Reagent Chemicals, A.C.S. Specifications

THE AMERICAN CHEMICAL SOCIETY's Committee on Analytical Reagents has completed a revised and greatly enlarged book on specifications. We have been assured by Mack Printing Company that copies will be available early in January of next year.

We are indebted to W. D. Collins, secretary of the Committee on Analytical Reagents, for the following brief summary of early attempts to raise the quality of laboratory chemicals:

One of the early pioneers was Edward Hart of Lafayette College, famous for many reasons, including the establishment of the *Journal of Analytical and Applied Chemistry*, which was incorporated into the *Journal of the American Chemical Society* in 1893, with Professor Hart as editor. Professor Hart continued his editorship of *J.A.C.S.* until 1902.

Professor Hart encouraged two of his students to form the Baker and Adamson Company, manufacturers of laboratory chemicals. He served as president of the company from 1881 to 1913. The two students, John T. Baker and George P. Adamson, were 21 and 17 years old, respectively, at the time the Baker and Adamson Company was formed.

At a meeting of the World Congress of Chemists in Chicago, August 21, 1893, C. B. Dudley and F. N. Pease presented a paper entitled "The Need of Standard Methods for the Analysis of Iron and Steel, with Some Proposed Standard Methods." The authors in the paper suggested four causes for the many observed discrepancies in analyses: (1) lack of uniformity of samples, (2) impurities in chemicals or defects in apparatus used, (3) the chemist, and (4) the method.

The comments of Dudley and Pease helped to stimulate the AMERICAN CHEMICAL SOCIETY into a program designed to improve the quality of laboratory reagents. A Committee on Uniformity in Technical Analyses was established, with W. F. Hillebrand of U. S. Geological Survey as chairman. In a report published in 1904, the committee referred to the Dudley and Pease paper and in substance expressed the hope that the Society's Committee on Purity of Reagents, working in cooperation with the National Bureau of Standards, would help to improve the quality of laboratory chemicals.

The Committee on Purity of Reagents held its first meeting on November 20 and 21, 1903, with John H. Long of the Northwestern Medical School as chairman. Other members of the committee were Charles Baskerville, College of the City of New York; L. N. Dennis, Cornell University; H. P. Talbot, Massachusetts Institute of Technology; and W. F. Hillebrand, who served as secretary.

The Committee on Purity of Reagents proposed a very elaborate and detailed program, but unfortunately its efforts were unsuccessful. At the New Orleans meeting of the AMERICAN CHEMICAL SOCIETY, December 29 and 30, 1905, there was some criticism of the delay in publication of the committee report. At a meeting in Washington, March 24, 1906, the committee decided to abandon the idea of publishing a complete book on specifications and instead suggested that its recommendations be published in the Society's journal.

The committee continued in a stand-by status dealing with questions relating to reagents until the spring meeting in New Orleans in 1915, when it was not reappointed. Individually and as a committee the members continued to exert pressure on manufacturers to produce reagents of higher quality.

Renewed interest by leading members of the Society in the question of specifications for laboratory reagents resulted in January 1917 in the formation of a Committee on Analyzed Reagents with W. F. Hillebrand as chairman, and Charles Baskerville and W. G. Bigelow of the National Canners Association as associates. The committee's report to the Council in April 1917 proposed that an effort be made to obtain an appropriation from Congress to enable the National Bureau of Standards to purchase reagents on the open market and publish results of analyses of the samples, along with the analyses on the labels. Financial support for this work did not materialize.

In 1919 the Council of the Society instructed the Committee on Analyzed Reagents to consider also the problem of standardization of scientific apparatus. It soon became evident, however, that this dual responsibility placed too great a burden on the committee. In 1924 two committees were authorized: the Committee on Guaranteed Reagents, and the Committee on Standard Apparatus. At a later date the name of the Committee on Guaranteed Reagents was changed to the Committee on Analytical Reagents. The membership of the committee consisted of W. D. Collins, U. S. Geological Survey, chairman; H. V. Farr, Mallinckrodt Chemical Works; Joseph Rosin, Powers, Weightman, Rosengarten; G. C. Spencer, Federal Food and Drug Administration; and Edward Wichers, National Bureau of Standards. Many changes in membership of the committee have occurred, but the pattern of the work of the committee from 1924 on has changed very little.

Sets of recommended specifications were published in batches of about 10 at different intervals from 1925 to 1947. In 1941 the specifications published up to that time were reproduced and issued in a single pamphlet. Since 1947 the main effort of the committee has been directed toward further refinement of previously published specifications and the development of additional ones.

The AMERICAN CHEMICAL SOCIETY, and analytical chemists in particular, are greatly indebted to the present committee responsible for the preparation of the new book "Reagent Chemicals A.C.S. Specifications, 1950." It has been our pleasure to cooperate closely with the committee. We are thoroughly aware of the excellent work performed by this group. We believe many readers of ANALYTICAL CHEMISTRY will be delighted to express their personal appreciation to the members of this committee: Edward Wichers, chairman; S. E. Q. Ashley, General Electric; A. Q. Butler, Mallinckrodt Chemical Works; B. L. Clarke, Merck; W. D. Collins; F. S. Eisenhauer, J. T. Baker Chemical; R. A. Osborn, Food and Drug Administration; J. F. Ross, General Electric; and John Wolf, Baker and Adamson Division, Allied Chemical & Dye Corporation.

Separations in Analytical Chemistry

Role of Separations in Analytical Chemistry

M. G. MELLON, *Purdue University, Lafayette, Ind.*

Some of the general aspects of separations in analytical chemistry are discussed:
the place of separations, the need for separations, their nature and kinds, and
the problems of nomenclature and source content that face the educator.

