Eastman Kodak Co. and was crystallized twice from acetone. The second crystallization yielded a product that melted at 65.2–65.8° C.; the value 66.4° C. has been reported (*4*).

Trimyristin was obtained from the Eastman Kodak Co. and had a melting point of 56.8–57.3° C.; reported value was 57.2° C. (*4*).

Trilaurin had been prepared by other workers in this laboratory and melted at 45.7–46.3° C.; reported value was 45–46.4° C. (*4*).

Hexane was obtained by the distillation of Skellysolve B through a Vigreux column. Only the fractions that distilled in the range 64.5–67° C. were used.

Nitroethane, highest purity (Eastman), was distilled at 106–108° C.

Acetonitrile, C. P., was distilled. Because water and acetonitrile form an azeotrope which boils at 76° C., while acetonitrile boils at 81° C., only the fractions that distilled above 80° C. were collected.

Chloroacetonitrile, highest purity, with a listed boiling point of 124–6° C. was obtained from the Eastman Kodak Co. However, at this temperature the material decomposed and so it was distilled under a reduced pressure of 85 mm. of mercury and a temperature of 62° C.

Determination of Critical Point. The critical points were determined by the use of the equal-volume path previously described. This path requires the addition of more hexane as the temperature is raised for the system hexane-nitroethane; it also requires the addition of more hexane as chloroform is added to the systems hexane-acetonitrile-chloroform and hexane-chloroacetonitrile-chloroform. For the system hexane-acetonitrile-chloroform-water, the system was maintained saturated with water by the addition of sufficient water to ensure that approximately one drop of water phase was present at all times. The critical temperature was reproducible to within 0.1° C. The plait points were reproducible to within 0.2% chloroform.

Partition Ratios were in some cases determined by two methods. The direct method consists of determining the amount of solute in aliquots taken from each phase. The second method involves the use of the countercurrent distribution curves as described by Craig and Craig (*2*). When the direct method was used to determine the partition ratios of tristearin, the system was in all cases saturated with tristearin; the weight of tristearin in the system, therefore, varied with the temperature, or the composition, but was always in the neighborhood of 50 mg. in 20 ml. of system (10 ml. of each phase). When the partition ratios of tristearin were determined from countercurrent distribution curves, the weight of tristearin in the tube at the maximum of the distribution curve ranged from 8 to 10 mg. in 20 ml. of system (10 ml. of each phase). The weight of triolein in 20 ml. of system for the direct method was always close to 86 mg., while the weight of triolein in the tube at the maximum of the distribution curve ranged from 9 to 17 mg. in 20 ml. of system. The partition ratios of trilaurin, trimyristin, and tripalmitin were determined only from countercurrent distribution curves; the weights of solute in the tube at the maximum of the distribution curve ranged from 7 to 11 mg. in 20 ml. of system.

The partition ratios determined by the direct method were reproducible to within less than 1% maximum deviation. Duplicate countercurrent distribution curves were not obtained. The countercurrent distribution apparatus used is a 60-tube, glass apparatus obtained from the H. O. Post Scientific Instrument Co. There was in all cases satisfactory agreement between the experimental and theoretical distribution curves (*10*).

APPLICABILITY OF THEORY TO SYSTEMS UNDER CONSIDERATION

While a model may be inadequate to predict the entropy and enthalpy of mixing, it may, nevertheless, be good enough for predicting the free energy of mixing and the equilibrium properties (*5*). A regular solution is one having an ideal entropy of mixing, even though it has an enthalpy of mixing. Factors that produce deviations from ideal entropies of mixing are differences in molal volumes and specific interactions of the type that produce association or solvation. The molal volumes of the solvents under consideration range from 53 for acetonitrile to 130 for hexane. This difference should not cause a serious departure from ideality (*5*, p. 117). The large molal volumes of the solutes are not significant, as the solutes are always present in low concentrations. The effects of specific forces associated with acetonitrile, chloroacetonitrile, and chloroform are difficult to estimate. One would expect some hydrogen bonding between chloroform and the nitriles, but this bonding should be fairly weak. The hydrogen bonding between the chloroform and the solutes (triglycerides) should be stronger, but this effect on the solvent system should be negligible; the hydrogen bonding between the chloroform and the solute should not produce an abnormal behavior of the partition ratios if the solvent system is approximately symmetric.

The composition at the critical points for the various systems studied in this work are given in Table I. The two-component system hexane-nitroethane is symmetric, at least near the critical temperature. For the three component system $x_c = y_c$ would indicate symmetry at the plait point. It is seen from Table I

Table I. Critical Compositions and Temperature

System	X	Y	Z	x_c	y_c	z_c	Water	ϕ_c	t_c
1	Hexane	Acetonitrile	Chloroform	0.38	0.46	0.16	0.00	15.13	25
2	Hexane	Chloroacetonitrile	Chloroform	0.35	0.43	0.22	0.00	19.44	25
3	Hexane	Nitroethane	....	0.497	0.503	..	0.00	....	19.4
4	Hexane	Acetonitrile	Chloroform	0.29	0.46	0.21	0.04	21.0	25

that the hexane-acetonitrile-chloroform system and the hexane-chloroacetonitrile system are symmetric only as a rough approximation. The effect of this asymmetry cannot be predicted, but the results given in the next section indicate that it is not serious.

The shift of the critical composition by the solute was found to be less than 1%, and, therefore, neglect of the effect of the solute on the solvent system seems justified.

EXPERIMENTAL RESULTS AND APPLICATION OF THEORY

The values of the constants γ, k, p, and h obtained by the application of the theory to the data for triolein and tristearin are given in Table II. The values of γ are the averages of the values of $\log K_s/\log K_o$ obtained at different values of θ or α. Subscripts s and o refer to tristerin and triolein, respectively.

Table II. Values of Theoretical Parameters

System[a]	Method[b]	k_o	k_s	p_o	p_s	h	γ
1	Direct	..	..	0.25	0.167	60	1.50
1a	c.d.	..	..	0.256	0.20	60	1.29
2	Direct	..	..	0.46	0.27	31	1.69
3	Direct	0.49	0.72	...	...	..	1.47
4	Direct	..	..	...	...	..	1.16

[a] System number corresponds to that given in Table I.
[b] Method of determining K; c.d., from countercurrent distribution curves.

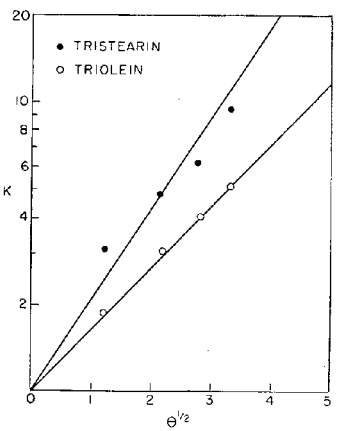

Figure 2. Partition ratio K as a function of $\theta^{1/2}$ on semilogarithmic coordinates for system hexane-nitroethane

The value of k_o was obtained from a plot of K_o against $\theta^{1/2}$ on semilogarithmic coordinates (Figure 2). Equation 13 was used to calculate θ. The value of k_s was then obtained from the values of γ and k_o. A straight line corresponding to this value of k_s is shown in Figure 2 with the experimental values of K_s. The values of p_o and h were found by fitting Equation 40 to the data graphically. These fits are shown in Figure 3. The values of p_s were then obtained from the values of p_o and γ. Curves for these values of p_s are also shown in Figure 3 with the experimental values of K_s.

The same value of h must be used for all curves that apply to a given solvent system. It follows that the curve (Figure 3) for triolein in system 1 (system numbers are as given in Tables I and II) is determined by two points, and the fact that the third lies on the curve is an indication that the system satisfies the theory. All other curves applying to system 1 (including those for system 1a) are then determined by the corresponding γ, and whether or not the points lie on these curves serves as a further test of the applicability of the theory. Analogous conditions apply to the curves for system 2.

In all cases the data for triolein lie on the theoretical curves, but the data for tristearin determined by the direct method do not fit the theoretical curves so well. The partition ratios of tristearin determined by the direct method, in which case the system was saturated with tristearin, are much higher than those determined from countercurrent distribution, in which case the concentration of tristearin after distribution was considerably below saturation. This strongly suggests that, for tristearin, K is concentration-dependent at the higher concentrations. The partition ratios of triolein determined by the direct method are only slightly greater than those obtained from countercurrent distribution curves.

For the system hexane-acetonitrile-chloroform saturated with water, the composition at the plait point and the partition coefficients of triolein and tristearin for one value of α were determined. By assuming that this system is a modified three-component one, the value of γ was calculated and is given in Table II. It is clear that the effect of water is large and is in

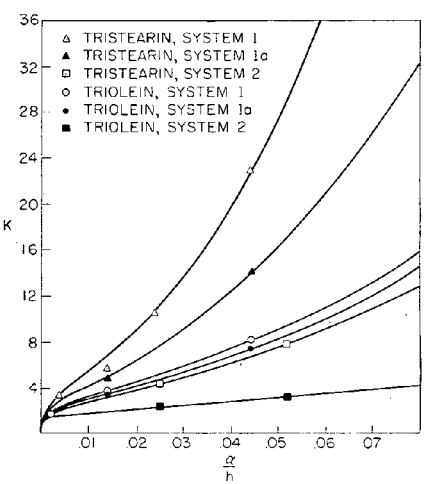

Figure 3. Partition ratio K as a function of α/h according to Equation 40 for systems 1, 1a, and 2

System number corresponds to that given in Tables I and II. Curves theoretical, points experimental

the direction to reduce the symmetry of the system and to lower the value of γ.

Because of the afore-mentioned discrepancies between the partition ratios of tristearin determined by the direct method and those obtained from countercurrent distribution curves, the results presented here cannot be used to obtain an accurate comparison of solvent systems with respect to the amount of separation that can be achieved by their use. Nevertheless, the results can be used for a rough comparison of the system and to obtain an idea of the magnitudes of the effects of certain variables. The predicted separation at optimum conditions for each system is given in Table III, where the separation has been expressed as both τ^* and $p^*(\sqrt{50}\ \tau)$; the optimum conditions θ^*, α^*, and K_o^* are also given in Table III. Figure 4 shows τ as a function of α for systems 1, 1a, and 2, and as a function of θ for system 3. Figure 5 shows $p^*(\sqrt{n}\ \tau)$ as a function of n, the number of transfers, for systems 1a, 2, and 3.

It is clear that the value of α or θ is not critical and that nearly optimum separation is predicted for a range of α of about 3% and for a range of θ of about 10° C. The value of γ is important. For example, from Figure 5 it can be seen that to get a given separation many more transfers are required for system 1a, for which we have $\gamma = 1.29$, then for system 2, for which we have $\gamma = 1.69$.

Table III. Optimum Conditions and Predicted Separations

System[a]	θ^*	α^*	K_o^*	τ^*	$p^*(\sqrt{50}\ \tau)$
1	..	2.2	7.0	0.135	82
1a	..	3.0	8.3	0.082	66
2	..	3.6	6.2	0.172	88
3	3.8	..	7.1	0.125	81
4	..	..	9.3	0.050	56

[a] System number corresponds to that given in Tables I and II.

Table IV. Values of γ and $p^*(\sqrt{50}\ n)$ for Ten Triglyceride Pairs in System Hexane-Acetonitrile-Chloroform

Triglyceride Pair		K^a	γ	$p^*(\sqrt{50}\ \tau)$
Trilaurin (C_{12})[b]	Trimyristin (C_{14})	2.69	1.14	63
Trilaurin (C_{12})	Tripalmitin (C_{16})	..	1.6	85
Trilaurin (C_{12})	Tristearin (C_{18})	..	1.78	90
Trilaurin (C_{12})	Triolein (C_{18})	..	1.39	87
Trimyristin (C_{14})	Tripalmitin (C_{16})	3.1	1.40	88
Trimyristin (C_{14})	Tristearin (C_{18})	..	1.56	84
Trimyristin (C_{14})	Triolein (C_{18})	..	1.21	68
Tripalmitin (C_{16})	Tristearin (C_{18})	4.9	1.11	61
Tripalmitin (C_{16})	Triolein (C_{18})	..	1.16	65
Tristearin (C_{18})	Triolein (C_{18})	5.84	1.29	73
Triolein (C_{18})	.....	3.95	..	..

[a] Partition ratios of triglyceride given in first column for $\alpha = 1.05$.
[b] Number of carbons in acid.

Partition ratios in the hexane-acetonitrile-chloroform system were determined from the countercurrent distribution curves of trilaurin, trimyristin, and tripalmitin. The distributions were made in a system for which the value of α was 1.05. The values of the partition ratios of triolein and tristearin for this value of α can be obtained from Figure 3, using the curves through the points that were determined by countercurrent distribution. In this way the partition ratios of five triglycerides are known for the same value of α, and it is, therefore, possible to calculate the values of γ for all these taken in pairs. These values of the partition ratios and γ are given along with the corresponding values of the separation $p^*(\sqrt{50}\ \tau)$ in Table IV. Because these values of γ were all determined from countercurrent distribution curves, they should be fairly reliable.

No difficulty due to temperature or composition sensitivity was encountered (*10*) in obtaining the distribution at $\alpha = 1.05$ or even at $\alpha = 0.84$, which is much nearer to the plait point than other nearly optimum composition. The variation with

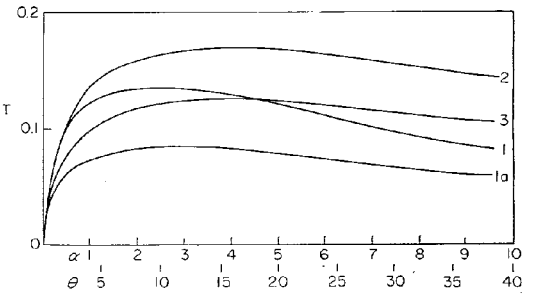

Figure 4. Separation parameter τ as a function of θ for system 3 and as a function of α for systems 1, 1a, and 2

Systems numbered according to Tables I and II

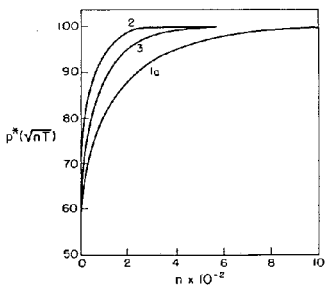

Figure 5. Optimum separation $p^*(\sqrt{n}\tau)$ as a function of n, number of transfers, for systems 1a, 2, and 3

Systems numbered according to Tables I and II

the temperature of the volumes of the two phases in the hexane-acetonitrile-chloroform was studied (*10*); this variation was never greater than 3% per degree, even at $\alpha = 0.84$ and at 26° C. (27° C. is the critical temperature for this value of α).

ACKNOWLEDGMENT

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Cryoscopic Determination of Purity of Highly Reactive Substances

AUGUSTUS R. GLASGOW, Jr., and MILTON TENENBAUM

National Bureau of Standards, Washington, D. C.

A freezing point apparatus was constructed of glass and noble metals for assaying the purity of reactive substances. The sample is stirred by a platinum-iridium stirrer sealed within a closed glass system. An iron armature protected by gold or platinum is attached to the upper portion of the stirrer. A solenoid encased in iron, mounted and guided outside the glass wall of the freezing point tube, holds the armature within its magnetic field, so that movement of the solenoid results in a corresponding movement of the stirrer within the sealed tube. The tube has openings into the cell for cleaning, introduction and removal of samples, temperature measurement, and crystal induction. The apparatus was used for experiments on titanium tetrachloride.

MANY compounds of scientific interest have high chemical reactivities or are poisonous, hygroscopic, or reactive with air. The evaluation of purity of such substances from temperature measurements of the solid-liquid equilibria requires that the system used be inert to these substances and that the operation be performed in a closed system. Because previous apparatus developed in these laboratories for the determination of purity from time-temperature freezing and melting curves (*2, 4–6*) were not satisfactory for such compounds, a new freezing point apparatus was constructed of glass and noble metals. In addition to measurements of purity, it is possible to determine directly the difference between the freezing point of the sample under its own vapor pressure (saturation pressure) and under the combined pressure and solubility effect of an inert gas at a controlled pressure. This report describes the details of construction of the apparatus and the experiments performed on titanium tetrachloride of different levels of purity.

APPARATUS

Essential features of the apparatus are:

Chemical inertness. All surfaces that come in contact with the sample are either borosilicate glass or noble metals (platinum, platinum-iridium alloy, or gold)

Provision for introduction and removal of volatile or nonvolatile samples without contact with air and without contamination

Provision for initiating crystallization, stirring, and obtaining precise temperature measurements of the sample sealed inside the freezing point cell

Provision for rigorous chemical cleaning of the internal surfaces.

The apparatus utilizes the reciprocating action of a double helical stirrer to maintain solid-liquid equilibrium. The direct

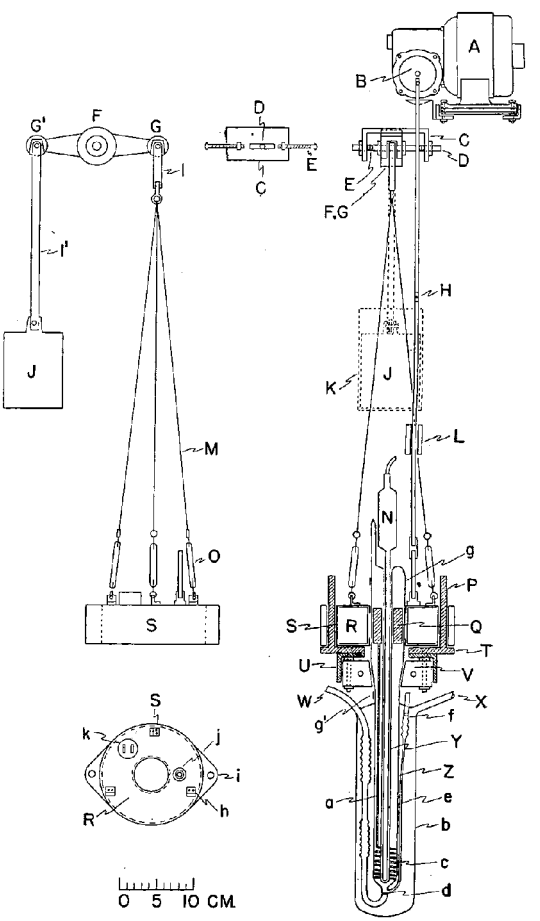


Figure 1. Assembly of Apparatus

A. Motor, gear reduction, 108 r.p.m.
B. Brass wheel, 2 1/2-inch diameter, 3/16 inch thick
C. Support, channel iron
D. Axle, 1/4-inch diameter, 4 inches long
E. Adjustment screws to permit 1 1/4-inch variation in position of axle for alignment of solenoid
F. Circular disk, brass, 2 1/2-inch diameter with ball bearing inserts
G, G'. Circular disk, brass, 1 1/2-inch diameter, 5/16 inch thick, slotted and pinned
H. Connecting rod, steel, 1/4-inch diameter, pinned at center
I. Connecting rod to wires supporting solenoid
I'. Connecting rod to brass counterweight
J. Counterweight, 11 pounds
K. Brass cylinder serving as guide and emergency support for counterweight, holes in bottom and sides to release air
L. Brass bearing to guide connecting rod *H*
M. Piano wire
N. Thermometer, platinum resistance, 25-ohm
O. Turnbuckle, 3-inch
P. Steel rod guide for solenoid, 3/8-inch
Q. Armature, soft-iron, protected by gold or platinum
R. Brass spool wound with magnet wire
S. Iron casing for solenoid
T. Steel plate, 3/8 inch thick to support guide rods *P*
U. Angle iron, 1-inch
V. Transite block with tapered hole to fit freezing point tube
W. Seeding well with expansion bellows
X. Glass tubing connected to vacuum pump
Y. Re-entrant well for insertion of thermometer
Z. Wall of freezing tube
a. Platinum-iridium rod, 1/8-inch diameter
b. Wall of freezing tube jacket, 80-mm. diameter
c. Stirrer, double helical, platinum-iridium
d. Glass partition
e. Glass tube, 3-mm.
f. Glass tube, 6-mm.
g, g'. Conducting strips, silver, attached to each end of heating tape which covers top half of freezing tube. Top of tube is heated with this tape when samples freezing above room temperature are measured
h. Turnbuckle, supports spaced 120° apart
i. Brass guide, soldered to iron casing of solenoid with 3/8-inch hole to center and guide solenoid
j. Threaded flange attached to connecting rod
k. Electrical connection for power supply to solenoid

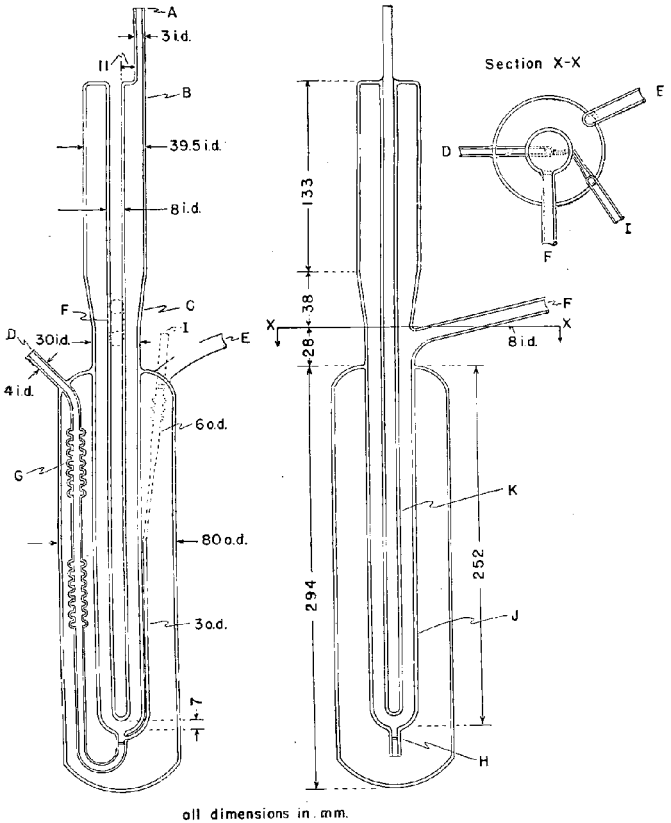


Figure 2. Details of freezing point tube

A. Glass tube, facilitates cleaning, sealed before introduction of sample
B. Point of final seal when tube is fabricated
C. Tapered section of tube to fit tapered section of transite block
D. "Seeding" well for inducing crystallization
E. Glass tubing, connected to vacuum pump for evacuating space between double walls
F. Glass tubing through which volatile samples are introduced and removed by distillation
G. Expansion bellows, preventing breakage when temperature changes occur
H. Glass partition, separating sample chamber and seeding well
I. Glass tube connected to sample chamber
J. Sample chamber
K. Thermometer well

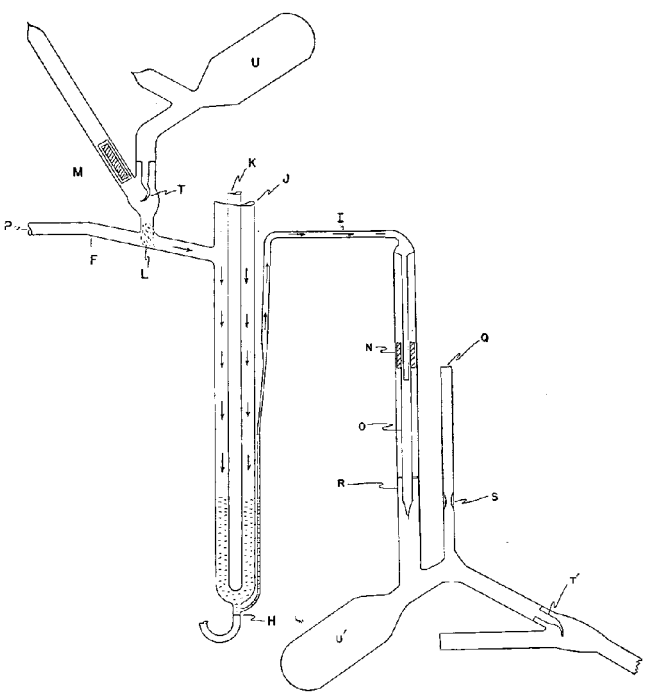


Figure 3. Introduction and removal of nonvolatile samples

F, H, I, J, K. Same as in Figure 2
L. Glass wool
M. Soft-iron rod, encased in glass
N. Soft-iron cylinder, encased in glass
O. Adjustable funnel, lowered to prevent splattering of liquid on glass around point *R* when sample is being transferred to ampoule *U*, then lifted with magnet to permit seal at *R*
P. Inlet for inert gas
Q. Outlet to vacuum system
R. Point at which ampoule is sealed after sample has been transferred to *U'*
S. Point at which final seal is made after sample is degassed
T, T'. Break-off tip
U. Ampoule containing sample to be measured
U'. Ampoule for receiving sample after measurement

drive stirrer used in equipment previously described (*2, 4, 5*) has been eliminated to permit confinement of the material in a sealed system. This makes it possible to measure temperature under triple-point conditions or in a controlled atmosphere at other pressures.

The iron armature to which the stirrer is attached is magnetically driven from outside the vessel. This armature and stirrer unit is permanently sealed within the freezing point tube. Vertical 1-inch strokes of the stirrer are produced by holding the armature in the magnetic field of a solenoid mounted around the outside of the stationary freezing point tube while lowering and raising the solenoid with a shaft attached to an electric motor. All internal parts of the system are constructed of glass or noble metals, so that measurements of purity can be made on reactive substances. The cell is constructed of borosilicate glass. The shaft and coil of the stirrer are made of an alloy composed of 80% platinum–20% iridium. The surface of the armature is plated with gold in one apparatus and encased in a platinum envelope in another. Because alignment is rather critical, the tube has been permanently mounted and is equipped with five different openings to allow necessary operations to be accomplished without the need for dismantling.

A drawing of the entire assembly is shown in Figure 1.

The solenoid, *S*, is attached to the bottom of shaft *H* and vertical motion is produced by attaching the top of the shaft 0.5 inch off-center on the motor-driven wheel, *B*. The solenoid is counterbalanced with a brass weight, *J*, suspended from a yoke at *G*. The freezing point tube is supported by a Transite block, *V*, machined to fit the tapered part of the tube. The block is split at the center and the two halves are bolted together so that the tube may be detached. Temperature is measured with a 25-ohm platinum resistance thermometer, *N*, placed in well *Y* and attached to a resistance bridge (Mueller type) and a galvanometer (not shown). The sensitivity of the thermometric system with a 2-ma. current flowing through the platinum thermometer is such that 1 mm. on the galvanometer scale is equivalent to 0.0003° C.

Details of construction of the freezing point tube which is designed for measuring freezing points of samples of 50-ml. volume are shown in Figure 2.

Openings *A* and *I* are used to flush cleaning agents through the tube. Final rinsing is done with distilled water, *A* and *I* are sealed, and the walls are thoroughly dried by pumping the system to a pressure of 10^{-5} mm. of mercury by means of a vacuum system connected to *F*.

Volatile samples are introduced by distilling them from break-off tip ampoules sealed to a glass manifold attached to the vacuum system at *F* (Figure 2). After completion of the experiment, the sample is distilled back into another ampoule on the manifold. The sample is then cooled and the ampoule sealed off. To prevent decomposition of any vapors from the sample in making this seal, it is important to keep another part of the manifold cooled. This permits the heated vapors to travel toward the cooled parts in both directions away from the point of sealing. Using this procedure for titanium tetrachloride, decomposition at the seal was eliminated.

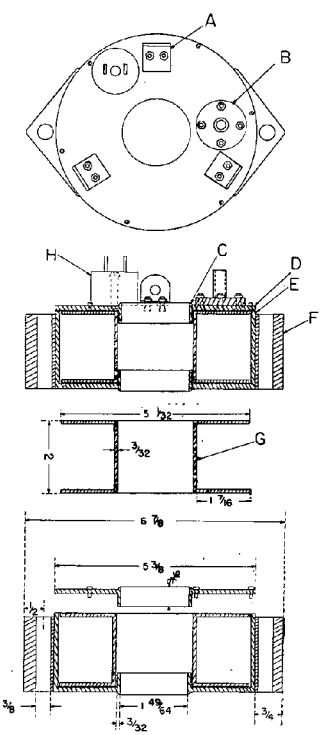
Nonvolatile samples are introduced by gravity flow from a specially designed ampoule, *U* (Figure 3), and are removed after completion of the measurement by admitting an inert gas through *F*, which forces the sample out through *I*. *N* is an iron cylinder encased in glass attached to glass tube *O*. The position of *O* can be adjusted to keep the wall at point *R* free of the liquid during transfer. Sealing at *R* is done with the sample under atmospheric pressure of an inert gas. This prevents sudden collapse of the heated glass, which would occur during sealing if large pressure difference existed between the inside and outside of the glass walls.

Dissolved gas is removed from the sample, using the technique of alternate freezing and melting in vacuum. Final sealing at *S* is done by fusion.

Heat flow to or from the sample is controlled by evacuating the space between the double-walled jacket. In this evacuation the air is removed through stopcock *E* (Figure 2). The walls are silvered to minimize heat losses from radiation. Any air admitted into the double jacket space is first freed of carbon dioxide and water vapor by means of a drying column containing Ascarite and magnesium perchlorate.

To prevent supercooling of the liquid during the freezing experiment, a small portion of the sample is cooled appreciably below its freezing point. Crystal nucleation is induced at the glass partition, *H* (*3*), by inserting liquid nitrogen or powdered solid carbon dioxide into tube *D* of Figure 2. A wire with a small flexible coil is used to force the solid refrigerant into contact with *H*. Nucleation of crystals by this method is referred to as "seeding" by thermal shock.

The solenoid (Figure 4) is made by winding 5 pounds of No. 26 B. and S. gage enameled copper magnet wire on the brass spool, *G*, and it is activated with a 110-volt direct current source. The magnetic field strength is increased in the vicinity of the stirrer



all dimensions in inches

Figure 4. Details of iron-encased solenoid

A. Turnbuckle supports (*h* in Figure 1)
B. Threaded flange, attaching solenoid to connecting rod (*j* in Figure 1)
C. Iron ring, welded to form part of iron lid
D. Iron lid, attached to rest of the iron casing by six screws
E. Iron casing, covering brass spool, machined from standard 5¼-inch o.d. iron pipe
F. Brass guide, soldered to iron casing (same as *i* in Figure 1)
G. Brass spool, wound with 5 pounds of No. 26 B and S gage magnet wire.
H. Electric outlet, power supply to magnet (same as *k* in Figure 1)

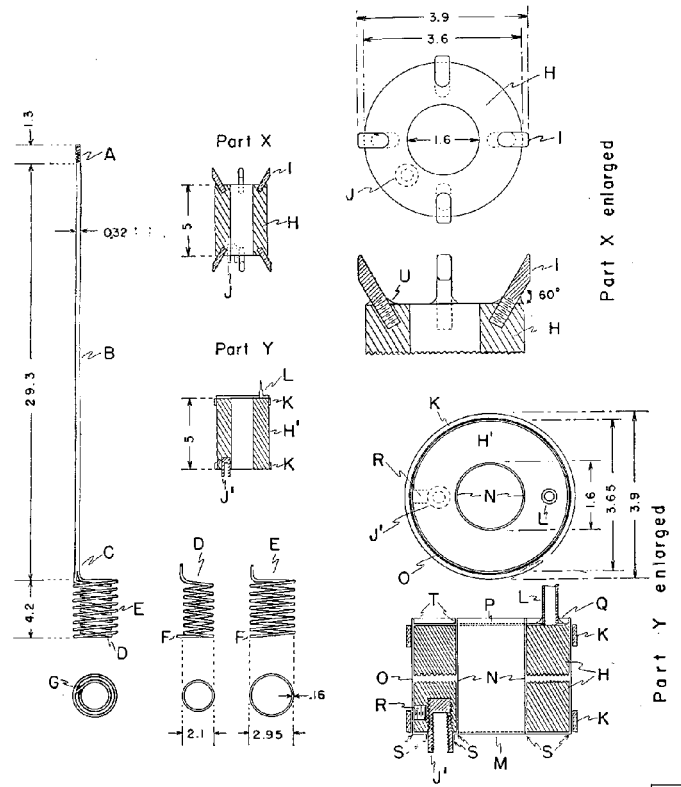


Figure 5. Details of stirrer

A. Thread, to fit *J* in iron core
B. Platinum-iridium rod
C. Platinum-iridium weld of helices to 1/8-inch rod
D. Inner helix, made by winding downward over cylinder of appropriate size (diameter of this cylinder depends upon any expansion in helical coil after winding tension is removed). Size specifications in drawing refer to this expanded condition, which is permanent set of coil.
E. Outer helix, wire continued at *F* to form outer coil, *E* (*D* and *E* are continuation of same strand of wire). *E* is made in same manner as *D*, by winding wire upward over another cylinder slipped over *D*. The two cylinders are removed and two coils welded together at *C* and to rod *B*.
Part *X*. Gold plated, flashed with copper, plated with 0.005 inch of silver, plated with 0.003 inch of gold, polished, and burnished
H. Iron cylinder
I. Eight rods, 80% platinum–20% iridium, screwed into iron cylinder and silver-soldered at points *U* before plating. Used to act as bearing surface to prevent wearing of gold plate
J. Threaded iron plug, attaching stirrer to iron cylinder, silver-soldered before plating
U. Silver-solder joints. Good plating surface is produced by rounding these fillets and eliminating sharp edges.
Part *Y* (platinum encased)
J'. Plug made of 80% platinum–20% iridium alloy, threaded to attach stirrer to iron core. Gold-soldered after assembly
K. Band, 80% platinum-20% iridium alloy, encircling platinum foil, 1/8 inch thick, acting as bearing surface. Protects against wearing of thin platinum foil
L. Platinum tubing, fold-soldered to platinum casing at *Q*, attached to vacuum pump so that casing may be tested for leaks, later crimped, gold-soldered closed, and cut off
M, P. Platinum disk, 25 mm. thick
N, O. Platinum foil, 15 mm. thick
Q. Soldered joint, made with high melting gold-platinum solder
R. Set screw to hold plug *J'*
S. Platinum fused joint
T. Gold-soldered joint

by encasing the spool in an iron jacket, *E*. Tests showed that the solenoid could support 4 kg. in addition to the weight of the stirrer. In freezing experiments stirring can be continued until one third to one half of the sample is frozen. This amount of solid prevents further stirring and there is no danger of breakage, since the armature of the stirrer slips in the magnetic field.

Details of the stirrer and the iron armature are shown in Figure 5.

The stirrer is made of an alloy containing 80% platinum and 20% iridium. This alloy has more elasticity and hardness than pure platinum. The double helical coil (*I*) is made by winding one strand of wire on cylinders of the required size. Two ends of the coil are then fused to shaft *B* at point *C*. The armature in one model, as shown in part *X*, was gold plated by the Electrodeposition Section of this bureau. In the other model the encasement of the armature in platinum, part *Y*, was fabricated to specifications by J. Bishop and Co. Platinum Works, Malvern, Pa. Both types have been satisfactory in preventing any reaction with the iron.

Extreme care must be taken to prevent flaws in the gold plate. The platinum type has the advantage of permitting the glass freezing-point tube to be annealed after the stirrer is sealed inside. In the other case this cannot be done, because the gold plate might blister.

To test for leaks in the seams of the platinum foil, tube *L* in part *Y* is attached to a vacuum pump and the space between the foil and the iron cylinder is evacuated. Part *Y* is then checked with a helium leak detector. Permanent closure at *L* is made by melting a small piece of gold which is placed in the platinum tube prior to evacuation. The tube is then crimped and cut off about 1 inch above *Q*.

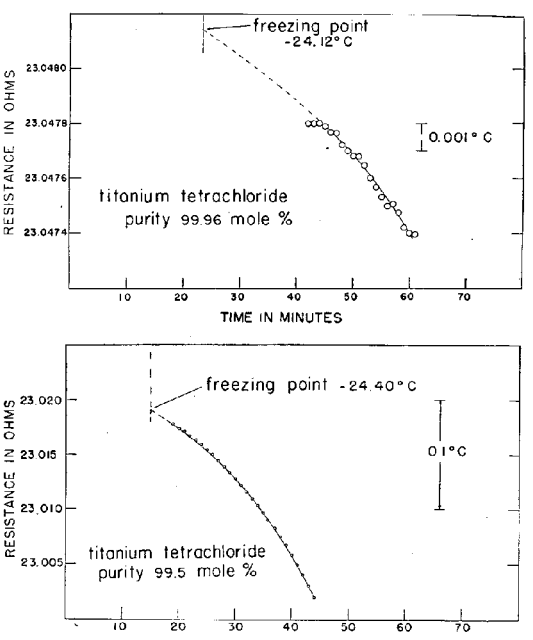


Figure 6. Freezing curve of titanium tetrachloride at saturation pressure

Scale of ordinates gives resistance in ohms of platinum resistance thermometer (0.1 ohm is approximately 1.0° C.)

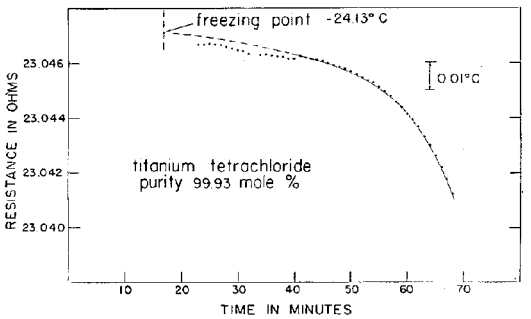


Figure 7. Freezing curve of titanium tetrachloride under 1 atm. of dry nitrogen

Scale of ordinates gives resistance in ohms of platinum resistance thermometer (0.1 ohm is approximately 1.0° C.).

EXPERIMENTAL DATA

The procedures for determining the purity from time-temperature freezing and melting curves and the principles involved are given in earlier publications (*1*, *2*, *4-7*). Three typical freezing point curves obtained with titanium tetrachloride samples of different levels of purity was shown in Figures 6 and 7. From a series of experiments such as these a value for the freezing point of titanium tetrachloride under saturation pressure with zero impurity, T_{f_0}, was calculated to be $-24.10° \pm 0.01°$ C. Figure 6 shows curves of experiments done under saturation pressure. The curve in Figure 7 was obtained with the sample under 1 atm. of dry nitrogen.

In other experiments, not shown in the figures, the temperatures of the freezing curve of a sample of titanium tetrachloride at saturation pressure were observed to be 0.007° C. lower than the corresponding temperatures of the freezing curve of the same sample under a pressure of 1 atm. of nitrogen.

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Factors Affecting Use of Dielectric Methods in Determination of Sea Water in Navy Special Fuel Oil

T. D. CALLINAN, R. M. ROE, and J. B. ROMANS
U. S. Naval Research Laboratory, Washington 25, D. C.

The dielectric constant, per cent power factor, dielectric loss factor, and conductivity of a number of boiler fuels were evaluated as a means of measuring the sea water content of Navy Special fuel oils on shipboard. These properties varied considerably from one fuel oil to another at comparable frequencies from 10 kc. to 75 Mc. When these oils were emulsified with synthetic sea water, the values so obtained increased with increasing sea water content but remained a function of the characteristics of the original fuel oil. The necessity of using a dry reference sample is emphasized.

IN THE course of investigating the causes of fuel slagging in Navy boilers, it became increasingly evident that information concerning the degree of contamination of Navy Special fuel oil by sea water would be of considerable value.

Present analytical methods, while highly accurate, are time-consuming and of little assistance under actual operational conditions. It would be desirable, therefore, to have a compact and rugged instrument that would indicate, or record continuously, variations in the salt water content of Navy Special boiler fuel. No suitable instruments or devices are available at the present time, although several methods have been proposed for the determination of sea water in fuel oil, each based on the measurement of some well-established electrical property of hydrocarbons or of water (*10*). Among several methods proposed were those for the determination of salt water content of emulsions by (*a*) determination of the dielectric constant of the emulsion or the change in dielectric constant as a function of salt water content, (*b*) change in per cent power factor, (*c*) change in dielectric loss factor, and (*d*) change in conductivity.

Although dielectric constant measurements have been used to follow the progress of oxidation in petroleum products, to determine impurities in transformer oils, for the detection of water in hydrocarbons, and the like (*12*), such determinations are made on highly refined, essentially nonpolar materials. The impurity usually represents only a trace or at least a very minor constituent of the product under examination. In contrast, boiler fuel oils, including Navy Special fuel oils, are complex mixtures of variable composition, chiefly hydrocarbon in nature, containing appreciable amounts of polar compounds. In addition to aromatic and paraffinic compounds known to be present, Navy Special fuel oil contains large amounts of asphaltic and resinous materials of unknown composition, oxygenated bodies, sulfur and nitrogen compounds, organometallic compounds, and adventitious material picked up in the course of refining or delivery.

THEORETICAL CONSIDERATIONS

Maxwell has given a rigorous calculation for the determination of the dielectric constant of a dispersion of two different substances of different dielectric constants. Maxwell's original formula can be replaced by the generalized empirical formula, (*13*)

$$\epsilon^K = \sum_i \Theta_i \epsilon_i K \qquad (1)$$

without great inaccuracy. The so-called logarithmic mixture rule results when the exponent K above is eliminated. The resultant formula which is used in practice (*2*, *13*) is

$$\log \epsilon' = \Sigma_i \Theta_i \log \epsilon_i' \qquad (2)$$

where ϵ' is the dielectric constant of the mixture; Θ_i is the volumetric fraction of ith component, where the total volume, $\Sigma\Theta_i$, is equal to 1; and ϵ_i' is the dielectric constant of the ith component.

This suggests the possible use of the above logarithmic formula for determining the moisture content of a vaporized mixture of fuel oil and water by dielectric means. While the principle is applicable, serious limitations are present; the dielectric constants of oils vary and, hence, a range of constants for oils containing identical amounts of water will result. The problem of determining the changes in the dielectric constant of mixtures of oil and water vapor has an additional difficulty. Since the values are 1.00059 for air, approximately 1.0035 for oil vapor, and 1.0126 for water vapor, a dry oil vapor would differ in dielectric constant from one containing 50% water by only 0.0031. Such a small change magnifies the instrumentation problem enormously.

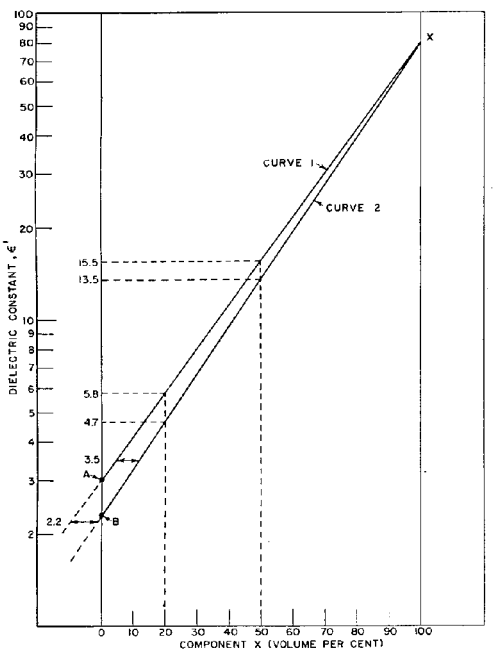

Figure 1. Theoretical relationship between dielectric constant and volume per cent of component X

In employing the dielectric method of measuring water in oil in the liquid state, two possible approaches exist: (*a*) relating the effect of water on the dielectric constant and (*b*) measuring the effect of water on the power factor of the oil. In both cases the values rise with increase in water content. The logarithmic mixture rule may be applied to liquids (as well as gases) where the components of the mixture are nonpolar and have no permanent dipole moment. Application of this theory is demonstrated in Figure 1, curve 1, for a mixture of two substances, *A* and *X*, one of which has a dielectric constant of 3.0 and the other a value of 80, respectively. Curve 1 predicts that the maximum dielectric constant to be expected from a mixture of 50% *A* and 50% *X* is approximately 15.5, and that a lower adulteration of 20% *X* results in a dielectric constant of about 5.8. As a second example, curve 2 predicts that the maximum value for another substance, *B*, with a dielectric constant of 2.3 originally, is approximately 13.5 when adulterated with 50% *X* and that a lower concentration of 20% *X* results in a dielectric constant of about 4.7. An examination of the theoretical curves indicates that, if the individual substances follow the logarithmic mixture rule, the initial dielectric constant value of the individual components will have a marked effect on the resultant dielectric constant of the mixture.

If it is assumed that the logarithmic mixture rule applies to mixtures of sea water and fuel oil and that the dielectric constants of the base oils under consideration are 3.0 and 2.3, respectively, while that of water is approximately 80, reference to Figure 1 (using curves 1 and 2 as limits) shows that an unknown mixture having a dielectric constant of 3.5 could contain as little as 5% or as much as 12% water. A second mixture with a dielectric constant of 2.2 would have an apparent negative water content, a conclusion which is obviously impossible. Since a variation in the dielectric constant of dry fuel oils will have a marked effect on the dielectric constant of emulsions of sea water and fuel oil, it has been necessary to determine the magnitude of this factor in a study of Navy Special fuel oils. If the variation is large, it is evident that, unless the dielectric constant of the dry fuel oil is known, it will be impossible to obtain the correct value of water content.

RESULTS

Studies were made of 19 samples of oils and approximately 130 emulsions of these oils, containing in some cases as much as 40% synthetic sea water (*1*) by weight.

Selected properties of 11 typical Navy Special fuel oils, conforming to Specification Mil-F-859A, are listed in Table I. The remaining samples not necessarily conforming to Specification Mil-F-859A consisted of a Venezuelan crude oil, a topped Venezuelan residuum, a high sulfur–high vanadium fuel oil, a low sulfur–low vanadium fuel oil, and four reference fuels.

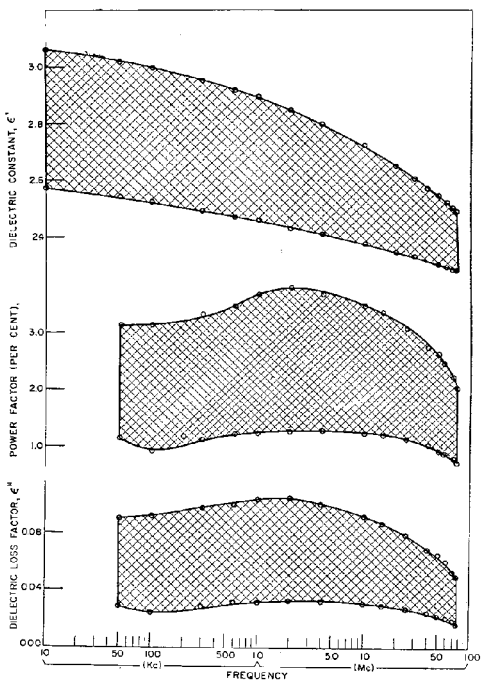

Figure 2. Range of dielectric properties obtained for boiler fuel oils as function of frequency

Data at 10 kc. were obtained by the bridge method; data from 50 kc. to 75 Mc. were obtained with a Q meter. The dielectric constants of emulsions containing more than 5% synthetic sea water could not be determined satisfactorily by the bridge method. The dielectric constant values are accurate to ±0.02

Table I. Selected Properties of Some Navy Special Fuel Oils

Sample No.	API Gravity, 60° F.	Viscosity at 122° F.	Ash, %	Water[a] by Distillation
1	17.2	218	0.06	0.05
2	14.9	212	0.03	0.05
3	18.3	202	0.04	0.05
4	16.2	204	0.04	0.05
5	15.4	218	0.04	0.05
6	17.3	223	0.01	0.05
7	15.6	224	0.01	0.05
8	15.9	211	0.03	0.1
9	12.8	213	...	0.05
10	11.7	200	0.05	0.05
11	17.4	141	0.035	0.05

[a] % by volume.

and the power factors to ±0.0002. All measurements were made within a temperature range of 75° to 85° F.

Dielectric Constant. Values of the dielectric constant of the 19 oils plotted against frequency are shown in Figure 2. The curves show that the dielectric constant is frequency dependent, decreasing with rising frequency, although the rate of decrease is not the same for all samples. The results show that relatively water-free fuel oils differ in dielectric constant by as much as 20% at audio-frequencies and by 9% at 75 Mc. Therefore, the extreme values would differ from a mean value of 2.82 at 10 kc. by 10% and from a mean of 2.40 at 75 Mc. by approximately 5%.

The particular characteristics which are responsible for the wide range in the dielectric constant of the fuel oils at a given frequency may be approximated by comparing the known dielectric constants of nonpolar liquids at equal density to the dielectric constants of 2.58 and 3.06 (the extremes of the dielectric constant range at 10 kc. as shown in Figure 2). This would indicate that electronic polarization constitutes about 88% and 74% respectively, of the total dielectric constant for fuel oils representing the two extremes of those studied. Because the part of the dielectric constant which arises from atomic polarization is usually about 10% of that due to electronic polarization (*6*), this leaves only 3.2% as arising from energy storage by permanent dipoles in the fuel oil of lower dielectric constant. This proportion changes appreciably for the fuel oil of highest dielectric constant, wherein 18.6% of the dielectric constant arises from the presence of permanent dipoles. This indicates strikingly that the original oils differ considerably, not only in the nature of the nonhydrocarbon impurities, but also in the nature of the hydrocarbons present.

Dielectric constant data on emulsions were readily obtained with sea water concentrations up to 20%; however, some of the emulsions at the higher concentrations of 30 and 40% were rather unstable. Examination of the data obtained (Figure 3) indicates that the dielectric constant of the mixture of synthetic sea water and fuel oil increases with increasing sea water content at all frequencies between 10 kc. and 75 Mc. The increase in dielectric constant, in general, follows the predicted curve for mixtures as shown previously in Figure 1. This is to be expected because the densities of the synthetic sea water and fuel oil components are nearly equal. Thus, a plot of the dielectric constant of the emulsion as a function of sea water content on a weight basis would be almost identical to the same data shown on a volume basis.

The applicability of the logarithmic mixture rule at 1 Mc. is further demonstrated in Figure 4 by plotting the values of dielectric constant as a function of synthetic sea water content for two emulsions made with two different fuel oils. It is obvious from Figure 4 that the dielectric constant of an emulsion with a given water content is dependent upon the dielectric constant of the dry oil from which the emulsion was made. Also, while the dielectric constant follows the predicted curve for each mixture (as mentioned earlier), the curves of two or more such mixtures are not necessarily parallel. This means that if the water content of two emulsions of oils from different sources be changed in like amount, the resultant change in dielectric constant of the emulsions will not necessarily be the same. In addition, extrapolation of the curves to 100% water content does not yield a dielectric constant of 80 in either case. This is not contrary to the logarithmic mixture rule but rather indicates that orientation and association (*5, 13*) of the water molecules in the disperse phase of the emulsion are different from that of the bulk synthetic sea water, and that a small correction factor must be applied. The difficulty of interpreting a change in dielectric constant in terms of a change in water content is complicated by the effects of the above factors.

The magnitude of error which may be expected in using the dielectric constant method for determining sea water content of

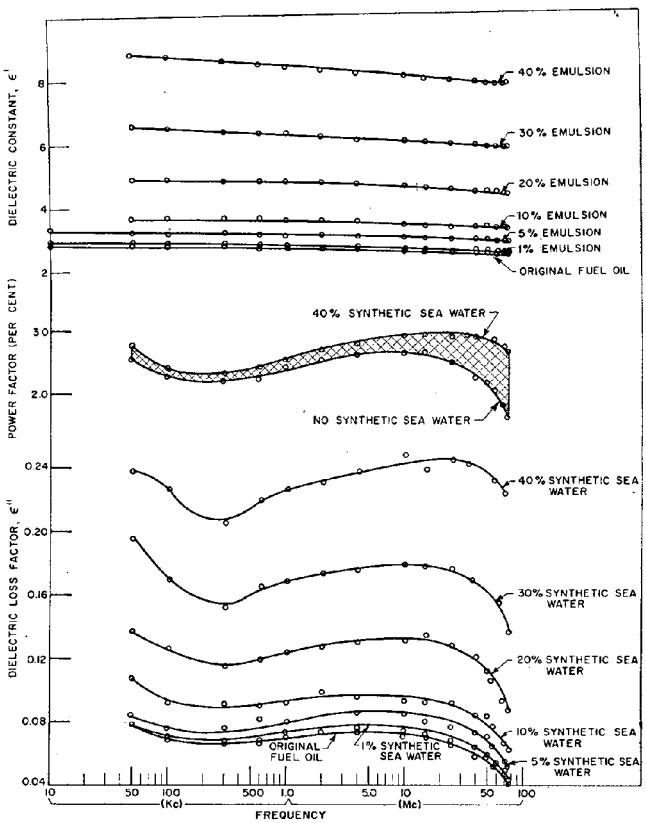

Figure 3. Variation in dielectric properties of emulsions of fuel oil sample 3 as function of frequency

Navy Special fuel oil emulsions is readily seen from an examination of the upper and lower limits obtained at 1 Mc. (Figure 5). It should be emphasized that the range shown is representative only of the fuel oils investigated and by no means includes all those which might be obtained under Navy Special fuel oil specification (*9*). The curves show that an unknown emulsion with a dielectric constant of 2.85 might contain no water or as much as 4%, while a second emulsion of dielectric constant of 5.00 might contain as little as 17% or as much as 23%. These approximations hold only if the dry fuel oils from which the emulsions were obtained had dielectric constant values within the limits of the curves—i.e., 2.52 to 2.85. Note that as the dielectric constant of an unknown emulsion of any fuel oil thus included in the range approaches the minimum value of 2.52, the error in estimating the *maximum* amount of water present approaches zero.

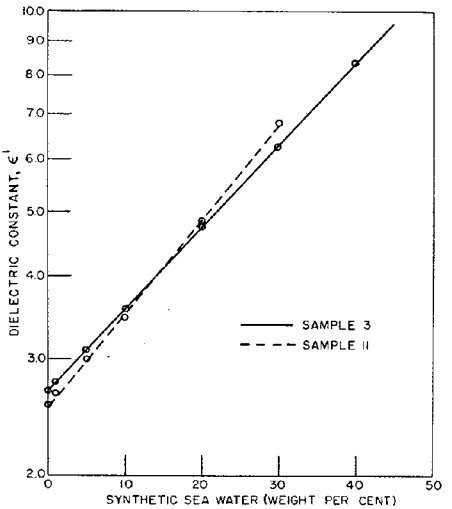

Figure 4. Variation of dielectric constant of emulsions of fuel oil samples 3 and 11 at 1 Mc. as function of per cent synthetic sea water

The uncertainty of the dielectric constant method of measuring water content of the Navy Special fuel oil emulsions becomes more apparent by taking the following example. If the dielectric constant of an unknown emulsion falls within the limits of curves 1 and 2 in Figure 5—e.g., 2.75—the maximum amount of water indicated is 3%. This does not necessarily represent the true value because it cannot be established that the original fuel oil from which this emulsion was obtained lies within the limits of the range. The real value can be found only by making an actual water determination by laboratory methods or by referring to the dielectric constant of the dry oil from which the emulsion was obtained. Obviously, if the dielectric constant of an unknown emulsion lies below the value of 2.52 the fuel oil from which the emulsion was obtained was not included in the previously established limits and it will be impossible even to estimate the amount of water present.

If an instrument were devised based on the dielectric constant method, using a zero-center meter, it would probably be calibrated in one of two ways:

(*a*) based on an average curve midway between the limits of curves 1 and 2, the zero water content corresponding to a dielectric constant of 2.68;

(*b*) based on the lower limit as represented by curve 2, where the zero water content corresponds to a dielectric constant of 2.52.

If the instrument is calibrated as in (*a*), values of dielectric constant above 2.68 would always indicate positive values of water content. For values below 2.68, the instrument would indicate negative values of water content—i.e., less than zero (an impossible situation). This will be true of all fuel oils.

If the calibration is based on (*b*), the values indicated by the instrument will be positive for all emulsions with a dielectric constant greater than 2.52. If the dielectric constant of an unknown emulsion is less than 2.52, the instrument will indicate negative values of water content. This immediately shows that the dielectric constant of the dry fuel oil is below the range shown in Figure 5. In this case it would be impossible to approximate the true value of the water content. Any attempt to readjust the instrument to read zero would, in effect, be extending the lower limit of the range shown in Figure 5 and, therefore would further increase the magnitude of error in the method. In measuring the water content of emulsions where the dielectric constant of the dry fuel oil lies above 2.85 (above the range shown in Figure 5), the instrument will indicate positive water content whether calibrated by method (*a*) or (*b*). However, the amount of water present will be less than that indicated.

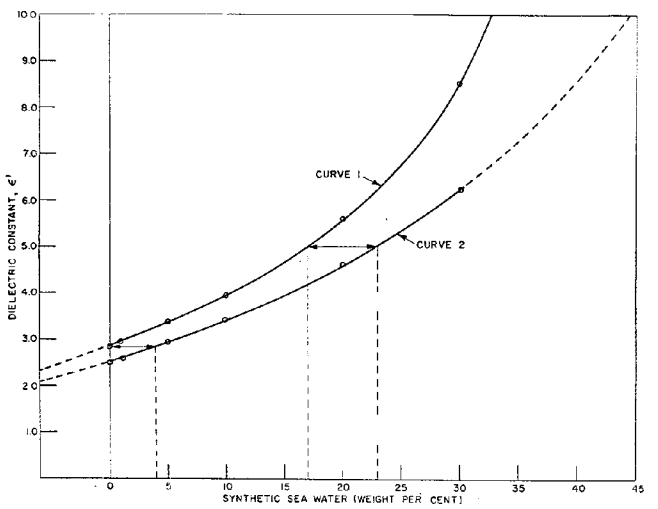

Figure 5. Range of dielectric constants at 1 Mc. for sea water emulsions of Navy Special fuel oil

It is evident, then, that for emulsions of Navy Special fuel oil, where the dielectric constant of the dry fuel oil lies within the range of Figure 5, errors in measuring the water content by the dielectric constant method may be as much as 4% at low concentrations to as much as 7% at about 25% water content. (At a frequency of 75 Mc., these errors range from 3% at low concentrations to as much as 5% at about 25% water content.) For emulsions where the dielectric constant of the dry fuel oil lies above the range, all readings of water content will be too high. Where the dielectric constant of the dry fuel oil lies below the range, some

readings may be negative and, therefore, meaningless, and the water actual content of the emulsion will be undeterminable. Thus, if the dielectric constant method is to be successful, it will be necessary to employ, as a reference standard, a dry sample of the fuel oil from which the emulsion was obtained.

The frequency spectrum beyond 75 Mc. was not explored for the following reasons.

(*a*) In mixtures of dielectrics in which the components differ in dielectric constant, electrical conductivity, and degree of dispersion, anomalous effects occur at frequencies near a frequency of maximum absorption. In a complex mixture such as Navy Special fuel oil, anomalies may be expected as the frequency is raised to higher values, particularly in the region of 10^{10} to 10^{12} c.p.s. (*8*).

(*b*) At frequencies above 10^8 c.p.s.(*7*), the dielectric constant of salt water falls rapidly from approximately 80 to a value of 1.76 at a frequency of 5×10^{14} c.p.s. Thus, the important advantage of the wide differences between the dielectric constant of fuel oil and water is lost.

Although the dielectric constant of the fuel oils cannot be obtained at optical frequencies by ordinary methods, the dielectric constant of hydrocarbons at optical frequencies follows Maxwell's law relating the dielectric constant of a substance and its index refraction, $\epsilon' = n^2$, where n is the index of refraction of the substance (*3, 6, 8*). The index of refraction of a hydrocarbon mixture is a function of composition and density (*12*). Because these factors vary widely in Navy Special fuel oils, considerable variation in the index of refraction (and hence, the dielectric constant) remains.

Power Factor. It had been suggested that the power factor (p.f.) might be used as a means of measuring the sea water content of fuel oil emulsions. For values less than 0.1 (10%), the power factor is equal to the ratio of the loss of energy within the dielectric medium to the total energy stored, multiplied by the reciprocal of the dielectric constant.

Determination of the power factor of the Navy Special fuel oils over the frequency range of 50 kc. through 75 Mc. revealed that the power factor is frequency dependent, exhibiting maxima and minima which vary from sample to sample. There were also wide differences in values at comparable frequencies, as shown graphically in Figure 2. Below 1 Mc., the range of all 19 original oils was greater than that shown in the graph. The per cent power factor of the emulsion below 1 Mc. was almost identical (within the accuracy of the method) with that of the dry fuel oil in each case. At higher frequencies the per cent power factor increased with increasing water content of the emulsion (Figure 3). This is further demonstrated by an examination of Figure 6, where emulsions of Navy Special fuel oil sample 3 show an orderly and readily observable increase in per cent power factor at a frequency of 40 Mc.

The fact that per cent power factor of Navy Special fuel oils varies widely at any given frequency and exhibits irregular maxima and minima over the frequency range enormously complicates the use of per cent power factor as a means of estimating water content. This necessitates standardization against a dry sample of the fuel oil being evaluated at the particular frequency employed. While the presence of sea water in fuel oil samples does raise the per cent power factor in a rather uniform manner at the higher frequencies, below 1 Mc. the addition of sea water causes no significant change. It must be emphasized that the per cent power factor of the dry fuel oils has been found to vary as much as 1% to 2.75% at 40 Mc. This is a greater difference in per cent power factor than that of typical emulsions containing from 0 to 40% sea water when measured at the same frequency. This point is shown graphically in Figure 3 because the change, even with 40% sea water, is small in comparison with the difference in initial per cent power factor of the dry fuel oils.

Dielectric Loss Factor. It was also proposed that the dielectric loss factor, if it could be determined directly, might prove a

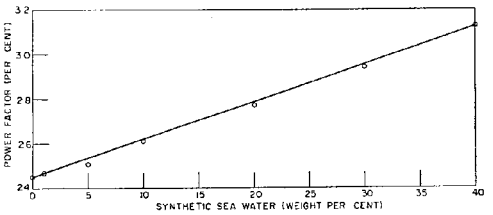

Figure 6. Variation in per cent power factor of emulsions of fuel oil sample 3 at 40 Mc. with per cent synthetic sea water

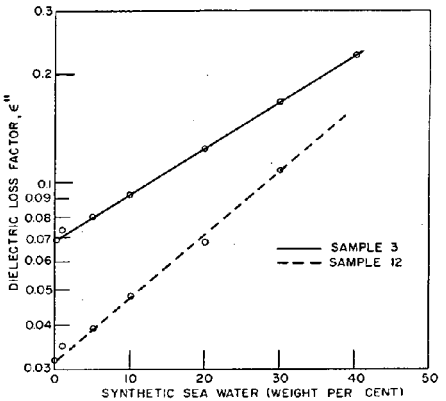

Figure 7. Variation of dielectric loss factor of emulsions of fuel oil samples 3 and 12 at 1 Mc. with per cent synthetic sea water

means of relating electrical and chemical properties of emulsions of sea water and fuel oil. Dielectric loss factor is defined as the ratio of the loss of energy within the dielectric medium to the total energy stored within it.

Dielectric loss factors of the Navy Special fuel oils examined previously were calculated; the range is shown in Figure 2. The loss factor at 1 Mc. varies from about 0.03 to 0.104, over a threefold variation. The range of the dielectric loss factor for all 19 oils as received from the supplier was greater at the lower frequencies. The dielectric loss factor of emulsions, as exemplified by Navy Special fuel oil sample 3, rises in an orderly manner with increasing sea water content (Figure 3). The loss factor of the dry oil (about 0.07 at 1 Mc.) is more than twice as great as the lower limit (0.03) of the range shown in Figure 2. Although it was found that dielectric loss factor increased linearly at a given frequency with increasing sea water content, examination of the curves for emulsions of Navy Special fuel oil samples 3 and 12 (Figure 7) indicates that the dielectric loss factor of an emulsion is dependent on the dielectric loss characteristics of the original oil. This method of determining sea water in fuel oil emulsions can be employed, therefore, only when data are obtainable on the original dry oil.

Conductivity. Because of the success of conductivity methods in estimating the salinity of sea water (*4*) and in determining the water content of petroleum products (*10*), it was suggested that this technique might be applied to the measurement of sea water in fuel oil. It was thought that if a given amount of sea water were capable of transporting a known current, then twice as much sea water would conduct proportionately more. Under-

lying this suggestion is the hypothesis that the emulsion remains uniform in a static electric field.

Experiments revealed that this was not the case and that an emulsion subjected to a constant field associated into chains of water droplets. Similar results have been reported by others (*11*). This chainlike formation resulted in high conductivity whenever a chain extended from one electrode to another but in low conductivity when the chain was broken. Because the conduction path was not through the mixture per se but through a sporadically generated path of droplets, neither reproducibility nor constancy in measurement was obtained. For these reasons the direct current conductivity method was abandoned.

In order to study the conductivity characteristics of the emulsions in an alternating electric field, the alternating current resistance was calculated from data taken with the Q meter during the dielectric constant measurements. Examination of this property of the emulsions indicated that the sea water content of fuel oil cannot be determined satisfactorily unless similar data are also obtainable on the dry oil. This is to be expected because the same variables that govern power factor and dielectric loss factor determine the alternating current conductivity characteristics.

SUMMARY AND CONCLUSIONS

This study of certain electrical properties of a number of Navy Special and other fuel oils has revealed that the per cent power factor, dielectric loss factor, and conductivity of the original fuel oils varied widely at comparable frequencies from 50 kc. to 75 Mc. These characteristics of the emulsions responded to changes in sea water content in an orderly manner. However, the relationships were of no practical value in measuring the water content because the actual values obtained were dependent on the characteristics of the original dry fuel oils from which the emulsions were made.

The dielectric constant of these same fuel oils varied considerably from one oil to another at any given frequency from 10 kc. to 75 Mc. The dielectric constant is frequency dependent, decreasing with increasing frequency, indicating that all oils studied contained quantities of polar compounds. It is evident that fuel oils from different sources differ in hydrocarbon composition as well as in content of polar materials.

When the fuel oils are emulsified with synthetic sea water, the dielectric constant increases with an increase in sea water content. The value of the dielectric constant of the emulsion was found to be a function of the dielectric constant of the dry fuel oil. The increase in dielectric constant corresponding to a given increase in sea water content was not always the same if fuel oils from different sources were used. These variables were found to be somewhat less at frequencies near 75 Mc., but they are sufficiently large to introduce serious errors when the dielectric constant is used to determine the sea water content of fuel oil emulsions.

Where an accuracy of $\pm 20\%$ or better is required, the data obtained indicate that the dielectric constant method is inapplicable.

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Spectrophotometric Method for Determination of Sugars

T. E. TIMELL, C. P. J. GLAUDEMANS, and A. L. CURRIE

McGill University and Pulp and Paper Research Institute of Canada, Montreal, Que., Canada

A new method for spectrophotometric determination of sugars involves the use of an acetic acid solution of o-aminodiphenyl. Aldopentoses, aldohexoses, methyl aldopentoses, hexuronic acids, and certain oligosaccharides as well as methylated monosaccharides can be rapidly and accurately estimated in a concentration range of 20 to 500 γ per ml. As Beer's law is strictly followed throughout and both the reagent and color developed are sufficiently stable, estimations can be based on standard curves. Galactose, glucose, and mannose show identical absorptivity, and the same is the case with arabinose, ribose, and xylose. The method has been found useful in conjunction with paper chromatography. The phosphate salt of o-aminodiphenyl in glacial acetic acid is a good spray reagent for paper chromatograms, with a sensitivity higher than that of the aniline salts.

A GREAT variety of methods for determination of microquantities of sugars has been developed within the last few years, especially in connection with paper partition chromatography. If direct photometric procedures (*6*) are disregarded, all of these procedures involve elution of the sugar from the paper with water followed by a quantitative estimation of the sugar content of the extract. The first technique to be adopted for this purpose, and one that is still widely used (*5, 9*), was the Somogyi copper method (*16*), which is applicable to very small amounts of reducing sugars but is not stoichiometric and also requires several steps. Oxidation with hypoiodite is superior in this respect and also has the added advantage of being quantitative for methylated sugars (*11*). Unfortunately, all reducing sugars do not react to completion with this reagent, mannose and rhamnose constituting two notable examples (*7*). Oxidation with sodium periodate and estimation of the formic acid formed, as suggested by Hirst and Jones (*8*), should theoretically be more

accurate. Methylated sugars, however, are not amenable to this treatment; even with free sugars, reproducible results are often difficult to obtain.

Colorimetric (or spectrophotometric) methods generally allow a more accurate and rapid determination of smaller quantities of material than do titration procedures. A number of such techniques have been developed for microanalysis of sugars; an earlier one involves the use of 3,5-dinitrosalicylic acid (*17*); and a more recent one, an adaptation of the Somogyi copper method (*18*). The anthrone–sulfuric acid (*15*) and the phenol–sulfuric acid (*4, 14*) methods have also found widespread use, particularly for oligosaccharides which are hydrolyzed to their constituent sugars under the conditions involved. In spite of the many attractive features of the last mentioned procedures, attempts have been made to avoid the use of concentrated mineral acid. Aniline phthalate has also been tried (*1, 3*), but a better technique seems to be the benzidine method of Jones and Pridham (*13*), which makes use of the yellow color developed when free and methylated reducing sugars are allowed to react with benzidine in glacial acetic acid. The condensation, which probably leads to the formation of an equilibrium mixture of a glycosylamine and the corresponding Schiff base, takes place under relatively mild conditions. Moreover, the color, which is proportional to the amount of sugar present, is very stable.

Unfortunately, the benzidine method has certain disadvantages. The reagent itself is unstable, requiring the addition of a reducing agent such as stannous chloride or potassium sulfite, and ordinary papers used for chromatographic purposes have a tendency to give high blanks unless subjected to special pretreatments (*12*). The chief drawback of the method, however, seems to be the fact that standard sugar solutions have to be analyzed together with the unknown, partly because of the reagent instability, but mostly because the absorbance-concentration relationship is nonlinear below a concentration of 100 γ per ml. The present investigation was undertaken to develop a new procedure which would possess the advantages of the useful benzidine method, but which would allow standard curves to be used over the entire range of concentration desired. Condensation with *o*-aminodiphenyl was eventually found to fulfill these requirements. This compound was also found to be a good spray reagent.

EXPERIMENTAL

Reagents. *o*-Aminodiphenyl, melting point 49.0° C., was obtained from a commercial product (Eastman Kodak Co., Rochester, N. Y.) after two recrystallizations from aqueous ethyl alcohol, charcoal being added to remove color. For the spray reagent, a material recrystallized once was satisfactory.

Analytical grade glacial acetic acid was used without further purification. In several cases the solution of *o*-aminodiphenyl in this solvent was found to be exceedingly unstable; a yellow color formed after boiling for only a few minutes or after standing for 1 or 2 hours. Although several brands were found perfectly satisfactory, caution should always be exercised and any reagent should be rejected which exhibits a transmittance lower than 93 to 95% after boiling for 1 hour, as measured against an untreated solution, the optimum range being 97 to 98%. Solutions containing exactly 0.4% of the amine were prepared shortly before use and, if possible, kept in the dark.

The sugars used for calibration were all crystalline reagent grade qualities, dried in vacuo at room temperature over phosphorus pentoxide prior to use.

When used as a spray reagent, 3.0 grams of *o*-aminodiphenyl was dissolved in 100 ml. of acetic acid, to which was added 1.3 ml. of 85% reagent grade phosphoric acid.

Apparatus. The reaction was carried out in test tubes, 18 × 150 mm.; provided with standard glass stopper No. 19/38. The use of open test tubes and cork stoppers resulted in lower reproducibility. A Beckman Model DU spectrophotometer with a photomultiplier and 1-cm. glass cells was used to measure the absorbance. The slit width was kept constant within 0.08 to 0.10 mm.

Procedure. One milliliter of the aqueous sugar solution, the concentration of which should be within the range of 10 to 500 γ per ml., was transferred with a calibrated pipet to a test tube and 5 ml. of a 0.4% solution of *o*-aminodiphenyl in glacial acetic acid was added from a buret. The test tube was inserted in a boiling water bath, stoppered after 1 minute, and heated for the desired length of time. Analyses were usually carried out in triplicate and duplicate blanks were always included—i.e., 1 ml. of water plus 5 ml. of the reagent. After completion of the reaction, the test tubes were cooled in water and the absorbance was measured at a wave length of 380 mμ against one of the two blanks (which should agree closely). From the average value thus obtained and the known relationship between absorbance and concentration, the amount of sugar present was immediately obtained.

RESULTS AND DISCUSSION

In the attempt to find an aromatic amine with the properties deemed necessary for the present purpose, a variety of compounds were tested in preliminary experiments, such as 1- and 2-naphthylamine and *o*-, *m*-, and *p*-phenylenediamine. Most of these proved unsuitable, either because they gave too high blanks or because the color developed was too unstable. The best reagent was eventually found to be *o*-aminodiphenyl, a compound which, although not commercially available in pure form, could be easily prepared from the technical product. This aromatic amine, when heated in glacial acetic acid to which had been added an aqueous solution of a reducing sugar, condensed with the sugar with the formation of a characteristic color for each class of sugar. The absorption curves obtained with glucose and two blanks are given in Figure 1. Within a range from 360 to 390 mμ, very little change in the absorbance occurred, while at the same time the blanks were low. Accordingly, the intermediate value of 380 mμ was selected as a standard for all future analyses. All sugars, when measured against a blank, exhibited similar curves; three typical ones are reproduced in Figure 2. The time of heating necessary to produce maximum absorbance varied from 30 minutes for aldopentoses and hexuronic acids to 120 minutes for oligosaccharides and higher methylated sugars (see Table II). A few examples of the variation of the absorbance with time are given in Figure 3.

Aldohexoses and some of their methylated derivatives developed the same green color when heated with *o*-aminodiphenyl.

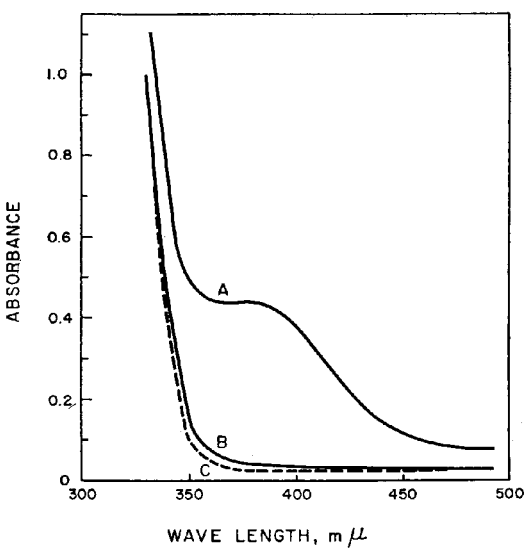

Figure 1. Absorption spectra for glucose and blanks

Reference: 1 ml. of water + 5 ml. of glacial acetic acid
A. 100 γ of glucose
B. Blank heated for 45 minutes
C. Untreated blank

With aldopentoses a yellowish brown color was formed and with hexuronic acids, a yellow one. Rhamnose and some methylated aldohexoses gave light brown solutions. Di- and trisaccharides also produced green solutions except *maltose*, which gave a color intermediate between green and yellow.

The absorbance usually remained constant for the first 24 hours, but after 4 days slightly higher values were noted (Table I); this also indicates the excellent reproducibility. The acetic acid solution of the reagent itself was stable for the first 2 to 3 days when kept in the dark; a slight yellow coloration became noticeable after this time. Addition of potassium sulfite (*12*) had a definite stabilizing effect on the reagent but turned all colors produced by the sugars into a light brown within a few hours, without, however, affecting the absorbance at 380 mμ. As the potassium sulfite was unable to eliminate completely the discoloration of the reagent, it was not added, but rather, new solutions were made every second or third day.

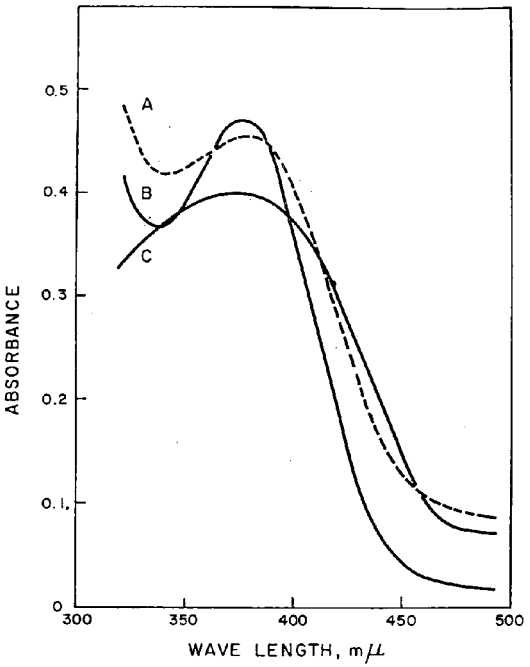

Figure 2. Absorption spectra for 100 γ of sugars measured against blank

A. Glucose
B. Galacturonic acid
C. Xylose

Table I. Change in Per Cent Transmittance with Time

Concn., γ/Ml.	% Transmittance[a]		
	A	*B*	*C*
5	97.7	97.8	95.2
10	93.3	93.7	91.8
20	82.8	83.0	82.5
35	71.5	72.9	70.0
50	60.9	61.8	58.2
75	46.3	46.1	45.2
100	38.6	38.9	36.8
150	22.5	22.2	20.8
200	12.6	12.9	11.9
250	8.47	8.39	7.60
300	5.33	5.00	4.86
350	3.37	3.20	2.71
400	1.94	2.04	1.90
450	1.10	1.10	1.04
500	0.70	0.70	0.78

[a] *A* and *B* are duplicate experiments; *C* are values found for *A* after 92 hours.

Throughout the entire concentration range studied—i.e., 5 to 500 γ per ml.—and with all sugars used, the relationship between the absorbance and concentration was strictly linear. Figure 4 shows that the absorbance also increases with increasing concentration of the reagent, thus making possible the use of smaller quantities of sugars. However, the 0.6% solution was considerably more unstable than the more dilute ones and this, together with the fact that it did not allow estimation of quantities of sugars larger than 300 γ, made the lower concentration of 0.4% more suitable. The fact that Beer's law was so closely followed made it possible to base the method on standard curves obtained for each sugar. Some examples are presented in Figure 5, where all the curves are based on experimental data obtained at 15 different concentrations, each measured in duplicate from duplicate sets of standard solutions from each concentration as indicated in Table I.

A summary of the characteristics of each sugar is presented in Table II. The three aldohexoses show similar absorptivity, as also do the aldopentoses, whereas the absorptivities of rhamnose and galacturonic acid are somewhat higher. The condensation product with glucurono-γ-lactone has a surprisingly strong absorptivity, which was the more unexpected as the absorptivity of the same compound when condensed with benzidine (*13*) was much lower than those of both aldopentoses and hexoses. Cellobiose and lactose can be estimated with the same accuracy as the monosaccharides but maltose, melibiose, and sucrose require somewhat larger quantities for a similar absorbance. Melezitose and

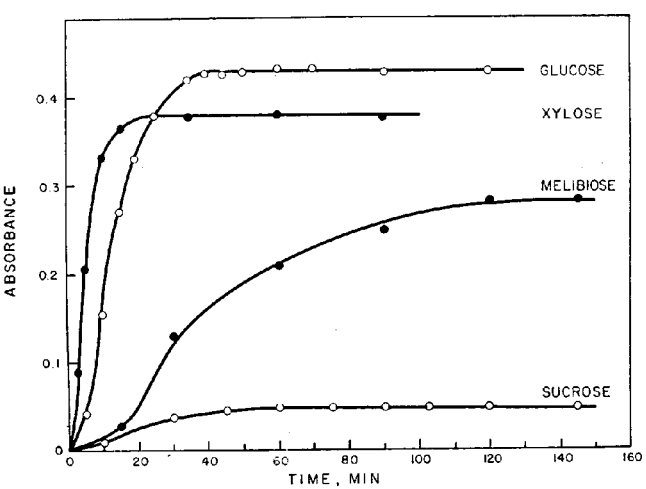

Figure 3. Change in absorbance with time of heating in boiling water bath

Sugar concentration, 100 γ per ml.

raffinose exhibit even lower absorptivity, while the method is completely inapplicable to fructose (*2*). 3-*O*-Methyl- and 6-*O*-methyl-D-glucose can both be determined as accurately as glucose but the 2-*O*-methyl derivative, which also gives a different color, has a lower absorptivity. Tetra-*O*-methyl glucose and the tri-*O*-methyl ethers of galactose and xylose exhibit a low absorptivity.

For an estimation of the accuracy of the procedure, seven standard solutions of glucose, ranging in concentration from 10 to 500 γ per ml., were each subjected to 40 to 50 separate analyses. Standard deviations and probable errors for a single measurement are summarized in Table III. The method is evidently useful for quantitative determination of glucose within a range of 20 to 500 γ per ml., with a probable error of ± 2 to 4% for concentrations below 100 γ per ml. and ± 1% for concentrations above that value. In actual practice, several analyses are usually carried out for each sugar solution, and under these circumstances the accuracy will be increased. In two test experiments two known mixtures of glucose, mannose, and xylose were separated on the paper chromatogram with the aid of two different solvent systems, the sugars eluted from the paper in the usual way, and analyzed as above. Five determinations were carried out in each case for both the sugars and the paper blanks. The latter exhibited 100% transmittance throughout when read against a reagent blank and no pretreatments of the paper were necessary in this particular case. However, it should be mentioned that later experience with other batches of Whatman No. 1 filter paper indicated the presence of a noticeable paper blank which could only be eliminated by thorough washing with distilled water prior to use. The results of the sugar analyses (Table

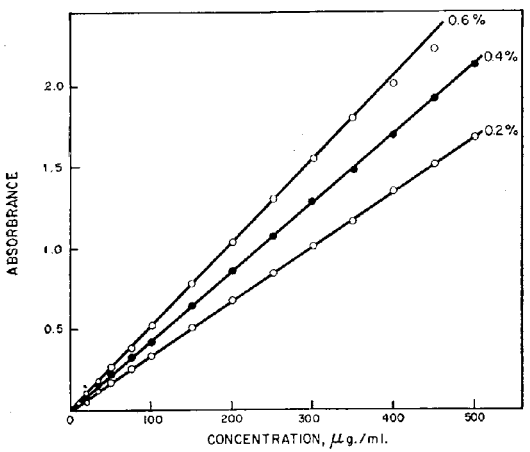

Figure 4. Change in absorbance with concentration of glucose at three reagent concentrations

Table II. Optical Properties of Glycosylamines of Various Sugars

Sugar	Color	Wave Length for Maximum Absorption, Mμ	Minutes of Heating Necessary for Maximum Absorption	γ per Ml. per 10^{-2} Absorbance Units[a]
Arabinose	Brownish yellow	370	30	2.62
Ribose	Brownish yellow	370	30	2.62
Xylose	Brownish yellow	375	30	2.62
Galactose	Green	380	45	2.33
Glucose	Green	380	45	2.33
Xylose	Green	380	45	2.33
Rhamnose	Brown	375	45	2.17
Galacturonic acid	Yellow	380	30	2.03
Glucuronolactone	Yellow	375	30	1.40
Cellobiose	Green	380	60	2.50
Lactose	Green	375	90	2.37
Maltose	Greenish yellow	380	120	3.45
Melibiose	Greenish yellow	375	120	3.53
Sucrose	Greenish yellow	380	60	4.22
Melezitose	Green	380	120	5.55
Raffinose	Green	380	120	5.37
2-*O*-Methyl-D-glucose	Brownish yellow	370	90	4.10
3-*O*-Methyl-D-glucose	Green	380	45	2.56
6-*O*-Methyl-D-glucose	Green	375	60	2.90
2,3,4,6-Tetra-*O*-methyl-D-glucose	Green	375	120	6.14
2,4,6-Tri-*O*-methyl-D-galactose	Yellow	370	120	5.07
2,3,4-Tri-*O*-methyl-D-xylose	Brown	375	120	5.07

[a] Calculated on anhydrous sugar.

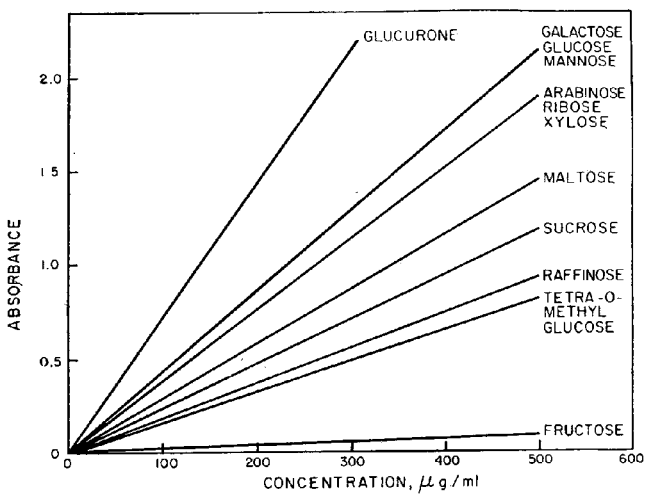

Figure 5. Absorbance *vs.* concentration for some sugars studied

Table III. Standard Deviation and Probable Error for Various Concentrations of Glucose

Concn., γ per Ml.	Std. Dev., %	Probable Error, %
10	15.0	10.0
20	6.0	4.0
50	3.0	2.0
100	1.6	1.1
200	1.5	1.0
350	1.2	0.8
500	1.8	1.2

Table IV. Sugar Recoveries after Separation in Two Different Solvent Systems

(Whatman No. 1 paper used)

Solvent System	Glucose, γ/ml.		Mannose, γ/ml.		Xylose, γ/ml.	
	Applied	Found	Applied	Found	Applied	Found
Pyridine–butyl alcohol–water (10 to 3 to 3)	100.0	100.5	100.0	100.0	100.0	101.0
Ethyl acetate–acetic acid–water (9 to 2 to 2)	112.0	111.0	96.2	97.0	70.0	70.3

IV) show that the accuracy attainable was satisfactory, 100 ±0.5% of the sugars being accounted for.

The *o*-aminodiphenyl also proved to be an excellent spray reagent for paper chromatograms. When used as the phosphate salt in acetic acid solution, its sensitivity is considerably higher than that of the aniline phthalate of phosphate (*10*). With light spraying and drying for 1 to 2 minutes at 105° C., brilliantly colored spots are produced on an almost white background with all sugars listed in Table II except fructose, melezitose, and raffinose. Aldohexoses and rhamnose give dark brown, aldopentoses bright red, and hexuronic acids an orange color, the latter changing to purple after heating for an additional 1 or 2 minutes. Unsubstituted monosaccharides, when applied directly to a paper and sprayed, could be detected with this reagent in quantities as small as 0.1 γ.

ACKNOWLEDGMENT

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Spectrophotometric Determination of Traces of Water in Acetic Acid

STANLEY BRUCKENSTEIN

School of Chemistry, University of Minnesota, Minneapolis, Minn.

During studies on acid-base reactions in acetic acid it became necessary to determine the water content of acetic acid containing approximately 0.001% water. As this is the lower limit for the Karl Fischer method using the visual end point, a 10 times more sensitive method was developed based on the reaction between acetic anhydride and water. The method involves adding acetic anhydride, heating for 90 minutes at 110° C., and determining the amount of unreacted acetic anhydride spectrophotometrically.

SEVERAL physical methods have been used to determine the purity of glacial acetic acid. The properties most used to check the purity of this solvent are freezing point, density, and specific conductance. The density is least sensitive, as solvent containing 1% water has a density approximately 7 parts per thousand lower than the anhydrous acid (*3*).

De Visser (*1*) found that 0.1% water lowered the freezing point of acetic acid 0.2° C., so that if an accuracy of a 0.01° C. is attained, as little as 0.005% water can be detected (provided water is the only impurity present). Kolthoff and Wilman (*5*) found the effect of water on the equivalent conductance to be small; 0.0485% water changed the equivalent conductance from 0.060 to 0.065 × 10^{-7} mho at 25°. Wilman (*6*) pointed out that samples of acetic acid with the same apparent melting point gave equivalent conductances which varied from 0.05 to 0.08 × 10^{-7} mho, an indication that the conductance method is not reliable for estimating water content.

The exact water content of acetic acid is of great importance when dissociation constants for acids and bases are to be determined. The visual Karl Fischer method gives satisfactory results for water contents above 0.01%, but for lower concentrations of water the uncertainty in the end point corresponds to about 0.001% water. Acetic anhydride absorbs appreciably at 2520 A., and a method has been developed based on the reaction of acetic anhydride with water. Experiments indicated that the reaction does not proceed at a measurable rate in 3 hours at

room temperature, but is quantitative at the end of 90 minutes at 110° C.

EXPERIMENTAL

Apparatus. All spectrophotometric measurements were obtained with a Cary recording spectrophotometer using 2-cm. quartz cells with ground-glass stoppers. Acetic acid was stored and dispensed as described previously (*4*).

Reagents. Acetic acid was purified and dried according to the method of Eichelberger and LaMer (*2*), which involves preliminary treatment of a C.P. material with chromium trioxide, drying with triacetyl borate, and, finally, fractional distillation.

Acetic Anhydride. A C.P. product was used.

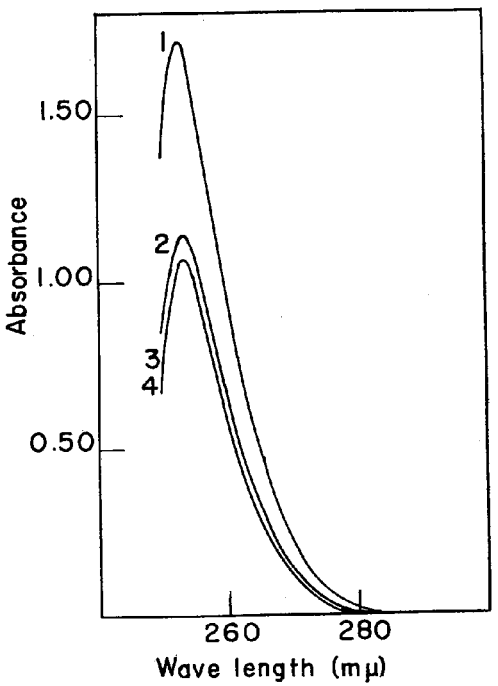

Figure 1. Spectra of acetic anhydride

1. Spectrum of 0.0247 *M* acetic anhydride in acetic acid. Cell length = 2.00 cm.
2. Same as 1, plus sufficient water to increase water content by $9.26 \times 10^{-3} M$, heated at 110° for 30 minutes
3. Same as 2, heated 60 minutes
4. Same as 3, heated 90 minutes

Development of Procedure. Curve 1 of Figure 1 represents the observed spectrum of 0.0247 *M* acetic anhydride in acetic acid. A maximum is observed at 2520 A., but because the slit of the spectrophotometer is opening rapidly and is wide open at 2500 A., the true molar absorptivities in this region are considerably higher than would be indicated by this curve. Beer's law is followed at 2520 A., and a molar absorptivity of 36.6 liters per mole-cm. was found. One milligram of water was added to the cell, corresponding to an increase of water content of $9.26 \times 10^{-3} M$, and the cell was allowed to stand for 3 hours at room temperature. No change in the spectrum was detectable, proving that the reaction of water with acetic anhydride does not proceed at a significant rate in pure acetic acid.

Curve 2 represents the spectrum obtained after the cell and contents have been heated at 110° C. for 30 minutes and cooled to room temperature. Curve 3 corresponds to a total heating time of 60 minutes. Curve 4, which is identical with curve 3, corresponds to a total heating time of 90 minutes. These data show that the reaction is substantially complete after 1 hour. A heating time of 90 minutes was chosen to allow a large safety margin in the actual analytical method.

The stoichiometry of the reaction was checked and the water content of a sample of acetic acid was determined.

Six milliliters of acetic acid was placed in a previously dried quartz cell and the blank absorbance determined at 2520 A. Using an ultramicroburet, 0.148 mmole of acetic anhydride was added, and the absorbance was determined before and after heating for 90 minutes at 110° C. This difference in absorbance corresponds to the amount of acetic anhydride which reacted with water. Then 0.0555 mmole of water was added, the solution was reheated to 110° C. for an additional 90 minutes and cooled, and the absorbance was noted. This difference in absorbance corresponds to the amount of acetic anhydride which reacted with 0.0555 mmole of water.

The actual experimental data are given in Table I.