THE assignment to the opening paper of this symposium has been taken to warrant a discussion of some of the general aspects of separations in analytical chemistry. Such a subject may impress one in different ways. In one direction a feeling of relief arises from the knowledge that others are to discuss the details of various kinds of methods. In the other direction a feeling of inadequacy results from the knowledge that only an analyst much more widely experienced than the author could present a satisfactory perspective of the broad subject of the theory and practice of all the different kinds of currently used analytical separations.

DEFINITIONS

Perhaps first of all certain definitions are in order. Desired constituents are the components to be identified or measured by a given method of analysis. These entities usually function in reactions as elements, ions, radicals, or compounds. Interfering constituents are the components which, when present along with a given desired constituent, prevent a satisfactory determination of this constituent. Such an interferer, of course, may itself be one of the desired constituents in a multicomponent system.

Separation is the process employed to remove the desired constituent from the range of action of the interferer. Whether it is perferable to isolate the interferer or the desired constituent—for example, from a solution—depends upon circumstances. Thus, the desired constituent arsenic may be distilled as the trichloride away from certain nonvolatile interferers. In contrast, the desired constituent uranium may be left in solution for measurement by electrodepositing certain interferers in a mercury cathode.

Occasionally someone considers as a kind of separation the mere prevention of interference by an action such as complexation of the colored ferric ion to form the colorless hexafluoroferrate ion. To the writer such a process seems rather a kind of preliminary treatment.

THE PLACE OF SEPARATIONS

In recent years analysts have begun to follow the lead of chemical engineers in referring to different steps in various kinds of chemical and physical procedures as unit operations. So considered, any method of analysis consists always of at least one, and usually of several, unit operations. Their number and nature depend upon the characteristics of the sample material and upon the kind and quality of information wanted. Separation, if used in a method, is one of these unit operations.

As a basis for discussion of some of the important topics considered in this paper, the analysis of an automobile antifreeze solution and of a granite rock may be taken as examples. In the liquid one wants to know the amount of the freezing point depressant, and in the rock some twenty desired constituents for a complete analysis.

The analysis of the antifreeze solution, as performed at gasoline filling stations to determine the adequacy of the system for a given temperature, involves the single unit operation of measurement, the instrument in this case being a hydrometer. The granite rock, however, is not so simple. For its analysis the methods of Washington (6) serve well to illustrate the place of separations in multioperational procedures as they apply to many kinds of materials. The specific determination of magnesium may be taken to bring out the nature of the different unit operations.

First comes the operation of sampling the rock material. If the mass to be sampled is a heterogeneous mountain range, supreme importance attaches to the selection of the portion which is to provide the gram of finely subdivided material to be used in the analysis. Preparation of this portion involves the suboperation of reduction of the particle size, the final step being grinding in an agate mortar until all particles pass a 200-mesh screen.

Next comes the unit operation of measuring the actual part of the sample portion to be analyzed, the specific process in this case being weighing. Because of the nature of the next step, the container into which the material is weighed is a platinum crucible.

Preliminary treatment is the third general unit operation applied to the sample of rock material in the process of analysis. Specifically, more than one step is involved. Fusion with sodium carbonate is the suboperation required to solubilize the rock. The following suboperation, dissolution with water and hydrochloric acid, really brings into solution the soluble salts and converts the silica to insoluble silicic acid or hydrous silica. Different suboperations of preliminary treatment often encountered are adjustment of pH, change in oxidation state, complexation or decomplexation, and, in the case of organic compounds, sulfonation or some similar transformation.

Following any necessary preliminary treatment, we reach separation, the subject of our present symposium. As we have assumed that our objective is the determination of magnesium by Washington's method, the problem at this stage is to remove from solution all constituents which might affect adversely the determination of the magnesium. In theory at least there are three possible situations: (1) If magnesium alone is desired, and if a suitable separative process for this element is available, it

would be removed from the interfering constituents; (2) if magnesium alone is desired, removal *en masse* of interferers might be possible by use of suitable reactions; and (3) if all constituents are to be reported, the separative procedures must provide for ultimate determination of each constituent.

The writer believes that the unit operation of separation as such has no essential connection with any particular kind of method used subsequently to measure a constituent which has been separated. If one may judge from many publications in the field, this view is not generally accepted. The peak of divergence is found when a text implies, or even states directly, that gravimetric methods include only those in which the desired constituent is weighed in the form of a compound which was separated by precipitation. It may be pointed out that in the determination of calcium the precipitation separation as the oxalate is the same, except for a final detail in washing, whether one is going to make a direct gravimetric measurement by weighing a suitable compound of the calcium, or an indirect titrimetric or colorimetric measurement of the metal by means of the reaction of permanganate ion with the precipitated oxalate ion.

NEED FOR SEPARATIONS

No analyst would voluntarily select a method involving a separative operation if an otherwise equally satisfactory nonseparative method were available. Separations take time, and time means money. The equipment required may be expensive and require skilled operators. Finally, analysts of wide experience recognize that, with the probable exception of sampling heterogeneous materials, separations are likely to be the seat of the most numerous and most serious errors in many methods of analysis.

The range of what the analyst encounters may be illustrated by two common liquid systems. Liquids for automobile radiators have already been mentioned as a type of material which requires only measurement of the desired constituent (disregarding the measurement of sample implicit in the calibration of the measuring instrument). Because in this case one assumes a binary system, consisting of water and an additive such as ethyl alcohol, the specific gravity measured is taken to be a function of the amount of ethyl alcohol present. There is no separation of the ethyl alcohol, as would be necessary with a system such as beer.

In the other direction, the analysis of a sample of crude petroleum from Oklahoma has been under way at the National Bureau of Standards for more than 20 years. Over ninety constituents were listed in a recent report on this famous project. The great problem with this material has been separation of the individual constituents, many of which are closely related chemically to each other. To the writer's knowledge, no more difficult separative problem has been reported.