Table I. Determination of Water in Acetic Acid by Acetic Anhydride Method

Operation	Absorbance at 2520 A.
Add 0.148 mmole Ac_2O.	1.83
Heat 1.5 hours at 110°, cool.	1.77
Add 0.0555 mmole H_2O, reheat, cool.	1.10

Calculations. Water present = (0.06/0.67) × 0.0555
= 0.005 mmole/6 ml. AcOH
= 0.0015% by volume

The water content found, 0.0015%, is in satisfactory agreement with the value estimated by the visual Karl Fischer method, 0.001 to 0.002%. The stoichiometry is as expected, 0.0555 mmole of water reacting with 0.054 mmole of acetic anhydride. Quintuple analyses of several samples of acetic acid containing approximately 0.002 *M* water have agreed to within 5%.

As a routine method for the determination of water in acetic acid it is not absolutely necessary to add a known amount of water after the first heating, the quantity of water being calculated from the amount of acetic anhydride which disappears and the molar absorptivity. In view of the rather large slit widths necessary at the wave length used, it does not seem advisable to place much faith in the reproducibility of the molar absorptivity of acetic anhydride on a given spectrophotometer over a long period of time. Therefore, the addition of a known amount of water is recommended, as it prevents instrument errors resulting from nonreproducible slit widths. It also makes unnecessary the use of 100% pure acetic anhydride, as this operation automatically determines the purity of acetic anhydride which is used.

The method is also suited for determining acetic anhydride in acetic acid, and was used to establish the absence of acetic anhydride in acetic acid as purified according to the method of Eichelberger and LaMer (*2*).

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Spectrophotometric Determination of Δ^4,3-Ketosteroids

DENIS ABELSON[1] and PHILIP K. BONDY

Departments of Medicine and Physiology, Yale University School of Medicine, New Haven, Conn.

A method is described for the spectrophotometric determination of Δ^4-3-ketosteroids. These substances react with potassium *tert*-butoxide in *tert*-butyl alcohol to produce a yellow color with absorption maxima at 260 and 385 mμ. The absorbance at 385 mμ varies with steroid concentration in accordance with Beer's law. The method is sensitive to 1 to 2γ of steroid. Estriol, estradiol, and estrone show absorption maxima at 250 and 310 mμ with the potassium butoxide reagent.

MOST quantitative chemical procedures for the determination of corticosteroids depend on properties of either the side chain or the Δ^4,3-ketone grouping. In addition, numerous qualitative or semiquantitative spot tests exist for the detection of corticosteroids of paper chromatograms. It has recently been shown (*1*) that the sodium hydroxide spot test for Δ^4,3-ketosteroids (*2*) may be adapted to the quantitative fluorometric estimation of these compounds in anhydrous solution. The spot test is based on the production of an orange-yellow fluorescence in ultraviolet light when Δ^4,3-ketosteroids on paper chromatograms are sprayed with 10% sodium hydroxide solution and allowed to dry. For the quantitative reaction the most suitable alkali was found to be potassium *tert*-butoxide dissolved in *tert*-butyl alcohol. A yellow color was observed in the solution when concentrations greater than about 10 γ of Δ^4,3-ketosteroid per ml. of reagent were used. This finding has been utilized in a spectrophotometric procedure for the quantitative analysis of Δ^4,3-ketosteroids.

EXPERIMENTAL

Reagent. Approximately 1 gram of metallic potassium is heated with *tert*-butyl alcohol for about 2 minutes, then washed with several rinses of *tert*-butyl alcohol. It is then refluxed in all-glass apparatus with about 40 ml. of *tert*-butyl alcohol under nitrogen until completely dissolved. The reagent is stored in a vacuum desiccator until use.

Preparation of Steroid Samples. The crystalline steroids were analyzed as received without further purification. When $E_{max.}$ measurements were to be made, the steroids were dried for 2 weeks over calcium chloride in a vacuum desiccator, weighed out in approximately 10-mg. quantities on an analytical balance, and made up to volume in volumetric flasks with absolute ethyl alcohol. The $E_{max.}$ of the alcoholic solutions at 240 to 242 mμ was compared with published values (*5*). In every case the observed $E_{max.}$ agreed with the published figures within 5%.

Apparatus. Spectrophotometric measurements were made with a Beckman DU spectrophotometer, using 1.000-cm. matched silica cells. Constant sensitivity was maintained by varying the slit width.

RESULTS

The absorption spectra of steroids containing the Δ^4,3-ketone configuration showed maxima at 260 and 385 mμ (Figure 1). Several steroids lacking the Δ^4,3-ketosteroid configuration absorbed in the region from 240 to 260 mμ, but, with the exception of cholestane-3,6-dione, only those steroids which contained the Δ^4,3-ketone grouping showed a maximum at 385 mμ. The maximum at 385 mμ was unchanged in position after standing for 2 hours at room temperature, whereas the maximum at the lower wave lengths shifted in some cases as much as 10 mμ in either direction on standing. Table I gives the absorbances of a number of steroids at 385 mμ, using a concentration of 20 γ per ml. In the absence of the Δ^4,3-ketone grouping, the absorbance did not usually exceed that of the reagent blank; in the few cases where a small reading was obtained, the absorption maximum was at a shorter wave length than 385 mμ. In the case of cholestane-3,6-dione, however, an absorption maximum was found at 385 mμ, the molar extinction coefficient being of the same order as that obtained with Δ^4,3-ketones.

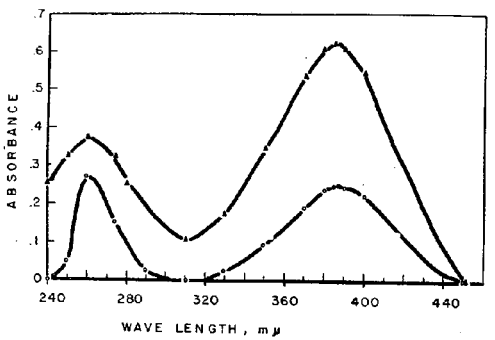

Figure 1. Absorption spectra of 17-hydroxycorticosterone (22.5 γ per ml.) in 0.3*N* potassium *tert*-butoxide reagent

Lower curve made after 10 minutes and upper curve made after 2 hours at room temperature

The rate of color development behaved in the same general manner as the fluorescence; thus 17-hydroxycorticosterone was the slowest steroid to reach both maximum fluorescence and maximum absorption, whereas 11-dehydrocorticosterone was the most rapid. There was more variation in the rate of color development than fluorescence development, and the latter in most cases was more rapid.

Table I. Absorbance at 385 mμ Produced after 1 Hour by 10 γ of Steroids in 0.5 Ml. of 0.1*N* Potassium *tert*-Butoxide Solution

	Absorbance[a]
Saturated	
Androstane-3,17-dione	0.024 (max. = 335 mμ)
Pregnane-3α,20α-diol (pregnanediol)	0.006
Pregnane-17α,21-diol,3,11,20-trione (dihydrocortisone)	0.062 (max. = 342 mμ)
Pregnane-3α,17α,21-triol,11,20-dione (tetrahydrocortisone)	0.006
Cholestane-3,6-dione	0.311 (max. = 385 mμ)
Δ^5-enes	
Cholesterol	0.000
Δ^5-Androstene-3β-ol,17-one (dehydroepiandrosterone)	0.000
Δ^1-ene-3-ones	
Δ^1-Cholestene-3-one	0.000
Δ^4-ene-3-ones	
Δ^4-Androstene-3,17-dione	0.460
Δ^5-one-7-ones	
7-Ketocholesteryl acetate	0.014
$\Delta^{8(9)}$-ene-7-ones	
$\Delta^{8(9)}$,^{22}-Ergostadiene-3-ol-7-one	0.023 (max. = 265 mμ)
$\Delta^{9(11)}$-ene-12-ones	
3-Hydroxy-12-keto-$\Delta^{9(11)}$-cholenic acid	0.000

[a] Read against butoxide blank in silica microcuvettes with 1-cm. light path.

[1] Present address, Department of Medicine, Postgraduate Medical School, Hammersmith Hospital, London, England.

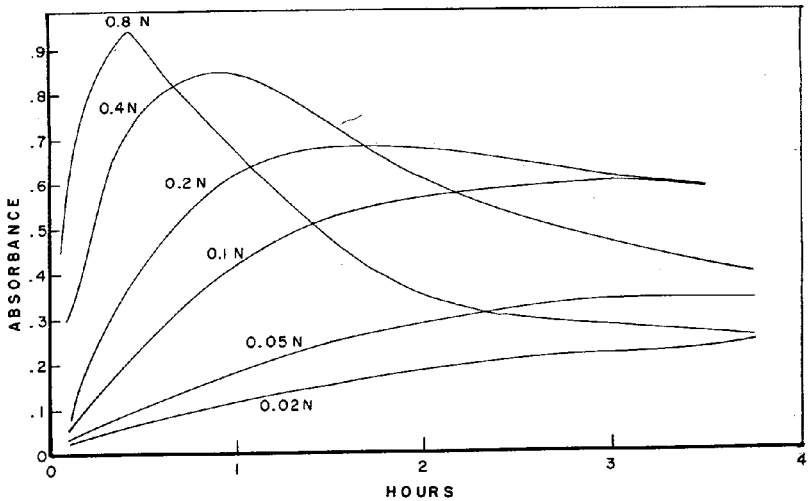

Figure 2. Effect of base concentration on rate and intensity of color development

17-Hydroxycorticosterone, 30.6γ per ml.

The rate of color development was also found to depend on base concentration in the same way as the rate of fluorescence development. In strongly alkaline solutions color development was more rapid, whereas in weaker solutions it was retarded (Figure 2). For routine purposes absorbance was most conveniently measured at 1 hour, using 0.4*N* butoxide solution.

For a given steroid, if the base concentration and time of color development were kept constant, the absorbance at 385 mμ varied with steroid concentration in accordance with Beer's law. Values of $E_{max.}$ for a number of Δ^4,3-ketosteroids in 0.4*N* butoxide are given in Table II. Because of the variation in both rate of color development and $E_{max.}$ values, the method is not suitable for analyzing mixtures of steroids. With single steroids the technique is highly reproducible, as the standard

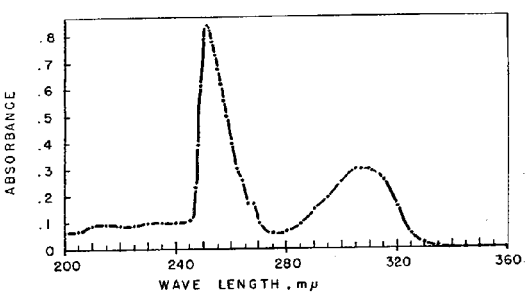

Figure 3. Absorption spectrum of estradiol (26.3 γ per ml.) in 0.3*N* potassium *tert*-butoxide reagent after 2 hours at room temperature

deviation calculated from six replicates of a single steroid solution was ±2.5% of the mean value.

Estradiol, estrone, and estriol, which normally absorb maximally at 280 mμ in neutral ethyl alcohol, showed absorption peaks at 250 mμ and 305 to 310 mμ in the potassium *tert*-butoxide solution (Figure 3). The $E_{max.}$ at 310 mμ after 2 hours in 0.3*N* potassium butoxide was approximately 3580 for estradiol, 3800 for estrone, and 3060 for estriol. At 250 mμ under identical conditions, the $E_{max.}$ for estradiol was 8820, for estrone 9360, and for estriol 7860.

DISCUSSION

The color produced by Δ^4,3-ketosteroids in potassium *tert*-butoxide appears to have the same significance as the fluorescence that develops in a parallel fashion, and it is possible that both are properties of the same structural grouping. The nature of this structural grouping has not yet been elucidated.

Results similar to those reported above were also obtained by Cross, Eisen, and Kedersha (*4*), who noted a maximum near 375 mμ for a number of Δ^4,3-ketosteroids after heating in 1.1*N* aqueous tetramethylammonium hydroxide. Meyer found a maximum near 380 mμ with Δ^4,3-ketones on exposure to alkaline ethyl alcohol at 23° and/or 60° C. (*7*). In both studies the maxima were much less intense than those reported here, and at a slightly different wave length. These differences are probably related to the different solvents used, and particularly to the use of aqueous solutions. Both the fluorescence and the color reaction with the butoxide reagent are strongly inhibited in the presence of water; indeed, the presence of as little as 0.1%

Table II. Values of $E_{max.}$[a] for Some Δ^4-3-Ketosteroids in 0.4*N* Potassium *tert*-Butoxide Solution

	$E_{max.}$
Testosterone	7,200
Progesterone	7,200
11-Desoxycorticosterone	5,600
11-Dehydrocorticosterone	7,800
17-Hydroxy,11-dehydrocorticosterone	8,760
17-Hydroxy,11-dehydrocorticosterone acetate	8,100
Corticosterone	11,000
17-Hydroxycorticosterone	10,300

[a] Development of color was followed in a Coleman Junior spectrophotometer until absorbance had reached a maximum. The solution was then transferred to a 1.0-cm. silica microcuvette, and the absorbance measured at 385 mμ in a Beckman DU spectrophotometer. $E_{max.}$ = absorbance at 385 mμ in 0.4*N* potassium butoxide solution/mole/liter/1-cm. light path.

water in the system produces appreciable changes in the relative intensity and location of the ultraviolet peaks.

The presence of a peak near 310 mμ in alkaline solutions of estrogens has previously been reported by Pedersen-Bjergaard and Schou (*8*), Hamburger (*6*), and Callow (*3*), and attributed by the last to the formation of a phenoxy salt in ring A. The peak at 250 mμ has not previously been reported, to the authors' knowledge, although Hamburger's curves show a continuous increase in absorbance as the wave length decreased to 250 mμ.

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Hydrocarbons in the 126° to 132° C. Fraction of Petroleum

MORTON B. EPSTEIN[1], CHARLES B. WILLINGHAM[2], BEVERIDGE J. MAIR, and FREDERICK D. ROSSINI

Carnegie Institute of Technology, Pittsburgh 13, Pa.

Seven hydrocarbons were found in the fraction of petroleum normally boiling between 126° and 132° C., which constitutes approximately 0.68% by volume of the representative petroleum that has been under investigation for many years by the API Research Project 6. These compounds were concentrated by extended use of the fractionating processes of distillation (both regular and azeotropic) and adsorption. The compounds were identified by infrared and mass spectrometric examination, coupled with measurements of the simple physical properties. The names and estimated relative amounts of the seven compounds in this fraction of petroleum, given in decreasing order of quantity, are: ethylcyclohexane, 53; 1-*trans*-2-*cis*-3-*trans*-4-tetramethylcyclopentane, 16; 1-*cis*-2-dimethylcyclohexane, 9; *n*-propylcyclopentane, 9; 1-methyl-*cis*-2-ethylcyclopentane, 6; 2,3,5-trimethylhexane, 5; and isopropylcyclopentane, 2.

AS PART of the continuing work of the American Petroleum Institute Research Project 6 on the composition of its representative petroleum (*7*), analysis has been completed of the hydrocarbons in that fraction of the petroleum normally boiling between 126° and 132° C., which constitutes approximately 0.68% by volume of the original crude. The status of this material prior to the present investigation is described in previous papers (*4*, *6*). The details of the analysis of the hydrocarbons in the adjacent lower-boiling fraction of this petroleum are given in another paper (*3*).

DETAILS OF PROCESSING

All of the material from the previous work, except a small amount of ethylcyclohexane, was blended and distilled to obtain in one lot all of the material from the original petroleum remaining in the range boiling normally from 126° to 132° C. The results of this distillation are given in Figure 1, which shows the location with respect to boiling point and refractive index of the compounds found in this material. It is apparent that the first portion of the distillate consisted largely of *n*-octane, which normally boils slightly below 126° C., and the portion just before the tail end consisted largely of ethylcyclohexane, which normally boils just below 132° C. The present analysis includes ethylcyclohexane but not *n*-octane, which is covered in the analysis of the next lower-boiling material (*3*).

The material was processed by distillation (regular, azeotropic, and at reduced pressure) and by adsorption in a sequence designed to concentrate the individual hydrocarbon compounds so that they could be identified with reasonable certainty. The amounts of the individual compounds were computed from the results of spectrographic analyses made on appropriate intermediate and final fractions by the Research Laboratory of the Humble Oil and Refining Co.

The processing of the material by distillation, following the distillation shown in Figure 1, is summarized as follows (see *8* for details of the distilling apparatus and procedures):

Lot 1-B, from Figure 1, Part B, 1870 ml., was distilled at 725 mm. of mercury. The results are shown in Figure 2, Part I.

Lot 2-I-C, from Figure 2, Part I-C, 1460 ml., was distilled at 56 mm. of mercury. The results are shown in Figure 2, Part II.

Lot 2-II-A, from Figure 2, Part II-A, 505 ml., was distilled azeotropically with ethylene glycol monoethyl ether (Cellosolve) at 725 mm. of mercury. The results are shown in Figure 2, Part III.

Lot 2-II-B, from Figure 2, Part II-B, 400 ml., was also distilled azeotropically with ethylene glycol monoethyl ether at 725 mm. of mercury. The results are shown in Figure 2, Part IV.

Lot 2-II-C plus 2-IV-A, from Figure 2, Part II-C plus Part IV-A, 580 ml., was also distilled azeotropically with ethylene glycol monoethyl ether at 725 mm. of mercury. The results are shown in Figure 2, Part V.

Lot 2-III-B, from Figure 2, Part III-B, 285 ml., was distilled at 725 mm. of mercury. The results are shown in Figure 3, Part I.

Lots 3-I-A and 3-I-C, from Figure 3, Parts I-A and I-C, plus cycloparaffin concentrates separated from Lot 1-A, from Figure 1, and Lot 2-III-A, from Figure 2, total charge of 250 ml., were distilled regularly at 725 mm. of mercury. The results are shown in Figure 3, Part II.

Lots 3-I-B and 3-II-B, from Figure 3, Parts I-B and II-B, 205 ml., were distilled azeotropically at 725 mm. of mercury. The results are shown in Figure 3, Part III.

Lot 2-V-A, from Figure 2, was further fractionated by adsorption with silica gel in a tall column (1 by 790 cm.) to give the results shown in Figure 4 (see *5* for details regarding the apparatus and procedure for fractionation by adsorption).

In the foregoing, the lots of material are identified with reference to the figure in which the results are plotted. Thus, Lot 2-I-B refers to Figure 2, Part I, Portion B.

[1] Present address, Onyx Oil and Chemical Co., Jersey City, N. J.
[2] Present address, Mellon Institute of Industrial Research, Pittsburgh 13, Pa.

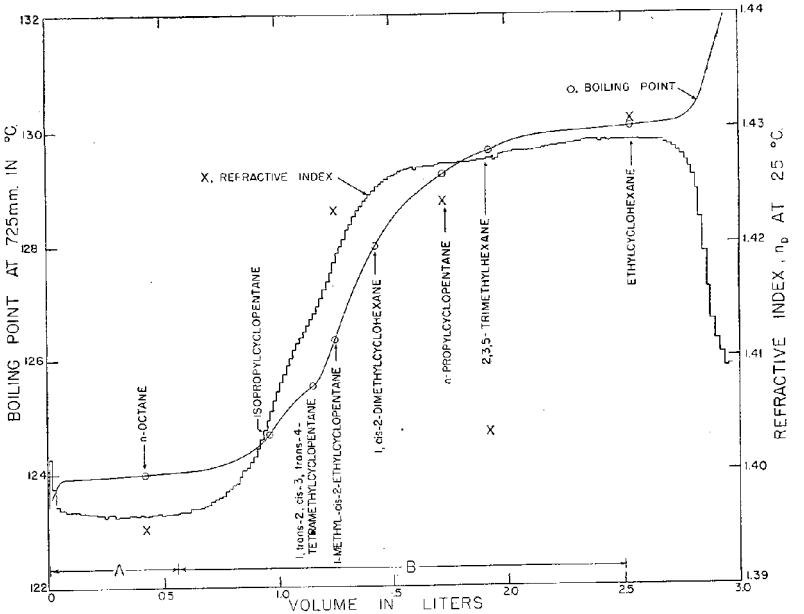

Figure 1. Results of regular distillation of 126° to 132° C. fraction of petroleum

Table I. Results of Spectrographic Analysis of Selected Lots[a]

Lot[b]	Compounds															
	n-Octane		Isopropyl-cyclopentane		1-*trans*-2-*cis*-3-*trans*-4-tetra-methylcyclo-pentane		1-Methyl-*cis*-2-ethylcyclo-pentane		1-*cis*-2-Dimethyl-cyclohexane		*n*-Propylcyclo-pentane		2,3,5-Trimethyl-hexane		Ethyl-cyclo-hexane	
	% by Volume in Lot															
	IR	M	IR	M	IR	M	IR	M	IR	M	IR	M	IR	M	IR	M
3-II-A	63	64	15	13	21	21	1	1								
3-II-C[c]					37	38	29	33	13	12	1	1				
3-III-B					45	41	52	54	0	1	2	2				2
4-A[c]					5		5		45	45	1		11		3	
4-B					2	0	1	7	13	17	49	48	16	14	8	11

[a] Spectrographic analyses made by Research Laboratory, Humble Oil and Refining Co., Baytown, Tex. Values in columns headed IR were obtained from infrared measurements. Values in columns headed M were obtained from mass spectrometer measurements.
[b] Lots identified in Figures 3 and 4. 3-II-A refers to Figure 3, Part II, Portion A.
[c] Spectrometric examination indicated that these samples contained an unidentified constituent, probably another tetramethylcyclopentane.

RESULTS OBTAINED

The distillation shown in Figure 1 served principally to separate the bulk of the *n*-octane at the front end and ethylcyclohexane near the tail end from the remaining six compounds. A small additional amount of ethylcyclohexane was separated at the tail end of the azeotropic distillation, which is shown in Figure 2, Part I. The distillation at reduced pressure (Figure 2, Part II) effected a considerable separation of the remaining material. The azeotropic distillation shown in Figure 2, Part III, concentrated 1-*trans*-2-*cis*-3-*trans*-4-tetramethylcyclopentane in the middle portion of the distillate and the 1-methyl-*cis*-2-ethylcyclopentane in the final portion. The azeotropic distillations shown in Parts IV and V of Figure 2 gave a portion (Lot 2-V-A) consisting almost entirely of 1-*cis*-2-dimethylcyclohexane, *n*-propylcyclopentane, and 2,3,5-trimethylhexane. Figure 3 gives the results of the distillation operations required to obtain the best sample (Lot 3-III-A) of 1-*trans*-2-*cis*-3-*trans*-4-tetramethylcyclopentane, and a concentrate (Lot 3-III-B) of 1-methyl-*cis*-2-ethylcyclopentane. The adsorption experiment shown in Figure 4 served to separate 1-*cis*-2-dimethylcyclohexane from *n*-propylcyclopentane.

The results of the spectrographic analyses are given in Table I. The spectrographic analyses were straightforward for six of the compounds, as API Standard samples of these were available. For 1-*trans*-2-*cis*-3-*trans*-4-tetramethylcyclopentane, no standard sample was available and the isolated sample, estimated to have a purity of 90 mole % was used for calibration for this compound. From the values of the simple physical properties of the C_8 and C_9 alkyl cyclopentanes given by the API Research Project 44, the identity of this compound appears certain (*1*). The spectrographic data were used in conjunction with the data on boiling points and refractive index as a function of volume to estimate the relative amounts of the individual components.

Table II summarizes the information regarding the seven hydrocarbon compounds found in the 126° to 132° C. fraction of petroleum, giving the name and formula of the compound, the normal boiling point of the pure compound, the highest concentration of the given compound isolated, the lot in which the highest concentration was found, the estimated relative amount of the given compound in the 126° to 132° C. fraction of this petroleum, and the estimated amount by volume of the given compound in the original petroleum. It is seen that the 126° to 132° C. frac-

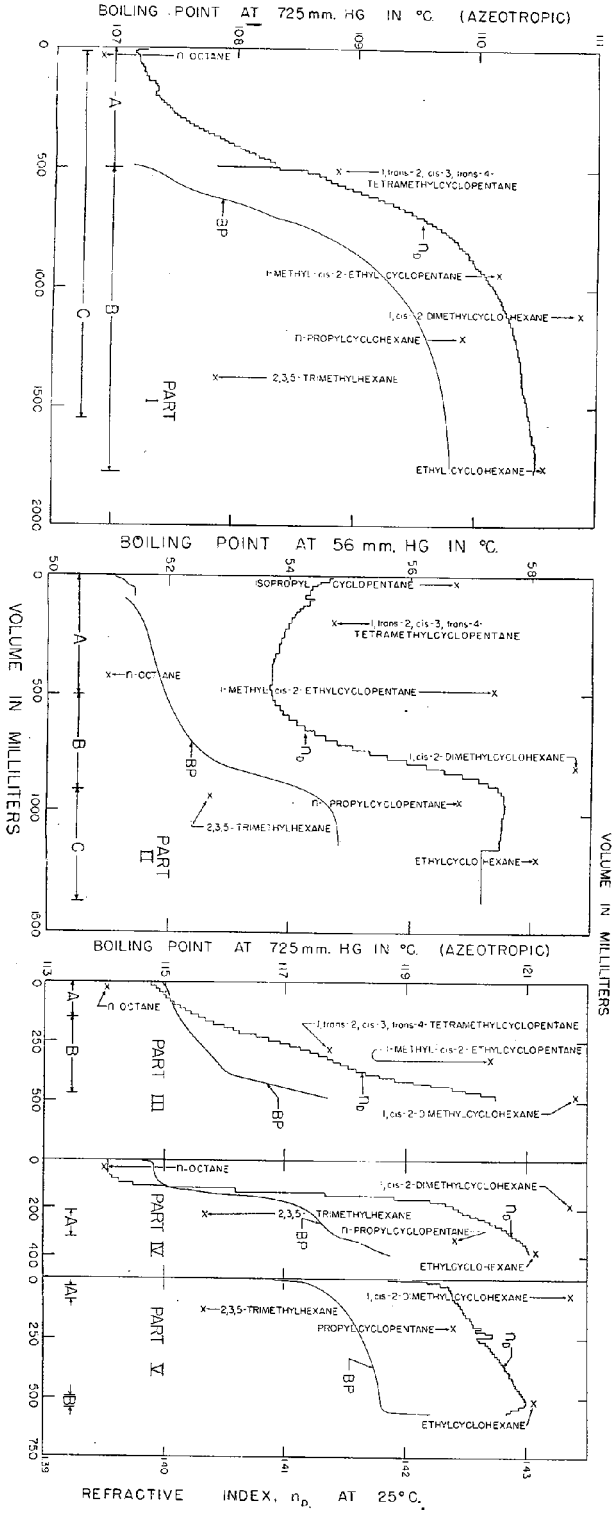

Figure 2. Results of distillation of Lots 1-B, 2-I-C, 2-II-A, and 2-IV-A

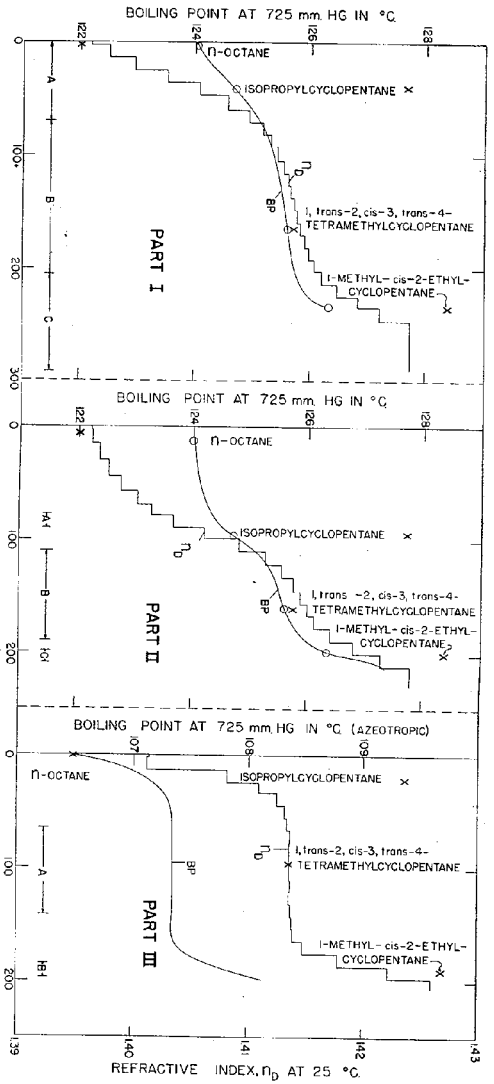

Figure 3. Results of distillation of Lot 2-III-B, involving concentration of 1-*trans*-2-*cis*-3-*trans*-4-tetramethylcyclo pentane

Table II. Summary of Seven Hydrocarbons Found in 126° to 132° C. Fraction of Petroleum

Compound Name	Formula	Boiling Point of Pure Compound at 1 Atm., ° C.	Highest Concn. Isolated, Mole %	Highest Concn. Found in Lot	Estd. Relative Amount of Given Compound by Vol.	Estd. Amount in Original Petroleum, Vol. %
Isopropylcyclopentane	C_8H_{16}	126.42	15	3-II-A	2	0.01
1-*trans*-2-*cis*-3-*trans*-4-tetramethylcyclopentane	C_9H_{18}	127.4	90	3-III-A	16	0.11
1-Methyl-*cis*-2-ethylcyclopentane	C_8H_{16}	128.05	52	3-III-B	6	0.04
1-*cis*-2-Dimethylcyclohexane	C_8H_{16}	129.73	45	4-A	9	0.06
n-Propylcyclopentane	C_8H_{16}	130.95	49	4-B	9	0.06
2,3,5-Trimethylhexane	C_9H_{20}	131.34	16	4-B	5	0.03
Ethylcyclohexane	C_8H_{16}	131.78	94	2-V-B	53	0.37
Total					100	0.68

tion of this petroleum is estimated to constitute 0.68% by volume of the original petroleum. The analyses reported by Bell (*2*) for an East Texas petroleum compare favorably with the results of this investigation.

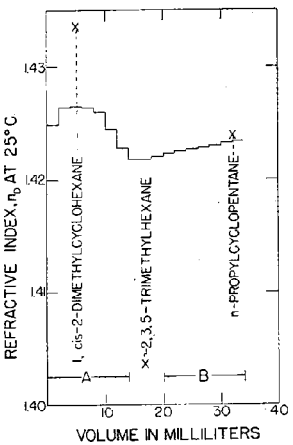

Figure 4. Results of fractionation of Lot 2-V-A by adsorption, involving separation of 1-*cis*-2-dimethylcyclohexane and *n*-propylcyclopentane

In addition to the seven hydrocarbon compounds found, the only other hydrocarbons of the paraffin, alkyl cyclopentane, and alkyl cyclohexane classes normally boiling in the range 126° to 132° C. are the following (*1*): 2,2,4-trimethylhexane at 126.54° C.; 2,4,4-trimethylhexane at 130.65° C.; 1,1-*cis*-2-*cis*-4-tetramethylcyclopentane and 1,1-*cis*-2-*trans*-4-tetramethylcyclopentane, both estimated to be near 130° C.; and 1,1-*cis*-2-*trans*-3-tetramethylcyclopentane, estimated to be near 131° C. The two trimethylhexanes are believed to be present only in trace amounts and the three tetramethylcyclopentanes, if actually normally boiling below 132° C., are believed to be present only in very small or trace amounts, as indicated in footnote ° of Table I.

From the data given in Table II, it is seen that the seven compounds which compose essentially all of the 126° to 132° C. fraction of this petroleum are of the branched paraffin, alkyl cyclopentane, and alkyl cyclohexanes classes. The relative amounts of these three classes of hydrocarbons in the 126° to 132° C. fraction are, respectively, 5, 33, and 62. This makes the cycloparaffin content of this fraction 95%.

ACKNOWLEDGMENT

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Relationship between Carbon-Type Composition, Viscosity-Gravity Constant, and Refractivity Intercept of Viscous Fractions of Petroleum

STEWART S. KURTZ, Jr., RICHARD W. KING, WILLIAM J. STOUT[1], DOROTHY G. PARTIKIAN, and E. A. SKRABEK[2]
Sun Oil Co., Marcus Hook and Norwood, Pa.

A triangular graph has been developed which relates carbon-type composition in terms of per cent aromatic carbons, per cent naphthenic carbons, and per cent paraffinic carbons to viscosity-gravity constant and refractivity intercept for viscous petroleum fractions. If both viscosity-gravity constant and refractivity intercept are known, carbon-type composition can be determined from this graph with reasonable accuracy. Viscosity, gravity, and refractive index are the only experimental data required for the use of this graph. It is useful in following the effect of solvent extraction, acid treating, hydrogenation of the viscous fractions of petroleum, and for comparing the composition of the viscous fractions from various crude oils.

TWO other laboratories have been working independently on the correlation of density, refractive index, and viscosity to provide a simple method for the analysis of petroleum fractions (*5, 41*). The method presented here is believed to be as accurate as the other methods, and more simple to use.

The information which has been accumulated in recent years concerning the lubricating oil fraction of petroleum indicates that the structures of the molecules in the lubricating oil fraction are fairly uniform (*1, 2, 5–11, 14, 16, 17, 20–22, 24–27, 29–33, 35–37, 39, 40, 43–45*). It seems probable that only a very small portion of the theoretically possible structures actually exist in lubricating oil.

Both viscosity-gravity constant (*12*) and refractivity intercept (*15, 18, 19*) were developed with the intent of obtaining constants which were indicative of the type of hydrocarbon composition and independent of molecular weight. Therefore, it seemed possible that lines of equal viscosity-gravity constant and equal refractivity intercept could be established on a three-component graph for carbon-type composition. Carbon type composition is used in the conventional sense (*30, 31, 43*). Specifically, per cent aromatic ring carbon means the per cent of the total carbon atoms in aromatic ring structures; per cent naphthenic ring carbon means the per cent of the total carbon atoms in naphthenic ring structures; and per cent paraffinic chain carbon means the per cent of the total carbon atoms in chain structures, free as well as combined with naphthenic and aromatic rings.

Van Nes and van Westen, in their book "Aspects of the Constitution of Mineral Oils" (*31*), have discussed both refractivity intercept (*33*) and viscosity-gravity constant (*32*) in relation to the carbon-type composition, and presented the following approximate equations:

$$r_i = 0.01065\,(\%\ C_A) + 11(\%\ C_A 10^{-3})^2 + 0.0103(\%\ C_N) + 0.0105\,(\%\ C_P) \quad (1)$$

$$\text{V.G.C.} = 0.0110(\%\ C_A) + 0.00925(\%\ C_N) + 0.00743(\%\ C_P) \quad (2)$$

These equations were presented as somewhat tentative, and were not recommended for general use because of the uncertainty in regard to the effect of aromatic carbons on the physical properties. These authors quote Leendertse (*20*) in regard to the reliability of the refractivity intercept for determining the naphthene carbon content and the paraffin carbon content of aromatic-free lubricating oil fractions. They were impressed with its reliability for saturated mineral oil fractions. The intercept for paraffin carbons chosen by Leendertse (1.0502) and the value used here (1.0500) both correspond closely with the value for the limiting point of the paraffin homologous series (1.0498) (*4*). A lower value (1.0480) has also been investigated, because there is no reason to believe that the limiting CH_2 increment is necessarily the best increment to use in the C_{20} to C_{30} molecular weight range. However, the higher value is better for data on lubricating oil fractions. This will be discussed in more detail below.

The basic problem was to collect enough data for viscous oils and fractions of viscous oils so that the relation between carbon-type composition, viscosity-gravity constant, and refractivity intercept could be established on an empirical basis. Carbon-type composition can be obtained by the n-d-M procedure if data are available for density, refractive index, and molecular weight (*31, 43*). If molecular weight is not available it can be estimated from published correlations of molecular weight with physical properties (*28*). Data were collected from the authors' own files (*42*) and from the literature (*10, 25, 31*) for approximately 258 lubricating oils and fractions of lubricating oils for which carbon-type composition, viscosity-gravity constant, and refractivity intercept were available.

Viscosity-gravity constants were calculated with the following equations or the corresponding nomographs:

$$\text{V.G.C.} = \frac{10G - 1.0752 \log (V_1 - 38)}{10 - \log (V_1 - 38)} \quad (3)$$

$$\text{V.G.C.} = \frac{G - 0.24 - 0.022 \log (V_2 - 35.5)}{0.755} \quad (4)$$

$$\text{V.G.C.} = \frac{d - 0.1384 \log (V_3 - 20)}{0.1526[7.14 - \log (V_3 - 20)]} + 0.579 \quad (5)$$

where

G = specific gravity 60/60° F.
d = density at 20° C./4° C.
V_1 = Saybolt viscosity at 100° F.
V_2 = Saybolt viscosity at 210° F.
V_3 = kinematic viscosity in centistokes at 20° C.

These equations all give viscosity-gravity constants equivalent to the Hill and Coats equation for 100° F., which is Equation 3. Some of the carbon-type composition data were obtained by the Martin method (*16, 26*) of calculation and some by the n-d-M method (*30, 31, 43*). For aromatic extracts and other compounds rich in aromatic rings, which are outside the range recommended for the n-d-M method, the Martin analytical technique was used.

VISCOSITY-GRAVITY CONSTANT CORRELATION

In development of Equation 2 van Nes and van Westen observed (*32*) that for saturated oils a linear relationship existed between the viscosity-gravity constant (V.G.C.) and percentage carbon in paraffinic structures (% C_P). There also seemed to be some relation between viscosity-gravity constant and % C_P for a number of oil fractions from widely differing crude sources. Their observations suggested that it might be possible to establish lines of constant viscosity-gravity constant on a triangular coordinate system by first establishing a relationship between viscosity-gravity constant and the percentage carbon in aro-

[1] Present address, University of Delaware, Newark, Del.
[2] Present address, University of Wisconsin, Madison 6, Wis.

Table I. Data Necessary for Construction of Viscosity-Gravity Constant Lines[a] in Figures 5 and 7

V.G.C.	Coordinate Point 1			Coordinate Point 2		
	% C_A	% C_N	% C_P	% C_A	% C_N	% C_P
0.78	4.0	17.0	79.0	0	23.0	77.0
0.79	5.7	18.0	76.3	0	27.0	73.0
0.80	7.5	19.5	73.0	0	31.6	68.4
0.81	9.8	20	70.2	0	35.8	64.2
0.82	12.5	20	67.5	0	40.0	60.0
0.83	15.5	20	64.5	0	45.0	55.0
0.84	18.2	20	61.8	0	50.0	50.0
0.85	21.0	20	59.0	0	54.8	45.2
0.86	23.6	20	56.4	0	60.0	40.0
0.87	26.4	20	53.6	0	66.1	33.9
0.88	29.0	20	51.0	0	73.0	27.0
0.89	31.6	20	48.4	0.7	79.3	20
0.90	34.0	20	46.0	7.5	72.5	20
0.91	36.3	20	43.7	13.7	66.3	20
0.92	38.2	20	41.8	19.9	60.1	20
0.93	40.0	20	40.0	25.0	55.0	20
0.94	41.5	20	38.5	30.0	50.0	20
0.95	43.0	20	37.0	34.5	45.5	20
0.96	44.4	20	35.6	38.4	41.6	20
0.97	45.7	20	34.3	41.9	38.1	20
0.98	46.9	20	33.1	44.5	36.0	19.5
0.99	48.0	20	32.0	47.3	34.7	18.0
1.00	49.2	20	30.8	50.0	33.0	17.0
1.01	50.5	20	29.5	52.0	31.7	16.3

[a] Coordinate points given are terminal points of the V.G.C. lines and define area of composition over which correlation has been tested.

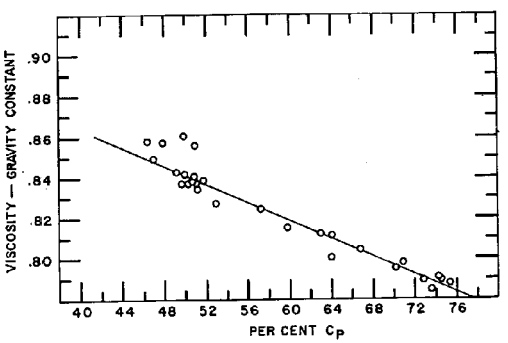

Figure 1. Viscosity-gravity constant *vs.* % C_P for saturated oils

Table II. Accuracy of Viscosity-Gravity Constant–Carbon-Type Correlation

Source of Data	Lit. Ref.	No. of Fractions	Av. V.G.C.	Std. Dev.	Dev. of Average[a]	Max. Dev.
Whole oils and cuts thereof						
Water White Oils	(25)	11	0.830	0.004	0.000	+0.009
Borneo Crude	(31)	5	0.926	0.004	−0.002	−0.006
Oklahoma Crude	(31)	5	0.845	0.004	−0.002	−0.007
Pennsylvania Crude	(31)	4	0.813	0.004	−0.004	−0.006
Webster Crude	(31)	4	0.858	0.006	+0.006	+0.010
Distillation fractions from Naphthenic Crudes	(31)	21	0.883	0.004	0.000	+0.010
Pa. 180 Neutral	(10)	20	0.819	0.002	0.000	−0.007
Midcontinent Neutral 1	(10)	17	0.860	0.003	+0.001	+0.005
California Neutral	(10)	18	0.892	0.002	0.000	−0.005
Gulf Coast Neutral	(10)	17	0.879	0.003	0.000	+0.006
Rodessa Neutral	(10)	15	0.830	0.002	−0.002	−0.004
Midcontinent Neutral 2	(10)	19	0.849	0.004	+0.001	+0.006
All whole oils		156	0.858	0.003	0.000	+0.010
Saturated oils						
Water White Oils	(25)	12	0.800	0.002	0.000	+0.004
Webster Crude	(42)	3	0.874	0.007	+0.006	+0.011
Distillation fractions from Naphthenic Crudes	(42)	21	0.836	0.004	+0.003	+0.009
All saturated oils		36	0.837	0.004	+0.001	+0.011
Aromatic extracts						
Aromatic conc. from solvent refined lube[b]	(42)	3	0.862	0.008	−0.007	−0.010
Aromatic conc. from light lubes[b]	(42)	3	0.956	0.008	−0.007	−0.010
Aromatic extracts	(42)	4	0.966	0.014	−0.014	−0.015
Aromatic conc. from Webster Crude[b]	(42)	2	0.945	0.014	−0.014	−0.015
Aromatic conc. from Duosol and furfural extractions[b]	(42)	6	0.969	0.005	−0.001	−0.010
Aromatic conc. of miscellaneous commercial oils from silica gel separations[b]	(42)	14	0.951	0.009	0.000	+0.014
All aromatic extracts		32	0.948	0.009	−0.006	−0.015
Complete total		224		0.003	−0.001	−0.015

[a] Deviation from average of each datum averaged, taking sign into account.
[b] Concentrated on silica gel; at least one aromatic ring per molecule.

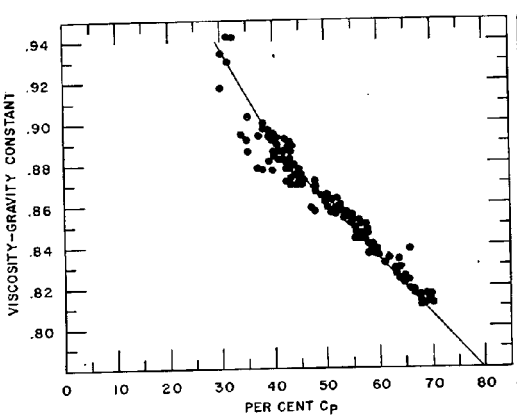

Figure 2. V.G.C. *vs.* % C_P

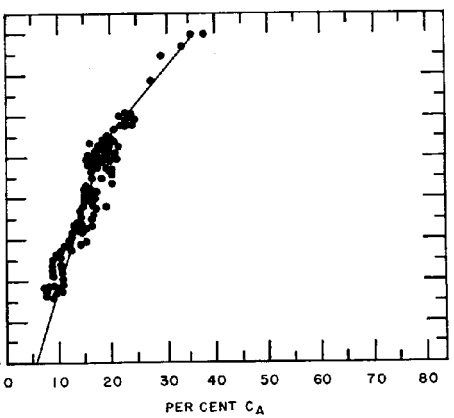

Figure 3. V.G.C. *vs.* % C_A

Viscosity-gravity constant plots for whole oils

matic, naphthenic, or paraffinic structures on rectangular coordinates.

For saturated oils, the linear relationship between viscosity-gravity constant and % C_P observed by van Nes and van Westen (*32*) was confirmed, as shown in Figure 1. Because these oils contained no carbon in aromatic structures, it was possible to transfer this line to the saturated base line of a triangular coordinate graph for % C_P, % C_N, and % C_A. This gives a series of viscosity-gravity constant points on the % C_P-% C_N side of the triangle.

In order to establish a second point for the viscosity-gravity constant lines, it was necessary to plot two of the composition variables as a function of viscosity-gravity constant for the series of whole oils. Per cent C_P and % C_A gave the best approximations to a linear relationship when so plotted (Figures 2 and 3).

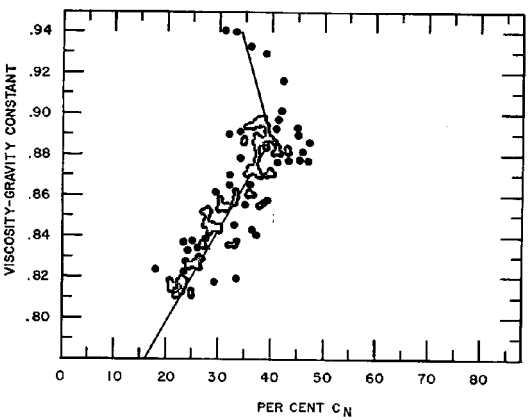

Figure 4. Viscosity-gravity constant *vs.* % C_N for whole oils

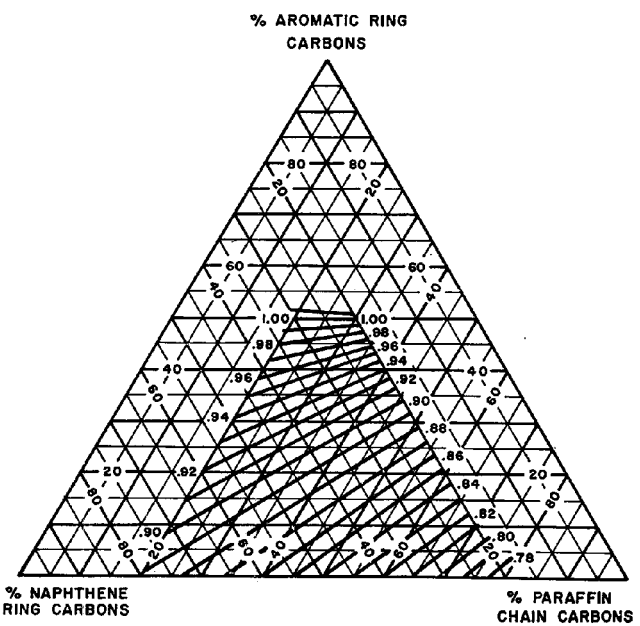

Figure 5. Viscosity-gravity constant in relation to carbon-type composition

A plot of % C_N showed considerably greater scattering, and is presented in Figure 4 merely to show that a line constructed from Figures 2 and 3 so that % $C_N = 100 - (\% C_P + \% C_A)$ fits the data reasonably well.

It was possible to fit the data for % C_P and % C_A with a straight line up to viscosity-gravity constant values of about 0.885. Above 0.885 the effect of the carbons in aromatic structures became large, and it was necessary to change the slope abruptly in order to fit the data in this region. These data were transferred to triangular coordinates and points of equal viscosity-gravity constant connected to give a series of lines covering the viscosity-gravity constant range from 0.790 to 0.910. In the range from 0.910 to 1.00 the lines were placed by inspection to give the best fit to the data.

Adjustments to the correlation were made until the average deviation was a minimum and the deviation of the average was close to zero. The viscosity-gravity constant lines on Figure 5 are the final adjusted lines.

Table I gives the data necessary to lay out the lines for viscosity-gravity constant on a three-component graph. For the present, at least, the lines are being restricted to that area of the graph for which supporting experimental data exist. Table II shows the degree of agreement obtained for 224 fractions between the viscosity-gravity constant determined experimentally and that derived from composition by using a chart corresponding to Figure 5. The agreement between experimental and calculated values, while not perfect, is satisfactory. It indicates that the reverse computation—that is, relating viscosity-gravity constant to composition—should be satisfactory, provided another function, also independent of molecular weight, could be plotted on the graph in order to obtain intersecting lines.

REFRACTIVITY INTERCEPT CORRELATION

It seemed reasonable to use refractivity intercept as the other plotted function, provided the effect of aromatic carbons could be evaluated on a reasonable basis. As the aromatic content of lubricating oil fractions increases, there is evidence that the proportion of condensed aromatic ring structures increases. Because the composition data for the 224 fractions that were available to the authors formed a fairly narrow band on the triangular diagram of carbon-type composition, it seemed reasonable to anticipate that a fairly smooth curve should be obtained if the equivalent refractivity intercept of the aromatic carbons were plotted against the observed refractivity intercept of the sample. Therefore, the equivalent refractivity intercept of the aromatic carbons was calculated using the following equation:

$$r_iA = \frac{r_i\text{sample}(100) - 1.0300(\% C_N) - 1.0500(\% C_P)}{\% C_A} \qquad (6)$$

Figure 6 shows the calculated refractivity intercepts for aromatic ring carbons plotted against the refractivity intercept of the sample for those samples which had 5% or more of aromatic ring carbons. Although some scattering is observed, the anticipated trend is clear. Because the available data did not include points rich in naphthene ring carbons and having low intercept values, some assumption was needed to establish tentative intercept lines in the more naphthenic portion of the composition chart. As there cannot be less than one aromatic ring per molecule and as it was not believed necessary to extend the chart below 1.035 refractivity intercept, the intercept value of benzene (1.0616) was plotted opposite the value 1.035 for refractivity intercept to provide a tentative terminal point for this curve. This was a rather arbitrary step which would only be justified if the chart ultimately developed was reliable.

The refractivity intercept lines on Figure 7 were established by interpolating between 1.0300 and 1.0500 on the naphthene and paraffin side of the triangle and between 1.0300 and r_iA on the naphthene and aromatic side of the triangle, and 1.0500 and r_iA on the paraffin and aromatic side of the triangle. r_iA is determined in each case using Figure 6 or Table III. The data necessary for establishing the intercept lines in Figure 7 are given in Table IV.

Study of the points in Figure 6 suggests the possibility that there should be a sharp downward curvature of the line for the calculated aromatic carbon intercept between the values 1.045

Table III. Data Needed for Drawing Curve of Equivalent Intercept of Aromatic Carbons *vs.* Intercept of Lube Oil as Shown in Figure 6

Intercept of Oil	Intercept of Aromatic Carbons
1.0350	1.0616
1.0400	1.0695
1.0450	1.0775
1.0500	1.0855
1.0550	1.0926
1.0600	1.0986
1.0650	1.1042
1.0700	1.1094
1.0750	1.1140
1.0800	1.1186

Table IV. Data for Establishing Refractivity Intercept Lines[a]

Refractivity Intercept	Naphthene-Paraffin Base Line		Naphthene-Aromatic Side of Triangle		Paraffin-Aromatic Side of Triangle	
	% C_P	% C_N	% C_A	% C_N	% C_A	% C_P
1.035	25	75	15.8	84.2		
1.040	50	50	25.3	74.7		
1.045	75	25	31.6	68.4		
1.050	100	0	36.1	63.9		
1.055			39.9	60.1	11.7	88.3
1.060			43.7	56.3	20.5	79.5
1.065			47.2	52.8	27.7	72.3
1.070			50.4	49.6	33.7	66.3
1.075			53.6	46.4	39.1	60.9
1.080			56.4	43.4	43.7	56.3

[a] In constructing Figure 7 values for intermediate lines can be obtained by plotting columns 2 to 7 *vs.* column 1 and interpolating. A working graph should have lines for each 2% of carbon-type composition, for each unit in the third decimal place of the refractivity intercept, and for each unit in the second decimal of viscosity-gravity constant.

and 1.050 for the intercept of the original oil. This was tried, but led to an irregular spacing of the intercept lines on the triangular diagram. The lines so placed did not agree well with the limited available data for this region. Therefore, as explained above, the coordinates 1.0616 and 1.0350 were tried as the terminal point of the curve. This led to more reasonable spacing of the intercept lines and better agreement with the data.

Considerable thought has been given to the significance of pure compound data in relation to locating the intercept lines on Figure 7. Consideration of data from the API 44 tables (*3, 38*) and for API 42 compounds (*2, 39, 40*) would indicate that a paraffin intercept value of 1.0480 would be better in the range from 20 to 40 carbon atoms than a value of 1.0500. The corresponding naphthene value is 1.0320. A complete graph was constructed and evaluated. A statistical study showed little difference between this graph and Figure 7. However, when compared by plotting data for a series of hydrogenated oils, the graph based on the paraffin intercept value of 1.0480 and a naphthene intercept value of 1.0320 showed the completely hydrogenated naphthene fractions falling about 2% below the base line representing 0% aromatic carbons. The graph based on 100% C_P = 1.0500 and 100% C_N = 1.0300 showed the completely hydrogenated fractions falling on the base line (Figure 8). For this reason it was decided to adhere to values of 1.0500 and 1.0300 for the paraffin and naphthene apexes, respectively.

In constructing this type of graph some thought needs to be given to what is meant by per cent composition. The data for per cent carbon type are in terms of percentage of aromatic, naphthenic, and paraffinic carbons in the molecule (*16, 31*). Refractivity intercept is, in general, additive on a volume per cent basis for mixtures of liquids. As shown by Leenderstse (*20*), there is good agreement between carbon-type composition and refractivity intercept for complex saturated molecules. The graph in Figure 7, as derived, represents carbon-type composition and not volume per cent composition or weight per cent composition. This should be kept in mind if it is applied to blends.

APPLICATION

The carbon-type composition of the lubricating oils and fractions of lubricating oils used in developing Figure 7, as well as a number of other oils on which data were available, was determined by plotting the viscosity-gravity constant and refractivity intercept for all these points on a large graph and reading off the corresponding composition. This study showed that the aromatic carbon contents are usually in agreement with the authors' best analyses to within 1 or 2%, although occasionally deviations as large as 4 or 5% may be observed. On the paraffin and naphthene compositions, the agreement is good for fractions containing 30% or less of aromatic carbons. Between 30% and 50% aromatic carbons, there is an increase of uncertainty in the values for the paraffin and naphthene carbons, because the angle at which the correlation lines intersect decreases rapidly. The chart should not be used for samples having viscosity-gravity constant values between 0.95 and 1.01 which fall below 20% C_N or 20% C_P. This is practical because very few samples having less than 20% C_N or 20% C_P have been found in this range. Table V presents data on a number of samples for which rather complete analytical data were obtained in connection with studies

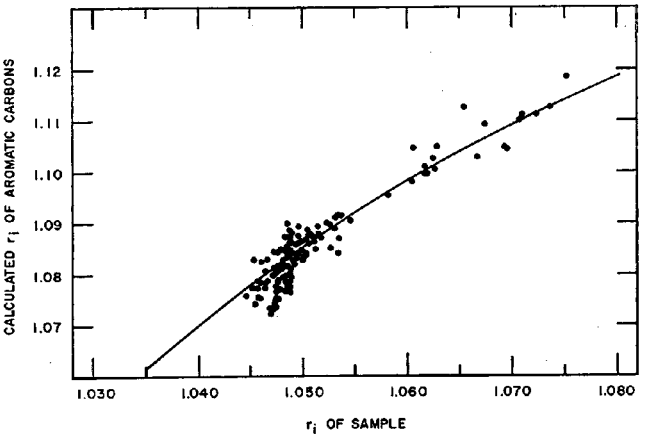

Figure 6. Refractivity intercept of aromatic carbons *vs.* refractivity intercept of sample

of rubber processing oils (*16*, *48*). In general, the agreement between composition obtained with Figure 7 and the composition obtained by more complete analysis is satisfactory—that is, within 1 or 2%. A few deviations larger than 4% are shown.

Table V also contains data obtained by the n-d-M procedure of Tadema, van Nes, and associates (*31*, *43*). In the range for which the n-d-M method is recommended—that is, for samples in which the ratio of % C_A to % C_N is 1.5 or less—the agreement is quite good. In the higher aromatic range the data obtained by Figure 7 are in better agreement with detailed analyses by the Martin (*16*, *26*) method than are the data by the n-d-M method.

Table VI compares carbon-type analyses obtained with Figure 7 and with the n-d-M procedure on the cuts of five typical oils studied by Hill and Ferris (*13*). The data on these oils were used by Hill and Coats (*12*) in deriving the viscosity-gravity constant. The two methods agree well for these typical oils. The range of carbon-type composition is about 20% for % C_A and % C_N and about 40% for % C_P. To prepare Table VI data were read from photostatic enlargements of the curves published by Hill and Ferris. Data were corrected to 20° C. when necessary.

A statistical study of all the data (Table VII) shows that, for oils having a viscosity-gravity constant of 0.900 or less, Figure 7 will give the value of % C_A with a standard deviation of about 1.0%. For % C_N and % C_P the standard deviation is roughly 1.5% for samples with a viscosity-gravity constant below 0.900. Most naturally occurring crude oils have viscosity-gravity constant values below 0.900.

For samples with viscosity-gravity constants between 0.900 and 1.000, the standard deviation for % C_A is approximately 2.0% and for % C_N and % C_P, approximately 4.5%. The samples having viscosity-gravity constant above 0.900 are, for the most part, aromatic concentrates obtained either by solvent extraction or gel separation. These samples are outside the range of materials for which the viscosity-gravity constant was originally developed.

Table VIII presents corresponding data arranged by groups based on per cent carbon in aromatic rings. For samples having less than 30% carbon in aromatic rings the standard deviation is as follows: per cent aromatic carbons, 1.2%; per cent naphthenic carbons, 2.0%; per cent paraffinic carbons, 1.7%.

The data used in developing this chart represent a wide variety of samples. Consideration of the data indicates that Figure 7 is sufficiently reliable for obtaining many of the carbon-type composition data which are needed in practical petroleum refining. The relation between refractivity intercept and composition, and between viscosity-gravity constant and composition is more accurately presented by Figure 7 than by Equations 1 and 2

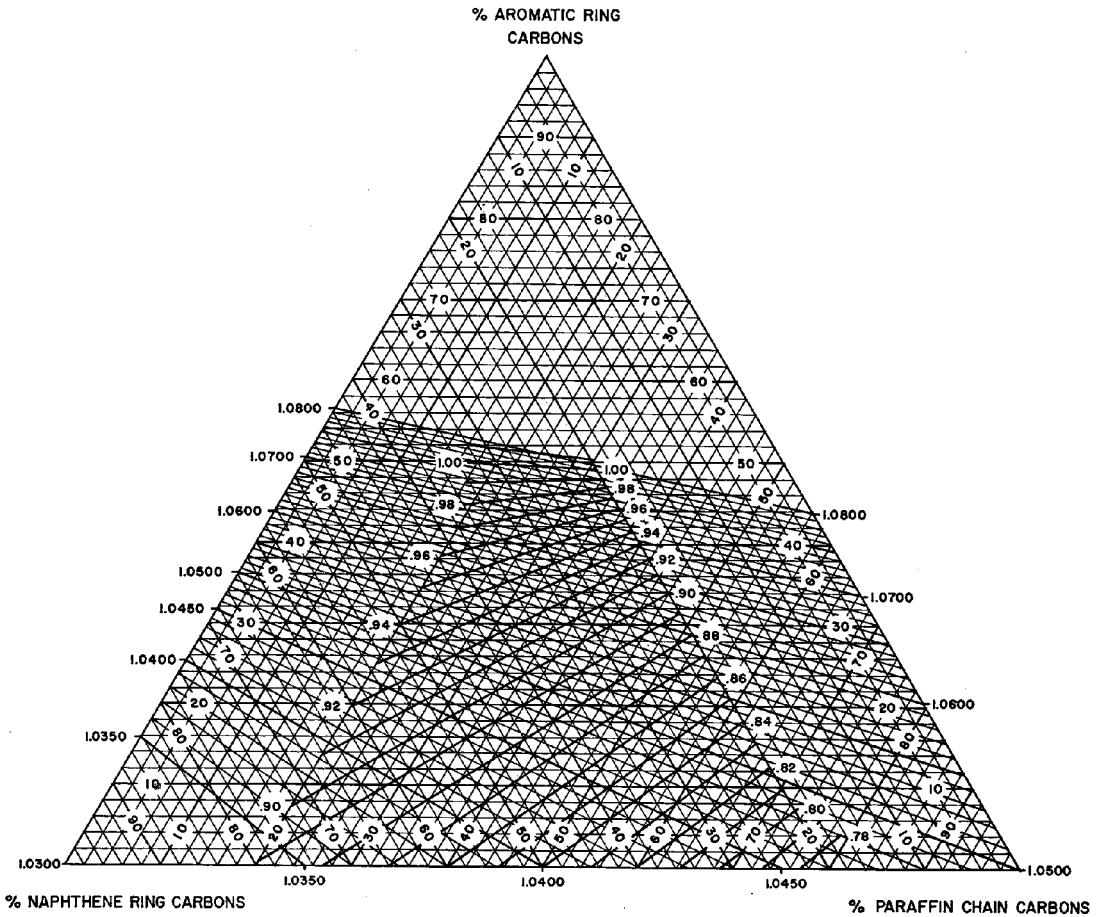

Figure 7. Viscosity-gravity constant and refractivity intercept in relation to carbon-type composition

Table V. Comparison of Carbon-Type Analysis by Viscosity-Gravity Constant-Refractivity Intercept and Other Methods

Oil No.	Property of Oil		Composition of Oil		% C_A	% C_N	% C_P
1	Mol. wt.	698	Fig. 7	x	2	28	70
	V.G.C.	0.798	n-d-M	y	3	28	69
	r_i	1.0448	Martin	z	2	28	70
	n	1.4865		$x-y$	− 1	0	+ 1
	d	0.8835		$x-z$	0	0	0
2	Mol. wt.	419	Fig. 7	x	3	33	64
	V.G.C.	0.815	n-d-M	y	3	33	64
	r_i	1.0441	Martin	z	3	33	64
	n	1.4793		$x-y$	0	0	0
	d	0.8704		$x-z$	0	0	0
3	Mol. wt.	352	Fig. 7	x	3	34	63
	V.G.C.	0.818	n-d-M	y	3	34	63
	r_i	1.0440	Martin	z	3	34	63
	n	1.4748		$x-y$	0	0	0
	d	0.8615		$x-z$	0	0	0
4	Mol. wt.	464	Fig. 7	x	4	45	51
	V.G.C.	0.842	n-d-M	y	4	45	51
	r_i	1.0419	Martin	z	5	45	50
	n	1.4971		$x-y$	0	0	0
	d	0.9105		$x-z$	− 1	0	+ 1
5	Mol. wt.	347	Fig. 7	x	2	49	49
	V.G.C.	0.846	n-d-M	y	3	47	50
	r_i	1.0407	Martin	z	3	47	50
	n	1.4847		$x-y$	− 1	+ 2	− 1
	d	0.8879		$x-z$	− 1	+ 2	− 1
6	Mol. wt.	399	Fig.7	x	20	38	42
	V.G.C.	0.883	n-d-M	y	19	39	42
	r_i	1.0491	Martin	z	16	42	42
	n	1.5210		$x-y$	+ 1	− 1	0
	d	0.9439		$x-z$	+ 4	− 4	0
7	Mol. wt.	442	Fig. 7	x	25	34	41
	V.G.C.	0.892	n-d-M	y	24	35	41
	r_i	1.0532	Martin	z	25	30	45
	n	1.5332		$x-y$	+ 1	− 1	0
	d	0.9600		$x-z$	0	+ 4	− 4
8	Mol. wt.	365	Fig. 7	x	25.5	45	29.5
	V.G.C.	0.915	n-d-M	y	22	43	35
	r_i	1.0501	Martin	z	20	45	35
	n	1.5291		$x-y$	+ 3.5	+ 2	− 5.5
	d	0.9580		$x-z$	+ 5.5	0	− 5.5
9	Mol. wt.	427	Fig. 7	x	36	28.5	35.5
	V.G.C.	0.927	n-d-M	y	36	22	42
	r_i	1.0631	Martin	z	33	26	41
	n	1.5550		$x-y$	0	+ 6.5	− 6.5
	d	0.9837		$x-z$	+ 3	+ 2.5	− 5.5
10	Mol. wt.	369	Fig. 7	x	39	26	35
	V.G.C.	0.936	n-d-M[a]	y	42	16	42
	r_i	1.0665	Martin	z	35	26	39
	n	1.5556		$x-y$	− 3	+10	− 7
	d	0.9783		$x-z$	+ 4	0	− 4
11	Mol. wt.	373	Fig. 7	x	37	30	33
	V.G.C.	0.936	n-d-M[a]	y	39	22	39
	r_i	1.0639	Martin	z	33	31	36
	n	1.5537		$x-y$	− 2	+ 8	− 6
	d	0.9797		$x-z$	+ 4	− 1	− 3
12	Mol. wt.	373	Fig. 7	x	39	29	32
	V.G.C.	0.943	n-d-M[a]	y	43	22	35
	r_i	1.0654	Martin	z	35	33	32
	n	1.5649		$x-y$	− 4	+ 7	− 3
	d	0.9990		$x-z$	+ 4	− 4	0
13	Mol. wt.	361	Fig. 7	x	45	23.5	31.5
	V.G.C.	0.970	n-d-M[a]	y	54	12	34
	r_i	1.0735	Martin	z	46	19	35
	n	1.5804		$x-y$	− 9	+11.5	− 2.5
	d	1.0138		$x-z$	− 1	+ 4.5	− 3.5
14	Mol. wt.	272	Fig. 7	x	46	30.5	23.5
	V.G.C.	0.982	n-d-M[a]	y	55	15	30
	r_i	1.0724	Martin	z	46	30	24
	n	1.5737		$x-y$	− 9	+15.5	− 6.5
	d	1.0026		$x-z$	0	+ 0.5	− 0.5
15	Mol. wt.	278	Fig. 7	x	46	37	17
	V.G.C.	0.985	n-d-M[a]	y	52	21	27
	r_i	1.0700	Martin	z	44	31	25
	n	1.5725		$x-y$	− 6	+16	−10
	d	1.0050		$x-z$	+ 2	+ 6	− 8
16	Mol. wt.	310	Fig. 7	x	49	31	20
	V.G.C.	0.997	n-d-M[a]	y	50	11	30
	r_i	1.0754	Martin	z	46	31	23
	n	1.5872		$x-y$	−10	+20	−10
	d	1.0236		$x-z$	+ 3	0	− 3
17	Mol. wt.	314	Fig. 7	x	50	15	35
	V.G.C.	1.010	n-d-M[a]	y	63	6	31
	r_i	1.0825	Martin	z	52	23	25
	n	1.5997		$x-y$	−13	+ 9	+ 4
	d	1.0343		$x-z$	− 2	− 8	+10

[a] Beyond range for which n-d-M method is recommended; also beyond range for which V.G.C. was derived.

Table VI. Comparison of Figure 7 and n-d-M Analysis

[Data of Hill and Ferris (*13*)]

	V.G.C.	Characterization Factor	Method	% C_A	% C_N	% C_P
Pennsylvania	0.808	12.4	Fig. 7	6.5	24.5	69
			n-d-M	6.5	24.5	69
Midcontinent	0.839	12.0	Fig. 7	12.5	29	58.5
			n-d-M	12.5	28.5	59.0
Gulf Coast No. 1	0.863	11.7	Fig. 7	16.5	34	49.5
			n-d-M	15	34.5	50.5
Gulf Coast No. 2	0.883	11.5	Fig. 7	17.5	42.5	40.0
			n-d-M	16	42.5	41.5
Gulf Coast No. 3	0.910	11.2	Fig. 7	24.5	44.5	31
			n-d-M	22	44	34
Range (maximum − minimum)				18.0	20.0	38

Table VII. Standard Deviation of Carbon-Type Analysis by Figure 7 for V.G.C. Groups

V.G.C. Group	No. of Data	Standard Deviation % C_A	% C_N	% C_P
Less than 0.819	36	0.7	1.2	1.0
0.820–0.849	75	0.8	1.9	1.4
0.850–0.899	103	1.3	2.3	2.0
0.900–0.949[a]	25	2.8	4.2	3.5
0.950–0.999[a]	16	1.8	3.5	3.4
Above 1.00[a]	3	1.2	6.1	7.3
	258			

[a] Maximum V.G.C. shown in Hill and Coats (*12*) is 0.935; above 0.935 V.G.C. is extrapolated function.

Table VIII. Standard Deviation of Carbon-Type Analysis by Figure 7 for Per Cent Aromatic Groups

% C_A Group	No. of Data	Standard Deviation % C_A	% C_N	% C_P
0– 9.9	64	1.1	2.2	1.4
10–19.9	118	1.1	1.6	1.4
20–29.9	41	1.4	2.7	2.9
30–39.9	18	2.5	3.9	3.4
40–49.9	15	2.3	4.5	4.1
Above 50	2	1.3	3.8	5.1
	258			

Table IX shows data for aromatic concentrates obtained by silica gel from five rubber processing oils. These data indicate that Figure 7 gives good values on the per cent aromatic carbons in such aromatic concentrates, but poor values for the % C_N and % C_P. By subtracting 0.015 from the viscosity-gravity constant value in each case, much better agreement is obtained, as shown in the table. In general, any method of this sort must be used with caution for fractions which are too homogenous as to type and, therefore, may not fit correlations based on averages.

The effect of sulfur on a correlation of this sort is important if it is to be used with high-sulfur oils. When data were used for approximately 60 oils on which sulfur data were available, the following correction factors were derived for % C_N and % C_P:

$$\text{Sulfur correction for } \%\ C_N = \frac{-\text{wt.}\%\ S}{0.288} \qquad (7)$$

$$\text{Sulfur correction for } \%\ C_P = \frac{+\text{wt.}\%\ S}{0.216} \qquad (8)$$

The corrected values for % C_A can be obtained from the equation

$$\%\ C_A = 100 - (\%\ C_N + \%\ C_P) \qquad (9)$$

Table X shows the effectiveness of the sulfur correction in

reducing the deviations between values read from Figure 7 and those obtained using more detailed methods of analysis. The tabulation only includes those samples containing more than 0.5% sulfur. In the region above 0.8% sulfur, the agreement between the viscosity-gravity constant-refractivity intercept method and other methods may be substantially improved by applying the sulfur correction.

In addition to viscosity-gravity constant another relation between viscosity and gravity, the characterization factor, has been widely used (*46, 47*). A graph similar to Figure 7, based on characterization factor, could undoubtedly be developed. The authors have preferred to provide tables so that data recorded in terms of characterization factor can be converted to viscosity-gravity constant and studied with the aid of Figure 7.

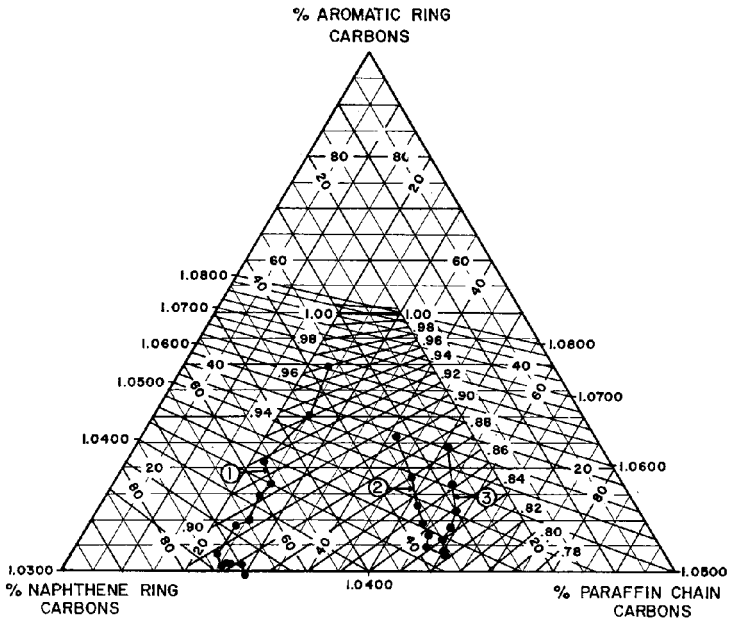

Figure 8. Hydrogenation and solvent extraction data in relation to carbon-type composition

Lines 1, 2, and 3 explained in text

Table IX. Aromatic Fractions Concentrated by Silica Gel

[From rubber processing oil (*48*)]

Aromatic Fraction of	Property of Oil				Composition of Oil % C_A	% C_N	% C_P
S_1, relatively naphthenic	Mol. wt.	366	Figure 7	x	26	36	38
	V.G.C.	0.900	Corrected[a]	y	24	32	44
	n_i	1.0536	Martin	z	27	28	45
	n	1.5269		x-z	− 1	+ 8	− 7
	d	0.9465		y-z	− 3	+ 4	− 1
S_2, relatively naphthenic	Mol. wt.	435	Figure 7	x	22	36	42
	V.G.C.	0.886	Corrected[a]	y	22	28	50
	n_i	1.0536	Martin	z	24	32	44
	n	1.5330		x-z	− 2	+ 4	− 2
	d	0.9588		y-z	− 2	− 4	+ 6
S_3, relatively paraffinic	Mol. wt.	350	Figure 7	x	27	33.5	39.5
	V.G.C.	0.898	Corrected[a]	y	25	29	46
	n_i	1.0547	Martin	z	27	27	46
	n	1.5225		x-z	0	+ 6.5	− 6.5
	d	0.9355		y-z	− 2	+ 2.0	0
S_4, relatively paraffinic	Mol. wt.	418	Figure 7	x	23	30.5	46.5
	V.G.C.	0.879	Corrected[a]	y	21	27	52
	n_i	1.0530	Martin	z	24	22	54
	n	1.5180		x-z	− 1	+ 8.5	− 7.5
	d	0.9300		y-z	− 3	+ 5	− 2
A_2, relatively aromatic	Mol. wt.	409	Figure 7	x	42	25	33
	V.G.C.	0.957	Corrected[a]	y	42	22	36
	n_i	1.0705	Martin	z	42	21	37
	n	1.5767		x-z	0	+ 4	− 4
	d	1.0124		y-z	0	+ 1	− 1

[a] 0.015 subtracted from V.G.C.

Table XI gives enough data so that viscosity-gravity constant can be obtained from characterization factor and viscosity by interpolation.

An example of the application of Figure 7 is given in Figure 8. Line 1 on this graph represents data from the paper by M. R. Lipkin, C. C. Martin, and R. C. Worthing (*23*) showing steps in the hydrogenation of a viscous oil fraction. The gradual decrease in aromatic carbon content and increase in naphthenic carbon content is clearly shown. There is also an indication that the final hydrogenation treatments, which were continued in an effort to eliminate the last trace of ultraviolet absorption, may have resulted in some ring opening, because there is a decrease of between 2 and 4% in the naphthene ring carbons and a corresponding increase in the paraffin chain carbons during these last hydrogenations. Other data for hydrogenated samples confirm the constancy of % C_P as aromatic rings are converted to naphthenic rings. Line 2 on this graph shows the change in an oil on repeated solvent extraction (*34*). In this case there is a progressive decrease in

Table X. Correction of Carbon-Type Composition Data for Effect of Sulfur

Sample No.	V.G.C.	r_i	% S	Deviation from Best Analyses: V.G.C. *vs.* r_i % C_A	% C_N	% C_P	V.G.C. *vs.* r_i (corr. for % S)[a] % C_A	% C_N	% C_P	Lit. Ref.
16	0.997	1.0754	0.57	+3.0	0	−3.0	+2.4	−2.0	−0.4	(42)
18	0.943	1.0607	0.73	+3.6	−1.3	−2.3	+2.7	−3.8	+1.1	(42)
20	0.970	1.0699	0.72	−2.1	+3.8	−1.7	−2.9	+1.4	+1.5	(42)
21	0.965	1.0693	0.67	−2.3	+0.9	+1.4	−3.1	−1.4	+4.5	(42)
23	0.982	1.0739	0.75	0	−0.9	+0.9	−0.9	−3.5	+4.4	(42)
24	0.973	1.0746	0.73	+2.5	−3.6	+1.1	+1.6	−6.1	+4.5	(42)
25	0.980	1.0700	0.56	+1.2	+7.6	−8.8	+0.5	+5.7	−6.2	(42)
26	1.011	1.0788	0.57	+1.8	+5.3	−7.1	+1.2	+3.3	−4.5	(42)
27	0.956	1.0642	0.77	−3.2	+3.7	−0.5	−4.1	+1.0	+3.1	(42)
11	0.936	1.0639	0.56	+4.3	−1.0	−3.3	+3.6	−2.9	−0.7	(42)
9	0.927	1.0631	0.62	+3.0	+2.5	−5.5	+2.4	+0.3	−2.7	(42)
14	0.982	1.0724	0.55	0	−0.5	−0.5	−0.7	−1.3	+2.0	(42)
10	0.936	1.0665	0.73	+3.8	0	−3.8	+2.9	−2.5	−0.4	(42)
33	0.831	1.0434	0.70	−1.5	+3.0	−1.5	−2.3	+0.6	+1.7	(34)
34	0.909	1.0670	0.79	+3.0	−3.0	0	+1.5	−5.2	+3.7	(42)
35	0.929	1.0560	0.77	+1.0	0	−1.0	+0.1	−2.7	+2.6	(42)
	Std. dev. (0.5 to 0.8% S)			2.6	3.1	3.8	2.4	3.2	3.2	
	Dev. of av.			+1.2	+1.1	−2.3	+0.3	−1.2	+0.9	
19	0.946	1.0629	0.82	+0.9	+4.6	−5.5	−0.1	+1.8	−1.7	(42)
22	0.971	1.0709	1.08	+0.6	+1.5	−2.1	−0.6	−2.3	+2.9	(42)
36	1.011	1.0816	0.92	−1.0	−3.0	+4.0	−2.1	−6.1	+8.2	(42)
7	0.892	1.0532	1.01	0	+4.3	−4.3	−1.2	+0.8	+0.4	(42)
13	0.970	1.0735	1.03	−1.0	+4.5	−3.5	−2.2	+0.9	+1.3	(42)
28	0.892	1.0543	2.05	+1.0	+8.0	−9.0	−1.4	+0.9	+0.5	(34)
29	0.870	1.0498	1.67	+0.5	+4.5	−5.0	−1.2	−1.5	+2.7	(34)
30	0.854	1.0468	1.35	+0.5	+3.0	−3.5	−1.1	−1.7	+2.8	(34)
31	0.844	1.0452	1.12	−1.0	+3.5	−2.5	−2.3	−0.4	+2.7	(34)
32	0.837	1.0441	0.89	−1.0	+3.0	−2.0	−2.0	−0.1	+2.1	(34)
37	0.838	1.0501	0.86	+1.5	+4.0	−5.5	+0.5	+1.0	−1.5	(5)
38	0.866	1.0505	1.50	+1.5	+5.0	−6.5	−0.2	−0.2	+0.4	(5)
39	0.871	1.0544	1.62	+4.0	+2.5	−6.5	+2.1	−3.1	+1.0	(5)
40	0.892	1.0515	1.70	+1.5	+6.0	−7.5	−0.5	+0.1	+0.4	(5)
41	0.859	1.0522	1.50	+0.5	+9.5	−10.0	−1.2	+4.3	−3.1	(5)
42	0.863	1.0534	1.51	+1.0	+8.0	−9.0	−0.7	+2.8	−2.1	(5)
43	0.871	1.0550	1.73	+1.5	+9.0	−10.5	−0.5	+3.0	−2.5	(5)
	Std. dev. (0.8 to 2.0% S)			1.4	5.5	6.3	1.4	2.4	2.8	
	Dev. of av.			+0.6	+4.6	−5.2	−0.9	0.0	+0.9	

[a] Correction applied to % C_N and % C_P; % C_A adjusted accordingly.

Table XI. Viscosity-Gravity Constant Corresponding to Indicated Viscosity and Characterization Factor

Viscosity, 100° F. Kinematic	Saybolt	Characterization Factor: 12.5	12	11.5	11	10.5	10
		Viscosity-Gravity Constant					
6	45.6	0.795	0.828	0.865	0.908	0.954	1.006
8	52.1	0.796	0.830	0.869	0.910	0.958	1.013
10	58.9	0.797	0.832	0.872	0.914	0.962	1.019
20	97.8	0.799	0.836	0.879	0.924	0.973	1.035
50	232	0.801	0.842	0.886	0.937	0.991	1.053
100	463	0.802	0.845	0.890	0.942	1.001	1.067
200	927	0.803	0.846	0.894	0.948	1.011	...
500	2317	0.804	0.848	0.898	0.953	1.023	...
1000	4635	0.805	0.849	0.901	0.957	1.030	...
210° F.							
5	42.7	0.796	0.837	0.884	0.938	0.995	1.062
10	59.3	0.803	0.844	0.892	0.947	1.005	1.073
20	98.5	0.806	0.849	0.898	0.954	1.015	1.080
50	234	0.809	0.854	0.904	0.960	1.021	1.086
100	467	0.811	0.856	0.906	0.963	1.023	1.087

aromatic carbon content and increase in paraffinic and naphthenic carbon content up to the last stage of extraction. In the last stage of extraction, aromatic carbon content changes little and naphthenic carbon decreases as paraffinic carbon increases.

The oil for which data are presented in Line 2 contained 2.05% sulfur before extraction. The composition of this oil as read from the graph is 26% C_A, 32% C_N, and 42% C_P. After applying the sulfur corrections, the composition is 24% C_A, 25% C_N, and 51% C_P. Van Nes and van Westen give 25% C_A, 24% C_N, and 51% C_P. Line 3 shows the composition data corrected for the effect of sulfur. These data confirm both the usefulness of the plot of the raw data to show trends, and the validity of the sulfur correction.

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Composition of Lubricating Oil

Use of Newer Separation and Spectroscopic Methods

F. W. MELPOLDER, R. A. BROWN, T. A. WASHALL, WILLIAM DOHERTY, and C. E. HEADINGTON

The Atlantic Refining Co., Philadelphia, Pa.

A study was made of the composition and physical properties of fractions separated from a solvent-refined oil heart cut. The oil charge was fractionated by means of 20-stage molecular distillation, silica gel chromatography, and liquid thermal diffusion to yield saturated fractions ranging from predominantly isoparaffins to multiring cycloparaffins. Hydrocarbon-type analyses were determined by mass and ultraviolet spectrometry and several molecular structures were postulated from mass and infrared data. One fraction which exhibited extreme physical properties was found to contain from four to ten rings per molecule.

THE present-day trend in the refining of petroleum products and the development of new and more powerful analytical techniques have promoted a growing interest in the composition of heavy petroleum products. Detailed information concerning the molecular structure of hydrocarbon types is needed because of the many factors related to performance and stability characteristics of lubricants.

A long-range approach to the problem has been extensively investigated during the past two decades by API Project 6 (*14*). This work has been directed toward a separation of oil according to hydrocarbon types, and measurements of numerous physical properties of the fractions. Additional data for a group of "homogeneous" fractions were recently reported for a cooperative spectroscopic study (*9*). Further progress in this field has been dependent on the development of more efficient separation techniques, extension of spectroscopic methods of analysis, and the synthesis of representative hydrocarbons as standards to guide the interpretation of spectra. Despite the lack of such standards, O'Neal (*18*) and Lumpkin and Johnson (*8*) were able to postulate the structure of many aromatic hydrocarbons and sulfur compounds in gas oil. Melpolder and coworkers were also able to make a mass spectrometric analysis of thermal diffusion fractions separated from a light lubricating oil (*10*).

In view of the significant new developments which have been made in the past few years in both separations and spectroscopic methods, the authors have undertaken a thorough study of the composition of a heart cut lubricating oil fraction. Working on the saturated portion only, many fractions were separated from the oil, in which specific hydrocarbon types of a narrow molecular weight range were concentrated. Physical properties and spectrometric analyses of the fractions were determined, and an effort was made to determine molecular structures from the interpretation of mass spectrometric data.

LUBRICATING OIL STOCK

The oil charge used in this work was a solvent-refined lubricating oil in the SAE-20-30 grade viscosity range. The oil was obtained from a mixed crude source as a pipe still distillate, solvent-extracted with nitrobenzene, dewaxed with methyl ethyl ketone, and filtered through clay. Inspections of the oil are shown in Table I.

SEPARATION PROCEDURES

The lubricating oil charge stock was separated by means of distillation, adsorption, and liquid thermal diffusion to yield 43 fractions containing concentrates of paraffin and cycloparaffin hydrocarbons. The procedures are summarized in the block diagram shown in Figure 1.

Starting with 5.5 liters of oil, having a molecular weight range of from C_{19} to C_{50}, a series of distillations was made in a 20-stage molecular still (*11*) at 1-micron pressure. A total of 14 separate equilibrium-type distillation runs and one batch distillation run was required to process the oil. The boiling range of the resulting

fractions was 196° to 535° F. (at 1 micron). The middle cut having a boiling range of 370° to 431° F. and a volume of 1.5 liters was then charged to the still for a second distillation.

In this second run the still was operated as a batch distillation unit at a throughput of 40 ml. per hour and a reflux ratio of 20 to 1. A heart cut having a boiling range of 393° to 414° F., a molecular weight range of from C_{31} to C_{39}, and a volume of 565 ml. was selected from this run.

The second step in the separation procedure involved the removal of aromatics from the heart cut by elution chromatography on silica gel. As thermal diffusion cannot readily distinguish between aromatic and cycloparaffin rings, it is advantageous to remove aromatics before effecting a separation according to molecular type.

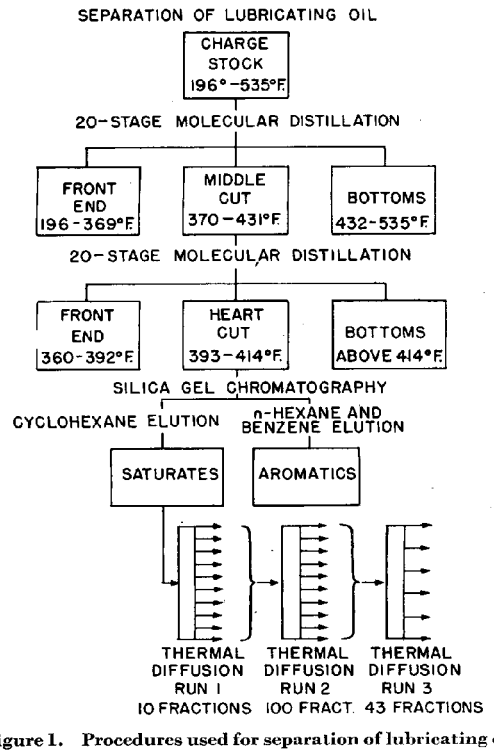


Figure 1. Procedures used for separation of lubricating oil

Table I. Inspections of Lubricating Oil Charge Stock

Gravity, °API, 60° F.	29.4
Refractive index, 176° F.	1.4610
Viscosity, 100° F. (SUS)	461
Viscosity, 210° F. (SUS)	61.8
Viscosity index	99
Pour point, ° F.	0

Distillation Data	° F. 2 mm.	Atm.[a]
I.B.P.	322	658
10	433	798
20	471	847
50	528	925
70	550	951
90	602	1020
95 (E.P.)	620	1045

[a] Temperatures converted to 760-mm. pressure by Beale and Docksey nomograph (*1*).

An 8-foot column, 40 mm. in inside diameter was packed with 1950 grams of 28–200-mesh Davison silica gel, No. 12-08, and 555 ml. of the heart cut from the distillation were diluted with an equal volume of cyclohexane and charged to the column. The sample was then eluted with 4 liters of cyclohexane, which was subsequently removed by evaporation on a steam bath. Final traces of solvent were removed by passing a stream of nitrogen gas through the oil. Cyclohexane was selected as the eluent because it was shown by Irish and Karbum (*5*) to possess weak elution properties as compared to *n*-hexane. The 435 ml. of oil eluted with cyclohexane was then used as the charge material for thermal diffusion.

The third and final step in the fractionation procedure consisted of a separation of the narrow boiling saturated hydrocarbons according to molecular type by thermal diffusion.

A battery of 10 columns of the type described by Jones and Milberger was assembled (*6*). Fourteen charges of oil of about 30 ml. each were processed in the preliminary separation. A temperature gradient of 200° F. was maintained across the column walls, 300° F. at the hot wall and 100° F. at the cold wall. At the end of 10 days of operation the fractions were collected by withdrawing from successive ports, starting at the top. Fractions which were removed from the same portion of each of the columns and having similar compositions were blended—that is, all of the topmost fractions from the 14 runs were combined, then the fractions taken from the second sections were combined, and so on down the columns. As a result of this blending procedure, 10 fractions were obtained of varying compositions, which ranged from predominantly paraffinic hydrocarbon types to predominantly cycloparaffinic types. The volume of each combined fraction was about 36 ml.

A further separation by thermal diffusion was made by charging each of the 10 combined fractions to a separate column. Again the columns were operated for 10 days with a temperature gradient of 200° F. The columns were then emptied by withdrawing 10 fractions from each of the 10 columns, starting at the top. In this manner 100 fractions were obtained. Refractive index was measured on each fraction, as seen in Figure 2.

Although a significant degree of separation was obtained, it was evident that a large amount of overlap in composition occurred, due to the lack of a sharp separation in the first thermal diffusion run. For example, fractions 9 (column 1) and 1 (column 4) which had identical refractive indices were run in the mass spectrometer to confirm the similarity in composition. Their mass spectra were almost identical. In view of the serious overlap in composition which existed, a third continuous run was made in a single 8-foot thermal diffusion column.

The 100 fractions from the second run were first arranged according to increasing refractive index. A sufficient number of fractions having the lowest refractive indices were charged to the column. A temperature gradient of 200° F. was maintained for 3 days. The topmost fraction of about 5 ml. was then withdrawn from the column, and a sufficient number of fractions in order of increasing refractive index from the previous run were charged into the center port, in order to refill the column to the top. This procedure was repeated every other day until 37 fractions were collected and all 100 fractions from the previous run had been charged. During this separation a bottommost fraction of 5 ml. was removed from the column every 10 days and recharged to the center of the column in the proper order according to its refractive index. This prevented a build-up of cycloparaffinic hydrocarbon types in the bottom of the column. The final six fractions were obtained after an additional 3 days by emptying the contents of the column.

A total of 43 fractions of about 5 ml. each was obtained for measurement of physical properties and spectrometric analysis. All the fractions were found to possess a slight odor, which was attributed to a trace amount of oxidation during the thermal diffusion runs. Consequently, in an additional purification step the oil was percolated over alumina in micro adsorption columns. The oil was diluted with 5 ml. of cyclohexane and added to a column, 5 mm. in inside diameter and 200 mm. long, filled with alumina. The oil was eluted with 100 ml. of cyclohexane. After evaporation of the solvent, the oil was found to be odorless and water-white.

MEASUREMENT AND INTERPRETATION OF PHYSICAL PROPERTIES

In order to note the effect of changes in composition on the physical properties of the fractions, a number of physi-

cal measurements were made (Table II). Refractive indices and pycnometer densities shown in Figure 3 were both measured at 70° C. The refractive indices ranged from 1.44016 to 1.49952, while densities ranged from 0.808 to 0.952 for the first and last fractions, respectively. Microviscosities at 100° and 210° F. are shown in Figure 4. Because of their extremely high viscosity at 100° F., the last four fractions could not be determined at this temperature. Viscosity indices were calculated and are plotted in Figure 5. The viscosity index was highest for fraction 1 at 166.5 and decreased steadily to −40 in fraction 39. Micro pour points of the fractions (Figure 6) showed a maximum in the curve. The "waxy" pour points decreased from a high of 65° F. for fraction 1 to a minimum of −30° F. for fractions 20 to 23. The "viscosity" pour points then increased to a maximum of 115° F. in fraction 43.

The physical properties of the original lubricating oil at different stages in the separation by distillation and chromatography, shown in Table III, exhibit only slight changes between the original oil and the material charged to the thermal diffusion columns, indicating that the fraction selected for analysis was a representative portion of the lubricating oil charge.

In an effort to obtain additional information which might substantiate the spectrometer analyses to follow, the n-d-M (refractive index, density, and molecular weight) ring analysis method of van Nes and van Westen (*12*) was employed. From the refractive index and density measurements and average molecular weights found from the mass spectra, it was possible to calculate the average number of rings per molecule for each fraction. As the oil fractions had been subjected to high efficiency distillation to reduce the spread in molecular weight, it was found that only a slight difference existed in molecular weight between the most paraffinic (fraction 1) and cycloparaffinic (fraction 43) fractions. The results given in Figure 7 show that the average number of rings in the molecule varied from 1.7 to 7.2. The number, 7.2 rings per molecule, is an extrapolation of the n-d-M correlation and therefore is only approximate. For the determination of aromatic rings it was found that negative values resulted for all the fractions.

A second attempt was made to determine independently the average number of rings in the molecule from the carbon-hydrogen ratio. This approach was feasible because of the narrow molecular range of the fractions and because the number of hydrocarbon types in each fraction had been reduced. Seven fractions, selected arbitrarily, were subjected to a carbon-hydrogen analysis. These data were then compared with the molecular weight of the fraction and the average number of rings per molecule was calculated. Only saturated hydrocarbon structures were considered in this case. The calculated average number of rings per molecule increased from 0.5 in fraction 2 to about 6 in fraction 43.

SPECTROMETRIC ANALYSIS

Hydrocarbon-type analyses were determined by means of high temperature mass spectrometry.

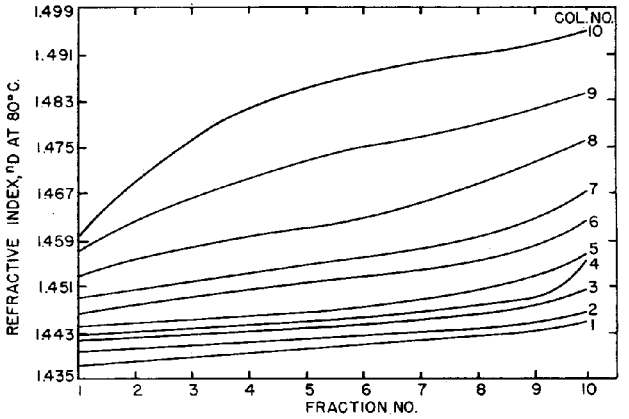


Figure 2. Refractive indices of fractions from second thermal diffusion run

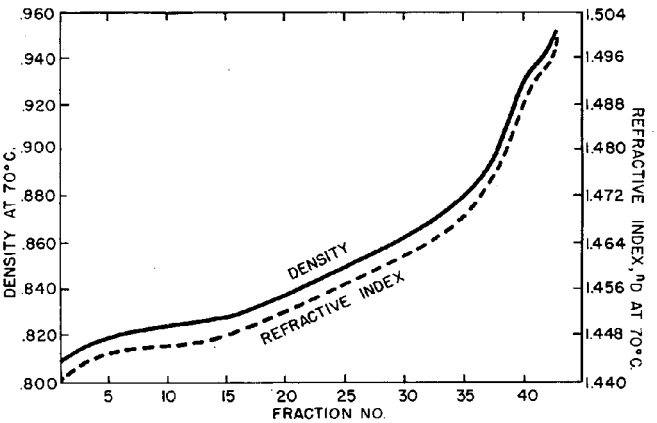


Figure 3. Densities and refractive indices of fractions from final thermal diffusion run

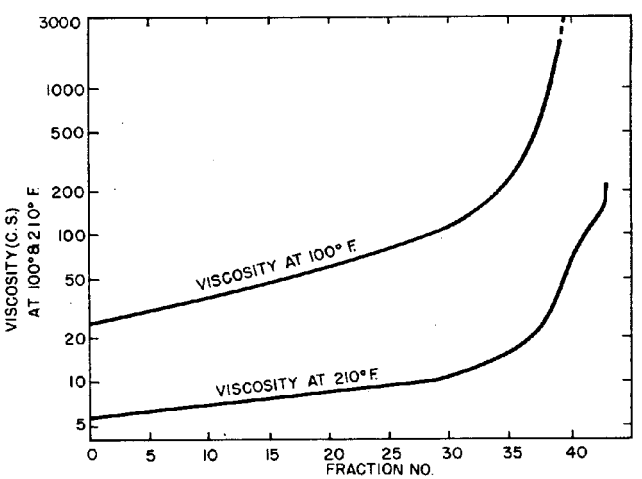


Figure 4. Viscosities of fractions from final thermal diffusion run

Table II. Physical Properties of Fractions from Final Thermal Diffusion Run

Fraction No.	Viscosity, Cs. 100° F.	Viscosity, Cs. 210° F.	Viscosity Index	Density at 70° C.	Refractive Index, n_D^{70}	Pour Point, ° F.	Molecular Wt. [a]	Molecular Wt. [b]	C/H Ratio	Av. No. of Rings/Molecule n-d-M (12)	Av. No. of Rings/Molecule MS	Av. No. of Rings/Molecule C-H ratio
1	25.0	5.74	167	0.808	1.4402	65	482			1.7		
2	28.2	6.05	158	0.813	1.4422	55			5.87	1.9	0.6	0.5
3	30.4	6.24	153	0.813	1.4437	45		461		1.8		
4	32.2	6.41	150	0.819	1.4447	40				2.2		
5	30.5	6.11	150	0.818	1.4442	35	473			2.1		
6	35.2	6.59	142	0.822	1.4456	30				2.3		
7	32.4	6.24	145	0.820	1.4448	25				2.1		
8	37.5	6.76	140	0.823	1.4459	20				2.3		
9	39.2	6.87	136	0.822	1.4461	15	478			2.2		
10	39.8	6.98	137	0.823	1.4462	10				2.2		
11	42.3	7.10	132	0.824	1.4465	5			5.82	2.2	1.2	0.2
12	41.7	7.18	136	0.824	1.4463	5				2.3		
13	45.1	7.31	129	0.825	1.4469	0				2.3		
14	46.3	7.43	128	0.826	1.4474	−5				2.3		
15	47.7	7.46	125	0.827	1.4478	−10				2.3		
16	50.4	7.68	123	0.830	1.4486	−15	480			2.6		
17	52.3	7.77	121	0.833	1.4497	−20				2.8		
18	54.9	7.98	117	0.834	1.4504	−25				2.8		
19	56.5	8.09	118	0.835	1.4510	−25				2.9		
20	54.9	7.96	119	0.836	1.4514	−30				2.9		
21	61.0	8.33	114	0.840	1.4528	−30			6.01	3.0	2.2	1.3
22	64.1	...	...	0.842	1.4536	−30		476		3.1		
23	70.7	8.96	109	0.845	1.4550	−30				3.2		
24	74.2	...	...	0.847	1.4556	−25				3.3		
25	78.6	9.25	102	0.849	1.4568	−25				3.4		
26	86.1	9.73	100	0.852	1.4578	−20	487		6.28	3.4	2.9	2.8
27	89.3	...	...	0.854	1.4583	−20				3.6		
28	94.6	10.2	96.5	0.856	1.4594	−15				3.6		
29	104	10.6	92.5	0.859	1.4603	−15				3.8		
30	118	11.2	87.0	0.862	1.4616	−10				3.8		
31	123	11.5	86.0	0.862	1.4619	−10				3.8		
32	139	12.0	79.0	0.865	1.4632	−10			6.32	3.9	3.6	3.0
33	149	12.3	76.0	0.867	1.4642	−5				4.0		
34	199	...	...	0.875	1.4669	0	491			4.3		
35	233	15.0	58.5	0.878	1.4684	5				4.4		
36	332	17.3	41.5	0.884	1.4712	10				4.6		
37	439	19.6	32.5	0.891	1.4735	20			6.59	4.9	4.8	4.4
38	723	24.1	11.0	0.897	1.4767	35	490			5.1		
39	1953	35.3	−40.0	0.912	1.4824	55				5.7		
40	...	64.5	...	0.928	1.4890	80				6.3		
41	...	99.5	...	0.938	1.4931	90				6.6		
42	...	110	...	0.941	1.4947	95		475		6.9		
43	...	215	...	0.952	1.4995	115	488		6.94	7.2	6.5	6.1

[a] MS determination.
[b] Ebullioscopic determination.

Table III. Physical Properties of Lubricating Oil at Various Stages of Separation

Physical Properties	Original Lubricating Oil Charge	Middle Cut from First Distillation	Heart Cut from Final Distillation	Saturated Portion of Heart Cut[a]
Molecular weight[b]	540	479	482	474
Refractive index, n_D^{70}	1.4642	1.4644	1.4635	1.4588
Density, d^{70}	0.876	0.865	0.864	0.856
Viscosity, Cs.				
100° F.	99.5	105.2	99.5	88.7
210° F.	10.7	10.9	10.6	10.0
Viscosity index	99	95	98	101
Pour point, ° F.	0	0	0	+10
n-d-M ring analysis				
% C_R (total)	55.0	48.5	48.0	46.9
% C_R (aromatic)	0	0	0	0
R_T (total rings)	5.1	3.8	3.8	3.6
R_A (aromatic rings)	0	0	0	0

[a] Charge material to thermal diffusion separation.
[b] Ebullioscopic molecular weight determination.

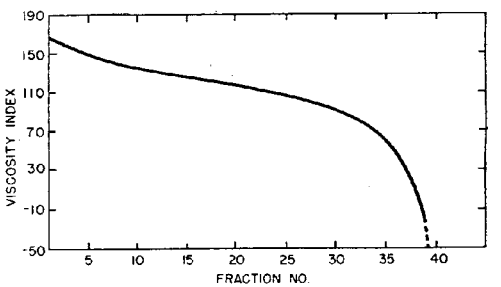


Figure 5. Viscosity indices of fractions from final thermal diffusion run

Supplementary information concerning molecular structure was found by measurement of total methyl groups and methylene groups present in aliphatic paraffin chains by infrared spectrometry. The presence of aromatic structures was found by ultraviolet spectrometry.

METHOD OF CALCULATION

In general, two different methods of mass spectrometric analysis were employed. In one method parent ions are used to determine compounds according to molecular weight. In this calculation it is assumed that the intensity of monoisotopic peaks is related directly to molar concentration. A second procedure is based on fragment ions in the spectrum, which are added together to act as a single peak to characterize all or part of a parent compound. Thus, the fragment ion method is considered to provide information regarding paraffins as parent compounds, and ring systems which generally are only one part of a molecule.

The fragment ion analysis used in this work was similar to that previously employed for an eicosane distillate (*10*). These samples were more complex in composition, however, so that the method had to be extended to include cyclic compounds having as many as nine rings. The final calculation procedure was devised to determine paraffins, mono- and/or noncondensed polycycloparaffins, condensed di- to nonacycloparaffins, free phenyls, free indans and/or Tetralins, and free naphthyls.

Polyisotopic peaks and calibration data used in the matrix solution are shown in Tables IV and V. These include two series.

of peaks each for paraffins and noncondensed cycloparaffins. In practice, results from Σ67 and Σ71 are accepted for the analysis, whereas Σ41 and Σ43 serve as a check matrix. This choice is based on the belief that Σ67 and Σ71 might provide greater precision. This is true because these sigmas include only peaks which are scanned at the same magnet field as the other peaks in the matrix. Some of the Σ41 and Σ43 peaks, on the other hand, are necessarily recorded at a lower magnet field. As a rule, paraffins by Σ43 are 10 relative % higher than when determined by Σ71. Cycloparaffins are correspondingly lower when based on Σ41.

These calibration data are subject to some uncertainty, particularly in the case of compounds having six or more rings for which no direct spectral data were available. Data for paraffins, monocycloparaffins, noncondensed polycycloparaffins, alkyl benzenes, and naphthylenes are probably reliable. This is true because a large number of pure compounds and concentrates of various kinds were examined to select average coefficients. For condensed ring compounds 23 di-, tri-, tetra-, and pentacyclics were studied. Although perhaps only one, cholestane, was representative of structures present in oil, considerable similarity existed between its spectrum and that of the other compounds. These spectra showed that condensed ring molecules may have major ions consisting of (1) the ring system intact, (2) fragments of a ring(s), (3) fragments having the ring system with two or four less hydrogen atoms, and (4) any of the major ions mentioned previously with its mass shifted one unit higher, owing to a heavy carbon atom or deuterium. Based on this information pattern, coefficients were estimated for compounds having as many as nine condensed rings.

These calibrations were obtained with an ion source temperature of 260° C. Subsequent data at 278° C. showed fragment ions to be more intense than parent ones. As a result, ring compounds contributed more to paraffin and noncondensed cycloparaffins. This effect must be taken into consideration before these data are applied to another mass spectrometer.

CHECKS ON METHOD

The accuracy of this method is difficult to determine. There is evidence, however, that gross errors do not exist. One independent check of the method consisted of analyzing synthetic blends made from two different pairs of thermal diffusion fractions. Blend 1 was a 50–50 mixture of fraction 1 (70% paraffins) and fraction 43 (75% condensed cycloparaffins), while blend 2 consisted of 50% fraction 2 and 50% fraction 19. The mass spectrometric analysis is compared with the "known" composition for each blend in Table VI. Reference to this comparison shows that the major constituents—paraffins, noncondensed cycloparaffins, and condensed di- and tricycloparaffins—generally agree within ±10 relative %. Smaller amounts of compounds differ by 0.2 to 2.3 absolute %. Examples of this type of error are the 0.8% tricycloparaffins in blend 2 determined to be 0.0%, and 4.9% tetracycloparaffins in blend 1 reported as 7.2%. Such errors, although relatively large, are not considered serious, in that they are believed to be constant incremental errors caused by several factors—(1) small errors in pattern coefficients of

Table V. Coefficients for Calculation of Saturated Lubricating Oil

(Magnet current = 0.9 ampere)

Peaks	Paraffins, %	Mono- and/or Noncondensed Polycyclo-paraffins, %	Condensed Cycloparaffins, Free Phenyls, Indans, %
Σ41, 55, 69, 83	33	100	45
Σ43, 57, 71, 85	100	51	35
Sensitivity, div./μ	330	270	..

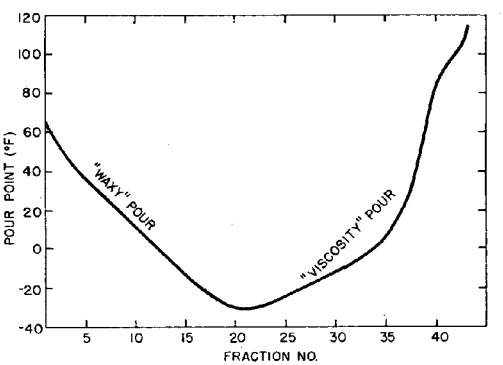


Figure 6. Pour points of fractions from final thermal diffusion run

Table IV. Coefficients for Calculation of Saturated Lubricating Oil

(Magnet current = 1.3 amperes)

Peaks	Paraffins, %	Mono and/or Non-condensed Polycyclo-paraffins, %	Condensed Cycloparaffins, %								Free Phenyls, %	Indans and/or Tetralins, %	Free Naph-thyls, %
			Dicyclic	Tri-cyclic	Tetra-cyclic	Penta-cyclic	Hexa-cyclic	Hepta-cyclic	Octa-cyclic	Nona-cyclic			
Σ 71, 85	100	17–10[a]	7	7	7	7	7	7	7	7	3	1	0.4
Σ 67, 68, 69, 81, 82, 83, 96, 97	64	100	57	57	57	57	57	57	57	57	5	3	1.4
Σ (123, 124—333, 334)	0	10–17[a]	100	20	10	0	0	0	0	40	0.2	0.3	3
Σ 149, 150—443, 444	0	0–7[a]	20	100	30	10	0	0	0	0	10	0.3	0.3
Σ 189, 190—483, 484	0	0	1	20	100	30	10	0	0	0	20	3	0.5
Σ 229, 230—509, 510	0	0	0.3	0	20	100	30	10	0	0	1.5	20	0
Σ 269, 270—507, 508	0.04	0.2	0.2	0	0	20	100	30	10	0	0	2	5
Σ 295, 296—505, 506	1.3	5–1[a]	0.5	0	0	0	30	100	30	10	0	0	20
Σ 321, 322—503, 504	0	0	2	1	0	0	0	30	100	30	0	0	2
Σ 347, 348—501, 502	0	0	3	1	1	0	0	0	30	100	0	0	0
Σ (91, 92—175, 176)	0.3	0	3	12	40	6	0	0	0	0	100	4	0.5
Σ (117, 118—187, 188)	0.3	0	1	3	3	40	0	0	0	0	13	100	0.3
Σ (141, 142—281, 282)	33	0	1	0.6	0.5	0	0	30	10	0	0.7	1	100
Sensitivity, div./μ	112	270	140	137	137	137	137	137	137	137	270	245	274

[a] Varies between monocycloparaffins and noncondensed polycycloparaffins in order given.

Table VI. Mass Spectrometer Fragment Ion Analysis of Synthetic Blends

Component	Blend 1, %		Blend 2, %	
	Known	Mass spec.	Known	Mass spec.
Paraffins	34.8	33.5	43.5	44.0
Mono- and/or noncondensed polycycloparaffins	25.1	23.9	37.5	40.0
Condensed cycloparaffins				
Di-	10.3	12.0	16.3	14.6
Tri-	11.4	11.7	0.8	0.0
Tetra-	4.9	7.2	0.3	0.3
Penta-	4.4	3.5	0.1	0.0
Hexa-	2.1	1.5	0.0	0.0
Hepta-	0.8	1.5	0.0	0.0
Octa-	0.2	0.7	0.0	0.0
Free phenyl	5.6	4.2	1.4	1.0
Free indans	0.4	0.3	0.1	0.1
Free naphthyls[a]	...	...	...	...
	100.0	100.0	100.0	100.0

[a] No attempt was made to determine naphthyls, so known composition is on a naphthalene-free basis.

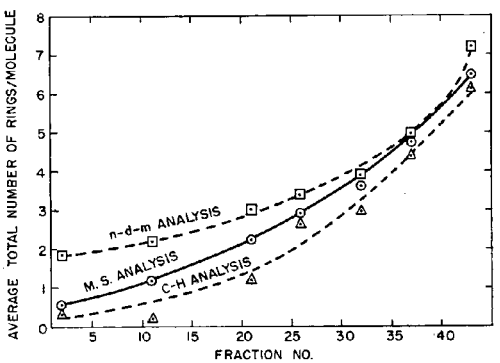


Figure 7. Average total number of rings per molecule in fractions from final thermal diffusion run

major constituents in a mixture, (2) the difficulty of selecting ions which are due solely to one type of ring system (Parent ions, for instance, are not included in sigma values because they are considered usually to consist of more than one ring system. Ions formed by the loss of a substituent on a ring also would be in this category.), and (3) the method of reading peak heights from a mass spectrometer record (simple tape measure used to read total peak intensities). The methods were internally consistent in that analyses of the original charge to the thermal diffusion columns agreed well with the composite of analyses for the 43 individual fractions. This agreement is shown in Tables IX and X.

Another over-all check on the method was obtained by comparing results on fractions 1, 26, and 43 with those obtained by using an alternative scheme of calculation (*2*). This latter method employs an entirely different combination of peaks and groups condensed cycloparaffins together. Comparison of results is shown in Table VII. This agreement is good, particularly in view of the fact that the calibrations presented by the authors of the alternative method were used directly.

Further confirmatory data have been obtained based on independent checks for individual compound types. Isoparaffins, for instance, are reported in fractions 1 to 39. This was expected, in that a preliminary study of the mixture spectra showed no isoparaffinic peaks in the parent mass region of fractions 19 and higher. For this reason a qualitative confirmation of

Table VII. Comparison between Two Different Mass Spectrometric Methods for Calculation of Lubricating Oil Composition

(Fragment ion analysis)

Component	Fraction 1		Fraction 26		Fraction 43		Fraction 1 from Elution of Fraction 26 on Alumina	
	This paper	(*2*)	This paper	(*2*)	This paper	(*2*)	This paper	(*2*)
Paraffins	70	67	16	0	0	0	24	16
Cycloparaffins								
Noncondensed	25	28	40	66	26	18	45	44
Condensed	4	4	41	29	62	64	23	27
Aromatics	1	1	3	5	12	18	8	13

their presence in higher fractions was sought. To do this, fraction 26 (16.2% isoparaffins) was eluted many times through alumina. Finally, the front and tail ends of this elution were analyzed by the mass spectrometer, as shown in Table VIII. Isoparaffins in the front end (No. 26, 1) were 23.5% as compared with 1.0% in the last fraction (No. 26, 19). This showed isoparaffin enrichment in sample 1 in a manner to be expected for the percolation. This lends considerable credence to the qualitative aspects of the method. No attempt was made to account for the unexpected enrichment of benzenes in the two fractions.

Table VIII. Separation of Fraction 26 by Elution Chromatography on Alumina

(Fragment ion analysis)

	Fraction 26, %	Eluted Fraction, %.	
		No. 1	No. 19
Paraffins	16.2	23.5	1.0
Noncondensed cycloparaffins	40.2	45.5	36.1
Condensed cycloparaffins			
Di-	29.1	18.9	19.4
Tri-	9.0	3.2	15.3
Tetra-	1.0	0.1	8.1
Penta-	1.1	0.6	3.0
Hexa-	0.2	0.3	1.4
Phenyl	3.1	6.4	12.1
Indan	0.1	1.5	3.6
	100.0	100.0	100.0

Infrared and ultraviolet analyses have also helped to affirm and supplement the mass spectrometric analyses. Molar absorptivities at 215 and 228 $m\mu$ were used to determine benzenes and naphthalenes by solving two simultaneous equations based on calibration data similar to those of Kinder (*7*). Typical comparisons between the two methods for total phenyl groups are shown below:

Fraction No.	Total Aromatics	
	MS	Ultraviolet
1	1.2	0.8
20	1.5	1.4
33	4.2	3.3
40	6.7	7.3
43	11.2	11.1
Original sample	3.08, 5.4	4.5

The ultraviolet data are summarized as total aromatic carbon atoms in Figure 8.

Infrared measurements of some selected fractions served to determine total methyl and aliphatic methylene groups as shown in Figure 9. The method of Hastings and others (*4*) and Francis (*3*) was used to do this, based on calibrations for a Beckman IR-2 instrument. A semiquantitative comparison can be drawn be-

tween such infrared results and the mass spectrometric analyses. Thus, 14% methyl groups and 72% aliphatic methylene groups were found in fraction 1 by infrared. For the same sample the mass spectrometer reported 70.1% isoparaffins and 29.9% cycloparaffins. Fragment ions in the mass spectrum indicated isoparaffins to be primarily mono- or dimethyl paraffins. Based on the parent ion analysis, the cycloparaffin molecules were found to contain, on the average, about ten carbon atoms in ring structures. For molecules having an average of 35 carbon atoms then, 25 carbons would be present as side chains. If, then, it is assumed that the average side chain contains four carbon atoms, methyl and methylene groups calculated from mass spectrometric data become 12.1 and 76.5%, respectively, which compare favorably with infrared results. Results on other fractions can be compared with less certainty. It is apparent, however, that trends of infrared and mass spectrometric results agree qualitatively with one another.

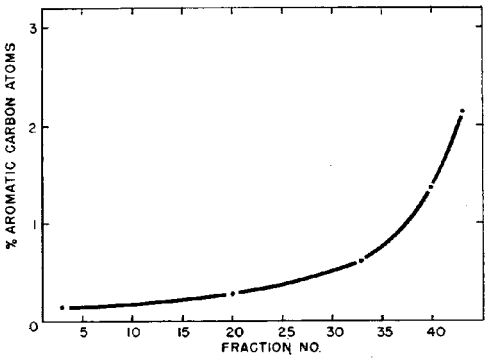


Figure 8. Total aromatic carbon atoms as determined by ultraviolet absorption

COMPOSITION OF LUBRICATING OIL

Results of parent and fragment ion analyses are tabulated in Tables IX and X. Data from parent ions show that fractions 1 through 43 increase in cyclization and decrease in paraffinicity. Fraction 1 contains 70% isoparaffins and 20% monocycloparaffins, whereas fraction 37 has none of these hydrocarbons. Dicylics also occur in fraction 1 and are absent from fraction 38. Heptacyclics appear from the first time in fraction 25, octacyclics in fraction 34, nonacyclics in fraction 39, and finally decacyclics in fraction 43.

Fragment ion calculations summarized in Table X are thought to furnish information of a different nature. However, these data are consistent with parent ion analyses, in that they show a steady increase in cyclic compounds from fraction 1 through 43. The most condensed material found was a small percentage of octacyclic compounds first appearing in fraction 41.

From the parent ion analysis data the average rings per molecule were calculated for a number of fractions. These results are shown and compared with the ring analyses of van Nes and van Westen (*12*) and carbon-hydrogen ratio in Figure 7. It is seen that the ring analyses calculated from mass spectrometric

Table IX. Parent Ion Analysis

Fraction No.	Iso-paraffin[a]	Cycloparaffin								
		Mono-	Di-	Tri-	Tetra-	Penta-	Hexa-	Hepta-	Octa-	Nona-	Deca-
1	70	20	9	1	..	..	..	..	..	..	..
2	57	25	16	2	..	..	..	..	..	..	..
3	51	19	17	5	3	1	1	..	..	..	..
4	50	19	21	6	2	1	1	..	..	..	..
5	49	18	22	6	3	1	1	..	..	..	..
6	48	17	23	7	3	1	1	..	..	..	..
7	46	15	23	9	4	2	1	..	..	..	..
8	44	15	24	10	4	2	1	..	..	..	..
9	46	14	23	10	4	2	1	..	..	..	..
10	44	14	23	11	5	2	1	..	..	..	..
11	47	13	22	11	4	2	1	..	..	..	..
12	45	12	21	11	6	4	1	..	..	..	..
13	44	13	21	11	6	4	1	..	..	..	..
14	42	12	21	12	7	4	2	..	..	..	..
15	41	12	22	13	7	4	1	..	..	..	..
16	36	11	22	17	8	4	2	..	..	..	..
17	32	11	24	17	10	4	2	..	..	..	..
18	31	10	23	19	10	5	2	..	..	..	..
19	30	10	23	20	10	5	2	..	..	..	..
20	26	7	20	24	12	7	4	..	..	..	..
21	25	8	24	22	12	6	3	..	..	..	..
22	22	7	22	24	14	8	3	..	..	..	..
23	20	7	21	25	15	8	4	..	..	..	..
24	18	6	20	27	17	8	4	..	..	..	..
25	17	5	20	25	18	9	5	1	..	..	..
26	16	3	19	27	19	10	5	1	..	..	..
27	16	3	17	27	20	10	5	2	..	..	..
28	15	2	16	27	21	11	6	2	..	..	..
29	13	2	15	26	22	12	7	3	..	..	..
30	12	..	13	29	24	13	7	2	..	..	..
31	12	..	13	28	24	13	7	3	..	..	..
32	9	..	11	27	26	15	8	4	..	..	..
33	9	..	9	26	27	16	9	4	..	..	..
34	5	..	5	20	30	21	11	6	2	..	..
35	5	..	4	20	28	21	12	7	3	..	..
36	4	..	2	16	29	24	14	8	3	..	..
37	..	..	1	14	32	27	15	8	3	..	..
38	..	..	..	10	30	29	17	10	4	..	..
39	..	..	..	3	22	33	22	12	6	2	..
40	..	..	..	1	16	34	24	14	8	3	..
41	..	..	..	1	11	32	25	16	10	5	..
42	..	..	..	..	10	32	25	17	11	5	..
43	..	..	..	..	5	28	24	17	13	9	4
Composite	26	8	15	15	13	11	7	3	1	1	..
Direct MS analysis	26	8[b]	15[c]	15	16	14	5	1	..	..	..

[a] Based on fragment ion analysis.
[b] Includes octacycloparaffins.
[c] Includes nonacycloparaffins.

Table X. Fragment Ion Analysis

Fraction No.	Iso-paraffin	Mono-cyclo-paraffin, Noncond. cyclo-paraffin	Condensed Cycloparaffins							Phenyl	Indan	Naph-thalene[a]
			Di-	Tri-	Tetra-	Penta-	Hexa-	Hepta-	Octa-			
1	70.1	24.4	3.8	0.2	0.1	0.2	...	...	...	1.2	...	...
2	57.4	36.1	5.2	...	...	...	...	...	...	1.3	...	...
3	54.4	38.2	6.3	0.2	...	...	...	...	...	0.9	...	...
4	49.7	40.4	8.6	0.4	...	...	...	...	...	0.9	...	...
5	49.2	40.8	8.7	0.2	0.1	0.1	...	...	...	0.9	...	...
6	48.4	36.7	13.3	0.4	0.1	0.1	...	...	...	1.0	...	...
7	45.7	35.3	17.2	0.4	0.2	0.1	0.1	...	...	1.0	...	...
8	43.8	34.8	19.6	0.3	0.3	0.1	...	...	...	1.1	...	...
9	45.6	33.8	18.8	0.4	0.1	0.1	...	...	...	1.2	...	...
10	44.2	34.1	18.9	0.8	0.6	0.1	0.1	...	...	1.2	...	...
11	47.1	32.8	18.2	0.4	0.2	0.1	...	...	...	1.2	...	...
12	44.7	32.1	20.8	0.9	0.1	0.1	...	...	...	1.3	...	...
13	43.0	33.1	21.3	0.9	0.4	...	...	...	...	1.3	...	...
14	42.1	33.7	21.4	0.9	0.6	...	...	...	...	1.3	...	...
15	40.8	34.7	22.0	0.2	0.9	...	...	...	...	1.4	...	...
16	36.0	37.6	23.1	0.9	0.9	0.1	...	...	...	1.4	...	...
17	32.4	38.4	25.3	0.9	1.1	0.5	...	...	...	1.4	...	...
18	31.0	38.8	26.4	1.2	0.8	0.3	...	...	...	1.5	...	...
19	29.6	39.2	27.5	1.5	0.6	0.1	...	...	...	1.5	...	...
20	25.7	41.7	27.0	2.2	1.2	0.4	0.3	...	...	1.5	...	...
21	24.7	42.2	26.1	2.6	0.4	0.6	0.1	...	...	3.3	...	...
22	21.7	40.2	29.5	3.1	0.9	0.8	0.2	...	...	3.5	...	0.1
23	20.3	42.3	27.0	5.0	0.9	0.8	0.2	...	...	3.4	...	0.1
24	18.2	43.7	26.1	7.1	1.1	0.6	0.2	...	...	2.9	...	0.1
25	17.0	46.5	24.1	6.3	1.2	1.0	0.2	...	...	3.6	...	0.1
26	16.2	40.2	29.1	9.0	1.0	1.1	0.2	...	...	3.1	...	0.1
27	16.3	42.0	29.3	6.5	2.4	0.5	0.2	...	...	2.7	...	0.1
28	15.2	41.7	28.6	8.3	1.8	1.1	0.4	...	...	2.8	...	0.1
29	12.7	43.2	27.0	11.7	0.8	1.1	0.2	...	...	3.0	0.2	0.1
30	11.7	41.2	29.6	10.9	1.8	1.1	0.3	...	...	3.2	0.1	0.1
31	11.6	39.8	30.2	11.0	3.2	0.8	0.3	...	...	2.8	0.2	0.1
32	9.4	37.7	31.4	14.4	2.1	1.2	0.4	...	...	3.2	0.1	0.1
33	9.1	38.0	25.9	19.5	1.8	1.8	0.4	...	...	3.3	0.1	0.1
34	4.6	37.8	27.2	16.5	6.1	2.5	0.9	...	...	3.7	0.5	0.2
35	5.1	37.0	26.0	16.2	8.1	2.5	1.2	...	...	3.0	0.6	0.3
38	3.8	34.1	25.9	17.6	9.1	3.7	1.5	...	...	3.5	0.5	0.3
37	3.9	33.3	23.5	20.1	7.9	4.2	1.4	...	...	5.1	0.2	0.4
38	3.8	34.1	20.9	18.7	10.1	4.3	1.4	...	...	5.8	0.5	0.4
39	3.8	32.7	19.4	17.2	11.9	5.7	2.1	...	...	6.5	0.2	0.5
40	...	24.9	19.9	21.6	11.9	9.6	3.2	0.4	...	7.7	0.3	0.5
41	...	25.1	18.7	21.4	10.8	10.8	3.7	0.5	0.3	7.8	0.3	0.6
42	...	23.2	18.9	22.8	11.1	9.5	3.3	1.0	0.5	8.7	0.3	0.7
43	...	25.9	16.1	21.9	9.7	8.3	4.8	0.6	0.7	10.2	1.0	0.8
Composite	25.81	36.37	21.72	7.50	2.89	1.77	0.63	0.06	0.03	2.96	0.12	0.14
Direct MS analysis	26.3	36.9	19.8	7.0	1.4	1.6	0.5	0.1	0.9	4.9	0.5	0.1

[a] Determined by ultraviolet.

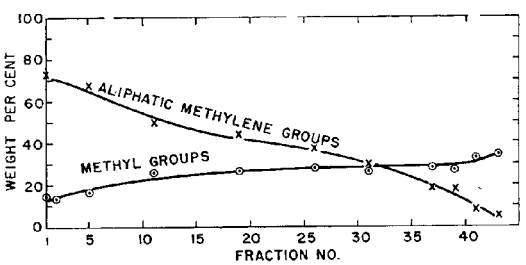


Figure 9. Functional groups determined by infrared absorption

data fall midway between the ring values by the other two methods.

STRUCTURE STUDY OF LUBRICATING OIL MOLECULES

Isoparaffins. Paraffins present in this sample are all branched-chain molecules, as indicated by the absence of parent ions which would result from normal paraffins. The amount of branching seems to increase in proceeding from fraction 1 to 39. Those present in fraction 1, for instance, have some ions near the parent mass region which are apparently due to the presence of a methyl group on the fourth or fifth carbon atom from the end of the chain. It is also possible that some molecules contain an ethyl or propyl side chain or two methyl groups along the chain. In higher numbered fractions fragment ions shift to lower masses, indicating long side chains or increased degrees of branching.

Monocycloparaffins. A study of the spectrum of fraction 1 indicated that these hydrocarbons were multisubstituted. It appeared that side chains generally consisted of two or more carbon atoms, because the spectra showed peaks which resulted from the loss of only ethyl and heavier groups from parent molecules.

Polycycloparaffins. The structure of these compounds unquestionably varies from rather simple molecules having only two rings with many side chains to highly cyclic ones having mostly methyl group side chains. This is borne out by a study of combined infrared and mass spectrometric data. The most cyclic separated material was fraction 43, as indicated by fragment and parent ion analyses. This sample was also of interest because of its high viscosity and other extreme physical properties. A thorough study was made of its spectroscopic data, therefore, to establish probable molecular structure.

STRUCTURE STUDY OF FRACTION 43

The parent ion analysis showed that mono-, di-, and tricyclic compounds were absent, and tetra- through decacyclics present. Fragment ion analysis on the other hand showed a preponderance of mono-, di-, tri-, tetra-, and pentacyclic systems. This indicated that more than one ring system was in an average molecule.

At this point an attempt was made to show how fragments might be arranged in parent molecules. To do this a statistical calculation was carried out to piece fragments together mathematically into combinations comprising these molecules. The calculation is based on the assumption that different rings in a

given molecule form ions with equal probability independent of the number of rings of a given kind. This means that the number of ions formed by dissociation is a function only of ring structure. According to this, a molecule having only one single ring would have single ring ions as intense as a molecule having two or more single rings. This assumption is obviously not absolutely valid, as indicated by the nonuniform distribution of rings. For instance, the progression of 21.9% tri-, 16.1% di-, and 25.9% monocyclics shows a higher amount of monocyclics than would be expected. This inconsistency does not appear to affect seriously the over-all conclusions as to structure. However, it does influence the distribution of the parent molecules which are calculated to have four, five, six, etc., rings. For this reason it was further assumed that single rings originating from different molecules had a concentration of 11% instead of 25.9%.

The first step in this calculation involved estimates of molecules which had only one system of rings in them. It seemed that molecules having seven (0.6%) or eight (0.7%) condensed rings as measured by fragment ions were in this category. In addition, a fraction of the molecules having five and six condensed rings were also assigned to this class. This is illustrated by the data in Table XI, third column.

Molecules having aromatic groups were considered next. Such compounds form ions consisting primarily of aromatic nuclei. For these molecules there would be essentially no ions to indicate saturated rings. For this reason phenyl, indan, and naphthalene nuclei were assumed to be evenly distributed in molecules having a total of three to five rings. The mathematical value of this assumption appears in column four of Table XI and the final probabilities used in the calculation are in the fifth column.

The procedure of piecing together fragments may be illustrated by considering how a few of the individual combinations were calculated. As parent ion analysis ruled out the presence of mono-, di-, and tricyclic compounds, the simplest one is a tetracyclic. Combinations of individual ring systems which would constitute a tetracyclic and their probabilities of occurrence would be:

Combination	Probability of Occurrence
1. Four single rings	$(0.11)^4 = 0.0002$
2. Two single rings and one two-ring	$3 \times (0.11)^2 \times 0.161 = 0.0058$
3. One single ring and one three-ring	$2 \times 0.11 \times 0.219 = 0.0482$
4. Two—two-ring	$(0.161)^2 = 0.0259$
5. One tetracyclic	$= 0.0000$
	0.0801

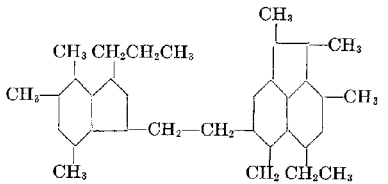
The sum of the individual probabilities, 0.0801, represents the total mole fraction of tetracyclic compounds.

More complex molecules result from an increasing number of combinations. Pentacyclics can arise from seven different ones and decacyclics from as many as 33. This latter number would have been even greater, except that it was assumed that no more than seven individual ring systems were present in a molecule. The complete calculation consisted of calculating probabilities for individual combinations and summing them to obtain the concentration of compounds having from four through ten rings. The sum of all probabilities was less than 100%, so that the final calculated composition was obtained by normalization. This result is given in Table XII and is compared with the corresponding values based on the parent ion analysis. This comparison is favorable enough to indicate that the piecing together process was fairly reasonable.

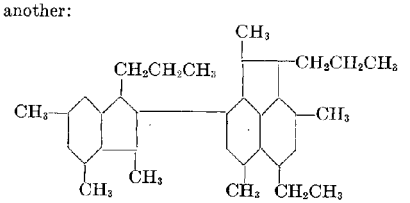
By combining the statistical picture with infrared structural data, some of the principal molecules can be visualized within certain limits. Pentacyclic compounds, for instance, show by statistical calculation a predominant molecule consisting of condensed di- and tricyclic systems. Infrared data show that of 35 carbon atoms in an average molecule 24% (or 8.4 atoms) are methyl groups and 6% or 2.1 carbon atoms are aliphatic methylene groups. Using these data and assuming hydrindan and perhydroacenaphthene ring structures, the number and kind of carbons in this molecule may be as follows:

Structure	No. of Carbon Atoms
Condensed two-ring (hydrindan)	9
Condensed three-ring (perhydroacenaphthene)	12
Methyl groups	8
Aliphatic methylene groups	2
Unaccounted for	4
	35

Based on the mixture spectrum, it also appeared at least one propyl group is present in some molecules. The composite molecules could then be:

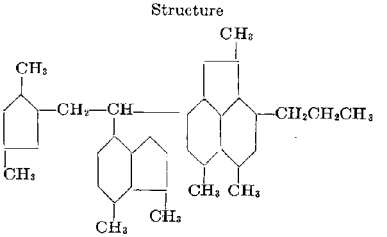
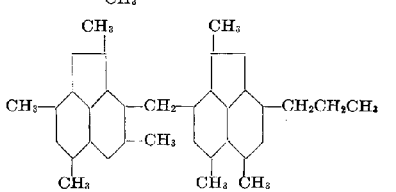
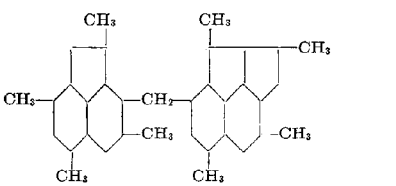


An alternative possibility is that the rings are bonded directly to one another:



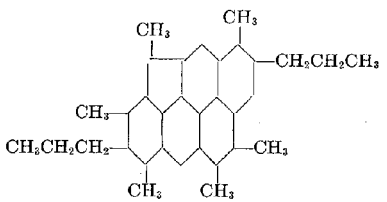
In these molecular formulas side chains, such as methyl, ethyl, and propyl groups, are positioned at random with no experimental data to indicate specific locations.

On this basis other abundant molecules would be of the nature shown below.

No.	No. of Rings in Parent Molecule	Structure
1	6	
2	6	
3	7	

Because fairly specific formulas have been proposed for compounds in a mixture as complex as lubricating oil, it is of interest to consider the likelihood of their existence. This problem narrows down to the reliability of structural information. In this respect it is felt that methyl and aliphatic methylenes are reliably determined. Similarly, the parent ion analysis appears reasonable, as indicated in Figure 7 by the degree of its agreement with the ring analysis calculated by the n-d-M and carbon-hydrogen ratios. The least reliable structural data are the degree of ring condensation that exists.

This latter information, which is based on fragment ion or functional group analysis, is subject to some uncertainty. Spectra of mono- through pentacyclic compounds verify the method. However, only one of these compounds was considered to be representative in structure. Because of this and the lack of spectra for pure compounds of greater condensation, it is impossible to be sure that these more highly cyclic compounds do not dissociate to yield major ions which appear to originate from compounds of lesser cyclization. If, for instance, the principal dissociation of a condensed octacyclic resulted in ions corresponding with one, two, and three rings, the conclusions regarding condensation would be erroneous. For this case the hexacyclic compound, No. 2 above, could then be of the nature:



No. of carbon atoms = 33

DISCUSSION OF RESULTS

The data on composition and physical properties for the series of 43 fractions indicate that two general groups of hydrocarbon types may be responsible for the characteristics of the oil. The first group, which includes fractions 1 to 34, is comprised largely of isoparaffins and cycloparaffins containing one to six rings or an average of about two rings per molecule. These fractions usually exhibited the favorable properties of the oil, such as good viscosity, viscosity index, and pour point. The second group, which includes fractions 35 to 43, contains cycloparaffins having three to 10 rings, or an average of about five rings per molecule. In this case the properties of the oil changed very rapidly as the number of rings per molecule increased. A sharp rise was noted in viscosities and in pour point, while the decrease in viscosity index was equally rapid. It is seen in Figure 9 that as the number of rings increased in the molecule, the length of aliphatic chains decreased.

Table XI. Fragment Data for Fraction 43

Fragment of Molecule	Fragment Ion Analysis, %	Molecules Containing Only One System of Rings, %	Fragments Assumed to Be Associated with Aromatic Nuclei, %	Fragments Free to Be Combined with Others (Probabilities), %
Monocycloparaffin ring	25.9	0.0	0.5	25.9[a]
Condensed cycloparaffin ring				
Di-	16.1	0.0	4.1	16.1
Tri-	21.9	0.0	4.0	21.9
Tetra-	9.7	0.0	3.4	9.7
Penta-	8.3	3.3	0.0	5.0
Hexa-	4.8	2.4	0.0	2.4
Hepta-	0.6	0.6	0.0	0.0
Octa-	0.7	0.7	0.0	0.0
Free phenyl[b]	10.2	. . .	0.0	..
Free hydrindan[b]	1.0	..	0.0	..
Free naphthalene[b]	0.8	..	0.0	..
	100.0		12.0	

[a] Value of 11% assumed for calculation.
[b] Only fragment of parent molecule determined.

Table XII. Comparison of Calculated with Parent Ion Analysis of Fraction 43

Cycloparaffin Component	Calculated, %	Parent Ion Analysis, %
Tetra-	9	5
Penta-	17	28
Hexa-	21	24
Hepta-	19	17
Octa-	16	13
Nona-	10	9
Deca-	8	4
	100	100

Although a small portion of the rings were aromatic, it is believed that the preponderance of cycloparaffin rings controls the physical behavior of these molecules.

In regard to the composition of fraction 43, the properties of this material are by far the most unusual for any predominantly saturated oil ever examined in this laboratory or reported in the literature to date. The oil has the appearance of a colorless, thick, tacky liquid which does not flow visibly below a temperature of 115° F. Mass spectrometric analysis has shown that this oil is comprised mainly of multiring cycloparaffins containing at least four and as high as 10 rings per molecule. Of particular interest to those concerned with the composition of petroleum is the appreciable concentrations of 8-, 9-, and 10-ring hydrocarbons in the sample.

ACKNOWLEDGMENT

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Determination of Saturated Hydrocarbons in Heavy Petroleum Fractions by Mass Spectrometry

H. E. LUMPKIN

Technical and Research Divisions, Humble Oil and Refining Co., Baytown, Tex.

A procedure for the type analysis by mass spectrometry of the saturate portion of petroleum materials of high molecular weight employs characteristic fragment masses of paraffins, noncondensed naphthenes, and condensed naphthenes containing two through six condensed rings per molecule to delineate these types. The sensitivity and interference coefficients are averages from pure compound spectra and extrapolated data. The method is simple and rapid, lending itself to inverted matrix and computer calculation. Any group with an instrument capable of resolving and pumping out high boiling petroleum materials should be able to use the method directly.

IN THE gasoline and lower distillate boiling ranges of petroleum, mass spectrometer methods of type analysis (*1*, *2*, *7*) generally determine both saturate and aromatic compound types. The three saturate types usually measured by these methods are paraffins, naphthenes, and condensed naphthenes. The condensed naphthenes in gasoline are primarily compounds containing two condensed naphthene rings per molecule, such as bicyclo-octane, hydrindane, and Decalin. In the higher distillate boiling ranges of petroleum it becomes necessary to separate the saturate and aromatic portions of oil prior to mass spectrometric determinations. This can be accomplished fairly completely using solid adsorbent chromatographic techniques (*4*, *5*). The two portions of oil are then examined separately by the methods available.

The mass spectrometer has been employed to identify many of the hydrocarbon and nonhydrocarbon compound types present in the aromatic portion of a gas oil (*6*), and methods have been published for the analysis of the saturate portion of lubricating oils and wax (*3*, *11*). The latter methods do not, however, determine the degree of condensation of the naphthenes. As the more complex fractions of petroleum, such as heating oil, gas oil, cycle stock, and lubricating oil, contain condensed naphthene compounds made up of more than two condensed naphthene rings per molecule, additional types should be determined for more complete characterization of the samples. A procedure recently described by Melpolder and associates (*9*) does provide for the analysis of condensed naphthalenes as well as aromatic nuclei. A method has been developed in these laboratories which determines paraffins, noncondensed naphthenes, and condensed naphthenes containing two to six condensed rings per molecule. The development of this method and its application to pure compounds and to separated petroleum fractions are described.

OBTAINING THE MATRIX

In the development of the type analysis it was desirable to use a sound theoretical basis entailing a minimum of assumptions. A simple, rapid method was sought, which would yield the maximum information concerning the extent of condensation of the naphthenes. It was also desirable that the method lend itself to inverted matrix and electronic computer calculation.

There are two major steps involved in the development of a type analysis by mass spectrometry: (1) the selection of a group of masses which are characteristic of the compound types to be determined; and (2) the determination of sensitivity and interference values of the types—i.e., the ion abundance (or peak height) on a relative or absolute basis of each type at its selected group of characteristic masses and at the masses chosen for all the other compound types.

In surveying the literature of mass spectral data, 138 spectra of pure saturate compounds of high molecular weight were found. These had been submitted to Research Project 44 of the American Petroleum Institute by the laboratories of the Shell Oil Co., Atlantic Refining Co., and Humble Oil and Refining Co. As there were several compounds available of each of the types being considered for inclusion in the procedure, except five and six condensed rings per molecule naphthenes, it was thought that these might provide sufficient data on which to base the method. It was hoped that the averaging effect of the few compounds of each type employed in setting up the procedure would give a result approaching that for the many thousands of compounds making up each type in the high boiling ranges of petroleum.

The mechanics of evaluating various selections of characteristic masses and computing the sensitivity and interference coefficients appeared to be so formidable that it was decided to employ high speed electronic calculators and sorters on the problem. Accordingly, the relative intensities (most abundant peak = 100.00) of each of the masses beginning at m/e 24 for each of the 138 spectra, as well as factors for computing absolute sensitivities in divisions per micron of reservoir pressure on a common sensitivity basis for each spectrum, were punched on data cards. Summation of the relative intensities for the selected m/e groups and computation of the sensitivity and interference values were made with a high speed computing machine. After various selections of mass groupings had been tried with varying degrees of success as indicated by sample analyses, the masses characteristic of the compound types given in Table I were chosen.

Table I. Characteristic Mass Groupings

Paraffins	71, 85, 99, 113
Noncondensed naphthenes	69, 83, 97, 111, 125, 139
Condensed naphthenes	
2 rings/molecule	109, 123, 137, 151, 165, 179, 193
3 rings/molecule	149, 163, 177, 191, 205, 219, 233, 247
4 rings/molecule	189, 203, 217, 231, 245, 259, 273, 287, 301
5 rings/molecule	229, 243, 257, 271, 285, 299, 313, 327, 341, 355
6 rings/molecule	269, 283, 297, 311, 325, 339, 353, 367, 381, 395, 409

The paraffin masses are the usual ones employed in type analyses and are the C_3 through C_8 alkyl ions. The naphthene masses were chosen so that the lowest mass in each group represented the minimum nuclear molecular weight, assuming all C_5 rings. The series advanced by 14 mass units (CH_2 groups) to the nuclear molecular weight corresponding to all C_6 rings; then four additional peaks in the same C_nH_{2n+z} series were added in order that alkyl substitution on the nucleus might contribute to the summation. After computation, the sensitivity and interference values were tabulated by compound type and by source of spectra in each type. Simple averages of the coefficients of the compounds in each type were computed. As there

were some rather large differences among the compound type sensitivities for the spectra from different laboratories, only the values from the Shell spectra, which represented the majority of those available, were employed further. In Table II the number of compounds of each type used in determining the final coefficients are shown. Although the pure compound sensitivity values varied widely within each type, no dependence of sensitivity of molecular weight could be found.

Because of the complete absence of pure compound spectra for condensed naphthenes having five and six rings per molecule, it was necessary to determine the sensitivity coefficients and the divisions per micron they would contribute to the mass summations selected for the other types (interference values) from extrapolation of curves constructed from the data for the other types. In plotting average divisions per micron for each summation against number of condensed naphthene rings per molecule (Figure 1), it was found that the curves were regular, leading to extrapolated values for the condensed naphthenes of five and six rings per molecule, which appeared satisfactory. Data from the curves for all the types were read and arranged in matrix form (Table III). The method contains no provision for determining small amounts of aromatic impurities which might be present in the saturate portion of a separated oil. Alkyl benzenes and indanes would interfere with and be determined primarily as four- and five-ring condensed naphthenes.

Table II. No. of Pure Compound Calibration Spectra Employed

Paraffins	24 (8 normal, 16 iso)
Noncondensed naphthenes	28
Condensed naphthenes	
2 rings/molecule	8
3 rings/molecule	6
4 rings/molecule	6
Total	72

Table III. Matrix for Saturate Type Analysis

	Paraffins	Noncondensed Naphthenes	Condensed Naphthenes 2-ring	3-ring	4-ring	5-ring	6-ring
Σ 71–113	561[a]	243	67	29	13.4	7	4.4
Σ 69–139	206	931	235	120	72	49	35
Σ109–193	3.4	48.7	410	130	75	50	38
Σ149–247	0.2	0.9	4.1	245	88	50	33
Σ189–301	0.1	0.1	0.9	7.6	168	50	28
Σ229–355	0	0	0.4	0.4	2.7	127	35
Σ269–409	1.5	0.3	0	0	0	2	102

[a] Divisions per micron of pressure with nC_{15} m/e 226 = 10.0 divisions per micron.

APPLICATION TO PURE COMPOUND SPECTRA

An analytical method for complex mixtures may be put to an extreme test by applying it to pure compounds. This is done regularly in the literature and in many cases is meaningful. The analyses of a few pure compounds by this method are given in Table IV. The compounds were selected at random, every second, or every third, in the tabulation of Shell data being chosen, according to the number of each type available. While some may view these data as indicating the probable accuracy of the method, they indicate, rather, the differences between each particular pure compound spectrum and the average spectra of those of that type employed in arriving at the matrix values. The analyses of the pure compounds further show that the masses chosen for each type are indeed characteristic of the type.

ANALYSES OF LUBRICATING OIL FRACTIONS

The method has been applied to a series of "homogeneous" saturate fractions of lubricating oil obtained from API Research

Table IV. Analyses of Pure Compounds

Type and Name	Paraffin, %	Noncond. Naph., %	Condensed Naphthenes, % 2-ring	3-ring	4-ring	5-ring	6-ring
n-Paraffins							
n-Hexacosane	99	0	0	0	0	0	1
n-Octacosane	97	3	0	0	1	0	0
n-Hexatriacontane	91	9	0	0	0	0	0
n-Dotriacontane	93	7	0	0	0	0	0
n-Tetracosane	98	2	0	0	0	0	0
Isoparaffins							
4-*n*-Propylheptadecane	98	2	0	0	0	0	0
9-*n*-Butyldocosane	99	1	0	0	0	0	0
5-*n*-Butyldocosane	92	8	0	0	0	0	0
11-*n*-Amyleneicosane	98	2	0	0	0	0	0
2,2,4,15,17,17-Hexamethyl-7-12-di-(3,5,5-trimethylhexyl)octadecane	85	14	1	0	0	0	0
Noncondensed naphthenes							
1,1-Dicyclohexyltetradecane	0	93	7	0	0	0	0
11-Cyclohexyleneicosane	41	59	0	0	0	0	0
13-Cyclohexylpentacosane	30	67	0	0	0	0	0
7-Cyclohexyleicosane	37	63	0	0	0	0	0
1,5-Dicyclohexyl-3(2-cyclohexyl-ethyl)pentane	0	93	7	0	0	0	0
1,7-Dicyclopentyl-4(3-cyclopentyl-propyl)heptane	0	93	7	0	0	0	0
1,4-Di-*n*-decylcyclohexane	0	100	0	0	0	0	0
1,2-Dicyclohexylethane	0	100	0	0	0	0	0
1-Cyclohexyldecane	0	100	0	0	0	0	0
2-ring condensed naphthenes							
11-α-decalinheneicosane	7	0	93	0	0	0	0
1,1-Di(α-decalyl)hendecane	0	4	88	4	2	2	0
9-[α(*cis*-0,3,3-Bicyclooctyl)-methyl]heptadecane	19	11	68	1	1	0	0
1-α-Decalylhendecane	0	0	100	0	0	0	0
1,1-Di(α-decalyl)ethane	0	0	100	0	0	0	0
3-ring condensed naphthenes							
9-*n*-Dodecylperhydroanthracene	0	0	2	98	0	0	0
9-*n*-Dodecylperhydrophenanthrene	0	0	5	85	10	0	0
1(5-Perhydroacenaphthyl)pentadecane	0	0	0	100	0	0	0
9-Cyclohexylperhydroanthracene	0	0	15	83	2	0	0
4-ring condensed naphthenes							
Cholestane	0	0	11	20	69	0	0
6-*n*-Octylperhydrobenz(de)-anthracene	0	0	1	3	96	0	0
9-*n*-Octylperhydronaphthacene	0	0	1	11	88	0	0

Project 6, on which a considerable body of analytical information is available (*8*). This includes the normal measurements of physical properties, from which the average number of naphthene rings per molecule (R_N) can be calculated employing van Nes and van Westen's n-d-M correlations (*10*). A modified Consolidated Model 21-103 analytical mass spectrometer was employed in obtaining the spectra of these samples and of those described later. The modifications made on the instrument and the heated inlet system used in this study have been discussed (*6*). In Table V the average number of naphthene rings per molecule (R_N) for API-6 homogeneous lubricating oil fractions 1 through 5 are shown. These values were calculated from the n-d-M method, from the known hydrogen content of the samples, and from a density correlation devised by B. H. Johnson of these laboratories. The R_N values are compared with the average number of rings per condensed nucleus calculated from the mass spectrometer analyses. The very good correlation between the mass spectrometer and the R_N values may indicate that most of the naphthene rings in the average molecule are condensed in one nucleus. Determination of the mass spectrometer value, which appears to correlate well with the important catalytic cracking feed stock characteristic, R_N, is possible from a type analysis only if a breakdown of the condensed naphthenes into number of rings per molecule is obtained.

ANALYSES OF THERMAL DIFFUSION FRACTIONS

Analyses of some thermal diffusion fractions from the saturate portion of a dewaxed light motor oil distillate by this method are shown in Table VI. As thermal diffusion is an analytical separation method known to concentrate paraffins in the top portion of the column and condensed naphthenes in the bottom of the column in the separation of saturates, the regularity of the calculated analyses shown is satisfying.

Table V. Comparison of Ring Values by Mass Spectrometer with Number of Naphthene Rings per Molecule Determined by Several Methods

	API-6 Homogeneous Lubricating Oil Fraction No.				
	1	2	3	4	5
MS	1.15	2.08	1.88	1.74	2.76
n-d-M	0.96	1.81	2.04	1.99	2.70
% H	1.00	2.00	2.00	2.00	3.00
Density correlation	1.06	2.02	2.02	2.08	2.50

Table VI. Analyses of Thermal Diffusion Fractions

Diffusion column port No.	2	6	8	10
Paraffins	64	44	39	18
Noncondensed naphthenes	34	43	44	47
Condensed naphthenes				
2 rings/molecule	2	9	13	23
3 rings/molecule	0	4	3	10
4 rings/molecule	0	0	1	2
5 rings/molecule	0	0	0	0
6 rings/molecule	0	0	0	0

CONCLUSION

A mass spectrometric method for the analysis of saturate fractions of high molecular weight has been developed. Considering the complexity of the samples to which the method can be applied, it is very rapid. The calculation, including numbering the masses on the record, reading the peak height of 55 masses, summing the groups, and solving the equations with an inverted matrix, requires about 40 minutes. Any group with an instrument capable of resolving and pumping out petroleum materials in the boiling range from heating oils to lubricating oils should be able to apply the method directly in analyzing saturate fractions.

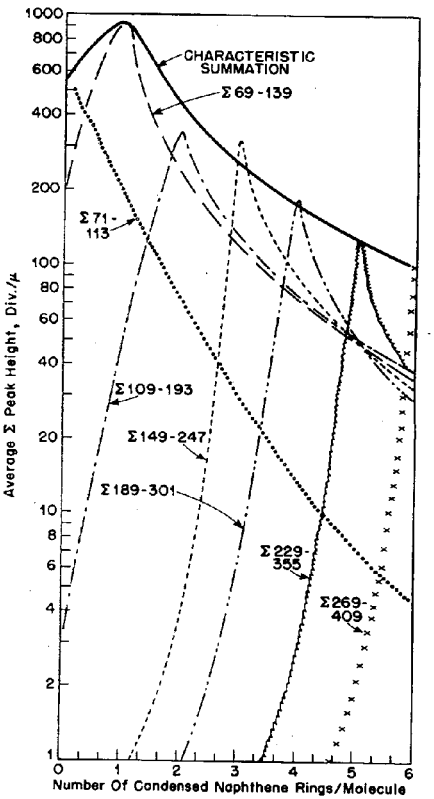

Figure 1. Coefficients of saturate compound types

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Fluorescent Indicator Adsorption Method for Hydrocarbon Type Analysis

Application to Traces and to Heavier Distillates

H. S. KNIGHT and SIGURD GROENNINGS

Shell Development Co., Emeryville, Calif.

The saturated, olefinic, and aromatic component types in lighter petroleum distillates are commonly determined by the fluorescent indicator adsorption (FIA) method in which a small sample is passed through a long narrow chromatographic column, and the composition is computed from the lengths of the zones. This simple method has been extended to the determination of hydrocarbon types in smaller than normal concentrations, and to the analysis of cracked gas oils and lubricating oils. For the determination of small quantities —0.1 to about 3%—of one type in the others, the pertinent zone developed by the usual procedure is too short to measure. This was circumvented by using a larger charge of measured volume and calculating the concentration of the trace by means of a calibration factor. Analysis of heavier distillates was accomplished by alteration of column dimensions, addition of a special dye, and dilution of the heaviest oils to reduce their viscosity.

IN 1948 Conrad (*2*) rendered the aromatic portion of gasoline in a chromatographic column visible in ultraviolet light by addition of a small amount of a fluorescent dye, whereby the aromatic content could be obtained simply by linear measurement. In 1951 Criddle and Le Tourneau (*3*) improved and extended the fluorescent indicator (FIA) method by using dyes which also marked the olefinic portion. Thus an excellent analytical tool was made available to the petroleum industry. By this means the concentrations of total saturates, total olefins, and total aromatics can be determined in gasolines, jet fuels, and kerosines more reliably and more simply than by any other routine procedure. (The aromatics aggregate includes olefinic aromatics which are classified as aromatics, together with sulfur, nitrogen, and oxygen compounds.) The method has found widespread use, and has been tentatively adopted by the American Society for Testing Materials (*1*). In principle, it operates as follows:

A small glass adsorption column with long narrow extension is packed with fine activated silica gel, a minute portion of which has been dyed with a fluorescent dye mixture. Approximately 0.75 ml. of sample is introduced and eluted with alcohol under pressure. The hydrocarbons separate according to their adsorption affinities into saturates, olefins, and aromatics, in that order, followed by the alcohol. The fluorescent dyes are also selectivcly adsorbed and appear at the boundaries of the hydrocarbon zones where they are visible under ultraviolet light. The volume per cent of each hydrocarbon type is computed from the length of each zone in the long narrow extension of the column, and of the sum of the zones, representing the whole sample. Results obtained with gasolines, jet fuels, and kerosines are usually accurate to ±1 or 2%, and 12 to 15 analyses can be completed in 8 hours.

In the present paper extensions of the scope of the FIA method are presented. Thus, with certain limitations, it has been made applicable to the determination of "trace" quantities of one hydrocarbon type in the others as well as to the analysis of heavier distillates.

HYDROCARRON TYPE ANALYSIS FOR TRACES

No reliable routine method has been available for the determination of relatively small quantities, in the order of 0.1 to 3%, of one of the hydrocarbon types in the others. It was therefore desirable to try to extend the FIA method to the analysis of materials like odorless kerosine and petroleum-derived aromatics, which contain predominantly one hydrocarbon type with traces of others. Moreover, by applying such a "Trace-FIA" method to the hydrocarbon-type aggregates, isolated by large scale development chromatography, slight overlapping of one type into another can readily be detected and accounted for.

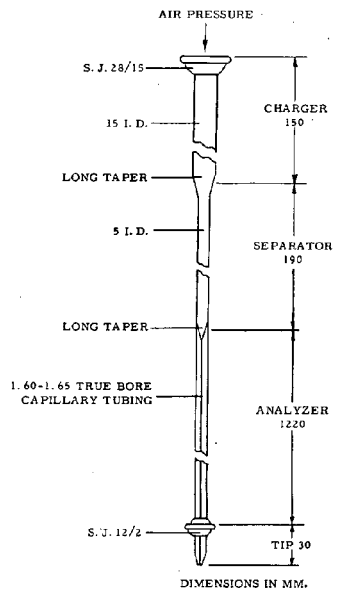

Figure 1. Fluorescent indicator adsorption column for lighter distillates

With the regular FIA method, as outlined above, the zone length of a hydrocarbon type present in very small concentration is too short for accurate measurement. The zone can be made longer by merely increasing the sample charge; but then the length of the zone in question cannot be related to the zone length of the total sample because the latter now more than fills the narrow extension of the column in which the measurements are made. However, this difficulty can be overcome by relating the volume of the liquid in the zone in question to the measured volume of the sample charge. The volume of the zone is obtained from its length by calibration of the packed column's long narrow extension made from true-bore capillary tubing.

The simplest form of trace analysis is represented by the cases where the type to be determined is more strongly adsorbed than

the rest of the sample—for instance, traces of aromatics and of olefins in saturates. A sample, larger than employed in the regular FIA analysis, is charged to the column, and the pertinent zone is measured and converted to volume as mentioned above. When the type to be determined is less strongly adsorbed than the rest of the sample, on the other hand, it is necessary first to pass the sample through a larger auxiliary column in which the weakly adsorbed trace material is allowed to develop and form a concentrate at the liquid front. The collected concentrate is then analyzed in the FIA column.

METHOD FOR TRACES

Apparatus and Materials. FIA COLUMN FOR LIGHTER DISTILLATES, consisting of a charger section, a separator section, and an analyzer section (long narrow extension), as shown in Figure 1. The analyzer section is made of true-bore capillary tubing of 1.60- to 1.65-mm. inner diameter. (Precision requirement for true-bore: 0.3-mm. maximum variation in the length of an approximately 100-mm. thread of mercury at several locations.) This column is also used for general hydrocarbon-type analyses of lighter distillates. It deviates from the original column in design (*5*) by elimination of the short capillary section between the charger and the separator sections, as superfluous; replacement of standard tubing in the analyzer section by true-bore tubing (permanently sealed on) to improve accuracy; and addition of a removable tip at the end of the column for convenience in inserting and removing the cotton plug which retains the adsorbent in the column.

CONCENTRATION COLUMN as shown in Figure 2.

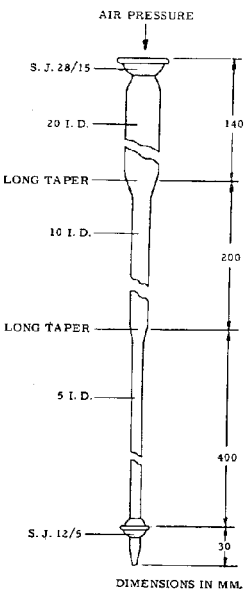

Figure 2. Concentration column

The columns should be mounted in a darkroom. A pipe manifold with a series of inner spherical joints for the columns and a series of meter rules placed adjacent to the analyzer sections makes a convenient arrangement. To facilitate the readings, every centimeter division on the rule may be marked with luminous paint, or the rule may be equipped with movable metal clips with similarly painted tips.

CONCENTRATE RECEIVER, graduated at 0.5 and 0.6 ml., as shown in Figure 3.

VIBRATOR for packing of the silica gel. A small rubber-padded massage machine is satisfactory.

ULTRAVIOLET LIGHT SOURCE. Radiation predominantly at 3660 A. A convenient arrangement consists of one or two 36-inch "black light" units mounted vertically along the apparatus.

HYPODERMIC TUBING for column cleaning; 19 stubs gage, about 90 cm. long, connected to tap water.

SILICA GEL, grade 923 (100 to 200-mesh) from Davison Chemical Corp., Baltimore 3, Md.

DYED SILICA GEL. The "dye mixture for the FIA method of hydrocarbon type analysis," supplied by Patent Chemicals, Inc., Paterson, N. J., consists of a yellow-green-fluorescent olefin marker, a blue-fluorescent aromatic marker, both of petroleum origin, and a nonfluorescent red dye, Sudan III, as alcohol marker. It has been found advantageous, however, to amplify the latter by including Ethyl Red.

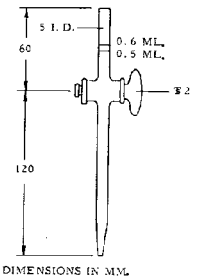

Figure 3. Concentrate receiver

While this dye mixture may be added to the sample, it is more convenient to affix it to a very small portion of the adsorbent, and insert the latter in the column. A supply of dyed silica gel is prepared by stirring 0.4 ml. of Patent Chemical's FIA dye mixture plus 7 mg. of Ethyl Red into 80 ml. of silica gel slurried in acetone, and evaporating the latter. A little acetone remaining does not interfere with the analysis. This quantity will suffice for about 1000 determinations. The dyed gel should be stored in the dark, as the aromatic marker will deteriorate in the light.

ISOPROPYL ALCOHOL refined 99%, hydrocarbon-free.

PRESSURING GAS. Air (or nitrogen), delivered to the top of the column at a regulated pressure up to 15 pounds per square inch.

The column for lighter distillates, vibrator, ultraviolet light source, hypodermic tubing, and silica gel, dyed silica gel, isopropyl alcohol, and pressuring gas apply also to the regular method of analysis for hydrocarbon types in lighter distillates (gasolines, jet fuels, and kerosines).

Procedure. COLUMN CALIBRATION. Put a piece of cotton in the tip of the FIA column (Figure 1) and pack it with silica gel, applying the vibrator as needed, until the separator section is about half full. Add a 3- to 5-mm. layer of dyed gel and continue vibrating and adding gel until it extends about 40 mm. into the charger section.

By means of a pipet introduce 0.50 ± 0.02 ml. of a hydrocarbon, such as iso-octane, and apply a pressure of 2 to 5 pounds per square inch until the sample is just absorbed. Cover with an approximately 15-mm. layer of additional gel (to prevent intermixing), and fill the charger section with isopropyl alcohol. Apply a pressure of 5 to 10 pounds per square inch, and when the red alcohol front has advanced about 300 mm. into the analyzer section, measure the hydrocarbon zone ahead of the alcohol in ordinary light. (For zone reading see below.)

Release the pressure, disconnect the column, and remove the used gel by inverting the column above a sink and rinsing with water from the inserted hypodermic tubing. Rinse with acetone or alcohol and dry.

Calculate the calibration factor, F, as follows:

$$F = \frac{50}{\text{zone, mm.}}$$

(With the prescribed column and silica gel F = ca. 0.11.)

The procedure for analysis is divided into three parts according to the nature of the hydrocarbon type to be determined in traces.

1. AROMATICS AND/OR OLEFINS IN SATURATES (one-column operation). Pack the FIA column (Figure 1) as described above.

Add by means of a pipet 5 ± 0.10 ml. of sample if the content of hydrocarbons to be determined is 1% or less, or 2 ± 0.05 ml. if it is greater than 1%, and apply a pressure of 2 to 3 pounds per square inch until the sample is absorbed. Cover with an approximately 15-mm. layer of additional gel, and fill the charger with isopropyl alcohol. Apply a pressure of 10 to 15 pounds per square inch; if olefins are present, their front will be sharper if the pressure is reduced to 3 pounds per square inch when the red alcohol front enters the analyzer section. When this front has advanced about 300 mm. further, take readings as directed below. (Collect the bulk of the saturates in a convenient receptacle, and discard.)

2. Saturates and/or Olefins in Aromatics (two-column operation). Pack the concentration column (Figure 2) with silica gel to about 25 mm. in the widest (top) section, omitting the dyed gel.

Add by means of a pipet 5 ± 0.10 ml. of sample if the content of hydrocarbons to be determined is 1% or less, or 2 ± 0.05 ml. if it is greater than 1%, and apply a pressure of 1 pound per square inch until the sample is absorbed. Cover with an approximately 15-mm. layer of additional gel, fill with isopropyl alcohol, and resume the pressure. Collect in the concentrate receiver (Figure 3) between 0.5 and 0.6 ml. of the first effluent, which represents a concentrate of the saturates and/or the olefins.

Transfer the concentrate to the packed FIA column, washing it in with a little alcohol, and proceed with the adsorption as above, but under a pressure of 3 to 5 pounds per square inch only. Read the saturates and/or olefins zone as directed below.

3. Olefins in Saturates Plus Aromatics (two-column operation). Pack the concentration column (Figure 2) as for saturates and/or olefins in aromatics, but insert an approximately 1-mm. layer of dyed gel in the middle section.

Proceed as above, but discard the saturates, and, in ultraviolet light, collect in the concentrate receiver 0.5 to 0.6 ml. of effluent. This will include the olefins, beginning just before the yellow-green zone appears and ending beyond the beginning of the blue zone. Transfer the concentrate to the packed FIA column and continue as for aromatics and/or olefins in saturates, but under a pressure of 3 to 5 pounds per square inch only.

4. Zone Reading and Calculation. The following directives for reading of the zones apply to the FIA method in general; in the case of trace FIA, the predominant hydrocarbon types are disregarded.

Measuring in ultraviolet light, the saturates extend from the colorless liquid front to the lowest point of maximum yellow-green fluorescence, the olefins extend from there to the lowest point of strong blue fluorescence, and the aromatics from there to the highest point of strong red or reddish brown color, the latter being best observed in ordinary light. Quickly mark the boundaries with a glass-writing pencil, or by means of movable metal clips on the meter rule, mounted close to the analyzer section. Take additional readings at 50- to 100-mm. intervals until repeatable measurements are attained. If a zone is only 1 or 2 mm. long, consider the pertinent hydrocarbon type as absent.

Calculate the trace hydrocarbon content for each type as follows:

$$\text{Trace hydrocarbon type, vol. \%} = F \frac{\text{zone, mm.}}{\text{sample, ml.}}$$

where F is the column calibration factor.

APPLICATIONS AND RESULTS

The method is applicable to lighter petroleum distillates when the hydrocarbon type present in traces is more strongly adsorbed than the predominant type. The analysis is carried out in one column and requires 2 to 5 hours of elapsed time, depending on the size of the sample, or about 0.5 hour of operating time.

When the hydrocarbon type present in traces is less strongly adsorbed than the predominant type, on the other hand, the method is applicable to simple mixtures only. Concentration of the trace material is required, and this analysis is therefore carried out with two columns and takes 4 to 5 hours of elapsed time or about 1 hour of operating time.

Examples of analyses of the first category are given in Table I. The samples represent known blends of saturates, olefins, and aromatics aggregates, isolated from a gasoline and a kerosine by large scale elution development chromatography. As may be seen from this table, the accuracy obtained is within ±0.05% for values below 0.5% and within ±0.10% for higher concentrations.

Table I. Determination of Traces of Hydrocarbon Types

(Petroleum distillates)

Main Constituents	Traces, Volume %: Known[a] Aromatics	Known[a] Olefins	Found Aromatics	Found Olefins	Error, Volume %: Aromatics	Error, Volume %: Olefins
Gasoline saturates	1.00	1.00	0.97	0.92	−0.03	−0.08
	1.00	1.00	0.99	1.01	−0.01	+0.01
	0.40	0.40	0.36	0.40	−0.04	0.00
	0.10	0.10	0.13	0.13	+0.03	+0.03
	0.50	..	0.46	..	−0.04	..
	..	0.40	..	0.40	..	0.00
Gasoline olefins	0.40	..	0.36	..	−0.04	..
Kerosine saturates	1.94	..	2.00	..	+0.06	..
	1.94	..	1.94	..	−0.04	..
	0.49	..	0.45	..	+0.01	..
	0.49	..	0.49	..	0.00	..

[a] Blends made from type aggregates isolated by large scale development chromatography.

Examples of analyses of the second category are given in Tables II and III; the reliability is about the same as above. Attempts to determine traces of saturates in olefins were not successful, but whether this is due to incomplete type separation or to inadequate marking of the olefin front by the dye is not known.

Table II. Determination of Traces of Saturates and Olefins in Aromatics

(Simple mixtures)

Sample	Traces, Volume %: Known Saturates	Known Olefins	Found Saturates	Found Olefins	Error, Volume %: Saturates	Error, Volume %: Olefins
Reference toluene	..	..	0.00	0.00	0.00	0.00
Iso-octane in ref. toluene	0.27	..	0.27	..	0.00	..
Methylcyclohexane in ref. toluene	0.33	..	0.27	..	−0.06	..
Diisobutylene in benzene, c.p.	..	0.40	0.28[a]	0.35	..	−0.05

[a] Apparently the benzene contained some saturates as impurity.

Table III. Determination of Trace of an Olefin in a Saturate-Aromatic Mixture

Sample	Trace, Volume %: Known	Trace, Volume %: Found	Error, Volume %
Diisobutylene in iso-octane and benzene	1.00	1.07	+0.07

Table IV. Applicability of Trace FIA Method

Trace Type	Predominant Type	Material	Procedure No.	No. of Columns
Aromatics	Saturates	Lighter distillates	1	1
	Olefins	Lighter distillates	1	1
	Saturates plus olefins	Lighter distillates	1	1
Olefins	Saturates	Lighter distillates	1	1
	Aromatics	Simple mixtures	2	2
	Saturates plus aromatics	Simple mixtures	3	2
Saturates	Olefins		None	
	Aromatics	Simple mixtures	2	2
	Olefins plus aromatics		None	

The scope of the trace FIA method is summarized in Table IV. So far it has not been extended beyond the kerosine boiling range, but it probably could be, if required.

HYDROCARBON TYPE ANALYSIS OF HEAVIER DISTILLATES

There is an increasing need of a reliable routine method, such as FIA, for the determination of the three principal hydrocarbon

types in cracked gas oils. This need prevails also with straight-run materials, including lubricating oils, because the sulfuric acid extraction method for determination of the saturates/aromatics split is not applicable to the heavier distillates.

A prerequisite to research along this line is the procurement of a collection of higher boiling distillates of reasonably well known composition with which to experiment. Such reference samples can now be realized as a result of work carried out here and elsewhere (*6, 8*) on the composition of gas oils and lubricating oils. Techniques have been established involving large scale elution development chromatography followed by spectrometric and chemical analyses of numerous cuts recovered; from these laborious analyses it was possible to arrive at figures for type composition which in most cases were accurate to ±1 to 2%.

Attempts to apply the FIA method to heavier distillates met with several difficulties. As would be expected, the high viscosity caused channeling in the column, at times to the extent of allowing the eluent to bypass a considerable portion of the sample. When the oil was not too viscous (light gas oils), these difficulties could be overcome simply by making the separator section narrower and longer (see Figure 4). With more viscous materials (lubricating oils) it was necessary also to dilute the sample with known quantities of solvents representing the three principal hydrocarbon types, such as iso-octane, diisobutylene, and benzene, and to make appropriate corrections in the calculation. (Reduction of the viscosity by increasing the temperature should be avoided because it affects the behavior of the dyes.)

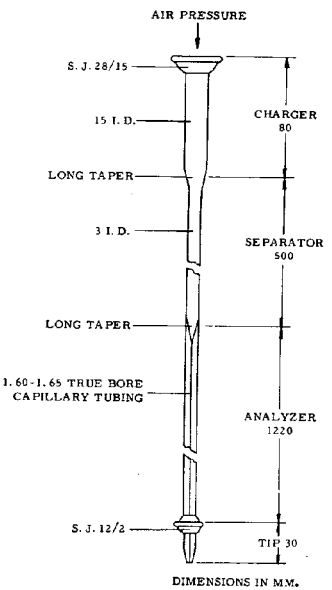

Figure 4. Column for heavier distillates

The aromatics marking component of the FIA dye is more strongly adsorbed than the highly alkylated monoaromatics, and therefore fails to mark the front of the aromatics zone. This behavior is, of course, due to the fact that the monoaromatics become more paraffinic with increasing molecular weight and, consequently, less strongly adsorbed. The difficulty was circumvented by supplementing the regular dye mixture with a less strongly adsorbed aromatics indicator, recovered from Patent Chemicals' Oil Color No. 50, the material from which this firm prepares the olefin marker.

Oxidation products, formed in some of the reference oils during storage, occasionally interfered with the separation. These dark products, even though present in very low concentration, migrated down the column and obscured the indicators. This situation could be corrected by replacing the upper portion (60 to 70 mm.) of the regular Davison's silica gel grade 923 (pore diameter 32 A. and surface area 800 square meters per gram) by Davison's silica gel grade 70 (pore diameter 100 A. and surface area 330 square meters per gram), which adsorbs the oxidation products more strongly than the regular gel. The latter is retained in the critical lower part of the column to provide better surface area. The oxidized molecules are relatively large, and the much improved retention on grade 70 gel may be due to the large pore size of this gel. It is also possible that the general reluctance of the oxidation products to separate can be explained by the formation of an asorbotropic mixture, one that will pass through the column unaltered (in analogy with azeotropic distillation). These hypotheses the authors have presented in connection with the chromatographic determination of gum (*7*).

In one instance of rather severe oxidation the dark materials were not sufficiently retarded even by grade 70 silica gel. However, such extreme materials can still be analyzed if isopropyl alcohol is replaced by isopropyl chloride. This eluent displaces the hydrocarbons but not the oxidation products. But isopropyl chloride does not displace the red eluent marking dye, and as no other dye has been found, the aromatics zone cannot be measured. In this case, therefore, a column with calibrated analyzer section (see trace FIA method) is used so that the volumes of the saturates and the olefins can be computed from their zone lengths and related to the known volume of the sample, and the aromatics, including the oxidation products, obtained by difference.

Wax may interfere by precipitation in the column if the quantity is too large to remain dissolved in the diluent. The tolerance has not been studied; therefore, if the oil contains much wax, it may be necessary to remove at least some of it prior to analysis.

In the course of this work it was also found that a fairly good value for the content of polyaromatics (including diaromatics and resins) in lubricating oils can be obtained. This is done in a separate test with the FIA column packed with alumina (Alcoa F-20) which is an excellent adsorbent for polyaromatics. No dyes are used because the polyaromatics are inherently strongly fluorescent in ultraviolet light and therefore self-indicating. As viscosity reducer, a solvent mixture containing only iso-octane and benzene is employed, diisobutylene being omitted because it interferes with the separation. This method is not applicable to gas oils because they contain very little fluorescent material and no suitable indicator dye is known.

METHOD FOR HEAVIER DISTILLATES

Apparatus and Materials. These items are the same as required for the FIA method for lighter distillates and for the trace FIA method, except for the following:

FIA column for heavier distillates, as shown in Figure 4. (The concentration column and receiver are not used.)

Syringe, 1-ml. capacity, graduated to 0.01 ml.

Two diluents. Iso-octane (technical) plus diisobutylene (technical) plus benzene (reagent grade), equal volumes, and isooctane plus benzene, equal volumes; the latter for the polyaromatics procedure.

Dyed silica gel for heavier aromatics, prepared as follows. Pack an adsorption column of approximate dimensions 20 × 200 mm. about three quarters full with Davison's Grade 923 silica gel, and charge it with a solution of 0.2 ml. of Patent Chemical's Oil Color No. 50 in 10 to 20 ml. of iso-octane. Add 25 ml. of diisobutylene, rinsing in the last of the iso-octane solution with the first small portions. Then follow with 25 ml. of benzene, in the same manner, and finally with isopropyl alcohol. In ordinary light, collect the approximately 2 ml. of rose-colored benzene effluent in a vessel containing 3 ml. of silica gel, and evaporate the benzene in a stream of air until the dyed gel is free-flowing. This quantity will suffice for about 40 determinations. Store the dyed gel in the dark.

Activated alumina, Alcoa, Grade F-20 (80 to 200-mesh) from the Aluminum Co. of America, Pittsburgh, Pa.; for the polyaromatics procedure.

Procedure. The procedure is divided into three parts according to the type of oil to be analyzed and hydrocarbons to be determined.

1. SATURATES, OLEFINS, AND AROMATICS IN LIGHT GAS OILS. Put a piece of cotton in the tip of the FIA column (Figure 4) and pack it with silica gel, applying the vibrator as needed, until the separator section is about half full. Add a 10-mm. layer each of the regular dyed gel and the dyed silica gel for heavier aromatics. Continue to vibrate and add gel until it fills all but 20 to 30 mm. of the separator section.

Add by means of a pipet 0.50 ± 0.05 ml. of sample and apply a pressure of 3 pounds per square inch until the oil is absorbed. Then carefully rinse the walls with a few drops of isopropyl alcohol. Cover with an approximately 10-mm. layer of gel, and fill the charger section with alcohol. Again apply the pressure of 3 pounds per square inch, and when the liquid front is half-way through the analyzer section, take readings as directed under the preceding trace FIA method.

Calculate the percentages of the hydrocarbon types as follows:

$$\text{Hydrocarbon type, volume \%} = 100 \frac{\text{zone, mm.}}{\text{sum of zones, mm.}}$$

2. SATURATES, OLEFINS, AND AROMATICS IN HEAVY GAS OILS AND LUBRICATING OILS. Pack the FIA column (Figure 4) as described above in the procedure for light gas oils.

Measuring with the syringe, dilute 0.70 ml. of oil with an equal volume (±0.01 ml.) of the iso-octane plus diisobutylene plus benzene diluent, and add 0.50 ± 0.05 ml. of the diluted sample to the column. Follow the procedure for light gas oil (above), but apply a pressure of only 1 pound per square inch, and, when the liquid front enters the analyzer section release the pressure.

Calculate the percentages of the hydrocarbon types as follows:

$$\text{Hydrocarbon type, volume \%} = 200 \frac{\text{zone, mm.}}{\text{sum of zones, mm.}} - 33.3$$

If the yellow-green-fluorescent olefins marking dye is closely followed by the blue-fluorescent aromatics marking dye, the olefins cannot be distinguished from the aromatics, and therefore only their sum can be determined.

3. POLYAROMATICS IN LUBRICATING OILS. Pack the FIA column (Figure 4) with activated alumina, F-20, applying the vibrator as needed, until the level is 20 to 30 mm. below the top of the separator section.

Measuring with the syringe, dilute 0.70 ml. of oil with an equal volume (±0.01 ml.) of the iso-octane plus benzene diluent and add 0.50 ± 0.05 ml. of the diluted sample to the column. Proceed as for heavy gas oils and lubricating oils (above).

In ultraviolet light, measure the length of the fluorescent polyaromatics zone, extending from the lowest point of strong blue fluorescence to the top of the reddish brown zone; also measure the length of the total sample zone.

Calculate the percentage of polyaromatics (including diaromatics and resins) as follows:

$$\text{Polyaromatics, volume \%} = 200 \frac{\text{polyaromatics zone, mm.}}{\text{sum of zones, mm.}}$$

RESULTS AND DISCUSSION

Table V shows examples of results that can be obtained with catalytically and thermally cracked light gas oils. The highest boiling fraction, 300° to 400° C., borders on a heavy distillate; it required dilution prior to analysis. As might be expected, the reliability is better for the lighter fractions than for the heavier ones. The deviations from the "true" compositions were 1 to 4% with an average of 2%, but for the 300° to 400° C. fraction, 2 to 6%; however, the true composition values for the latter are relatively uncertain.

It was discovered that these oils could be analyzed just about as well when the special dye for indication of heavier aromatics was omitted, using only the regular dye as employed in the analysis for lighter distillates (gasolines, jet fuels, and kerosines); the difference in results was not statistically significant. As mentioned earlier, the ability of the aromatics to displace the regular dye depends on their molecular weight. For lubricating oils the special dye is indispensable, and it may therefore be advisable to include it in the borderline cases discussed here.

Examples of the analyses of dewaxed lubricating oil base stocks are shown in Table VI. These oils are straight-run distillates; all but one are olefin-free, which greatly simplifies the analysis. In spite of the relatively high molecular weight of the oils, therefore, the results are rather good, the errors being 0 to 4%, or 2% on the average. The exceptional oil (the first in the series in Table VI) is derived from a Pennsylvania crude oil, and contains a substantial amount of olefins. The presence of olefins in a virgin crude oil is extraordinary, but has definitely been established here and in other laboratories in oils of similar origin (*4*, *5*).

The fact that this unsaturated heavy oil could be analyzed satisfactorily by means of the FIA method indicates that cracked heavy gas oils can be so analyzed, although, with the exception of the 300° to 400° C. fraction (Table V), no tests with the latter were carried out. However, the olefins-aromatics split could not be observed in oils of higher average molecular weight than about 400, corresponding to a mid-boiling point of ca. 450° C. (as referred to atmospheric pressure), because strong blue fluorescence then appeared just above the olefin marking dye. This is attributed to displacement of certain highly alkylated and therefore weakly adsorbed polyaromatics by diisobutylene. This displacement of fluorescent components of heavy oils by diisobutylene was observed even in a column of alumina which is considered superior for segregation of polyaromatics. Hence the olefin was eliminated from the diluent mixture in the analysis for polyaromatics.

The errors in the values for polyaromatics were likewise 0 to 4%, with an average of 2%.

This analysis requires about 0.5 hour of operator time, but the elapsed time may be as much as 10 to 15 hours, depending on the viscosity of the oil.

On the whole, the reliability of the FIA method as applied to heavier distillates is within about ±2%, but errors as high as 5 or even 6% have occasionally been observed. Better accuracy is desirable and will no doubt be achieved, for it is now generally realized that in routine analyses usable values for hydrocarbon-type distribution can only be obtained by chromatography. An

Table V. Analyses of Cracked Distillates of Light Gas Oil Boiling Range

Sample	Boiling Range, ° C.	Composition, Volume % Known[a] Saturates	Known[a] Olefins	Known[a] Aromatics	Found Saturates	Found Olefins	Found Aromatics
Catalytically cracked gas oil fractions	230–337	55	4	41	53	5	42
	230–320	55	4	41	51	6	43
	286–314	59	3	38	58	6	36
	314–337	62	3	35	61	6	32
Thermally cracked gas oil fractions	170–310	48	16	36	47	15	38
	300–400[b]	36	9	55	34	5	61

[a] Accuracy of known values ±1 to 2%; 2 to 3% for 300°–400° C. fraction.
[b] This sample was more viscous and, like lubricating oils, required dilution.

Table VI. Analyses of Dewaxed Lubricating Oil Base Stocks

Average Molecular Weight	Composition, Volume %: Known[a] Saturates	Olefins	Monoaromatics	Polyaromatics[b]	Found Saturates	Olefins	Monoaromatics	Polyaromatics[b]
340	66	11	11	9	66	14	7	13
390	60	1	14	25	60	0	12	28
400[c]	48	0	15	37	46	0	13	41
420	61	0	19	20	60	0	23	17
440	61	0	17	22	60	0	18	22
450	58	0	14	28	55	0	18	27
460	46	0	14	40	46	0	13	41

[a] Accuracy of "known" values, ±1 to 2%.
[b] Including diaromatics and resins.
[c] Owing to presence of dark products of oxidation, isopropyl chloride was used as eluent in this case.

alternative that naturally comes to mind would be the determination of saturates by acid absorption, olefins by halogenation, and aromatics by difference. As might be expected, however, this approach fails because the olefin-aromatic ratio so obtained is entirely erroneous. This may be illustrated by the results of a cooperative testing carried out by several laboratories with the lightest of these oils, the thermally cracked gas oil of boiling range 170° to 310° C. (see Table V). Its true composition is considered accurate to within ±1%. This oil is still light enough for determination of saturates by acid absorption to within 1 or 2% of the known value of 48%. Bromine numbers by various methods ranged from 31 to 38 grams per 100 grams. In calculating the olefin content from these bromine numbers by aid of the determined molecular weight of the sample, 191, one obtains values of between 37 and 45% as compared with the known value of 16%; this leaves only 8 to 16% for the aromatics, the known content of which is 36%. With the FIA method the same laboratories obtained results which, on the average, deviated from the known values by only −1.9, −0.5, and +2.4% for saturates, olefins, and aromatics, respectively.

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Full Luminescence at Liquid-Air Temperature of Methyl-1,2-benzanthracenes and Methylbenzo[*c*]phenanthrenes

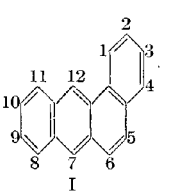
YEHUDA HIRSHBERG[1]

Daniel Sieff Research Institute, Weizmann Institute of Science, Rehovoth, Israel

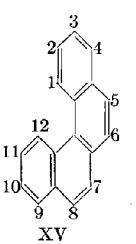
At liquid-air temperature, in a mixture of solvents which sets to a rigid clear glass, the full luminescence of the monomethyl derivatives of the methyl-1,2-benzanthracene and methylbenzo[*c*]phenanthrene series shows distinctive spectra in relation to that of the parent compound. The significant changes in the spectrum caused by the introduction of the methyl group in different positions can be used for the identification of any methyl derivative of 1,2-benzanthracene or benzo[*c*]phenanthrene. The afterglow of the most carcinogenic compounds of the benzanthracene series is specifically different from that of all the other members of these series.

IN ACCORDANCE with the reversible nature of absorption and emission of light it has been found that groups of compounds produce characteristic patterns of fluorescence spectra. On this basis biologically active polycyclic hydrocarbons have been identified by fluorescence spectrography in the past 20 years (*1, 2, 4, 10*). Because the accuracy of the fluorescence data depends on the sharpness and fine structure of the bands, better results may be obtained when the fluorescence is studied at low temperatures.

In the case of the methyl derivatives of 1,2-benzanthracene (I) and benzo[*c*]phenanthrene (XV) the methyl position has little influence on the fluorescence spectra of the parent hydrocarbons at room temperature.



I



XV

The benzanthracenes and the benzo[*c*]phenanthrenes are sensitive to ultraviolet irradiation; therefore, when their fluores-

[1] Present address, University of California, Berkeley 4, Calif.

cence is studied at room temperature, not only is a loss of reradiative power of the light-absorbing molecules caused by thermal collisions, but the photochemical process produced by the ultraviolet-exciting light disguises the fluorescence. At liquid-air temperature the compounds are more stable toward irradiation, thermal collisions are minimized, and the fluorescence spectra are sharper. In the full luminescence spectrum at liquid-air temperature, not only the bands of the singlet → singlet emission (fluorescence) appear, but also the triplet → singlet emission (phosphorescence) is recorded (*6*, *8*); therefore the spectrum of each methyl derivative is more detailed and distinctive.