Unless one can determine a desired constituent in the presence of whatever else happens to be present in the system to be measured, separation is obviously necessary. That such operations will be required for a long time to come seems reasonably safe to predict. For example, what measurement is now feasible, or seems likely to be, in terms of which one could calculate the amounts of the twenty unknowns in our granite rock?

The possibilities of improving, decreasing, or eliminating separative operations constitute an almost inexhaustible supply of analytical research problems. Thus, by far the major part of the time and the difficulty in practically all precipitation-gravimetric methods centers in the precipitation separation. Weighing either the sample, or the product derived therefrom, is a relatively easy and rapid unit operation.

One striking example of progress in avoiding separations is found in many recent absorptiometric methods, especially those based on measurements in the infrared region of the spectrum. Routine infrared work particularly in the petroleum industry,

regularly yields data for a half-dozen constituents in a multi-component distillation fraction or cut. To the writer's knowledge, eleven is the maximum number of constituents thus far found determinable in this way. Even so, time, skill, and expensive equipment are necessary. Perhaps the real analytical research problem is the invention of a gadget which, when one presses a switch, will indicate on dials, or better record on a chart, the amounts of any and all desired constituents in any given sample. A further desideratum for this automaton would be the achievement of any degree of reliability needed in a particular situation.

Table I. Types of Separable Systems

Phases Involved	Processes	Examples Constituent (from)
1. Solid-solid	Sieving	C (cast iron)
	Magnetic action	Fe (nonmagnetic material)
2. Solid-liquid	Precipitation	Se (solution)
	Electrodeposition	Cu on Pt (solution)
	Adsorption	
	General	$BaSO_4 + Fe^{+++}$ (solution)
	Columnar	
	No exchange	Chlorophylls (solution)
	Ion exchange	Na on Dowex 50 (solution)
3. Solid-gas	Condensation	Ice (water vapor and air)
	Adsorption	H_2 on Pd (air)
4. Liquid-solid	Dissolution	Sugar (sand)
	Extraction	Fat (peanuts)
5. Liquid-liquid	Distillation	Fractions (petroleum)
	Partition	$UO_2(NO_3)_2$ (interferers)
	Electrodeposition	Fe^{+++} in Hg cathode (UO_2^{++})
6. Liquid-gas	Condensation	Hg (air)
	Absorption	CO_2 in KOH (air)
7. Gas-solid	Volatilization	H_2O $(BaCl_2.2H_2O)$
		CO_2 $(CaCO_3 + H_2SO_4)$
8. Gas-liquid	Volatilization	NH_3 (aqueous solution)
9. Gases	Diffusion	$U^{235}F_6$ $(U^{238}F_6)$
	Magnetic action	Ions (those having different ratio of mass to charge)

NATURE OF SEPARATIONS

As pointed out many years ago by Blasdale (*2*), separations may be considered in terms of the phase transformation concerned. In recent papers Cassidy (*3*) has chosen to consider all of them as different kinds of partition processes.

The phases concerned refer, of course, to the three familiar states of matter: solid, liquid, and gas. Theoretically, at least, we have the various possibilities listed in Table I.

Now to the problem of interpreting the processes of separations. Some of those listed in Table I seem purely physical; no chemical transformations are involved. Examples are sieving, diffusion, and probably magnetic action.

Some of the others seem just as certainly to be chemical—that is, material transformations are involved. There are many familiar examples of this type. In precipitation, selenium is reduced to the elemental form, or the barium ion reacts with the sulfate ion to produce insoluble barium sulfate. In electrodeposition the cupric ion is reduced at the cathode to the elemental form, and the chloride ion is oxidized at a silver anode and reacts with it. In an absorption, such as carbon dioxide in aqueous potassium hydroxide, the absorbee reacts with the absorbant. On heating barium chloride dihydrate at 300° C., water is volatilized and the anhydrous chloride remains. Heating a steel at 1000° to 1200° C. in a stream of oxygen volatilizes the carbon as the dioxide but leaves the iron as nonvolatile ferric oxide.

There remain several processes less certainly assignable to the physical or the chemical categories. One faces various questions of interpretation. What is the nature of processes such as the following: dissolution of sugar in water; volatilization of ammonia from water; decolorization (general adsorption) of vinegar by charcoal; selective retention (columnar adsorption) of chlorophylls by sucrose; condensation of water vapor to ice; partition

of iron(III) chloride and nickel(II) chloride between diethyl ether and water; and the exchange of hydrogen ions for potassium or sodium ions by Dowex 50? Perhaps for these and other similar cases it is adequate to assume that one is dealing with forces ranging between coulombic attraction and the chemical bond, as conceived by Pauling. Physisorptive and chemisorptive bonds probably are intermediate types. Obviously, satisfactory separations by such processes rest upon enough practical knowledge to enable one to adapt the technique to the forces concerned.

KINDS OF SEPARATIONS

As far as the writer is aware, nothing has been published which could be considered a systematic, comprehensive survey of the analytically useful kinds of methods of separation. Such a publication would require at least one monograph of impressive size to treat in detail all kinds of these methods. Lack of such treatment complicates intelligent discussion by workers in the field and hinders productive study by students attempting to familiarize themselves with the phenomena concerned.

Such systematization, if perspectively balanced in treatment, would require an over-all knowledge of the subject from at least the following viewpoints: (1) the different kinds of processes applicable for effecting separations quantitatively; (2) the distinctive nature of each process; (3) the basic physical chemistry involved in the functioning of each process; (4) the most common means employed to make given kinds of separations; (5) the merits of each kind of method; and (6) the possibilities of application.

Although new information is accumulating steadily, especially in fields such as columnar adsorption and ion exchange methods, we already have an extensive stock of knowledge. Every textbook of merit must deal with the subject, even though the material included may not be designated specifically as separation. Most of the methods in the great compilations covering industrial materials include separations as necessary incidental parts of the procedures. Textbooks of physical chemistry deal with at least part of the theory. The periodical literature contains a wealth of scattered information, usually referred to only incidentally, if at all, as separations. Because of the inescapable importance of separations in many methods of analysis, the writer has felt for some years that the information on this kind of unit operation needs to be gathered together, coordinated, and emphasized more in our teaching of analytical courses.

Even though all the remaining papers on this symposium program are devoted to specific kinds of methods of separation, or to some aspects of particular methods, it seems desirable at this time to take a hasty over-all view of current practice. Some methods are so new that they are mentioned thus far, if at all, in only an occasional book, while others date from the earliest days of analytical chemistry. The two annual reviews thus far published in ANALYTICAL CHEMISTRY (1) contain much valuable material together with many references to recent literature.

Volatilization and Condensation. It seems likely that the calcinations, distillations, and sublimations of the alchemists led to the first separation by volatilization. Through the intervening years this process has been, and still remains, one of our most useful methods. Many variations may be found in details of treatment of the sample and in the apparatus employed. However, the general principle in all is the evolution of a constituent volatile under the conditions established. The evolution is accomplished either by controlled heating alone, or by heating accompanied by, or following, some chemical transformation used to produce a volatile constituent. Thus, the process is a separation of a gas phase from a liquid or a solid phase.

Whether the sample material is a solid or a liquid, the term "volatilization" seems generally appplicable for the evolution process involved. A more restricted term, "distillation," is rather generally used when the system heated is a liquid. Use of a carrier gas, such as carbon dioxide in the volatilization of arsenic trichloride or steam in the volatilization of various organic compounds, represents a modified kind of distillation. Rotary columns, molecular stills, and other innovations are included here.

Although a considerable number of inorganic constituents are volatilized as such, or can be transformed chemically to some volatile form, the major application of volatilization is to organic systems. The peak of gadgetry is the automatic Podbielniak still.

If an originally gaseous sample is converted to the liquid or the solid state by lowering the prevailing temperature, the process is known as condensation. Other less generally applicable terms may be used in certain cases. It is evident that the phase transformation is the reverse of that in volatilization.

Although on first thought it might seem feasible to analyze a multicomponent gas sample by selective condensation, few practical methods employ the principle of successively "freezing out" the various constituents. Adequately controlled equipment is operationally not easily used, besides being relatively expensive. The process is used somewhat, as in determining dew points. One may remove interfering constituents, such as water vapor, in this way in preparing a sample for absorptiometric measurement in the infrared.

In many practical applications volatilization is a more involved process than is condensation. Thus, gaseous constituents are condensed as such, without the necessity of any chemical transformation; but solid and liquid materials often have to be subjected to one or more chemical transformations in order to render some constituent(s) volatile under suitable conditions.

Precipitation and Dissolution. The formation of a solid phase in a liquid system generally is referred to as precipitation. Like volatilization, it is one of the oldest separative operations used by analysts.

The process involved is usually the production of a solid substance insoluble in the prevailing solvent system. Occasionally this substance is the actual element desired, such as selenium or gold; but nearly always it is some compound containing the element or radical desired. Only this latter possibility is considered here, for relatively it is by far the most important practice.

The classical schemes of qualitative inorganic analysis, especially those including more than the most common ions, are fine examples of this technique. Lundell and Hoffman (4) illustrate systematic schemes for the quantitative analysis of important industrial materials.

Much chemistry is concerned here, particularly as it applies to aqueous solutions. Many an analyst has acquired his first practical experience with sols in going through the inevitable von Weimarnian succession: solution, molecular aggregates, colloidal dispersion, visible particles, and filterable precipitate. If one goes more into detail, there may be involved something, at least, of most of the topics mentioned below under precipitation in the section on what to teach.

It is not to be assumed that all these subjects are necessarily concerned with every precipitation, nor that they are of importance only in precipitation operations. Their application is much wider, as every analyst knows.

Although most writers have not so considered the subject, there is some merit in including here mention of dissolution. As a separative process it is coordinate with precipitation. In one process something is selectively precipitated from solution by conversion of the constituent to an adequately insoluble form. In the other process something is dissolved out of a solid (occasionally a liquid system, such as milk) through the selective action of a solvent. Separation of sugar from sand by the latter means is a simple example. The same general principles of solid-solution equilibria apply to both the precipitation and dissolution processes.

Many analysts consider selective dissolution as a form of extraction. This viewpoint is reflected in the designation as "ex-

tractors" of a variety of equipment. The Soxhlet and Bailey-Walker forms are well known examples. Such apparatus is designed to bring the solvent into contact with the sample material in a way to facilitate the removal of the desired constituent. Extensive use of the general principle is made in the analysis of many agricultural and pharmaceutical materials.

Electrodeposition. The foundation of present electrodeposition methods rests upon a discovery of Wolcott Gibbs. In 1864 he noted that, under suitable conditions, passage of a direct electrical current through an aqueous solution of certain cupric salts resulted in the quantitative deposition of the copper upon the cathode. The chemistry involved consists of the conversion of each cation to an atom through the supply of electrons. This cathodic process is now known as reduction. As such, it obviously requires the introduction of no foreign ions, an advantage in multicomponent work.

A variation of the process consists in accomplishing the deposition without the use of external current. An old example is the displacement of copper by boiling a cupric ion solution with metallic aluminum. Electrochemical action results in deposition of the copper upon the aluminum foil.

A few metals, such as lead, can be and are deposited from aqueous solution as oxides upon the anode. However, from our viewpoint the general process of oxidation involved at this electrode is more likely to be concerned with removal of electrons from an anion, such as the chloride ion. Although it is possible to handle a few constituents in this way, in general anions are not so treated.