Although the fluorescence and phosphorescence of some of the compounds reported in this paper have been studied at liquid-nitrogen temperature (*5*, *9*, *11*, *12*), no systematic investigation of the full luminescence of all the monomethyl derivatives of 1,2-benzanthracene and benzo[*c*]phenanthrene has been recorded. This paper shows that the significant changes in the full luminescence spectra of the parent polycyclic hydrocarbons, caused by the introduction of the methyl group in different positions, can be used to identify any methyl derivative of 1,2-benzanthracene (I) or benzo[*c*]phenanthrene (XV).

EXPERIMENTAL

All the compounds investigated were kindly sent by Melvin S. Newman, Ohio State University.

Solvents. Pure absolute ethanol and methanol were prepared by the usual methods. Dry ether was purified by passing it through a column of activated silica gel. The rigid clear glass formed by the mixture of ethanol plus methanol plus ether (in proportions of 8 to 2 to 1 by volume) at liquid-air temperature had no luminescence.

Apparatus. To measure the full luminescence and the afterglow of the compounds studied, an apparatus was constructed similar to that described by Farrow, Reckers, and Germann (*3*). The apparatus (*3*, Figure 3) consists of a blackened, light-tight iron box containing a quartz Dewar flask and the sample. On one side of the box, two gear-driven synchronous shutters are mounted so that the surface of the sample that is excited by ultraviolet light may radiate the luminescent or phosphorescent light directly to the slit of the spectrograph, with a minimum loss due to absorption or reflection. In order to photograph the full luminescence spectrum of a compound, the shutters are held stationary and both are open at the same time. To photograph the phosphorescence, one shutter is placed at 90° out of phase with the other and both are driven by a $^1/_8$-hp. motor up to speeds of 3450 r.p.m. In this arrangement, the surface of the sample was excited by the 3560 A. group of a General Electric mercury arc (Type A-H6). The angle between exciting and luminescent radiation was about 45°.

Luminescence and Phosphorescence Spectra. These were photographed with a Fuess glass spectrograph on Kodak P1500 2.5 × 3.5 inch panchromatic plates and evaluated by means of a Leeds & Northrup recording microphotometer. The slit of the spectrograph was held at a constant width of 0.1 mm. and the time of exposure for all the compounds studied was 15 minutes.

RESULTS AND DISCUSSION

Monomethyl-1,2-benzanthracenes. At room temperature the fluorescence of 1,2-benzanthracene (I) is of a weak violet color. Its spectrum consists of three bands, two of them of relative medium intensity with maxima at 4130 and 4360 A. When dissolved in a mixture of ethanol plus methanol plus ether (8 to 2 to 1 by volume) which sets at liquid-air temperature to a rigid clear glass, the luminescence is of a strong bluish color and has a brick-red afterglow of about 0.5 second. The spectrum consists of 14 well defined bands. Five of the first eight bands, which belong to the singlet → singlet emission, are intense, having maxima at 4070 A. [1], 4100 A. [2], 4160 A. [3], 4310 A. [4], and 4600 A. [5], two bands are of about half the intensity of the latter, having maxima at 4810 A. [6], and 4920 A. [7], and there is a weak one at 5200 A. [8]. The triplet → singlet emission is presented by the six remaining bands with maxima at 5740 A. [9], 5980 A. [10], 6100 A. [11], 6220 A. [12], 6340 A. [13], and 6450 A. [14]. The most intense band of the afterglow is the tenth one (I, Figure 1).

Although the luminescence and the afterglow of most of the methyl derivatives of 1,2-benzanthracene seem visually to be the same as those of the parent compound, different significant changes in the spectrum of each methyl derivative show that the methyl position in 1,2-benzanthracene may be identified in this way.

The maxima and the relative intensities of the full luminescence band of 1,2-benzanthracene and its most important methyl derivatives are presented in Figure 1 and Table I.

The methyl group introduced into position 1 (compound II) causes a hypsochromic shift of maxima [1], [2], [3], [5], [8] [10], [11], and [14], and the disappearance of bands [6], [7], [9], [12], and [14]. At the same time, the intensities of the maxima of the afterglow bands [10], [11], and [13] are strongly reduced (compare II with I in Figure 1).

In the case of the 2-methyl derivative (III) there is a bathochromic shift in the maxima relative to those of derivative II and the spectrum of III is distinguished from that of the parent hydrocarbon in that bands [6], [7], [9], [12], and [13] are absent in the former and in the strongly reduced intensities of [10], [11], and (14) (compare III with II and I in Figure 1).

When the methyl group is in position 3 (compound IV) the spectrum differs from I in that bands [6], [7], [8], [9], [12], and [13] are absent in the former; the maxima [1], [2], [3], [4], [5], [10], and [11] are hypsochromically shifted relative to those in III and [8] is absent; and its spectrum is bathochromically shifted relative to that of II (compare IV with I, II, and III in Figure 1).

The spectrum of the 4-methyl derivative (V) is distinguished from those of all the former methyl derivatives by the reappearance of bands [7], [9], and [12] and by the higher intensities (compare V with I, II, III, and IV in Figure 1). The strong hypsochromic shift of maximum [1] and the strong bathochromatic shift of maxima [7], [8], [9], [10], [11], [12], and [14] in relation to those of the parent hydrocarbon are helpful in distinguishing between the spectrum of V and that of I (compare V with I in Figure 1).

The spectrum of the 5-methyl derivative (VI) differs from those

Table I. Maxima (in A.) of Bands of Full Luminescence Spectra of 1,2-Benzanthracene and Its Methyl Derivatives

Compound	1	2	3	4	5	6	7	8	9	10	11	12	13	14
I	4070	4100	4160	4310	4600	4810	4920	5200	5740	5980	6100	6220	6340	6450
II	3980	4070	4100	4320	4560	..	..	5040	..	5810	5900	..	6280	..
III	4085	4120	4210	4340	4600	..	..	5270	..	5950	6080	..	..	6420
IV	4060	4100	4150	4320	4590	..	..	..	..	5940	6050	..	..	6420
V	4010	4110	4150	4370	4620	..	4980	5260	5790	6080	6200	6300	..	6570
VI	4020	4120	4150	4390	4620, 4660	..	4960	5380	5710	5980	6100	6170	..	6490
VII		4070	4110	4330	4600	4810	4960	5240	5680	6000	6120	6200	..	6500
VIII	4000	4120, 4150	4220	4370	4590, 4630	..	4950	5230	5390	5660	..	..	6140	6440
IX	4080	4110	4160	4330	4600	4820	..	5270	..	6010	6140	6210	..	6500
X	4070	4110, 4145	4190	4340	4550, 4600	4810	..	5200	..	5950	6080	6180	6410	6520
XI	4020	4100	4140	4360	4620	..	..	5250	..	5930	6060	..	..	6500
XII	3990	4080, 4125	4190	4330, 4370	4520, 4550	..	..	5300	5720	6000	6120	..	6360	6520
XIII	4030	4165	4210	4430	4690	..	5080	5580	..	..	..	6230	..	6500
XIV	4100	..	4270	4520	4800	..	5140	5500	5670	..	..	6460	..	6570

of all the former compounds in the splitting of band [5] into two bands, [5a] and [5b], while there is a bathochromic shift of maxima [4] and [5] (compare VI, with I, II, III, IV, and V in Figure 1). The afterglow of compound VI is twice as long as that of each compound described above.

The 6-methyl derivative (compound VII) can be identified by the reappearance in its spectrum of band [6] and the disappearance of band [1]. The maxima of its phosphorescence are of much higher intensities than those of the former compounds (compare VII with I to VI in Figure 1).

7-Methyl-1,2-benzanthracene (VIII) is distinguished from the compounds described above by the fact that its afterglow is of such short duration that it is not perceived visually. In its spectrum, bands [2] and [5] are split into two bands [2a], [2b], [5a], [5b]; bands [6], [11], and [12] are not present, and there is a strong hypsochromic shift in maxima [9], [10], [13], and [14] (compare VIII with I to VII in Figure 1).

While the spectrum of the 8-methyl derivative (IX) is similar to that of the parent compound (I), the absence of bands [7], [9], and [13] allows a distinction between them. The brick-red afterglow of IX is twice as long as in the case of I, II, III, IV, and V (compare IX with I in Figure 1).

In the spectrum of the 9-methyl derivative (X), seven bands appear instead of the first five bands; therefore compound X is easily differentiated from all the former compounds (compare X with I to IX in Figure 1).

Although the spectrum of 10-methyl-1,2-benzanthracene (XI) is similar to that of compound II, the fact that all its maxima are bathochromically shifted with regard to those of II and its afterglow half as long as that of II makes it possible to distinguish between them (compare XI with II in Figure 1).

The spectrum of the 11-methyl derivative (XII) has eight bands instead of the first five appearing in the spectrum of the parent compound (I). This distinguishes the spectrum of compound XII from all the others described (see XII in Figure 1).

The spectrum of the 12-methyl derivative (XIII) is easily recognized by the strong bathochromic shift of maxima [2], [3], [4], [5], [7], and [8] in relation to the corresponding maxima of all the former compounds (see XIII in relation to I to XII in Figure 1). In the case of XIII, which is strongly biologically active, like compound VIII, the afterglow has a short life and is not perceivable visually as in the case of the latter.

The full luminescence of 7,12-dimethyl-1,2-benzanthracene (XIV) is presented in this paper, because this compound is the most biologically active in this series. The luminescence of XIV will help in the discussion which follows on the correlation between luminescence and biological activity.

The three most carcinogenic of the methyl derivatives of the 1,2-benzanthracene series (derivatives VIII, XIII, and XIV) are distinct from all the others, in that the triplet → singlet emission (the afterglow) of each is of short duration and is not visually perceivable, whereas all the other methyl derivatives have a relatively long phosphorescence. In this respect compounds VIII, XIII, and XIV resemble the best known polycyclic carcino-

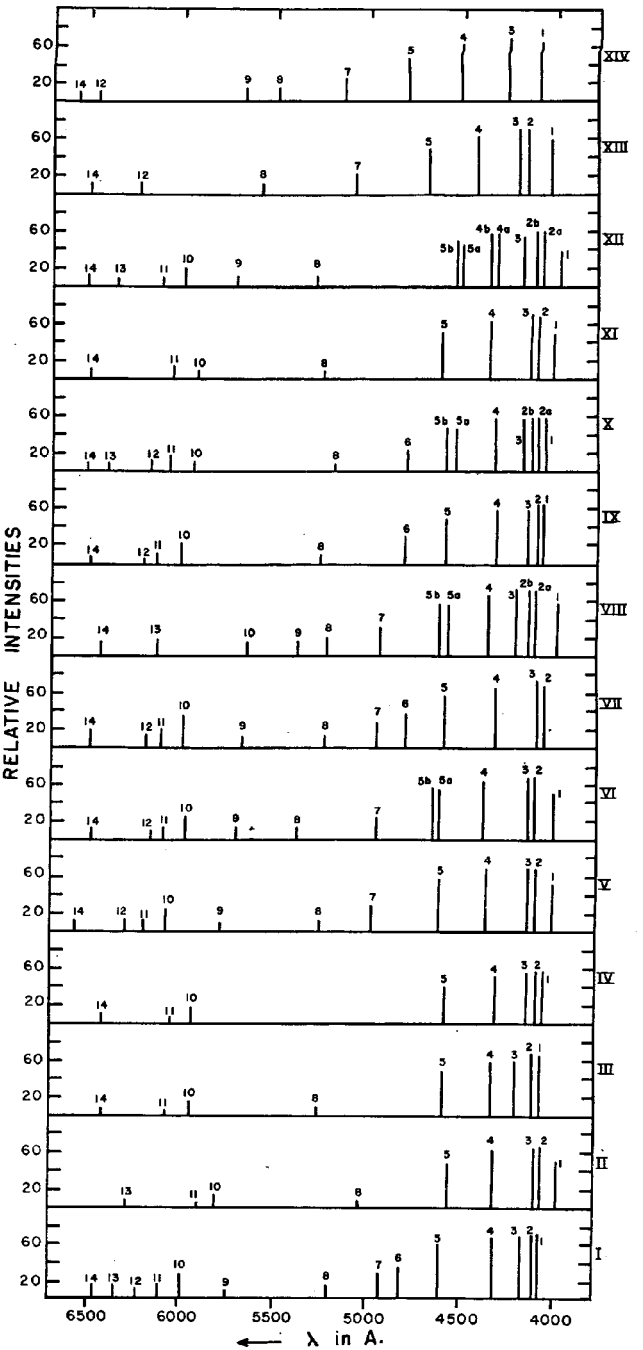


Figure 1. Maxima and relative intensities of full luminescence bands of 1,2-benzanthracene and its methyl derivatives

I.	1,2-Benzanthracene (1,2-BA)	VIII.	7-Methyl-1,2-BA
II.	1-Methyl-1,2-BA	IX.	8-Methyl-1,2-BA
III.	2-Methyl-1,2,-BA	X.	9-Methyl-1,2-BA
IV.	3-Methyl-1,2-BA	XI.	10-Methyl-1,2-BA
V.	4-Methyl-1,2-BA	XII.	11-Methyl-1,2-BA
VI.	5-Methyl-1,2-BA	XIII.	12-Methyl-1,2-BA
VII.	6-Methyl-1,2-BA	XIV.	7,12-Dimethyl-1,2-BA

Table II. Maxima (in A.) of Bands of Full Luminescence Spectra of Benzo(c)phenanthrene and Its Methyl Derivatives

Compound	1	2	3	4	5	6	7	8	9	10	11
XV	4070	4170	4195	4290	4410	4450	4960	5080	5370	5620	5800
XVI	4070	4130	4150	4290	..	4530	5120	5260	..	5610	5830
XVII		4110	4190	..	..	4450	5010	5100	5440	..	5880
XVIII	4070	4120	4210	..	..	4460	5040	5150	5460	..	5910
XIX	4050	4130	4230	..	..	4490	5040	5160	5470	5650	5920
XX	4070	4130	4215, 4240	..	..	4480	5040	5170	5470	..	5930
XXI	4040, 4090	4140	4240, 4260	..	..	4490	5030	5150	5470	..	5920

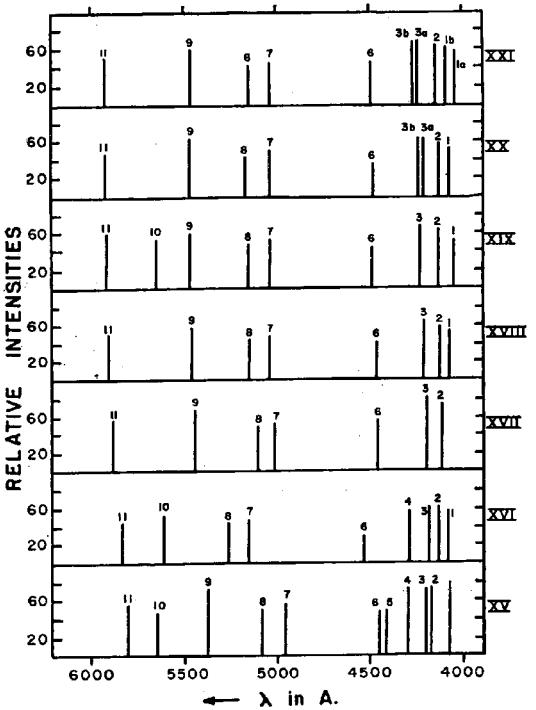


Figure 2. Maxima and relative intensities of full luminescence of benzo(c)phenanthrene and its monomethyl derivatives

XV. Benzo(c)phenanthrene [B(c)Ph]
XVI. 1-Methyl-B(c)Ph
XVII. 2-Methyl-B(c)Ph
XVIII. 3-Methyl-B(c)Ph
XIX. 4-Methyl-B(c)Ph
XX. 5-Methyl-B(c)Ph
XXI. 6-Methyl-B(c)Ph

genic hydrocarbons, 3,4-benzopyrene and 20-methylcholanthrene. This important fact has not been mentioned by other investigators, although they have discussed the correlation between biological activity and the chemical and physical properties of these series (*1, 5, 7, 9, 12*).

Monomethylbenzo[c]phenanthrenes. The maxima of the bands and the relative intensities of the full luminescence spectra of benzo[c]phenanthrene (XV) and its monomethyl derivatives are presented in Figure 2 and Table II.

At room temperature the fluorescence of benzo[c]phenanthrene (XV) is violet; its spectrum consists of one broad band with a maximum at 4230 A. In the rigid glass medium at liquid-air temperature its luminescence is strong grayish white and it has a strong greenish yellow afterglow of about 10 seconds. Its full luminescence spectrum consists of 11 bands. The first six bands of the shortest wave lengths are connected with the singlet → singlet emission of the compound and the remaining seven bands are due to the triplet → singlet emission, the afterglow.

The introduction of a methyl group in position 1 (XVI) changes the luminescence to a whitish rose color and the yellowish green afterglow has a shorter lifetime, about 7 seconds. In the spectrum the changes are represented by the different spacing of the first three bands, by the absence of bands [*5*] and [*9*], and by a strong bathochromic shift of maxima [6], [7], and [8] (compare XVI with XV in Figure 2).

When the methyl group is in position 2 (XVII) a very strong white luminescence appears, having a strong yellow afterglow of a lifetime twice as great as in the case of XVI. The spectrum of XVII is distinguished from those of XV and XVI by the disappearance of bands [1], [4], [5], and [10] (compare XVII with XV and XVI in Figure 2).

In the case of 3-methylbenzo[c]phenanthrene (XVIII) the luminescence is grayish white and it has a strong greenish yellow afterglow. Its spectrum can be recognized by the reappearance of band [1] and disappearance of bands [4], [5], and [10]. Bands [9] and [11] are bathochromically shifted with regards to those of all the former benzo[c]phenanthrenes (compare XVIII with XV, XVI, and XVII in Figure 2).

The 4-methyl derivative (XIX) has a strong white luminescence and a green afterglow of about 16 seconds. Its spectrum lacks bands [4] and [5] and there is a reappearance of band [10] (compare XIX with XV to XVIII in Figure 2).

When the methyl group is in position 5 of benzo[c]phenanthrene (derivative XX), although its luminescence and afterglow are visually like those of XIX, the spectrum of XX is different from that of the former in the splitting of band [3] into two bands and the absence of band [10] (compare XX with XIX in Figure 2).

The luminescence of 6-methylbenzo[c]phenanthrene XXI is also visually similar to those of XIX and XX, but the spectrum of XXI is distinct from that of XX in the appearance of an extra band in the beginning of the spectrum, 1a (compare XXI with XIX and XX in Figure 2).

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A Radiological Detector for Gas Chromatography

C. H. DEAL, J. W. OTVOS, V. N. SMITH, and P. S. ZUCCO

Shell Development Co., Emeryville, Calif.

A method for sensing changes in the composition of a gas stream has been developed, which exploits differences in beta ionization cross sections and is suitable for use as a detector in gas chromatography. It gives a detector instrument of very rapid response, high stability, high sensitivity, and broad applicability, which is insensitive to gas flow rate. The fundamental principles of the method are outlined, and the apparatus and its application to gas chromatography are described.

IN THE use of gas chromatography for separation or analysis of mixtures of volatile substances (*2*) a sensing device is required that will respond to the presence of any of the components in the carrier gas, usually nitrogen or helium. Various types of detectors have been reported, their principle of operation being based on chemical reactions (*2*), thermal conductivity (*7*), gas density (*3*), and heat of combustion (*9*). In some applications the authors have successfully used an ionization chamber detector, which has the desirable features of high sensitivity, good stability and precision, rapid response, and insensitivity to changes in rate of gas flow.

PRINCIPLES OF DESIGN AND OPERATION

The principles of ionization chamber operation are well known and instruments for gas analysis based on ionization chamber techniques have been described (*1, 8*). This discussion is therefore restricted to principles that bear on the design and operation considerations discussed below.

Production of Ions. If ions are formed by a source of β-particles, for example, in a gas at or near atmospheric pressure and if a potential difference is applied to a pair of electrodes placed in the gas, then current will be carried by the ions. The current will increase with increasing voltage until a "saturation" current is reached. At saturation, all the ions that are being formed reach the electrodes before they recombine, whereas at lower voltages the drift rate of the ions is smaller and the rate of recombination becomes comparable with the rate of collection at the electrodes. The voltage required for saturation depends on the electrode spacing, the pressure, and the nature of the gas. Hence, to eliminate the effect of voltage on ion current under a variety of conditions, it is desirable to work considerably above the saturation voltage. In the apparatus described below, 100 volts was found to be adequate.

The rate of production of ions depends on the strength of the ionizing source, the nature of the gas, and the concentration of gas molecules, which in turn depends on temperature and pressure. If the current is to be proportional to the concentration, the size of the chamber and the energy of the β-particles must be so related that only a small part of the β-particle energy is dissipated in the gas. Under these conditions the ionization produced per unit length of path is constant throughout the chamber and the rate of ion production is given by

$$i = kcQ \qquad (1)$$

where c is the concentration of gas molecules per unit volume and Q is the ionization cross section of the gas molecules (*6*). For a mixture of gases one can write

$$i = \frac{kP}{RT} \sum_j x_j Q_j \qquad (2)$$

where the x_j's are the mole fractions of the components and P and T are the total pressure and the absolute temperature. In the absence of recombination reactions this rate of ion production is equal to the collected ion current.

Effect of Pressure, Temperature, and Composition. The extent to which the conditions that lead to Equation 2 are satisfied in the instrument under consideration may be seen in Figures 1 to 3, where the total response in millivolts, before any current is balanced out, is plotted as ordinate. The data given in Figures 1 and 2 show that for a flow of pure nitrogen the ion current is proportional to total pressure and to the reciprocal of the absolute temperature. When heptane is introduced into the stream, the current rises, as shown in Figure 3. The cross sections of heptane and nitrogen may be estimated from the data of Otvos and Stevenson (*6*) as 45.1 and 7.7 relative to 1.0 for the hydrogen atom. From these figures it can be shown that the ion current should increase by 4.6% of its value between pure nitrogen and 1 mole % heptane in nitrogen, and should be linear with the mole fraction. Actually, Figure 3 shows an in-

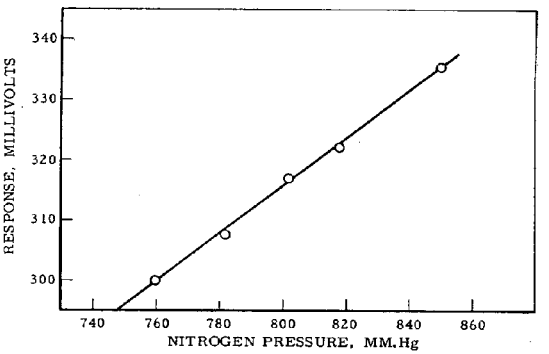

Figure 1. Response of nitrogen-filled cell to changes in pressure at 50°C.

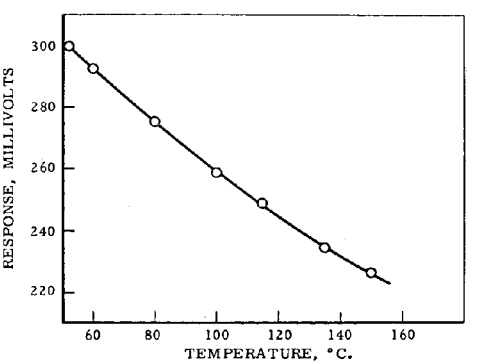

Figure 2. Response of nitrogen-filled cell to changes in temperature

Atmospheric pressure, 50 ml. per minute nitrogen flow

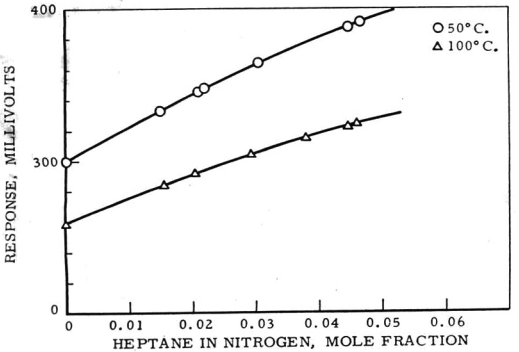

Figure 3. Response to heptane in nitrogen

Atmospheric pressure, 50 ml. per minute nitrogen flow

itial increase of 7% per mole % heptane and a slowly decreasing slope with increasing heptane concentration. A complete discussion of the reasons for this discrepancy is beyond the scope of the present paper, but the effect is believed to be similar to that found by Jesse and Sadauskis (*4*), who explained such a nonlinear behavior by the formation of additional ions by collision of un-ionized excited molecules and normal molecules. Such an effect indicates that relative ionization cross sections should be used only as a qualitative guide to the behavior of gas mixtures at other than very low pressures.

Sensitivity and Noise. The statistical fluctuations in the intensity of the β-particle source produce a noise in the ionization current that sets a limit on the concentration of a second gas that can be detected in nitrogen. This noise depends on the source strength and on the time constant of the recorder. For example, in the instrument described here, a 10 mc. source is used with a 1-second filter circuit in the recorder. Assuming a reasonable geometry, and allowing for absorption of some β-particles in the source holder, we can estimate that 2×10^8 ionizing particles traverse the gas in the period of one time constant. The random fluctuation associated with this rate is $\sqrt{2 \times 10^8}$, which is a noise-to-signal ratio of 7×10^{-5}. The noise level shown in Figure 11 is about 0.1 mv. out of 300, or 33×10^{-5}.

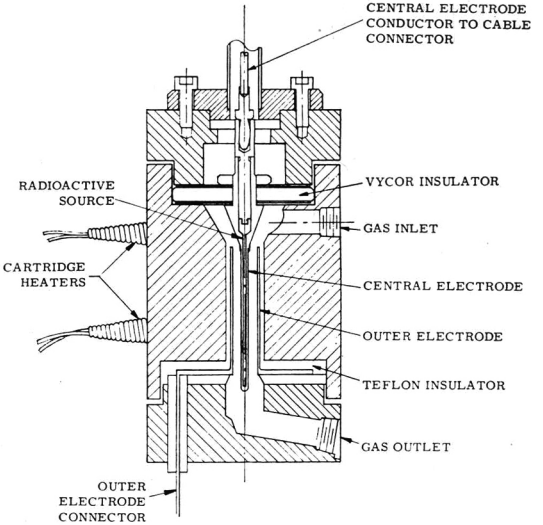

Figure 5. Ionization chamber assembly

This is not bad agreement for such a crude calculation, considering that there are other sources of noise as well, and that the 0.1 mv. is a peak to peak value rather than an average value. The heptane results, together with the noise figure, indicate that a concentration of 0.01 mole % heptane would produce a signal-to-noise ratio of 2 to 1 and would thus be detectable under the standard conditions of operation.

Flow Sensitivity. An ionization chamber detector is inherently insensitive to changes in flow rate as long as the residence time of the gas in the chamber is long compared to the drift time of the ions in reaching the electrodes. The latter can be roughly estimated to be 10^{-3} to 10^{-2} second under the applied electric field (δ). The residence times are always much longer, even at the unrealistic rate of 9 liters per minute shown in Figure 12. The small increase in current with increasing flow rate is probably a pressure effect due to flow restriction in the exit tube from the chamber.

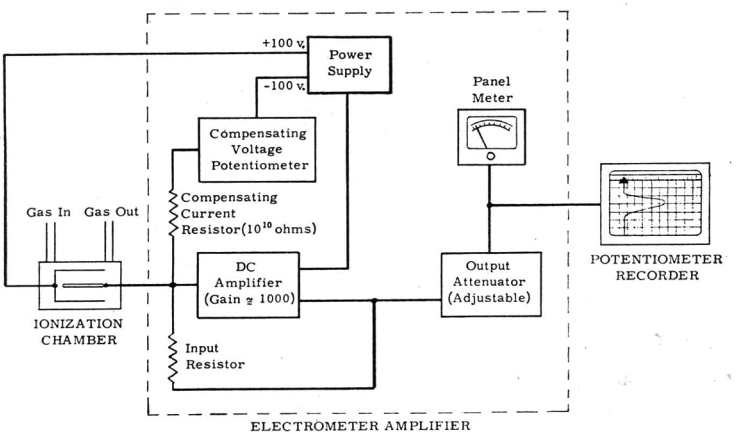

Figure 4. Schematic block diagram of radiological detector for gas chromatography

GENERAL DESCRIPTION OF APPARATUS

The complete detecting apparatus consists of a special ionization chamber with self-contained radioactive source, an electrometer amplifier with built-in compensating voltage supply, a potentiometer-type strip chart recorder, and an electronic temperature controller for thermostating the ionization chamber. Diagrams and photographs of the over-all assembly and essential parts are shown in Figures 4 through 9. The cost of the equipment, exclusive of the recorder, is approximately $1100. Of this total, approximately $325 is for the ionization chamber and source, $525 is for the electrometer amplifier, and $250 is for the temperature controller.

Ionization Chamber. The present design of the ionization chamber has evolved from experience with several designs over the past 3 years. The most important requirements that must be met by the design are:

1. Safety from radiation and electrical shock hazards
2. Small volume for fast response to changing concentration
3. Large outlet passage for minimum pressure rise due to flow
4. Ability to operate at temperatures up to 250° C.
5. Ease of cleaning by flushing with solvent without disassembly
6. Simplicity to minimize cost and simplify maintenance

The ionization chamber shown in Figure 5 in cross section, and in Figures 6 and 7 in photographic views, meets the foregoing requirements very well.

The body of the cell is a rectangular stainless steel block having over-all dimensions of $2^1/_2 \times 2^1/_2 \times 4^1/_2$ inches. A hole $^1/_2$ inch in diameter bored through the block provides space for the electrodes and is the active region of the cell. The outer electrode is a stainless steel tube $^3/_8$ inch in outside diameter with 0.035-inch wall thickness, supported by a circular flange. The flange is clamped between Teflon gaskets that serve as insulators as well as gas-tight seals. Electrical connection to the electrode

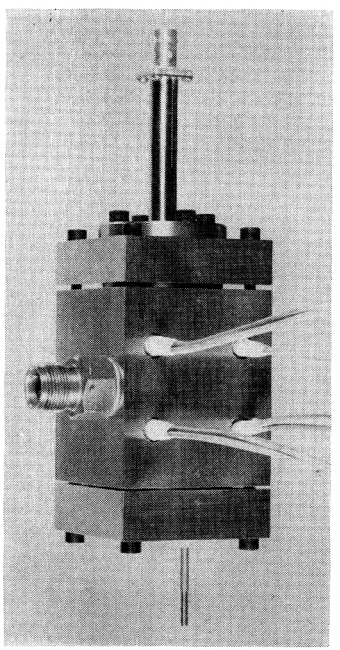

Figure 6. Ionization chamber assembled

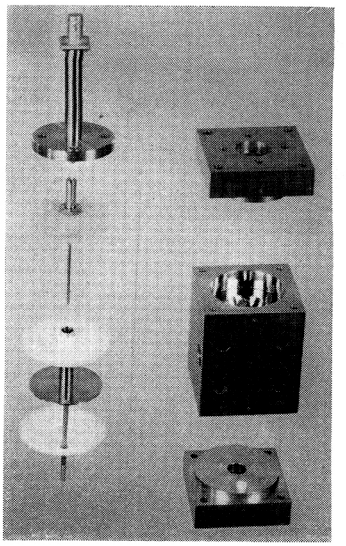

Figure 7. Components of ionization chamber

is made by a rod $^1/_8$ inch in diameter, extending through the gasket and bottom cover plate. Three holes at the lower end of the electrode permit gas flow through the annular space outside the electrode and permit complete draining of solvent after cleaning.

The central electrode is a stainless steel hypodermic tube with 0.063-inch inside diameter and 0.005-inch thick wall to permit penetration of β-particles into the active volume from the enclosed source. This electrode is supported by a conical end piece into which the radioactive source is screwed. The central electrode assembly is mounted on a Vycor (96% silica glass manufactured by the Corning Glass Works.) disk insulator and sealing is provided by Teflon gaskets. The Vycor or fused quartz insulator is required to maintain high insulation resistance at high temperatures. Glass is not satisfactory because its resistivity drops rapidly at temperatures above 200° C. The electrical connection to the central electrode is made through a coaxial conductor to a conventional connector at the top of a $2^1/_2$-inch extension tube. The $2^1/_2$-inch long stainless steel extension tube provides thermal isolation of the connector and cable from the hot cell.

The cell block is bored for insertion of four cartridge-type electrical heaters and a nickel resistance thermometer element. The cell temperature is controlled by means of an electronic temperature controller (Resistotrol temperature controller manufactured by Hallikainen Instruments, Berkeley, Calif.) with the resistance thermometer element connected as one arm of the bridge input circuit. Temperature control is better than ±0.1° C., which is more than adequate for the stability requirements.

Flow line connections are made through tapped holes at the side near the top of the block and on the bottom cover plate. These holes are located to minimize the escape of direct β-radiation from the chamber when flow lines are disconnected. The total volume of the chamber is approximately 13 ml., less than 5 ml. of which is active volume. The design is such that a larger bore and larger outer electrode may be used to accommodate flows from larger columns, if desired.

The grounded shell construction used here has the advantage of shielding the high voltage electrode and simplifying connection of flow lines because they need not be insulated from ground. It also provides an inherent "guard ring" for the central collector electrode, preventing electrical leakage paths between the outer electrode and the collector electrode other than through the ionized gas. A word of caution is due here concerning the selection of the collector electrode. If the outer electrode is

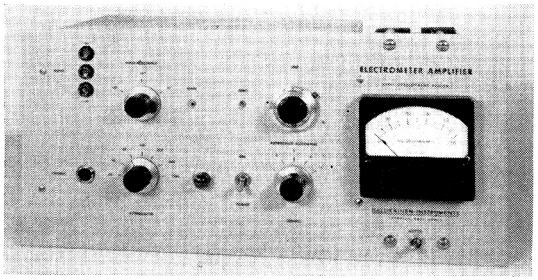

Figure 8. Electrometer amplifier

used as the collector—i.e., connected to the amplifier input circuit—the measured current includes ions produced in the annular space between the outer electrode and the cell body. The drift velocity is very low for these ions because of the low potential difference between the grounded cell body and the amplifier input. This results in excessive sensitivity to gas flow, sensitivity to surface conditions owing to surface potentials, and sensitivity to polarity of the high voltage electrode, because the external current may either add to or subtract from the ion current in the active region. When the central electrode is used as the collector, these difficulties do not arise.

Radioactive Source. For the radioactive source strontium-90–yttrium-90 has been chosen because it is a pure β-emitter and has a relatively long half life (approximately 19 years). A γ-emitter is not desirable for this type of instrument because of the low ionization efficiency of γ-rays and the greater shielding problem. Although α-emitters are desirable for their high specific ionization (*1*), their poor penetrating power makes it necessary to expose the active material to the gas stream, which may permit contamination of the gas or of solvents used for cleaning the cell. The strontium-90 in equilibrium with its daughter product, yttrium-90, emits β-particles with energies up to about 2,200,000 electron volts, which permits the use of two isolating stainless steel tubes between the active material and the sample gas without undue loss of sensitivity.

The source consists of 10 mc. of the radioactive strontium in the form of a sliver of activated foil in a thin-walled (0.002 inch thick) stainless steel hypodermic tube having an outside diameter of 0.042 inch and a length of $1^1/_2$ inches. The active material is sealed in place by silver solder plugs in the ends, and an 8-32 socket head setscrew is silver-soldered to one end to facilitate handling and stable mounting in the chamber. These special "needle sources" were designed and fabricated to specifications by the U. S. Radium Corp., 535 Pearl St., New York, N.Y. A special handling tool is used for inserting or retracting the source from the cell. A photograph of this tool with a "dummy" source attached is shown in Figure 9.

The cylindrical geometry permitted by the needle source greatly increases the efficiency of ionization of the gas and improves the uniformity of irradiation. All β-particles penetrating the wall of the inner electrode must pass through the gas and produce ions. A high percentage of those reaching the outer wall are back-scattered and produce further ionization. The ion current with this 10 mc. source is approximately equal to that obtained with a similar chamber using a 25-mc. capsule-type source mounted at one end.

Radiation Hazard. The radiation hazard with this apparatus is negligible during normal operation. The heavy walls of the ionization chamber stop all the β-particles, so that the external radiation is only low intensity secondary x-ray (Bremsstrahlung). The radiation level at the surface of the cell body is approximately 15 milliroentgens per hour (mr per hour), and this is further reduced to less than 3 mr per hour by $^1/_8$-inch-thick lead shielding fastened to the cell walls. However, exposure to intense radiation that can produce serious burns is possible if the cell is disassembled. For this reason the source should be removed and placed in a shield block by qualified personnel, and the cell should be checked for internal contamination before the disassembly is begun.

Electrometer Amplifier and Recorder. The ion current obtained with nitrogen in the cell is of the order of 5×10^{-10} ampere and the minimum changes to be detected are approximately 0.25×10^{-12} ampere ($\pm 0.05\%$ of total current). In order to accomplish this satisfactorily, the ion current due to nitrogen must be balanced out either by current from a compensating ion chamber filled with a flowing reference gas (*8*) or by a current obtained from a compensating voltage applied through a high resistance. Although the compensating ion chamber has the advantage of compensating for changes in temperature and pressure, the single chamber with compensating voltage has proved completely satisfactory and has been used in most applications because of its simplicity and lower cost.

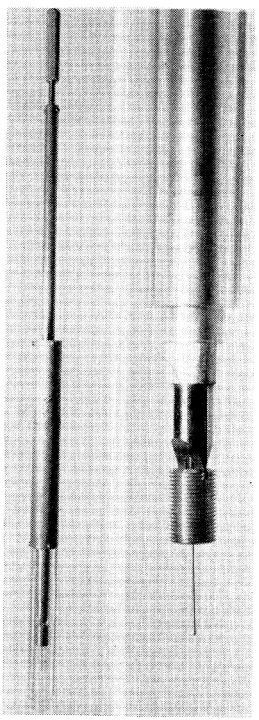

Figure 9. Radioactive source handling tool

The electrometer amplifier (manufactured by Hallikainen Instruments, Berkeley, Calif., according to Shell Development Co. design) used with this detector is an improved and modified version of one used previously with an apparatus for measuring β-particle absorption in liquids (*10*). The amplifier is direct coupled, uses all conventional vacuum tubes, and incorporates 100% negative feedback for stabilization of gain. Voltages are stabilized by a constant voltage transformer and gas discharge-type voltage regulator tubes. Panel-mounted coaxial connectors are provided for the input current from the ion chamber and for either +100 or −100 volts for the ion chamber accelerating electrode. A selector switch permits use of 10^9, 10^{10}, or 10^{11} ohms in the input circuit, and an additional 10^{10}-ohm resistor

connected to an adjustable compensating voltage supply is connected to the input grid. Normally the 10^{10}-ohm input resistor is used and the compensating voltage is adjusted by means of a panel switch and 10-turn dial to balance out the current due to nitrogen. The amplifier output is connected to a panel meter and recorder jack through a step attenuator. The output circuit is designed so that panel meter readings agree with the recorder when a 10-mv. recorder is used (this may be modified easily for use with recorders to 50-mv. sensitivity). The time constant normally used is approximately 1 second and is determined by a resistive, capacitive filter in the output attenuator circuit.

OPERATION AND MAINTENANCE

To operate the apparatus the electrometer amplifier and temperature controller are turned on and the desired temperature is set on the temperature control dial. The cell may be operated at a temperature above the highest column temperature to be used, if desired, to avoid resetting of controls. By the time the cell has reached the operating temperature, the electrometer amplifier will be sufficiently stabilized for zero adjustments to be made. First the amplifier zero adjustment is made with the input cable disconnected and the compensating voltage set at zero. Then the input cable is reconnected and the compensating voltage is adjusted to give zero output signal with nitrogen (or other carrier gas) flowing through the chamber. Subsequently, the amplifier zero and the setting of the compensating voltage should be checked occasionally to correct for further warm-up drift or changes in pressure. Normally the amplifier zero drift is negligible and need be checked only once a day, and the compensating voltage setting needs to be reset only when the operating temperature or pressure is changed.

Occasionally deposits will build up in the ionization chamber owing to condensation of high boiling materials, dirt in the system, etc. Cleaning can usually be accomplished by flushing the cell several times with a solvent such as acetone, followed by air drying. In cases where solvent flushing is inadequate, it is necessary to remove the radioactive source and dismantle the cell for cleaning. Dismantling has rarely been found necessary with the present cell design.

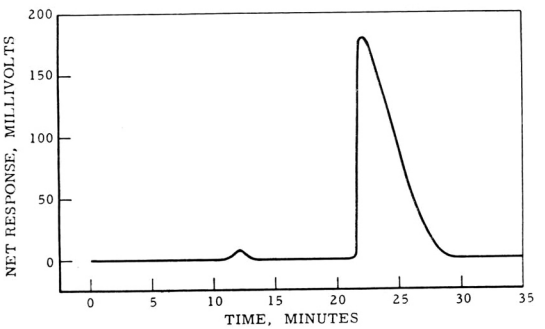

Figure 10. Detection of separation of 1% *n*-hexane in *n*-octane

Atmospheric nitrogen pressure, 40 ml. per minute flow, 150°C. cell temperature. Current due to nitrogen balanced out

OPERATIONAL CHARACTERISTICS

The signal from the detector cell is sensitive to the composition of the gas in the cell, the operating temperature of the cell, and the operating pressure in the cell, but is insensitive to the rate of flow of gas in the cell. In practical operation the cell temperature and pressure may be fairly easily controlled to the degree required to provide a stable base line trace on the recorder with regard to both short-term variations which might be confused with trace sample components and long-term drifts. Amplifier noise and incidental noise are normally small compared to the statistical noise associated with the β-ionization source. The latter imposes the practical limit at which a change in gas composition can no longer be detected.

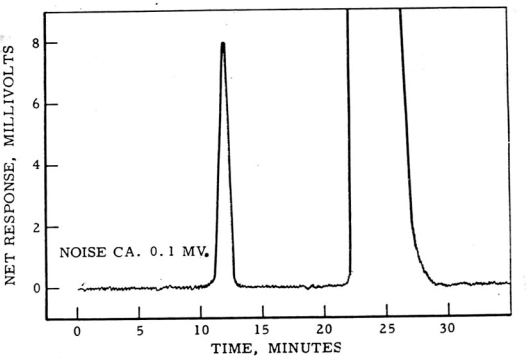

Figure 11. Detection of separation of 1% *n*-hexane in *n*-octane

Atmospheric nitrogen pressure, 40 ml. per minute flow, 150°C. cell temperature. Current due to nitrogen balanced out

In gas liquid partition chromatographic application the inherent flow insensitivity of the present detection system is particularly valuable, because an interfering surge in total flow of gas as a band is stripped from a column can frequently be detected with flow-sensitive detectors. The design of the present cell with a "through"-flow pattern and with a holding time of 0.05 to 0.10 minute at the 50 to 100 cc. per minute flows usually used ensures a rapid response with the cell providing an accurate measure of the average composition of the gas in the cell at any instant. Time delays in the electrical circuits and the recorder may be expected to give only slight distortions in the peaks plotted by the recorder. An illustrative chromatogram of a mixture of 1% *n*-hexane in *n*-octane obtained with the unit operated in conjunction with a gas partition column 2 meters in length and 8 mm. in diameter containing SF-96 silicone fluid (General Electric Co.) suspended on crushed C-22 (Johns Manville Co.) is shown in Figure 10. The same chromatogram at higher recorder sensitivity is shown in Figure 11.

With nitrogen at 50° C. and atmospheric pressure flowing in the cell, the ionization current is about 6×10^{-10} amperes, which

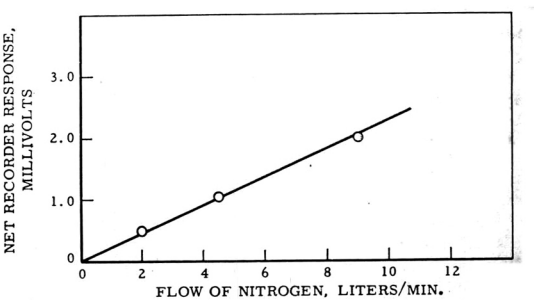

Figure 12. Response to changes in nitrogen flow

Atmospheric pressure, 25°C. cell temperature

corresponds to a potential of 6 volts across the 10^{10}-ohm input resistor. At an amplifier attenuation of $1/_{20}$ this corresponds to a 300-mv. output, as shown in Figures 1, 2, and 3. Under operating conditions this current is balanced out by means of the compensating voltage, and the recorder sensitivity is set at 1 mv. per inch, so that, for example, the response to heptane vapor is 560-mm. displacement (22 mv.) per mole per cent of heptane. The net response is substantially linear in the composition of the gas up to 0.02 or 0.03 mole fraction (Figure 3). Because there is a rough proportionality between ionization cross section and molecular weight, the net response of the unit to different vapors is about the same when the compositions are expressed on a weight basis. The net response to changes in cell pressure and temperature is on the order of 0.4 mv. per mm. of mercury (3.3-mm. displacement per mm. of mercury) and 0.8 mv. per °C. (6.7-mm. displacement per °C.), respectively (Figures 1 and 2). An increase in nitrogen flow of 1 liter per minute produces a net response of only 0.2 mv. up to flow rates of at least 5 liters per minute (Figure 12). The statistical noise corresponds to a net response of about 3 mm. (0.1 mv.) and is equivalent in magnitude to the net signal from a change in heptane concentration in the gas stream of about 0.005 mole %.

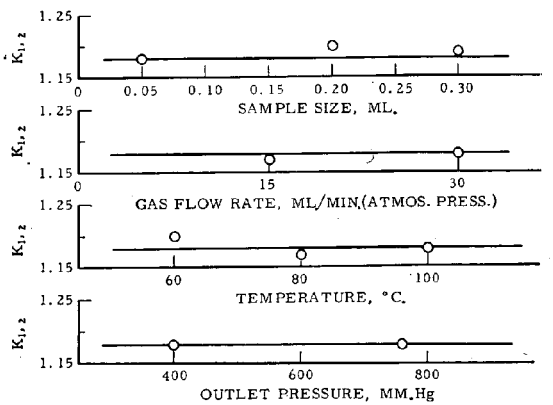

Figure 13. Effects of column operating conditions on calibration parameters for equiweight solution of *sec*-butyl alcohol (1) and propyl alcohol (2)

Cell operated at column temperature

APPLICATION TO QUANTITATIVE ANALYSES

When the unit is applied in conjunction with a chromatographic column, it is to be expected that the area A_i, of each of the chromatographic peaks representing the separated components of a sample will be proportional to the product of the total moles of the component, m_i, and the difference between its ionization cross section and that of the carrier gas, ΔQ_i,

$$A_i = k' m_i \Delta Q_i$$

where k' depends upon the flow rate, the temperature, and the pressure of the gas in the cell. (It is implied here that rate of flow of total gas effluent from the column is constant and that the concentrations of noncarrier gas components detected are sufficiently small that the net response is linear in the effluent gas concentration.) Usually, however, it is not convenient to reproduce gas flows from chromatogram to chromatogram quantitatively or to measure the flow quantitatively, and an internal standard method is usually used for quantitative analyses. In this case, for any pair of sample components, 1 and 2, a parameter which is to be expected to be independent of operating conditions and the relative concentrations of the sample components may be defined as

$$k_{1,2} = \frac{A_1}{X_1} \Big/ \frac{A_2}{X_2} = \frac{M_2 \Delta Q_1}{M_1 \Delta Q_2}$$

where X's are weight fractions of the components in the sample charged and the M's are their molecular weights. As indicated earlier, the ΔQ's may be estimated from the cross sections of the constituent atoms (*6*).

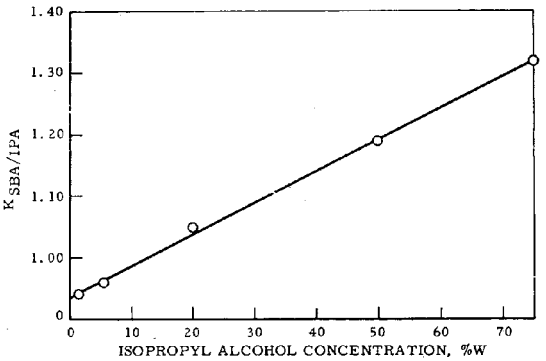

Figure 14. Effect of sample composition of binary sample on calibration parameter

sec-Butyl alcohol–isopropyl alcohol solutions, 100°C.

In practice, parameter $K_{1,2}$ is found to be substantially independent of sample size, gas flow rate, temperature, and pressure. The parameter for *sec*-butyl alcohol (2-butanol), 1, and isopropyl alcohol (2-propanol), 2, is plotted as a function of these variables in Figure 13. It is found also to be independent of the mechanical details of the detector cell over a wide range of designs. It is, however, somewhat dependent upon the relative concentrations of the pair of components and its magnitude can be estimated only roughly from atomic cross sections. A typical plot of $K_{1,2}$ *vs.* X_2, where the concentrations have been calculated on a two-component basis ($X_1 + X_2 = 1$), is shown in Figure 14. For a large number of cases, plots of this sort have been shown to be linear within experimental errors of 1 to 2%, regardless of whether the data are taken from binary or multicomponent samples. Data which allow the comparison of calculated parameters and experimental parameters are given in Table I.

Table I. Comparison of Experimental and Calculated $K_{1,2}$

Binary Pair		$K_{1,2} = \frac{A_1}{X_1} \Big/ \frac{A_2}{X_2}$ at $X_1 = X_2$	$K_{1,2} = \frac{M_2 \Delta Q_1}{M_1 \Delta Q_2}$ (Calcd.)
1	2		
2-Butanol	2-Propanol	1.18	1.12
Acetone	2-Propanol	0.88	0.91
Methyl ethyl ketone	2-Propanol	0.99	1.05
Diisopropyl ether	2-Propanol	1.14	1.13
2-Butanol	Acetone	0.88	0.91
Methyl ethyl ketone	Acetone	1.27	1.16

ACKNOWLEDGMENT

The authors are indebted to D. J. Pompeo for suggestions and encouragement in the use of ionization chamber detectors, to S. T. Abrams, W. B. Conner, Jr., and S. M. Brassington for their part in the design and construction of the cells, and to J. F. Waller and H. U. Cole for their part in applying the cells in practical gas partition chromatography.

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Quantitative Determination of Phenylalanine on Paper Chromatograms

ARTHUR E. PASIEKA and JOSEPH F. MORGAN

Laboratory of Hygiene, Department of National Health and Welfare, Ottawa, Canada

A quantitative method for the determination of phenylalanine in the presence of varying proportions of 19 other amino acids utilizes the characteristic blue color formed by phenylalanine when ninhydrin-developed paper chromatograms are treated with dilute sodium bicarbonate. The ninhydrin colors of the other amino acids can be removed by water washing without eluting the specific phenylalanine color, which is then extracted with 1-butanol and measured in a spectrophotometer at 600 mμ. The intensity of the clearly defined phenylalanine spot can also be read directly on the chromatograms with a densitometer. The application of the method to complex biological media is reported.

DURING studies on the amino acid metabolism of animal tissues cultivated in vitro in synthetic media (*8*), paper chromatography indicated that an uptake of phenylalanine occurred during the cultivation period. In these studies, the synthetic medium employed was M 150 (*4, 5*), which contains 60 ingredients including 20 amino acids dissolved in a modified Tyrode's solution (*2*). The DL-phenylalanine content of this medium is 50 mg. per liter, representing 4.5% of the total amino acids present. The disappearance of phenylalanine from the medium suggested its importance for tissue culture nutrition and metabolism. Under certain conditions, phenylalanine forms a characteristic gray color when developed by the conventional ninhydrin procedure, and by this method microgram quantities can be detected (*1, 3, 9*). Under the conditions of neutral and acidic solvent systems used in the present study, however, the phenylalanine-ninhydrin color was found to be nonspecific and indistinguishable from that of various other amino acids. For this reason, an effort was made to develop a selective method for phenylalanine that could be applied in the presence of high concentrations of other amino acids following development by neutral and acidic solvents.

Previous studies from this laboratory (*7*) have shown that a characteristic blue color, specific for phenylalanine, is produced when the ninhydrin-developed chromatograms are subsequently treated with dilute sodium bicarbonate. Development of this specific color is associated with a shift in the absorption maximum from 560 to 600 mμ as well as increased color stability. The results reported in the present communication show that this characteristic blue color can be used as the basis for a quantitative method that permits the specific determination of phenylalanine on paper chromatograms in the presence of 19 other amino acids, even under conditions of poor separation and resolution.

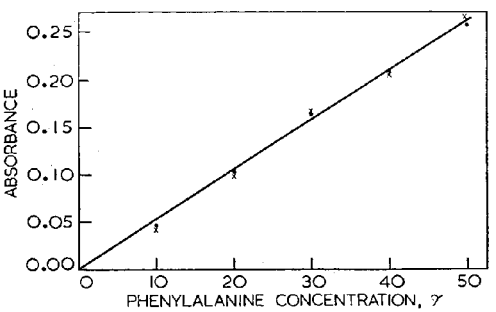

Figure 1. Standard curve for specific phenylalanine determination

● Graded concentrations of DL-phenylalanine dissolved in M 150 with variable ratio of phenylalanine to other amino acids present
× Graded concentrations of DL-phenylalanine with constant ratio of phenylalanine to other amino acids

PROCEDURE

Chromatography. Samples for analysis (5.0 ml.) are concentrated to dryness in vacuo over concentrated sulfuric acid and reconstituted in 0.2 ml. of deionized water. With the biological media studied, 10-μl. aliquots of the concentrates were found suitable for analysis. One-dimensional descending paper chromatograms are employed with Schleicher and Schuell No. 597 or Whatman No. 1 paper. The solvent systems recommended for use are either 1-butanol–acetic acid–water or 1-butanol–ethanol–water, prepared as described previously (*6–8*). The chromatograms are developed at room temperature by the descending technique for 18 hours, dried at 110° C. for 2 to 3 minutes, and redeveloped in the same solvent for an additional 18 hours in the same dimension. Separation and resolution were considerably increased by this second development period.

The chromatograms are then dried at 110° C. for 2 to 3 minutes and sprayed with 0.4% ninhydrin dissolved in either water-saturated 1-butanol or 95% ethanol. The chromatograms are dried at room temperature for 5 to 10 minutes, reheated to 110° C. for 3 minutes, and dipped into 1.0% sodium bicarbonate. The phenylalanine region on the chromatograms immediately appears as a deep blue spot, which is clearly visible even in the presence of the purple color of other amino acids. This blue color does not fade on prolonged standing, although the color intensity of the other amino acids on the chromatograms decreases steadily (*7*).

Measurement of Concentration. SPECTROPHOTOMETER. The blue phenylalanine area is then cut into several strips, which are placed in a test tube with 5.0 ml. of deionized water. The tube from each spot is shaken mechanically for 1 minute, the liquid decanted, and the washing procedure repeated. The tubes are

then drained, 5.0 ml. of butanol is added to each, and shaking continued for 10 minutes. This extract is then decanted and the color intensity read in a spectrophotometer at 600 mμ (a Beckmann Model DU was used), employing a 1-butanol blank. The phenylalanine concentration is calculated from a standard curve prepared by the same procedure.

DENSITOMETER. As an alternative method, the ninhydrin- and bicarbonate-treated chromatograms may be washed with water until the contaminating colors have been removed. The period of washing will depend on the concentration of contaminating ninhydrin-positive materials, but is usually complete within 5 minutes. The intensity of the clearly defined blue phenylalanine spot may then be measured with a densitometer (Welch Densichron), and the phenylalanine concentration calculated from a standard curve prepared in the same way.

Because the phenylalanine spots are somewhat irregular, both area and peak density must be measured in the densitometer procedure. For this reason, the butanol extraction method is recommended as the procedure of choice. In the development of this method, specific types of paper and developing solvents were used, but it appears probable that other papers and solvent systems would prove equally satisfactory.

Standard Curves. Graded levels of DL-phenylalanine were dissolved in medium M 150, samples concentrated to dryness, and reconstituted in deionized water as described previously. At the same time, samples of M 150 containing 50 mg. per liter of DL-phenylalanine were concentrated to dryness and reconstituted in varying quantities of deionized water. Portions of 10 μl. of these concentrated samples were then spotted on paper chromatograms so that the concentration of phenylalanine per spot ranged from 10 to 50 γ. In this manner two series of phenylalanine spots were prepared. In one series, the ratio of phenylalanine to other amino acids remained constant, while in the second series the ratio changed progressively.

The specific phenylalanine color was then developed, followed by butanol extraction and measurement of absorbance. The results of these determinations (Figure 1) show a linear response over the concentration range of 10 to 50 γ. Higher concentrations of phenylalanine could not be measured in this system because of solubility limitations. Because the response obtained is linear and identical whether the ratio of phenylalanine to other amino acids remains constant or changes, interference by other amino acids is precluded. In preparing these curves, eight replicate chromatograms were used in each series and separate measurements were made at each phenylalanine concentration. Calculation of the standard error in terms of the absorbance measurements (0.047 ± 0.004, 0.168 ± 0.011, and 0.257 ± 0.016 for 10, 30, and 50 γ of phenylalanine, respectively) shows that the precision of the method is good.

RESULTS AND DISCUSSION

Data from a typical recovery experiment, summarized in Table I, show that excellent recoveries can be obtained by this method.

Table I. Determination of Known Amounts of DL-Phenylalanine Added to Medium M 150

DL-Phenylalanine, γ per Ml.		Recovery,
Added	Recovered	%
30	30.4	101.3
30	29.3	97.7
30	30.4	101.3
30	31.5	105.0
40	38.3	95.8
40	41.3	103.1
40	40.8	100.2
40	40.5	100.1
40	39.3	98.3
40	39.3	98.3
50	47.6	95.2
50	52.4	104.8
50	48.8	97.6
50	49.1	98.2

Removal of Contaminating Amino Acids. In exploratory experiments, chromatograms of medium M 150 treated with ninhydrin and bicarbonate as described previously (7) gave the characteristic blue phenylalanine spot, but heavily contaminated with valine and occasionally with methionine and leucine. Because the phenylalanine color was bound to the paper more strongly than that of the other amino acids present (7), attempts were made to remove the contaminants by solvent extraction. The phenylalanine areas, together with their contaminants, were cut from the chromatograms, placed in test tubes, and 5.0 ml. portions of appropriate solvents added. The tubes were shaken mechanically for 5 minutes, the liquid was decanted, and absorption curves were prepared. The results of these experiments are summarized in Table II. With the exception of chloroform, the organic solvents tested failed to elute the ninhydrin-positive materials. Water or 1.0% sodium bicarbonate removed most of the ninhydrin and amino acid colors but did not elute the phenylalanine color. After washing with water or bicarbonate, however, treatment with 1-butanol was found to elute the specific phenylalanine spot effectively; this two-step elution procedure was selected as a differential method.

Table II. Selective Elution of Contaminating Amino Acids and Phenylalanine from Ninhydrin- and Bicarbonate-Treated Paper Chromatograms

	Removal of[a]	
Eluting Solvent	Contaminants	Phenylalanine
Chloroform	++++	++++
1-Butanol	+	+
Acetone	−	−
Ethanol, 95%	−	−
Carbon tetrachloride	−	−
Diethylamine	−	−
Water, deionized	++++	−
Sodium bicarbonate, 1.0%	++++	−
Hydrochloric acid, 0.1N[b]	−	−
1-Butanol (after water extraction)	−	++++

[a] ++++ = complete removal; + = very slight removal.
[b] Dilute hydrochloric acid caused characteristic phenylalanine color to revert to typical nonspecific ninhydrin color.

Extraction of contaminating amino acid and ninhydrin colors from a paper chromatogram of medium M 150 (containing 50 mg. per liter of DL-phenylalanine), after development with ninhydrin and treatment with sodium bicarbonate, is illustrated in Figure 2. A 1-minute extraction with water has removed the majority of the ninhydrin-positive materials, as shown by the

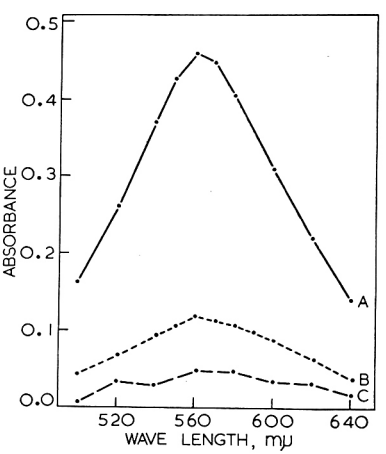

Figure 2. Removal of contaminating ninhydrin colors by extaction with water

A. First 1-minute water extract
B. Second 1-minute water extract
C. Third 1-minute water extract

high reading of the characteristic absorption maximum at 560 mμ in the eluted material. At the same time, the lack of a peak at 600 mμ indicates that the characteristic phenylalanine color has not been eluted. Small amounts of color were removed by a second water extraction but only insignificant amounts appeared during the third extraction.

Following two 1-minute water washes of the chromatogram, the specific phenylalanine color was eluted by 1-butanol, as shown in Figure 3, curve *A*. This graph shows clearly the characteristic absorption peak at 600 mμ of the specific phenylalanine color. The regularity of this curve and the absence of a peak at 560 mμ show that only negligible amounts of extraneous color have been carried into the butanol extract. For comparative purposes, a graph of the third water extract, following two 1-minute water extractions of a duplicate chromatogram, is included (Figure 3, curve *B*). This curve shows the typical ninhydrin absorption maximum at 560 mμ. The regularity of this curve and the absence of a peak at 600 mμ indicate that negligible amounts of the specific phenylalanine color have been extracted by the water wash.

APPLICATION TO BIOLOGICAL MEDIA

The new method was tested on synthetic medium M 150 and on a modified synthetic medium (M 496) in which the total amino acid content was approximately double that of M 150. Concentrated water solutions (30%) of yeast extract (Difco) and enzymatic casein hydrolyzate (Difco) were also tested for the presence of phenylalanine. The results of these experiments are shown in Figure 4. The left half (*A*, *B*, *C*, and *D*) shows development of these four solutions by the conventional ninhydrin procedure and illustrates the difficulty of detecting phenylalanine in the presence of other ninhydrin-positive substances. The right half (A_1, B_2, C_3, and D_4) shows a similar chromatogram which has been developed with ninhydrin, treated with bicarbonate, and washed with water. The characteristic blue spots of phenylalanine (position 16) are clearly defined and washed free of contamination with other amino acids. Yeast extract and casein hydrolyzate (C_3 and D_4) show an appreciable content of phenylalanine, although on development by the conventional ninhydrin procedure alone (*C* and *D*) the presence of this amino acid was impossible to detect. Better resolution of the amino acids in the yeast extract and casein hydrolyzate on these chromatograms could have been obtained by the use of less concentrated samples but the conditions were deliberately made as rigorous as possible.

The major advantage of this new method is that it permits the specific determination of phenylalanine in the presence of large amounts of other amino acids, even under conditions of poor separation and resolution on the chromatograms. In the application of this procedure to biological media, it has been possible to determine phenylalanine readily in synthetic tissue culture medium M 150, in which DL-phenylalanine constitutes 50 mg. in 1100 mg. per liter of total amino acids, a concentration of only 4.5%. An unusual feature of this method is that it can be subsequently applied to paper chromatograms that have been developed with ninhydrin for the measurement of other amino acids or peptides. Because the specific color reaction is undergone by free phenylalanine but not by derivatives or peptides of phenylalanine (7), the method may possibly be applied, in conjunction with the conventional ninhydrin procedure, for quantitative measurements of the degree of protein hydrolysis.

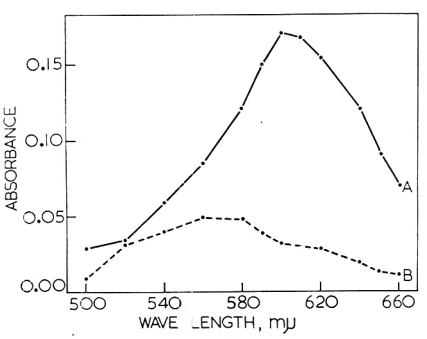

Figure 3. Elution of specific phenylalanine color with 1-butanol

A. 10-minute extraction with 1-butanol following two 1-minute water extractions
B. Third 1-minute water extraction following two initial 1-minute water extractions as for *A*

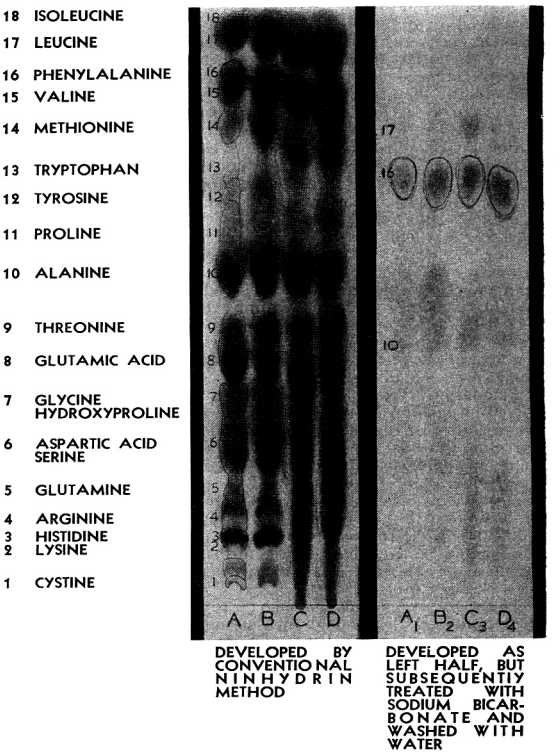

Figure 4. Application of specific phenylalanine method to paper chromatograms

A, A_1. Medium M 150
B, B_2. Medium M 496
C, C_3. Yeast extract
D, D_4. Enzymatic casein hydrolyzate

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Determination of Sugars on Paper Chromatograms with *p*-Anisidine Hydrochloride

JOHN B. PRIDHAM[1]

The Institute of Paper Chemistry, Appleton, Wis.

A new method for the determination of aldopentoses, aldohexoses, hexuronic acids, and 6-deoxyaldohexoses involves the paper chromatographic resolution of the sugar mixture, spraying of the chromatogram with *p*-anisidine hydrochloride reagent, and heating the paper in an oven. The resulting colored spots are cut out, the colors eluted from the paper with aqueous methanol containing stannous chloride, and then the absorbance is measured with a spectrophotometer. The absorbances of the sugar–*p*-anisidine complexes are directly proportional to the weights of the sugars over a range of 5 to 50 γ. The method has been used as a rapid analytical tool for the determination of the monosaccharide components of wood pulps and hemicelluloses.

PAPER partition chromatography has proved to be an invaluable aid to the quantitative determination of the components of complex mixtures of sugars (*1*). However, the chromatographic procedure which is normally used has the following disadvantages: Relatively large amounts of the sugars must be applied to the paper; the location of the bands by the use of marker strips may be inaccurate; and the complete elution of the sugars is time-consuming.

In the procedure described here, the solution to be analyzed is applied to the paper as small discrete spots, thus ensuring good chromatographic separation when only a relatively short solvent development time is used. After development the chromatogram is dried, then sprayed with *p*-anisidine hydrochloride (*2*) reagent and heated. The resulting colored spots, the boundaries of which are clearly discernible, are then cut from the chromatogram. The colors can be rapidly eluted and measured in a spectrophotometer. The intensity of color bears a linear relationship to the amount of sugar over the range from 5 to 50 γ.

The method has been successfully used for the determination of aldohexoses, aldopentoses, hexuronic acids and 6-deoxyaldohexoses, and, therefore, has been particularly useful for the analysis of wood pulps and hemicelluloses.

REAGENTS

p-Anisidine Hydrochloride Solution. Dissolve 1.0 gram of the crystalline reagent in 10 ml. of absolute methanol and make up to 100 ml. with 1-butanol. Add 0.1 gram of sodium hydrosulfite. Store the solution in the refrigerator.

Eluent. Dissolve 1.0 gram of stannous chloride in 5 ml. of water. Add 90 ml. of absolute methanol and filter the solution.

PROCEDURE

Quantitative analysis of sugar solutions was carried out by spotting suitable volumes onto Whatman No. 1 filter paper with an ultramicroburet. Three or four spots of standard mixed sugar solutions, the components of which corresponded qualitatively to those in the unknown samples, were also applied to the chromatograms. The standard solutions were spotted so that each sugar component was present in varying amounts over a range of 5 to 50 γ.

The chromatograms were developed with 1-butanol–pyridine–water solvent (6 to 4 to 3 v./v.) or ethyl acetate–acetic acid–water (9 to 2 to 2 v./v.) solvent for a minimum of 20 hours. The chromatograms were air dried, then sprayed as uniformly as possible with the *p*-anisidine hydrochloride reagent. They were then heated in an oven at 130° C. for 10 minutes. The colored sugar spots, together with suitable blanks, were cut out with a scissors, the areas of the pieces of paper being kept constant for each sugar series and as small as possible.

The color was eluted from the paper by shaking mechanically for 5 minutes with 3 ml. of methanol–stannous chloride solution in rubber-stoppered test tubes, 6 × 3/4 inch. The blanks were eluted similarly.

The absorbances were then measured in 1-cm. cells in a Beckman Model DU spectrophotometer at the following wave lengths:

Aldopentoses and hexuronic acids	510 mμ
Aldohexoses	400 mμ
6-Deoxyaldohexoses	385 mμ

Absorbance measurements on aldopentoses or hexuronic acids were carried out within a period of 30 minutes after development of the color.

Absorbance values were plotted against the weights of sugars for the standard determinations and the resulting graphs then used to determine the unknowns.

RESULTS AND DISCUSSION

An examination of the absorption spectra of the colored compounds formed by the interaction of sugars with the *p*-anisidine hydrochloride reagent showed that both aldopentoses and hexuronic acids gave compounds which had absorption maxima at 510 mμ. This suggests that the same reaction mechanism occurs with both types of sugar, possibly an initial degradation to furfural followed by a condensation of the furfural with the *p*-anisidine to form a compound with a characteristic red color. Small

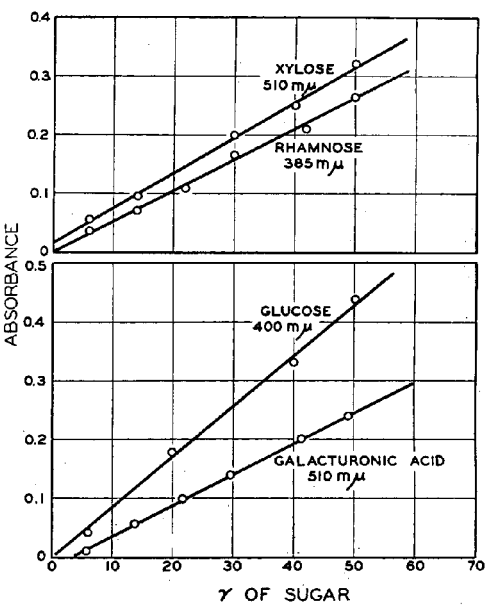

Figure 1. Increase in absorbance with increase in weight of various sugars

[1] Present address, Department of Chemistry, University of Edinburgh, Edinburgh 9, Scotland.

Table I. Quantitative Analysis of Spruce Pulp Hydrolyzed with 72% Sulfuric Acid

Sugar	Volume of Hydrolyzate Applied to Chromatogram, μl.	Determined Weight of Sugar, γ	Calcd. Sugar Concn. in Hydrolyzate, Mg./Ml.
Glucose[a]	5	12.2	24.4
	10	24.9	24.9
Mannose[b]	20	28.3	1.30
	30	38.2	1.40
Xylose[b]	40	39.0	0.97
	60	55.0	0.92

Sum of av. of sugar in hydrolyzate, 27.0 mg./ml.

[a] Hydrolyzate diluted 10 times; calculated sugar values corrected for dilution.
[b] Hydrolyzate undiluted.

variations in the shade of this color for different sugars, however, indicate that the reaction mechanism may be somewhat more complex than this.

The absorption maxima of the brown-colored compounds formed with aldohexoses and 6-deoxyaldohexoses were at 400 mμ and 385 mμ, respectively. The colors obtained with these sugars were relatively stable, but for best results, the absorbance should be measured shortly after color development.

The compound produced by reaction of aldopentoses or hexuronic acids with the *p*-anisidine hydrochloride reagent was rather unstable, but the addition of stannous chloride to the eluting solution enhanced the color stability. Nevertheless, for a pentose determination, it is advisable to measure the absorbance of the solution within a period of 30 minutes after the development of the color on the chromatogram.

The determination of standard sugars together with the unknowns on the same paper chromatogram has alleviated the use of exactly standardized conditions, so that small variations in the procedure given will not affect the final results. Some typical examples of curves obtained with standard sugars are shown in Figure 1. The errors are within ±4%.

Table I shows data obtained for the quantitative analysis of spruce pulp hydrolyzed with 72% sulfuric acid, using the procedure developed by Saeman and coworkers (*3*). In order to determine glucose, which was present in a high concentration in the pulp, the hydrolyzate was diluted 10 times before it was applied to the chromatogram. Mannose and xylose determinations were made using undiluted hydrolyzate.

A determination of the total sugar present in the hydrolyzate was carried out by cautious evaporation of a known volume at 50° C. under reduced pressure to a constant weight sirup. This gave a value of 27.3 mg. per ml. On this basis the figure given for the total sugar concentration in Table I represents a 99% recovery.

ACKNOWLEDGMENT

The author wishes to thank Maija Lakstigala for her interest and criticism.

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Colorimetric Estimation of Dialkyl Phosphites in Presence of Trialkyl Phosphites, Phosphates, and Phosphonates

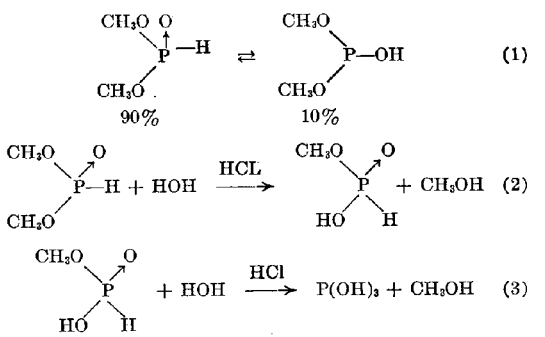
SAMUEL SASS and JAMES CASSIDY

Chemical Research Division, Chemical Warfare Laboratories, Army Chemical Center, Md.

A method for the detection and quantitative estimation of dialkyl hydrogen phosphites in the presence of other phosphatics is based on the reaction of these phosphites with trinitrobenzene to form a red color measurable on a colorimeter or spectrophotometer at 465 mμ. The method is sensitive to 0.2 to 0.5 γ of dialkyl hydrogen phosphite per ml. of solution.

MANY phosphorus compounds used for insecticides and related purposes are made in several synthetic steps which require alkyl phosphites or yield them as intermediates. No micromethod was available for distinguishing between dialkyl hydrogen phosphites and the monoalkyl and trialkyl phosphites, among others. In this particular case a method was required for the estimation of dialkyl hydrogen phosphites in the presence of larger quantities of compounds with varying similarity in chemical properties.

Evidence that the dialkyl hydrogen phosphite exists as an equilibrium between the hydrogen phosphite and phosphonate came from unpublished infrared and nuclear magnetic resonance studies made in these laboratories, and from its hydrolytic characteristics (Reactions 1, 2, 3), studied here and also reported by Fox (*3*), among others.

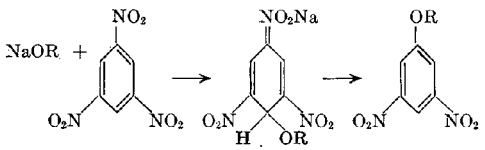


However, its oxidative characteristics in the presence of iodine or bromine show an apparent 100% trivalent phosphorus character or 100% as the apparent hydrogen phosphite form. The tautomeric character of the dialkyl hydrogen phosphite appeared to be reminiscent of the enol keto equilibrium of carbon ketones, thus suggesting the use of aldehyde and ketone techniques.

The use of dinitro- and polynitrobenzenes to form colored compounds with ketones (*1*, *2*, *4*) was of interest in these labora-

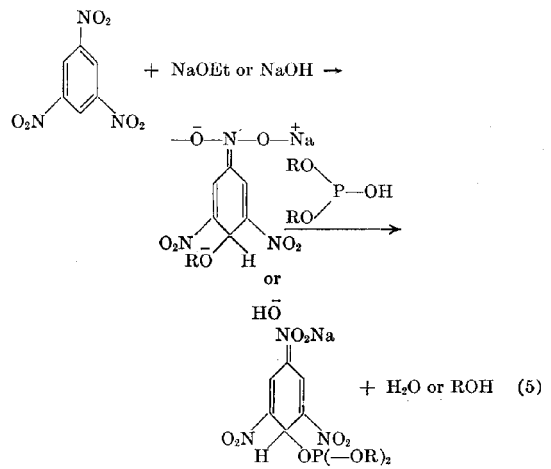
tories because it helped to supply a technique for the determination of small quantities of chloroacetophenone. Bost and Nicholson (*2*) suggested the use of ketones to distinguish between mono- and polynitrobenzenes and toluenes. Baerstein (*1*) used the reaction to determine benzene and toluene in solvent mixtures by introducing a differential oxidation technique, followed by treatment with butanone. The mononitro compounds did not form color. The suggested mechanism (*1*) was a condensation between the enol form of the ketone and the aci form of *m*-dinitrobenzene with the elimination of a molecule of water.

Exploratory and developmental work done in these laboratories had shown that small quantities of ketones, including chloroacetophenone, could be estimated if conditions were modified to maintain a measurable stability of color. When expanded to the dialkyl hydrogen phosphites, it was found that *m*-dinitrobenzene, while forming a color with these compounds, did not allow for a sensitivity in the desired area (at least 1 γ per ml. of solution) with satisfactory accuracy. 2,4,6-Trinitrobenzoic acid, which was available, produced a greater sensitivity. 1,3,5-Trinitrobenzene produced an even greater sensitivity with the dialkyl hydrogen phosphite. Whitmore (*5*) stated that 1,3,5-trinitrobenzene reacts with sodium alcoholates eventually to give replacement of one NO_2 by alkoxyl. "The intermediate product is a highly colored compound probably of quinoid structure" (Reaction 4).



(4)

Trinitrobenzene was made to react with the dialkyl hydrogen phosphites in the presence of alcoholic sodium hydroxide. The postulated mechanism for the formation of colored product, extended from the work of Baerstein (*1*) and Whitmore (*5*) with ketones, is shown in Reaction 5.



(5)

One difference is that the ketone product, while showing up as color in the basic solution, loses the color in the acid. The color formed with the dialkyl hydrogen phosphites remains after acidification. In fact, the proposed method is based on an acidification after previous reaction and color formation when basic. This treatment was required, because the trinitrobenzene itself is strongly colored in basic solution.

REAGENTS, APPARATUS, AND PROCEDURE

Reagents. Absolute ethyl alcohol.

Sodium hydroxide, 0.005*N* in absolute ethyl alcohol.

Glacial acetic acid, 0.05*N* solution in absolute ethyl alcohol.

1,3,5-Trinitrobenzene (TNB), melting point 121–122° C., Eastman Kodak Co., 0.05% solution in absolute ethyl alcohol.

Dialkyl hydrogen phosphite.

Apparatus. Absorbance measurements were made on a Cary recording spectrophotometer. Measurements of concentration *vs.* instrument units (absorbance) were made on a Klett-Summerson colorimeter using Klett filter No. 44 (410 to 480 mμ), and on a Beckman DU spectrophotometer at a wave length of 465 mμ.

Procedure. Prepare a solution of the dialkyl hydrogen phosphite in absolute ethyl alcohol, such that a 5-ml. aliquot will represent from 5 to 50 γ of compound.

Pipet 5 ml. of the specimen solution into a Klett tube, add 1 ml. of trinitrobenzene solution, and mix. Then add 1 ml. of 0.005*N* ethanolic sodium hydroxide, mix, and allow to stand for 1 minute. Add 3 ml. of 0.05*N* ethanolic acetic acid, mix, and allow to stand for 6 minutes. Measure the developed color on a colorimeter using Klett filter No. 44 or on a spectrophotometer at 465 mμ. Run a suitable reagent blank.

For specimens containing materials of relatively high acidity, adjust to pH 10.5 with ethanolic sodium hydroxide after the addition of trinitrobenzene. Proceed with ethanolic acetic acid, etc. The sensitivity by this procedure is approximately 0.5 γ per ml. of solution. The sensitivity can be doubled by restricting the total volume of reagents and specimen to 5 ml.

Preparation of Standards. Prepare standards containing 5, 10, 15, 20, 25, 30, and 40 γ of dialkyl hydrogen phosphite per 5 ml. of alcohol. The curve, which is reproducible, follows Beer's law through 40 γ.

DISCUSSION

Spectral Characteristics. The spectral characteristics of the color produced by the reaction of trinitrobenzene with dialkyl hydrogen phosphite were determined on a Beckman DU spectrophotometer and later on a Cary recording spectrophotometer in the range 300 to 600 mμ. Figure 1 shows the absorption curve when dimethyl hydrogen phosphite is treated under the procedural conditions. Figure 2 shows the calibration curves obtained for a number of different alkyl hydrogen phosphites using the Beckman DU at a wave length of 465 mμ, the sensitivity in micrograms per instrument unit being proportional to the molecular weight of compound.

Effect of Water. The red colored product can be formed in an aqueous medium, but under less stable conditions (approximately one half the stability of the nonaqueous medium).

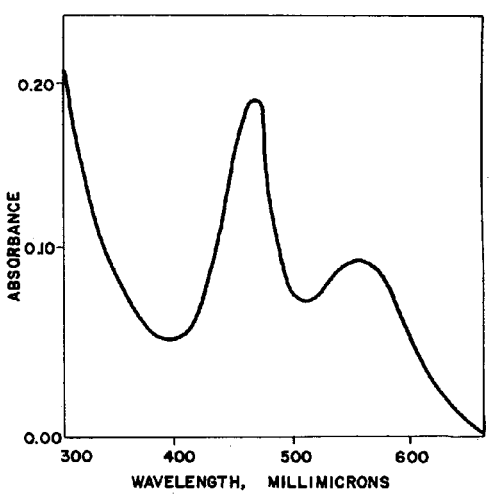


Figure 1. Spectral absorbance curve for 10 γ of dimethyl hydrogen phosphite and trinitrobenzene

Effect of pH, Time, and Temperature. Specimens of dimethyl hydrogen phosphite were dissolved in water, ethyl alcohol, and methyl Cellosolve. Trinitrobenzene, in the proper proportions, was added to each and the resulting mixtures were treated with sodium hydroxide in the range of pH 7 to 12. A color formed rapidly through most of this pH range (pH 8 to 12) at ambient temperature (25° C.), but maximum results were obtained at pH 10.5, if the specimens were kept alkaline for no longer than 1.5 minutes. Good sensitivity resulted, but the reagent trinitrobenzene blank was relatively high. Tests made on the acidification of the colored material between pH 7 and 2 showed maximum stability for the developed color at pH 6.5, with less than 1.5% color decrease after 40 minutes.

Table I. Specificity of Method for Dialkyl Hydrogen Phosphites

Sample	Dimethyl Hydrogen Phosphite, γ Added	Recovered
Trimethyl phosphite (1000 γ)	0	<1
	30	30
Triisopropyl phosphite (1000 γ)	0	1
	150	152
Bis (hydroxymethylphosphonic acid) anhydride (150 γ)	0	0
	167	166
Methylphosphonic acid (120 γ)	0	0
	25	26
Triethyl phosphate (1000 γ)	0	0
	180	182
Dimethyl methylphosphonate (200 γ)	0	0
	30	30
Phosphorous acid (100 γ)	0	1
	90	89
Monomethyl hydrogen phosphonate (1000 γ)	0[a]	0
	200	201

[a] Prepared in aqueous solution by treating dimethyl hydrogen phosphite with hydrochloric acid.

Specificity of Reaction. Specimens of trialkyl phosphite, dialkyl phosphoric acid, trialkyl phosphate, and alkyl phosphonates were treated both separately and as mixtures with dialkyl hydrogen phosphites in ethanolic solution, using the trinitrobenzene procedure. Practically no interference was encountered from the presence of the above compounds. These results are shown in Table I.

Table II. Analytical Recovery of Diethyl Hydrogen Phosphite from Known Mixtures Containing 2 Mg. of Triethyl Phosphite in Absolute Ethyl Alcohol

Added, γ	Present, γ	Found, γ
0	10	10
30	40	40
32	42	42
68	78	79
71	81	81
123	133	132
142	152	150
180	190	189
220	230	230

Reproducibility of Method. Excellent reproducibility is obtained with the trinitrobenzene method when the procedure outlined is followed. Table II shows the reproducibility obtained with different dilutions of diethyl hydrogen phosphite in 2 mg. of triethyl phosphite containing a small quantity of the hydrogen phosphite.

Tables I and II indicate a reliability of the method within 2 γ over a relatively large range of dialkyl hydrogen phosphite concentration.

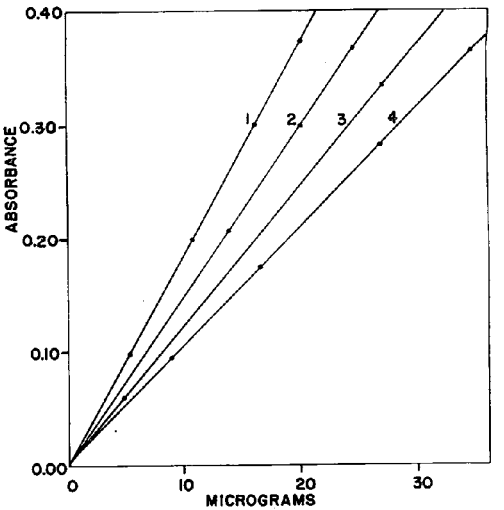


Figure 2. Calibration curves for dialkyl hydrogen phosphites

1. Dimethyl hydrogen phosphite
2. Diethyl hydrogen phosphite
3. Diisopropyl hydrogen phosphite
4. Dibutyl hydrogen phosphite

Comparison of Dialkyl Hydrogen Phosphite and Acetone Using Trinitrobenzene Procedure. Although not a problem during the experimental work for specifically determining dialkyl hydrogen phosphite, a study of the reaction of ketones with trinitrobenzene indicated that acetone in the same concentration as the hydrogen phosphite did not interfere. Although the ketone reaction with trinitrobenzene proceeds in alkaline solution, no color is evident on subsequent acidification.

CONCLUSION

A method used for distinguishing between mono- and polynitrobenzenes using a ketone as a reagent has been modified for the specific estimation of dialkyl hydrogen phosphites. The developed color after acidification shows a maximum absorption at 465 mμ with a lesser absorption at 560 mμ. The method can be made sensitive to 0.2 to 0.5 γ of dialkyl hydrogen phosphite per ml. of solution. No interference is encountered due to the presence of ketones, other phosphites, phosphates, or phosphonates.

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Analysis of Acid Chlorides Containing Free Carboxylic Acid and Hydrogen Chloride

CLARENCE R. STAHL and SIDNEY SIGGIA

Central Research Laboratory, General Aniline & Film Corp., Easton, Pa.

A system of analyses is presented for the determination of acid chlorides and the direct titration of free carboxylic acid and hydrogen chloride in acid chlorides. The acid chloride and free carboxylic acid values are obtained in a single potentiometric titration with sodium hydroxide after reaction with *m*-chloroaniline. Hydrogen chloride is determined on a separate sample by direct titration with *N*-tripropylamine.

IN MOST existing methods for the determination of acid chlorides no attention is given to the determination of the hydrogen chloride and the free carboxylic acid which they contain. In fact, the hydrogen chloride present is often an interference which is determined as acid chloride. Thus, in the sodium acetate titration of Usanovich and Yatsimirshii (*7*), the sodium methylate titration of Fritz (*3*), and the silver nitrate titration of Drahowzal and Klamann (*2*), any hydrogen chloride present titrates, giving high values for acid chloride. Mitchell and Smith (*5*) were able to determine acid chlorides without interference from hydrogen chloride by making the chloride react with pyridine, hydrolyzing with water, and titrating the excess water. Ackley and Tesoro (*1*) determined the free carboxylic acid in acid chloride by making the chloride react with ammonia, neutralizing with hydrochloric acid, and extracting and titrating the carboxylic acid. This method, however, is useful only for chlorides of long-chain fatty acids. Pesez and Willemart (*6*) determined both hydrogen chloride and free carboxylic acid by indirect means. The subtraction of two large figures to obtain the small values for hydrogen chloride and free carboxylic acid in this method makes its use undesirable. Klamann (*4*) determined the hydrogen chloride content of acid chlorides by a direct titration with silver nitrate in acetone; however, the carboxylic acid determination is also indirect.

As the amounts of hydrogen chloride and free carboxylic acid present in acid chlorides are usually small, it is desirable to determine these compounds directly. In the present method this is accomplished by titrating the hydrogen chloride in chlorobenzene-ether with *N*-tripropylamine, and the free carboxylic acid with sodium hydroxide after the acid chloride has reacted with *m*-chloroaniline. In the latter titration, two potential breaks are obtained (Figure 1). One corresponds to the neutralization of the amine hydrochloride formed from the acid chloride and the hydrogen chloride, and the other represents the neutralization of free carboxylic acid. Thus, both hydrogen chloride and free carboxylic acid are determined by direct titration, and the only value obtained by difference is that for acid chloride, which is calculated by subtracting the free hydrogen chloride value from the amine hydrochloride titration. This subtraction introduces no serious error, as a small value is subtracted from a large value.

Although amines have been used in several previous methods—Klamann (*4*), Ackley and Tesoro (*1*), and Pesez and Willemart (*6*)—the amines employed in those methods were too strongly basic to allow differential titration of the amine hydrochloride and free carboxylic acid. *m*-Chloroaniline was selected for use in the present method after several aromatic amines had been tried. The nitroanilines were found to be too weakly basic to prevent loss of hydrogen chloride during the reaction, and *p*-chloroaniline caused poor breaks on titration. The naphthylamines caused poor breaks and also gave trouble by precipitating during the titration. *m*-Chloroaniline was found to be a strong enough base to prevent loss of hydrogen chloride but not too strong to interfere with the titration.

REAGENTS

C.P. acetone, anhydrous diethyl ether, chlorobenzene, standard 0.5*N* and 0.1*N* sodium hydroxide, standard 0.1*N* *N*-tripropyl-

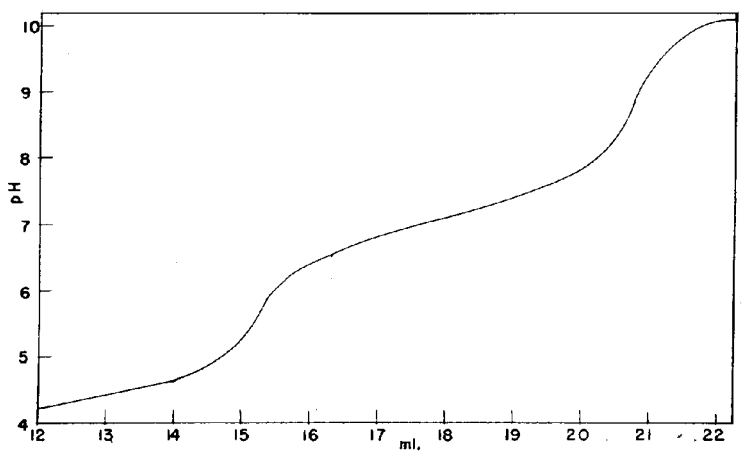

Figure 1. Titration of amine hydrochloride plus carboxylic acid with sodium hydroxide

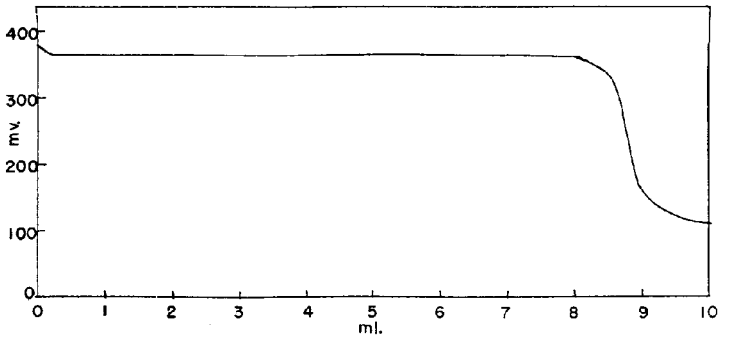

Figure 2. Titration of hydrochloric acid with tripropylamine

amine in chlorobenzene, and freshly distilled *m*-chloroaniline are used.