This separative process may be taken as an example of what seems a fairly general historical phenomenon. A method is discovered. Sooner or later the idea spreads. Even wide interest or popularity may result. Then follows a decline in use, in some cases surprisingly rapid. Finally, if the proposal is really of general value, its rightful place among competitive methods is achieved. The whole thing is roughly analogous to a section of a sine curve.

In the case of electrodeposition with current, Gibbs's discovery was followed by a fairly slow rise in interest until the enthusiasm for this technique probably peaked in the heyday of E. F. Smith, roughly the decade of 1905 to 1915. Many prominent chemists trace their inspiration to Smith's electrochemical laboratory during this period. The sixth edition of his famous book, "Electro-Analysis," appeared in 1918 (5). Shortly thereafter the decline started, for the following quarter of a century the interest lagged so much that the publishers apparently could find no one in this country to undertake a revision of the book.

Although various elements were separated in this manner all through the past four decades, especially in industrial laboratories, only in the past five years have signs of life appeared again. Now a new book is under way. Apparatus for use of rotating electrodes is widely advertised. Diehl, Lingane, and others have proposed equipment for operating at constant electrode potentials. The mercury cathode has come into its own, not so much for handling desired constituents directly, as suggested by Hildebrand many years ago, as for "cleaning up" a solution of interfering metals.

One may well keep this story and similar ones in mind when enthusiasts for some new gadget or method seem about to supplant everything else with their contribution. Occasionally something is really revolutionary, but thus far no one item is a panacea for all analytical troubles. More likely each new item has its place. The wise analyst will determine this and then act accordingly.

Extraction. The term "extraction" may mean different things to different people. The range is wide enough to include at least the following processes listed in Table I, including all their variations: absorption, adsorption, dissolution, partition, and extraction. Some individuals include only selective dissolution and partition between two immiscible liquids. Because dissolution has been grouped with precipitation, and adsorption

is considered separately in this paper, the author chose to limit the term to partition between immiscible solvents.

Such liquid-liquid extractive processes take two forms. The old process involving a separatory funnel is well known. The relatively new countercurrent technique is becoming increasingly important.

Whatever the method, various environmental factors are important, such as the solubilizing action of various components on the desired constituent.

Adsorption. A generally acceptable, precise definition of adsorption may be elusive. Roughly, the author has in mind a process in which a constituent of a multicomponent gas or liquid system is removed by condensation upon a solid phase with which the gas or liquid is brought into contact.

There are several variations in this type of action. In one variation the separation is effected in the course of the formation of the solid phase. Thus, in an A.S.T.M. method for bronze analysis precipitation of enough hydrous ferric oxide will carry down with it constituents such as arsenic and antimony. Analysts are more generally familiar with this phenomenon as it is encountered in the production of precipitates contaminated with only part of the unwanted constituent. Ferric iron adsorbed on barium sulfate is a well known example.

In a second variation the sample material is brought into contact with an already formed solid adsorbant. Thus, hydrogen may be adsorbed from a gaseous mixture by passage over finely divided palladium. Adsorbant carbon may be used to remove interfering colored material in sugar analysis.

In both types the process may be distinguished as being general, or nonlocalized. Frequently only one component is removed by the action. If there is more than one, no differentiation is possible between any two on the adsorbant.

In contrast to this kind of action, we have differential or columnar adsorption. This variation, as widely practiced, consists in passing a liquid solution down through a column of the adsorbant. Thus, a mixture of the two chlorophylls may be separated in this manner on a sucrose adsorbant. Presumably there is no ordinary chemical action between adsorbates and adsorbant.

A modification of this differential process is based on the use of paper as the adsorbant. It may be impregnated before use with some reagent.

For many columnar and differential methods the unfortunate term "chromatography" has come into general use. Often there is no distinguishing hue (color) and the ending "-graph" seems questionable. Anyway, it is inconsistent with our other terms ending in "-tion."

Thus far no exchange of ions between adsorbant and adsorbate has been assumed. If ion-exchange methods may be included here, they comprise the processes in which there is exchange of an ion in an ionic adsorbant with an ion in solution. Separation of potassium and sodium on Dowex 50 is an example. Work is just well started in this field.

Absorption. The analysis of various gaseous mixtures has long been made by volumetric (by volume) measurement of the components. Starting with a known volume of the mixture, each constituent is removed in turn. The decrease in volume with each such removal is taken as the volume of the respective gases removed. The process of removal is known as absorption. The measurement might, of course, be manometric.

Familiar examples of such separations are the absorption of carbon dioxide by aqueous potassium hydroxide, oxygen by pyrogallol, and unsaturated hydrocarbons by sulfuric acid. In all these cases the absorbant is a liquid phase. However, it may be a solid phase, as illustrated by the use of Ascarite to absorb carbon dioxide from air, or of yellow phosphorus to absorb oxygen from air.

Thus far, the examples cited have not involved any preparative transformations to render a constituent absorbable under given conditions. Such preseparative treatment may be necessary, as

in the combustion of methane, a saturated hydrocarbon, to carbon dioxide and water by reaction with excess oxygen. The carbon dioxide is then absorbed.

Magnetic Action. In a few cases the separative process involves magnetic action on the desired constituent. (The author suggests the term "magnetition" for this kind of separation.) Two variations of the process seem evident, the seat of the variance being the nature of the entity attracted.

In the first variation, old but relatively uncommon, one component of the sample is magnetic and the others are not. Thus, iron particles might be mixed with sand. The metallic component may be separated by means of a magnet brought close to the mixture. Obviously, the possibilities are limited.

In the second variation, relatively new and increasingly important, ionizable constituents are ionized and then subjected to a magnetic force, as in a mass spectrometer. Because of the difference of the ratios of mass to charge for most constituents, electrical or other differentiation of the presence and the amounts of different constituents is possible. Components so separable are either gaseous or readily convertible to this state.