The tripropylamine may be standardized against maleic acid dissolved in acetone or against a solution of dry hydrogen chloride in ether-chlorobenzene, which has been standardized by dissolving an aliquot in acetone-water and titrating with standard 0.1*N* sodium hydroxide. If the maleic acid standardization is used, it should be remembered that only one carboxy group on the maleic acid can be titrated with tripropylamine.

PROCEDURES

A. An exactly weighed sample of acid chloride containing not more than 0.001 mole of hydrogen chloride is dissolved in a one to one mixture of ether-chlorobenzene and titrated potentiometrically with standard 0.1*N* tripropylamine in chlorobenzene, using a 10-ml. buret. Only the hydrogen chloride titrates and the break occurs between 350 and 150 mv. Per cent hydrogen chloride is calculated using the following equations:

$$\frac{\text{Milliliters} \times N\text{TPA}}{\text{weight of sample} \times 1000} = \text{mole of HCl per gram of sample}$$

$$\text{Mole of HCl per gram of sample} \times 100 \times 36.5 = \%\ \text{HCl}$$

B. A sample containing approximately 0.01 mole of acid chloride plus free carboxylic acid is weighed in a glass-stoppered weighing bottle or in a sealed ampoule. Sealed ampoules should be used for all volatile acid chlorides. The weighed sample is placed in a 250-ml. glass-stoppered flask containing 5 ml. of *m*-chloroaniline and 25 ml. of acetone. If the sample is weighed in a weighing bottle, the stopper should be removed just before the sample is placed in the flask and the weighing bottle slid down the side of the flask, so that the sample and reagent do not mix. The flask is sealed with stopcock grease and is shaken to mix the sample and reagent. The contents of the flask are cooled slightly below room temperature in running tap water or in ice, and the flask is allowed to stand 5 minutes to ensure complete reaction.

After the reaction is complete, the stopper is removed and 5 ml. of distilled water are added. The stopper is replaced and the flask is shaken to dissolve the amine hydrochloride formed in the reaction. Then the contents of the flask are washed into a beaker with acetone. Using a pH meter equipped with a glass-calomel electrode system, standard 0.5*N* sodium hydroxide is added from a buret until the pH of the solution is approximately 4. The volume of 0.5*N* sodium hydroxide is read, then the solution is titrated potentiometrically with standard 0.1*N* sodium hydroxide.

The first break, which occurs between pH 5 and 6, represents the neutralization of the amine hydrochloride formed by the reaction of the *m*-chloroaniline with the acid chloride and free hydrogen chloride. The equivalents of 0.1*N* sodium hydroxide plus the equivalents of 0.5*N* sodium hydroxide added, equal the equivalents of acid chloride plus hydrogen chloride in the sample. The second break occurs between pH 8 and 9.5 and represents the titration of the free carboxylic acid.

Two concentrations of standard sodium hydroxide are used. A rather large sample is required to obtain a sufficiently large titration for the free carboxylic acid, which is usually present in relatively small quantities. The total titration would be large if 0.1*N* hydroxide were used, and the titration for free carboxylic acid would be small if 0.5*N* hydroxide were used in the total titration. In this procedure, the bulk of the acidity is neutralized with 0.5*N* reagent, and the 0.1*N* hydroxide is used to carry the titration through the two neutral points. Per cent acid chloride is calculated as follows:

$$\frac{(\text{Ml. of } 0.5N\ \text{NaOH} \times N) + (\text{ml. of } 0.1N\ \text{NaOH} \times N)}{\text{Weight of sample} \times 1000} = \text{moles of acid chloride + HCl per gram of sample}$$

$$(\text{Mole of acid chloride + HCl per gram}) - (\text{mole HCL per gram} = \text{mole acid chloride per gram}$$

$$\text{Mole of acid chloride per gram} \times 100 \times \text{mol. wt. of acid chloride} = \%\ \text{acid chloride}$$

Per cent free carboxylic acid is calculated using the following equation:

$$\frac{(\text{Ml. to second break} - \text{ml. to first break}) \times N\ \text{of NaOH} \times \text{mol. wt. of acid} \times 100}{\text{Weight of sample} \times 1000} = \%\ \text{free carboxylic acid}$$

Table I. Analysis of Synthetic Mixtures of Acid Chlorides and Carboxylic Acid

Synthetic Mixture	Added, % Acid chloride	Added, % Carboxylic acid	Found, % Acid chloride	Found, % Carboxylic acid
Benzoyl chloride	99.2	0.8	98.6	0.8
Benzoic acid	97.5	2.5	97.5	2.7
	96.6	3.4	96.4	3.5
	96.5	3.5	96.2	3.7
	93.7	6.3	93.3	6.4
	92.5	7.5	92.2	7.5
	92.0	8.0	91.4	7.8
	90.6	9.4	90.6	9.5
Lauroyl chloride	97.3	2.7	97.5	2.6
Lauric acid	94.4	5.6	94.2	5.2
	93.0	7.0	93.0	6.9
	90.1	9.9	90.0	9.7
Acetyl chloride	98.7	1.3	98.3	1.4
Acetic acid	97.0	3.0	96.0	3.2
	95.0	5.0	94.7	5.2
	90.6	9.4	90.5	9.4
Palmitoyl chloride	98.7	1.3	98.1	1.5
Palmitic acid	96.7	3.3	96.7	3.2
	93.5	6.5	93.0	6.8
	91.8	8.2	91.9	8.4
Fatty acid chloride	96.9	3.1	97.0	3.1
(av. mol. wt. = 293.5)	95.1	4.9	95.2	4.7
Stearic acid	92.8	7.2	92.2	6.9
Propionyl chloride	97.1	2.9	97.2	3.2
Propionic acid	95.1	4.9	94.5	5.0
	91.9	8.1	91.8	8.2
Benzoyl bromide	98.1	1.9	98.0	2.0
Benzoic acid	97.0	3.0	96.8	3.2
	94.6	5.4	94.4	5.2
	89.6	10.4	89.3	10.5

Table II. Determination of Hydrogen Chloride in Presence of Acid Chlorides

Acid Chloride	Hydrogen Chloride, % Added	Found
Acetyl chloride	2.02	2.07
	3.85	3.93
	6.14	6.30
	16.50	17.08
Propionyl chloride	1.95	1.94
	3.49	3.65
	6.72	6.19
	14.72	14.47
Lauroyl chloride	0.72	0.70
	1.67	1.65
	3.08	3.24
	4.00	4.21
Palmitoyl chloride	1.24	1.37
	2.35	2.47
	3.45	3.60
	7.88	8.49
Benzoyl chloride	1.42	1.57
	2.64	2.75
	5.10	5.17
	10.53	10.64
Naphthoyl chloride	1.14	1.21
	2.10	2.14
Fatty acid chloride (av. mol. wt. = 293.5)	0.11	0.13
	0.81	0.80
	1.87	1.83

Table III. Analysis of Succinyl and Naphthoyl Chlorides

Acid Chloride	Hydrogen Chloride, %	Acid Chloride, %	Carboxylic Acid, %
Succinyl chloride	0.0	99.4	..
		99.4	..
		99.1	..
		99.1	..
		99.2	..
		99.2	..
		98.9	..
Naphthoyl chloride	0.0	93.6	6.3
		93.7	6.3
		93.6	6.3

DISCUSSION AND RESULTS

All reagents were used as obtained, except the *m*-chloroaniline, which was distilled. After distillation the *m*-chloroaniline can be used for 2 months or more without redistillation. The acetone employed contained about 0.2% water, but the acid chlorides react rapidly enough with the *m*-chloroaniline to prevent any hydrolysis from taking place. Acetone dried over Drierite gave the same results as undried acetone.

Synthetic mixtures of acid chlorides and the corresponding acids were prepared and analyzed by Procedure B (Table *I*) and synthetic mixtures of acid chlorides and hydrogen chloride were analyzed by Procedure A (Table II) to test the method. The acid chlorides used in these mixtures were distilled from the best available samples to obtain acid chlorides free of hydrogen chloride and carboxylic acid. Because of the difficulty of adding known amounts of dry hydrogen chloride directly to acid chlorides to obtain synthetics of known composition, the hydrogen chloride–acid chloride synthetics were prepared by adding aliquots of an ether solution of hydrogen chloride of known composition to weighed samples of acid chlorides.

Results obtained for succinyl chloride and naphthoyl chloride are given in Table III. No synthetic mixtures were prepared for these compounds, because in the case of succinyl chloride the second chloride group reacts incompletely and the free carboxylic acid values obtained cannot be used. The unreacted acid chloride group forms carboxylic acid when water is added, and high results are obtained for free carboxylic acid. In the case of naphthoyl chloride the authors were unable to obtain a pure sample from which to prepare synthetic mixtures.

The analysis of three acid bromide samples was attempted, but good results were obtained only for benzoyl bromide. In the analysis of benzoyl bromide 25 ml. of ether were used in Procedure B instead of 25 ml. of acetone. Low results for acid bromide were obtained when acetone was used. Results obtained for acetyl and valeryl bromides varied greatly.

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Colorimetric Determination of Biphenyl in Biological Materials

ROBERT B. BRUCE and JOHN W. HOWARD
Hazleton Laboratories, Falls Church, Va.

A colorimetric method has been devised for the determination of biphenyl in biological materials. Biphenyl is nitrated in acetic acid, using concentrated nitric acid. The product is shown to be 4-nitrobiphenyl. The nitro derivative is subsequently reduced and the resulting amine coupled with *N*-(1-naphthyl)ethylenediamine to give a purple dye. The absorbance of this solution is proportional to the concentration in the range of 10 to 100 γ. This method has been successfully used in the study of the metabolism of biphenyl.

DURING the investigation of the metabolism of biphenyl it was necessary to have a method suitable for its determination in biological materials. Among the methods available in the literature (*1–4*), that of Dickey and Green (*1*) appeared to offer the best advantages for the determination of biphenyl in biological materials. However, on treating urine by this method extremely high blanks were obtained which could not easily be eliminated. A method which has proved to be satisfactory involves separation of the biphenyl with subsequent nitration to 4-nitrobiphenyl, reduction to the corresponding amine, and colorimetric determination of the amine by diazotization and coupling with *N*-(1-naphthyl)ethylenediamine. This procedure has been used in this laboratory and elsewhere (*5*) for several months with satisfactory results.

ANALYTICAL PROCEDURE

Reagents. Reagent grade chloroform, glacial acetic acid, reagent grade nitric acid, and reagent grade sodium sulfate, conforming to ACS specifications.

Sodium carbonate, 5% (w./v.) in distilled water
Ethyl alcohol, 95%
Sodium hydroxide, 5*N*
Hydrochloric acid, reagent grade
Potassium permanganate, 6% (w./v.) in distilled water
Zinc dust, certified reagent grade
Sodium nitrite, 0.25 gram of reagent grade sodium nitrite in water to make 100 ml. Make up fresh daily.
Ammonium sulfamate, 2.5 grams of technical ammonium sulfamate in water to make 100 ml. Make up fresh weekly.
N-(1-Naphthyl)ethylenediamine dihydrochloride, Eastman Kodak Co., 1 gram in water to make 50 ml. Make up fresh weekly.
Biphenyl. Standard Solution A, 0.1000 gram of biphenyl in chloroform to make 100 ml. 1 ml. = 1000 micrograms of biphenyl.
Standard Solution B, 2 ml. of Standard Solution A diluted to 100 ml. with chloroform. 1 ml. = 20 γ of biphenyl.
Apparatus. A Beckman Model DU spectrophotometer was used with 1.000-cm. cuvettes.
Test tubes, 22 by 200 mm., fitted with bulb condenser
Volumetric flasks, 50-ml. and 100-ml.
Soxhlet apparatus
Centrifuge tubes, 50-ml., fitted with glass stoppers

PREPARATION OF STANDARD CURVE

Aliquots of 0.5, 1.0, 2.0, 3.0, and 4.0 ml. of Standard Solution B are run into 22 × 200 mm. test tubes, 0.5 ml. of glacial acetic acid is added, and the chloroform is evaporated at 50° C. under a gentle stream of air to 1 or 2 ml. or less.

Then 0.5 ml. of concentrated nitric acid is added, the solutions are mixed well, and the tubes are placed in a water bath at 70° C. for 1 hour. The nitration is stopped by addition of 5 ml. of ice water.

Two milliliters of chloroform are added to each tube and the nitro derivative is extracted into the chloroform by shaking the tubes for 2 to 3 minutes. The acid layer is drawn off and discarded.

The tubes are placed in a warm water bath (50° to 60° C.) and the chloroform layer is evaporated under a gentle stream of air. One milliliter of 95% ethyl alcohol and 2 ml. of 5*N* hydrochloric acid are added and the tubes are shaken well to wash down the sides. Then 0.2 gram of zinc dust is added and the tubes are placed in a boiling water bath for 15 minutes. Each tube is fitted with a small bulb condenser.

After reduction, the contents of each tube are filtered through Whatman No. 42 paper into a 50-ml. volumetric flask. The condenser and tube are well rinsed with water and the rinses are added to the flask to make the volume 40 ml.

One milliliter of 0.25% sodium nitrite is added to each flask and the solution is mixed well and allowed to stand 10 minutes. One milliliter of 2.5% ammonium sulfamate is added to each solution, which is again mixed well and allowed to stand 10 minutes more. Finally, 2.0 ml. of 1% *N*-(1-naphthyl)ethylenediamine dihydrochloride are added to each solution and the solutions are made to 50 ml., mixed, and allowed to stand 1 hour for full development of the purple color. The absorbance is read at 570 mμ, using a blank solution prepared by carrying 2.0 ml. of chloroform through the entire procedure.

DETERMINATION OF BIPHENYL IN BIOLOGICAL MATERIAL

Blood. Five milliliters of blood (oxalated) are pipetted into a 22 × 200 mm. test tube, shaken for 2 to 3 minutes with 10 ml. of chloroform, and then filtered through glass wool (wetted with chloroform) into a 50-ml. glass-stoppered centrifuge tube. The test tube and precipitate are washed well with additional small aliquots of chloroform.

The chloroform layer is washed with 10 ml. of 5*N* sodium hydroxide by shaking for 2 to 3 minutes. The water layer is drawn off and the chloroform layer is washed twice more with a 10-ml. portion of water. The chloroform layer is then washed with 10 ml. of 6% potassium permanganate plus 5 ml. of glacial acetic acid. For this wash the tubes are mechanically shaken for 1 hour. After this the permanganate layer is drawn off and the chloroform layer is shaken with 20 ml. of 5% sodium carbonate for 2 minutes. The carbonate layer is removed and the chloroform layer is washed twice again with 20 ml. of water.

After removal of the water layer, the chloroform layer is filtered through glass wool (wetted with chloroform) into a 22 × 220 mm. test tube with adequate rinsing; 0.5 ml. of glacial acetic acid is added, and the chloroform is evaporated to 1 or 2 ml. in a water bath at 50° to 55° C. under a stream of air. The remainder of the procedure is the same as for preparation of the standard curve.

Urine. Five milliliters of urine are pipetted into a glass-stoppered 50-ml. centrifuge tube and shaken for 2 to 3 minutes with 10 ml. of chloroform. After removal of the urine layer, the chloroform layer is washed with water, followed by a wash with 10 ml. of 5*N* sodium hydroxide. The remainder of the procedure is the same as for the blood analysis. Centrifugation may be necessary in many of these steps, for adequate separation of layers.

Feces. Five grams of a well-mixed sample of feces are placed in a mortar, followed by a portion of anhydrous sodium sulfate; the feces and sodium sulfate are adequately mixed until the fecal sample is in a dry state. The sample is then quantitatively transferred to a Soxhlet cup and extracted with chloroform for 3 hours. The extract is transferred to a 100-ml. volumetric flask and adjusted to volume with chloroform.

A suitable aliquot for analysis is pipetted into a glass-stoppered centrifuge tube. The aliquot is shaken with 5*N* sodium hydroxide for 2 to 3 minutes and the procedure as described for the blood and urine is continued.

DISCUSSION

The absorbance curve of the colored compound formed by carrying 69 γ of biphenyl through the procedure is presented in Figure 1. Maximum absorption lies at 570 mμ. An absorbance-concentration curve determined for 10 to 100 γ of biphenyl showed that the Beer-Lambert relationship is followed over this range.

Recoveries of known amounts of biphenyl added to samples of blood, urine, and feces (Table I) appear to be satisfactory.

The method described is empirical in nature and each step should be followed exactly as given. However, some investigation was made of the reactions that occur during the nitration and subsequent reduction of the biphenyl.

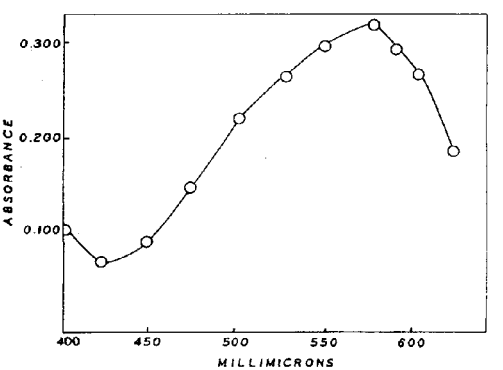

Figure 1. Absorption curve

One gram of biphenyl was dissolved in 5 ml. of chloroform, and 5 ml. each of glacial acetic and nitric acids were added. The procedures described above were followed with proportionate increases in the amounts of reagents. After extraction of the nitro derivative into chloroform and washing, the chloroform extract was evaporated to dryness and the residue recrystallized from alcohol. The melting point of this compound was 113° C., corresponding to that of 4-nitrobiphenyl. The yield was well above 90% based on this derivative. Reduction of this nitro derivative by the methods described in the procedure for analysis and subsequent acylation with acetic anhydride gave a product with a melting point of 171° C., corresponding to that of *N*-acetylbiphenylamine. This evidence indicates that the primary product of nitration under the conditions of the analytical procedure is the mononitro derivative.

Samples containing known amounts of 4-nitrobiphenyl- and 4-biphenylamine were carried through the analytical procedure,

Table I. Recoveries of Biphenyl Added to Blood, Urine, and Feces

(5.0 ml. of blood and urine, and 5 grams of feces)

Biphenyl, γ		
Added	Recovered	% recovery
	In Blood	
10	9.2	92
20	18.5	93
25	22.7	91
40	40.5	101
	Av.	94
	In Urine	
20	17.2	86
25	30.4	121
40	41.4	103
40	40.3	101
50	44.0	88
75	77.4	103
	Av.	100

Biphenyl, Mg.		
Added	Recovered	% recovery
2.50	2.30	90
4.00	3.96	99
5.00	4.73	95
7.50	6.07	80
8.00	7.55	94
10.0	8.70	87
	Av.	91

beginning at the appropriate steps. The absorbances per micromole were 0.875 for the nitro derivative and 0.872 for the amino derivative. The corresponding absorbance found when biphenyl was carried through the procedure was 0.705. These results indicate that approximately 20% is lost either during or before nitration.

In preliminary work it was found that during the evaporation of chloroform solutions of biphenyl considerable and variable amounts of biphenyl were lost. The addition of acetic acid prior to evaporation prevented this loss. To solutions containing 5 and 10 γ of biphenyl in 10 ml. of chloroform, 0.50 ml. of acetic acid was added. The solutions were evaporated under gentle air streams again until no odor of chloroform remained. The resulting acetic acid solutions were diluted to 10.0 ml. with iso-octane and their absorbances compared at 248 mμ with that of pure biphenyl in iso-octane containing the same concentrations of acetic acid. The absorbances indicated that no biphenyl had been lost in the evaporation steps despite the marked volatility of biphenyl.

The procedure used for purification of extracts of biological tissues is similar to that described by Dickey and Green (*1*).

The preliminary wash with sodium hydroxide is intended to remove phenols that may have formed from metabolism of biphenyl. In order to determine the efficiency of this wash, solutions containing 1 mg. each of *o*- and *p*-phenylphenol and 4,4′-dihydroxybiphenyl were carried through the procedure. No color was formed with any of these phenols. Control samples of blood, urine, and feces carried through the procedure gave only small blank readings. Although these were negligible, corrections were made.

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Use of 2,4-Dinitrophenylhydrazones of *p*-Phenylphenacyl Esters as Second Derivatives in Identification of Organic Acids

HAWKINS NG, A. DINSMOOR WEBB, and RICHARD E. KEPNER

Departments of Chemistry and of Viticulture and Enology, University of California, Davis, Calif.

The 2,4-dinitrophenylhydrazones of the *p*-phenylphenacyl esters of 18 fatty acids were prepared. In several cases a greater difference was observed between the melting points of the hydrazones than between the melting points of the corresponding esters. The double derivatives of the straight-chain saturated acids from acetic through octadecanoic were found separable on silicic acid–nitromethane chromatographic columns. The relative rates of travel with respect to that of the hexanoate derivative were determined and should be of assistance in the identification of small amounts of unknown organic acids.

THE identification of small amounts of organic acids present in the volatile aroma materials from grapes and wines has been of interest in this laboratory for some time. The *p*-phenylphenacyl derivatives have proved valuable for this purpose when only a single acid or a mixture of acids of low molecular weight was present in a fraction. The chromatographic method for separation of mixtures of *p*-phenylphenacyl esters on silicic acid columns described by Kirchner, Prater, and Haagen-Smit (*3*) has permitted the separation and identification of these esters when there is a considerable difference in molecular weight of the acid portion of the esters. Column chromatographic separations of *p*-phenylazophenacyl esters, as developed in this laboratory (*2*), have provided slightly better separations of the higher molecular weight acid derivatives. When only milligram quantities of *p*-phenylphenacyl ester are available, purification by either recrystallization or by chromatography is sometimes not effective enough to permit positive identification. The value of being able to prepare a second derivative from the small amount of *p*-phenylphenacyl ester available in such cases is obvious. This paper reports the melting points and the chromatographic behavior of a number of the 2,4-dinitrophenylhydrazones of the *p*-phenylphenacyl esters of the saturated fatty acids from acetic through stearic acids.

MATERIALS

2,4-Dinitrophenylhydrazine Reagent. The reagent solution for preparation of the 2,4-dinitrophenylhydrazones of the *p*-phenylphenacyl esters was made by dissolving 5.9 grams of 2,4-dinitrophenylhydrazine in 130 ml. of reagent grade concentrated hydrochloric acid solution and then diluting it with 870 ml. of 95% ethyl alcohol. Aliquots of this stock solution were filtered shortly before use.

***p*-Phenylphenacyl Esters.** Esters were prepared from known

acids by the method of Shriner and Fuson (*5*) and were purified by the chromatographic method of Kirchner, Prater, and Haagen-Smit (*3*).

Chromatographic Adsorbent. The chromatographic columns were packed with an adsorbent prepared from analytical reagent grade silicic acid (Mallinckrodt No. 2847) activated by drying for 3 days at 105° C. and then thoroughly mixed with nitromethane (Eastman No. 189). Eight milliliters of nitromethane were mixed with 10 grams of the dried silicic acid. This is essentially the adsorbent developed by Kramer and van Duin (*4*).

Developing Solvent. The developing solvent for the chromatographic separation of the derivatives was prepared by saturating redistilled Skellysolve B (boiling range 60° to 70° C.) with nitromethane. The Skellysolve B was shaken in a separatory funnel with 0.01 its volume of nitromethane for 5 minutes. After separation, the lower nitromethane layer was discarded.

APPARATUS

Chromatographic Columns. The chromatographic columns used were the same as those described by Ikeda, Webb, and Kepner (*2*).

PROCEDURE

Preparation of *p*-Phenylphenacyl-2,4-dinitrophenylhydrazones of Acids. The double derivatives of the acids were prepared by adding slowly twice the theoretical amount of the filtered 2,4-dinitrophenylhydrazine solution to a warm solution of the *p*-phenylphenacyl ester in 95% ethyl alcohol with stirring. After standing several hours at room temperature, the crystalline derivative was filtered from the solution, washed with small quantities of water, and dried in air. Mixtures of varying proportions of ethyl alcohol, ethyl acetate, and water were used for recrystallization.

Chromatography of *p*-Phenylphenacyl-2,4-dinitrophenylhydrazones of Acids. The chromatographic columns were packed by transferring a slurry prepared from approximately 15 grams of the adsorbent and 30 ml. of the development solvent into the tubes through a funnel. The adsorbent was compacted in the column by applying a pressure of 10 pounds per square inch of nitrogen at the top of the column. The pressure was released when there was about 1 cm. of solvent left above the adsorbent in the column. From approximately 10 γ to 2.5 mg. of the double derivative or mixture of the double derivatives dissolved in the minimum amount of the developing solvent was carefully pipetted into the top of the column. The solution of derivatives was then forced into the adsorbent layer by the application of pressure from a cylinder of nitrogen at the top of the column. One or more small washings of the flask and pipet with the developing solvent were transferred into the column by the above sequence of operations, after which the reservoir of developing solvent was attached at the top and the column development was started. It was found important always to maintain a layer of solvent above the adsorbent in the column.

Measurement of *R* Values. The facts that the chromatographic columns are packed with adsorbent in the form of a slurry and that the derivatives move very slowly with respect to the solvent front prohibit the determination of R_f values as such. The relative rates of travel of the various derivatives investigated in this work were measured with respect to the rate of travel of *p*-phenylphenacylhexanoate-2,4-dinitrophenylhydrazone on the chromatographic column. Three sets of measurements were usually taken; in each case the distance from the top of the adsorbent layer to the point of greatest color density in each of the derivative zones on the column was measured. The average of the ratios of distance moved by a second derivative divided by distance moved by the hexanoate derivative was recorded as the *R* value for the particular compound.

RESULTS AND DISCUSSION

The 2,4-dinitrophenylhydrazones of 18 different saturated fatty acid *p*-phenylphenacyl esters were prepared by the procedure outlined above, with yields of from 93 to 100%. Repeated crystallizations from ethyl alcohol or mixtures of ethyl alcohol and ethyl acetate were usually required to secure material of constant melting point. The melting points of the *p*-phenylphenacyl esters and their 2,4-dinitrophenylhydrazones and the results of combustion analyses for the double derivatives prepared are listed in Table I.

Table I. Melting Points and Combustion Analyses of Acid Derivatives

Acid	Melting Point[a], °C. *p*-Phenylphenacyl ester	Melting Point[a], °C. 2,4-DNH[b] of *p*-phenylphenacyl ester	Combustion Analysis of 2,4-DNH of *p*-Phenylphenacyl Esters % C Calcd.	% C Found	% H Calcd.	% H Found
Acetic	110.5–110.8	183.5–184.0	60.82	60.94	4.18	4.06
Propionic	103.5–104.0	139.0	61.60	61.82	4.50	4.64
Butyric	82.0–82.2	142.5–143.5	62.33	62.52	4.80	4.72
Isobutyric	89.2–90.0	155.4–156.4	62.33	62.10	4.80	4.94
Valeric	68.2–69.0	149.5–150.0	63.01	63.01	5.08	5.34
Isovaleric	79.0–79.5	149.0–150.0	63.01	62.92	5.08	4.99
Hexanoic	70.2–71.0	136.2–137.2	63.66	63.77	5.34	5.37
Isohexanoic	70.9–71.9	145.0–146.0	63.66	63.70	5.34	5.12
Heptanoic	64.5–65.0	121.0–122.0	64.27	64.02	5.59	5.80
Octanoic	68.2–69.3	113.3–114.0	64.85	64.93	5.83	5.91
Nonanoic	70.5–71.5	104.0–105.0	65.40	65.64	6.06	6.04
Decanoic	76.0–76.5	99.2–100.0	65.92	66.11	6.27	6.27
Undecanoic	80.0–80.7	101.0–102.0	66.41	66.65	6.47	6.61
Dodecanoic	84.4–84.8	103.0–103.7	66.88	67.06	6.67	6.52
Tridecanoic	87.0–87.5	101.0–102.0	67.33	67.38	6.85	7.05
Tetradecanoic	90.3–91.0	101.0–101.6	67.75	67.65	7.02	7.25
Hexadecanoic	93.0–94.0	101.0–102.0	68.55	68.78	7.35	7.23
Octadecanoic	96.3–97.0	101.5–102.2	69.27	69.42	7.65	7.57

[a] All melting points corrected.
[b] 2,4-Dinitrophenylhydrazone.

Examination of the melting points listed in Table I shows that in several cases where the *p*-phenylphenacyl esters of acids have similar melting points, the 2,4-dinitrophenylhydrazones prepared from them show considerable differences in melting point. The C_6, iso-C_6, C_8, and C_9 esters have an inclusive melting range of 4° C., for instance, while the corresponding double derivatives are distributed over a range of 42° C. with the closest interval being equal to 8° C. Examination of Table I also shows, however, that for the double derivatives of the acids of molecular weight greater than that of undecanoic acid which were investigated, the melting points were remarkably constant at 101° to 102° C. Measurement of the melting points of both the *p*-phenylphenacyl derivative and the *p*-phenylphenacyl-2,4-dinitrophenylhydrazone derivative of the acids, therefore, will be of great assistance in establishing the identity of an unknown acid in some cases, but of only limited assistance in others.

The value of the melting points of the 2,4-dinitrophenylhydrazones of the *p*-phenylphenacyl esters as a means of identifying unknown acids is somewhat lessened because of difficulty in attaining a constant melting point by recrystallization of these derivatives. This difficulty is, however, probably not due to the possible presence of geometrical isomers, since only one zone is obtained on chromatographing each of these derivatives under conditions which have been shown to separate the syn and anti forms of certain other 2,4-dinitrophenylhydrazones (*1*). It is thought more likely that in this case the difficulty in securing constant melting points is due to polymorphism in these derivatives. This hypothesis is supported by the fact that differently

Table II. Relative Rate of Travel of *p*-Phenylphenacyl-2,4-Dinitrophenylhydrazones with Respect to Hexanoate Derivative

Acid	*R* Value	Acid	*R* Value
Acetic	0.23	Octanoic	1.8
Propionic	0.38	Nonanoic	2.4
Butyric	0.53	Decanoic	3.3
Isobutyric	0.56	Undecanoic	4.0
Valeric	0.74	Dodecanoic	5.3
Isovaleric	0.75	Tridecanoic	6.5
Hexanoic	1.000	Tetradecanoic	8.8
Isohexanoic	1.0	Hexadecanoic	12
Heptanoic	1.4	Octadecanoic	15

Table III. Chromatographic Separations of *p*-Phenylphenacyl Ester–2,4-Dinitrophenylhydrazones

(S = separated, O = not separated)

	Propionic	Butyric	Isobutyric	Valeric	Isovaleric	Hexanoic	Isohexanoic	Heptanoic	Octanoic	Nonanoic	Decanoic	Undecanoic	Dodecanoic	Tridecanoic	Tetradecanoic	Hexadecanoic	Octadecanoic
Acetic	S	S	S	S	S	S	S	S	S	S	S	S	S	S	S	S	S
Propionic	..	S	S	S	S	S	S	S	S	S	S	S	S	S	S	S	S
Butyric		..	O	S	S	S	S	S	S	S	S	S	S	S	S	S	S
Isobutyric			..	S	S	S	S	S	S	S	S	S	S	S	S	S	S
Valeric				..	O	S	S	S	S	S	S	S	S	S	S	S	S
Isovaleric					..	S	S	S	S	S	S	S	S	S	S	S	S
Hexanoic						..	O	S	S	S	S	S	S	S	S	S	S
Isohexanoic							..	S	S	S	S	S	S	S	S	S	S
Heptanoic								..	S	S	S	S	S	S	S	S	S
Octanoic									..	S	S	S	S	S	S	S	S
Nonanoic										..	S	S	S	S	S	S	S
Decanoic											..	S	S	S	S	S	S
Undecanoic												..	S	S	S	S	S
Dodecanoic													..	S	S	S	S
Tridecanoic														..	S	S	S
Tetradecanoic															..	S	S
Hexadecanoic																..	S
Octadecanoic																	..

colored and differently formed crystals may be obtained from the same preparation of a derivative simply by changing the solvent used for crystallization. In general, no depression of melting point was observed with a mixture of the two crystalline forms of a derivative of a single acid—that is, the melting range was the same as that observed when the lower melting form was melted by itself. The melting-points listed in Table I are those of the higher melting, more stable crystal modifications.

The greatest value of the 2,4-dinitrophenylhydrazones of the *p*-phenylphenacyl esters lies in the fact that extremely small amounts of the orange colored derivatives may be chromatographed to give measurable R values which may be helpful in the identification of a particular compound. Table II lists the R values for the 18 derivatives investigated. All the derivatives chromatographed have significantly different R values, with the exception of the three cases of the normal and iso acid derivatives of the same molecular weight. It is possible that with a column of greater length the isobutyrate derivative could be separated from the normal butyrate derivative, but the two hexanoate derivatives moved with identical speeds, as nearly as could be determined. The values recorded for relative travel rates are reproducible when the chromatographic columns are carefully prepared. It was found that a column could be used repeatedly for separations but that variations in the R values occurred as the column aged. Therefore, when a R value was desired to assist in the identification of an unknown acid, a freshly prepared chromatographic column was always used.

In Table III are recorded the results of experimental chromatographic separations of various combinations of the double derivatives. In every chromatogram three different derivatives were run at the same time, one of which was always the hexanoate or reference derivative. Examination of Table III shows that with the exception of the normal and iso acid derivatives of the same molecular weight, the separations on the chromatographic column were excellent. In the case of the structural isomers no separation was evident.

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Determination of Primary Aliphatic Amines by an Acidimetric Salicylaldehyde Reaction

JAMES B. JOHNSON and GREGORY L. FUNK

Development Department, Carbide and Carbon Chemicals Co., Division of Union Carbide and Carbon Corp., South Charleston, W. Va.

An acidimetric method for the determination of primary amines uses an indicator end point. A measured excess of salicylaldehyde reacts with a primary amine and the excess reagent is titrated as an acid with sodium methylate in a pyridine medium. Aliphatic secondary and tertiary amines do not interfere. The interference of ammonia, alcoholamines, aniline, heterocyclic amines, and the ethyleneamines is discussed. Data are presented for the determination of 12 primary aliphatic amines. The method is rapid, easy to perform, and applicable over a wide range of concentrations.

THE methods available for the determination of primary amines have been reviewed by Critchfield and Johnson (*2*). The reaction of salicylaldehyde with primary amines to form the corresponding imines was used by Wagner, Brown, and Peters (*6*) as a basis of a method for the analysis of amine mixtures. In their procedure the unreacted secondary and tertiary amines are titrated in a nonaqueous medium. Primary amine content may be calculated as the difference between a total base and secondary plus tertiary amine determination. As this method does not employ an indicator end point, it is necessary to determine the entire potentiometric titration curve for each titration.

This paper is a presentation of an unpublished method originally cited by Hillenbrand (*5*) and more recently by Critchfield and Johnson (*2*) for the direct determination of primary amines by the salicylaldehyde reaction employing an indicator end point. Moss, Elliott, and Hall (*4*), Fritz and Keen (*3*), and others have shown that many phenols may be quantitatively titrated as acids in basic solvents. The method described herein is based upon the fact that in pyridine medium, salicylaldehyde is acidic and can be titrated with sodium methylate. The reaction products of a primary aliphatic amine and salicylaldehyde are imine and water, which are neutral in pyridine medium. The amount of salicylaldehyde consumed, determined by titrating the excess reagent with sodium methylate, is a measure of the primary amine.

REAGENTS

Methanol, anhydrous, Carbide and Carbon Chemicals Co.
Pyridine, redistilled.

Salicylaldehyde, approximately 0.5*N*. Dilute 5 ml. of reagent grade salicylaldehyde to 100 ml. with redistilled pyridine.

Sodium methylate, 0.1*N* solution in pyridine. Prepare 4*N* sodium methylate by dissolving 217 grams of dry sodium methylate in sufficient methanol to make 1 liter of solution. Transfer 25 ml. of the 4*N* sodium methylate to a 1-liter reagent bottle containing 75 ml. of methanol and dilute to 1 liter with redistilled pyridine. Standardize this solution against Bureau of Standards benzoic acid, using pyridine as solvent and thymolphthalein indicator. For the change in normality with temperature use ΔN per ° C. = −0.0001. The reagent readily absorbs carbon dioxide from the air and is best preserved in a bottle equipped with a 50-ml. automatic buret. All vents open to the air must have protective Ascarite tubes.

Phenolphthalein indicator, 1.0% solution in pyridine.

Thymolphthalein indicator, 1.0% solution in pyridine.

PROCEDURE

Pipet exactly 10 ml. of the 0.5*N* salicylaldehyde into each of two 250-ml. glass-stoppered flasks. If the sample is an aliquot portion of a dilution, add an equivalent volume of the diluent to one of the flasks, stopper, and reserve as a blank. In the other flask place an amount of sample containing not more than 3 meq. of primary amine. For volatile amines, use a sealed-glass ampoule and add several pieces of 8-mm. glass rod to a pressure bottle. Alternatively an aliquot from a pyridine dilution may be used for volatile amine samples. Cap the bottle and shake to break the ampoule or swirl the flasks to effect adequate mixing of reagent and sample. Allow the sample and blank to stand for 15 minutes at room temperature. Carefully remove the stopper or cap and wash any adhering liquid into the vessel with a few milliliters of redistilled pyridine. To each vessel add 1 ml. of the preferred indicator (phenolphthalein or thymolphthalein; see discussion) and titrate with standard 0.1*N* sodium methylate in pyridine to the end point. The difference between a blank and sample titration is a measure of primary amine.

DISCUSSION

Reaction Rate. The reaction of primary aliphatic amines with salicylaldehyde goes rapidly to completion at room temperature. Table I illustrates the rate of reaction of isopropylamine and butylamine with the reagent. In the determination of all the amines shown in Table II, the reaction was complete in 15 minutes. The difference between the per cent primary amine obtained by this method and by total base titration is undoubtedly due to the presence of small percentages of the corresponding secondary and tertiary amines in the commercial samples.

Ammonia Interference. Primary amines cannot be determined in the presence of ammonia by this method. Ammonia reacts with salicylaldehyde to give an apparent primary amine value. However, the reaction is not stoichiometric under these conditions. All attempts either to obtain a quantitative reaction of salicylaldehyde with ammonia or to prevent reaction have been unsuccessful.

Effect of Alcoholamines. Ethanolamine does not react quantitatively under the conditions employed and, as in the case of ammonia, the reaction could not be forced to completion. Furthermore, diethanolamine also reacts with salicylaldehyde. For example, a sample of refined diethanolamine (total base as diethanolamine 99.9%) reacted to the extent of 67% in 15 minutes at room temperature. A sample of ethanolamine (total base as ethanolamine 99.3%) analyzed 86% in the same time. The explanation of the phenomenon has been adequately discussed by Wagner, Brown, and Peters (*6*).

Effect of Aromatic Amines. Attempts to obtain quantitative results with aniline also were unsuccessful. A highly refined sample gave a reaction of 70% in 1 hour. Presumably other aromatic amines also fail to react completely under the specified conditions.

Other Interferences. Amine salts interfere quantitatively and a correction must be applied if they are present. Inasmuch as some amine carbonates form readily, care must be exercised to prevent atmospheric contamination of the samples. Heterocyclic secondary amines such as piperidine, piperazine, and morpholine react partially under the specified reaction conditions and therefore must be absent from the sample.

Alcohols and water do not interfere and have been used in certain cases to prepare dilutions of amines for analysis.

Indicators. In most cases phenolphthalein and thymolphthalein indicators may be used interchangeably. The proper selection of indicator seems to be a matter of individual preference. In some cases the color of reaction products may dictate the ultimate choice.

Accuracy. An indication of the accuracy of the method is given by the analysis of a synthetic sample of the following composition: ethylamine, 2.4%; diethylamine, 22.6%; triethylamine, 2.3%; ethyl alcohol, 0.9%; and water, 71.8%. The procedure described herein gave duplicate results of 2.3% for ethylamine.

Table I. Reaction Rate of Primary Amines with Salicylaldehyde

Amine[a]	Time, Minutes 1	5	15	30	45	120
Isopropylamine	95.6	97.7	98.2	98.2	98.2	...
Butylamine	...	...	97.2	97.3	...	97.3

[a] All values are per cent by weight.

Table II. Determination of Primary Amines by Acidimetric Salicylaldehyde Reaction

Amine[a]	This Method[b]	Total Base[c]	Prim. plus Sec. Amine[d]
n-Butyl	97.3 ± 0.2	99.2	99.2
Isopropyl	98.6 ± 0.2	99.2	...
tert-Butyl	96.8 ± 0.0	97.6	...
Isoamyl	91.0 ± 0.4	92.4	...
n-Amyl	84.6	85.8	...
n-Hexyl	97.6 ± 0.2	99.1	98.9
Isobutyl	97.2 ± 0.3	98.8	99.3
Propyl, aqueous	44.7 ± 0.2	45.4	...
2-Ethylhexyl	96.4 ± 0.2	99.5	100.1
Diethylaminoethyl	96.2 ± 0.3	...	...
Ethyl	98.3 ± 0.1	101.9	...
Methyl, aqueous	28.8 ± 0.0	29.7	...

[a] Commercial grade materials containing small percentages of corresponding secondary amines.

[b] Average of at least 2 determinations; all values are per cent by weight.

[c] By titration in water with 0.5*N* hydrochloric acid using bromocresol green–methyl red indicator.

[d] By carbon disulfide procedure of Critchfield and Johnson (*1*). Calculated as primary amine.

Table III. Determination of Ethylamine in Refined Diethylamine

	Ethylamine, Wt. % Present	Found: Salicylaldehyde reaction	Found: Van Slyke method[a]
Sample 1		0.033 0.027 0.014 0.027 Av. 0.025	0.017
Sample 1 plus 0.274%	0.299	0.287 0.294 0.287 Av. 0.289	0.330
Sample 1 plus 0.599%	0.624	0.596 0.609 0.623 Av. 0.609	0.594
Sample 2		0.268 0.285 0.288 0.301 Av. 0.286	0.273

[a] Modified Van Slyke nitrogen-evolution method (*7*).

Low Concentrations. The salicylaldehyde procedure has been slightly modified for the determination of low concentrations of ethylamine in diethylamine and presumably is adaptable to other amine combinations.

For this determination pipet 25 ml. of 0.1*N* salicylaldehyde in pyridine into a suitable glass-stoppered flask. Add 75 ml. of pyridine and introduce a 10-ml. sample of known specific gravity. Allow to react 15 minutes at room temperature and titrate with standard 0.1*N* sodium methylate reagent to a phenolphthalein end point which should last 15 seconds. The use of a blanket of nitrogen above the liquid helps to prevent fading of the end point thereby increasing the precision. Diethylamine and salicylaldehyde produce an orange color in this determination, which obscures the thymolphthalein end point.

A sample of refined diethylamine was carefully fractionated, and samples of known ethylamine content were prepared and analyzed. Table III shows the results obtained.

ACKNOWLEDGMENT

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Detection of Surface-Active Alkylaryl Sulfonates by Alkaline Fusion and Formation of an Azo Dye

MILTON J. ROSEN and GERALD C. GOLDFINGER

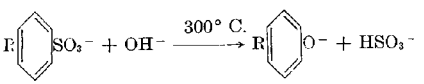
Department of Chemistry, Brooklyn College, Brooklyn, N. Y.

Surface-active agents containing the alkylaryl sulfonate group may be detected by the purple, red, or orange color produced when the phenol obtained from their fusion with potassium hydroxide reacts with diazotized dianisidine. Compounds containing nitro or halo substituents on the benzene ring give false negatives.

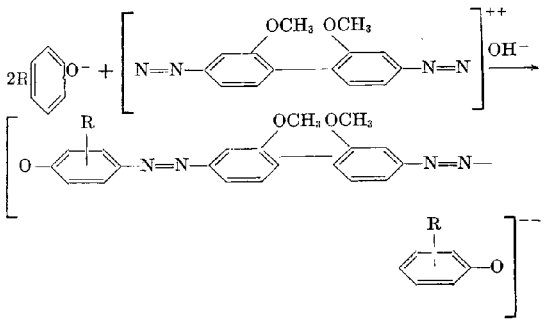
ALTHOUGH the alkylaryl sulfonate group is the functional group most commonly found in surface-active agents (*1*), the literature contains no simple, convenient, and definitive test for the qualitative detection of this grouping. Published tests for this group are based on formation of a precipitate with 10% cupric sulfate solution (*5*); nitration of the aromatic nucleus, reduction of the product, and detection of the resulting aromatic amine (*4*); or alkaline fusion of the aromatic sulfonate and detection of the resulting phenol (*6*, *7*).

The first type of test (cupric sulfate precipitation) is unsatisfactory, as a number of types of surfactants which do not contain this functional group are also precipitated by cupric sulfate (*3*), while certain alkylaryl sulfonates are unaffected by the reagent. The second type also suffers from lack of specificity, because it is given by all aromatic nuclei, sulfonated or unsulfonated. For example, it gives positive results with all alkylphenol–ethylene oxide condensates. The third test seems to have the greatest potential specificity; the fact that it is given by all phenols, sulfonated or not, is not considered a serious disadvantage, as unsulfonated phenols are not ordinarily used as surface-active agents and phenol–ethylene oxide condensates would give negative results. However, the published procedures (*6*, *7*) for performing the alkaline fusion type of test are inconvenient, require a good deal of experience, or are not specific to aryl sulfonates. The test as outlined by Müller (*6*) suffers from a lack of specificity, as it gives false positive results with many easily oxidized compounds, while the fusion devised by Wurzschmitt (*7*) must be done under carefully controlled conditions and, according to the author, needs experience to be performed correctly. The procedure outlined below has been devised to remedy these deficiencies.

The aryl sulfonate first reacts with molten potassium hydroxide in the usual fashion to give a phenol, according to the equation



The phenol produced is then detected by reaction with diazotized dianisidine to form an azo dye.



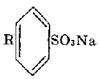
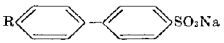
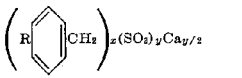
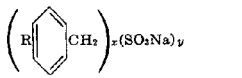
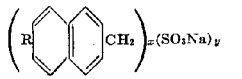
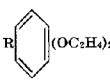
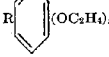
Diazotized dianisidine was chosen for this purpose because, under the conditions of the test, it forms azo dyes that are more intensely colored than those of any other amine tested.

Because diazotized amines produce colors not only with the phenols produced by the fusion with molten alkali, but also with the by-products formed during the fusion, it was necessary to remove these by-products by solvent extraction before the coupling reaction. For this purpose, the reaction mixture was first extracted with benzene, while still alkaline, to remove benzene-soluble by-products and unreacted sulfonate and then, after acidification, extracted with petroleum ether to remove the phenol from the remaining by-products. Ethyl ether, which is used to extract the phenol in other tests of a similar nature (*6*), was found to dissolve by-products of the fusion reaction as well as the phenol and thereby give false positive results in a number of cases.

PROCEDURE

Preparation of Diazonium Salt Solution. Dissolve 20 mg. of dianisidine in 10 ml. of 1 to 4 (by volume) hydrochloric acid.

Table I. Reactions of Commercial Surfactants to Alkaline Fusion and Coupling with Diazotized Dianisidine

Product	Source	Structure[a]	Color Produced	Result
Alkanol B	Du Pont		Purple	+
Aerosol OS	Am. Cyanamid		Purple	+
Nacconol NR	Natl. Aniline		Red	+
Ultrawet K	Atlantic Refg.		Red	+
Santomerse No. 1	Monsanto		Red	+
Detergent D-40[b,c]	Oronite		Red	+
Wetting Agent S[d]	Oronite		Orange, then red	+
Ultrawet 30[d]	Atlantic Refg.		Orange	+
Aresket 300	Monsanto		Red	+
Daxad 21	Dewey & Almy		Amber	–
Daxad 23	Dewey & Almy		Red	+
Daxad 11	Dewey & Almy		Purple	+
Duponol LS[b]	Du Pont	$C_{18}H_{38}OSO_3Na$	Amber	–
Orvus WA[b]	Procter & Gamble	$C_{12}H_{25}OSO_3Na$	Yellow-amber	–
Tergitol 7[d]	Carbide & Carbon	$C_{17}H_{35}OSO_3Na$	Yellow	–
Stepanol M-1[d]	Stepan	$ROSO_3Na$	Yellow-amber	–
Aerosol 18[d]	Am. Cyanamid	CH_2COONa $\vert$ $CH(SO_3Na)CONHC_{18}H_{37}$	Amber	–
Tergitol EH	Carbide & Carbon	$C_4H_9CH{=}C(C_2H_5)CH_2SO_3Na$	Amber	–
Aerosol OT	Am. Cyanamid	$ROOCCH_2CH(SO_3Na)COOR$	Amber	–
Monopole oil 48[b]	Antara	Sulfated castor oil	Amber	–
Igepon T	Antara	$RC(=O)N(CH_3)CH_2CH_2SO_3Na$	Yellow-amber	–
Sulfonate OA5[d]	Tenn. Corp.	$RCH(CH_2)_nCOOH$ $\vert$ SO_3Na	Amber	–
Lathanol LAL	Natl. Aniline	$C_{12}H_{25}OOCCH_2SO_3Na$	Colorless	–
Igepon AC-78	Antara	$RCOOCH_2CH_2SO_3Na$ (coconut f.a. deriv.)	Yellow	–
Igepon AP-78	Antara	$RCOOCH_2CH_2SO_3Na$ (oleic acid deriv.)	Amber	–
Phi-o-Sol WA[b]	Onyx	$RCH(OSO_3Na)(CH_2)_nCOOR$	Light tan	–
Alrosene 31	Geigy	$RC(=O)N(H)(CH_2)_nOSO_3Na$	Colorless	–
Triton X-200[b]	Rohm & Haas		Amber	–
Triton 770[b]	Rohm & Haas		Red[e]	+
Alipal CO-436[b]	Antara		Amber	–
Petronate H	Sonneborn	Petroleum sulfonate	Amber	–
Hyponate L50[b]	Sonneborn	Petroleum sulfonate (oil-free)	Yellow-amber	–
Albatex PO	Ciba		Amber	–
Nekal NS[b]	Antara	$ROOCCH_2$ $\vert$ $ROOCCHSO_3Na$ $\vert$ $ROOCCH_2$	Amber	–

[a] R = alkyl or alkenyl group.
[b] Dried and suspended in methanol.
[c] Made into paste with water and sodium sulfate, dried, and crushed.
[d] Dried and crushed with sodium sulfate.
[e] Product gives same color with diazotized anisidine before fusion.

Cool to 0° to 5° C. in an ice bath, add 100 mg. of sodium nitrite, and agitate well. The red color that forms at first turns yellow after 5 to 10 minutes. About 10 minutes after the yellow color appears, add about 0.1 gram of urea to the test tube to remove excess nitrous acid.

Fusion Reaction. Fuse 2 to 2.5 grams of potassium hydroxide in a nickel crucible. Add 200 mg. of finely divided, anhydrous surfactant (obtained by solvent extraction or other suitable procedure from a surfactant-containing composition) to the melt. (Compounds that are not in the form of a finely divided powder are made into a paste with water and an equal weight of sodium sulfate, dried, and ground. Compounds that form pastes upon drying are dissolved or suspended in methanol and added to the crucible by means of a long medicine dropper.) Stir the molten mixture well for 3 to 4 minutes while heating with a flame that barely touches the bottom of the crucible. Cool, add 5 ml. of water, stir well to dissolve all water-soluble material, and centrifuge (or filter) the suspension.

Extract the clear centrifugate (or filtrate) once with an equal volume of benzene, acidify the extracted aqueous layer to Congo red paper with concentrated hydrochloric acid, cool, and extract the phenol twice with 5-ml. portions of petroleum ether. (It may be necessary to centrifuge in order to break any emulsions that form.) Evaporate the petroleum ether extracts to dryness, add 3 ml. of 10% sodium hydroxide to the residue, and stir well to dissolve all alkali-soluble material. Test the mixture with litmus paper, and add more 10% sodium hydroxide solution if it is not strongly alkaline. Transfer the alkaline solution to a test tube and add about 1 ml. of the diazonium salt solution. Note the color.

DISCUSSION OF RESULTS

Table I describes the results obtained with various types of surface-active agents. All of the alkylaryl sulfonates tested, with the one exception noted below (Daxad 21), gave colors ranging from orange or red to purple. Naphthalene derivatives gave purple colors, while benzene derivatives gave red dyes. These are considered positive results. Yellow or amber colors are considered negative. A sulfonated benzimidazole (Albatex PO), gave negative results.

It has been reported that the alkaline fusion of alkylaryl sulfonates containing nitro or halo substituents in the aromatic nucleus will not produce a phenol (*2*). Although no surface-active agents with this type of grouping could be obtained, the test was tried on sodium *p*-chlorobenzene sulfonate and *m*-nitrobenzenesulfonic acid. Negative results were obtained with both compounds.

Daxad 21, a calcium salt of a sulfonated alkylphenylmethylene polymer, was the only alkylaryl sulfonate tested which gave a negative result. This was probably due to the insolubility of the calcium salt in the molten alkali, as both Daxad 23, a sodium salt of similar structure, and Daxad 11, a sodium salt of an alkylnaphthalene homolog of similar structure, gave positive results.

The only compound that gave a false positive was Triton 770, a sodium alkylphenyl polyoxyethylene sulfate. However, when this compound was tested with diazotized dianisidine before the fusion reaction, it gave the same red color, indicating that the original compound contained some free phenol. An ammonium salt of similar structure from a different source gave the expected negative result. All other alcohol sulfates gave negative results, as did many types of alkyl sulfonates, sulfated oils, and petroleum sulfonates.

Compounds containing double bonds, which are subject to oxidation during the fusion reaction, gave positive results when the by-products formed in the fusion reaction were not removed by extraction, and gave amber colors after these extractions.

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Determination of Specific Surface Area of Colloidal Silica by Titration with Sodium Hydroxide

GEORGE W. SEARS, Jr.

Grasselli Chemicals Department, Experimental Station, E. I. du Pont de Nemours & Co., Inc., Wilmington, Del.

A rapid method determining the specific surface area of silica particles of colloidal size involves a titration of the silica surface with sodium hydroxide, in a medium of 20% aqueous sodium chloride between pH 4 and 9. At pH 9, 1.26 hydroxyl ions are adsorbed per square millimicron of surface. The titer, therefore, is a measure of the total surface present and can be related by an empirical equation to the specific surface area of the colloidal particles as determined by nitrogen adsorption. Advantages of the method are rapidity, accuracy for particles of very high specific surface area, and applicability to particles in colloidal solution as well as to powders.

THE specific surface area of amorphous silica has been commonly determined either by calculation from particle size observed in electron micrographs, or by adsorption techniques involving nitrogen (*5*, *8*) or methyl red (*2*, *15*). Methods for determining the size and shape of particles of colloidal silica and the relation between particle diameter and specific surface area have been reviewed by Iler (*9*).

In the study of polymerization and depolymerization of colloidal silica, a simple, rapid method for determining the specific surface area of silica in the form of a colloidal solution, especially in the range of extremely small particles (below 10 mμ in diameter) has been needed. Although particle size in this range can be measured with the aid of the electron microscope, the process is slow, and equipment is often unavailable. Specific surface areas cannot be measured by conventional adsorption methods without first drying the silica requiring special techniques to avoid coalescence of particles and reduction of surface area (*1*, *14*).

The ion exchange capacity of silica and silicate minerals has been the subject of frequent investigation (*7*, *13*). Bryant (*6*) has shown that for a given SiO_2:Na_2O ratio, the pH of a silica sol increases with increasing particle size and decreases with increasing electrolyte concentration of the medium. These studies indicate the possibility of developing a quantitative method of determining the specific surface area of colloidal silica or silica powders by titration with a base.

EXPERIMENTAL

In the work reported here, the amounts of alkali reacting under closely controlled conditions with various samples of

colloidal silica were measured, and were then related empirically to the actual specific surface areas of the samples as determined by nitrogen adsorption. The relationship holds not only for particles in colloidal solution, but also for gels and even silica powders ignited to temperatures as high as 450° C.

Preparation of Samples. The colloidal or high-surface silicas used in this study included various aqueous silica sols, and gels both aqueous and dried. Sols of smallest particle size were prepared by deionization of dilute sodium silicate as described by Bird (*4*), followed by stabilization with sodium hydroxide (ca. 1% based on the silica). Sols of larger particles—e.g., 10 to 100 mμ—were prepared by the technique of Bechtold and Snyder (*3*). Gels were prepared from colloidal solutions by heating after deionization to pH 5 to 6.

For all except the largest particles (dried directly from deionized solution), dry powders were prepared by the following procedure. The sol, deionized to pH 3 to 4, or gel prepared as described above, was dehydrated by azeotropic distillation with 1-propanol, after which the silica was dried by evaporation of the propanol. In this way, interparticle fusion or coalescence, or structure collapse in the case of gels, was minimized (*10*). In order to remove propoxy groups which remain to some extent on the silica surface under these conditions (*12*), the dry samples were ignited in air at 350° to 450° C., until the silica, which initially turned dark, again became white.

Determination of Specific Surface Area by Nitrogen Adsorption. All samples were converted to dry powders by the techniques described above, and their specific surface areas were measured by the low-temperature nitrogen adsorption technique (*5*).

Reaction of Silica Surface with Alkali. Initial studies of the reaction of hydroxyl ions with colloidal silica particles were carried out on a sol containing particles having a specific surface of 210 sq. meters per gram. The pH titrations of this sol (deionized to remove the free alkali used for sol stabilization) with 0.10*N* sodium hydroxide in several media are shown in Figure 1. Each titration involved 1.50 grams of silica in 150 ml. of solution. As was shown by Bryant (*6*), the charge on the silica surface at a given pH, due either to the reaction of surface

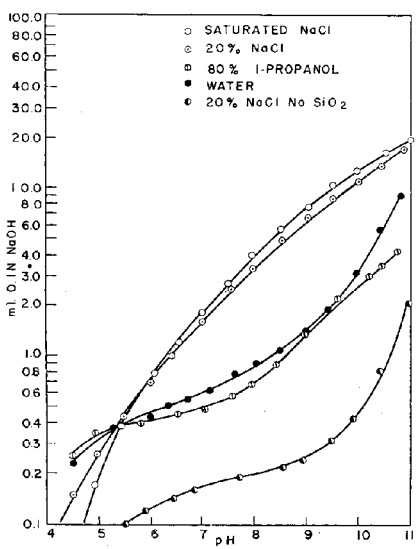

Figure 1. Alkali titration of silica sols in various media

Titration at 25°C. of 1.50 grams of silica in 150 ml. of solution, except where noted

Table I. Charge on Silica Surface as Function of pH

(During titration of a solution of *1.5 grams of silica* and 30 grams of sodium chloride per 150 ml. at 25° C. with 0.10*N* sodium hydroxide)

pH of Medium	Charge, or No. of ;SiO⁻ Ions Formed per Sq. mμ of Surface
9.0	1.26
10.0	2.2
11.0	3.3
11.5	3.7

silanol groups with hydroxyl ions,

$$;SiOH + OH^- \rightarrow ;SiO^- + H_2O$$

or to an adsorption of hydroxyl ions by the silanol surface, increases markedly with increasing electrolyte concentration. It is influenced to only a slight extent by the presence of organic media such as 1-propanol.

In order to measure the reaction of hydroxyl ions with the colloidal particles in a medium containing approximately 20% sodium chloride, alkali added to a similar medium containing no silica was subtracted from that added to the sodium chloride–sol mixture for each pH value. The number of ;SiO⁻ ions formed per square millimicron of silica surface was calculated by dividing the total number of ions formed by the total area of surface exposed. This number of ions or charge per square millimicron of silica surface was found to be independent of the specific surface area of the particles. Variation in charge with pH as determined for a series of sols of varying specific surface (200 to 400 sq. meters per gram) is shown in Table I.

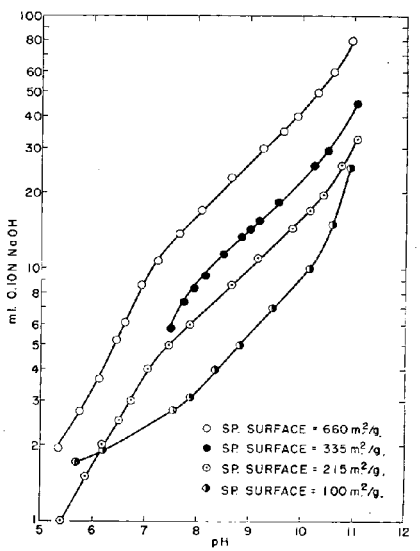

Figure 2. Alkali titration of silica sols in a concentrated solution of sodium chloride

Titration at 25°C. of 1.50 grams of silica in 150 ml. of 20% sodium chloride

In highly alkaline medium (ca. pH 12 and higher), the colloidal silica is unstable and slowly depolymerizes to form monomeric sodium silicate.

It has been calculated (*11*) that there are about eight surface silanol groups per square millimicron of silica surface and that, at maximum charge, about four of these groups are ionized.

The above data are consistent with these calculations, and indicate further that no distinct end point in the relation between pH and charge exists.

Figure 2 shows a series of titrations for sols of differing specific surface. These sols were deionized to pH 3.5 to 4 to remove the free alkali used for stabilization. A significant feature of these titrations is the fact that from about pH 8 to 10, all the curves are essentially parallel and linear. Because the linear relation between log of volume and pH permits more accurate estimation of volume for a given pH, the approximate mid-point of this straight line—pH 9.00—was chosen for the end point of the titration.

A comparison of sols initially deionized to pH 3.5 to 4 with similar sols merely acidified with dilute hydrochloric acid to pH 4.0 showed essentially no difference in the subsequent titration. The latter method, both simpler and quicker and giving a constant starting pH, was adopted.

Titration of suspensions of dried silica powders was also investigated. It was found that alkali consumption is the same for a surface which has been dried as for the same surface before drying.

Titration Procedure. Based principally on the above observations, the technique adopted for the determination of specific surface of colloidal silica particles by alkali titration is as follows:

A sample containing 1.50 grams of silica is acidified with dilute hydrochloric acid to a pH of 3 to 3.5. To this sol is added 30 grams of C.P. sodium chloride and the volume is made up to 150 ml. with distilled water. The temperature is adjusted to 25° ± 0.5° C. and the titration is carried out with standard 0.10*N* sodium hydroxide. The pH is measured with a high pH (Beckman Type E) glass electrode and calomel reference electrode, the electrodes being checked against a pH 10 buffer solution. Base is added to give pH 4.0, and added further until the pH rises to a steady value of 9.00. The titer is that volume required to raise the pH from 4.0 to 9.00.

Relationship of Added Alkali to Specific Surface Area. Figure 3 shows a plot of volume of base added against specific surface by nitrogen adsorption. A straight line is obtained, the equation for which is

$$S = 32\,V\text{-}25$$

where S is specific surface in square meters per gram and V is volume in milliliters of 0.100*N* sodium hydroxide required for a 1.50-gram sample of silica.

Thus, by a simple titration, usually requiring not more than 10 to 15 minutes, the specific surface and, from this, the average particle diameter of a silica sol of known concentration can be determined. The technique works equally well on large and small particles, and because drying of the sample is unnecessary, gives more accurate results than the nitrogen adsorption method for particles less than 4 to 5 mμ in diameter.

DISCUSSION

This is an empirical method. A reproducibility to within 2 to 5% can readily be achieved, but only by very accurate measure of pH. Thus, a 0.01-unit error in the measurement of the final pH results in an error of 0.5 to 1.0%, which increases within this range with decreasing specific surface.

Reaction of hydroxyl ions with a silica surface has been shown to be independent of the state of the surface, to the extent that silica gels and dry silica powders ignited to as high a temperature as 450° C. can be titrated in the same manner as colloidal solutions. Titrations of solid ignited samples are shown in Figure 3 as solid circles. Before such silica samples were added to the sodium chloride solution, each sample was ground to pass a 100-mesh screen to reduce the time required to reach equilibrium (usually not longer than 5 to 10 minutes).

Although the silica samples used in the development of this technique were all prepared by deionization of sodium silicate solutions, the method was also tested on silicas of other origin to determine the range of applicability of the method. Included in these samples were silica prepared by burning ethyl orthosilicate in air, silica produced as an aerogel from alcoholic suspension of silicic acid, and silica obtained by neutralization of sodium silicate with sulfuric acid. In all cases, the titration method checked well with the low temperature nitrogen-adsorption method.

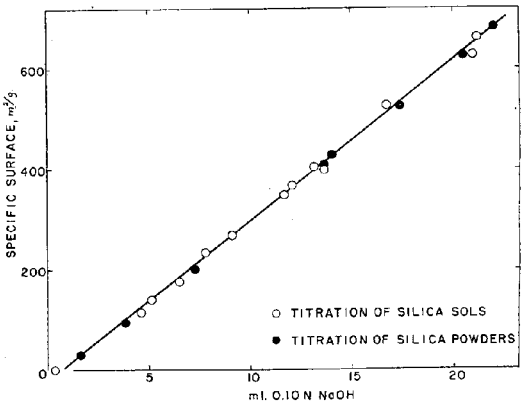

Figure 3. Titer as a function of specific surface area

Specific surface area determined by nitrogen adsorption. Titration at 25°C. of 1.50 grams of silica in 150 ml. of 20% sodium chloride

The titration of a silica surface requires the absence of all weak electrolytes such as the ammonium ion, and metal ions forming insoluble hydroxides such as iron and aluminum, unless their concentrations are accurately known and their effect is calculated. Such ions can easily be removed by deionization. Aluminum as the aluminate ion must first be converted to the hexa-coordinate form by acidification to pH 1 to 2, in which form it can then be effectively removed along with excess acid with mixed cation and anion exchange resin.

ACKNOWLEDGMENT

The author is indebted to E. B. Sledz for the many measurements of specific surface area by low temperature nitrogen adsorption.

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Determination of Urea-Formaldehyde Resins in Coatings via Urea Analysis

M. H. SWANN and G. G. ESPOSITO

Coating and Chemical Laboratory, Aberdeen Proving Ground, Md.

The release of ammonia from urea-formaldehyde coating resins on treatment with alkali is characteristic. It provides a rapid quantitative means of analyzing coatings for urea resin modification, or of determining urea in urea-formaldehyde resins.

ALKYD resins used for baking finishes are frequently modified with 10 to 20% of a nitrogen resin such as urea- or melamine-formaldehyde. Class B enamels of Federal Specifications TT-E-489b and TT-E-529 are of this type. For some time, the extent of this modification has been measured by determining total nitrogen, using the well-known Kjeldahl method. With resinous products the Kjeldahl method is time-consuming but highly accurate.

Recently, an infrared spectrophotometric method was developed (*1*) for determining relative amounts of urea- and melamine-formaldehyde resins in alkyd blends. The method is rapid and applicable to mixtures of these nitrogen resins, but is not so accurate as the chemical method described here. It is also subject to interference from other resins.

Table I. Determination of Total Nitrogen in Urea-Formaldehyde Resins

(Solution basis)

Sample	Nitrogen Found, %	
	Kjeldahl	Alkali digestion
Uformite F-233	10.7	10.7
Uformite F-210	10.8	10.7
Uformite F-240	11.8	10.7
Beckamine 2530	10.9	10.4
Syn-U-Tex 400	10.7	10.4

The urea resins appear to be unique among resins in their reaction with alkali under high-temperature saponification conditions. They release ammonia, which can be collected and measured in standard acid, giving results in good agreement with the nitrogen content of the resin as determined by the Kjeldahl method. Melamine-formaldehyde, polyamide, and butadiene-acrylonitrile copolymer resins do not interfere; isocyanate and polyacrylamide resins have not been tested. In principle, the urea-formaldehyde resin is dissolved in ethylene glycol containing potassium hydroxide. Dry air is drawn through this reaction flask, then through standard sulfuric acid. The reaction medium is gradually heated to boiling and after 1 hour the ammonia absorbed by the acid is determined by titration with alkali.

If the coating contains mixed urea- and melamine-formaldehyde resins, the latter can be measured by determining the difference in the total nitrogen and urea nitrogen content. The factor of 6.58, used to calculate the urea resin, is based on the average nitrogen content of a variety of resins analyzed by the Kjeldahl method. Some analytical results obtained by both methods are shown in Tables I and II.

PROCEDURE

A 250-ml. Erlenmeyer flask with 24/40 ground joint is arranged on an electric heater having a variable transformer heat control. Two adapters with 24/40 joints (Ace Glass, Inc., Nos. 5190 and 5235) are attached to the flask and connected to two gas-washing bottles so that air drawn through the apparatus bubbles first through concentrated sulfuric acid, then over the sample, and finally through another washing bottle. The latter contains 100 ml. of standard 0.1*N* sulfuric acid and is provided with a fritted glass disk of medium porosity to subdivide the air into fine bubbles. A vacuum source is used to draw the air slowly through the apparatus.

Table II. Determination of Urea-Formaldehyde Resin in Alkyd Blends

(Nonvolatile basis)

Alkyd Resin	Nitrogen Resins Present, %		Urea-Formaldehyde Found, %
	Melamine	Urea	
Soybean oil, high phthalic	0.0	19.7	19.8
	13.1	10.6	10.8
Coconut oil, high phthalic	0.0	31.5	31.0
	10.6	11.1	11.3
	0.0	19.1	18.6
	9.8	10.8	10.7
None	50.0	50.0	49.4
	50.0	50.0	48.3

A sample of resin solution containing 0.2 to 0.4 gram (nonvolatile basis) of urea-formaldehyde resin is weighed into the flask, and 25 ml. of 14% potassium hydroxide in ethylene glycol is added. The addition of a Berl saddle is recommended. The flow of air is started and the heat applied gradually so that gentle boiling is reached in not less than 30 minutes. Boiling is continued for 1 hour. A small Bunsen burner flame is played over the outer walls of the vertical adapter for approximately 1 minute. The upper joint is disconnected and washed with water on the inside in such a manner that the wash water flows into the washing bottle of standard acid. The acid is then titrated with 0.1*N* sodium hydroxide to the methyl purple end point. A blank titration on 100 ml. of the acid is also made.

$$\% \text{ urea-formaldehyde resin} = \frac{(V_1 - V_2) \times \text{normality of alkali} \times 6.58}{\text{sample weight}}$$

or

$$\% \text{ nitrogen} = \frac{(V_1 - V_2) \times \text{normality of alkali} \times 1.401}{\text{sample weight}}$$

where V_1 = ml. NaOH for blank.
V_2 = ml. NaOH for sample.

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Quantitative Microdetermination of Gaseous Ammonia by Its Absorption at 204.3 Mμ

F. A. GUNTHER, J. H. BARKLEY, M. J. KOLBEZEN, R. C. BLINN, and E. A. STAGGS

Citrus Experiment Station, University of California, Riverside, Calif.

A direct spectrophotometric method for the quantitative determination of ammonia gas at atmospheric pressure utilizes the absorption maximum of ammonia at 204.3 mμ (ε, 3127) which allows determinations from 7 p.p.m. (5 γ per liter) to 1000 p.p.m. of ammonia in air. Data are presented to indicate sensitivities achievable at 10 other absorption maxima of ammonia within the region from 190.3 to 224.4 mμ. Comparisons of fused silica and crystal quartz spectrophotometers in this application are reported in detail.

AMONG the many recorded micromethods for the determination of gaseous ammonia, some require collection of the ammonia in a scrubbing solution followed by colorimetric assay (*4*, *5*, *7*), while others are capable of more direct determination, as by the ordinary thermal diffusion process (*1*, *8*, *11*) and by changes in electrical resistance of very hot (1200° to 1300° C.) platinum wires immersed in the gas mixture (*3*). Quantitative utilizations of the striking and ideally suited absorption maxima of ammonia in the ultraviolet region from 226 mμ to about 190 mμ have not appeared in the literature. The present report is concerned with the analytical exploitation of the electronic absorption of the ammonia molecule; details of the utilization of this method with automatic recording in evaluating sorption of ammonia by citrus fruits and by fiberboard will be reported elsewhere.

In 1935, Mulliken (*6*) proposed electron configurations for some of the possible transition assignments of one of the electrons of the absorbing electron pair in ammonia, and in 1946 Thompson and Duncan (*10*) reported oscillator strengths and positions of bands for the ultraviolet spectrum of ammonia in the range from 45,000 cm.$^{-1}$ (222 mμ) to 120,000 cm.$^{-1}$ (83 mμ). Recently, Tannenbaum and coworkers (*9*) published their detailed ammonia spectrum from 45,000 cm.$^{-1}$ (222 mμ) to 60,000 cm.$^{-1}$ (167 mμ) as obtained with a vacuum spectrograph and the flowing vapor technique. Their spectrum exhibited doublets at about 217 mμ, 213 mμ, and 209 mμ, as estimated from their spectral plot.

In the present study ammonia was determined in an especially rebuilt Beckman Model DU spectrophotometer.

EXPERIMENTAL

Instrument. A Beckman Model DU spectrophotometer was modified by the manufacturer by replacing the 30° crystal quartz prism by a 33° fused silica prism. This instrument is now available as a Beckman Model DUS spectrophotometer. To gain detection sensitivity and to improve resolution in the region of interest, the instrument was equipped with the standard Beckman photomultiplier attachment.

Because of possible interferences in the low ultraviolet region from chemicals in the laboratory atmosphere, the following changes were made by this laboratory. The instrument was drilled and tapped, and 1/8-inch tubing fittings were inserted for continuously purging the resistor box (back side), the lamp house (bottom; the lamp house cover was replaced with a gasketed solid plate), and the cast monochromator housing (1 inch away from the prism baffle plate) with the quantities of dry nitrogen shown in Table I. Also, the standard DU four-turn wave length paper scale was replaced with the lower wave length portion of the six-turn paper scale from a Beckman DK-2 spectrophotometer. Because both scales and the DU scroll were made for crystal quartz instruments, the wave length scale had to be recalibrated for the present purpose. The new scale was positioned and calibrated in the usual manner by maximum instrument response to the emission spectrum of mercury vapor from 185 mμ to 302 mμ and to minimum instrument response to the six strong oxygen absorption bands between 184 mμ and 195 mμ (Table II). From these calibration data a smoothed correction curve of apparent *vs.* actual readings was prepared. In all subsequent discussions reported, wave length values are the corrected ones unless otherwise indicated.

Table I. Rates of Introduction of Dry Nitrogen[a] into Spectrophotometer

Position	Approximate Flow Rate, Liter/Minute	
	Initial[b]	Stabilized
Resistor box	0.30	0.10
Lamp house	0.15	0.05
Monochromator	1.20	0.40

[a] Water-pumped nitrogen passed over calcium chloride and Ascarite.

[b] For approximately 15 minutes, or until instrument readings stabilized.

Table II. Calibration in Millimicrons of Wave Length Scale Using Mercury Emission Lines and Atmospheric Oxygen Absorption Bands

Hg or O_2 Line	Scale Reading	Hg or O_2 Line	Scale Reading
184.6 (O_2)	Off-scale	225.3	225.0
184.9	185.0	226.0	225.5
186.3 (O_2)	186.3	239.9	238.3
188.2 (O_2)	188.2	248.3	246.3
190.2 (O_2)	190.3	253.7	251.3
192.35 (O_2)	192.3	265.2	262.1
194.2	194.2	275.3	271.3
194.7 (O_2)	194.6	289.4	284.2
202.7	202.5	296.7	290.8
205.3	204.9	302.2	295.7
222.5	221.6		

Subsequently, a Beckman DK-2 spectrophotometer was utilized for some of the routine analytical work with gaseous ammonia. This spectrophotometer was equipped with the standard Beckman dry nitrogen purge kit for this model instrument. Calibration of the DK-2 against the modified manual DU through the range of interest (202 mμ to 206 mμ) indicated scale agreement within ±0.2 mμ.

For quantitative applications both instruments were carefully preset to fixed wave length via optimum instrument response corresponding to the absorption maximum of ammonia at 204.3 mμ. This broad intense band was chosen to have minimum effect when slit width was changed, as well as to avoid interference from absorption by water vapor.

Cells. Both 1-cm. and 10-cm. sealed silica cells were used, with a high-vacuum, silicone-type lubricant as sealant. All cells were cross calibrated with dry air. In all subsequent discussions the corrected cell values are used.

Calibration with Ammonia. Initial semiquantitative measurements to ascertain the expected sensitivity and precision of the analytical method at different absorption maxima were made by mixing known volumes of anhydrous ammonia gas and dry nitrogen in a calibrated 100-cc. syringe. For example, ammonia gas in a continuous, rapid stream was introduced at the bottom of a 1-liter beaker until the beaker was overflowing, then 10 cc. was drawn into the syringe from near the bottom of the beaker; similarly, dry nitrogen was then drawn into the syringe to make 100 cc. total volume. This mixture was allowed to stand briefly, then was flushed through the cells through a hypodermic needle.

More precise establishment of the sensitivity and precision of this method for ammonia was accomplished with the aid of the apparatus shown schematically in Figure 1. All pertinent glassware was immersed in a water bath held at 26.0° ± 0.2° C. All-glass connections were used, with the only nonglass portions of the system occurring within the pulsing diaphragm Dynapump. The 10-cm. cell arrangement, adopted from a previous use (*2*), is shown in Figure 2. This device permits shifting either the reference cell or the sample cell into the energy beam without interrupting gas flow through the sample cell. All spherical and standard taper connections were generously lubricated with a high-vacuum, silicone-type lubricant. The system was maintained at atmospheric pressure.

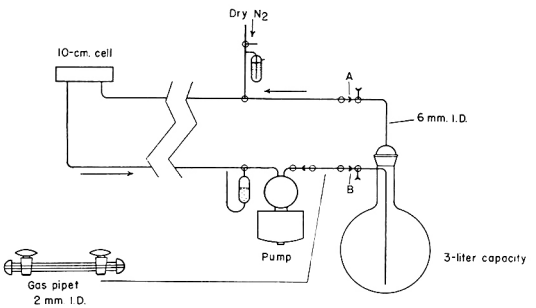

Figure 1. Schematic drawing of apparatus used in preparing standard curves

The gas introduction pipet (shown in detail in Figure 1) when calibrated with mercury in the usual manner was found to have a reproducible volume of 1.544 ± 0.003 cc. at 26.0° C., including the bores of both stopcocks. The pipet was connected to a cylinder of ammonia gas by a lubricated spherical joint, and the gas was passed through it at 2 pounds pressure for 30 seconds. The stopcock remote from the cylinder was closed first, then the other stopcock was closed, and the pipet was disconnected from the spherical joint. Both stopcocks were quickly rotated twice through 360° to equalize pressure to atmospheric both within the body of the pipet and within the bores of the stopcocks, after equilibration to 26° C. Then the cavities between the stopcocks and the terminal spherical joints were swept with dry air through fine capillary tubing pushed into them. The pipet was introduced into the assembly shown in Figure 3 at the 18/5 semiball joint and acid-washed air passed over activated charcoal was drawn through the system at the rate of 4 liters per minute for 10 minutes. The scrubber contained 25.0 to 100.0 ml. of 0.00302*N* sulfuric acid solution made with distilled water which had been previously deionized and boiled. Back titrations of the scrubbing solutions (back washed into the 250-ml. flask) with 0.00331*N* sodium hydroxide solution gave the ammonia capacity of the pipet as 1.06 ± 0.01 mg. of ammonia at 734 mm. and 26.0° C.; the calculated value was 1.053 mg. Normality of the acid above was established by the micro-Kjeldahl procedure, using ammonium sulfate recrystallized three times from freshly distilled water. Typical standardizations involved 0.099 mg. of ammonia as ammonium sulfate per milliliter of stock acid solution. Pipetted volumes of acid and back titers of alkali were plotted to give a slope value or ratio of alkali to acid of 0.936 ± 0.005 from six separate runs; the calculated value for this ratio was 0.937 ± 0.020. The titration indicator was a mixture of 10 mg. of methylene blue and 20 mg. of methyl red in 40 ml. of 95% ethyl alcohol. In the presence of ammonium sulfate this indicator has a transition point at about pH 5.4.

The volume of the large flask and accessory glassware to points *A* and *B* in Figure 1 was found to be 3260 ± 1 cc. by measuring the water required to fill. The total volume of the assembled and nitrogen-filled apparatus shown in Figure 1 was established in the following manner. Multiples of 1.06 mg. of ammonia were introduced into the system from the gas pipet previously described. The contents of the system were allowed to circulate through the pump until the balance meter needle on the spectrophotometer steadied (from 2 to 4 minutes, at 204.3 mμ). The

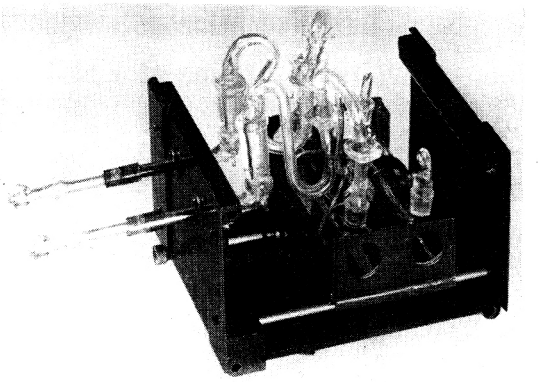

Figure 2. All-glass flexible cell arrangement

portion of the apparatus between points *A* and *B* was isolated from the system. The scrubber (Figure 3), containing from 25.0 to 100.0 ml. of the standard dilute sulfuric acid, was attached at point *B*. Then, with dry nitrogen flowing at 1 liter per minute, the 3260 cc. of ammonia-nitrogen mixture was flushed through the scrubber for 15 minutes. The scrubbing solution was titrated as described above to give the fraction of the original ammonia resident in the 3260-cc. portion of the system.

In Table III are recorded the data obtained, including the derived volume of the total system. In order to establish possible strongly retentive sorbtion of ammonia by any of the components of the system, including the pump, 3.18 mg. of ammonia was introduced and equilibrated with nitrogen, then the entire system was flushed with fresh dry nitrogen through the scrubber for 15 minutes; 3.09 mg. (97%) was recovered.

Standard Curve. The average total volume of 3710 cc. (Table III) was assumed for all subsequent calculations. The reference cell was filled with dry nitrogen at atmospheric pressure.

Unit portions of ammonia were introduced into the system as described above, and the stabilized absorbance readings were taken. Stabilization of the reading usually occurred within 2 to 4 minutes. In Table IV are recorded typical concentration-absorbance data. Less than unit quantities (1.06 mg.) of ammonia were achieved by mixing ammonia and dry nitrogen in a 100-cc. hypodermic syringe as described earlier; portions of each mixture were forced through the gas pipet to secure unit volumes, which were then absorbed in the dilute acid and back titrated in the usual manner, and other portions were introduced into the spectrophotometer system by means of the same gas pipet. Slit width was adjusted daily to get maximum response for the initial reading. The width varied from 0.013 mm. with a new hydrogen discharge lamp to 0.040 mm. with an aged lamp. The sensitivity control was adjusted with each measurement to afford maximum response. After the completion of each determination, the entire system was flushed with dry nitrogen until the original background absorbance was achieved (Table IV).

Table III. Volume of System

NH_3 Introduced, Mg.	Acid Consumed[a], Ml.	Calcd. Volume of System, Cc.
1.06	18.64	3690
1.06	18.45	3726
1.06	18.50	3720
4.24	73.64	3650
5.30	91.50	3760
		Av. 3710

[a] 0.00302*N* sulfuric acid solution; 1.06 mg. of ammonia requires 21.13 ml. of this acid for neutralization to pH 5.4.

RESULTS

In Figure 4 is reproduced the transmittance–wave length curve for ammonia gas as obtained with the manual, fused-silica prism spectrophotometer in 1-cm. cells. Dry nitrogen was in the reference cell. The uncorrected wave length values are those from the scale fitted to the spectrophotometer; the correction darts are derived from calibration (Table II) and indicate horizontal displacement of the appropriate absorption maximum necessary to correct for the nonlinearity of the adapted scale.

In Figure 5 is reproduced the log molar absorptivity (ϵ)–wave length curve for ammonia gas under the same conditions, but with corrected wave length scale. Figure 4 is included to demonstrate the precision obtainable with the manual fused-silica prism spectrophotometer, whereas Figure 5 demonstrates the analytical sensitivity obtainable throughout the entire spectrum. It is interesting to note the five sets of absorption doublets between 225 mμ and 208 mμ; Tannenbaum and coworkers (*9*) recorded only those three sets of doublets between 217 mμ and 208 mμ with a vacuum spectrograph, even though they started scanning at 230 mμ.

A typical absorbance-concentration curve for ammonia gas in dry nitrogen and *vs.* dry nitrogen may be reproduced from the data in Table IV. These data were established at 204.3 mμ with 10-cm. sealed silica cells on the manual instrument. Apparent deviation from the Beer-Lambert relationships above 0.8 mg. of ammonia per liter is possibly a curvilinear instrument response because of the very minute amounts of energy involved in the measurements with finite slit width.

The molar absorptivity (ϵ) data in Table V support the generality of a curvilinear relationship between energy record and amounts of ammonia above 0.28 mg. per liter. They also demonstrate the sensitivity of the analytical method at any of the indicated absorption maxima in this portion of the ultraviolet region.

A graphical comparison of the absorbance-concentration curves for ammonia gas in dry nitrogen with dry nitrogen as reference is shown for both the modified manual instrument and the Model

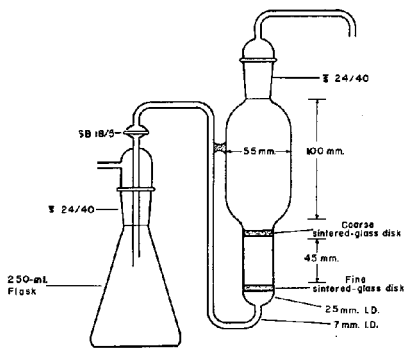

Figure 3. Apparatus for calibration of ammonia pipet

Table IV. Concentration-Absorbance Data for Ammonia at 204.3 Mμ

(10-cm. cells)

Ammonia, Mg./Liter	Number of Replicates	Absorbance, Corr. for Background
0.000	40	0.043 ± 0.003
0.013	6	0.011 ± 0.001
0.028	6	0.044 ± 0.001
0.056	4	0.083 ± 0.002
0.142	1	0.220
0.285	11	0.485 ± 0.005
0.57	4	0.890 ± 0.008
0.86	4	1.298 ± 0.008
1.14	3	1.621 ± 0.020

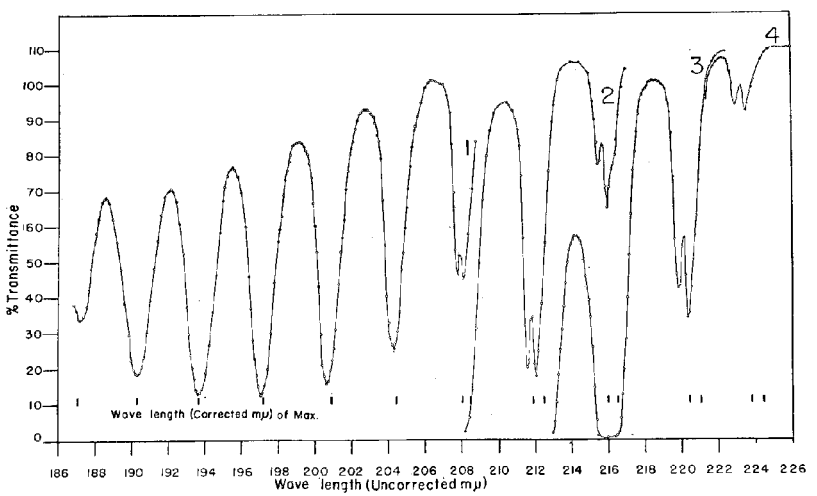

Figure 4. Transmittance–wave length curve for ammonia gas *vs.* dry nitrogen in 1-cm. cells

Mg. of ammonia per liter of dry nitrogen at 724 mm. pressure and 26.0° C.:
1. 3.4
2. 17.9
3. 111
4. 120

DK-2 recording instrument in Figure 6. The absorbance-concentration relationships with both instruments are essentially linear within the range of concentrations utilized, using 10-cm. sealed silica cells at 204.3 mμ. From Figure 4 and Table V the molar absorptivity for ammonia gas, corrected for cell absorption at 204.3 mμ with the manual instrument, is 2730 liters per mole-cm.; with the recording instrument the corresponding corrected value is 2790. From Figures 4 and 6 and from the absorptivities cited, it is clear that the two instruments possess equivalent sensitivity at 204.3 mμ. Furthermore, at this wave length and for the present purpose, an ordinary purged manual DU instrument with natural quartz prism and with photomultiplier attachment could have been used. Natural quartz does not transmit so well as fused silica at the shorter wave lengths,

Table V. Comparative Molar Absorptivities[a] for Ammonia at Several Absorption Maxima[b] with Manual Instrument

Corrected Wave-length, Mμ	0.285 mg./l.	0.570 mg./l.	0.855 mg./l.	1.140 mg./l.	1.425 mg./l.
190.3	3715	..	..	..	..
193.6	4487	..	..	..	..
197.2	4577	4122	3474	..	..
200.8	4131	3816	3389	2767	..
204.3	3127	2980	2570	2410	..
208.0	1891	1857	..	..	..
208.5	1987	..	1782	..	..
212.4	1058	930	873	855	839
221.1	..	..	..	104	88
223.8	..	..	..	80	63
224.4	..	..	..	79	63

[a] $\epsilon = \frac{\text{Absorbance} \times \text{liters}}{\text{mole} \times \text{cm.}}$

[b] In uncorrected 10-cm. cells, zero setting on sensitivity control, varying slit width.

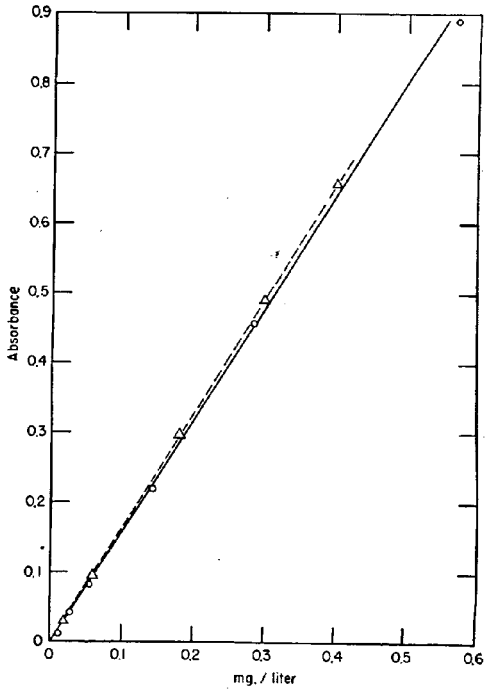

Figure 6. Absorbance-concentration curves for ammonia gas *vs.* dry nitrogen

——— Manual instrument
– – – – Recording instrument

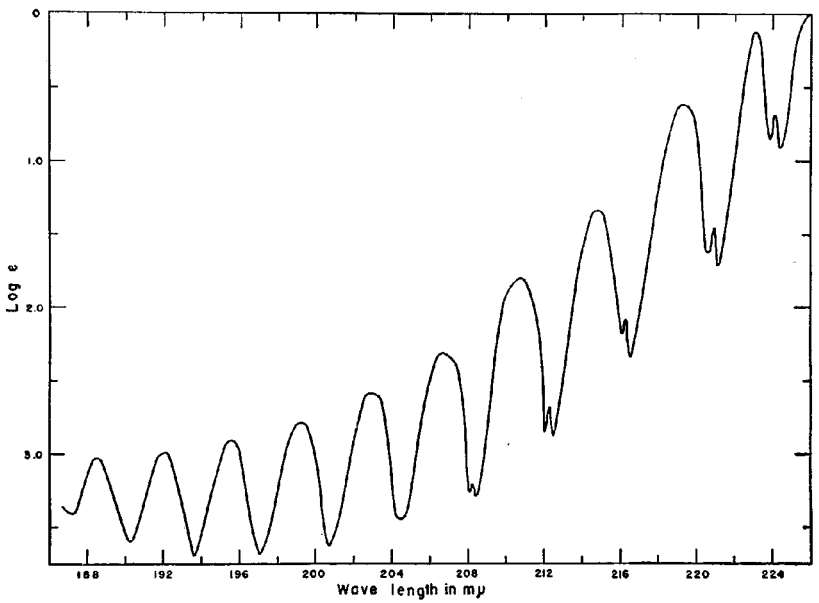

Figure 5. Log molar absorptivity–wave length curve for ammonia gas *vs.* dry nitrogen in 1-cm. cells

however. For example, in Figure 5 there are clean maxima both at 190.3 mμ and at 187.0 mμ, with apparent ε values of 3715 liters per mole-cm. (Table V) and 2370 liters per mole-cm., respectively. The DK-2 instrument recorded the maximum at 190.3 mμ with an apparent ε value of 1106 liters per mole-cm. but failed to record the maximum at 187.0 mμ.

At 204.3 mμ both instruments are capable of detecting about 5 γ (7 p.p.m.) of ammonia per liter of air or nitrogen under optimum instrument conditions with 10-cm. cells.

Mulliken (*6*) states that, in regard to the electronic configuration of ammonia, the structure, $[sa_1]^2[\pi e]^4\ [za_1]\ (3sa_1)$, $^3A_1$, $^1A_1$, indicates that the NH_3^+ core per se should be stable because the electron removal is essentially nonbonding, but that the possibility of predissociation of excited NH_3 exists. Thus, the excited electron may interact with the core as follows:

$$NH_3^+ + e \rightarrow NH_2 + H$$

but predissociation should in general tend to diminish with increase in the principal quantum number of the excited electron.

To test the effect of prolonged radiation at 204.3 mμ upon ammonia gas, two 1-cm. cells carefully matched at this wave length were filled at 724 mm. with a mixture of ammonia gas (3 mg. per liter) and dry nitrogen. One cell was exposed continuously to the ultraviolet energy, whereas the companion cell was exposed only for the few seconds necessary to make readings. Typical results against dry nitrogen are shown in Table VI. At the end of this period the two cells were quickly scanned from 200 to 206 mμ, with essentially parallel absorption curves resulting. These data and curves indicate that prolonged irradiation of ammonia gas in this region does decrease the effective concentration of the absorbing species of interest, unless this predissociation is reversible in that concentration varies with elapsed time between exposure and concentration measurement.

Table VI. Photodecomposition of Ammonia Gas at 204.3 Mμ and 26° C.

Elapsed Time, Minutes	Transmittance	
	Unexposed	Exposed
0	31.2, 31.1	31.1, 31.3
20	31.3, 31.4	38.2, 38.2
80	31.4, 31.5	40.0, 40.1
110	31.8, 31.9	42.6, 42.5
130	31.9, 31.9	43.8, 44.0

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Determination of Thorium in Urine

R. W. PERKINS and D. R. KALKWARF

General Electric Co., Richland, Wash.

A bioassay procedure can be used to determine thorium in submicrogram amounts in urine. Thorium is separated from interfering materials by coprecipitation with lanthanum fluoride, followed by an extraction using 2-thenoyltrifluoroacetone in benzene. The amount of thorium is determined colorimetrically as the thorium-morin complex.

IN ORDER to determine the relationship between urinary excretion of thorium and the amount of thorium present in the body, a procedure must be available to detect the small amount of thorium that can be expected in the urine. A maximum permissible limit of 89 mg. (0.01 μc.) of thorium in the body has been recommended by the International Commission on Radiological Protection (*9*). The available information on the rate of excretion of thorium has been recently summarized (*8*); however, it is not sufficient to define the sensitivity required of a bioassay procedure for determining a given body burden of thorium. An estimate based on the biochemical similarity of thorium and plutonium (*7*) indicated that a sensitivity of 0.2 γ of thorium would be sufficient to detect any significant thorium content in an individual and thus be suitable for future studies of the relationship between urinary excretion and body burden of thorium.

Several possible analytical techniques for estimating the thorium content of urine samples were considered. An alpha-particle counting procedure sensitive to 0.05 disintegration per minute (0.2 γ of thorium-232) can be realized; however, complicating factors in the case of thorium make this approach undesirable. One of the thorium-232 decay products is thorium-228, which is also an alpha emitter. The relative amounts of the two isotopes present are a function of the time since the decay chain between them had been broken. The alpha emissions of thorium might be counted immediately on separation and then again 1 to 4 weeks later, when the amount of thorium-228 could be determined by the build-up of alpha-particle-emitting daughters of thorium-228. However, this would be difficult to evaluate at present because only nuclear track counting has the required sensitivity and 1 week or more of exposure would be required for each count, further confusing the analysis.

The direct determination of as little as 0.3 γ of thorium in animal tissue samples with an emission spectrograph has been reported (*6*). Because urine contains the same inorganic salts as tissue but in a higher concentration (by a factor of about 10^3), a spectrographic analysis might be performed after a preliminary separation of the thorium from the bulk of the urine salts. A recently reported mass spectrometric determination of thorium indicated (*19*) that 0.1 γ of thorium could be detected; however, a preliminary separation would again be required.

Both of these methods require elaborate instrumentation which, together with the technical difficulties associated with sample preparation, make their use undesirable.

Of the colorimeteric reagents for thorium reported in the literature, morin, 2′,3,4′,5,7-pentahydroxyflavone, is the most sensitive. The sensitivity of this reagent has been reported (*3*) to be such that 0.1 to 0.2 γ of ThO_2 in 50 ml. of solution can be determined. As this sensitivity compares favorably with those of the other methods, a colorimetric procedure utilizing morin appeared to be most suitable for routine bioassay application.

OUTLINE OF METHOD

The urine sample is first freed from organic matter by a series of wet ashings with concentrated nitric acid. Two lanthanum fluoride precipitations remove the thorium from the bulk of urine salts. Thorium in 0.2*N* nitric acid is separated from any remaining urine salts and the lanthanum carrier by extraction with 0.45*M* 2-thenoyltrifluoroacetone (TTA) in benzene. Thorium is stripped from the 2-thenoyltrifluoroacetone–benzene solution with 2*N* nitric acid and evaporated to dryness with perchloric acid to remove the last traces of organic material. Then the thorium is taken up in pH 2.0 perchloric acid and determined colorimetrically as the thorium-morin complex.

A direct precipitation method was developed to replace the wet-ashing procedure, which is time-consuming as well as a possible source of an occasionally low result, possibly due to the formation of a difficultly soluble, refractory thorium oxide during the heating. The acidified urine sample is boiled down to a small volume and the lanthanum fluoride is precipitated directly from this solution. This procedure gave a higher yield and precision than the wet-ashing procedure.

REAGENTS AND APPARATUS

Standard Thorium Perchlorate. A solution of thorium perchlorate was prepared and purified by the method of Willard and Gordon (*21*). The solution was standardized gravimetrically by the oxalate procedure (*17*) and dilutions of this stock solution were prepared using doubly distilled water.

Lanthanum Nitrate Solution. A solution containing 25 grams of lanthanum nitrate tetrahydrate (Lindsay Light and Chemical Co.) in 50 ml. of water was washed for 10 minutes with each of three 10-ml. portions of 0.45*M* 2-thenoyltrifluoroacetone in benzene. The purified lanthanum nitrate solution was then diluted with doubly distilled water to give a concentration of 10 mg. of lanthanum per ml.

2-Thenoyltrifluoroacetone (TTA) Solution. A solution of 2-thenoyltrifluoroacetone (Midcontinent Chemicals Corp.) was prepared by dissolving 10 grams in redistilled benzene to give a total volume of 100 ml. Portions of this solution required for the extractions were washed 5 minutes with each of three 20-ml. portions of 2*N* nitric acid in the separatory funnel just prior to use.

Morin Solution. Morin (2′,3,4′,5,7-pentahydroxyflavone) was purified from technical grade morin (Eastman T4475) in the following manner. A sample of the technical grade material was stirred with ten times its weight of absolute ethyl alcohol at room temperature and the suspension was allowed to settle overnight. The alcoholic extract was filtered and evaporated under a heat lamp to one tenth its volume. An equal quantity of water was added and the precipitated morin was filtered. The precipitate was dissolved in a minimum amount of ethyl alcohol and again precipitated with an equal volume of water. The precipitate was then filtered, washed with water, and dried at 110° C. for 1 hour. A 2.5% yield was obtained; the product was light yellow with a melting point of 289–92° C. The solution for the colorimetric measurements was prepared by dissolving 25 mg. of purified morin in 100 ml. of absolute ethyl alcohol.

Acid Solutions. Nitric acid and perchloric acid were both redistilled and all dilutions were made with doubly distilled water. Hydrofluoric acid (ACS Code 1100, General Chemical Division, Allied Chemical and Dye Corp.) was used without further purification.

Glassware. Erlenmeyer flasks were cleaned with boiling nitric acid and rinsed with distilled water. Separatory funnels and Vycor (No. 7900) evaporating dishes were boiled in chromic acid cleaning solution for 10 minutes, followed by boiling in concentrated nitric acid for 5 minutes and rinsing with doubly distilled water. Silicone grease (Dow Corning) was used on the separatory funnel stopcocks.

Other Equipment. A Beckman Model DU spectrophotometer and 1-cm. Corex cells were used to obtain the absorbance measurements. A Beckman Model H-2 pH meter was used for the pH determinations. A Burrell Model DD shaker was used in the extraction operations. An International centrifuge Model V was used in the centrifugation operations.

DETAILED PROCEDURE

Ashing Procedure. To a 500-ml. urine sample in a 1000-ml. Erlenmeyer flask add 1 ml. of lanthanum nitrate solution (10 mg. of lanthanum) and 50 ml. of concentrated nitric acid and evaporate to dryness. Add 10 ml. of concentrated nitric acid and evaporate. Repeat this step until only white salts remain. Dissolve the salts in 60 ml. of 2*N* nitric acid, add 1 ml. of lanthanum nitrate solution, and stir thoroughly. Transfer flask contents to a 100-ml. Lusteroid centrifuge tube. Wash the flask with three 10-ml. portions of 2*N* nitric acid, adding washings to the centifuge tube.

Direct Precipitation Modification. To a 500-ml. urine sample in a 1000-ml. Erlenmeyer flask add 2 ml. of lanthanum solution and 100 ml. of concentrated nitric acid and evaporate to 25 to 35 ml. Allow the sample to cool 5 minutes. Transfer the sample to a 100-ml. Lusteroid centrifuge tube containing 10 to 20 ml. of distilled water. Wash the flask with three 10 to 15 ml. portions of 2*N* nitric acid, adding washings to the centrifuge tube. The first lanthanum fluoride precipitation can be made directly on this solution.

Thorium Separation and Determination. Add 5 ml. of concentrated hydrofluoric acid, stir thoroughly, and allow it to stand 1 hour. Centrifuge at 1600 r.p.m. for 2 minutes. Decant the solution, taking care to leave the precipitate undisturbed, and dissolve the precipitate in 10 to 20 ml. of 2*N* nitric acid directed in a fine stream from a wash bottle; dilute to 80 to 90 ml. with 2*N* nitric acid. Add 5 ml. of concentrated hydrofluoric acid, stir, and allow to stand 5 minutes. Centrifuge at 1600 r.p.m. for 2 minutes. Decant the solution and transfer the precipitate to a 45-ml. Vycor evaporating dish with the aid of 10 to 15 ml. of 2*N* nitric acid. Add 3 ml. of concentrated perchloric acid and evaporate to dryness on a hot plate. Dissolve the residue in 3 ml. of 1*N* nitric acid and transfer the solution to a separatory funnel containing 10 ml. of 0.45*M* 2-thenoyltrifluoroacetone in benzene. Wash the Vycor dish with three 1-ml. portions of water, adding the washes to the separatory funnel. Shake for 5 minutes at maximum agitation on a mechanical shaker, then add 10 ml. of distilled water and shake for 15 minutes. Discard the aqueous layer. Wash the inside of the separatory funnel with 25 to 35 ml. of distilled water by spraying from a wash bottle, then discard the wash water. Wash the 2-thenoyltrifluoroacetone–benzene layer by shaking it with three 5-ml. portions of 0.2*N* nitric acid 5 minutes each, discarding the aqueous layer each time. Wash the inside of the separatory funnel with 25 to 35 ml. of distilled water by spraying from a wash bottle and discard the wash water. Add 10 ml. of 2*N* nitric acid and shake 15 minutes. Let stand for 30 minutes to allow complete separation of the phases. (Incomplete separation here may lead to a mild explosion and loss of the sample during the next steps.)

Withdraw the aqueous phase into a 45-ml. Vycor dish containing 3 ml. of concentrated perchloric acid. Place the samples

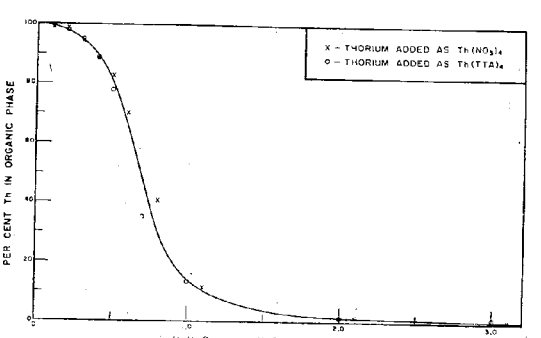

Figure 1. Thorium distribution between nitric acid and 0.45*M* 2-thenoyltrifluoroacetone as a function of nitric acid concentration

on an asbestos-covered hot plate and cover them with an inverted rectangular borosilicate glass dish raised slightly at the back to allow the fumes to escape while preventing entrance of dust from the hood ventilating air. Evaporate to dryness. Remove the dishes from the hot plate and allow them to cool. Add 3.3 ml. of perchloric acid at pH 2.0, swirl 0.5 minute, allow to stand 5 minutes, and swirl again. Transfer 3.0 ml. of the sample to the spectrophotometer cell and add 0.50 ml. of morin solution. Prepare a blank solution containing 3.0 ml. of perchloric acid at pH 2 and 0.50 ml. of morin solution. Place the cap on the cells and invert several times to mix. Allow to stand 1 hour and measure the absorbance at a wave length of 412 mμ and a slit width of 0.03 mm. on a Beckman Model DU spectrophotometer.

DISCUSSION OF METHOD

A preliminary study of possible methods of separating thorium from urine samples indicated that a lanthanum fluoride carrier precipitation of thorium followed by a solvent extraction separation of the thorium from the carrier should be suitable. Several organic solvents and chelating agents were considered for the extraction, among which 2-thenoyltrifluoroacetone–benzene (*4, 5, 16*) mesityl oxide (*1, 2, 4, 11, 14*) and methyl isobutyl ketone (*18*) seemed most promising. A brief study of these systems indicated that 2-thenoyltrifluoroacetone–benzene required no salting agent, which could introduce contamination, and greater selectivity for thorium could be obtained.

The distribution of thorium between 0.25 *M* 2-thenoyltrifluoroacetone–benzene and nitric acid solutions as a function of pH has been determined (*5*). For the present work a 0.45*M* 2-thenoyltrifluoroacetone–benzene solution (10 grams per 100 ml.) was chosen to permit the use of a more acid solution for the initial extraction step.

To determine suitable acid concentrations for thorium extraction into and out of 0.45*M* 2-thenoyltrifluoroacetone–benzene, thorium distribution as a function of nitric acid concentration was studied. Thorium-228 was used as a tracer to permit the use of low thorium concentrations, similar to the thorium-232 concentrations to be studied in urine, and at the same time have a sufficient quantity of radioactivity for accurate measurements. Thorium distribution was studied with thorium-228 added both as $Th(NO_3)_4$ and as $Th(TTA)_4$ in benzene. Equal volumes of the acid and the organic solutions were equilibrated 20 minutes by vigorous shaking; then the phases were separated and their alpha activities measured. The results of this study are summarized in Figure 1.

Table I. Locations of Thorium Loss

Location	Th Found, %
Supernatant solution from first precipitation	0.2
Supernatant solution from second precipitation	0.2
Aqueous layer from extraction	2.0
First acid wash	2.9
Second acid wash	3.3
Third acid wash	3.8
Organic layer	1.3
Total	13.7

From the data obtained in this study a 0.2*N* nitric acid concentration for extraction of thorium into 2-thenoyltrifluoroacetone–benzene and a 2*N* nitric acid concentration for back-extraction were chosen. These acidities give excellent purification of thorium with reasonably small loss of thorium.

The efficiency of the lanthanum fluoride carrier precipitation of thorium was studied as a function of nitric acid concentration to determine a suitable range for this step. For nitric acid concentrations of 2*N* to 12*N* no appreciable effect of the completeness of the thorium precipitation was observed.

To determine the approximate loss of thorium in each of the separation steps (exclusive of wet ashing) of the analytical procedure, an analysis was performed using thorium-228 tracer on a 75-ml. aliquot of 2*N* nitric acid. The thorium present in the various solutions normally discarded in the analysis was measured and is tabulated in Table I.

The data in Table I indicate the size of the small thorium losses that occur in the procedure, and that an over-all yield of about 85% could be expected.

The major loss of thorium is due to its equilibrium distribution between the organic and aqueous phases in the extraction and washing steps. These washing steps, while reducing the yield slightly, were required to give a product of sufficient purity for colorimetric analysis.

Using thorium-228 as a tracer the yields were determined on eight 500-ml. urine samples for both the wet-ashing and direct precipitation procedures. The average yield for the wet-ash procedure was about 70% and for the direct precipitation procedure above 80%.

In the 2-thenoyltrifluoroacetone–benzene extraction step the extraction proceeds initially from 0.5*N* nitric acid and finally (without separation) from 0.2*N* nitric acid. Shaking with the more concentrated acid at first prevents an occasional formation of a solid material at the interference, which is redissolved only with difficulty. This solid material has not been identified but may be a lanthanum–2-thenoyltrifluoroacetone complex.

In dilute perchloric acid solutions, thorium forms a complex with morin which has an absorption maximum at 412 mμ, as shown in Figure 2. Because thorium precipitates or is absorbed on the container walls in solutions with pH greater than 3.0 (*15*), a pH of 2.0 was chosen for the medium on which to make the absorbance measurements. This value is a compromise to ensure keeping the thorium in solution while maintaining a high absorptivity.

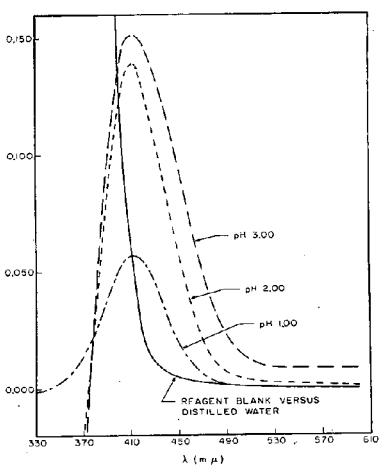

Figure 2. Absorbance–wave length curves for thorium-morin complex and excess morin in dilute perchloric acid

The absorbances of aqueous solutions at pH 2.0 containing 0.036% of morin by weight, 14% of ethyl alcohol by volume, and up to 2 p.p.m. of thorium were determined at 412 mμ *vs.* a similar reference solution containing no thorium. The solutions were found to obey Beer's law and have an absorptivity of 0.179 p.p.m.$^{-1}$ cm^{-1}. Two other colorimetric reagents proposed for thorium, naphthazarin (*15*), and thorin (*1*) form complexes with absorptivities of 0.096 and 0.073 p.p.m.$^{-1}$ cm^{-1},

respectively, as calculated from data in the literature and are thus only half as sensitive as morin. The fluorescent light intensities from $Th(morin)_2$ solutions were also examined with the Beckman DU spectrophotometer using the fluorescence attachment; however, no improvement in sensitivity was found when this technique was used.

The ratio of thorium to morin in the complex formed at pH 2.0 in a solution containing 14% ethyl alcohol by volume was determined by the method of continuous variation (*10*). The value of the ratio found corresponds to the formula $Th(morin)_2$ as illustrated in Figure 3. The coincidence of the absorbance maxima at 412 and 440 mμ indicates that only one complex is formed (*20*). The dissociation constant of the complex was evaluated as 3×10^{-10} mole^2 liter^{-2} by comparing the concentrations of thorium and morin in two different solutions which have the same concentration of the complex (*12*). Fletcher and Milkey (*3*) also reported the formula $Th(morin)_2$ and gave the value 2×10^{-10} for the dissociation constant, although they reported no details of the solution composition or the procedure.

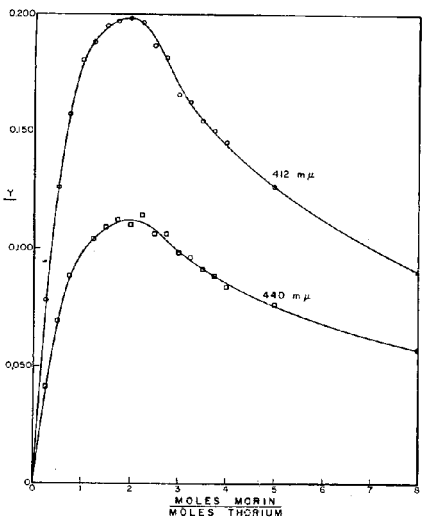

Figure 3. Relation of absorbance function *Y* to molar ratio of morin-thorium in perchloric acid solution at pH 2.0

Function *Y* is absorbance of solution minus calculated absorbance for no reaction

Morin is extremely sensitive to many metal ions and organic materials. The use of Vycor dishes for the perchloric acid evaporation was found to be advisable, because some interfering material that increased the measured absorbance was leached from borosilicate glass and even from silica vessels. The absorptivity of the $Th(morin)_2$ complex decreases at a rate of only 0.1% per minute after mixing; however, trace impurities carried through the bioassay procedure exhibit an initial high absorbance which fades rapidly. As it was not possible to eliminate these impurities, the procedure incorporates a delay of 1 hour between mixing the reagents and reading the absorbance, in order to minimize their effect. The difference between these two values reflects the difference in recovery efficiencies of the two procedures.

SENSITIVITY OF PROCEDURE

Aliquots of the standard thorium perchlorate solution containing 0.87γ of thorium were added to each of a series of 500-ml. urine samples and then thorium was determined in these samples, as well as a number of blank urine samples, by either the wet-ashing procedure or direct precipitation. The results from the final absorbance measurements are listed in Table II. For the wet-ashing procedure, an absorbance of 0.0215 unit greater than the urine blank reading is equivalent to 1γ of thorium and, similarly, an absorbance of 0.0328 is equivalent to 1γ of thorium in the direct precipitation modification.

Table II. Comparison of Absorbances Obtained by Ashing and Direct Precipitation Modification of Procedure

Ashing Procedure		Direct Precipitation Modification	
Blank	0.87 γ Th	Blank	0.87 γ
0.008	0.041	0.010	0.034
0.011	0.039	0.009	0.036
0.017	0.038	0.006	0.036
0.022	0.037	0.008	0.035
0.020	0.027	0.008	0.036
0.011	0.034	0.008	0.038
0.011	0.040	0.009	0.039
0.015	0.034	0.010	0.038
0.009	0.028	0.013	0.043
0.009	0.029	0.007	0.035
0.008	0.022	0.008	0.038
0.012	0.023	0.009	0.036
0.014	0.037		0.042
0.009	0.022		0.039
0.014	0.026		0.034
0.003	0.026		
0.003	0.027		
0.008	0.026		
0.003	0.029		
0.012	0.021		
0.017			
0.017			
0.014			
0.0116	0.0303	0.00875	0.0373
Net absorbance, absorbance unit/γ Th	0.0187		0.0285

Table III. Sensitivity Limits

(γ Th per 500-ml. sample)

Probability Level, %	Ashing Procedure		Direct Precipitation	
	Limit 1	Limit 2	Limit 1	Limit 2
75	0.16	0.38	0.037	0.091
90	0.32	0.73	0.073	0.18
95	0.41	0.94	0.095	0.24
99	0.60	1.38	0.15	0.36

The sensitivity of the procedure may be stated in two ways. One is the amount of thorium equivalent to an absorbance reading which would be higher than a given confidence level for the blanks. The second is the amount of thorium which, if present in the sample, would give a reading higher than the first sensitivity limit a given percentage of the time—e.g., the first sensitivity limit gives the amount of thorium that would yield absorbances above a given confidence level for the blanks only 50% of the time, if the absorbance values were assumed to be symmetrically distributed.

Both these limits were calculated at various probability levels, on the assumption that absorbance values for both the blank and standard samples could be represented by normal distribution curves. Values of these limits shown in Table III refer to the analysis of one 500-ml. urine sample. For example, by the direct precipitation procedure, 0.24γ of thorium in a sample would give a reading higher than that corresponding to the 95% confidence level of the blanks (equivalent to 0.095 γ of thorium)

95% of the time. These sensitivities should be adequate to estimate any significant amount of thorium present in the urine.

ACKNOWLEDGMENT

The authors wish to express their appreciation to L. J. Kirby for his work in testing the analytical procedure and to H. T. Norton for his help in the statistical analysis. Much of the laboratory work in the development of the procedure was performed by D. R. Edwards, whose efforts have been greatly appreciated.

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Report on Recommended Specifications for Microchemical Apparatus

Volumetric Glassware. Flasks, Pipets, and Centrifuge Tubes

Committee on Microchemical Apparatus, Division of Analytical Chemistry, AMERICAN CHEMICAL SOCIETY

AL STEYERMARK, Chairman, Hoffmann-La Roche Inc., Nutley, N. J.

H. K. ALBER, Arthur H. Thomas Co., Philadelphia, Pa.

V. A. ALUISE, Hercules Powder Co., Wilmington, Del.

E. W. D. HUFFMAN, Huffman Microanalytical Laboratories, Wheatridge, Colo.

E. L. JOLLEY, Corning Glass Works, Corning, N. Y.

J. A. KUCK, College of the City of New York, New York, N. Y., and American Cyanamid Co., Stamford, Conn.

J. J. MORAN, Kimble Glass Co., Vineland, N. J.

C. L. OGG, Eastern Utilization Research Branch, Agricultural Research Service, U. S. Department of Agriculture, Philadelphia, Pa.

IN PREVIOUS reports (*2*, *3*) of the Committee on Microchemical Apparatus, recommended specifications were published for pieces of apparatus that were either the most widely used for the work in question or else an improvement over such apparatus according to tests made by the members of the committee or cooperating chemists. In this report, specifications are

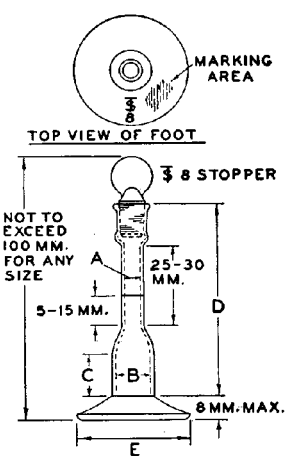


Figure 1. Microvolumetric flask

Capacity, Ml.	*A*, Inside Diameter, Mm.	*B*, Inside Diameter, Mm.	*C* (Approx.), Mm.	*D* (Maximum), Mm.	*E* (Maximum), Mm.	*F*, Tolerance, Ml.
1	4.2–4.6	8.0–8.5	10	70	37	±0.010
2	5.0–5.4	10.5–11.0	13	70	39	±0.015
3	5.0–5.4	13.25–13.75	14	72	39	±0.015
4	6.2–6.6	13.75–14.25	18	75	39	±0.020
5	6.2–6.6	15.5–16.0	18	75	39	±0.020

To be marked "T.C. (capacity) 20° C."
1-ml. size to weigh less than 19 grams empty (stopper included).
Shape of bases may be either round or hexagonal. Dimensions given in column *E* are maximum permitted for distance between parallel sides of hexagonal bases and are maximum diameters of round bases.

recommended for volumetric flasks (Figure 1), pipets to be used with the flasks (Figure 2), and centrifuge tubes (Figures 3 to 6).

The volumetric flasks are of a new design which combines convenience in use with accuracy. A wide base affords greater stability against upset. In the case of the 1-ml. size, the diameter of the base is small enough to permit placement on the microchemical balance pan and the weight is restricted to a maximum of 19 grams when empty.

To increase the usefulness of these flasks, special measuring pipets have been designed. The long narrow delivery stems of the pipets reach to the bottom of the flasks, permitting almost complete withdrawal of the contents. Tests by members of the committee show that all but a few hundredths of a milliliter can be withdrawn.

Four types of centrifuge tubes are recommended: with conical bottom, plain (Figure 3); with conical bottom, stoppered (Figure

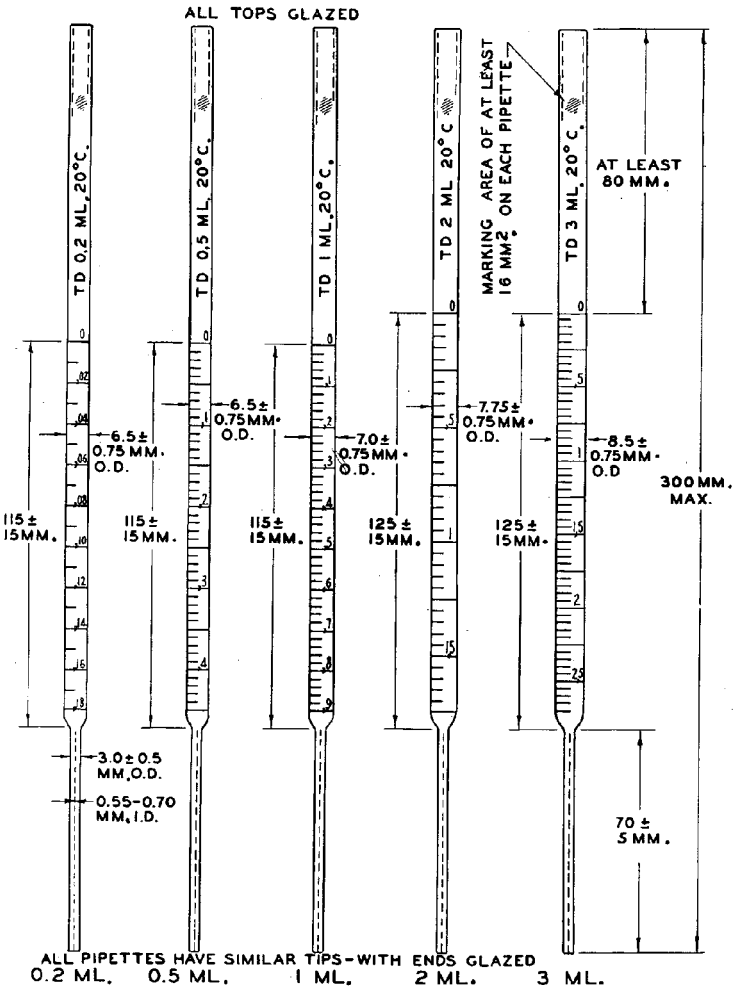


Figure 2. Micropipet with cylindrical tip

Capacity, Ml.	Subdivision, Ml.	Interval Graduated, Ml.	Lining: Ring at each ml.	Lining: ½ ring at each ml.	Number at 0 and each ml.	Tolerance, Ml.
0.2	0.01	0 to 0.18	0.02	0.01	0.02	±0.005
0.5	0.01	0 to 0.45	0.05	0.01	0.1	±0.01
1	0.02	0 to 0.90	0.1	0.02	0.1	±0.02
2	0.05	0 to 1.75	0.25	0.05	0.5	±0.04
3	0.05	0 to 2.70	0.25	0.05	0.5	±0.06

No graduations to appear in tapered portion
Tip may be tapered at junction with body, but outside diameter at this point may not exceed 4.5 mm.
Tip outlet to be glazed, with least possible constriction
Calibrated to deliver at 20° C. touching off last drop

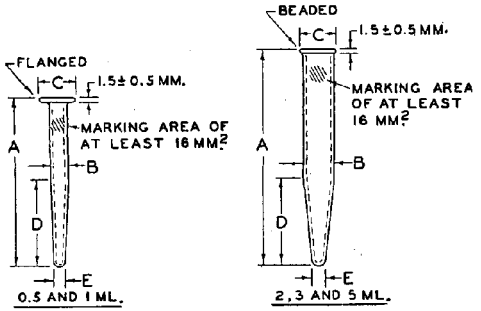


Figure 3. Microcentrifuge tube with conical bottom, plain

Nominal Capacity, Ml.	*A*, Over-All Height, Mm.	*B*, Outside Diameter Cylindrical Portion, Mm.	*C*, Outside Diameter Top Finish, Mm.	*D*, Length of Taper, Mm.	*E*, Outside Diameter at Bottom, Mm.
0.5	58 ± 2	6.0 ± 0.25	13 ± 1.0	30 ± 2	3.5 ± 0.5
1	61 ± 2	8.25 ± 0.25	13 ± 1.0	30 ± 2	3.5 ± 0.5
2	66 ± 2	10.75 ± 0.25*	13.5 ± 1.0	30 ± 2	4.0 ± 0.5
3	74 ± 2	10.75 ± 0.25*	13.5 ± 1.0	30 ± 2	4.0 ± 0.5
5	101 ± 2	13.0 ± 0.50	16.25 ± 0.75	40 ± 2	4.0 ± 0.5

Wall thickness of all sizes to be approximately 1 mm.
* The outside diameter of 2 and 3 ml. must not exceed 11.0 mm.; otherwise tubes will not fit into centrifuge shields.
Bottoms to be rounded

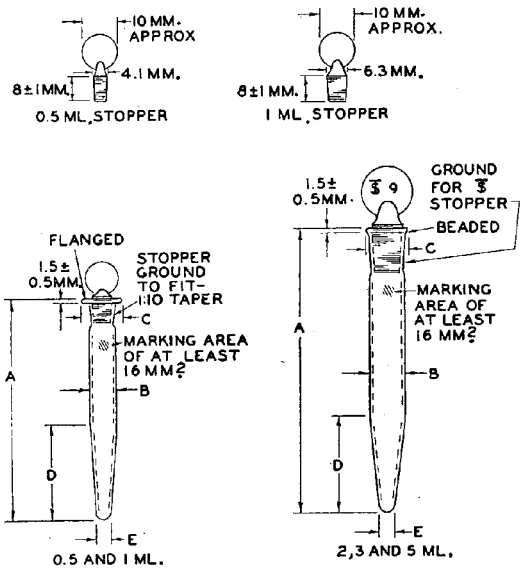
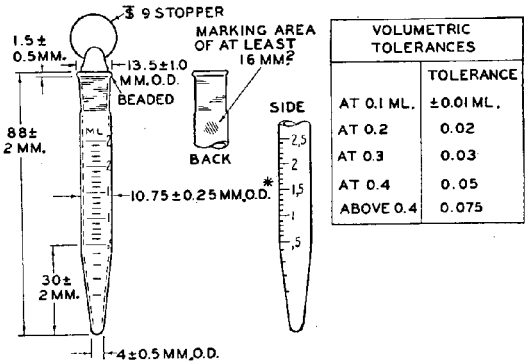


Figure 4. Microcentrifuge tube with conical bottom, stoppered

Nominal Capacity, Ml.	*A*, Over-All Height, Mm.	*B*, Outside Diameter Cylindrical Portion, Mm.	*C*, Outside Diameter Top Finish, Mm.	*D*, Length of Taper, Mm.	*E*, Outside Diameter at Bottom, Mm.
0.5	66 ± 2	6.0 ± 0.25	13 ± 1.0	30 ± 2	3.5 ± 0.5
1	69 ± 2	8.25 ± 0.25	13 ± 1.0	30 ± 2	3.5 ± 0.5
2	80 ± 2	10.75 ± 0.25*	13.5 ± 1.0	30 ± 2	4.0 ± 0.5
3	88 ± 2	10.75 ± 0.25*	13.5 ± 1.0	30 ± 2	4.0 ± 0.5
5	115 ± 2	13.0 ± 0.50	16.25 ± 0.75	40 ± 2	4.0 ± 0.5

Wall thickness of all sizes to be approximately 1 mm.
* The outside diameter of 2 and 3 ml. must not exceed 11.0 mm.; otherwise tubes will not fit in centrifuge shields.
Bottoms to be rounded



VOLUMETRIC TOLERANCES	
	TOLERANCE
AT 0.1 ML.	±0.01 ML.
AT 0.2	0.02
AT 0.3	0.03
AT 0.4	0.05
ABOVE 0.4	0.075

Figure 5. Microcentrifuge tube with conical bottom, stoppered, graduated, 2.5 ml. in 0.1 ml.

Wall thickness to be approximately 1 mm.
* Outside diameter must not exceed 11.0 mm.; otherwise, tube will not fit into centrifuge shields
Bottom to be rounded

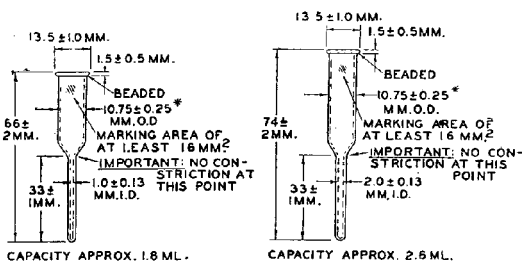


Figure 6. Microcentrifuge tube with cylindrical bottom, plain

Wall thickness of both sizes to be approximately 1 mm.
* The outside diameter of both sizes must not exceed 11.0 mm.; otherwise tubes will not fit into centrifuge shields
Bottoms to be rounded

4); with conical bottom, stoppered, graduated (Figure 5); and with cylindrical bottom, plain (*1*) (Figure 6). These centrifuge tubes fit into the metal shields that are supplied with commercially available centrifuges. Removal of glass stoppers during actual centrifugation is advised.

Additional reports will be made on other microvolumetric apparatus.

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Determination of Nitrate in Fresh Water

Concentration of Samples by an Ion Exchange Procedure

A. D. WESTLAND[1] and R. R. LANGFORD[2]

Opeongo Limnological Laboratory, Department of Lands and Forests, Province of Ontario, Whitney, Ont., Can.

An analytical procedure has been developed which is applicable to determination of nitrate in fresh waters in a concentration range one order of magnitude lower than previous methods have allowed. Samples are concentrated by an ion exchange process before the strychnidine color determination is applied. Direct application of the color reaction to natural samples may lead to results which are much too high.

A STUDY of the biological productivity of lake waters necessitated a knowledge of the organic, ammonia, nitrite, and nitrate nitrogen in inland waters. Existing analytical procedures sufficed for the determination of the first three, but no method sufficiently sensitive for the estimation of the low concentrations of nitrate in northern Ontario waters has been reported. The most recent methods for nitrate (*3*, *4*), using the polarograph, are no more sensitive than older colorimetric ones.

Natural water samples cannot be concentrated for nitrate determination by evaporation because the resulting decomposition and hydrolysis of organic nitrogen compounds vitiate determination of the original nitrate content. Previous studies on the concentration of phosphate samples by an ion exchange process (*1*) suggested the possibility of similarly concentrating nitrate samples. Nydahl (*2*) determined a variety of constituents following an ion exchange procedure, but gave little attention to nitrate. It was felt that adsorption of nitrate on a chloride-form resin at room temperature should be attended by little or no disruption of organic nitrogen compounds. The nitrate, along with other strong acid radicals, should be eluted by a relatively small volume of elutriant, the concentration being then high enough for colorimetric determination. This was found to be the case and tenfold concentrations were effected.

Preliminary examination of colorimetric methods for nitrate determination led the authors to choose strychnidine as a reagent, because this procedure of Zwicker and Robinson (*5*) gave the best results for low concentrations of nitrate. The strychnidine procedure suffers from the disadvantage that a curve, which does not obey Beer's law, must be obtained from standard samples determined simultaneously with each set of unknowns.

Various techniques for carrying out the color development were investigated in order to establish conditions which gave the most reproducible absorbance values. The color intensity is sensitive to the method of mixing the color reagent with the sample solution and also to the time of standing, so that a precise manipulation technique had to be maintained. The mixing method described below gave reproducible results. The time allowed for color development was selected with regard to the slow color development in samples of low concentration and fading in samples of high concentration. The choice of the chloride concentration of the solution was based on the study of the ion exchange process described further on.

Because nitrite ion reacts with strychnidine to give an intense coloration, the possibility of eliminating it by diazotization was investigated. The addition of an amine reduces the nitrate color as well as the nitrite concentration, so a search was made for a compound which would not reduce the sensitivity for nitrate by too much. Of the compounds tested, sulfanilic acid gave the best results. The final absorbance was influenced by the quantity of this reagent; therefore, it was added accurately from a micropipet. A study of the efficiency of the nitrite removal showed that 0.002 gram of sulfanilic acid was sufficient to eliminate interference from nitrite when present in an amount comparable to the amount of nitrate.

[1] Present address, Department of Chemistry, University of Toronto, Toronto, Can.

[2] Present address, Department of Zoology, University of Toronto, Toronto, Can.

EXPERIMENTAL

Apparatus. COLORIMETRIC. A Rubicon Co. Evelyn photoelectric colorimeter equipped with a 540-mμ filter was used for the absorbance measurements. The strongly acid strychnidine reagent was delivered from an automatic buret greased with silicone stopcock compound. The vent to the atmosphere was connected to a drying tower containing anhydrous magnesium perchlorate.

ION EXCHANGE. Glass columns 0.8 cm. in inside diameter contained analytical grade Amberlite IR-4B ion exchange resin to a depth of 8 cm. The column effluent was delivered through a siphon tube 0.5 mm. in inside diameter. It was found that large bore tubing allowed back-diffusion of the solutions, thus preventing quantitative recovery by the necessarily small volume of elutriant used.

Reagents. COLOPIMETRIC. For the color reagent, 1.0 mM strychnidine solution was prepared by dissolving 0.320 gram of the reagent, obtained from Bios Laboratories, New York, N. Y., in 1 liter of concentrated, low nitrate sulfuric acid. For sulfanilic acid solution, 0.6 gram of the reagent (Distillation Products Industries, No. T238) was dissolved in 70 ml. of hot water, 20 ml. of hot concentrated hydrochloric acid was added, and the volume adjusted to 100 ml. Standard nitrate solution was prepared by adding 0.722 gram of analytical grade potassium nitrate and 1 ml. of chloroform to sufficient water to make 1 liter of solution containing 100 p.p.m. of nitrate nitrogen. Dilutions to the desired concentration were made immediately before use.

ION EXCHANGE. Analytical grade sodium chloride solutions of various concentrations were used for elutions. The water used was distilled from a Barnstead still and passed through a column of Amberlite IRA-400 ion exchange resin in the hydroxyl form to produce anion-free water. In early experiments, large volumes of double-distilled water used for washing and preparing solutions introduced considerable nitrate and nitrite. This condition might have been remedied by distilling the water from alkaline medium, but the authors chose to use the more convenient but effective device of further treating once-distilled water by passing through Amberlite IRA-400.

Procedure. The pH value of a fresh sample is adjusted to between 5 and 7 with 0.01N acetic acid or sodium bicarbonate. If the chloride concentration is below 0.001M, it is brought to this value by the addition of sodium chloride solution. The sample is passed at a rate of 1.0 to 1.5 ml. per minute through an Amberlite IR-4B column. The column is cleared of residual sample water by passing through it 25 ml. of anion-free water. The nitrate is eluted with 45 to 50 ml. of 1% sodium chloride solution and made up to 50.0-ml.

A 5-ml. aliquot (which contains from 0.10 to 1.0 p.p.m. of nitrate nitrogen) of this solution is placed in a comparison tube. A 0.40-ml. volume of sulfanilic acid solution is added with mixing. The solution is allowed to stand for at least 10 minutes. Meanwhile, a 5.4-ml. volume of strychnidine reagent solution is delivered to another comparison tube. The reagent is poured quickly but carefully into the sample, the solution is poured back into the first tube, and then forth and back once again. The color is allowed to develop for 20 ± 1 minutes and the absorbance is measured, using the 6-mm. aperture and the 540-mμ filter. The sample should be protected from bright light. If several samples are to be determined at once, a schedule of about one sample per minute should be followed during the color development.

To prepare the column for the next analysis, it is washed free of chloride with 0.5 liter of anion-free water.

Preparation of Standard Curve. Dilutions of the standard nitrate solution, containing from 0.1 to 1.0 p.p.m. of nitrate nitrogen, were made. The dilutions were adjusted to contain 1% of

sodium chloride and the volume was made up to 5 ml. Color was developed in the same manner as for the samples.

RESULTS

Five independent analyses of a large sample of stream water, from which the precision of the method can be ascertained, appear in Table I.

Table I. Precision of Replicate Nitrate Determinations in Stream Water by Ion Exchange

(500-ml. taken for each sample)

Sample No.	Nitrate Nitrogen Concn., P.P.M.
1	0.058
2	0.061
3	0.062
4	0.061
5	0.057

DISCUSSION

In exploratory experiments, samples prepared by adding known amounts of the diluted nitrate and nitrite standards to 1 liter of the anion-free water were passed at a rate of 1.0 to 1.5 ml. per minute through the column. The column was eluted at the same rate with 45 ml. of 3% sodium chloride solution and the eluate made up to 50 ml. with 3% sodium chloride solution. A 5-ml. aliquot was taken for analysis.

The results of some determinations on such samples appear in Table II. These show a slight tendency to positive errors, as blank solutions did also. This was at first assumed to be due to incomplete removal of nitrate in the water purification process, but the error was increased by slower passing of the eluting solution and by high concentrations of salt.

Table II. Recovery of Nitrate from Synthetic Samples

Nitrite Taken, γ	Nitrate, γ Taken	Nitrate, γ Recovered	% Recovery
2.5	10.0	10.4	104
2.5	10.0	9.4	94
10.0	10.0	10.4	104
10.0	10.0	10.4	104
	10.0	10.7	107
5.0	20.0	19.8	99

It was subsequently found that the resin was slightly dissolved by the elutriant to give a solution capable of forming a red color with strychnidine. It was further noticed that a slight brown color was imparted to elutriant solutions by the resin. To examine this quantitatively, it was necessary to measure the color of eluates using a 150-mm. layer of solution in a Lumetron Model 450 colorimeter with a 420-mμ filter. The intensities of the color of eluates of various sodium chloride concentrations are listed in Table III. Nitrate samples were passed through the columns and eluted with solutions of the same chloride concentrations. The recoveries are recorded in the same table. An elutriant containing 1% sodium chloride gives quantitative recovery and dissolves only about half as much resin as the solutions used in the earlier experiments.

A major consideration in the ion exchange process is the pH of the sample. The exchange process will not operate if the pH is above 7. The waters dealt with in this laboratory are

Table III. Effect of Elutriant Chloride Concentration on Eluate Color and Nitrate Recovery

(9.8 γ of nitrate nitrogen taken)

Sodium Chloride, %	Absorbance of Eluate	Nitrate Recovered γ	Nitrate Recovered %
0.25	0.014	2.0	20
0.50	0.026	8.4	86
1.0	0.032	9.9	101
2.0	0.045	11.2	114
3.0	0.060	10.1	103

almost invariably slightly acid, so that no adjustment of pH was usually necessary. Unless the sample was only feebly acid, the resin was partly dissolved; this process induced flocculation of the humic material in the resin bed. It was found advisable to keep the pH within the range from 5 to 7. The adjustment with base or acid was not tedious because the organic acids present had a slight buffering effect. Weak acid or base should be used for this, otherwise hydrolysis of nitrogen compounds may occur.

The choice of a chloride-form resin was opportune. A hydroxyl-form resin evokes an abrupt change in acidity as the sample is passed through. The hydroxyl and the sulfate forms of the resin adsorb the tannins almost quantitatively, whereas the extent of adsorption of the chloride-form resin is small. Any adsorbed and subsequently eluted organic nitrogen which can be hydrolyzed to nitrate by the strychnidine solution results in positive errors. The interference caused in this way was found to be roughly proportional to the color of the humic matter in the eluate solution when measured with a 420-mμ filter and a 150-mm. light path. Approximately 7% of the colored organic matter in water obtained from a very dark stream was adsorbed on the chloride-form resin and was quantitatively eluted. The effluent showed an apparent nitrate nitrogen concentration of 0.048 p.p.m. Assuming that the 7% of adsorbed organic matter could hydrolyze upon acidification to a proportionate amount of nitrate, the error resulting would be 0.048 p.p.m. $\times$ $^7/_{93}$ = 0.004 p.p.m. This is near the lower limit of the concentration range in which the method would be applicable; therefore it was desirable to decrease this error. It was discovered that if the sample were made to contain chloride in a concentration of 0.001M, the extent of adsorption of organic matter was reduced to about two thirds of the former value. Higher concentrations effected no further decrease, however. The adsorption of nitrate from dark-colored natural stream water was not inhibited by the presence of chloride in concentrations at least as high as 0.002M. The optical absorbance of the organic matter itself was negligible at 540 mμ.

When the strychnidine procedure was applied to stream water from which strong acid anions had been removed by passing through an Amberlite IR-4B column, a red color appeared indicating the presence of an oxidizing agent, probably nitrate. Presumably, this was not present as free nitrate ion during the exchange process but was released when the strong acid reagent was added. An attempt was made to further justify this assumption.

Dark-colored stream water was passed through the Amberlite IR-4B exchanger to free it from available nitrate. Known quantities of standard solution were added to the effluent water and the nitrate was then determined by the ion exchange concentrating procedure. Quantitative recoveries of the nitrate as reported in Table IV indicate the validity of the method.

It is significant that when the strychnidine procedure was applied directly to the water samples—i.e., omitting the ion exchange process—results high by several hundred per cent were often obtained. The same phenomenon was observed with phosphate when determined both directly with acid molyb-

Table IV. Recovery of Nitrate Added to Blank Stream Water

Sample No.	Color of Feed Water, Absorbance Unit	Nitrate, γ Added	Nitrate, γ Recovered	% Recovery
1	0.010	2.11	2.16	102
2	0.010	5.05	5.85	116
3	0.010	5.05	4.84	96
4	0.057	5.05	4.93	98
5	0.057	5.05	5.08	101
6	0.057	10.6	11.3	107
7	0.057	10.6	10.5	99

date and after an ion exchange concentration procedure similar to that for nitrate. The authors believe that the extent of the hydrolysis of organic nitrogen and phosphorus in conventional methods of analysis has not been sufficiently appreciated.

No attempt was made to modify this procedure for application to sea water. If use of the ion exchange process for saline samples were desired it might be possible to reduce the halide concentration sufficiently by complexing the chloride with mercury(II) acetate.

ACKNOWLEDGMENT

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Calculation of Transfers Needed in Countercurrent Distribution

EINO NELSON

School of Pharmacy, University of California Medical Center, San Francisco, Calif.

A method of calculating the number of transfers needed to effect a given degree of separation between a pair of solutes distributed in the countercurrent process is described. It is based on finding the number of transfers to obtain a given fraction of either solute between the peak of its distribution and the intersection of the distribution curves for the solutes distributed. Applications of the equations developed are illustrated and possible sources of error due to the method are discussed.

SEVERAL methods are available for calculating the number of transfers needed to obtain a given degree of separation in the Craig countercurrent distribution process or for estimating the degree of separation obtained after a given number of transfers are applied. Among the methods available for calculating either or both of these quantities are those of Gregory and Craig (*2*), Hecker (*3*), Nichols (*5*), and Weisiger (*6*). In determining the number of transfers needed to obtain a given degree of separation between a pair of solutes distributed, the number calculated will vary, depending on the method of calculation chosen. This note describes a generally applicable method that is as accurate as possible when using Laplace's approximation to the binomial expansion that describes a countercurrent distribution.

In the Craig countercurrent distribution process, the distribution of a solute may be described by

$$Tn,r = \frac{n!}{(n-r)!r!}(X)^r(Y)^{n-r} \qquad (1)$$

where Tn,r is the fraction in tube r after n transfers, X is the fraction transferred with the moving phase (assumed to be the upper phase), and Y is the fraction remaining in the stationary phase (*1*). If a pair of solutes are distributed in the process, each solute is assumed to be distributed independently of the other and describable by Equation 1 with known values of X and Y. After the distribution of a pair—for example, solutes 1 and 2 with X and Y values, respectively, of X_1,Y_1 and X_2,Y_2—there will be some tube, r_i, in which equal fractions of solutes 1 and 2 will be found. This corresponds to the intersection of the two distribution curves (*5*). Therefore,

$$(Tn,r_i)_1 = (Tn,r_i)_2$$

from which on substitution with Equation 1 and solving for r_i,

$$r_i = \frac{n \log\left(\frac{Y_2}{Y_1}\right)}{\log\left(\frac{X_1 Y_2}{X_2 Y_1}\right)} \qquad (2)$$

The fact that Equation 1 is not defined for other than integral values of r results in no loss of generality.

The fractions of each solute between the peaks of their distributions, nX_1 and nX_2, and r_i may be found by use of the following equation and tabulated values for its integral (*4*):

$$Tn,r = \frac{1}{\sqrt{2\pi nXY}} e^{-\frac{(nX-r)^2}{2nXY}} \qquad (3)$$

This expression is generally accepted as a good approximation for Equation 1 when n is large and the quantity $(nX-r)$ is small in relation to nX and nY. Here, $(nX - r_i)$ is the absolute number of tubes between the peak of the distribution and the tube corresponding to the intersection of the two distribution curves. Tabulated values of the integral of Equation 3 are so arranged that the tables are entered with a number,

$$t = \frac{(nX-r)}{\sqrt{nXY}} \qquad (4)$$

and the area (fraction) between nX and r is available directly.

Thus, after n transfers, the fraction of solute 1 or 2 between the peak of its distribution and r_i may be easily found.

CALCULATION OF TRANSFERS TO EFFECT SEPARATION

A problem of greater interest than the above is the determination of the number of transfers needed to obtain a given fraction of either solute between its peak and r_i. This calculation is possible using Equations 2 and 4. Writing Equation 4 in terms of solute 2 and r_i,

$$t = \frac{(nX_2 - r_i)}{\sqrt{nX_2Y_2}}$$

and substituting 2 for r_i

$$t = \frac{(nX_2 - nA)}{\sqrt{nX_2Y_2}} \text{ where } \left[A = \frac{\log \frac{Y_2}{Y_1}}{\log \left(\frac{X_1}{X_2} \frac{Y_2}{Y_1} \right)} \right]$$

give an equation which may be solved explicitly for n:

$$n = \frac{t^2 X_2 Y_2}{(X_2 - A)^2} \tag{5}$$

To use Equation 5, a t from the tabulated values of the exponential function is found that corresponds to the fraction (area) of solute 2 desired between the peak of its distribution, nX_2, and r_i. Then n is readily calculated. Equation 5 may also be written in terms of X_1 and Y_1 to obtain n for a given fraction between nX_1 and r_i.

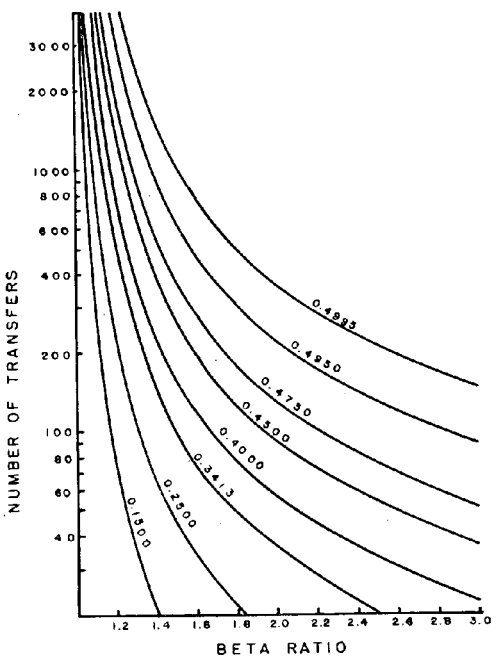

Figure 1. Number of transfers needed to obtain various fractions between peak of a solute's distribution and tube corresponding to intersection of its band with other solute's of the pair distributed as a function of beta ratio

Fractions marked on each curve. Curves drawn for solute 2 having partition ratio of 2. Solute 1 of pair with partition ratio of 1

Figure 1 shows n as a function of beta ratio and fraction of solute 2 between nX_2 and r_i. Here $\beta = \frac{K_2}{K_1}$, $K_1 = 1$.

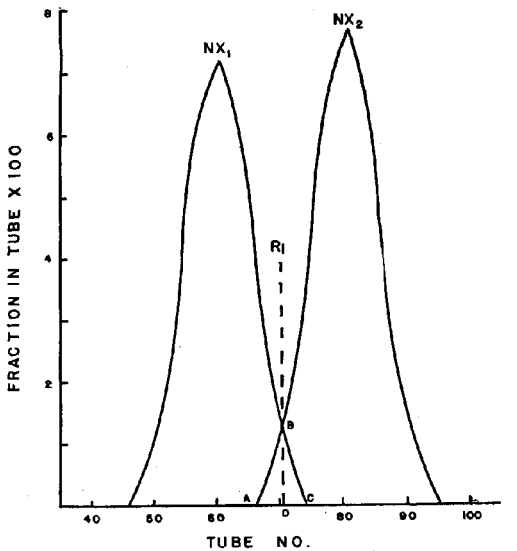

Figure 2. Hypothetical countercurrent distribution for two solutes

R_i. Tube corresponding to intersection of bands
K_1. 1
K_2. 2

The plot of Figure 2 is for the distribution of two solutes with partition ratios $K_1 = 1$ and $K_2 = 2$. It was calculated from Equation 5 that 121 transfers would be needed to obtain 47.2% of solute 2 between $nX_2 = 80.7$ and $r_i = 70.7$. Then 97.2% of solute 2 would be contained in all tubes from the extreme right to r_i. If the contents of these tubes were recovered, the percentage of solute 2 in sample would be:

$$\% S_2 = \frac{0.972 \times 100}{0.972 + F}$$

where F is the fraction of solute 1 in tubes r_i and others to the right of r_i (corresponding to area DBC in Figure 2). This quantity is readily found by subtracting the fraction between nX_1 and r_i from 0.5; the fraction between nX_1 and r_i is found by entering the tabulated values of the exponential function with

$$t = \frac{(nX_1 - r_i)}{\sqrt{nX_1Y_1}}$$

In this case area DBC is equivalent to the fraction 0.032 of solute 1. Therefore,

$$\% S_2 = \frac{0.972 \times 100}{1.004} = 96.8$$

For other than 1 gram of either solute initially present, the above expression would require insertion of the amount of the fraction. A similar calculation may be made to determine the percentage of solute 1 in all tubes from the extreme left to r_i.

SOURCES OF ERROR IN CALCULATIONS

The validity of the calculations described depends on how well

a particular distribution curve is approximated by the exponential function, Equation 3. One source of error is the symmetry of the exponential function. A perfectly symmetrical distribution results only when the fraction in the stationary or moving phase is 0.5 ($K = 1$). The error from this source decreases both with approach to this condition and with increasing n. If n calculated for $t = 1$ was in error by Δn, then the error in n for some larger value of t would be $t^2\Delta n$. However, t varies only from 1 to 3.27 for fractions between nX and r_i of 0.3413 and 0.4995, respectively.

In all the preceding, it has been assumed that the solutes behave ideally and that the volumes of the moving and stationary phases are equal.

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Direct Titration of Oxirane Oxygen with Hydrogen Bromide in Acetic Acid

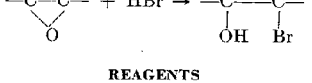
A. J. DURBETAKI

Becco Chemical Division, Food Machinery and Chemical Corp., Station B, Buffalo 7, N. Y.

A direct method for titrating oxirane oxygen with hydrogen bromide in acetic acid makes possible the determination of a variety of epoxy compounds, epoxy resins, and epoxy plasticizers with increased speed and accuracy. Carboxylic acids, aldehydes, ethers, esters, and peroxides do not interfere. Hydroperoxides react slowly with the reagent but give no interference.

EPOXY compounds have assumed commercial importance in recent years with the advent of resins, epoxy plasticizers, epoxy stabilizers, and epoxy insecticides. This has focused increased attention on analytical methods for oxirane oxygen. Until now oxirane oxygen has been determined by indirect methods (*1–3, 5, 6, 8, 9, 11*). The methods that have found the widest applicability because of their specificity employ hydrogen chloride in ether, dioxane, and pyridine (*2, 6, 9, 11*). All these methods are based on the addition of hydrogen chloride to oxirane oxygen to form the corresponding chlorohydrin. The difference between the amount of unconsumed hydrochloric acid and that of the corresponding blank is a measure of the epoxy content. As carboxylic acids interfere with these determinations, a correction for the amount of acid present in the sample has to be made. In general, these methods require appreciably more time and operations and involve errors of three, as compared with one, separate titrations to obtain the oxirane oxygen content.

The first direct titration procedure for oxirane oxygen (*4*) employed an acetic acid–hydrochloric acid reagent. Titrations were performed potentiometrically. The method presented here is an improved and simplified procedure, which utilizes an acetic acid–hydrobromic acid reagent. Visual end points can be employed and the general range of applicability is considerably extended. Hydrogen bromide is a much stronger acid than hydrogen chloride in glacial acetic acid (*7*) and reacts to a faster rate with the α-epoxy group.



REAGENTS

Acetic acid, glacial, analytical reagent grade.
Benzene, analytical reagent grade.
Chlorobenzene, Eastman Kodak Co.
Crystal violet indicator solution, 0.1% crystal violet (Eastman) in glacial acetic acid.
Hydrogen bromide, anhydrous, Matheson Co.
Hydrogen Bromide in Acetic Acid, 0.1*N*. Bubble anhydrous hydrogen bromide at a slow rate through 1 liter of glacial acetic acid, until the desired normality is attained. Standardize against 0.1 gram of sodium carbonate, dissolved in 5 ml. of glacial acetic acid, and titrate to the blue-green end point of the crystal violet indicator.
Sodium carbonate, primary standard grade, Mallinckrodt. Dry to constant weight at 120° C.

APPARATUS

Reservoir Buret, Karl Fischer Type, Arthur H. Thomas Co., No. 2484-B. Fill the drying tubes of the reservoir and buret with Todd universal absorbent. Replace the drying tube of the reservoir with a ball joint stopper when the buret is not in use.
Rubber Stopper, made of soft red rubber with section perforated to within 1 mm. of the top (Will Corp., No. 6402). Make a spherical opening large enough to accommodate the buret tip snugly with a very small side opening to allow escape of replaced air during titration.
Magnetic stirring bar, Teflon-sealed, Schaar.
Magnetic stirrer, variable speed.

PROCEDURE

Weigh accurately a sample of 0.3 to 0.6 gram in a 50-ml. Erlenmeyer flask. Dissolve epoxy resins in chlorobenzene, other compounds in chlorobenzene or benzene. Add 5 drops of 0.1% crystal violet indicator solution, place the rubber stopper in position, and lower the buret tip to a point just above the solution. Titrate the sample to the blue-green end point while stirring at a slow speed with the magnetic stirrer.

RESULTS AND DISCUSSION

A variety of purified epoxy compounds and commercial epoxy plasticizers were analyzed. In order to evaluate the method, especially where the purity of the epoxy sample was not known, the results were compared with those obtained by the hydrochloric acid–ethyl ether method (*11*) or the pyridinium chloride–pyridine method (*2*). The oxirane oxygen content obtained by the acetic acid–hydrobromic acid method is in excellent agreement with those obtained by the other two methods (Table I). The reaction with all compounds tested so far is almost instantaneous and proceeds at a speed equal to that of aqueous acid–base titrations. Epoxides, such as styrene oxide, which isomerize readily in acid media cannot be titrated quantitatively by this method. This is also true of other methods employing acidic reagents (*5*).

Although glacial acetic acid can be used as a solvent, in the presence of chlorobenzene or benzene sharper end points are obtained without sacrificing the speed of the reaction. Because of its greater polarity, chlorobenzene is preferable, especially in the titration of epoxy resins. In cases where desired, the titration can be followed potentiometrically using the glass-calomel electrode system as in the acetic acid–hydrochloric acid method (*4*). The sample is dissolved in 10 ml. of glacial acetic acid and a mechanical stirrer is used. Three potentiometric titration curves for a plasticizer, epoxy resins, and an epoxy compound are given in Figure 1.

The specificity of the reagent to the α-epoxy group was checked by investigating the possible interference of other functional groups. With peroxides such as oleyl peroxide, lauroyl peroxide, and benzoyl peroxide, the end points were stable for more than 5 minutes. A slow reaction of hydroperoxides was noticed but with no observable interference, as indicated by the study of mixtures of varying concentrations of cumene hydroperoxide and 9,10-epoxystearic acid and similar mixtures of *tert*-butyl peroxide and 9,10-epoxystearic acid (Table II). The end point is sharp and stable for about half a minute. The apparent reaction rate of hydroperoxides is slower than that of the oxirane oxygen and no apparent reaction of the hydroperoxide prior to the complete reaction of the epoxy group was observed.

Table I. Determination of Oxirane Oxygen by Hydrogen Bromide in Acetic Acid

Compound	% Oxirane Oxygen: Acetic acid–HBr[a]	Other	Theory
1,2-Epoxydodecane	8.65 ± 0.01 (6)	8.63[b]	8.68
9,10-Epoxystearic acid	5.34 ± 0.01 (6)	5.34[b]	5.32
Butyl epoxystearate	4.48 ± 0.01 (3)	4.49[b]	4.49
9,10-Epoxyocta-1-decanol	5.61 ± 0.00 (4)	5.62[b]	5.59
Cyclohexene oxide	16.22 ± 0.01 (4)	16.2[b]	16.30
Limonene monoepoxide	10.49 ± 0.02 (12)	10.44[b]	10.51
Glycidyl phenyl ether	10.58 ± 0.02 (5)	10.54[c]	10.65
Epoxy soybean oil	6.62 ± 0.00 (6)	6.5[c]	...
Epon 828	8.54 ± 0.02 (5)	8.5[c]	...
Armstrong epoxy resin C-4	9.43 ± 0.01 (6)	9.4[c]	...

[a] Figures in parenthesis represent number of determinations.
[b] Ether–hydrochloric acid method (*11*).
[c] Pyridinium chloride–pyridine method (*2*).

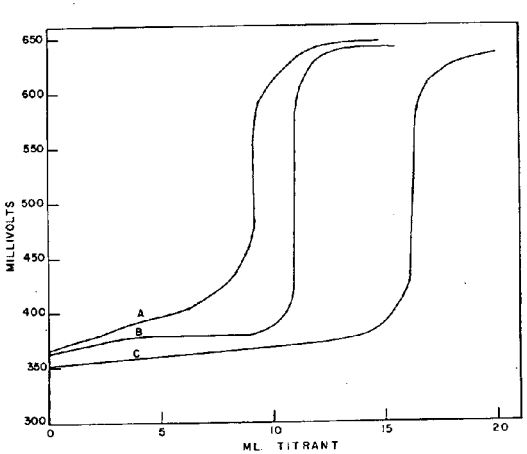


Figure 1. Potentiometric titration of oxirane oxygen by hydrogen bromide in acetic acid
A. **Epon 828**
B. **Limonene monoepoxide**
C. **Epoxy soybean oil**

Table II. Effect of Hydroperoxides on Oxirane Oxygen Determination by Hydrogen Bromide in Acetic Acid

Composition of Mixture, %: 9,10-Epoxystearic acid	Hydroperoxide	% Oxirane Oxygen: Calculated	Determined
99.2	0.8[a]	5.31	5.24
82.6	17.4[a]	4.43	4.37
71.9	28.1[a]	3.85	3.85
69.9	30.1[a]	5.01	4.93
49.0	51.0[a]	2.62	2.63
16.7	83.3[a]	0.89	0.95
92.9	7.1[b]	4.98	4.93
78.5	21.5[b]	4.20	4.19
53.2	46.8[b]	2.85	2.92
4.1	95.9[b]	0.22	0.28

[a] *tert*-Butyl hydroperoxide.
[b] Cumene hydroperoxide.

Other oxygenated compounds, carboxylic acids, aldehydes, alcohols, ethers, and esters were tested for interference by using 9,10-dihydroxystearic acid, 1-ketostearic acid, oleic acid, oleyl alcohol, furfuryl alcohol, dioxane, 2-butyraldehyde, benzaldehyde, eleostearic acid, butyl oleate, and methyl oleate in concentrations varying from 1 to 100%. No interference by these compounds was encountered. Solvents such as chloroform, carbon tetrachloride, and hexane did not interfere nor indicate any slowing in the apparent reaction rate of the oxirane oxygen with the titrant when present in the sample. Amines are readily titrated in glacial acetic acid and accordingly, as in the case with other oxirane oxygen methods, they interfere (*10*). The potentiometric differentiation of the amines in the presence of oxirane oxygen is possible. Although 1 to 1.5% of water does not seem to interfere, its effect on the epoxy titrations was not fully investigated and therefore it should be kept as low as possible. Acetic anhydride in general cannot be used to eliminate water. Addition of acetic anhydride resulted in poor end points and inconsistent results. Olefins were tested for possible addition of hydrobromic acid to the double bonds, with no apparent interference, and the end points were stable.

Although daily standardization of the reagent is preferable, no significant change of the titer was observed at temperatures of 25° to 27° C. and with the Karl Fischer-type buret. The method is very fast and eliminates long periods of reaction required by the indirect methods. The apparatus and technique used are simple and give excellent reproducibility when applied under the conditions described.

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Some Components of the Gas Phase of Cigarette Smoke

ROGER J. PHILIPPE and MARCUS E. HOBBS
Duke University, Durham, N. C.

The analysis of the gas phase of cigarette smoke by application of an infrared absorption compensation technique has been extended to cigarette smoke from two additional tobacco compositions. Compounds identified and quantitatively determined that were not reported previously include butane, isobutylene, benzene, toluene, furan, and 2-methylfuran. A table lists the most useful absorption bands for the compounds identified, and several absorption bands for substances not yet identified are discussed. The differences observed in the concentrations of several constituents are discussed on the basis of the different types of tobaccos investigated.

EXTENSION of previous studies of the gas phase of cigarette smoke to two additional tobacco compositions—a blend of 50% cased burley—50% bright and turkish tobacco samples—was desirable to supplement data previously reported (*21*). The results reported in the present paper and the previous one (*21*) essentially complete the authors' study of the gas phase of smoke from cigarettes made from the chief types of cigarette tobaccos. It is felt that with the exception of some saturated hydrocarbons and possibly a heterocyclic compound as yet unidentified, the major components of the gas phase have been qualitatively and quantitatively established. There remains a considerable number of minor constituents on which further study could be made, but pursuit of such a program will require rather large numbers of cigarettes as a sample and would advisedly make use of more effective methods of fractionation than have been used in the present or previous studies. The LeRoy distilling column (*19*) and gas chromatography (*14–16*) hold considerably more promise in this respect than the method used in the present investigation, which employs trap-to-trap type of distillation.

APPARATUS AND EXPERIMENTAL PROCEDURES

The apparatus and experimental procedures required for this study have been described (*21*), and in the present investigation all experimental variables such as puffing time, puff volume, cigarette weight tolerances, conditioning procedures, etc., were made to conform as nearly as was practicable to conditions previously used. One point of difference resulted from the use of a different syringe in the present work. The average volume per puff was approximately 36.8 cc. at room temperature and pressure rather than the 35 cc. per puff used in the previous work. This accounts for a puff volume at normal pressure and temperature of approximately 34 cc. in the present work as recorded in Table I in contrast to approximately 32 cc. in previously reported data. The results, using infrared absorption measurement, of the analysis of the gas phase of smoke from cigarettes made from bright, burley, cased burley, and a blend of 50% bright–50% burley tobaccos were given in the previous paper (*21*). The same procedure was used in the present investigation for the analysis of the gas phase of the smoke from cigarettes made from a blend of 50% bright–50% cased burley (10% dextrose) and from turkish tobaccos.

A sample spectrum obtained on the model 21 Perkin-Elmer instrument, using a sodium chloride prism, shows the essential features of the method used (Figure 1). In Figure 1 the compensated blank, or upper trace, shows slight overcompensation.

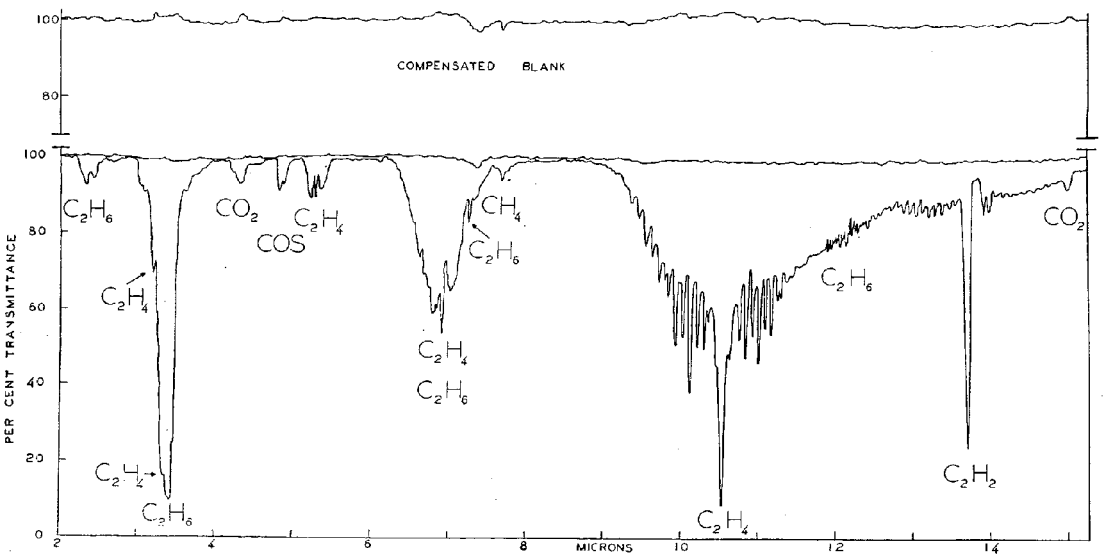

Figure 1. Sample spectrum of condensable fraction collected at −154° C. from gas phase of smoke of sixty 50% bright–50% cased burley cigarettes

Showing absorption bands for constituents present, cell blank, and blank after compensation

Table I. Summary of Analyses by Infrared Methods of Gas Phase of Cigarette Smoke

Component	Volume, Cc./Puff at NPT		Mole % of Total Gas Phase	
	Blend 50% bright-50% cased burley	Turkish	Blend 50% bright-50% cased burley	Turkish
CO_2	3.0	2.5	8.7	7.3
CO	1.4	0.95	4.2	2.8
CH_4	22.0 $\times 10^{-2}$	16.0 $\times 10^{-2}$	0.64	0.47
Ethane	4.1 $\times 10^{-2}$	3.2 $\times 10^{-2}$	12.0 $\times 10^{-2}$	9.3 $\times 10^{-2}$
Propane	1.6 $\times 10^{-2}$	....	4.7 $\times 10^{-2}$	....
Butane	0.2 $\times 10^{-2}$	....	0.5 $\times 10^{-2}$	....
Propane + butane	....	2.5 $\times 10^{-2}$	....	7.2 $\times 10^{-2}$
Ethylene	2.3 $\times 10^{-2}$	1.8 $\times 10^{-2}$	6.8 $\times 10^{-2}$	5.4 $\times 10^{-2}$
Propylene	0.68 $\times 10^{-2}$	0.74 $\times 10^{-2}$	2.0 $\times 10^{-2}$	2.2 $\times 10^{-2}$
Acetylene	0.38 $\times 10^{-2}$	0.33 $\times 10^{-2}$	1.1 $\times 10^{-2}$	1.0 $\times 10^{-2}$
Isoprene	3.1 $\times 10^{-2}$	4.8 $\times 10^{-2}$	9.2 $\times 10^{-2}$	14.1 $\times 10^{-2}$
Butadiene	0.17 $\times 10^{-2}$	0.18 $\times 10^{-2}$	0.5 $\times 10^{-2}$	0.5 $\times 10^{-2}$
Acetaldehyde	9.7 $\times 10^{-2}$	3.9 $\times 10^{-2}$	28.3 $\times 10^{-2}$	11.3 $\times 10^{-2}$
Acetone	1.4 $\times 10^{-2}$	1.1 $\times 10^{-2}$	4.1 $\times 10^{-2}$	3.1 $\times 10^{-2}$
Methyl ethyl ketone	0.18 $\times 10^{-2}$	0.08 $\times 10^{-2}$	0.5 $\times 10^{-2}$	0.2 $\times 10^{-2}$
Methanol	0.85 $\times 10^{-2}$	2.2 $\times 10^{-2}$	2.5 $\times 10^{-2}$	6.5 $\times 10^{-2}$
HCN	3.8 $\times 10^{-2}$	0.26 $\times 10^{-2}$	11.2 $\times 10^{-2}$	0.8 $\times 10^{-2}$
Diacetyl	0.09 $\times 10^{-2}$	0.09 $\times 10^{-2}$	0.3 $\times 10^{-2}$	0.3 $\times 10^{-2}$
COS	0.07 $\times 10^{-2}$	0.23 $\times 10^{-2}$	0.2 $\times 10^{-2}$	0.7 $\times 10^{-2}$
Methyl chloride	3.2 $\times 10^{-2}$	1.6 $\times 10^{-2}$	9.3 $\times 10^{-2}$	4.7 $\times 10^{-2}$
Isobutylene[a]	0.07 $\times 10^{-2}$	0.26 $\times 10^{-2}$	0.2 $\times 10^{-2}$	0.8 $\times 10^{-2}$
Benzene	0.15 $\times 10^{-2}$	0.11 $\times 10^{-2}$	0.4 $\times 10^{-2}$	0.3 $\times 10^{-2}$
Toluene	0.04 $\times 10^{-2}$	0.15 $\times 10^{-2}$	0.1 $\times 10^{-2}$	0.5 $\times 10^{-2}$
Furan	0.11 $\times 10^{-2}$	0.08 $\times 10^{-2}$	0.3 $\times 10^{-2}$	0.2 $\times 10^{-2}$
2-Methylfuran	~0.11 $\times 10^{-2}$[b]	0.02 $\times 10^{-2}$	~0.3 $\times 10^{-2}$[b]	0.07 $\times 10^{-2}$
Condensed phase analyzed[c]	3.3	2.7	9.7	8.0
Condensed phase not analyzed[d]	0.3	0.4	0.9	1.2
Total condensables	3.6	3.1	10.6	9.2
Total noncondensables	30.6	31.2	89.4	90.8
Total volume (NPT)	34.1	34.3		

Average of mass spectral analyses of infrared inactive constituents (mole %):

Air	~57% (±3%)
Nitrogen (excess)	~24% (±1%)
Hydrogen	~ 1.6%
Argon	~ 0.3%

[a] Isobutylene was previously determined for cigarettes made from bright and burley tobaccos. The mole % concentrations were, respectively, 0.6 $\times 10^{-2}$ and 0.7 $\times 10^{-2}$. This compound was not determined for cigarettes made from cased burley and from 50% bright–50% burley tobaccos.

[b] Estimated directly from spectrum.

[c] Sum of volumes in cc./puff at NPT and of mole % of condensables quantitatively accounted for. Essentially all CO and CH_4 were obtained in noncondensable fraction.

[d] Based on mass spectral analysis, this material consists of approximately 80 mole % water and 20 mole % of other constituents, including methanol and acetone.

In the regions between 3.2 and 3.3 microns near 6.9 and between 10.0 and 11.0 microns, the overcompensation resulted from impurities in the sample of ethane used for compensation. The ethane sample analyzed 95% of ethane with the remainder essentially ethylene. Slight overcompensation near 3.4 and 6.8, 4.3 and 15, and near 4.9 microns is due to ethane, carbon dioxide, and carbonyl sulfide, respectively. A small amount of uncompensated methane shows near 7.7 microns. The apparent undercompensation in the region of 7.4 microns is attributable to impurities on the cell windows, as may be seen from the cell blank trace.

The gas phase of smoke obtained from sixty regular size cigarettes, 70 mm. long, was used for the analysis of the condensable fraction. For the analysis of the blend, six fractions were collected at temperatures of −154°, −141°, −125°, −100°, −60°, and −20° C. The condensable gas phase of turkish cigarette smoke was separated into eight fractions collected at temperatures of −160°, −140°, −100°, −80°, −60°, −40°, −25°, and −15° C. The noncondensable fraction of the gas phase in the present investigation was analyzed by the procedure described (*21*).

RESULTS AND DISCUSSION

Table I gives a summary of the analyses. It is seen by comparison with the previously reported data (*21*) that some components in addition to those previously reported were identified and quantitatively determined: benzene, toluene, furan, and 2-methylfuran. Isobutylene was also determined on the new samples and had been determined on some of the samples previously reported, but was not included in the published data. Butane was identified, but it was rather difficult to estimate quantitatively because of the similarity of the useful absorption bands of ethane and propane. The figures for butane obtained for cigarettes made from the blend are given separately, but for turkish cigarettes, because the spectra did not allow one to distinguish between propane and butane, the results are given for the mixture of the two hydrocarbons. This difficulty is general for the saturated hydrocarbons containing more than three carbon atoms, and more efficient fractionation and identification techniques such as vapor chromatography, are very desirable in this connection. In addition to the difficulties experienced with the saturated hydrocarbons, there are some compounds, hydrogen sulfide for example, which may be present in the gas phase but which might not be detected at low concentrations by infrared absorption technique because of rather low absorptivity.

The characteristic absorption bands for benzene, furan, and 2-methylfuran were present in the spectra of the gas phase of smoke from tobaccos previously studied, but these compounds were not definitely identified at the time. In the present investigation toluene was identified in the fraction collected at approximately −20° C. and had not been found in previous work because the fractionation was carried only to −50° C. In the identification phase of this work, it was most useful to run reference spectra of pure gases or vapors at different pressures to locate the strongest and most specific absorption bands. The choice of an absorption band suitable for compensation depends, of course, on the partial pressure of the constituent in the specific mixture to be analyzed. For the components identified and quantitatively determined in the gas phase of cigarette smoke, the most useful absorption bands are listed in Table II along with the relative intensities and the absorption frequency values quoted from other authors. This table, by no means complete, is presented only as a working tool to facilitate identification of the components and selection of suitable bands for compensation. The agreement with other authors is generally good, except for a few cases such as carbon dioxide at 4.32 microns. In this case, the lack of agreement is primarily attributable to the accentuation

Table II. Band Location and Identification

λ, μ (±0.01 μ)	ν, Cm.⁻¹	ν, Cm.⁻¹ (Other Authors)		Relative Intensity	Component
2.69, 2.77	3717, 3610	3716, 3609	(17)	s.	Carbon dioxide
2.73	3663	3682	(17)	v.s.	Methanol
		3683	(27)		
3.01, 3.05 doublet	3322, 3279	3312.0	(17)	s.	Hydrogen cyanide
		3312.9	(27)		
3.18	3145	3120	(3)	s.	Ethylene
3.24	3086	3085	(6)	s.	Isoprene
					Ethylene
3.26	3067	3095	(5)	s.	Butadiene, 1,3
		3086	(2)		
3.32	3012	3020	(27)	s.	Ethylene
3.34	2994	3019.6	(17)	v.s.	Methane
		3020.3	(27)		
3.35	2985	2965	(6)	s.	Isoprene
3.37	2967	2959	(2)	s.	Butadiene, 1,3
3.37, 3.41 doublet	2967, 3933	2966.2	(17)	s.	Methyl chloride
		2967	(27)		
3.40	2941	2968.0	(17)	v.s. +	Propane
					Butane
3.43	2915	2894	(17)	v.s.	Ethane
		2895	(27)		
					Methanol
3.47	2882	2915	(3)	s.	Butane
3.52	2841	2844	(17)	v.s.	Methanol
		2845	(27)		
3.70	2703	2704	(25)	s.	Acetaldehyde
		2710	(20)		
4.32	2315	2349.3	(17)	v.s. +	Carbon dioxide
		2350	(27)		
4.61, 4.72 doublet	2169, 2119	2146, 2116.7	(18)	m.	Carbon monoxide
4.83, 4.86 doublet	2070, 2058	2079, 2050.5	(11) (12)	v.s.	Carbonyl sulfide
5.48, 5.53 doublet	1825, 1808	1821, 1812	(5)	s.	Butadiene, 1,3
		1828, 1812	(2)		
5.67	1764	1760, 1755	(25) (20)	v.s.	Acetaldehyde
5.75	1739	1725	(23)	v.s. +	Acetone
		1715	(26)		
					Methyl ethyl ketone
5.80	1724			v.s.	Diacetyl
6.00, 6.10 doublet	1667, 1639	1647	(17)	s.	Propylene
		1656, 1642	(4)		
6.23	1605	1608	(6)	s.	Isoprene
6.23, 6.30 doublet	1605, 1587	1608, 1597	(5)	s.	Butadiene, 1,3
		1603, 1587	(2)		
6.82	1466	1486	(17)	v.s.	Ethane
		1465	(27)		
		1477	(27)		
		1470	(17)		Propane
		1475	(7)		
		1462	(8)		Butane

λ, μ (±0.01 μ)	ν, Cm.⁻¹	γ, Cm.⁻¹ (Other Authors)		Relative Intensity	Component
6.93	1443	1440	(3)	s.	Ethylene
		1443	(4)		Propylene
		1445	(1)		Isobutylene
		1445	(6)		Isoprene
7.10	1408	1405	(25)	s.	Acetaldehyde
		1414	(20)		
7.27	1376	1375	(17)	s.	Propane
		1364	(7)		
7.33	1364	1354.9	(17)	s.	Methyl chloride
		1370	(25)		Acetaldehyde
		1373	(20)		
		1363	(23)		Acetone
		1388	(26)		
					Methyl ethyl ketone
					Diacetyl
7.36	1359			s.	Hydrogen cyanide
7.67	1304	1306.2	(17)	v.s. +	Methane
		1305	(27)		
8.23	1215	1202	(23)	v.s.	Acetone
		1221	(26)		
8.55	1170			v.s.	Methyl ethyl ketone
8.93, 9.07 doublet	1120, 1103	1114	(25)	s.	Acetaldehyde
		1121	(20)		
9.00	1111			v.s.	Diacetyl
9.68	1033	1033.9	(17)	v.s. +	Methanol
		1034.2	(27)		
10.08	992.1	991.1	(6)	v.s.	Isoprene
10.53	949.7	949.2	(17)	v.s.	Ethylene
		950	(27)		
		950	(3)		
10.97	911.6	910.7	(4)	v.s.	Propylene
11.02	907.4	909	(24)	v.s.	Butadiene, 1,3
		908.7	(5)		
		909	(2)		
11.05, 11.20 doublet	905.0, 892.9	905.8, 892.9	(6)	v.s. +	Isoprene
11.25	888.9	890	(1)	v.s.	Isobutylene
12.63	791.8			s.	2-Methylfuran
13.37	747.9	748	(17)	s.	Propane
		747	(7)		
13.45	743.5	725	(23)	v.s.	Furan
		763	(23)		
13.67	731.5	732.1	(17)	v.s.	Methyl chloride
		732.3	(27)		
13.71	729.4	729.1	(17)	v.s.	Acetylene
		729	(27)		
13.73	728.0	730	(10)	v.s.	Toluene
13.78	725.7			v.s.	2-Methylfuran
13.90	719.4	720.5	(17)	s.	Carbon dioxide
		720.9	(27)		
14.03	712.8	712.1	(17)	v.s.	Hydrogen cyanide
		712.3	(27)		
14.43	693.0	694	(10)	s.	Toluene
14.88	672.0	671	(17)	v.s.	Benzene
		671	(9)		
14.97	667.5	667.3	(17)	v.s.	Carbon dioxide
		667.5	(27)		

Relative band strengths. v.s. very strong (+ indicates stronger of two very strong bands for same substance); s. strong; m. moderate.

of the 4.32-micron band at the partial pressures of carbon dioxide encountered in these investigations. The data recorded in columns 1 and 2 of Table II have not been corrected to vacuum, whereas most of the data recorded in column 3 are corrected values. This accounts for some of the discrepancies observed and in other cases the data in columns 1 and 2 give the doublet, whereas the literature values may be for the unresolved band or for the band center. Some authors give the values for the P and R branches—for example, furan at 725 and 763 cm.$^{-1}$. The authors' value is for the Q branch and agrees well with the average of 744 cm.$^{-1}$ for the P and R branches given in the literature. The instrument used in their work was calibrated using atmospheric water vapor, carbon dioxide, and polystyrene film over the range from 2 to 15 microns. The maximum deviation from correct values found over this range was ±0.015 micron and in general the deviations were less than ±0.01 micron.

Several absorption bands are not yet identified. First, some strong bands occurring in the spectrum of −80° C. fractions are undoubtedly related to one or several saturated linear or branched hydrocarbons. As mentioned above, saturated hydrocarbons containing more than three carbon atoms, when examined at low pressure and over the limited spectral range used, are not readily distinguishable by the infrared technique. Table III gives the location of the bands the authors believe to be indicative of saturated hydrocarbons, along with the correlation given by Bellamy (*18*).

Table III.

	λ, μ	ν, Cm.$^{-1}$	ν, Cm.$^{-1}$ and Assignment (Bellamy, *13*)		
Sharp bands (strong)	3.45	2899	2853–2962	(25)	—CH stretching vibrations
	6.85	1459	1450 ± 20	(17)	—C—CH_3 asymmetrical deformation frequency
Broad bands (strong)	6.90	1449	1465 ± 20	(17)	—CH_2 deformation frequency
	7.25	1379	1380–1370	(25)	—C—CH_3 symmetrical deformation frequency
			1385–1365	(25)	—C—$(CH_3)_2$ deformation frequency
	8.80	1136	1170–1140	(25)	—C—$(CH_2)_2$ skeletal vibrations

Another absorption band occurs at 12.35 ± 0.01 microns or 809.7 cm.$^{-1}$ (*Q* branch) in the fraction collected at about −110° C. and seems to be most characteristic for smoke from burley tobacco cigarettes. The intensity of this band decreases rapidly in the sequence burley, cased burley, 50% bright–50% burley, 50% bright–50% cased burley, and is almost absent in the spectra of the gas phase of turkish and of bright tobacco cigarette smoke.

Two other absorption bands which appear in the spectrum of fractions collected at −80° C., are at 12.87 ± 0.01 microns or 777.0 cm.$^{-1}$ and 15.10 ± 0.01 microns or 662.2 cm.$^{-1}$. The out-of-plane vibrations of hydrogen atoms in planar systems such as benzene or heterocyclic structures seem to be associated with these bands, but as yet the authors have not identified the specific compound or compounds. The identity of the substances responsible for these two bands has recently been established on the basis of information given the authors by personnel of the American Tobacco Co. Research Laboratories. The band at 12.87 microns is characteristic of 2,5-dimethylfuran and the one at 15.10 microns is highly characteristic of cyclopentadiene.

Table I shows that, in general, the same constituents were present in the gas phase of smoke from cigarettes made from the blend and turkish tobaccos. The same conclusion was reached for the four previously studied (*21*) samples. On the other hand, the relative amount of some of the components showed considerable variations with the type of tobacco investigated. Table IV gives the mole per cent of the total gas phase of several constituents of the smoke for the types of cigarettes so far investigated, along with the average number of puffs required to smoke the cigarette to a standard butt length and the average weight of the cigarettes. In general, a decrease in the concentrations of carbon dioxide, carbon monoxide, ethane, ethylene, acetaldehyde, acetone, and methanol is apparent as one proceeds from burley to turkish cigarettes. The somewhat scattered results obtained for acetone and methanol might be explained by the relatively low vapor pressure and the high solubility of these compounds in water. This increases their tendency to remain in the unanalyzed water residue to an extent dependent on the fractionation procedure. Mass spectrographic analysis (*21*) of the water residue indicates a moderate amount of methanol and some acetone.

For the series of samples examined, the average number of puffs required to smoke one cigarette to a standard butt length increases from burley to turkish cigarettes. Combined with the over-all decrease of the total of the condensable fraction as we go from burley to turkish, this appears to reflect the graduation in the burning rates of the different tobaccos investigated.

The data in Table IV show that low molecular weight hydrocarbons like methane and acetylene did not vary significantly among the various types of tobaccos. No significant correlation was found for two other readily detected constituents—namely, isoprene and hydrogen cyanide. Each of these substances would need a more detailed and individualized study than was made in the present and previous investigations before one could reasonably suggest why they appear to follow no set pattern or whether the lack of a trend was attributable to variability in the procedures used.

The very low concentration of hydrogen cyanide found in turkish cigarettes—namely, about 1×10^{-2} mole % for turkish samples as compared with 10 to 30×10^{-2} mole % for the other samples investigated—is worthy of note, in that such differences may furnish useful leads as to the origin of the various components of the gas phase.

The techniques employed have given reasonably consistent results for the qualitative and quantitative analysis of the major components of the gas phase of cigarette smoke. The infrared technique must be supplemented by other methods to obtain a complete analysis, as some of the chief constituents of the gas phase such as nitrogen, oxygen, and hydrogen are infrared inactive. In spite of such limitations, it appears that the compensation technique is satisfactory where it can be used and is, in general, far superior to any other methods reported thus far in the literature.