EDUCATIONAL PROBLEMS

In this broad consideration of separations the author, as a teacher, ventures to raise two educational questions—namely, nomenclature and course content. Only brief mention of the nature of the problem is possible.

Nomenclature. Because the separative operation is so important in the analytical methods for most multicomponent systems, and because the measuring operation occurs in every quantitative determination, it is suggested once more that the general nature of each of these two unit operations be indicated in naming the over-all method. Anyone having occasion to make much use of indexing serials and abstracting journals must have been irked by the lack of such functional nomenclature. The author, for example, has spent much time trying to find out whether a given method is colorimetric and how the desired constituents are separated.

Suitable naming and indexing would have made such work unnecessary. A combination term would indicate the general nature of both principal unit operations—namely, separation and measurement. A few examples are volatilization-volumetric, precipitation-gravimetric, electrodeposition-titrimetric, and extraction-absorptiometric. If there is no separation, the measurement term alone would suffice.

What to Teach. Of more importance to many, no doubt, is the question of what one should try to include on this unit operation in an elementary quantitative course. Because

isolation of the desired constituents for measurement encompasses most of the chemistry in a procedure, the question really is what chemistry can and should be taught.

Broadly considered, the chemistry involved is of two kinds. The first kind is factual. Examples are the photochemical sensitivity of silver chloride and the hygroscopicity of ignited calcium oxide. If the student does enough analyses and is alert to these facts, he should emerge as something more than a Lundell determinator. He would know that things are, but not why they are.

The second kind is interpretative. Because it involves understanding, as far as this is possible, it is the more important. Such understanding of a procedure concerns the how and why of things, or, as some would say, the underlying theory. Basically this theory comprises the physical chemistry relevant to the various unit operations of a method.

Taking precipitation as an example of a separative operation, we find concerned such subjects as the following: choice of precipitant, solubility of precipitates, colloidal dispersions, ionic equilibria, common and diverse ion effects, activity of ions, pH, buffer solutions, purity of precipitates, oxidation-reduction, complexation, washing precipitates, and igniting precipitates.

To interpret all such phenomena relevant to the analytical process in terms of modern physical chemistry is no small assignment. Teachers of physical chemistry know that extensive problem drill, rather than superficial descriptive treatment, is required to fix such concepts in workable form. Mere mention of the subjects by the analytical instructor will do no harm, but probably little lasting good.

Most students now reach quantitative analysis with not more than three semesters of foundation chemistry and often without physics. Then the great majority take one semester of quantitative work. On this background one must treat the rapidly expanding subject of chemical analysis. With this statement of the problem, the serious instructor is left to contemplate the dilemma.

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3rd Annual Summer Symposium — Separations

Partition Chromatography and Countercurrent Distribution

LYMAN C. CRAIG, *The Rockefeller Institute for Medical Research, New York, N. Y.*

EVERYONE interested in separation processes soon learns that he must deal with some form of heterogeneous equilibrium involving the selective transport of solute from one phase to another, and that only under the most favorable circumstance will a single transfer suffice to give an adequate separation. Repeated transfers are required.

It was noted many years ago that if the two phases involved

could be made to flow past each other in sufficiently intimate contact, surprisingly good separations could often be achieved. The effect was broadly interpreted in terms of repeated stepwise contacts or transfers. Many investigators have tried to give a satisfactory theory for the continuous process, and every year brings a fresh supply, undoubtedly a reflection on the yet unsatisfactory nature of our understanding.

In evaluating the efficiency of continuous fractionation processes such as partition chromatography, a common procedure is that of calculating the height of equivalent theoretical column. This involves an experimental determination of the effect of a single stepwise equilibrium separation for comparison to the effect of passage through the column. This by no means implies a full understanding of the events taking place in the column. In fact, many of the various factors bearing on the column separation are so interdependent as to be difficult to study clearly. Because countercurrent distribution is a stepwise equilibrium procedure which has now been carried to several thousand actual stages, it is interesting in the light of the continuous process to review the factors influencing its successful operation. A slightly different concept of the continuous process is thus reached.
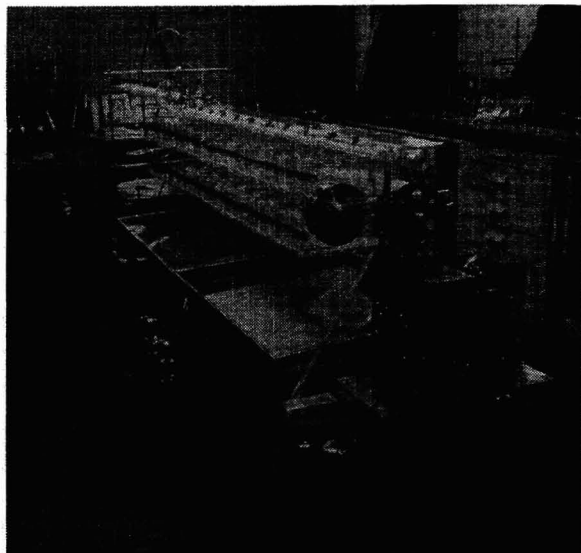
Figure 1. Automatic 220-Cell Glass Distribution Train

In general, the approach has been to formulate a theory and then attempt to prove it by carrying out separations on an artificial mixture under specified conditions in a given extraction train or column. By correlation of effects the result is interpreted for proof of the theory. The fundamental weakness of this approach lies in the fact that certain assumptions which may or may not hold during such a complex interplay of events are always required and the evidence in the final analysis is only circumstantial at best. Often the theory is known to hold for limiting cases only and to deviate widely in actual practice.