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Table IV. Summary of Results on Some Selected Components

Type of Tobacco	Av. No. of Puffs	Av. Weight of Cigarette, G.	Mole % of Total Gas Phase: Total condensables	CH_4	C_2H_2 (× 10^2)	CO_2	CO	C_2H_6 (× 10^2)	C_2H_4 (× 10^2)	C_3H_6 (× 10^2)	Acetaldehyde (× 10^2)	Acetone (× 10^2)	Methanol (× 10^2)
Burley	7	0.92	16.2	0.6_3	0.9_3	12.2	5.7	12.0	8.1	7.2	49.0	21.2	7.9
Cased burley	8	0.86	14.6	0.6_7	2.8_0	10.8	4.4	13.5	7.6	12.4	37.0	17.7	7.8
50% burley and 50% bright	8	0.94	14.3	0.6_6	1.1_0	9.2	4.5	12.2	7.8	4.1	55.0	16.2	11.9
50% cased burley and 50% bright	10	0.97	10.6	0.6_4	1.1_0	8.7	4.2	12.0	6.8	2.0	28.3	4.1	2.5
Bright	10	1.23	10.3	0.6_0	1.3_0	8.0	3.3	9.7	5.0	3.6	11.0	5.3	4.5
Turkish	13	1.11	9.2	0.4_7	1.0_0	7.3	2.8	9.3	5.4	2.2	11.3	3.1	6.5

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Determination of Oxygen in Titanium, Zirconium, Chromium, Vanadium, and Steels by Bromination–Carbon Reduction Method

MAURICE CODELL and GEORGE NORWITZ

Pitman-Dunn Laboratories, Frankford Arsenal, Philadelphia, Pa.

Improvements have been made in the bromination–carbon reduction method for the determination of oxygen in titanium and titanium alloys. The factors contributing to the blank were investigated and the blank was reduced considerably by purification of the bromine. The method has been extended to the determination of oxygen in zirconium, chromium, vanadium, and steels.

RECENTLY this laboratory developed a new procedure for the determination of oxygen in titanium and titanium alloys by means of a bromination–carbon reduction technique (*7*). The sample was mixed with graphite and treated with bromine at 825° C., helium being used as a carrier gas. The oxygen in the sample was converted to carbon monoxide, which was oxidized to carbon dioxide with hot copper oxide and absorbed into a weighted bulb containing Ascarite. The titanium tetrabromide and bromine were frozen out by means of a dry ice and water trap, followed by two dry ice and alcohol traps.

As a result of further investigations, improvements have been made in the method as applied to titanium and titanium alloys, and the method has been extended to the determination of oxygen in zirconium, chromium, vanadium, and steels.

SPECIAL REAGENTS

Granular blister copper (Ledoux and Co., Teaneck, N. J.).

Fluorolube, MG grade, and liquid grade S (Hooker Electrochemical Co., Niagara Falls, N. Y.).

AGR graphite powder, prepared by scraping 0.75-inch graphite rods, grade AGR (National Carbon Co., Niagara Falls, N. Y.), with a clean razor blade. Discard the scrapings from the exterior surface of the rod. Store in a glass-stoppered bottle.

Spectrographic graphite powder. National spectrographic graphite powder, Grade SP-2, National Carbon Co., Niagara Falls, N. Y.

Purified Bromine. Set up a purification train by assembling the following items in consecutive order: tank of oxygen, column of Ascarite and Anhydrone to purify oxygen, inlet tube of bromine bottle, 1-liter bottle with a ground-glass mouth, outlet tube of bromine bottle, reaction tube packed with pieces of broken Vycor glass, a dry ice and water trap (250-ml. capacity), first dry ice trap, and second dry ice trap. Add about 500 ml. of C.P. bromine and 200 ml. of sulfuric acid to the 1-liter bottle. Heat to about 30° C. by means of a beaker of warm water. Bubble oxygen through the bromine at a fairly fast rate and pass the mixture of oxygen and bromine through the reaction tube heated to 1000° C. Condense the bromine in the traps in the usual manner. Allow the bromine to melt and store it in a dry glass-stoppered bottle.

Copper Sulfate–Asbestos Reagent. Ignite high purity asbestos in a muffle for 1 hour at 1000° C. to drive off organic material. Mix about 3 parts of asbestos with 1 part of C.P. anhydrous cupric sulfate by shaking in a closed bottle. Heat the mixture in an oven at 150° C. for 2 hours.

APPARATUS

The parts of the absorption train are identified in Figure 1. Kallmann (*17*) has modified the adapter which connects the bromine bottle to the reaction tube, so that samples can be inserted without disassembling the apparatus or turning off the heat. The adapter consists of a Vycor tube, 6 inches long and 1 inch in diameter, with a vertical tube in the center which connects to the bromine bottle. Large socket joints (35/25) are attached to the ends of the adapter. One of the joints fits on a ball joint attached to the end of the reaction tube; the other is fitted with a ball stopper which is removed to introduce new samples or to remove completed ones.

PROCEDURES

Titanium and Titanium Alloys. CASE I. SAMPLES CONTAINING LESS THAN 0.5% OXYGEN. Prepare the train as shown in Figure 1. Turn on all heaters except the one used to heat the reaction tube. Add to the bromine bottle approximately 150 ml. of purified bromine and 50 ml. of sulfuric acid. With the system disconnected before the reaction tube, pass helium through the bromine bottle for 15 minutes. Now turn the stopcocks so that the helium bypasses the bottle containing the bromine.

Prepare the sample in the form of chips about 0.02 inch thick. Clean with carbon tetrachloride and dry by heating at 50° C. Weigh out 2 grams of the sample and 1.5 to 2 grams of spectrographic graphite powder or AGR graphite powder. Place about one half the graphite on the bottom of a platinum or a gold boat. Place the sample on the carbon and cover the sample with the remainder of the carbon. Push the sample to the center of the heater. Assemble the system but do not connect the absorption bulb. Adjust the flow of helium to a fast rate and allow the system to flush for a few minutes. Decrease the flow of helium to 210 bubbles per minute. Turn on the heater for the reaction tube. While this heater is coming up to temperature, add about 150 ml. of water and several pieces of dry ice to the beaker for the dry ice and water trap. Fill the beaker for the first dry ice trap two thirds full and the beaker for the second dry ice trap entirely full with pieces of dry ice about 0.5 cubic inch in volume. Use of dry ice alone, instead of dry ice and alcohol (*7*), eliminates erratic results found with the latter.

When the temperature of the heater for the reaction tube has reached 925° C., connect the absorption bulb, and allow the helium to pass through the system for 10 minutes. Close the stopcock of the absorption bulb and disconnect. Open the stop-

cock momentarily to the atmosphere and weigh. Reconnect the bulb and weigh again after 10 minutes. If constant weight has not been reached, repeat the process.

Turn the stopcocks so that bromine flows through the system. Continue the flow of bromine for 30 minutes after the reaction is ended, as indicated by the complete disappearance of the cloud in the vertical portion of the reaction tube. Turn off the bromine and switch off the heater for the reaction tube but allow the helium to flow. Weigh the absorption bulb. Calculate per cent oxygen as follows:

$$\text{Per cent oxygen} = \frac{36.36\,(W - BT)}{M}$$

where

W = weight of carbon dioxide, grams
B = blank, grams of carbon dioxide per hour
T = time for run, hours
M = weight of sample, grams

Determine the blank by carrying 1.5 to 2 grams of graphite through the determination. Continue the flow of bromine for 2 hours and divide the gain in weight by 2 to obtain the hourly blank.

To prepare for the next run disconnect the reaction tube and three traps. Cautiously pour the contents of the dry ice and water trap into a 4-liter beaker containing about 1 liter of tap water. Allow the dry ice traps to thaw out for a few minutes, then add water and pour the contents into the 4-liter beaker. Add ammonium hydroxide (technical grade) or sodium thiosulfate (technical grade) to the contents of the beaker to destroy the bromine. Rinse all three traps thoroughly with hot water and dry by heating in an oven at 200° C. Remove the boat from the reaction tube and wash the reaction tube with ordinary household cleanser using a brush. It may be necessary to soak the reaction tube a few minutes in 1 to 3 hydrofluoric acid. Rinse the reaction tube well with hot water and dry it by heating with a blast burner while holding it with an asbestos glove. Remove the carbon from the boat and clean the boat by rubbing with steel wool and cleanser on a small glass plate. Soak the boat for a few minutes in an acid mixture made of equal parts of nitric and hydrofluoric acids stored in a plastic beaker. Wash the boat with water and dry it by heating in a Bunsen flame. Cool the heater used for heating the reaction tube to approximately room temperature by means of an air blast, or substitute another heater. Two or three successive runs on the same day may be made without cleaning the traps.

Case II. Samples Containing 0.5 to Approximately 1% Oxygen. Crush the sample with a steel mortar and pestle. Weigh out 1 gram of sample and 2 grams of spectrographic graphite powder. Place about one third of the graphite on the bottom of a platinum boat and mix another third of the graphite intimately with the sample. Place the mixture on the graphite contained on the bottom of the boat, and cover with the remaining third of the graphite. Compress with a small spatula. Proceed as in the regular method.

Case III. Samples Containing Approximately 1 to 3% Oxygen. Proceed as above, but use a 0.5-gram sample and after the run is finished transfer the graphite from the boat to a tared platinum crucible. Ignite in a blast burner, tilting the crucible to allow free access of air. Weigh the residue as titanium dioxide. Calculate per cent oxygen in the sample as follows:

$$\text{Per cent oxygen} = \frac{36.36\,(W - BT) + 40.05\,P}{M}$$

where P = weight of titanium dioxide, grams

Zirconium. Oxygen in zirconium has been determined by vacuum fusion (*35, 36*), isotopic dilution (*20*), chlorination using chlorine or hydrogen chloride (*22, 27*) and by igniting in oxygen and observing the gain in weight (*22*). Because of the similarity in the metallurgical and chemical properties of the zirconium-oxygen and titanium-oxygen systems (*8, 25*), the method can be readily applied to zirconium.

Zirconium tetrabromide (white) is produced in the bromination reaction (*31*). As with titanium, the end of the reaction is noted by the disappearance of the cloud in the vertical portion of the reaction tube. Zirconium tetrabromide and also chromium, vanadium, and iron bromides sublime on heating and do not have definite melting or boiling points at atmospheric pressure. This is in contrast to titanium tetrabromide, which has a definite melting and boiling point at atmospheric pressure. Commercial zirconium and zirconium alloys contain about 0.03 to 0.5% oxygen.

The determination of oxygen in zirconium is carried as for titanium

Chromium. Oxygen has been determined in chromium by vacuum fusion (*15, 33*) and by digesting with hydrochloric acid and filtering off the chromic oxide after annealing in a vacuum at 800° C. (*4, 30, 37*). Oxygen is present in chromium as chromic oxide inclusions (*37*). In electrolytic chromium the oxygen may be present as hydrous chromic oxide inclusions (*4, 37*).

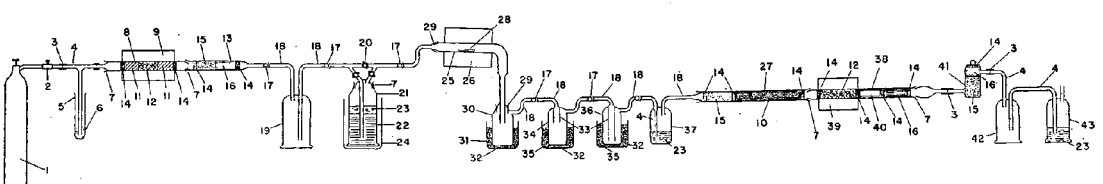

Figure 1. Apparatus for determining oxygen in metals

1. Tank of helium
2. Needle valve
3. Gum rubber tubing, small piece
4. Borosilicate glass tubing, 7 mm.
5. Mercury blow-off valve (7)
6. Mercury
7. Ground-glass joint (29/42)
8. Copper–copper oxide tube, 96% silica, 1 inch in diameter and 16 inches long
9. Electric heater for copper–copper oxide tube, 500° C., 11 inches long
10. Ascarite–copper sulfate tube, borosilicate glass, 1 inch in diameter and 11 inches long
11. Granular blister copper, or purified granular copper used in powder metallurgy
12. Copper oxide, fine wire form
13. Ascarite–Anhydrone purification tube, borosilicate glass, 1 inch in diameter and 8 inches long
14. Glass wool
15. Ascarite
16. Anhydrone
17. Ball joint (18/9)
18. Borosilicate glass tubing, 10 mm.
19. Suck-back trap for bromine, capacity about 250 ml.
20. Stopcock
21. Bromine bottle, 250-ml. gas washing bottle with 29/42 ground-glass joint
22. Purified bromine
23. Sulfuric acid
24. Beaker to protect bromine
25. Reaction tube (7)
26. Electric heater for reaction tube, 925° C., 10 inches long
27. Copper sulfate mixed with ignited asbestos
28. Boat about 3.5 inches long
29. Ground-glass joint (24/40)
30. Dry ice and water trap (7)
31. Dry ice and water
32. Dewar flasks, 500-ml. capacity, 3.5 inches wide and 6 inches high
33. Borosilicate glass tubing, 18 mm.
34. First dry ice trap (7)
35. Dry ice
36. Second dry ice trap (7)
37. Sulfuric acid bubble counter (7)
38. Copper oxide–Anhydrone tube, 96% silica, 1 inch in diameter and 13 inches long
39. Heater for copper oxide, 400° C., 7 inches long
40. 96% Silica tube, 0.75 inch in diameter and 2 inches long, to separate copper oxide from Anhydrone
41. Small absorption bulb, or U-tube with stopcocks
42. Small suck-back trap for sulfuric acid
43. Small sulfuric acid bubble counter

On heating electrolytic chromium the hydrogen is given off as elemental hydrogen and not as water vapor (*4, 37*). The bromination–carbon reduction method was found to be applicable to chromium. A reaction temperature of 925° C. must be used to obtain complete reaction of the oxides. Also, the sample should be powdered and mixed well with the graphite. No decomposition of the chromic oxide or reaction between the graphite and oxygen in the chromium would be expected to take place when the temperature of the reaction tube is raised to 925° C. (*9, 37*). The latter point was checked by obtaining constant weight of the absorption bulb while the reaction tube was at room temperature, then heating the reaction tube to 925° C. and holding it at this temperature for 1 hour. It is not possible to check for completion of the bromination reaction by examination for a cloud of chromic bromide in the vertical portion of the reaction tube, because most of the chromic bromide condenses toward the end of the horizontal part of the reaction tube. Therefore, an adequate time interval should be allowed for completion of the reaction; 2 hours were required for the samples used by the authors.

Chromic bromide rather than chromous bromide is formed in the reaction (*31*). Chromic bromide, once heated to redness, was found to be an extremely insoluble substance. The only effective solvent was a hydrochloric acid solution containing some chromous chloride. Such a solution has been used previously for dissolving anhydrous chromic chloride (*31*). The effect of the chromous chloride is probably catalytic (*31*). The solution for cleaning the reaction tube is best prepared by adding sodium or potassium dichromate to dilute hydrochloric acid (1 to 3) and then adding several grams of granulated zinc. The reduction of the chromium to the divalent state is not quantitative but sufficient chromous ion will be formed.

The oxygen content of commercial chromium is approximately 0.1 to 0.5%. The procedure for the determination of oxygen in chromium is the same as for titanium, Case II. Allow the reaction to proceed for 2 hours after turning on the bromine.

Vanadium. Oxygen in vanadium has been determined by vacuum fusion (*35*), and by difference (*29*). The vanadium-oxygen system bears some resemblance to the titanium-oxygen system and the zirconium-oxygen system, but the solubility of oxygen in vanadium is not as great as in the other two metals (*11, 29*). As with chromium a temperature of 925° C. and intimate mixing of the graphite with the crushed sample is recommended. No decomposition of the vanadium oxide or reaction between the graphite and the oxygen in the vanadium would be expected to take place when the temperature of the reaction tube is raised to 925° C. (*11, 24*). This point was checked in the same way as for the oxygen determination in chromium. No evidence of the formation of vanadium oxybromide ($VOBr_3$) (*31*) was noted, probably because there is an excess of carbon in close contact with the sample. The bromide formed in the bromination is vanadium tribromide (black) (*31*). Gold boats used for vanadium samples were severely attacked; therefore, platinum boats are recommended. To test for completeness of the bromination reaction it is convenient to form a "window" by playing a flame on about 1 square inch of the vertical portion of the reaction tube, as has been suggested by Kallmann (*17*). The presence or absence of a cloud can then be readily observed.

Kallmann (*17*) found that, in analyzing vanadium alloys containing large amounts of aluminum, sometimes about 1 mg. of oxide, identified spectrographically as aluminum oxide (not yellow vanadic oxide), was left on igniting the graphite residue. It is, therefore, necessary to calculate this aluminum oxide to oxygen and add this figure to the amount of oxygen found on weighing the absorption bulb. Occasionally, a small amount of silicon dioxide is found with the aluminum oxide. Since the factor for converting aluminum oxide to oxygen is 0.471 and the factor for converting silicon dioxide to oxygen is 0.533, no significant error is made for the small residue encountered if it is assumed that the residue is all aluminum oxide. In analyzing titanium samples containing several per cent of aluminum, the presence of unreacted aluminum oxide was *never observed*.

Commercial vanadium and vanadium alloys contain about 0.1 to 2% oxygen. The samples available to the authors contained less than 0.75% oxygen. There are a great number of experimental vanadium alloys being produced and it is not certain that the method would be applicable to all of them.

The determination is the same as given for titanium, Case II. Use a 1-gram sample of vanadium when the oxygen content is less than 0.5% and a 0.5-gram sample when the oxygen content is greater than 0.5%.

If the sample contains appreciable amounts of aluminum, proceed in the same way, but after the run transfer the graphite to a tared platinum crucible. Ignite in a blast burner and weigh the residue as aluminum oxide. Convert the weight of aluminum oxide to oxygen, using the factor 0.471, and add this figure to the weight of oxygen in the absorption bulb.

Steels. Oxygen in steels has been determined by the following methods: vacuum fusion (*1, 38*); reduction with carbon at 1200° C. in an atmosphere of nitrogen (*32*); reduction with hydrogen (*6, 21*); solution methods whereby the metal is dissolved and the oxides remain (*26*); electrolytic methods whereby the specimen is made the anode, the metal dissolving while the oxides remain unattacked (*26*); chlorination methods (*26*); isotopic dilution methods (*19*); and reduction with aluminum at a high temperature to form insoluble aluminum oxide (*26*).

Deoxidized steels usually have an oxygen content of approximately 0.01 to 0.04% (*26*). In rimming steels the total oxygen content usually lies between 0.05 to 0.2%. Most of the oxygen is present in solid steel as duplex oxides and silicates of iron and manganese. In silicon killed steels, as much as 40 to 75% of the oxygen is present as combined silica. Aluminum causes submicroscopic inclusions of alumina to predominate. In rimming steels a considerable portion of oxygen is present as iron oxide. Traces of dissolved or entrapped gaseous oxygen may sometimes be present in steels.

Steel drillings have an oxide coating. If the sample is drilled carefully with the drill kept at room temperature, the oxide coating produced on the drilling will give an increase in oxygen content of the sample of 0.02 to 0.04% (*6, 21*). If the sample is drilled under oil, and the drillings are washed with benzene and stored in a desiccator, the oxygen content of the oxide coating will give an increase of 0.003 to 0.005% in oxygen content of the sample (*6, 21*). If solid polished pieces are used, the oxide coating is insignificant (*1, 38*).

Another important fact to be considered is that the oxides and carbides in the steel react on heating to give carbon monoxide (*9, 12, 16, 34*):

$$FeO + Fe_3C \rightarrow CO + 4Fe$$

The exact temperature at which this reaction takes place is uncertain. However, with solid pieces of iron and steel it would not be expected to take place below about 650° C. (*12, 34*). Because of the reaction indicated in the above equation, it is necessary to connect the absorption bulb before turning on the heater for the reaction tube. This increases the total blank for the run by about 0.4 mg.

There is no danger of direct reaction between oxides of iron contained in the sample and the graphite powder according to the following equation (*8*):

$$FeO + C \rightarrow Fe + CO$$

The diffusion rate of carbon into solid steel specimens that have been packed in graphite and heated to redness is insignificant (*24*). There is no danger that iron carbonyl will form according to the reaction:

$$Fe + 5CO \rightarrow Fe(CO)_5$$

This compound can be formed only by reacting iron and carbon monoxide in the temperature range from 100° to 300° C. (*31*). Above this temperature the compound decomposes and it is not formed with solid iron (*31*). Iron oxide will not decompose to iron and oxygen on heating (*9*).

Carbon monoxide might possibly combine with the ferrous bromide to form iron tetracarbonyl bromide [$Fe(CO)_4Br_2$]. It is known that this compound will be formed if the carbon monoxide is under pressure or if the ferrous bromide is dissolved in an inert solvent such as petroleum ether (*13*). Iron tetracarbonyl bromide is a yellow solid that decomposes above 55° C. To prove that iron tetracarbonyl bromide is not formed in reacting steel with bromine, 2 grams of pure iron were mixed with 2 grams of a titanium sample containing 0.34% oxygen. The sample was analyzed for oxygen by the bromination–carbon reduction method. No tendency toward low results for oxygen was observed. Ferrous bromide and not ferric bromide is formed when steel reacts with bromine at red heat (*31*).

The layer of graphite over the iron or steel should be tightly compressed to reduce any carbon dioxide that might possibly be produced by the following reactions (*3*, *9*):

$$FeO + CO \rightarrow Fe + CO_2$$

$$3Fe + 2CO \rightarrow Fe_3C + CO_2$$

The following reaction will not take place:

$$2CO \rightarrow CO_2 + C$$

because this reaction occurs above 925° C. only when there is an excess of carbon monoxide (*3*).

The specimens must be cleaned mechanically and not by pickling. If the samples are pickled, they will become saturated with hydrogen and, on heating in the reaction tube, may lose some oxygen as water:

$$H_2 + FeO \rightarrow Fe + H_2O$$

After standing for a few days, the hydrogen content of the pickled specimens drops to the normal solubility limit of hydrogen in steels (less than 0.0001%).

Either gold or platinum boats can be used for the determination of oxygen in iron and steel. The end of the reaction cannot be noted by observing whether there is a cloud in the vertical portion of the reaction tube, because the ferrous bromide collects mostly at the end of the horizontal portion of the reaction tube. Therefore, about 2 hours should be allowed after turning on the bromine. A sample larger than 2 grams cannot be used because the reaction tube becomes clogged.

The method is presently recommended for the determination of oxygen in steels containing more than 0.05% oxygen. The method may not be applicable without modification to the usual aluminum or silicon killed steels of commerce because of the microscopic inclusions of alumina or silica which such steels frequently contain.

Remove the external surface of the specimen with an abrasive wheel. Prepare strips of the sample about 1/8 inch thick. Polish with carborundum paper, brush with a camel hair brush, and wash well with acetone followed by carbon tetrachloride. Allow the sample to dry by standing in air for a few minutes. Place 2 grams of the sample on 1 gram of spectrographic graphite powder or AGR graphite powder contained on the bottom of a gold or platinum boat. Cover with another gram of graphite and compress the graphite with a spatula. Proceed as for titanium, but obtain constant weight with the reaction tube at room temperature. Then turn on the heater for the reaction tube, heat to 925° C., and turn on the bromine. Continue the flow of bromine for 2 hours. Deduct a blank run in the same manner as the sample.

RESULTS

Results on various samples for which methods are presented are given in Table I. For the most part results are in good agreement with those obtained by other methods. Difficulty was encountered in obtaining reproducible results for vanadium samples by the vacuum fusion method.

DISCUSSION

Preliminary studies were made of the factors involved in the

Table I. Results for Oxygen Determination

Sample	Bromination Method, %	Vacuum Fusion, %
	Titanium	
WA 9	0.135	0.134[a]
	0.136	
	0.124	
	0.124	
	Av. 0.130	
WA 10	0.135	0.130[a]
	0.133	
	0.127	
	0.140	
	Av. 0.134	
WA 12	0.339	0.336[a]
	0.349	
	0.344	
	0.351	
	Av. 0.346	
WA 53	1.24	1.25[b]
	1.24	
	1.31	
	1.24	
	1.17	
	Av. 1.24	
	Zirconium	
1	0.32	0.35[c]
	0.35	
	Av. 0.34	
2	0.04	0.03[c]
	0.02	
	Av. 0.03	
	Chromium	
1	0.31	0.30[c]
	0.30	
	0.29	
	0.30	
	0.31	
	Av. 0.30	
	Vanadium	
1[d,e]	0.70	0.53 (by diff.)
	0.71	
	0.72	
	Av. 0.71	
2[e,g]	0.55	0.71 (by diff.)[f]
	0.52	
	0.55	
	Av. 0.54	
	Steel	
1 NBS, Steel #7	0.115	0.107
	0.101	
	0.091	
	0.117	
	0.107	
	Av. 0.106	
2	0.060	0.068[c]
	0.059	
	Av. 0.060	

[a] Average of results by Task Force on Vacuum Fusion Analysis, Metallurgical Advisory Committee on Titanium.
[b] Result from T. D. McKinley (*23*).
[c] Determined by E. Schneider (*28*).
[d] Contains 93.68% V, 3.68% Al, 1.38% Fe, 0.73% Si.
[e] Obtained from E. Brown, Vanadium Corp. of America, Cambridge, Ohio.
[f] Results obtained from Vanadium Corp. of America (*5*).
[g] Contains 69.02% V, 28.43% Fe, 1.42% Ni, 0.09% N, 0.05% C, 0.17% Mn, 0.05% Cr, 0.06% Cu.

blank, which was approximately 0.5 mg. of carbon dioxide per hour (*7*). Some lots of C.P. bromine gave a blank as high as 1.5 mg. per hour. By passing bromine through the hot or cold reaction tube without the boat or graphite, almost the entire blank amount was obtained. This was probably caused by halogenated hydrocarbons present in the bromine (*18*).

Organic compounds in bromine are eliminated industrially by shaking with sulfuric acid (*39*). Various modifications of such a purification method were not entirely satisfactory. Bromine prepared by fusing pure potassium bromide with permanganate to oxidize the organic material and then treating with dichromate to release the bromine (*2*) gave no better blank than bromine prepared by treating with sulfuric acid.

With the bromine purified as recommended under Special Reagents, the blank could be reduced to 0.2 mg. per hour; by placing a column of copper sulfate mixed with asbestos after the Ascarite, it could be reduced further to 0.1 mg. per hour. What compound the copper sulfate eliminates is not known. Hillebrand, Lundell, Bright, and Hoffman (*14*) have used copper sulfate to remove hydrogen sulfide, hydrogen chloride, and chlorine. With the purified bromine it was not necessary to use a zinc column heated to 350° C. to purify the carbon monoxide. The elimination of the zinc column proved advantageous, because the zinc [and also silver (*7*)] was a considerable source of trouble.

Blanks obtained at 815° C. were slightly lower than those obtained at 925° C., but the latter temperature is recommended because the reaction proceeds faster.

The graphite probably contributes to the blank because it contains some oxygen. AGR graphite gives blanks of about 0.05 mg. more per hour than spectrographic graphite. However, if cost is a factor, the AGR graphite is recommended. If the graphite residue is to be ignited, as for titanium alloys containing more than 1% oxygen, spectrographic graphite powder should be used because the AGR graphite gives an added blank of 0.8 mg. from conversion of carbides to oxides. Igniting spectrographic powder gives no blank.

When the method described here is used, the effect of the boat on the blank, under ordinary circumstances, is not very great. The fact that platinum boats give higher blanks than gold boats (*7*) was attributed to the oxide coating found on platinum but not on gold. However, it is now believed that the reason for this is some catalytic effect of the platinum, which causes the carbon compounds in the impure bromine to break down into interfering substances (*10*).

The same blank was obtained with platinum boats as with gold boats that weighed less than 50 grams and were not spongy. The blanks with gold boats weighing more than 50 grams were somewhat greater than blanks obtained with smaller gold boats. However, by pretreating these larger gold boats in hydrogen at 700° C., the blanks were reduced to those obtained with small gold boats. Higher blanks will be obtained with gold boats that have become spongy. The sponginess in gold boats can be eliminated by flattening the gold with a clean hammer on a clean surface. This tendency to become spongy can be reduced considerably by covering the bottom of the boats with a thick layer of graphite when making a determination. The precaution should be especially observed if gold boats are used for titanium alloys containing vanadium. It is advisable to use platinum boats when the graphite residue is to be ignited for determining unreacted oxide. If gold boats are used in this ignition procedure, the results for oxygen will be somewhat high because a small quantity of gold is picked up by the graphite (*17*). For ordinary commercial titanium alloys, either platinum or gold boats can be used, but platinum boats are recommended because of their greater durability. The boats may be of the regular combustion type or made from sheet. If they are made from sheet, care must be taken that the graphite does not spill out of the ends onto the reaction tube.

The ground-glass joints and ball joints between the exit end of the reaction tube and the Ascarite should be sealed with a small amount of liquid Fluorolube grease S. The use of sulfuric acid (*7*) is not recommended, because the acid corrodes the metal clamps. The stopcocks for the bromine bottle should be greased with regular Fluorolube grease, MG grade (*7*). It has been definitely established that Fluorolube grease is not a cause of difficulty in the method.

Glass wool, if placed outside the heaters, can be used in place of the balls of fine copper wire previously recommended for holding the copper and copper oxide in place (*7*).

All the heaters are regulated by pyrometer control. The heater for the final copper oxide should be 400° C., rather than 500° C. (*7*). The helium flow rate is controlled at 210 bubbles per minute merely by counting the bubbles in the first bubbler. This rate is reproducible if an inlet tube of similar diameter (7 mm.) is used for the bubbler and if the height of the sulfuric acid in the bubbler is 1 to 3 inches.

An extremely important precaution to be observed with this method is frequent changing of the copper in the purification train. Consistently high results and failure to obtain constant weight of the absorption bulb is almost a certain indication that the copper needs to be changed. It may look fairly bright and still not be completely effective.

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Determination of Potassium as the Metaperiodate

RALPH E. JENTOFT[1] and REX J. ROBINSON

Departments of Chemistry and Oceanography, University of Washington, Seattle 5, Wash.

An analytical procedure for the determination of potassium with periodic acid is described, which is very sensitive, has wide range, and is free from the empiricism usually associated with the determination of this element.

A FEW years ago Willard and Boyle (*13*) developed a new procedure for the determination of potassium, in which the potassium was weighed as potassium metaperiodate or estimated iodometrically through reduction of the potassium metaperiodate to iodate with iodide at a pH of 7.5. To minimize the relatively large solubility error of potassium metaperiodate in water, a rather large volume of 1 to 1 ethyl alcohol–ethyl acetate was added and the temperature of the solution was lowered to about 0° C. Because the procedure of Willard and Boyle did not yield the accuracy desired for a particular application, it has been investigated thoroughly by the present authors. It was ascertained that the chief factors limiting the accuracy of the method were: the relatively great solubility of the potassium metaperiodate due to the dilution effect of the organic solvents, an insufficient common-ion effect, and the deposition of difficultly soluble sodium metaperiodate by surface evaporation of the volatile solvent.

To reduce the loss of potassium metaperiodate through solubility to its barest minimum, the following steps have been taken by the authors in their proposed method. The volume of water used for solution of the potassium sample was reduced to 4 ml. from 7 to 8 ml. as specified by Willard and Boyle. A 33% (by volume) ethyl alcohol solvent medium was used instead of the 90% ethyl alcohol–ethyl acetate medium of Willard and Boyle. The former medium was shown by the authors to be preferable because of its simplicity, lesser volatility, and lesser solvent effect. The pH of the solution was buffered to 3.5 with lithium acetate to give maximum common-ion effect. The temperature of the solution was lowered to 0° C. as was done by Willard and Boyle.

These measures are not without their disadvantages. Using a small volume of water for solution limits the amount of sample which can be dissolved. It also increases the ionic strength of the solution, which increases the solubility of potassium metaperiodate as shown by Jones and Heckman (*9*). The use of an added organic solvent produces a dilution effect and also decreases the activity of the common-ion. The adjustment of pH involves the use of a buffering agent, which also adds to the ionic strength of the solution. Cooling the solution to 0° C. reduces the common-ion effect of the excess metaperiodate as indicated by Crouthamel, Hayes, and Martin (*2*). Finally, these measures also suppress the solubilities of the periodate salts of other ions which may be present in the solution. In spite of these limitations, all the foregoing measures to suppress solubility may be utilized to net advantage.

Ammonium metaperiodate and the alkali metaperiodates have low solubilities and may interfere in the determination of potassium. Because rubidium and cesium are rarely present in significant quantities and ammonium salts are easily volatilized by ignition, sodium is the chief source of interference.

An excessive concentration of sodium is conveniently reduced to an allowable amount by a single separation of potassium as the insoluble potassium-sodium cobaltinitrite. Cobaltous ion is formed in the solution during subsequent destruction of the cobaltinitrite to render the potassium soluble again. This caused serious difficulties in the present investigation, until it was realized by the authors (*7*) that a redox reaction occurred between cobaltous ion and periodic acid. Fortunately, cobaltous ion may be rendered passive in the presence of periodic acid by converting it to the insoluble cobaltous oxalate with oxalic acid. The sodium present is precipitated as sodium acid oxalate at the same time. This suggested the possibility of initially removing sodium and the alkaline earths, if present, by precipitating as the oxalates rather than by some other separation procedure. However, because of difficulties in washing large bulks of insoluble oxalate, this procedure is feasible only in removing small amounts of these cations.

Many other aspects of the chemistry of periodic acid and its salts were involved in the development of this procedure (*5*).

SELECTION OF ORGANIC SOLVENT MEDIUM

The organic solvent medium for this procedure was selected only after careful consideration of a number of factors, the most important of which were the solubility of potassium metaperiodate and the effect of the solvent medium on the common ion.

The solubility of potassium metaperiodate was measured in a number of organic solvent–water mixtures cooled to 0° ± 0.1° C. in a chest type of refrigerator. In order to simulate as nearly as possible the solubility of potassium metaperiodate under the actual conditions of its precipitation in the analytical procedure

[1] Present address, California Research Corp., Richmond, Calif.

for potassium, the solubility measurements were made by precipitating an excess of a definite amount of potassium metaperiodate from a known volume of solution, 0.1*M* in periodic acid and buffered to pH 3.5 with lithium acetate. The organic solvent concentration was adjusted and the solution was agitated at 0° C. for at least 24 hours to allow for solubility equilibration. The precipitated potassium metaperiodate was filtered from the solution, washed with cold ethyl alcohol, and finally determined iodometrically. The difference between the amount of potassium taken and that found was considered to be the amount soluble as the metaperiodate. Complete details of the experimental procedure are given by Jentoft (*5*).

The data for the various organic solvent–water mixtures are presented in Table I, arranged in the order of decreasing efficiency of the solvent as solubility suppressors. The dielectric constants of the organic solvents have also been listed in Table I because of the correlation of dielectric constant with the common-ion effect.

The initial study was made with ethyl alcohol as the solvent over the entire range of concentrations. The authors (*6*) have shown by a graphical method that the minimum solubility for potassium metaperiodate occurred at an ethyl alcohol concentration of 35% by volume. A few pertinent data for ethyl alcohol have been presented in Table I for comparison with the other organic solvents. Preliminary solubility measurements with two or three appropriate concentrations of other organic solvent–water mixtures did not reveal a solvent which was considered more suitable than ethyl alcohol; consequently detailed solubility studies similar to that made for ethyl alcohol were not made for the other solvent systems. On the basis of the solubility data shown in Table I, ethyl alcohol and isopropyl alcohol are almost comparable in efficiencies. However ethyl alcohol was selected over isopropyl because of its ready availability, lesser cost, and higher dielectric constant which favors common-ion activity. A solution of high dielectric strength is preferable to keep the relative solubility of sodium metaperiodate high.

Table I. Solubility Data for Potassium Metaperiodate in Various Organic Solvent–Water Mixtures, 0.1*M* in Periodic Acid at pH 3.5

Organic Solvent	Dielectric[a] Constant	% Solvent	Solubility KIO_4, Mg. K/100 Ml.
Ethyl alcohol	22.0 (20° C.)	0	2.82
		16	0.86
		24	0.57
		32	0.43
		36	0.37
Isopropyl alcohol	15.7 (20° C.)	16	0.80
		24	0.50
		32	0.48
1 to 1 ethyl alcohol–isopropyl alcohol		16	0.80
		24	0.53
		32	0.43
tert-Butyl alcohol	6.6 (19° C.)	16	0.77
		24	0.55
		32	0.58
Methanol	33.1 (20° C.)	16	1.00
		24	0.65
		32	0.53
n-Propyl alcohol	12.3 (20° C.)	16	0.93
		24	0.70
		32	0.65
5 to 1 ethyl alcohol–ethyl acetate	6 (20° C.)	24	0.73
Ethyl Cellosolve		24	1.10
		32	1.18
Acetone	21.2 (20° C.)	16	1.95
		24	2.05
Butanone	18.1 (17° C.)	16	1.88
		24	2.20

[a] All dielectric constants measured at radio-frequency by Drude (*3*).

The solubility of potassium metaperiodate was determined to be equivalent to 0.009 mg. of potassium per 4 ml. of water under these conditions of determination. Since sodium commonly occurs with potassium, it seemed desirable to know the solubility of sodium metaperiodate. Under the conditions used for the determination of potassium a solubility value of 2.7 mg. of sodium per 4 ml. of water was obtained.

REAGENTS AND SOLUTIONS

Reagent grade chemicals were used throughout this investigation unless otherwise stated.

Periodic Acid. The periodic acid, prepared by the G. F. Smith Chemical Co., was checked for purity as described by Willard and Boyle (*13*) and found to be free of iodic acid. A reagent solution, containing 0.5 gram of H_5IO_6 per ml., was prepared as needed, as it was found to deteriorate on standing.

Potassium Metaperiodate. This salt was purified by recrystallization, dried first at 110° C. and then at 180° C. to constant weight according to Jones (*8*).

Lithium Carbonate. Lithium carbonate was suspended in distilled water and dissolved by bubbling carbon dioxide. Solution of the gas was aided by cooling the reaction vessel with an ice pack. The carbon dioxide was first washed through concentrated sulfuric acid, then through saturated sodium bicarbonate solution, and finally through distilled water. The lithium bicarbonate solution was filtered through a fritted-glass filter funnel and lithium carbonate was precipitated by heating the solution until evolution of carbon dioxide was complete. During this operation vigorous stirring of the suspended lithium carbonate was necessary to avoid bumping. The hot solution was decanted and the lithium carbonate was washed several times with boiling water. This procedure was repeated on the recovered product. The second crystalline precipitate of lithium carbonate was dried at 120° C. for 24 hours. The over-all yield was 65%.

Lithium Acetate. A 2.5*N* lithium acetate solution was prepared by dissolving 18.5 grams of lithium carbonate in 30 ml. of glacial acetic acid and diluting to 200 ml.

Oxalic Acid. Two solutions of oxalic acid were prepared; one had a concentration of 100 grams of oxalic acid dihydrate per liter, the other 10 grams per liter.

2,6-Dinitrophenol. A 0.1% solution was made up in water with the aid of an equivalent amount of lithium carbonate.

Potassium Iodate. The potassium iodate was purified by recrystallization, and dried at 100° C. and then at 180° C. to constant weight according to Scott (*12*). A series of standard solutions of appropriate concentrations was prepared on which to standardize all the sodium thiosulfate solutions except the 0.35*N* solution. Equivalent concentrations of potassium bromate were made according to Kolthoff and Sandell (*10*).

Sodium Thiosulfate. Solutions were prepared which were 0.35, 0.12, 0.04, 0.014, and 0.007*N*. These solutions were stabilized with sodium furoate, according to Platow (*11*). The sodium thiosulfate solutions were standardized against potassium iodate or potassium bromate. When standardized against potassium bromate, 4 or 5 drops of 3% ammonium molybdate solution were added to catalyze the oxidation of iodide as recommended by Kolthoff and Sandell (*10*). The 0.35*N* sodium thiosulfate solution was standardized with weighed amounts of solid potassium iodate or potassium metaperiodate.

Potassium Nitrate. The potassium nitrate was purified by recrystallization from water, and dried at 100° C. and then at 210° C. to constant weight according to Scott (*12*). Standard solutions were prepared to contain approximately 3, 1, 0.4, 0.12, 0.06, and 0.02 mg. of potassium per ml.

Organic Solvents. All the organic solvents were redistilled, using those portions which distilled over within a range of 1° to 2° C. A 2 to 1 ethyl alcohol–isopropyl alcohol wash liquor was also prepared.

Asbestos. Asbestos of good grade was digested with concentrated nitric acid for 4 hours, filtered, and washed with distilled water. This treatment was necessary to prevent retention of periodic acid which could not be washed free from the asbestos, causing high results.

ANALYTICAL PROCEDURE

The sample containing no more than 75 mg. of potassium is put into a 100-ml. beaker. Oxidizing and reducing agents may not be present. Halides are removed by evaporation just to dryness with nitric acid. Only lithium, sodium, and the alkaline earth cations (except barium) may be present.

With only small amounts of the alkaline earth cations and less than 2.5 mg. of sodium present, the potassium may be precipitated directly with periodic acid. Moderate amounts of these

cations (less than 1.5 times the equivalents of potassium) may be prevented from interfering by precipitation as the oxalates. A solution of oxalic acid in excess of that required to convert the cations to oxalates is added, together with 3 ml. of concentrated nitric acid. The solution is taken to dryness on the steam bath. Sublimed oxalic acid on the sides of the beaker is evidence that an excess has been added.

With large amounts of sodium, lithium, or alkaline earths present (except barium which forms insoluble cobaltinitrite), the potassium is separated by precipitation as potassium-sodium cobaltinitrite. The solution is adjusted to 25 ml. and 0.2 ml. of 0.1% gelatin solution is added. One gram of sodium cobaltinitrite is added and dissolved. The solution is cooled to 0° C., 25 ml. of 95% ethyl alcohol are added, and the solution is refrigerated at 0° C. for 8 hours. The solution is filtered and the precipitate and containers are washed once with 95% ethyl alcohol cooled to 0° C. The alcohol is evaporated completely on the steam bath and the precipitate is dissolved in 10 ml. of hot 5*N* nitric acid. The sodium is precipitated by adding oxalic acid in the ratio of 10 mg. of oxalic acid dihydrate per milligram of potassium in the sample. The solution is taken to dryness on the steam bath in preparation for precipitation with periodic acid.

The potassium is dissolved in 2 ml. of water and precipitated slowly by adding 1 ml. of periodic acid, containing 0.5 gram, in such a manner to attain maximum crystal size. Dropwise addition of the reagent over a period up to 30 minutes is required for maximum amounts of potassium. The solution must be stirred rapidly whenever the reagent is added and occasionally for a time thereafter.

About 10 minutes after the last addition of periodic acid, the pH of the solution is adjusted by adding 0.4 ml. of 2.5*N* lithium acetate dropwise with stirring. About 10 minutes later a drop (0.03 ml.) of 2,6-dinitrophenol indicator is added and the dropwise addition of lithium acetate is continued until the indicator turns a dark yellow, indicating a pH of 3.0 to 3.5. Usually a total volume of about 1 ml. of lithium acetate is required. Then 2 ml. of 95% ethyl alcohol are added. The beaker and contents are cooled for 30 to 40 minutes in an ice-bath or refrigerator, at 0° C.

The solution is decanted through a 10-ml. Gooch crucible (with an asbestos pad made from finely shredded fibers) cooled previously to 0° C. The precipitate and containers are washed 10 to 12 times, with minimum amounts of 2 to 1 ethyl alcohol–isopropyl alcohol at 0° C.

The potassium periodate is dissolved in 10 ml. of 4*N* sulfuric acid and 25 ml. of water. One to 5 grams of potassium iodide are added depending upon the amount of the precipitate. The liberated iodine is titrated with standard sodium thiosulfate solution of appropriate concentration, starch being used as the indicator.

DISCUSSION OF PROCEDURE

The available lithium carbonate always contained some potassium as an impurity, which necessitated purification before it was suitable for use in the preparation of the lithium acetate reagent.

Nitric acid must be present when the solution of oxalates is evaporated to dryness in order to deposit potassium as the soluble nitrate rather than the difficultly soluble potassium acid oxalate.

The authors have shown (*6*) that the minimum solubility loss of potassium periodate is experienced when a 35% (by volume) ethyl alcohol solution is used. In the previously outlined procedure the alcohol concentration is about 33% because it is impractical to adjust the concentration to 35%.

Under the conditions of this experimental work, no evidence was ever noted of oxidation of ethyl alcohol to aldehyde by periodic acid with subsequent reduction of potassium periodate. Consequently, the addition of ethyl acetate to retard the oxidation of ethyl alcohol was not required, as had been done by Willard and Boyle (*13*) when using a medium of higher ethyl alcohol concentration.

It is important to evaporate the ethyl alcohol wash solution completely before attempting to dissolve the potassium-sodium cobaltinitrite precipitate in hot nitric acid; otherwise there may be a reaction of near explosive violence between the hot nitric acid and the ethyl alcohol.

2,6-Dinitrophenol was chosen as the indicator both for its transition interval and for its resistance to oxidation by periodic acid.

Although the data of Crouthamel and coworkers (*2*) show that the maximum concentration of metaperiodate ion is attained at pH 5 for a temperature of 0° C., it is undesirable to adjust the pH to this value because of the danger of precipitating $Li_2H_3IO_6$. For this reason it seemed best to adjust the pH of the solution to between 3.0 and 3.5.

Table II. Analyses of Potassium Nitrate Samples by Periodate Method

K Taken, Mg.	No. of Samples	Mean of K Found, Mg.	Error for Set, Mg.	Group Average, Mg.	Standard Deviation, Mg.
74.92	3	74.77	−0.15		
74.95	3	74.83	−0.12	−0.13	±0.027
44.95	6	44.88	−0.07		
44.94	3	44.90	−0.04	−0.06	0.025
24.69	6	24.60	−0.09		
	3	24.63	−0.06		
24.68	3	24.66	−0.02		
24.71	4	24.65	−0.06	−0.06	0.026
14.81	6	14.79	−0.02		
	3	14.78	−0.03	−0.02	0.014
8.967	6	8.951	−0.016		
8.962	6	8.957	−0.005		
9.247	2	9.228	−0.019		
9.241	2	9.228	−0.013		
9.243	3	9.232	−0.011		
9.368	3	9.336	−0.032		
9.352	3	9.335	−0.017	−0.016	0.012
5.378	6	5.372	−0.006		
5.375	6	5.369	−0.006	−0.006	0.009
3.157	6	3.154	−0.003		
	7	3.160	+0.003		
3.751	3	3.729	−0.021	−0.007	0.009
1.511	6	1.513	+0.002		
	3	1.501	−0.010	−0.004	0.003
0.906	6	0.908	+0.002		
	3	0.893	−0.013	−0.006	0.004
0.507	6	0.512	+0.005		
	6	0.507	0.000	+0.003	0.005
0.304	2	0.298	−0.006	−0.006	0.008
0.203	6	0.204	+0.001	+0.001	0.007
0.101	8	0.098	−0.003	−0.003	0.009

The sodium cobaltinitrite was added as a solid as suggested by Burkhart (*1*) to encourage immediate precipitation of potassium-sodium cobaltinitrite. This technique was permissible because the stoichiometric composition of the precipitate was of less importance than the complete separation of the potassium. This also accounts for the fact that the precipitate does not need to be washed free of the excess reagent.

Gelatin is precipitated upon the addition of the ethyl alcohol and sweeps down the fine particles of the precipitate. This assists in the completeness of the precipitation.

Special care must be given to dissolve the evaporated sample completely in only 2 ml. of water. The oxalic acid which may have sublimed onto the sides of the beaker may be disregarded.

A light green color is often observed in the solution when potassium is precipitated as potassium metaperiodate in the presence of cobaltous oxalate. It is probably due to a cobaltic oxalate complex and causes no difficulty. Gmelin (*4*) reports that potassium and sodium cobaltic oxalate salts are dark green and very soluble.

The evaporate from the solution of potassium-sodium cobaltinitrite in nitric acid should not be heated above 100° C., as cobaltous oxalate may decompose to cobalt sesquioxide. If formed, this compound would later oxidize iodide to free iodine and invalidate the final determination of potassium.

The fundamental reaction for the volumetric determination of potassium as described indicates an equivalent weight of one eighth its atomic weight.

$$KIO_4 + 7I^- + 8H^+ \doteq K^+ + 4I_2 + 4H_2O$$

By the method of Willard and Boyle the equivalent weight of potassium is one half its atomic weight.

$$KIO_4 + 2I^- + 2H^+ = K^+ + I_2 + IO_3^- + H_2O$$

Thus the proposed method has a sensitivity four times that of the Willard and Boyle method, making it particularly suitable for the estimation of small amounts of potassium.

For amounts of potassium greater than 25 mg. the potassium metaperiodate may be determined by arsenite titration as described by Willard and Boyle (*13*). In their method the potassium metaperiodate is reduced to iodate with iodide in a buffered solution at pH 7.5 and the liberated iodine is titrated with standard arsenite solution. This obviates the use of a high normality sodium thiosulfate solution. By preference sodium thiosulfate solutions were used throughout the present study.

EXPERIMENTAL

Conditions of Measurement. The analytical weights were calibrated against Class M weights calibrated by the National Bureau of Standards. All weighings involved in the various analyses were corrected for air buoyancy effects. Calibrated Normax volumetric equipment was used throughout. Standard solutions were calculated to 20° C. In order to minimize errors in the calculated results, the normalities of the titrants were adjusted so that the titration volumes fell between 40 and 50 ml. whenever possible. Each titrant was always standardized in respect to two independent standard solutions and check values were demanded which differed by no more than 0.1%.

Proof of the Method. The reliability of the method previously presented was verified by analysis of known amounts of potassium. This was accomplished in two stages, because it was necessary to prove the method of determining the potassium with periodic acid before proving the method of separating the potassium with sodium cobaltinitrite. To test the recovery of potassium by the periodate procedure, known amounts of potassium nitrate were analyzed over a range of 0.1 to 75 mg. of potassium. The results of 139 analyses are presented in Table II. For verification of the entire procedure, known amounts of potassium nitrate were first precipitated as potassium-sodium cobaltinitrite and then estimated as the metaperiodate according to the prescribed procedure. The results of 56 analyses are given in Table III. No attempt was made to separate potassium from other than a solution of sodium cobaltinitrite, because the precipitation of potassium-sodium cobaltinitrite under various experimental conditions has been well treated in the literature.

Discussion of Results. Because of the large number of data involved, it is impractical to list the individual data for the analysis of the various amounts of pure potassium nitrate taken. Rather the mean of each set of analyses has been calculated as well as its deviation from the known amount of potassium taken for analysis, and these values are presented in Tables II and III. For a particular amount of potassium the average of these deviations has been taken as a measure of the error in the method for this amount. The deviation of each set has been given equal weight in this calculation because the results for a particular set are dependent upon the same experimental conditions. The standard deviation of the method for a particular amount of potassium has been calculated from all the results for that amount by treating the deviation of an individual result from the mean of the set. These values give a measure of the precision of the method.

These results for the proof of the periodate separation and estimation are recorded in Table II and have been plotted on a semilogarithmic scale in Figure 1. The standard deviation of the method has been plotted for amounts of potassium ranging from 0.1 to 75 mg. The error in the method as defined above also has been plotted for the same range.

Taking into account that a semilogarithmic plot has been used, it is seen that both the standard deviation and the error gradually increase for larger amounts of potassium. For amounts of potassium greater than about 3 mg. the results are low by less than 0.2% on the average. For amounts of potassium between 0.1 and 3 mg. the results are low by 0.005 mg. of potassium or less. The low results are attributed to the solubility error.

The standard deviation for amounts of potassium greater than 3 mg. is about ±0.1% on the average, being somewhat greater for small amounts and somewhat less for larger amounts. The standard deviation for amounts of potassium between 0.1 and 3 mg. is about ±0.005 mg. on the average, increasing somewhat for the smallest amounts.

The data for the analysis of various amounts of potassium nitrate after the preliminary separation of the potassium as the cobaltinitrite are presented in Table III. These results have been treated and presented in the manner described above.

From Figure 2 it is seen that the data present much the same picture as Figure 1. However, the solubility error is somewhat greater for these data for amounts of potassium greater than 3 mg. It varies from about 0.3% for 3-mg. amounts to less than 0.2% for 75-mg. amounts.

The standard deviation of these data for the largest amounts of potassium is a little greater than that shown by the data in Figure 1. However, it is still less than ±0.1% on the average for the amounts greater than 3 mg.

Undoubtedly there has been compensation of the solubility error to a small extent in almost all the analyses. The low solu-

Table III. Analyses of Potassium Nitrate Samples with Cobaltinitrite and Metaperiodate Precipitations

K Taken, Mg.	No. of Samples	Mean of K Found, Mg.	Error for Set, Mg.	Group Average, Mg.	Standard Deviation, Mg.
74.99	4	74.87	−0.12	−0.12	±0.050
44.94	3	44.86	−0.08		
44.98	4	44.95	−0.03	−0.05	0.046
24.68	3	24.61	−0.07	−0.07	0.010
14.80	3	14.78	−0.02		
14.84	3	14.80	−0.04	−0.03	0.017
8.969	4	8.944	−0.025		
8.967	3	8.956	−0.011		
9.368	3	9.336	−0.032		
9.369	5	9.342	−0.027		
9.377	3	9.354	−0.023	−0.023	0.009
5.624	5	5.614	−0.010	−0.010	0.002
1.491	4	1.487	−0.004	−0.004	0.005
0.507	2	0.505	−0.002		
0.508	4	0.504	−0.004	−0.003	0.003
0.203	3	0.201	−0.002	−0.002	0.002

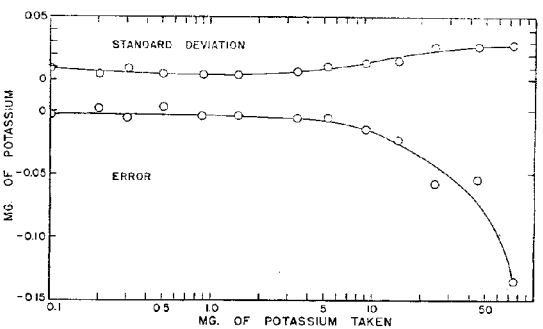

Figure 1. Analysis of results on potassium nitrate samples

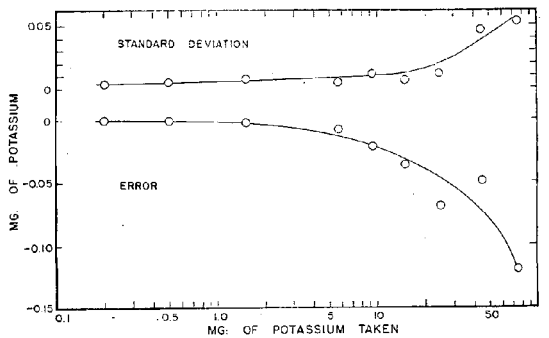

Figure 2. Analysis of results on potassium nitrate sample with cobaltinitrite and metaperiodate precipitations

bility error for small amounts of potassium is probably due to this. Since the precipitation of small amounts of potassium as the metaperiodate is slow and incomplete in aqueous solution, most of it precipitates upon addition of the ethyl alcohol, with resultant coprecipitation of periodate. The faster rate of precipitation inherent with the largest amounts of potassium taken for analysis would also be likely to cause some coprecipitation of periodate. The results for both sets of data diverge from the curves in Figures 1 and 2 for 25-mg. amounts of potassium. This is probably due to practically no compensation by coprecipitation for this amount, because the rate of precipitation was relatively slower than for the largest amounts.

Although it was recognized that there was always some coprecipitation, efforts were directed to minimizing it in order to evaluate the real magnitude of the solubility error as nearly as possible. On the other hand, there is good reason to believe that coprecipitation may be controlled so as to compensate for the solubility error if desired. This could be accomplished by adding the ethyl alcohol before the complete neutralization of the periodic acid with lithium acetate. This measure may be of the greatest advantage, should the method be adapted to microtechniques. Although this possibility is noted here in the light of experience with the method, there is no real need to use such a technique in macro work. The solubility error may be corrected for by means of the experimental curves, in which case the uncertainty in the results will be of the order of ±0.1% for amounts of potassium greater than 3 mg. Even if no correction is applied, the uncertainty in this range would probably not exceed −0.3% and in most cases would appear to be less than this.

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Coprecipitation of Rare Earth Iodates with Thorium Iodate Precipitated from Homogeneous Solution

KENNETH J. SHAVER[1]

Mound Laboratory, Monsanto Chemical Co., Miamisburg, Ohio

The separation of thorium from rare earths by precipitation of thorium iodate from homogeneous solution is evaluated. The extent of coprecipitation is given when thorium is precipitated in the presence of the rare earths; lanthanum, praseodymium, promethium, and europium; and the related elements, yttrium and scandium. The extent of coprecipitation is determined by the use of radioactive tracers of these elements. The distribution of rare earths with thorium follows the logarithmic or heterogeneous distribution law. It is concluded that trivalent rare earths coprecipitate with thorium iodate by a type of isomorphous replacement within the thorium iodate lattice. A correlation is given between ionic radii and extent of coprecipitation.

THE precipitation of thorium iodate from a nitric acid solution has long been used for the qualitative separation of thorium from rare earths. This separation depends on the solubility of rare earth iodates in a moderately concentrated nitric acid solution. As a quantitative method, however, the separation is not satisfactory because rare earths are coprecipitated to an appreciable extent.

Recently, this situation has been improved through the application of the technique of precipitation from homogeneous solution. Stine and Gordon (*8*) at Syracuse University applied this technique to the precipitation of iodates in a unique manner.

In this method, iodate ion is produced in solution from the reduction of periodic acid with ethylene glycol. The rate-controlling reaction is the production of glycol from the hydrolysis of β-hydroxyethyl acetate. Thorium iodate slowly precipitates as iodate ion is produced homogeneously throughout the solution. The degree of separation of thorium from rare earth was determined by Stine and Gordon by precipitation of thorium iodate in the presence of trivalent cerium.

The present work is a detailed investigation of this separation. The separation efficiency is given in terms of the degree of coprecipitation of a number of rare earths and related elements.

[1] Present address, Inorganic Chemicals Division, Monsanto Chemical Co., Everett Station, Boston 49, Mass.

For simplicity of discussion these related elements are generally included under the term "rare earths."

Coprecipitation data obtained in this evaluation are further interpreted to gain information concerning the nature of this coprecipitation. From the standpoint of coprecipitation theory this is a particularly interesting system, for two reasons. The extent of coprecipitation is extremely small and does not become significant until the extent of precipitation of thorium approaches 100%. This is a typical case of a separation which is nearly quantitative. Coprecipitation theory is more generally applied to the opposite extreme, where two more similar elements are involved and where coprecipitation is appreciable regardless of the extent of precipitation of the major components. The other factor which makes the thorium–rare earth iodate system of particular interest is the difference in charge between the two cations involved. If these coprecipitate by a type of isomorphous replacement, one must assume the likelihood of vacancies within the lattice and a corresponding degree of lattice distortion.

THEORETICAL DISCUSSION

When one material coprecipitates with another, there are two systematic ways in which the minor constituent may be distributed throughout the main component of the precipitate. It may be distributed homogeneously throughout each individual particle of the precipitate, or it may be distributed in a logarithmic manner such that the concentration is zero at the center of each particle and increases layer by layer to a maximum at the outermost layer. The opposite direction of increase in concentration would exist in an enrichment system.

The first type of distribution has been expressed mathematically in terms of a direct proportionality between the extent of precipitation of the major constituent and the extent of coprecipitation of the minor constituent. This relationship, which is usually referred to as the homogeneous distribution law, is generally associated with the investigations reported by Henderson and Kracek (*3*) dealing with the radium-barium chromate system. These authors did not derive the mathematical expression but similar relationships have been derived before and since this work based in some cases on the Berthelot-Nernst distribution law (*10*) and in other cases on simple equilibrium solubility relationships (*2*). This mathematical expression was derived for and has previously been employed with systems where the two ions are of like charge. This expression is used in the present work to interpret data obtained with a system where the two cations do not have the same charge. It has been tacitly assumed that the expression used by Henderson and Kracek is sufficiently valid for the interpretation of data in the thorium–rare earth iodate system.

$$\frac{\text{Rare earth in precipitate}}{\text{Rare earth in solution}} = D\,\frac{\text{thorium in precipitate}}{\text{thorium in solution}}$$

The proportionality constant D is the homogeneous distribution coefficient. As this law expresses homogeneity in the crystal, it assumes equilibrium between the entire solid phase and the liquid phase.

The other type of distribution is represented by the logarithmic distribution law derived by Doerner and Hoskins (*1*). This law may be expressed in terms of the thorium–rare earth system as follows:

$$\text{Log}\,\frac{\text{total rare earth}}{\text{rare earth in solution}} = \lambda\,\log\,\frac{\text{total thorium}}{\text{thorium in solution}}$$

The logarithmic distribution law assumes only that equilibrium exists between the solution and each newly formed infinitesimal surface layer of the solid phase. At the start of precipitation, it is evident that the two laws are equivalent and that D is equal to λ. As precipitation occurs, however, the simple distribution law must be integrated over the period of crystal growth to obtain the logarithmic relationship.

From a common initial value of the distribution coefficient, a precipitation may be carried out in such a manner that either D or λ will remain constant. If the method of precipitation results in a homogeneous distribution of rare earths, calculated values of D will remain constant while values of λ will increase continuously as thorium is precipitated. Conversely, if conditions of precipitation lead to a logarithmic distribution, calculated values of λ will remain constant while values of D will decrease continuously. This is a general relationship which is always true where D and λ are less than 1.

In any case, however, for a given initial value of the distribution coefficients the extent of coprecipitation will be less if the method of precipitation is such that λ remains constant rather than D.

This is illustrated graphically in Figure 1, which shows how coprecipitation increases as precipitation occurs and approaches completion for two cases where D and λ have the same numerical value. For any degree of precipitation, the corresponding extent of coprecipitation is less when λ is constant rather than D. With any proposed separation procedure, then, a logarithmic distribution must be demonstrated to ensure that this procedure will give a maximum separation. The technique of precipitation from homogeneous solution generally tends toward this result. Also shown in Figure 1 is the same relationship between extent of precipitation and extent of coprecipitation for a very much smaller value of the distribution coefficient where λ is 5×10^{-4}. This is the situation which would exist in the case of a separation which is nearly quantitative. Nearly complete precipitation is accompanied by only slight coprecipitation. However, at some point prior to complete precipitation, coprecipitation will start to increase sharply, as is shown by an enlargement of the corner of the graph. If information is available in this extreme range, it is possible to control the extent of precipitation to obtain any desired degree of purity of the precipitate and to avoid the sharp increase in coprecipitation.

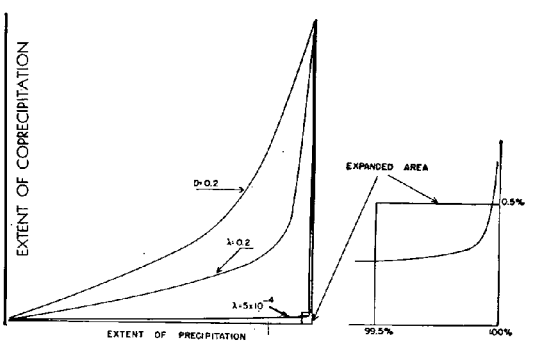

Figure 1. Relative rate of increase of coprecipitation as precipitation occurs for different values of the distribution coefficient

The separation of thorium iodate from rare earth iodates is a separation which is nearly complete and most of the coprecipitation data in the present work fall within this extreme range.

EXPERIMENTAL

The method of precipitation of thorium iodate which was employed for the present work was essentially that of Stine and Gordon, with two modifications. First, the concentration of nitric

acid was increased slightly to 4*N*. The greater rare earth solubility at this concentration avoids the possibility of direct precipitation of rare earth iodates, because the concentration of rare earth was greater in most cases than that specified in the method of Stine and Gordon. Secondly, ethylene diacetate was the source of ethylene glycol rather than the monoacetate ester, so that all of the ester could be added at the start and to achieve a slower rate of precipitation. The amounts of ester and periodic acid added at the start were adjusted so that the final concentration of iodate would be 5% as in the method of Stine and Gordon. After the ester and periodic acid were added to the mixture of thorium and rare earth nitrates in 4*N* nitric acid, the solution was allowed to stand at room temperature with stirring for 1.5 hours. At the end of this time, the ester was completely hydrolyzed and the periodic acid was reduced to iodate by the ethylene glycol. The precipitate, which in most cases consisted of approximately 10 mg. of thorium, was filtered on a 1-cm. glass frit and washed with a minimum volume of dilute iodic acid wash solution. The washing procedure was standardized at four 1-ml. washes and all coprecipitation data were determined on the basis of this washed precipitate.

In determining distribution data for a system of this type where the extent of coprecipitation is very low, the problem of analysis becomes considerable. It can be greatly simplified, however, by the use of radioactive tracers as a means of analysis. In the present work, radioactive rare earth tracers were added to the mixture of thorium and rare earth nitrates before precipitation. The fraction of the rare earth which coprecipitated with thorium was then recovered and determined by comparing the activity in the fraction with that remaining in solution. The coprecipitated rare earth was recovered by dissolving the washed thorium iodate precipitate in hydrobromic acid. The resulting bromide solution was converted to nitrate by evaporating the solution to near dryness with nitric acid. Finally, the concentration of nitric acid was adjusted to 4*N* and thorium was reprecipitated by the direct addition of iodic acid. When this procedure was used, no more than 1% of the rare earth which had initially coprecipitated was coprecipitated again with the second thorium precipitate. The major portion of the rare earth which remains in the filtrate from this second thorium precipitate can then be determined by a counting procedure. An aliquot of this solution was mounted on a 2-inch stainless steel disk and evaporated to dryness. The total amount of solids on the disk was negligible. The β-activity of the tracer was then determined in a Nuclear Measurements Corp., Model PC-1 proportional counter. The use of tracers as an analytical tool generally results in three significant figures. Coprecipitation data are given in terms of only two figures, however, as this more nearly expresses the degree of reproducibility of the results.

The tracers employed to obtain coprecipitation data were lanthanum-140, praseodymium-143, promethium-147, europium-152, 154, yttrium-90, and scandium-46. In the case of lanthanum, promethium, and yttrium, it was possible to obtain tracers which were carrier-free, so that the coprecipitation of tracer alone with thorium could be determined. Lanthanum-140 and yttrium-90 were obtained from the parent materials, barium-140 and strontium-90, by a chemical separation according to the method of Salutsky and Kirby (*5*, *6*). These parent materials and all of the other tracers were obtained from the Isotopes Division, Oak Ridge National Laboratory.

The small quantity of thorium remaining in solution due to the normal solubility of thorium iodate was determined by an α-counting technique using thorium-228 which was available from Mound Laboratory stocks.

Data are given in Table I for the coprecipitation of various rare earths, yttrium and scandium, when 10 mg. of thorium is precipitated from homogeneous solution as the iodate in the presence of about 15 mg. of stable rare earth and 10 microcuries of radioactive tracer. The extent of precipitation of thorium is 99.96% when this quantity of thorium is precipitated in a volume of 6 ml. Data are also given in some cases where the same quantity of thorium was precipitated but no rare earth carrier was present. In addition, the coprecipitation of praseodymium was determined in the presence of a mixed carrier consisting of 10 mg. each of lanthanum and praseodymium.

Table I. Extent of Coprecipitation of Rare Earths, Yttrium and Scandium with Thorium[a]

Rare Earth or Related Element Present during Precipitation	Extent of Coprecipitation, %		
	Homogeneous Precipitation		Heterogeneous precipitation
	Rare earth carrier present	Rare earth carrier absent	
Lanthanum	0.49	0.61	1.13, 0.97
Praseodymium	0.44 (0.44)[b]	...	
Promethium	...	0.53	
Europium	0.19	...	
Yttrium	0.079	0.088	
Scandium	0.48	...	

[a] Thorium precipitation of 99.96%.
[b] Mixed carrier present.

In order to show the advantage of the procedure for precipitation from homogeneous solution, thorium iodate was also precipitated in the presence of lanthanum by a comparable heterogeneous procedure. Iodic acid was added dropwise with stirring to a hot nitric acid solution containing 10 mg. of thorium, 20 mg. of lanthanum, and 10 microcuries of lanthanum-140. The final volume was 6 ml.; the final acidity, 4*N*; and the final iodic acid concentration, 5%. The solution was then cooled, filtered, and washed as described. The extent of coprecipitation of lanthanum is given in Table I.

In order to calculate distribution coefficients, additional coprecipitation data were needed. Those shown in Table I correspond to 99.96% precipitation of thorium. Additional data are shown in Figure 2 where different amounts of thorium are precipitated. Incomplete precipitation of thorium for this purpose was readily achieved by precipitation in a greater volume of solution. As the volume of solution during precipitation is increased from 3 to 30 ml. the extent of precipitation of thorium decreases from 99.98 to 99.8%. The extent of coprecipitation of the various rare earths, lanthanum, praseodymium, eruopium, and yttrium, was determined, and the data are plotted in Figure 2 opposite the corresponding extent of precipitation of thorium. The single value for cerium was taken from the work of Stine and Gordon (*9*). It falls, as would be expected, between lanthanum and praseodymium.

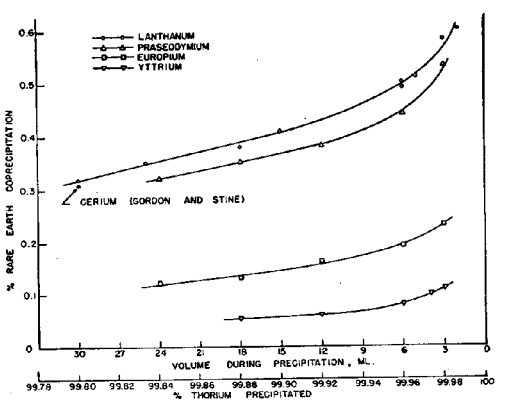

Figure 2. Rate of increase of rare earth coprecipitation as precipitation of thorium approaches completion

In addition to the data shown in Figure 2, some coprecipitation data were obtained for lanthanum and praseodymium where less than 99.8% of the thorium was precipitated. Incomplete precipitation of thorium in this case was achieved by adding a quantity of ester insufficient for complete reduction of the periodate present. As the iodic acid concentration is then less than 5%, there is an increase in the thorium solubility. The single low value for praseodymium was obtained by precipitating 10 mg. of thorium in a volume of 24 ml. and adding half the normal quantity of ester. The three values for lanthanum were obtained by precipitating 10 mg. of thorium in a volume of 12 ml. and adding one half, one third, and one fourth the normal quantity of ester. These data are given in Table II.

Table II. Calculated Distribution Coefficients

Thorium Precipitated, %	Rare Earth Coprecipitated, %	λ	D
		Lanthanum	
88.2	0.15	7.0×10^{-4}	200×10^{-6}
96.2	0.24	7.3	95
99.0	0.33	7.2	33
99.800	0.32	5.2	6.4
99.835	0.35	5.5	5.8
99.880	0.38	5.6	4.6
99.900	0.41	5.9	4.1
99.920	0.46	6.4	3.7
99.960	0.49	6.3	2.0
99.967	0.51	6.4	1.6
99.987	0.60	6.7	0.8
		Av. 6.4×10^{-4}	
		Praseodymium	
98.810	0.26	5.9×10^{-4}	31.6×10^{-6}
99.840	0.32	5.0	4.9
99.880	0.35	5.2	4.0
99.920	0.38	5.3	2.9
99.960	0.44	4.9	1.7
99.980	0.53	6.2	1.0
		Av. 5.4×10^{-4}	

Both the logarithmic and homogeneous distribution coefficients have been calculated in all cases for lanthanum and praseodymium and are given in Table II.

DISCUSSION

It is evident from the data in Table I that there is little change in the extent of coprecipitation, whether the quantity of rare earth is present at the microgram level where tracer alone is present or at the milligram level where rare earth carrier is added. It is probable, therefore, that adsorption does not occur. Instead, a systematic replacement must occur within the crystal lattice of thorium iodate. This is further supported by the fact that the coprecipitation figure for praseodymium alone was exactly duplicated when an equal quantity of lanthanum carrier was also present.

The lattice replacement of one cation by another of different charge when a single species of anion is present is not without precedent in nature. Examples of this are the replacement of potassium with divalent lead in feldspars and the replacement of trivalent yttrium with divalent calcium in yttrofluorite. Replacement by an ion of lesser charge probably results in a vacancy or defect in the lattice and perhaps even some degree of lattice distortion. The quantity of foreign ion that can be tolerated in such a situation may be related to the difference in the ionic radii of the two cations (*4*). Such a correlation between ionic radii and extent of coprecipitation has been reported for the coprecipitation with lanthanum fluoride of various rare earths, ceric fluoride, and uranium fluoride (*7*). A list of ionic radii are given in Table III, which were taken from the work of Zachariasen (*12*). For convenience of comparison, coprecipitation data from Table I are also listed opposite the proper rare earth. There is a general trend of relationship between decreasing ionic radii and decreasing extent of coprecipitation.

Table III. Correlation between Ionic Radii and Extent of Coprecipitation

Element	Ionic Radii, A.	Extent of Coprecipitation, %
La^{3+}	1.04	0.49 (0.61)[a]
Ce^{3+}	1.02	...
Pr^{3+}	1.00	0.44
Th^{4+}	0.99	...
Pm^{3+}	(0.98)[b]	(0.53)[a]
Sm^{3+}	0.97	...
Eu^{3+}	0.96	0.19
Y^{3+}	0.88	0.079 (0.088)[a]
Sc^{3+}	0.68	0.48

[a] Coprecipitation in absence of rare earth carrier.
[b] Interpolated value.

The apparent irregularity of scandium may be due to the fact that scandium is somewhat removed from the rare earths in its chemistry, and such a direct comparison with rare earths may not be valid. The effective ionic radius—that is, the hydrated radius for scandium—may be similar to lanthanum.

It appears from the data in Table I for lanthanum that precipitation from homogeneous solution is approximately twice as effective as heterogeneous precipitation with regard to rare earth contamination in thorium iodate.

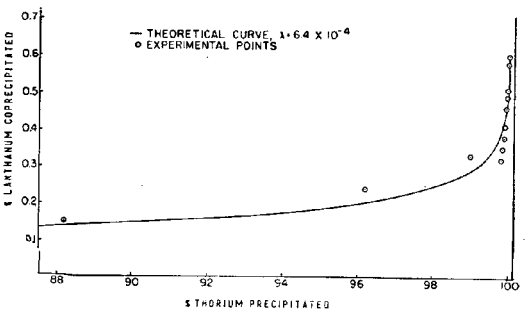

Figure 3. Comparison between experimental rate of increase in coprecipitation and that calculated for an average value of λ for lanthanum

The data shown in Table II indicate that this coprecipitation follows the logarithmic rather than the homogeneous distribution law. The calculated values of λ are approximately constant, while the corresponding calculated values of D vary continuously. Over the range of precipitation of thorium between 88.2 and 99.-99%, this variation for lanthanum is 200-fold.

The single value for praseodymium and the three values for lanthanum corresponding to an extent of precipitation of thorium less than 99.8% are in general agreement with the remaining values in each series in spite of the fact that, in these cases, a lower final concentration of iodic acid was employed. It is evident from the data that the calculated values for λ in these four cases are essentially equal to the remaining values in each series, while the values of D continue the variable trend established by the other data. Therefore, all of these data have been listed in a single table and are treated as continuous.

In order to illustrate further the constancy of λ, curves have been plotted similar to the enlarged portion of Figure 1 showing

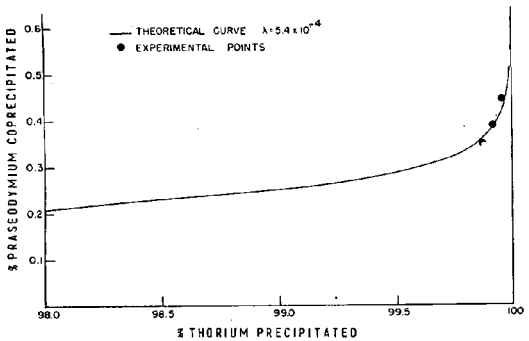

Figure 4. Comparision between experimental rate of increase in coprecipitation and that calculated for an average value of λ for praseodymium

the variation between extent of precipitation of thorium and extent of coprecipitation of rare earth for two theoretical cases which show a λ type of distribution, with λ equal to the average value of lanthanum (Figure 3) and praseodymium (Figure 4) as given in Table II. Actual coprecipitation data have been superimposed on these theoretical curves to illustrate the extent of agreement.

The application of coprecipitation theory in general areas such as this can serve as a very useful tool. Where a separation is good but not quite good enough, it can tell first of all whether or not the contaminant carries by systematic replacement or by some nonsystematic means such as adsorption. If the coprecipitation is systematic, it will tell whether the maximum possible separation is being achieved—i.e., whether the distribution is logarithmic. Finally, once the nature of the systematic distribution has been established, the process of precipitation can be controlled to achieve any predetermined purity in the precipitate. A two-step precipitation process (*11*) can be designed with assurance that it will be successful to a predetermined extent. As an added advantage, it may be possible to predict qualitatively or semiquantitatively the behavior of other similar contaminants without actual experimentation.

The limiting factor with regard to general application, however, is the fact that in many cases the type of coprecipitation may be such that neither distribution law is followed, because coprecipitation is nonsystematic or the systematic distribution is something intermediate between logarithmic and homogeneous distribution.

ACKNOWLEDGMENT

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Determination of Zirconium and/or Hafnium Using 1-Naphthylglycolic Acid

R. B. HAHN and P. T. JOSEPH[1]

Chemistry Department, Wayne University, Detroit 2, Mich.

Both zirconium and hafnium are precipitated quantitatively from dilute acid solution by 1-naphthylglycolic acid. No interference is caused by aluminum, ferric, lanthanum, stannic, thorium, titanium, and uranyl ions. The method was tested by the analysis of a zircon ore. The results obtained using 1-naphthylglycolic acid compare favorably with those obtained with mandelic acid.

MANY organic compounds have been used for the determination of zirconium (*8–10*). The most specific reagents are phenylglycolic acid (mandelic acid) and other derivatives of glycolic acid. These reagents, however, do not differentiate between zirconium and hafnium, both of which are precipitated quantitatively (*2*). According to Feigl (*1*), mandelic acid is a specific reagent for the precipitation of zirconium (or hafnium) because of the presence of the zirconium-binding $-CH(OH)-COOH$ group. Although glycolic acid contains this group, the reaction is not quantitative, because of the absence of the weighting effect of the phenyl group. It was expected, therefore, that the substitution of a group like naphthyl in place of the phenyl group of mandelic acid would produce an effective reagent for zirconium. Oesper and Klingenberg (*7*) prepared a number of such substituted compounds, including 2-naphthylglycolic acid, and studied their reactions with zirconyl ions. Because 1-naphthylglycolic acid has not been studied previously, this investigation was undertaken.

[1] Present address, Titanium Alloy Division, National Lead Co., Niagara Falls, N. Y.

PREPARATION OF 1-NAPHTHYLGLYCOLIC ACID

The acid was prepared by treating 1-naphthyl magnesium bromide with chloral and hydrolyzing the resulting product (*6*). The acid was purified by steam distillation and recrystallization from water. The product was obtained as white needle-shaped

crystals, melting at 97–98° C. Reported values for the melting point are the same (*6*). An over-all yield of 26% was obtained.

ANALYSES. $C_{12}H_{10}O_3$ requires C, 71.29; H, 4.95; found C, 71.22; H, 4.91.

1-Naphthylglycolic acid is only slightly soluble in water; hence the sodium salt was prepared in order to increase the solubility.

EXPERIMENTAL

Solutions. A 0.1*M* solution of the sodium salt of 1-naphthylglycolic acid was prepared as stock solution.

Stock solutions of zirconium oxychloride and hafnium oxychloride were prepared by dissolving the chemically pure salts in 0.1*M* hydrochloric acid. The solutions were standardized with mandelic acid, using the method of Kumins (*5*), and with cupferron, using the method of Hillebrand and Lundell (*4*). The results given in Table I are averages of duplicate determinations.

Table I. Standardization of Solutions

Reagent Used	ZrO_2, G.	HfO_2, G.
Mandelic acid	0.0825	0.4875
Cupferron	0.0824	0.4876
1-Naphthylglycolic acid (sodium salt)	0.0826	0.4877

A wash solution containing 0.5% sodium salt of 1-naphthylglycolic acid and 2% hydrochloric acid was prepared.

Procedure for Precipitation of Zirconium with 1-Naphthylglycolic Acid. Ten milliliters of the standard solution of zirconyl chloride containing the equivalent of about 0.1 gram of zirconium oxide was mixed with 5 ml. of 12*M* hydrochloric acid and 5 ml. of distilled water. To this was added 25 ml. of the stock solution of the sodium salt of 1-naphthylglycolic acid. A white precipitate formed immediately. The mixture was digested on a water bath at 85° C. for 20 minutes. The precipitate settled rapidly and was filtered, using Whatman No. 40 filter paper. After filtration, the precipitate was washed with the wash solution mentioned above, then with 95% ethyl alcohol, and finally with acetone, and dried. The dry precipitate was ignited in a platinum crucible to constant weight of zirconium oxide. The results given in Table I are averages of duplicate determinations.

Table II. Effect of Acidity

Acid	Acid Concn., *N*	ZrO_2 Taken, G.	ZrO_2 Found,[a] G.	Difference, G.
HCl	0.1	0.0825	0.0824	−0.0001
	0.3	0.0825	0.0824	−0.0001
	0.5	0.0825	0.0821	−0.0004
H_2SO_4	0.36	0.0825	0.0824	−0.0001
	1.08	0.0825	0.0824	−0.0001
	1.80	0.0825	0.0823	−0.0002
	2.52	0.0825	0.0820	−0.0005

[a] Average of duplicate determinations.

Effect of Acidity. As the acid strength plays an important and often critical role in effecting complete precipitation, the influence of varying the acidity was investigated. The same procedure was used in each experiment but the acid strength was varied. The weight of zirconium oxide formed by igniting the precipitate was determined (Table II).

Interference of Other Cations. Because zirconium usually occurs along with compounds of iron, aluminum, titanium, and rare earths, the possible interference of these and other ions was studied. Nitrates or chlorides of the cations were used for this purpose. Ten milliliters of the standard zirconyl chloride solution was mixed with known amounts of the cation and the zirconium was precipitated according to the procedure described before. The results of these separations are given in Table III.

Masking Action. Zirconium 1-naphthylglycolate dissolves in sodium hydroxide, but a precipitate of zirconium hydroxide quickly forms. With ammonium hydroxide, however, a solution is obtained and no precipitate is formed. This behavior resembles that of zirconium tetramandelate, in which an inner complex salt is formed (*3*).

Precipitation of Hafnium. Standard solutions of hafnyl chloride were treated with the sodium salt of 1-naphthylglycolic acid, using the procedure outlined for zirconium. A 30-minute period of digestion at 85° C. was required for the complete precipitation of the hafnium. The precipitate was filtered, washed, dried, and ignited in the same manner as the zirconium precipitate. The results, which are averages of duplicate determinations, are given in Table I.

The effect of varying the acidity was found to be the same for hafnium as for zirconium (Table II). The effect of foreign ions upon the determination of hafnium is summarized in Table III. These results are averages of duplicate determinations. The reactions of hafnium 1-naphthylglycolate with solutions of sodium hydroxide and ammonium hydroxide are the same as those of zirconium 1-naphthylglycolate.

Table III. Effect of Diverse Ions

Ion Added	Ion Added, G.	ZrO_2 Taken, G.	ZrO_2 Found, G.	Difference, G.
		On Zirconium		
Aluminum(III)	0.1	0.0825	0.0826	+0.0001
Lanthanum(III)	0.1	0.0825	0.0827	+0.0002
Iron(III)	0.1	0.0825	0.0828	+0.0003
Titanium(IV)	0.1	0.0825	0.0829	+0.0004
Uranium(VI)	0.1	0.0825	0.0826	+0.0001
Thorium(IV)	0.1	0.0825	0.0824	−0.0001
Tin(IV)	0.1	0.0825	0.0826	+0.0001
		On Hafnium		
		HfO_2	HfO_2	
Iron(III)	0.1	0.4875	0.4877	+0.0002
Aluminum(III)	0.1	0.4875	0.4877	+0.0002
Titanium(IV)	0.1	0.4875	0.4878	+0.0003
Thorium(IV)	0.1	0.4875	0.4873	−0.0002

Determination of Zirconium Plus Hafnium in Travancore Zircon. Powdered zircon was opened by borax fusion and converted to zirconyl chloride by the usual methods (*9*). The zirconium plus hafnium was determined by precipitation with mandelic acid and with the sodium salt of 1-naphthylglycolic acid. The results, given in Table IV, show good agreement between the two methods.

Table IV. Analysis of Travancore Zircon

Zircon, G.	Reagent	$ZrO_2 + HfO_2$ Found G.	$ZrO_2 + HfO_2$ Found %	Zr + Hf Found G.	Zr + Hf Found %
1	Mandelic acid	0.6508	65.08	0.4812	48.12
		0.6509	65.09		
1	1-Naphthylglycolic acid	0.6498	64.98	0.4808	48.08
		0.6501	65.01		

Comparison of 1-Naphthylglycolic Acid with Other Reagents. The precipitate of zirconium 1-naphthylglycolate is more voluminous than the corresponding mandelate and *p*-bromomandelate precipitates. In this respect it is probably inferior to mandelic acid and *p*-bromomandelic acid as a reagent for zirconium. The properties of the 1-naphthylglycolate and the 2-naphthylglycolate, as described by Oesper and Klingenberg (*7*), are practically identical. The reagent is more selective than cupferron and the precipitate is more compact than the corresponding cupferrate.

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CRYSTALLOGRAPHIC DATA

141. Thorium Tetranitrate Pentahydrate, $Th(NO_3)_4 \cdot 5H_2O$

EUGENE STARITZKY
The University of California, Los Alamos Scientific Laboratory, Los Alamos, N. M.

THE partial structure of this compound has been determined by Templeton and Dauben (*2*), who referred to it as the hexahydrate, though admitting that the exact composition is in doubt. The number of waters per thorium has been established to be five by density measurements. Templeton and Dauben's x-ray data lead to a calculated density of 2.80 ± 0.03 grams per cc. if the compound is assumed to be a pentahydrate, and 2.89 grams per cc. if the number of hydration waters is assumed to be six. The density measured by the flotation method was 2.787 grams per cc. Furthermore, a recent investigation of the system thorium nitrate–water–nitric acid by Ferraro, Katzin, and Gibson (*1*) showed the pentahydrate and the tetrahydrate to be the only stable hydrates of thorium nitrate at 25° C. Crystals of the pentahydrate have been prepared by allowing a solution of thorium nitrate in concentrated nitric acid to evaporate at room temperature.

Templeton and Dauben (*2*) established the space group of this compound to be *Fdd2* (C_{2v}^{19}) and determined the dimensions of the cell containing eight formular units as a_0 = 11.2 A., b_0 = 22.8 A., c_0 = 10.6 A. They observed a pyroelectric effect.

Partial Powder X-Ray Diffraction Pattern of Thorium Tetranitrate Pentahydrate

hkl	*d*, A., Calcd.	*d*, A., Detd.[a]	*I*[b]
111	7.30	7.32	100
040	5.70	5.69	35
131	5.41	5.38	55
220	5.03	5.00	50
022	4.81	4.78	60
240	3.99	..	..
151	3.92	3.91	25
202	3.85	3.82	10
222	3.65	..	..
311	3.48	3.46	25
113	3.33	3.31	15
331	3.19	3.18	30
242	3.19		
260	3.14	..	..
062	3.09	3.08	45
133	3.08		
171	3.00	3.00	15
080	2.85	2.851	5
400	2.80	2.786	25
351	2.79		
420	2.72	..	..
153	2.71	2.702	15
262	2.70	..	..
004	2.65	2.636	10
313	2.55	2.540	15
280	2.54	..	..
440	2.51	2.505	10
333	2.43	..	..
422	2.42	2.405	30
191	2.41		
044	2.40	2.393	10
371	2.39		
224	2.34	2.336	35
173	2.34		
282	2.29	2.289	20
442	2.27	..	..
460	2.25	..	..
353	2.24	2.230	10
244	2.21	..	..
511	2.18	2.172	15

[a] Philips 114.6-mm.-diameter powder camera, Straumanis mounting; $\lambda(CuK\alpha)$ = 1.5418 A.
[b] Relative peak intensities above background from densitometer measurements.

Crystal Morphology

System and Class. Orthorhombic, pyramidal.
Habit. Bipyramidal {111}, {11$\bar{1}$} with subordinate {010}. No evidence of hemihedrism was observed.

Optical Properties

Refractive Indices (5893 A.). n_X = 1.518; n_Y = 1.528; n_Z = 1.628; geometric mean 1.557$_2$. Molecular refraction 65.88 cc. (based on measured density).
Optic Orientation. $X = b$; $Y = c$; $Z = a$.
Optic Axial Angle (5893 A.). $2V_Z$ = 38°.
Colorless.

THERMAL DATA. On heating in air the crystals decompose at 85° C. to microcrystalline aggregates of another compound.

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WORK done under the auspices of the Atomic Energy Commission. Contributions of Crystallographic Data for this section should be sent to Walter C. McCrone, 500 East 33rd St., Chicago 16, Ill.

142. Plutonium Tetranitrate Pentahydrate, $Pu(NO_3)_4 \cdot 5H_2O$

EUGENE STARITZKY, The University of California, Los Alamos Scientific Laboratory, Los Alamos, N. M.

WELL developed crystals of plutonium tetranitrate pentahydrate, up to 2 mm. in length, grew on long standing in a solution of plutonium in 10*N* nitric acid. Ordinarily, such solutions tend to become supersaturated and many attempts to prepare crystalline plutonium nitrate have resulted in the formation of extremely viscous liquids and, eventually, of vitreous solids without development of crystals. Prolonged gentle heating of such a solid generally resulted in the development of dendritic

growths and poorly formed crystals of the pentahydrate. Plutonium tetranitrate pentahydrate, which is isomorphous with corresponding nitrates of thorium and cerium, is rather hygroscopic.

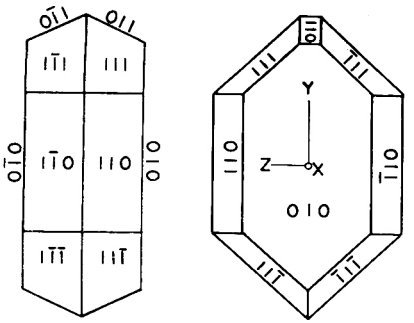

Figure 1. Crystal of plutonium tetranitrate pentahydrate

Orthographic projection parallel to *a* and on (010)

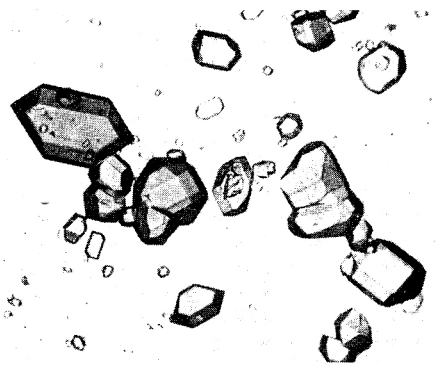

Figure 2. Crystals of plutonium tetranitrate pentahydrate

Crystal Morphology

System and Class. Orthorhombic, pyramidal.

Axial Elements. $a:b:c$ = 0.493:1:0.465 (derived from unit cell dimensions).

Habit. Variable, equant or prismatic {001}, flattened {010}. Forms usually developed are {010}, {110}, {111}, and {11$\bar{1}$}. Form {011} is also frequently present, alone or accompanied by {01$\bar{1}$}.

Interzonal Angles. [011] ∧ [001] = 65.0°; [101] ∧ [001] = 46.7°.

X-Ray Diffraction Data

Space Group. *Fdd2* (C_{2v}^{19}).

Cell Dimensions. a_0 = 11.14 ± 0.02 A.; b_0 = 22.58 ± 0.03 A.; c_0 = 10.51 ± 0.03 A.

Formula Units per Cell. 8; volume per formula unit 330.5 A.^{3}

Formula Weight. 577.17.

Density. 2.90 grams per cc. (x-ray); 2.896 (flotation).

Optical Properties

Refractive Indices (5893 A.). n_X = 1.554$_3$; n_Y = 1.556; n_Z = 1.667; geometric mean 1.591$_6$. Molecular refraction 67.41 cc. (based on measured density).

Optic Orientation. $X = b$; $Y = c$; $Z = a$.

Optic Axial Angle. $2V_Z$(441 mμ.) = 20°; $2V_Z$(470 mμ.) = 17°; $2V_Z$(533 mμ.) = 13°; $2V_Z$(589 mμ.) = 7.5°.

Color. $X \approx Y$ = yellowish green, Z = green. The absorption spectrum, as observed through a Zeiss prism microspectrometer eyepiece, is given in Table II.