An example of such an approach is the published theory for the technique called "partition chromatography." Martin and Synge first experimented with a stage continuous liquid-liquid extraction train (9) designed for the separation of amino acids. They found the procedure laborious and evolved the ingenious idea of immobilizing one of the liquid phases by adsorbing it on some mechanical support known to have weak adsorptive properties, such as silica, starch, or paper (10). This permits a mechanical state of affairs most nearly ideal for the countercurrent effect from both a practical and theoretical standpoint, because the operation can be performed as simple percolation. They called the process partition chromatography in the thought that it really was a form of liquid-liquid extraction and not based on adsorption.

By now nearly every chemist knows something of the great practical value of the method, not to mention the stimulation it has given to the further development of many other types of countercurrent separation processes.

Martin and Synge proposed a theory which probably gave more insight into the nature of chromatography than previous viewpoints, even though it was not entirely correct. Their theory was developed along the lines proposed by previous workers such as Jantzen (7) and Cornish, Archibald, Murphy, and Evans (4) in terms of the "theoretical plate" concept.

No one doubts that the effects of the ideal discontinuous process and the truly continuous become nearly identical when high numbers of stages are in the former. It is the reasoning of calculus. Furthermore, chromatography presents mechanical conditions which should give almost the equivalent of infinite numbers of stages, provided there is uniform linear flow of solvent with no channeling or turbulence such as that caused by a packing which is not uniform; equilibrium conditions—e.g., the partition or adsorption isotherm—are satisfied at any point in the column at a practical rate of flow; and the isotherm involved is strictly linear. None of these conditions is ever completely met in practice. A measure of the efficiency of a column is therefore an indication of the combined effects of the various deviations from ideality. Some of the deviations may be favorable to separation, others unfavorable.

COUNTERCURRENT DISTRIBUTION

Several years ago it occurred to the writer that a profitable approach to an understanding of many of the finer points of fractionation theory might be reached by intensively studying a strictly discontinuous extraction process (5) carried to high numbers of stages—i.e., "countercurrent distribution." High
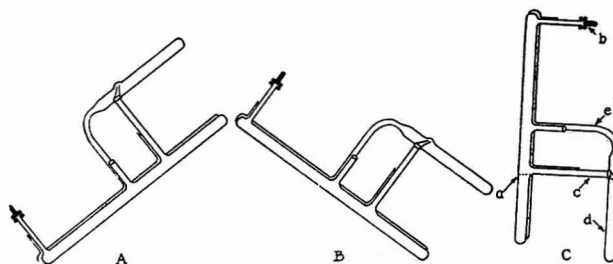

Figure 2. Individual Cell of Distribution Apparatus

resolving power was not expected at first, but it was thought that because the theory of such a process would be known, certain assumptions necessary for interpretation of continuous processes could be more critically examined. However, the first separations obtained were encouraging and soon the program necessitated the development of adequate mechanical equipment for performing the thousands of extractions desired. This phase of the study is partly covered in the literature (6).

The extractor currently in use in the author's laboratory (Figure 1) contains 220 glass equilibration cells connected in series.

It therefore performs 220 actual extractions in from 1 to 3 minutes, depending on the speed of equilibration and separation of the phases. It is fitted with electric motors, timers, a filling device, a fraction collector, etc., so that the operation is fully automatic. It will run without attention through the night. Twenty-four hours of operation give from 100,000 to 200,000 actual extractions, which are integrated to give the "column" effect.

The design of a single cell is given in Figure 2. Each cell contains 10 ml. of the lower phase, sufficient to bring the interface to a in position C. An arbitrary volume no greater than 15 ml. of upper phase is used. Equilibrium is established by rocking from position A to B. The phases separate at position B. On tilting to position C the upper phase decants through c to chamber d. Now on tilting to position A the contents of d flow through e to the adjoining cell. b is a flat ground-glass stopper.

Several methods of operating the apparatus are useful. In each method the sample is placed initially either in one cell or, in order to give greater capacity, in a number of the first cells.

Fundamental Procedure. The train is operated until the first upper phase has migrated to cell 219. If the train is examined analytically at this point, the result is analogous to chromatography in which an effluent has not been obtained but the column is cut into segments. It is also analogous to paper chromatography (3).

Single Withdrawal (6). The train is operated further than in the first by permitting the upper phases to flow from the train at cell 219 into the fraction collector. The upper phases flowing out are analogous to the effluent from a chromatogram.

Recycling. The third procedure is used when the mixture consists of two or three closely related components and higher separating power is desired. The apparatus contains two parallel rows of 110 cells, one row above the other, so arranged that the upper phases move in opposite directions. Therefore cell 219 is under cell 0 and the upper phases leaving 219 can be caused to flow back into cell 0 instead of into the fraction collector. The effect of this method of operating is to increase greatly the number of transfers which can be applied in the fundamental procedure. It can be considered as accomplishing part of the result of reflux in a fractional distillation column. Various combinations of the three procedures can be used conveniently in a single separation.

The result of a given experiment can be grasped most readily from a distribution pattern. This is simply a graph of the fraction of the original solute found in each cell at the end of the operation, or a figure proportional to it, plotted as ordinate against the cell number. Fractions in withdrawn phases are plotted against the transfer number on which they emerge. Figure 3 is an experimental result obtained in the fractionation of an artificial mixture of amino acids, 300 mg. of each.

MATHEMATICAL EXPRESSION OF RESULTS

With such large numbers of individual cases to be followed, adequate mathematics must be available for expression of the result. It so happens that the mathematics of probability or statistics are nearly identical with the mathematics needed for this work. Both are based on the binomial series. Previous workers (4, 10) have used the binomial series in developing a theory for the operation of continuous columns. Stene (14) began a theoretical study of extraction from the same viewpoint as the author's and at about the same time, but did not implement his views practically with the required apparatus.