Table I. Partial Powder X-Ray Diffraction Pattern

hkl	*d*, A., Calcd.	*d*, A., Obsd.[a]	*I*[b]
111	7.24	7.16	100
040	5.645	5.58	40
131	5.364	5.30	50
220	4.995	4.98	45
022	4.764	4.72	45
240	3.965	...	...
151	3.888	3.86	30
202	3.822	3.80	10
222	3.620	...	...
311	3.460	3.44	20
113	3.306	3.28	15
331	3.175	3.15	30
242	3.165		
260	3.118	3.10	< 5
062	3.060	3.04	35
133	3.054		
171	2.972	2.952	10
080	2.823	2.805	10
400	2.785	2.767	25
351	2.767		
420	2.704	...	...
153	2.686	2.669	15
262	2.682	...	...
004	2.627	2.614	10
313	2.532	2.519	15
280	2.518	...	...
440	2.498	2.485	10
333	2.414	...	...
422	2.404	2.395	20
191	2.384	2.368	25
044	2.382		
371	2.372		
224	2.326	2.315	25
173	2.321		
282	2.271	2.262	20
442	2.256	...	...
460	2.239	...	...
353	2.219	2.213	10
244	2.190	...	...
511	2.170	2.158	15

162 additional lines were measured.

[a] Philips 114.6-mm.-diameter powder camera, Straumanis mounting; λ(Cu*Kα*) = 1.5418 A.

[b] Relative peak intensities above background from densitometer measurements.

Table II. Absorption Spectrum of Plutonium Tetranitrate Pentahydrate

(Band maxima in millimicrons and relative intensities)

Vibration, Direction *X* or *Y*	Vibration, Direction *Z*
655, strong	650, strong
622, medium	635, medium
	620, medium
590, very weak	...
...	564, weak
556, medium weak	556, medium weak
548, medium	546, weak
532, very weak	535, medium weak
516, weak	521, medium weak
506, weak	506, medium strong
488, very strong	488, very strong
468, medium weak	477, medium strong
447, medium strong	

Thermal Data

On heating in air the crystals decompose slowly at 70° C. to a viscous isotropic mass, which at slightly higher temperatures devitrifies to microcrystalline birefringent aggregates of another compound.

Work done under the auspices of the Atomic Energy Commission. Data for publication in this section should be sent to Walter C. McCrone, 500 East 33rd St., Chicago 16, Ill.

143. Cerium Tetranitrate Pentahydrate, $Ce(NO_3)_4 \cdot 5H_2O$

EUGENE STARITZKY, The University of California, Los Alamos Scientific Laboratory, Los Alamos, N. M.

Crystals of cerium tetranitrate pentahydrate, isomorphous with corresponding compounds of thorium and plutonium, were prepared by allowing a solution of ceric nitrate in concentrated nitric acid to evaporate at 35° C.

Crystal Morphology

System and Class. Orthorhombic, pyramidal (from isomorphism with corresponding compounds of thorium and plutonium).

Axial Elements. $a:b:c$ = 0.493:1:0.464 (derived from unit cell dimensions).

Habit. Dipyramidal by equal development of {111} and {11$\bar{1}$}, usually with subordinate {010} and often with {110}. No hemihedral development was noted.

X-Ray Diffraction Data

Space Group. $Fdd2$ (C_{2v}^{19}).

Cell Dimensions. a_0 = 11.17 ± 0.03 A.; b_0 = 22.68 ± 0.06 A.; c_0 = 10.53 ± 0.04 A.

Formula Units per Cell. 8; volume per formula unit 333.5 A.^{3}

Formula Weight. 478.24.

Density. 2.38 grams per cc. (x-ray); 2.403 (flotation).

Partial Powder X-Ray Diffraction Pattern

hkl	d, A., Calcd.	d, A., Obsd.[a]	I[b]
111	7.26	7.23	100
040	5.67	5.64	40
131	5.38	5.36	45
220	5.01	4.98	40
022	4.78	4.76	50
240	3.98	3.97	< 5
151	3.90	3.88	20
202	3.83	3.82	10
222	3.63	3.61	< 5
311	3.47	3.46	15
113	3.31	3.30	10
331	3.18	...	...
242	3.17	3.16	15
260	3.13	...	...
062	3.07	3.06	40
133	3.06		
171	2.984	2.977	10
080	2.835	2.825	5
400	2.792	...	...
351	2.776	2.770	15
420	2.711	...	...
153	2.694	2.683	15
262	2.691		
004	2.632	2.625	10
313	2.588	2.529	10
280	2.528	...	...
440	2.505	2.496	5
333	2.420	...	...
422	2.411	2.401	15
191	2.394	...	...
044	2.388	2.374	25
371	2.381		
224	2.330	2.324	25
173	2.328		
282	2.279	2.274	15
442	2.262	...	...
460	2.246	...	...
353	2.226	2.216	5
244	2.195	...	...
511	2.175	2.164	15

[a] Philips 114.6-mm.-diameter powder camera, Straumanis mounting; λ(Cu$K\alpha$) = 1.5418 A.

[b] Relative peak intensities above background from densitometer measurements.

Optical Properties

Refractive Indices (5893 A.). n_X = 1.586; n_Y = 1.590; n_Z = 1.691; geometric mean 1.6216. Molecular refraction 70.05 cc. (based on measured density).

Optic Orientation. $X = b$; $Y = c$; $Z = a$.

Optic Axial Angle (5893 A.). $2V_Z$ = 34° with strong dispersion $r < v$.

Color. $X \approx Y$ = yellow; Z = orange-red.

Thermal Data. On heating in air the crystals decompose at 61° C. to a mixture of a liquid and a new crystal species.

Work done under the auspices of the Atomic Energy Commission. Data for publication in this section should be sent to Walter C. McCrone, 500 East 33rd St. Chicago 16, Ill.

144. Yttrium Sesquioxide, Y_2O_3
145. Dysprosium Sesquioxide, Dy_2O_3
146. Erbium Sesquioxide, Er_2O_3
147. Ytterbium Sesquioxide, Yb_2O_3

EUGENE STARITZKY, The University of California, Los Alamos Scientific Laboratory, Los Alamos, N. M.

The rare earth oxides used were prepared by ion exchange methods at the Institute of Atomic Research, Iowa State College. Spectrographic analysis indicated their purity to be considerably in excess of 99%. The yttrium oxide, from another source, is estimated to be at least 99% pure. All oxides were recrystallized by melting in an oxyacetylene flame to aggregates of anhedral crystals exhibiting octahedral cleavage.

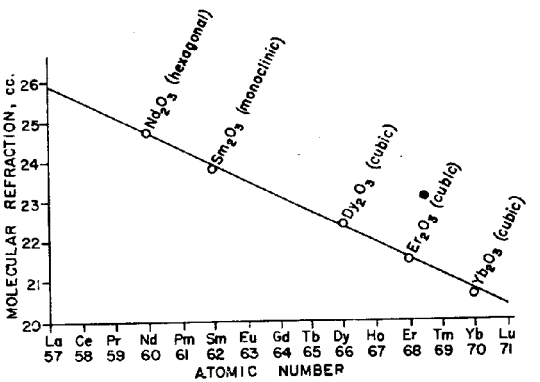

Figure 1. Molecular refraction of some rare earth sesquioxides

Table I. Partial Powder X-Ray Diffraction Pattern

$h^2 + k^2 + l^2$	Y_2O_3 d, A., obsd.[a]	Y_2O_3 I[b]	Dy_2O_3 d, A., obsd.[a]	Dy_2O_3 I[b]	Er_2O_3 d, A., obsd.[a]	Er_2O_3 I[b]	Yb_2O_3 d, A., obsd.[a]	Yb_2O_3 I[b]
6	4.31	14	4.33	8	4.29	12	4.23	8
12	3.06	100	3.07	100	3.04	100	2.997	100
14	...	...	...	...	2.810	2	2.775	3
16	2.646	31	2.660	40	2.631	40	2.606	30
18	2.494	7	2.505	9	2.481	9	2.453	7
20	2.366	2	...	...	2.352	2	2.327	2
22	2.258	9	2.268	7	2.243	10	2.217	8
24	2.160	2	...	...	2.148	2	2.127	3
26	2.076	14	2.087	14	2.064	16	2.042	16
30	1.933	5	...	...	1.922	8	1.901	5
32	1.873	61	1.883	58	1.861	62	1.843	53
34	1.816	3	1.828	8	1.806	5	1.787	7
36	1.767	2	...	...	1.755	1	1.739	3
38	1.718	8	1.727	9	1.710	10	1.691	11
40	1.675	2	1.681	2	1.665	2	1.647	3
42	1.634	8	1.644	8	1.626	9	1.609	10
44	1.597	43	1.606	53	1.589	53	1.572	52
46	1.562	11	1.570	9	1.553	12	1.538	13
48	1.528	10	1.537	11	1.521	14	1.504	17
50	1.498	4	1.506	8	1.490	5	1.474	7
52	1.469	3	1.478	5	1.462	3	1.444	4
54	1.442	6	1.449	6	1.434	7	1.418	8
56	1.416	4	1.422	4	1.400	4	1.395	5

More than 50 additional lines were observed in each case.

[a] Philips 114.6-mm.-diameter powder camera, Straumanis mounting; λ(Cu$K\alpha$) = 1.5418 A.

[b] Relative peak intensities above background from densitometer measurements.

All the oxides crystallized from their melts with the cubic C structure belonging to the space group $Ia3$ (T_h^7), with 16 formular units per cell (*5*). The lattice constant of yttrium sesquioxide has been determined recently by Swanson and Fuyat (*3*) as 10.604 A. Templeton and Dauben (*4*) reported $a_0 = 10.667 \pm 0.006$ A. for dysprosium sesquioxide, $a_0 = 10.547 \pm 0.003$ A. for erbium sesquioxide, and $a_0 = 10.439 \pm 0.007$ A. for ytterbium sesquioxide.

X-Ray Diffraction Data

	Cell Dimension, a_0; A.	Formula Weight	Density, Grams/Cc.
Yttrium sesquioxide	10.605 ± 0.001	225.84	5.030
Dysprosium sesquioxide	10.667 ± 0.001	372.92	8.161
Erbium sesquioxide	10.550 ± 0.001	382.4	8.651
Ytterbium sesquioxide	10.435 ± 0.001	394.08	9.213

The above cell dimensions have been determined by least-squares linear extrapolation of the a_0 values calculated from high-angle diffraction lines against the function $(\cos^2\theta/\sin\theta + \cos^2\theta/\theta)$ to the zero value of that function. Between 20 and 30 Cu$K\alpha_1$ and Cu$K\alpha_2$ lines in the angular region $\theta = 65°$ to $85°$ were used in each case.

Optical Properties

Refractive Indices.

	Wave Length		
	Hg 4358 A.	Na 5893 A.	6640 A.
Yttrium sesquioxide	1.935	1.915	1.903
Dysprosium sesquioxide		1.974	
Erbium sesquioxide	1.984	1.960	1.952
Ytterbium sesquioxide		1.947	

Molecular Refraction (5893 A.).21.13 cc. for yttrium sesquioxide, 22.4 cc. for dysprosium sesquioxide, 21.50 cc. for erbium sesquioxide, 20.6 cc. for ytterbium sesquioxide. The above values of molecular refraction for the three cubic rare earth sesquioxides have been plotted on Figure 1, together with corresponding values for the hexagonal neodymium oxide (*1*) and the monoclinic samarium oxide (*2*). The molecular refraction of rare earth sesquioxides appears to be closely approximated by a linear function of the atomic number and not markedly affected by differences of crystal structure.

Color. Yttrium sesquioxide is pale brown, erbium oxide pink. Dysprosium and ytterbium sesquioxides are colorless. Erbium sesquioxide exhibits an absorption spectrum with many bands in the visible range, the half-width of the bands not exceeding 10 to 30 A. except in the case of three red bands. The maxima and relative intensities of the absorption bands are listed in Table II. These were measured with a Cary Spectrophotometer on a sample of crushed melt mounted in an immersion liquid with the refractive index 1.96 for sodium light.

Table II. Absorption Spectrum of Erbium Sesquioxide

Band Maxima, mμ	Relative Intensity	Band Maxima, mμ	Relative Intensity	Band Maxima, mμ	Relative Intensity
487.4	1	522.4	6	540.6	1
488.3	1	524.2	10	541.3	3
489.0	2	525.2	4	547.8	1
489.7	3	526.2	4	548.9	1
490.7	5	527.1	8	550.5	2
492.8	4	528.2	6	551.5	1
493.9	3	529.3	4	553.1	1
494.9	3	530.6	3	555.9	2
496.9	1	531.5	3	558.3	1
499.4	1	533.4	1	566.0	1
505.5	1	534.3	1	650.9	1
513.5	1	536.1	1	656.2	2
521.4	9	537.0	1	662.6	2

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Work done under the auspices of the Atomic Energy Commission. Contributions of Crystallographic Data for this section should be sent to W. C. McCrone, 500 East 33rd St., Chicago 16, Ill.

SCIENTIFIC COMMUNICATION

Precision Plating of Polonium

Sir: The ease with which polonium spontaneously plates out on metal foils and disks has been utilized in most procedures for its analysis. Accordingly, the experimental conditions affecting the plating have been extensively investigated (*1–5*). However, a perusal of these published reports leaves the definite impression that the plating procedure is at best somewhat inaccurate. For example Fink and others (*3*) state that the reproducibility of their method was "probably not better than ±5%." The Los Alamos group (*2*) reported an accuracy of 98 ± 10% in analyzing urine. Smith, Della Rosa, and Casarett (*5*) demonstrated a direct relation between recovery by a single plating and the amount of polonium which can be plated—i.e., total for original plating plus several successive platings of supernatants until the radioactivity in the disk approximated background of counter – with recoveries varying from 90 to 96% in a single plating.

While these recoveries are sufficient for many purposes, a procedure giving better precision was needed as a prerequisite to a program of investigation of the physicochemical properties of polonium. By combining the best features of the various published methods, it is conveniently possible to obtain single plating recoveries of 99% and better, an accuracy within the probable counting error, and a reproducibility within the pipetting error.

PROCEDURE

The apparatus used was similar to that of Eutsler, Milligan and Robbins (*2*), in that a metal foil disk (0.003 inch thick and 1.5 inches in diameter; silver in our case) was suspended in the polonium solution by means of a glass stirring rod hooked through a 1-mm. hole in the foil. The polonium solution was contained in a 300-ml. tall-form beaker without lip, which was suspended in a water bath through a sheet of copper containing six holes, each large enough to pass all but the lip of the beaker. Thus, six solutions could be plated simultaneously. The idea first suggested by Baxter and Wood (*1*) of operating all the stirrers with one motor by means of a pulley and belt system was adopted. After plating, both sides of each silver foil were counted in scintillation counters.

RESULTS AND DISCUSSION

In Table I are shown the results of a typical plating experiment with polonium-210 solutions containing about 3000 c.p.m. For each experiment, 1 ml. of stock polonium-210 solution was diluted with 200 ml. of 0.5N hydrochloric acid. When the bath reached 97° C., plating was started. The first disk was exposed for 1½ hours. Then a second disk was exposed for 2 hours. Finally a third disk was exposed for 2 hours. The sides of the beakers were washed down with distilled water after 1 hour of plating each time.

The three solutions showed a plating efficiency (in terms of total recoverable counts) of 99.8 ± 0.2% for one plating. This

Table I. Typical Plating Experiment with Polonium-210 Solutions[a]

1st Plating, C.P.M.[b]	2nd Plating, C.P.M.	Total Recoverable Counts, C.P.M.[b,c]	% Efficiency, 1st Plating[d]
3467	4	3471	99.9
3354	15	3369	99.5
3390	3	3393	99.9
Av. 3404 ± 42	7 ± 4	3411 ± 37	99.8 ± 0.2

[a] Data corrected for background, 3 c.p.m. per foil (both sides).

[b] Probable counting error = $100\% \times 0.67 \frac{\sqrt{\text{total no. of counts}}}{\text{total no. of counts}} = 0.5\%$.

[c] Total recoverable = 1st plating plus 2nd plating. Third platings always showed background only.

[d] Per cent efficiency of plating = 100% × counts on disk/total recoverable counts.

Table II. Relationship between Total Recoverable Counts and Dilution[a]

1st Plating, C.P.M.	2nd Plating, C.P.M.	Total Recoverable Counts, C.P.M.	Efficiency of 1st Plating, %	Probable Counting Error, %
205	1	206	99.5	0.9
521	0	521	100.0	0.9
1020	1	1021	99.9	0.9
4075	48	4123	98.9	0.4
		Av.	99.6 ± 0.4	

[a] Aliquots of 10, 25, 50, and 200 ml. of stock polonium-210 solution were diluted to 200 ml. with 0.5*N* hydrochloric acid. Data corrected for decay to same data as Table I experiments.

is well within the probable counting error of 0.5%. These results have been reproduced repeatedly. Experiments also showed that failure to wash down the sides of the beaker during the experiment introduces an error of about 1%—i.e., recoveries of only 98.9 ± 0.4% were obtained.

The data for Table II show that, over a 20-fold variation in concentration, there is a strict proportionality between the total recoverable counts and dilution. This would not be expected if more than a negligible amount of polonium remained unplated. Furthermore, soaking the beakers in 6*M* hydrochloric acid after each plating yielded no further counts, indicating that any polonium remaining adsorbed on the beakers was negligible. We have also counted pieces of glass from the bottom of the beakers used for plating and obtained only the background count, again indicating negligible absorption, if any.

ACKNOWLEDGMENT

We are happy to acknowledge the aid of Taft Toribara in constructing the apparatus.

This paper is based on work performed under contract with the United States Atomic Energy Commission at the University of Rochester Atomic Energy Project, Rochester, N. Y.

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ISAAC FELDMAN
MARGARET FRISCH

Department of Radiation Biology
School of Medicine and Dentistry
University of Rochester
Rochester, N. Y.

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MEETING REPORTS

Society for Analytical Chemistry

AT A meeting of the Midlands Section, held September 11, in Birmingham, the following paper was read and discussed.

Recent Advances in the Analysis of Cast Iron and Foundry Materials. W. E. CLARKE, British Cast Iron Research Association, Alvechurch.

The heterogeneous nature of cast iron gives rise to sampling difficulties. Different types of graphite, flake and nodular, were illustrated, and sampling for carbon determination was described. Many different sampling techniques have to be used, because the size of the casting and the type of graphite affect the type of sample required for accurate results. New methods include radio-frequency induction heating of samples for the determination of carbon and sulfur. The conditions required for steel samples, gray and white cast-iron drillings, and solid samples, including ferroalloys, were discussed, as well as the advantages and disadvantages of this type of heating. The analysis of nodular irons was outlined. Methods for the determination of small amounts of cerium, rapid chemical methods for magnesium, and methods for analysis of nickel-magnesium alloys were described.

At a joint meeting of the Scottish Section of the Society for Analytical Chemistry and the Methods of Analysis Panel (Glasgow), formerly the Spekker Group, held in Glasgow September 28, three papers were presented.

Photometric Determination of Molybdenum as the Thiocyanate. R. KERR, Imperial Chemical Industries Ltd., Nobel Division, Stevenston, Ayrshire.

The paper covered a study of the molybdenum-thiocyanate complex and its applicability to the routine determination of molybdenum photometrically in various classes of steels.

Determination of Copper in Steel. L. J. A. HAYWOOD AND P. SUTCLIFFE, Catton & Co., Ltd., Yorkshire Steel Foundry, Hunslet, Leeds.

Bis-cyclohexanone oxalyldihydrazone has been established as a reagent for the determination of copper in steels and ferrous metals generally. The method has been particularly developed for routine analysis, with an absorptiometric finish, and is appreciably more simple and rapid than any method hitherto published. No separations, either chemical or physical, are involved, and the solvent acids will cover almost all types of steel alloys. Interfering elements are very few, and in all cases except one, can be virtually ignored.

Analysis of Titanium and Its Alloys. W. T. ELWELL, Imperial Chemical Industries, Ltd., Metals Division, Witton, Birmingham.

Only within the past 4 or 5 years has titanium metal become a commercial product. It is not surprising, therefore, that published data covering methods of analysis are scanty. The recent rapid growth of the titanium industry, the increasing use of the metal, and the development of an ever-increasing number of titanium alloys, make it essential that information on analytical methods be available.

In the course of considerable research over the whole field of titanium technology, Imperial Chemical Industries, Ltd., have given much attention to methods for the determination of a large number of different elements in titanium, whether present as impurities or purposefully added. The development of recommended procedures associated with this new branch of analytical chemistry was discussed.

On October 3 a meeting was held in London, at which two papers were presented.

Determination of Vitamin D and Related Compounds. Introduction and Preparation of Compounds in the Irradiation Series. Analysis of Irradiation Products. W. H. C. SHAW, J. P. JEFFERIES, AND T. E. HOLT, Glaxo Laboratories, Ltd., Greenford.

Physical and chemical methods for the determination of the vitamins D were re-examined, particularly those for determining the composition of the complex mixtures formed during the ultra-

violet irradiation of the provitamins D (ergosterol and 7-dehydrocholesterol). By preliminary adsorption on activated alumina of the correct grade and development of the chromatogram with a mixture of light petroleum and acetone, the components of such mixtures were separated into two main fractions; individual compounds were then determined by ultraviolet adsorption spectroscopy and application of the antimony trichloride color reaction.

The preparation, mainly by chromatographic methods, of purified precalciferol 2, precalciferol 3, lumisterol 2, tachysterol 2, and other compounds closely related to the vitamins D was described. The required ultraviolet absorption characteristics and behavior in the color reaction of each compound were established with these materials.

Full details for carrying out the chromatography on the analytical scale for the analysis of the chromatographic fractions and the determination of residual provitamin were given. Products obtained by irradiating the provitamins under different conditions were examined, and the results were discussed in relation to the structural changes that take place during and subsequent to irradiation and in relation to the results of biological assays.

The methods were also applicable to the determination of the precalciferols and the vitamins D in high-potency preparations, but in their present form were unsuitable for materials of low potency or those containing vitamin A.

Some Examples of the Use of Paper Chromatography in Toxicological Analysis. A. S. CURRY, Home Office, Forensic Science Laboratory, Harrogate.

The use of paper chromatography in the analysis of viscera for barbiturates formed the subject of the first example. A case involving the ingestion of two barbiturates was discussed. The second example concerned the analysis of the contents of 73 ampoules. Each was supposed to contain 1 ml. of morphine sulfate solution. The role of paper chromatography in showing their actual content was described.

Five papers on the subject of submicromethods in inorganic and organic analysis were presented and discussed at a joint meeting of the Microchemistry Group and the Midlands Section at a meeting held October 5 in Cambridge.

Introduction. R. BELCHER, Birmingham University.

Methods of submicro inorganic analysis came into prominence after the war, when their application to the study of the trans-uranic elements was revealed. Methods of submicro organic analysis have so far received only occasional attention. As far as routine application is concerned, the smallest amount of sample used in organic analysis is the level reached by Pregl of 3 to 5 mg.

Several years ago we initiated a research program with the object of developing a new system of organic analysis which required sample weights of only about 0.05 mg. This technique should be of value in biochemistry and physiological chemistry and many other applications.

The first problem was to devise a simple balance capable of weighing accurately the sample weights required. After this had been achieved, several methods were developed which have the same order of accuracy as is attainable on the microscale. The technique is comparatively simple. Work in this field is continuing and several other methods are now being perfected.

General Review of Submicromethods. T. S. WEST, Birmingham University.

A general review was given of some of the techniques used in submicro inorganic and organic analysis. Reference was made to various balances. The balance developed at Birmingham University was described.

Determination of Alkoxyl. M. K. BHATTY, Birmingham University.

The determination of alkoxyl groups on samples weighing about 50 γ was described.

Determination of Nitrogen. M. WILLIAMS, Birmingham University.

The determination of nitrogen in organic compounds on the submicro scale was described. A sealed tube technique is used; the digest is titrated in this tube without transference.

Determination of Iodine. A. R. SHAH, Birmingham University.

The determination of iodine in organic compounds on the submicro scale was described. The compound is decomposed with sodium in a sealed tube and the iodide is then determined titrimetrically.

A joint meeting of the Physical Methods Group and the North of England Section of the Society was held October 19 at Manchester University. The following papers were presented and discussed.

Ion Exchange in the Study of Complexes. T. V. ARDEN, Permutit Co., Lit.

The early uses of ion exchange resins in analysis were largely concerned with separations in which the resins conveniently replaced standard chemical techniques. A recent development has been the study of inorganic complex ions in solution by methods using the fundamental structure of the resin. These techniques have given information which cannot be obtained by standard chemical methods. The principles used in the investigation of complexes were discussed and illustrated, with particular reference to the study of the complex uranyl sulfate anion.

Some Recent Applications of Ion Exchange in Biochemistry. T. S. WORK, Medical Research Council.

Rapid progress has been made in recent years in the study of proteins, peptides, and nucleic acids. Ion exchangers made by adding basic or acidic groups to cellulose seem likely to be particularly useful for the fractionation of large molecules. Thus, for example, deaecellulose made by reaction of cellulose with diethylamino ethyl chloride has been used in the successful fractionation of plasma proteins and seems to offer some promise also in the fractionation of nucleic acids.

Carboxylic acid resins of the acrylic acid series have been found to give excellent fractionation of smaller proteins and large peptides. Several enzymes have been purified by chromatography in IRC 50.

Polystyrene sulfuric acid resins are particularly successful in the fractionation of peptides and amino acids, extremely high resolving power being achieved. The optimum conditions for the applications of these resins in column chromatography were discussed.

The quarternary ammonium type resins give excellent fractionation of nucleotides and several new nucleotides have recently been isolated in different laboratories by the use of these resins.

American Oil Chemists' Society

ABSTRACTS of papers of analytical interest presented at the meeting of the American Oil Chemists' Society at Chicago, September 24 to 26, appear below. Many of these will be published in the *Journal of the AOCS*. Information concerning publication plans is available from the American Oil Chemists' Society, 35 East Wacker Drive, Chicago 1, Ill.

Analysis of Corn Oil for Tocopherol. KATHERINE HIVON AND F. W. QUACKENBUSH.

A method has been developed to overcome difficulties in the analysis of corn oil for tocopherol. The poor recovery of tocopherol added to corn oil, experienced in the Parker-McFarlane treatment, does not occur with the present method. The interfering substance causing this decrease is present in corn oil but not in other common edible oils.

The interfering substance did not distill appreciably in a molecular still at 170° C., and attempts to remove it from the oil by selective adsorption or solvent extraction were unsuccessful. It was extractable with dilute alkali from a hexane solution of the oil and could be transferred from the alkali to a benzene solution. Extracts containing the substance showed strong absorption at 290 and 315 mμ and reacted slowly with ferric chloride α,α'-bipyridine to give absorption at 520 mμ.

A combination of the alkali treatment with adsorption on diatomaceous earth reduced the content of interfering substances sufficiently to permit analysis by the Emmerie-Engel method. By this method it was found that the oil from different inbreds varied over a sixfold range in tocopherol content.

J. N. SHAW, AND H. A. SCHUETTE.

In the Wheeler method for the determination of peroxides in oils there is an apparent increase in the observed value with increase of contact time in the reagent. This suggests that errors caused by this factor are larger than formerly estimated. Light has an accelerating effect on atmospheric oxidation and tends to bring increased values. The peroxide values increase indefinitely in the presence of light but tend to approach a maximum if air is excluded.

When a halogen-substituted acetic acid is present in the solvent, higher peroxide values are obtained initially. When these values are plotted against reaction time, the curve rises abruptly and then gradually until after 120 minutes values are substantially in agreement with those in the unmodified Wheeler method.

A modified method was developed, using 0.1*M* monochloroacetic acid in the chloroform–acetic acid solvent, which results in peroxide values showing less deviation and greater precision than the standard Wheeler test. The latter method has shown variations as high as 300% with samples ranging in size from 0.1 to 5.0 grams.

Substitution of an inert atmosphere, carbon dioxide, and retaining monochloroacetic acid in the solvent give more uniform values with varying time of contact with the reagent and varying sample size. The increased acidity leads to a more complete reaction between peroxide and potassium iodide and concurrently reduces atmospheric oxidation so that more nearly replicate results are obtained with varying samples. A recommended procedure was given.

Polarographic Investigation of Autoxidation in Lard. EDWIN J. KUTA AND F. W. QUACKENBUSH.

The peroxide formation in deodorized bleached lard autoxidized at 55° and 100° C. was followed polarographically and by total peroxide number. Also the autoxidation was followed when the deodorized bleached lard contained pro-oxidants (1.5 p.p.m. copper ions, 0.02% chlorophyll, and 0.18, 0.36, and 1.5% phosphoric acid); synergists (0.05% ascorbic acid, 0.05% citric acid); and antioxidant and synergists (1 micromole per gram of catechol alone, catechol with 0.05% ascorbic acid, catechol with 0.05% citric acid).

In all cases studied the polarographic method showed three reduction waves, which generally increased in height as the peroxide number increased. At 100° C. the time of autoxidation necessary for each reduction wave to reach a maximum concentration depended on the pro-oxidant, antioxidant, and synergist added to the lard. At 55° C. only one of the reduction waves ($E^1/_2 = -0.15$ volt) reached a maximum. The other two reduction waves ($E^1/_2 = -0.66$ volt, $E^1/_2 = -1.10$ volts) as well as the peroxide number did not reach a maximum after 300 hours of autoxidation.

Complete Color Characterization of Vegetable Oils and Its Correlation with Lovibond Values. E. H. MELVIN. M. M. GILBERT, AND JEAN M. MALLAN.

That vegetable oils may appear different to the eye and yet have the same trade color values has long been known. That, as used in American practice, the Lovibond values do not usually give a complete color description has not perhaps been as well known. In order to understand the apparent anomalies as well as to improve the knowledge of oil composition and quality, complete color determinations on about 200 commercial vegetable oil samples as well as on many of the Lovibond glasses have been made. The method of measurement, calculation, and a single-numbered expression of color differences were discussed.

The data prove that in very few cases (usually peanut oils) is there agreement between the tristimulus values (complete color designations) of oils and glasses and that the usual cases, particularly with soybean and cottonseed oils, are in wide disagreement. There is usually agreement between the trichromatic coefficients (partial color designations) of oils and glasses. This means that usually the oils are made to appear to have higher pigment concentrations than they really have.

Since photometric color correlates very highly with the Lovibond red value, the same difficulties are experienced with the newer method. Some proposals that would provide a more direct correlation with type of pigment and concentrations were discussed.

Determination of Pyrophosphate in Commercial Triphosphate. HERMAN J. WEISER, JR.

has been a direct method of determining pyrophosphat isotope dilution method was first to give accurate result presence of large amounts of triphosphate. More recently pa ion exchange chromatographic procedures were set up. exchange procedure appeared to be capable of giving greater a and therefore has been modified for use with commercial triph

Since commercial triphosphate samples contain only 5 pyrophosphate, it was necessary to change the elution proc ensure complete separation of pyro- and triphosphate. The and Doty colorimetric procedure was adapted to the analys chromatographic fractions.

The method shows an average deviation from the true 0.21% at the 8 to 10% sodium pyrophosphate level. It standard deviation of 0.10% when replicate determinations v on a single sample. Ortho-, tri-, and trimetaphosphate can separated and determined. The method can be applied to phate built detergents after separating the organic materia alcohol separation. The pyrophosphate determination can in about 4 hours.

Separation of Esters of Mono- and Dicarboxylic Fatty A Gas-Liquid Chromatography. JANINA NOWAKOWSKA, E. H. M AND RICHARD WIEBE.

An apparatus has been set up to study the separation of e mono- and dicarboxylic acids by means of gas-liquid chr raphy. Separations were obtained of mixtures of diethyl m diethyl succinate, dimethyl adipate, and dimethyl sebacate as mixtures of mono- and dicarboxylic acid esters such as d adipate, methyl caproate, methyl pelargonate, methyl azel methyl sebacate, and methyl caprate. Products of oxidatio unsaturated fatty acids and their mixtures—for example, ol (pelargonic and azelaic acids) and of linoleic acid (azelaic and acids) can be separated. A method is being used to study th tion of fatty acids and is being developed as a possible analyt for the quantitative separation of fatty acids in vegetable oils.

Analysis of Fatty Acids and Their Esters by Vapor-Phase C tography. W. J. PODBIELNIAK, S. T. PRESTON, AND P. J. T

The basic principles of vapor-phase chromatography a equipment required for this method of analysis were explain specific application to the analysis of fats and oils was de Recently developed techniques were described, together wit niques used by others working in this field, for the analysis acids and their esters.

Organic Detergent Test Methods. W. G. SPANGLER.

The principal analytical methods for determining organic gents of commercial importance were reviewed. A detailed violet absorption procedure for determining alkyl aryl sulfona included, together with a nonaqueous titration of acid mixes.

Analytical Test Methods for the Inorganic Portion of the De Products. J. C. HARRIS.

Evaluation of available methods for preliminary examina the inorganic portion of detergent compositions indicates th phase of the analysis has a relatively satisfactory status. Uti of various spectrographic devices can prove most helpful preliminary and final determination of detergent components.

Several integrated schemes of analysis are available. N them are as yet incomplete with respect to a good determ of sodium tripolyphosphate, but recently described techniqu considerable promise. These general schemes are under revi the objective of using more effective techniques for certai ponents.

Individual component analyses are under critical exam particularly those for the phosphates. A recently int chromatographic technique promises improvement here. Im techniques for the determination of silica merit examinat integrated schemes as well as for single-component analysis. sulfate analysis may be improved if published methods are ind

Analyses for optical brighteners, corrosion inhibitors, inhibitors, and carboxymethylcellulose are needed and do n exist in satisfactory form.

Rapid Argentimetric Determination of Halides by Direct Potentiometric Titration—Addendum

the appearance of the original article on this subject
iner, V. J., Jr., and Smith, M. L., ANAL. CHEM. 28, 1043
several errors have been called to the attention of the
.

ıann (W. Riemann III, private communication) has
out that the values in column 3 of Table I should be
ted with the mid-points of the interval of columns one and
stead of with the ends, as was done. This produces an
f 0.02, 0.04, and 0.02 ml., respectively, in the end point
determined for chloride, bromide, and iodide and would
e a constant error of +0.0004, +0.0008, and +0.0004 meq.,
ively, for chloride, bromide, and iodide in subsequent
ns. The fact that the data in Table V came out so well
due to compensatory systematic errors of the same order
nitude, or it may indicate that there is a slight error in the
titrations and that the end point values taken were very
correct. In any analysis one should determine a titration
by a series of standard determinations; if this is done in
se, the value taken for the end point e.m.f. is not critical,
ed it is on the steep part of the e.m.f. curve. If it is deter-
that there is a small blank, it can be eliminated by a
in the e.m.f. used for the end point.

use of the correction noted above, the end point e.m.f.
given in column 4 of Table II should be 254, 174, and 55
of 257, 197, and 114. Riemann also points out that
alue given for silver iodide is a typographical error and
be 1.5×10^{-16}. Table I also contains some typographical
thmetic errors: 207.08 in column 2 should read 223.28;
mn 3 the corrections in order are, 2.00 to 0.70, 9.87
, 62.55 to 63.10, 8.13 to 8.10, 11.55 to 11.58, 74.70 to
and 72.00 to 144.00.

bylowicz (E. P. Przybylowicz, private communication)
led to the authors' attention the fact that, as written, the
ndicates that the end points used in the titration of the
halides were the same as those obtained in the titration of
parate halides. This is incorrect; the end point e.m.f.'s
mixed halide titrations should be determined as the
rium e.m.f.'s exhibited by the cell when enough standard
itrate has been added to a standard mixed halide solution
ipitate in turn all of the iodide, bromide, and chloride. A
e.m.f. *vs.* standard silver nitrate added, for such a titra-
hould give breaks which include the equivalence points
h halide. However, the mid-points of these breaks will
cessarily coincide exactly with the calculated end points.
d point e.m.f.'s chosen should, of course, be the ones which
e correct titer. We have found these end points to be re-
ible over periods of 4 or 5 days.

bylowicz has also pointed out that for widely different
of chloride, bromide, and iodide these end points will not
tly the same, so that standardization should be done with
lard sample approximating the composition of the unknown.
cking our procedure Przybylowicz reports that he con-
y obtained the break in the e.m.f. curve at the bromide
int 10 to 14% high and at the chloride end point low by the
been associated with a nonequilibrium condition in the cell brought on by coagulation of the precipitate. This can be avoided by using additional detergent (as much as 5 ml.), stirring vigorously, and allowing a little time for the cell to come to equilibrium near the end point. With enough detergent present, this time need be only about 1 or 2 minutes.

We have not been able to obtain satisfactory reproducible e.m.f. curves without using the detergent, because of excessive potential drift, and therefore believe the detergent to be necessary for satisfactory results. Przybylowicz reports that he has not been able to obtain the bromide break very near the bromide end point in the presence of the detergent, even using the additional precautions mentioned above. He also reports that he is able to obtain satisfactory e.m.f. curves without detergent in solutions of high ionic strength (0.6*M* sodium acetate–0.6*M* acetic acid), and therefore claims that the detergent is not useful in the mixed halide determination. We believe that it is significant that prior to our work, none of the published procedures for potentiometric halide determination involved titrations to fixed end points. We also did not find this practical for separate or mixed halide determinations, except in the presence of the detergent. Both sets of experimenters agree that the potentiometric method is useful for mixed halide determination in the concentration ranges around 0.001*M*, although there is disagreement as to the usefulness of the detergent.

V. J. SHINER, JR
MORRIS L. SMITH

Indiana University
Bloomington, Ind.

Components of Gas Phase of Cigarette Smoke

In the article on "Some Components of Gas Phase of Cigarette Smoke" [Osborne, J. S., Adamek, Stephen, and Hobbs, M. E. ANAL. CHEM. 28, 211 (1956)] the values for COS given in Table VI under the heading "Volume, Cc./Puff at NPT" should be reduced by a factor of 10. The correct values are 0.24, 0.08, 0.51, and 0.11 $\times 10^{-2}$.

MARCUS E. HOBBS

X-Ray Powder Diffraction Patterns of Benzoic Acids

In Tables I and II of the article on "X-Ray Powder Diffraction Patterns of Benzoic Acids" [Rose and Van Camp, ANAL

Liquid-Liquid Continuous Extractor for Solvents Heavier Than Water

Charles E. Pierce and Ralph E. Peterson, National Institute of Arthritis and Metabolic Diseases, National Institute of Health, Bethesda, Md.

MANY modifications of the original Wehrli (*7*) liquid-liquid continuous extractor for solvents heavier than water have been described. Attempts to improve the Wehrli-type extractor have been directed toward increasing the surface area for contact of the two solvent phases, so that the solvent leaving the extraction chamber is more nearly in equilibrium with the aqueous solution. This has been accomplished by mechanical stirring in the extraction chamber (*6*), stirring by injection of the vapors from distillation (*5*), injection of the solvent from a fine jet (*4*), addition of long spiral for the solvent to be in contact with the aqueous phase (*1*), and provision of a diffuser plate (*2*) to disperse the solvent condensate. However, these modified extractors are still relatively inefficient because the extracting solvent does not extract sufficient solute to satisfy the partition ratio during a single passage through the aqueous phase. Thus, there is still a need for a liquid-liquid extractor for solvents heavier than water, which has more versatility and gives a more efficient extraction rate.

The following apparatus meets many of these requirements. A greatly increased boundary surface for contact of the two solvent phases has been achieved by the continual exposure of the organic solvent to a rapidly changing thin film of the aqueous solvent through the use of a rotating glass ball.

OPERATION

The extractor is assembled as shown in Figure 1.

A few hundred milliliters of solvent (dichloromethane has been used in all of these experiments) are placed in a 1-liter round-bottomed distillation flask, which is then attached to the ground joint at the lower end of *C*.

Approximately 500 ml. of dichloromethane are added to the reservoir, *A*, which has a capacity of about 4500 ml. with the 1-liter round glass ball in place. The aqueous phase (water or urine in these experiments) is carefully introduced into *A*. From 200 ml. to a maximum of 4000 ml. of aqueous material may be used in a reservoir of this size.

Urine should be at room temperature or slightly higher (25° to 40° C.) during the entire operation of this extractor. Cold urine has a tendency to form emulsions, but no troublesome emulsions have been experienced with warm urine.

The adjustable side arm, *B*, is set at the proper angle, depending upon the volume of urine added to the reservoir. The angle should be adjusted so that between 300 and 350 ml. of dichloromethane remain in the bottom of the reservoir. This should bring the level of dichloromethane in *A* to just below the center of the circular ball, *D*.

The heating mantle for the distilling flask is connected to a variable transformer and distillation of the solvent is begun. A few boiling chips may be added to the distillation flask to achieve more even distillation of solvent.

The solvent vapors pass up the side arm, *C*, and the condensate collects at the condenser, *G*. This condensate then drops into the side-arm tube and mixes with the solvent in the bottom of the reservoir.

After the solvent has started to distill over, the variable-speed electric motor with the magnet is started. This in turn rotates the magnet encased in Teflon in the hollow glass ball, *D*, enclosed in the reservoir. As the ball turns, it carries a thin film of the aqueous phase through the solvent, and produces a very efficient and continuous mixing of the upper phase. The ball, operating at the slowest speed that is necessary to keep it turning continuously, must turn at a rate of approximately 50 r.p.m. Faster rates produce no more efficient extraction, and too rapid turning may produce emulsions.

The dichloromethane-soluble solutes in the urine reach the distilling flask by way of the ball-and-socket joints are lubricated with water.) *B* has a opening at the top of the bend and a trap on the outer desc arm, to prevent siphoning of the solvent from the reserv the distilling flask. A small hole in *G* prevents a positive p in the distillation system.

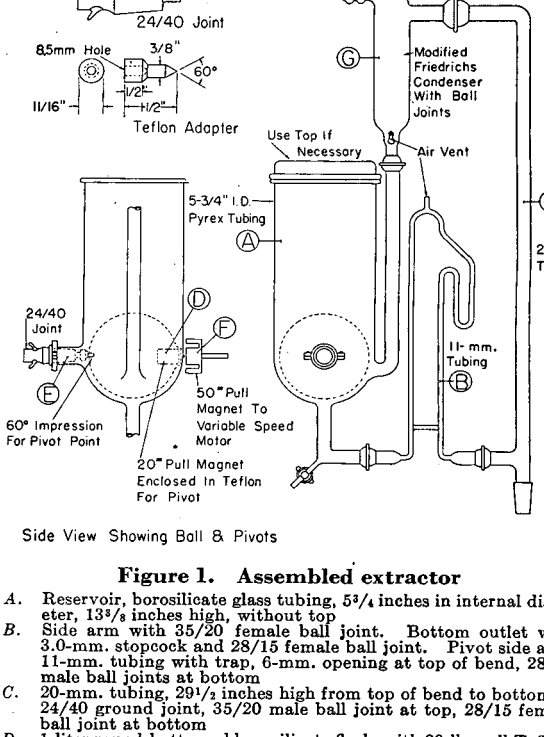


Figure 1. Assembled extractor

- *A.* Reservoir, borosilicate glass tubing, 5¾ inches in internal di eter, 13⅜ inches high, without top
- *B.* Side arm with 35/20 female ball joint. Bottom outlet v 3.0-mm. stopcock and 28/15 female ball joint. Pivot side a 11-mm. tubing with trap, 6-mm. opening at top of bend, 28 male ball joints at bottom
- *C.* 20-mm. tubing, 29½ inches high from top of bend to botton 24/40 ground joint, 35/20 male ball joint at top, 28/15 fem ball joint at bottom
- *D.* 1-liter round-bottomed borosilicate flask, with 20-lb. pull Tef coated magnet embedded in glass flask
- *E.* 24/40 ground-glass joint with Teflon adapter
- *F.* 50-lb. pull magnet to attach to variable-speed motor
- *G.* Modified Friedrichs condenser with 35/20 female ball joint top and 35/20 male ball joint at bottom, 6-mm. air vent n bottom

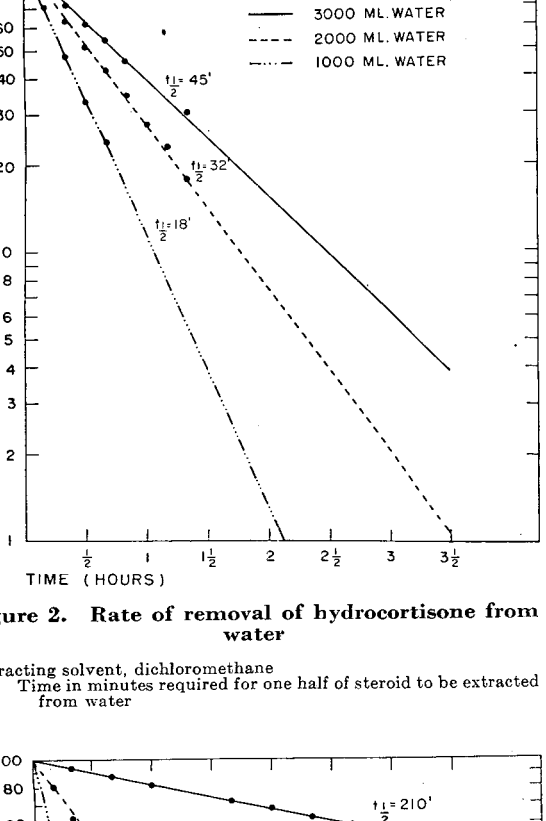
After the extraction operation has been completed, the s in the reservoir may be drained directly into the distillatio by closing the small opening in the tip of the adjustable sid and lowering the angle of the side arm. This adjustable side similar to that described by Iffland (*3*), but makes it po to adjust the liquid level in the extractor over a wider ra volumes. The reservoir may be completely emptied by pla finger over the air vent and lowering the side arm. Aft solvent has drained into the distilling flask, the side arm turned to a vertical position, and the urine drained out th the stopcock at the bottom of *A*.

RATE OF REMOVAL OF STEROIDS FROM WATER

A graphic plot on semilogarithmic coordinates of the fr of steroid removed from the water per unit time produ single straight line (Figure 2). This demonstrates the exp tial nature of the removal process and the efficiency of the r of the aqueous solution. The rate of removal was found t function of the volume of the aqueous phase. Using the s ard Hershberg-Wolfe extractor (*2*) with 1000 ml. of hydrocortisone was removed at a rate that indicated a hal of 84 minutes as compared with 18 minutes with the rotar extractor and 1000 ml. of water. In all experiments wit

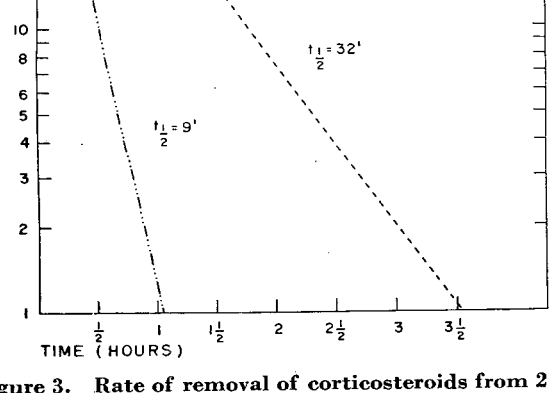
s makes it possible to adjust the liquid level in the extrac-
er a wider range of volumes. The reservoir may be
tely emptied by placing a finger over the air vent and
g the side arm.

rate of removal of the steroids from the water was corre-
ith the partition coefficient of the particular solute be-



ure 2. Rate of removal of hydrocortisone from water

racting solvent, dichloromethane
Time in minutes required for one half of steroid to be extracted from water



gure 3. Rate of removal of corticosteroids from 2 liters of water

tracting solvent, dichloromethane

coefficient ($K = \frac{\text{concentration upper phase}}{\text{concentration lower phase}}$, with solvents equilibrated with each other at 25° C.), the slower the rate of removal of solute. Figure 3 shows the removal rates for three different steroids, using a constant volume of water (2 liters), and also the partition coefficients of the various steroids between water and dichloromethane.

ADVANTAGES

The extraction rate is rapid because of the large surface area of fresh aqueous phase continuously exposed to solvent by the turning of the glass ball, and the continuous mixing of the aqueous phase by the turning of the glass ball. Thus, a rapid equilibration of the solute between the two solvent phases is achieved.

There is little tendency to emulsion formation, because air is not introduced into the system.

Various volumes of urine (200 to 4000 ml.) can be extracted with a small volume of solvent. The extractor may be designed to extract even large volumes of urine.

This extractor, like any continuous extractor, permits extraction of a solute from a large volume of water into a small volume of solvent, especially desirable where the solute is not particularly soluble in the solvent.

ACKNOWLEDGMENT

The authors are indebted to T. D. Perrine for many helpfu suggestions regarding the design of this extractor, and to the Rinco Instrument Co., Greenville, Ill., for aid in the construction. The extractor is commercially available from the Rinco Instrument Co.

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Thermistor-Operated Temperature Control

Charles M. Proctor, Department of Oceanography, Agricultural and Mechanical College of Texas, College Station, Tex.

FOUR things are desirable in a water-bath temperature control system: good regulation, easy temperature selection reliability, and simplicity of design. The regulator described permits temperature control to ±0.01° C. in an uninsulated bath operating 15° above room temperature, a dial setting gives the desired operating temperature. The unit has been in use intermittently for a year at temperatures from 0° to 80° C. with no change in calibration, and the circuit is less complicated than a small "hi-fi" preamplifier.

The thermistor is the most responsive of the temperature sensitive resistance elements. Its thermal coefficient of resistance is about 4% per degree Centigrade, compared with 0.39% for the platinum resistance thermometer. A thermistor does not have the power-handling capability of the metallic resistance elements, so that a much smaller bridge voltage must be used. The bridge output signal for a 0.01° change in temperature may thus be lower with a thermistor than with a metallic resistance thermometer. This lower output can be compensated by slightly higher gain in the amplifier. The lower cost of the thermistor and associated low-power bridge elements, combined with its low thermal lag, makes it a logical choice for the temperature sensing element.

sufficient gain for operation of a shield-biased Type 2050 thyratron (*1*, *5–7*) with a heater control relay in the anode circuit. Figure 1 gives the schematic diagram of the controller; Figure 2 shows the assembled unit.

CONSTRUCTION

Bridge Circuit. The thermistor (Victory Engineering Type 32A1) is used in a modified bridge circuit with the lower arms of the usual Wheatstone bridge replaced by a tapped winding, ten turns of plastic insulated wire added to the power transformer and taped in place. The need for this special winding is eliminated by an alternative bridge circuit (*3*).

Figure 3 is a calibration chart of temperature against potentiometer setting. The thermistor resistance decreases logarithmically with rising temperature, so that switching is necessary to allow accurate adjustment at higher temperatures with a linear taper potentiometer. (Precision log-taper potentiometers are usually available only on special order.)

The thermistor is being operated near its maximum voltage range. Both short- and long-term stability have been satisfactory, however.

Protective Mount for Thermistors. As a commercial source for thermistor mountings could not be found, the one shown in Figure 4 was made from gas pipe fittings and radio chassis grommets.

Amplifier. This amplifier has an over-all voltage gain of about 4500. Use of a lower gain tube, such as 12AT7 or 12AU7, reduces the control sensitivity by a factor of about 3 or 10, respectively.

The 300-volt plate supply comes from a midget power transformer with a half-wave selenium rectifier. Two 130-volt, 20-ma. rectifier units connected in series will withstand 260 volts (r.m.s.) at about 15 ma. (*2*). This amplifier draws only about 1 ma. The filter is more than sufficient to reduce ripple to a satisfactory level and voltage regulation is adequate at this low power drain.

Line noise is reduced by the filter network in the primary circuit of the power transformer. It could probably be omitted in most locations, or replaced by a 0.05-mf., 1600-volt condenser across the high voltage winding. Although line noise (as from an electrical hand drill) seems to cause the relay to operate erratically at times, no effect on bath temperature has been noticed.

In assembling the bridge and amplifier, good audio layout and wiring practice should be followed.

Thyratron and Relay. The thyratron is connected for positive-grid operation (*1*, *5–7*). The heater winding supplies out-of-phase bias for the shield. The heater is isolated from the cathode circuit by a resistor (*4*). The relay connection and operation have been described (*4*). Because of the antiarcing condensers across the relay contacts, both indicator lights will stay on until a heater is plugged into one of the receptacles.

Phasing. With the control grid of the thyratron connected temporarily to the cathode, the relay should remain open, except for an occasional random firing of the tube. If the relay remains closed (thyratron conducting) the shield grid bias will have to be changed by reversing the connection to the heater winding.

With the potentiometer set for balance slightly above room temperature, the relay can be made to operate by breathing on the thermistor. The relay should open as the thermistor is warmed. If the relay closes when the thermistor is warmed, the power line connection should be reversed to either the bridge supply transformer or the thyratron transformer.

PERFORMANCE

In Uninsulated Tank. The unit was tested in an open-top, round borosilicate glass tank 16 inches in diameter and 10 inches in height, holding about 5 gallons of water. The stirrer, 250-watt heater, thermistor, and differential thermometer were arranged in that order around the edge of the tank. After the bath came to equilibrium at about 37° C., the differential thermometer was watched for 2 minutes (through several heating cycles) and the highest and lowest observed temperatures were estimated to the nearest 0.001° C. and recorded over a 16-day period. All readings were within a 0.020° range. Room temperature varied from about 23° to 25° C. during the test.

In an Insulated Flask. A Dewar flask, 7 inches in diameter and 14 inches deep, without cover, was used for a further test of performance. Temperature excursions during a 2-minute period were less than 0.002° C. with 1 volt on the thermistor (*A* scale of Figure 3). In one test at 42° C. over a 24-hour period, the observed temperature readings on the differential thermometer were all within ±0.001° C. The heater input was 50 watts to reduce overshoot.

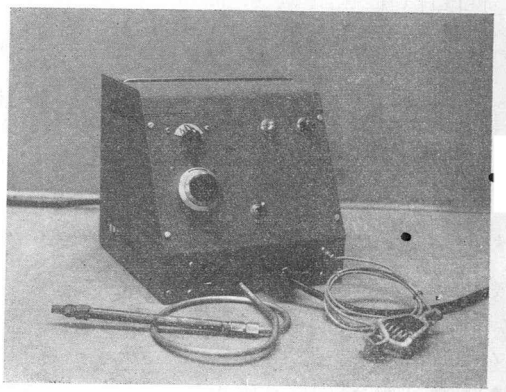

Figure 2. Assembled regulator

With 0.2 volt on the thermistor (*B* scale) the temperature variation was ±0.02° C. with either 50 or 250 watts on the heater. The variation was ±0.03 with very slow stirring.

Stability. No significant temperature drifting was observed during the tests mentioned above and the temperature could be

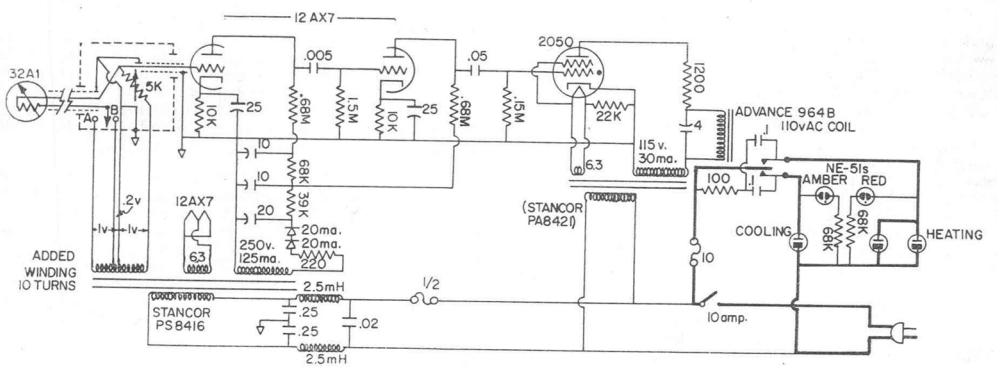

Figure 1. Thermistor-controlled relay circuit

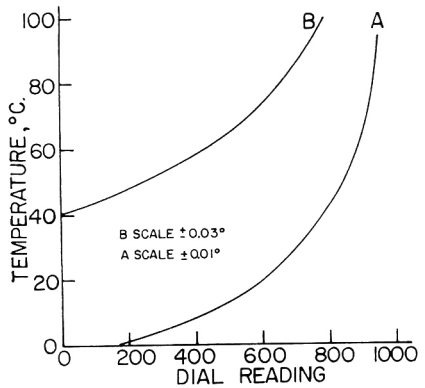

Figure 3. Calibration chart

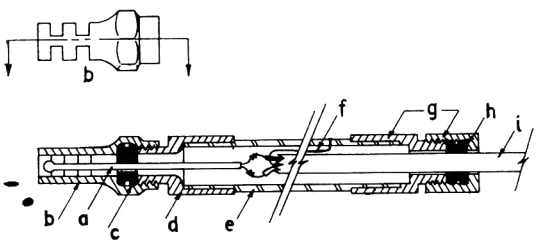

Figure 4. Protective mount for probe-type thermistors

a. Thermistor, Victory 32A1, 32A11, 51A1, or Stantel F type
b. 3/16-inch tubing flare nut, long type. Water circulation slots cut with hack saw
c. 1/4-inch rubber grommet. Fits Victory, ream out for Stantel
d. 3/16-inch tubing × 1/8-inch female IPS compression connector. Nut not used. Ream out for Stantel
e. 1/8-inch brass nipple. At least 4 inches long for Victory 32A11, 6 inches or longer for others. *d* and *g* sweat-soldered to nipple
f. Flexible grounding wire from shield to hole in nipple
g. 1/4-inch tubing × 1/8-inch female IPS compression connector with nut. Ream out to fit cable
h. 3/8-inch rubber grommet. Trim edges to fit inside nut
i. Microphone cable, Belden type 8422, two-conductor, shielded, vinyl insulation

reset to within 0.02° C. (test at 42° C). A year after the original calibration the instrument setting was rechecked at several temperatures from 0° to 80° C. No change in calibration was observed.

Line voltage changes from 100 to 130 volts have little effect on performance of the controller.

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Power Supply for Zone Electrophoresis, Electrodialysis, and General Use

Charles M. Proctor, Department of Oceanography, Agricultural and Mechanical College of Texas, College Station, Tex.

IN ZONE electrophoresis, evaporation will cause the resistance of the strip to go down, because of an increase in concentration of the supporting electrolyte. Constant current is therefore recommended for most applications, in order to limit heat dissipation in the strip [Raymond, Samuel, *Science* **120**, 677–8(1954)]. The conditions are different in electrodialysis, where the cell resistance rises to a very high value as salts are removed from the solution. As dialysis progresses, the voltage across the cell should be increased to speed removal of the last traces of salt. Inverse current regulation is needed, however, to avoid overheating the cell.

The power supply shown in Figure 1 was built for exploratory scale electrophoresis and electrodialysis studies.

A 6AG7 is used as regulator tube with switching for pentode operation to give constant current, triode operation for inverse current regulation, and the regulator tube made inoperative when the unit is used as a straight power supply with either choke or condenser input filter. The same basic circuit could be used for higher voltages and currents by selecting a larger tube and appropriate components.

Circuit Design Considerations. The eight terminals at the right of Figure 1 are connections to an octal socket on the front panel. Separate cords are used for regulated or unregulated output, and for condenser or choke input. The labels on the drawing indicate the pin jumpers that should be placed in the cord plug for various operating conditions. The no-load output from the filter is about 300 volts with choke input, 370 volts with condenser input. The 1-megohm resistor allows the first section of the filter condenser to charge, the time constant (RC) is 10 seconds, with no output plug in the socket. This prevents a current surge if an output cord is connected to the supply while the rectifier is operating. The regulator tube heats only when there is a plug jumper between terminals 2 and 3.

Pentode Operation at Constant Current. The screen grid current of a pentode varies as an inverse function of the plate current. Cathode degeneration cannot be used for plate current regulation, if the screen return current flows through the cathode biasing resistor. A separate screen voltage supply is therefore necessary for good regulation.

It is obtained from a small 115-volt, 15-ma. transformer with a 6.3 volt, 0.3-ampere heater winding. A 12AU7, with grids and plates connected together, is a satisfactory rectifier. (A transformer such as Stancer PS-8415 and a 6 X 4 rectifier could be substituted.) The No. 48 lamp (2 volts, 0.06 ampere) serves as a screen current indicator and fuse. Under normal operation, the lamp will never show more than a barely perceptible glow.

With the operation control switch in position 1, the screen supply transformer is connected to the power line, the regulator tube is pentode-connected, and the control grid potentiometer is connected to the bleeder resistor to provide a positive reference potential for operation with cathode degeneration. A functional outline of the pentode-connected circuit is given in the lower right corner of Figure 1 for greater clarity.

The 6AG7 is rated for 9-watt plate dissipation. With a very small value of load resistance, the plate to cathode potential may reach 300 volts. The regulator is therefore designed for maximum operating current of 30 ma. This operating current is covered in two ranges: 0 to 10 ma. and 0 to 30 ma. With the range switch in "low" position, the cathode resistor is 8500 ohms and the meter operates with normal scale. When the range switch is moved to "high," the value of the cathode resistor is reduced to 2500 ohms and a 3x shunt is connected across the meter. For the various models of panel mount, 10-ma. meters are currently being listed in the radio supply catalogs; those made by Triplett have a nominal resistance of 3.1 ohms; by Simpson, 10 ohms. The shunt should be one half of the meter resistance.

The load current *vs.* voltage curves are shown in Figure 2.

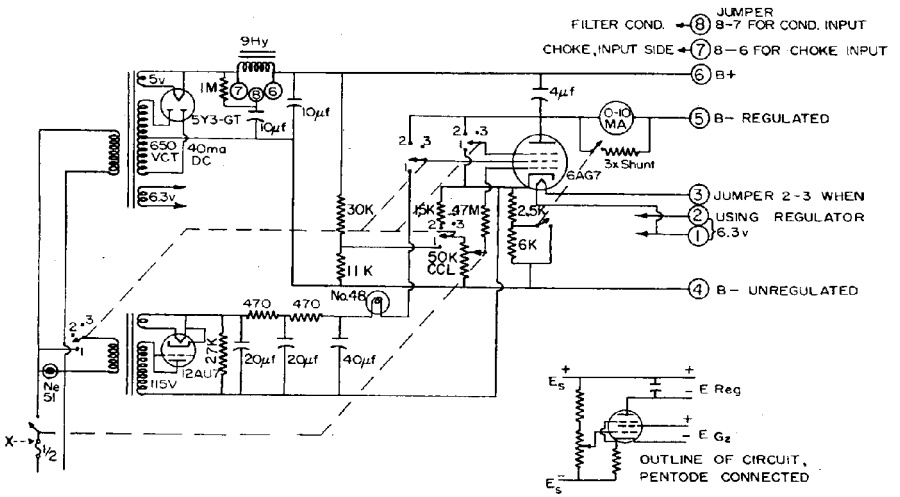

Figure 1. Circuit of regulated power supply

This power supply gives constant or inverse current regulation at the turn of a switch. It may also be used unregulated for plate and heater supply. A safety interlock switch may be connected at point *X*. The potentiometer is Ohmite-type CB 5031, with switch.

The power supply regulation curve, measured at the output of the filter, is given at the right of the figure. With the 4-μf. condenser across the load, the ripple at 300-volt output is less than 0.01% as estimated with the aid of an oscilloscope. Voltage regulation of the screen supply is rather poor. The performance could be improved by using a voltage regulator tube in the screen supply, but the degree of regulation shown in Figure 2 is adequate for present use.

If the load circuit were opened while the power supply is on, cathode bias would be removed. Screen current would then soar, burning out the No. 48 lamp. The 0.47-megohm resistor would limit the control grid current to a safe value. The only damage to the circuit would thus be one burned-out bulb.

Triode Operation, Inverse Current Regulation. For triode operation the control switch is set in position 2, the screen supply is turned off, the tube is triode-connected, and the grid potentiometer is connected for variable cathode bias. The allowable plate voltage for triode connection is higher with the suppressor grid tied to the plate than if it were at cathode potential. Power dissipation by the screen should also be lower. The 1.5-kilohm resistor in series with the grid potentiometer provides a minimum grid bias when the potentiometer is in full range position. The 0–10- and 0- 30-ma. range switch functions as before.

The triode operating curves are given in Figure 3. For each setting of the grid potentiometer, the load resistance was increased in six to ten steps, starting from zero. Current through the load varies inversely with the voltage drop across it. The dotted curves show the calculated load power dissipation for each of the current-voltage curves. In actual operation with an electrodialysis cell, load resistance and load voltage will start not at zero but at some point along an operating curve. As dialysis proceeds, the current-voltage relations can be predicted from these curves.

Unregulated Operation. With the operation control switch in position 3 and no connection between pins 2 and 3 of the cable plug, the unit acts as a choke or condenser input power supply, depending on the connection of pin 8. The output voltage-current curve for condenser input operation is the same as the supply voltage curve shown at the right of Figures 2 and 3. Maximum output current from the specified transformer is 40 ma. of which the bleeder takes 10.

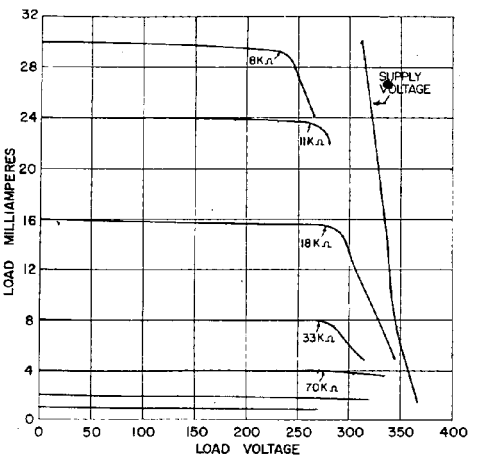

Figure 2. Pentode operation at constant current

For each curve, the current-control (grid bias) potentiometer was set with zero load resistance. The load resistance was then increased until the current dropped sharply. The maximum usable value of load resistance is given beside the break in each current curve. The supply voltage changes with load current, vertical curve at the right of the figure, and was measured between terminals 4 and 6.

With choke input connection: the no-load voltage drops to 300, regulation improves considerably, maximum available output current is 45 ma. (Langford-Smith, F., "Radiotron Designer's Handbook," 3rd ed., chap. 22, 23, RCA, Harrison, N. J., 1945) and filtering efficiency much lower.

NOTES AND COMMENTS

For convenience in handling, the unit was built into a 6 × 9 × 5 inch steel cabinet. The cabinet should be large enough to provide a compartment for storage of output cables with the various plug connections.

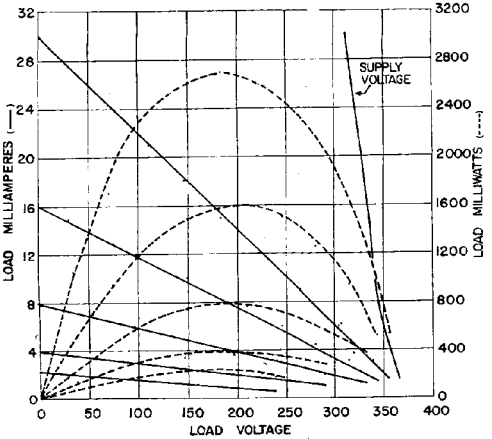

Figure 3. Triode operation, inverse current regulated

As the load resistance is increased from zero, the load voltage rises and current drops. The power dissipation in the load is shown by dashed lines. Supply voltage curve is as for Figure 2.

An unexpected use for the current-regulated supply was found in determining the closing and opening currents of a group of plate circuit relays.

For safety in the chemical laboratory, no part of the circuit should be connected to the chassis. The chassis should be grounded; 300 volts at 30 ma. can be very uncomfortable and can be dangerous when the hands are wet. For this reason a safety-interlock switch is provided on most commercial electrophoresis cells, so that power is removed when the cell cover is opened. This safety switch should be connected between the fuse and the power switch. The filter can be permanently connected for condenser input, leaving socket terminals 7 and 8 for the safety switch leads.

For less critical current control the separate screen supply may be omitted and screen voltage obtained from the high voltage supply through a 25-kilo-ohm, 10-watt dropping resistor. The control grid is connected to B^- and cathode bias used. The cathode resistor may consist of two 4-watt wire-wound potentiometers in series, a 5000 ohm and a 500 ohm for coarse and fine control, respectively. The current drop with increasing load is about 5 times as great with this modification.

When half-wave rectification is used for the plate supply the ripple is only about 0.02%. The above circuit may thus be adapted for operation up to about 1200 volts by using a type 5R4GY as half-wave rectifier with a good quality receiver-type transformer for the plate supply and using an 807 (or higher voltage) transmitting type pentode for the regulator tube. Adequate precautions against shock are mandatory.

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Analysis of Pickling Bath Solution Using Ion Exchange

Florence Nesh and Edward C. Haas, Naval Material Laboratory, New York Naval Shipyard, New York, N. Y.

THE reagent control of pickling bath solutions used to clean the surfaces of aluminum and aluminum alloys preparatory to spot welding is effected by a weekly titration for acid content and a monthly sulfate determination. In this laboratory a method has been developed involving the titration to a pH of 3.5 for nitric acid content, a continued titration to a pH of 7.0 for the aluminum salt content, and an ion exchange method for the determination of sodium sulfate. This method eliminates the long and tedious gravimetric procedures previously used, without sacrifice of accuracy.

Ion exchange has been used for total cation determination in inorganic analysis (Samuelson, O., "Ion Exchangers in Analytical Chemistry," Wiley, New York, 1935), and recently a method was brought to the authors' attention in which the ion exchange principle was applied to the analysis of iron pickle liquor [Fisher, S., Kunin, R., ANAL. CHEM. **27**, 1649 (1955)].

The cleaner is composed of 15% by volume of 42° Baumé nitric acid, 13 ounces per gallon of sodium sulfate decahydrate (Glauber's salt), and the balance water. The solution, when in use, is maintained at a temperature of 180° to 190° F. The ion exchange column used consisted of 40 grams of the cation resin Amberlite IR-100, the hydrogen form, packed in a 100-ml. buret with a plug of glass wool at the bottom. The total exchange capacity of this resin is 1.7 meq. per gram and 0.6 meq. per ml. It was determined by experiment that 24 meq. of sodium ion would saturate 25 grams of resin.

The following procedure is recommended for the analysis of prespot weld aluminum pickling bath solution.

Take 5 ml. of the pickling bath solution and dilute to 250 ml. in a volumetric flask.

Take a 25-ml. aliquot of the diluted solution and titrate to a pH of 3.5 (or to a methyl orange end point); continue titrating to a pH of 7.0 (or to a phenolphthalein end point).

Take another 25-ml. aliquot of the diluted solution and pass it through the ion exchange column.

The figure at pH 3.5 gives the nitric acid content and the figure at pH 3.5 to 7.0 gives the aluminum salt content. The total of these two figures subtracted from the eluate figure gives the sodium sulfate content.

To verify the procedure, a solution was prepared from accurately weighed amounts of pure anhydrous sodium sulfate, nitric acid (specific gravity 1.42) and pure aluminum wire and the whole was diluted to simulate a partially depleted pickling bath. This synthetic solution was analyzed, with the following results.

	Meq. in Aliquot	Meq. Found
Na_2SO_4	1.37	1.32
HNO_3	2.20	2.15
$Al(NO_3)_3$	0.110	0.104

THE opinions or assertions contained in this paper are the private ones of the authors and are not to be construed as official or reflecting the views of the Naval Service at large.

Buret Pump for Handling Two-Phase Liquids in Quantitative Analysis

W. R. Dunnavant, Chemistry Research Branch, Aeronautical Research Laboratory, Directorate of Research, Wright Air Development Center, Wright-Patterson Air Force Base, Ohio

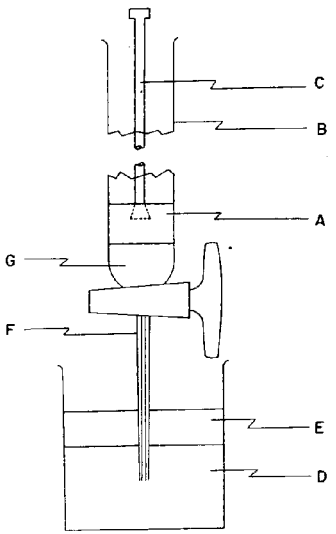
IN ANALYTICAL work it is sometimes necessary to standardize solutions which are unstable in contact with air. These solutions are commonly stored under a protective layer of a less dense immiscible liquid and are handled during titration by means of an apparatus requiring an inert gaseous atmosphere, or an evacuated system in order to prevent decomposition. These types of systems generally use a buret connected to the supply of solution to be titrated and frequently result in titrations of solution contained only in the connecting tube and not truly representative of the bulk of the solution, regardless of how well it has been mixed.

The pump described is a rapid, convenient, and accurate means of titrating unstable solutions or liquids which have been

prepared, or are stored under a protective liquid layer, and allows the sample to be withdrawn from the main bulk of the solution.

The essential features of this apparatus are the constant maintenance of the two liquid phases existing in the storage vessel at all times during the transfer operations required in the titration and the elimination of the elaborate apparatus setups required by the other methods for accomplishing the same results.

A piston is constructed by cutting a rubber cylinder, with a diameter slightly larger than the bore of the buret to be used, from a rubber stopper by means of a cork borer. This cylinder is drilled out to grip the flared end of the glass rod, *C*, which is slightly longer than the buret, *B*, and enables the piston to be raised or lowered. The rubber cylinder is placed on a rotating glass rod held in the chuck of a stirrer motor and its diameter is decreased by holding it against a piece of fine emery cloth on a wood block until it barely slides smoothly through the buret.



In use, the air-sensitive solution, *D*, is prepared, or stored, under a protective layer of a less dense, immiscible liquid, *E*. The buret tip, *F*, and a portion of the buret barrel, *G*, are filled with liquid *E* or an equivalent and the stopcock is closed.

The piston is pushed into the buret with sufficient force to cause the leakage of all air trapped above the surface of *G* around the piston, *A*. When the piston touches *G*, a tight seal is formed between the piston and the inner wall of the buret. The tip of the buret is now placed beneath layer *E* in the liquid to be transferred, *D*, the stopcock is opened, and the buret is filled by slowly withdrawing the piston. When the desired volume has been withdrawn, the stopcock is closed and the piston removed from the buret. The unstable liquid is now in the buret, still protected by a layer of *E*.

In performing a titration, the buret tip should be flushed for each sample removed by allowing a small volume of solution to run out (assuring fresh solution in the tip). Any droplet remaining on the tip is removed, and the tip is immediately immersed in the liquid to be titrated. The titration is then carried out in the normal way.

In this laboratory this method proved to be extremely advantageous for the standardization of chromous chloride solutions. The measured volumes of chromous solution were run in under the surface of excess ferric ammonium sulfate solutions, which were then back-titrated with standard dichromate using diphenylaminesulfonic acid indicator. A large number of chromous determinations by this method, using dodecane as the protective liquid phase, indicated a precision of >99.7% when carried out with a 50-ml. buret.

Micro Test Tube Marker

Sjoerd L. Bonting[1] and Gerald R. Walters, Department of Physiology and Physiology-Pharmacology Machine Shop, College of Medicine, State University of Iowa, Iowa City, Iowa

In work on the microliter scale, diluting to volume is usually avoided by employing known and reproducible volumes of sample and reagents. However, in some cases this is not possible—e.g., in determinations involving a digestion at high temperature, in the course of which varying amounts of fluid may evaporate.

A micro test tube marker has been constructed, which allows the marking of micro test tubes to contain volumes of from 20 to 500 μl. An exploded view of the apparatus is shown in Figure 1.

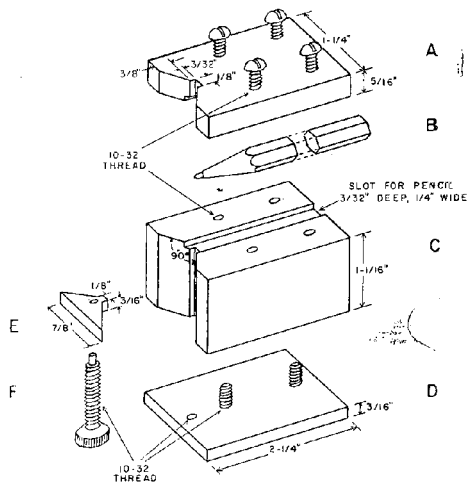


Figure 1. Apparatus

D, *E*, and *F* are made of brass, while *A* and *C* consist of aluminum to reduce the total weight of the apparatus. *B* is a diamond marking pencil (Fisher Scientific Co., No. 8-675). *A* and *C* both have a slot 3/32 inch deep and 1/4 inch wide to hold the marking pencil. They have a V-shape cut on one side, which takes triangular stage *E*. The dimensions are given in Figure 1. Plate *D* is permanently fastened to block *C* with two 10-32 flat-head machine screws. Screw *F* runs through the hole in plate *D*. Triangular stage *E* is lightly riveted to *F*.

The marking pencil is positioned in the slots in *A* and *C*, and is then held in place by tightening the four 10-32 round-head machine screws in *A*. A volume of water, equal to the volume at which the tubes are to be marked, is added to each of the tubes by means of a Lang-Levy constriction pipet (Microchemical Specialties Co., Berkeley 3, Calif.).

The tube is placed on stage *E* in the V-shape groove, and held there with the index finger of one hand. The whole assembly is held at eye level against a well-lighted background. The test tube and diamond point can be observed through the space remaining between *A* and *C*. The stage is lowered or raised until the dia-

[1] Present address, Department of Medicine, Presbyterian Hospital, and Department of Biological Chemistry, University of Illinois College of Medicine, Chicago 12, Ill.

mond point is exactly opposite the lower side of the meniscus. As the upper part of block *C* is just below the meniscus, the bottom of the meniscus appears dark, and can therefore be aligned with the diamond point with great accuracy. The test tube is then rotated once or more, while being pressed gently into the V-shape groove and onto the stage. This gives a very fine mark all around the tube.

The reproducibility in actual use was determined for 20 tubes, calibrated to contain 100 μl.

Each tube was first weighed dry to 0.02 mg., then placed in a holder on a rack and pinion stage, and filled to the mark with water from a vertically clamped capillary pipet. The addition of fluid from the pipet was controlled by means of a 1.0-ml. hypodermic syringe, connected with the pipet through plastic capillary tubing. Observing the tube through a magnifying glass facilitated the setting of the meniscus. The tube was weighed again, and the volume of water contained in the tube was calculated from the difference in weight.

The average volume was 99.03 μl., with a standard deviation of 0.72 μl. The constriction pipet, used to add the water prior to marking the tubes, had a calibrated volume of 99.0 μl. As the inner diameter of these tubes was 4.0 mm., this reproducibility means that the meniscus can be set to within $\pm$0.058 mm. from the mark. Parallax can easily be avoided, as the mark extends completely around the tube.

Plastic Vessel for pH Measurements of Small Samples

Kenneth M. Richter, Department of Anatomy, University of Oklahoma School of Medicine, Oklahoma City, Okla.

One principle which seems to have been followed in designing electrodes for pH and electromotive force measurements has been to make electrodes fit the amount of sample available. Thus, electrodes are listed commercially for large samples, for samples from 3 to 5 ml., for 1-drop samples, and for those even smaller.

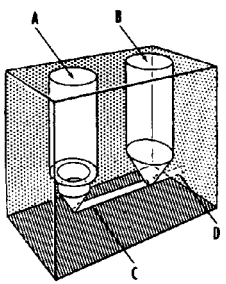


Figure 1. Plastic pH vessel

A, B. Wells, 1/2-inch diameter. *A* has bottom shoulder.
C. Connecting channel
D. Cemented plug

A vessel has been fabricated in which the sample chamber closely reflects the size and shape of standard Beckman electrode tips, and which can accommodate samples as small as 0.25 ml. The vessel illustrated (Figure 1) is designed for use with the No. 4990-80 and No. 4970 Beckman standard electrodes measuring approximately $^7/_{16} \times 5^1/_4$ inches. It consists of a block of Plexiglas, 1 × 1.5 × 2 inches, in which two closely spaced wells $^1/_2$ inch in diameter are drilled. One well has a shoulder at the bottom to conform to and at the same time prevent damage to the small elevated tip of the calomel electrode (Figure 1,*A*). The wells are connected at the bottom by a narrow channel drilled in from one end only. The portion of the channel not connecting the wells is plugged with a cemented-in rod of Plexiglas. The sample chamber is cleared and smoothed by flushing with Plexiglas solvent. Dimensions for this particular vessel may be obtained from Figure 2.

The scale near the left edge of the vessel (Figure 2,*A*) indicates, from bottom to top, the levels reached in the wells by 0.25-, 0.50-, 0.75-, and 1-ml. samples, respectively. When electrodes are inserted to the bottoms of the wells, the level of each of these various sized samples is raised and more electrode surface is bathed by a given sample than is indicated by the scale.

Hundreds of check pH determinations with the indicated electrodes have shown that this vessel does not change the accuracy of measurement. For greatest accuracy the sample chamber and electrodes should be dry before adding sample. Also, rather serious errors may be incurred in the measurement of thin layers of poorly buffered solutions due to the solubility of the glass.

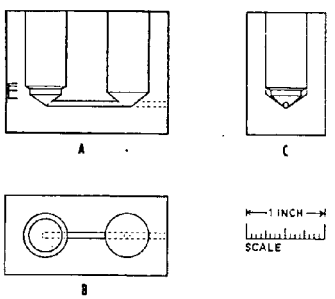


Figure 2. Orthographic projection of plastic pH vessel

This type of vessel has been used for 4 years to make pH measurements on supernatants of 2 ml. and less from roller tube cultures, as well as in the routine preparation of tissue culture media, buffer solutions. and the like.

A plastic cell of small capacity has also been suggested by Dietz [Dietz, V. H., *Science* **108**, 338 (1948)] but its shape does not conform to that of the electrodes as does the vessel described here.

ACKNOWLEDGMENT

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Ultraviolet Scanner-Camera for Paper Chromatography

Norman A. Drake, William J. Haines,[1] Raymond E. Knauff,[2] and Eldon D. Nielson, The Upjohn Co., Kalamazoo, Mich.

Brief descriptions of scanner-cameras for the visual and photographic detection of ultraviolet-absorbing steroids on paper chromatograms have been published from this laboratory previously (*1*, *2*). Details are presented here for the construction

[1] Present address, Armour Laboratories, Chicago, Ill.
[2] Present address, G. D. Searle and Co., Chicago, Ill.

and operation of a scanner-camera which has now found extensive use in the field of steroid research both in this and other laboratories. (A similar machine will be manufactured commercially by Labline, Inc., Chicago, Ill.)

Obviously, the usefulness of this apparatus is not limited to work with steroids. In fact, the ultraviolet photography of paper chromatograms was proposed independently by Markham and Smith (*4*), who employed the technique for the detection of purines, pyrimidines, and derivatives of these compounds.

CONSTRUCTION

Ultraviolet Scanner-Camera. The ultraviolet paper chromatogram scanner-camera consists of a lighttight box containing a light source, an adjustable shutter and its enclosure, a transmission filter, a fluorescent screen, and a pressure plate. The box, which is constructed of stainless steel to resist the corrosive vapors of laboratory atmospheres, is 20 × 7 × 14 inches (length × width × height). The open top of the box is surrounded with a ledge to hold an exposed filter in place. A 15-watt ultraviolet lamp (Germicidal Type WL-15 Sterilamp, Westinghouse) is centered in the bottom of the box. The top surfaces of the shutter and its enclosure are 6 inches above the box floor. The transmission filter consists of three 6.5-inch squares of Corning filter glass No. 9863 (transmission characteristics: range, 230 to 420 mμ; maximum, 320 mμ; 50%, 250 to 390 mμ). Three squares of filter glass are needed to cover the top of the box because a single piece of appropriate size is not obtainable. The top surface of the filter must be higher than the retaining edges of the box.

The fluorescent screen consists of Du Pont zinc silicate phosphor No. 609 (activated maximally by light of 254 mμ wave length) deposited on double-strength window glass. The phosphor vehicle and adhesive, which must transmit ultraviolet light, is poly(vinyl alcohol) (Elvanol 71-24, Du Pont). The screen is encased in a metal band with a hinge along the rear. The screen must be large enough for the metal encasement to rest outside of the filter glass. This is necessary so that the screen will press tightly against the paper. The pressure plate, used with the adjustable shutter when the apparatus is employed as a camera, is simply a piece of aluminum sheet stock, 20 × 7 × 0.5 inches, which has one evenly flat side and an attached handle on the other side. A schematic diagram of the scanner-camera is given in Figure 1.

Visible-Light Camera. The ultraviolet scanner-camera can be modified for use as a camera to photograph spots made visible by color development on paper chromatograms. This adapted camera is useful not only as an aid in the preparation of permanent records, but also as a means to obtain photographs for comparison with ultraviolet photographs of the same paper chromatograms taken before color was developed. The visible-light camera can be constructed by the use of a 15-watt fluorescent lamp instead of the germicidal lamp, and plate glass instead of the Corning filter glass.

OPERATION

Detection of Ultraviolet-Absorbing Compounds. When compounds having ultraviolet absorption are to be detected on chromatograms, the paper strip is placed on the filter glass, and the fluorescent screen is lowered to rest directly on the paper. The light source is turned on in a darkened room to view the fluorescent screen. The filter paper background appears as a uniform, light greenish fluorescence, whereas areas bearing ultraviolet-absorbing materials appear as distinct, dark shadows. These shadows are due to the absence of fluorescence in the regions where ultraviolet light is prevented from impingement upon the screen.

Lengthy observations (for more than several minutes) of the chromatogram should be avoided because of the possible decomposition of compounds on the paper by ultraviolet light and as a precaution against possible damage to the screen by the chromatographic solvents. The chromatogram should be air-dried for about 5 minutes or longer prior to viewing in order to allow the evaporation of volatile solvents which may otherwise render it overly moist or opaque to ultraviolet light.

If the paper chromatogram is cut with channels as described by Zaffaroni, Burton, and Keutmann (*5*), the use of a complementary mask, cut from thin cardboard and placed between the chromatogram and the filter, prevents an excessive amount of fluorescence on the screen and renders the ultraviolet-absorbing substances more readily detected.

A photograph can be made of the chromatogram if the fluorescent screen is replaced by photographic paper (Kodagraph Contact Standard), weighted down by the pressure plate. Such photographs can be used for prolonged study and can be filed as permanent records. If the data pertinent to the chromatogram are written on the paper with a soft pencil (No. 1 lead), they appear on the photograph as well. The chromatographic record, therefore, is complete on the photograph. Ultraviolet-absorbing spots appear white on the black background on the photograph. Exposure time varies relative to the type and amount of solvent on the paper. Two to 4 seconds, standardized as a certain number of shutter strokes, is generally satisfactory. It is sometimes of value to over- or underexpose photographs to reveal features not observable under standard exposure conditions. Low concentrations of material are more readily detected by underexposure; two components, not completely resolved, may be revealed by overexposure.

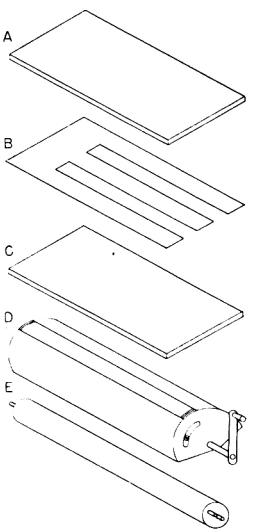

Figure 1. Schematic diagram of scanner-camera

A. Fluorescent screen
B. Papergram
C. Transmission filter
D. Adjustable shutter
E. Ultraviolet light

Should it be desirable to elute the compounds from channeled chromatograms for further study, the paper strips may be placed off-center over the photograph, and the area containing the compound accurately marked for subsequent segmentation. Marking for segmentation on nonchanneled chromatograms can be accomplished with a blunt scriber while viewing on the scanner. If color tests are run on channeled paper, the location of chromogenic compounds and ultraviolet-absorbing compounds can be compared in a fashion similar to that described for segment elution.

The amount of ultraviolet-absorbing steroid detectable by the visual and photographic methods is about 5 γ per square cm. of filter paper.

Photography of Chromogenic Compounds. The use of the visible-light modification of the scanner-camera derives its greatest utility in the preparation of permanent photographic records of developed paper chromatograms. This is especially true if the color developed on the paper fades rapidly after development. Contact paper is used as in the ultraviolet photography; however, a somewhat longer exposure is necessary in this case. In the use of this device to photograph chromatograms with developed tetrazolium color (*3*), a pretreatment of the processed paper is desirable. This pretreatment consists of: (1) washing excess tetrazolium reagent and alkali from the paper with water (deionized water is used in this laboratory), and (2) moistening the washed paper with 50% (by volume) aqueous propylene glycol. The washing and moistening operations are performed while the chromatogram is supported on a sheet of stainless steel at an angle of 45° in a sink. The use of propylene glycol enhances the transparency of the paper.

Figure 2 shows photographs of the same paper chromatogram, first, by ultraviolet photography and, second, by visible-light photography after tetrazolium color has been developed on the paper.

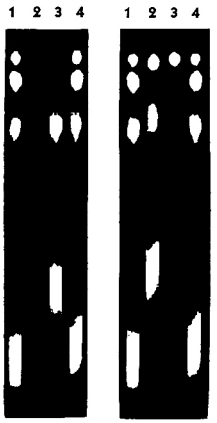

Figure 2. Comparison of photographs of same papergram

Papergram developed on Whatman No. 1 paper in toluene–propylene glycol (*5*).

UV. Ultraviolet photography
TC. Visible-light photography after tetrazolium color development

Channels, top to bottom:
1, 4. 11-Epihydrocortisone, hydrocortisone, cortisone, 11-desoxyhydrocortisone
2. Tetrahydrocortisone (TC), tetrahydro-11-desoxyhydrocortisone (TC), tetrahydro-11-dehydrocorticosterone (TC)
3. Tetrahydrohydrocortisone (TC), pregnenetriolone (UV), 21-desoxyhydrocortisone (UV)

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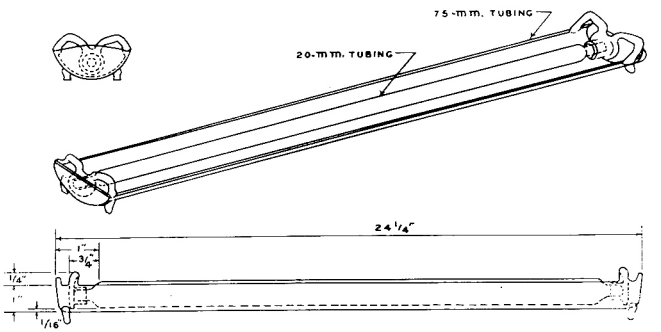
Tray for Dipping Chromatograms

Nelle J. Morris and Austin C. F. Mason, Southern Regional Research Branch, Agricultural Research Service, U. S. Department of Agriculture, New Orleans, La.

Paper chromatograms, after development, generally require the application of reagents for locating the positions of the separated components. Depending on the reagent, the solvent in which the reagent is dissolved may be allowed to evaporate and the dried chromatogram heated or allowed to stand at room temperature until reactions have produced colored spots on the paper. The reagents are usually sprayed on the chromatogram. However, it is often better to dip the chromatograms in solutions of the reagents in organic solvents (*1–3*), in which the separated components are not readily soluble. Among the advantages of dipping are uniform application of the reagent to the chromatogram and the avoidance of mists. In order to dip the chromatograms conveniently, an apparatus is needed that will achieve positive and uniform wetting of either large or small papers, will not exert much drag on the paper (danger of tearing wet paper), will require only a small volume of solvent, and will be easy to clean, inert to corrosive reagents, and free from sources of contamination—e. g., metals.



A tray that meets these requirements and provides a convenient means for dipping large chromatograms is made from a longitudinally split section of borosilicate glass tubing. For a roller to hold the paper beneath the surface of the reagent solution, a glass tube of smaller diameter, sealed at the ends, is fitted into fixed glass sleeves in such a manner that the tube rotates freely. A 24.5 × 2.75 inch tray will accommodate chromatograms up to 22.5 inches in width. The exact dimensions of the tray (or roller) are not important; however, trays much smaller in diameter would not be convenient for use with large papers. The glass sleeves were prepared from glass tubing having an inside diameter slightly larger than the short pieces of glass rod that seal the ends of the roller and fit into the sleeves. The sleeves were slipped on the roller and then sealed permanently to the tray. In use, a dried paper chromatogram is slipped under the roller tube and drawn quickly through the reagent solution (approximately 50 ml.). This device is probably suitable for other laboratory coating and impregnating processes.

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