Glycine   Tyrosine
Alanine   Leucine
α-amino butyric   Isoleucine
Valine   Phenylalanine
Methionine   Tryptophane
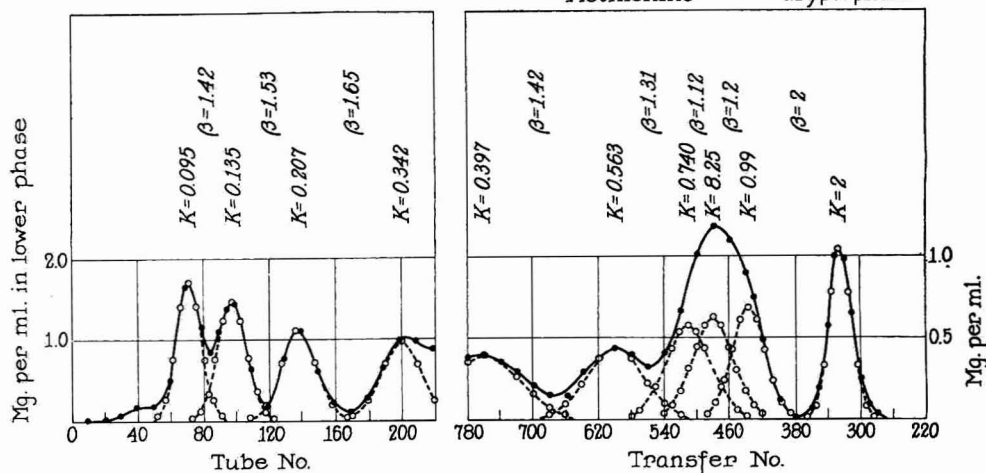

Figure 3.   Distribution Pattern of Synthetic Mixture of Amino Acids

System ● n-butyl alcohol, 5% HCl
●—● Experimental
○—○ Calculated

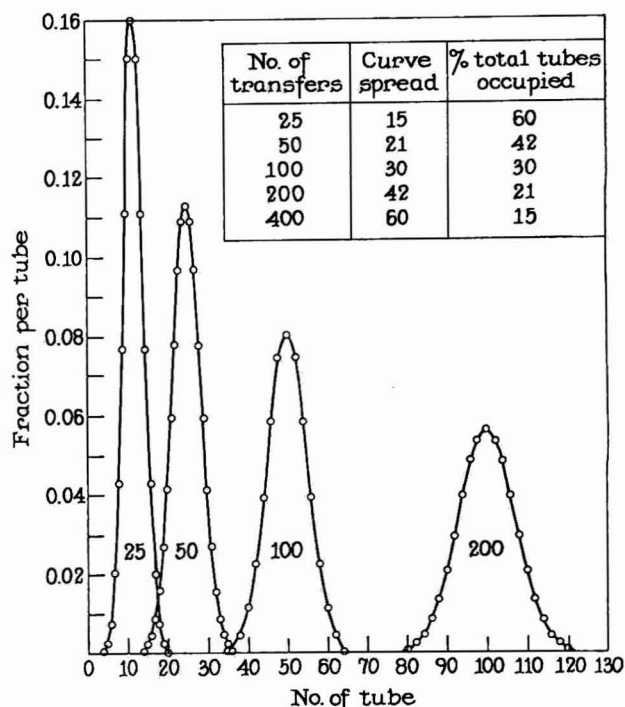| No. of transfers	Curve spread	% total tubes occupied
25	15	60
50	21	42
100	30	30
200	42	21
400	60	15

Figure 4.   Relation of Curve Spread and Height with Increasing Transfers

A given solute if it behaves ideally—i.e., complete equilibrium at each stage and constant partition ratios—will migrate through the series of cells according to the binomial expansion

$$\left(\frac{K}{K+1}\right) + \left(\frac{1}{K+1}\right)^n \tag{1}$$

where K is the partition ratio and n is the number of transfers applied (6).

A useful approximation of the binomial for numbers of transfers greater than 25 is Equation 2, which is taken directly from the normal curve of error, the equation so familiar in the mathematics of probability. Y is the fraction of the original solute in a

given cell and X is the number of cells that particular cell is removed from the cell of maximum concentration. The degree to which actual experiment and the calculation agree can be seen from Figure 3.

$$Y = \frac{1}{\sqrt{2\pi n K/(K+1)^2}} e^{-X^2/2nK/(K+1)^2} \qquad (2)$$

The mathematics applicable to the elution series, the bands in the right hand pattern of Figure 3, can be derived from Equation 2 and may be expressed by the approximation of Equation 3. This series is most important if one is interested in the analogy to chromatography.

$$Y = \frac{1}{\sqrt{2\pi n/K}} e^{-X^2/2n/K} \qquad (3)$$

The concentration shifts taking place in a stepwise extraction train for a single solute, $K = 1$, when increasing transfers are applied are shown in Figure 4. The bands become broader and lower. This means that a basic part of the process is dilution.

Even after 200 transfers a small fraction, $(0.5)^{200}$, remains in the 0 cell. Obviously, so small an amount is of no practical significance and is neglected. But progressively up the series the amount of solute in each cell increases and a point is finally reached where a significant amount of solute is present. In the present discussion a significant amount will be 1.0% of that present in the maximum cell.

Perhaps a better grasp of the effect of higher and higher numbers of transfers is given by viewing the process in a somewhat different light.

In a 10-transfer distribution, $K = 1$, the pattern could be curve A of Figure 5. Here there is little space for throwing off impurity, all except cells 1 and 10 having significant amounts of the main solute in them.

But if 100 transfers were applied, in the same total volume of solvent, arbitrarily taking sufficiently more solute so that the maximum cell would contain the same amount as in A, and the result were plotted on the same pattern by renumbering the abscissa, curve B would result. Now there is significant solute in only 30% of the cells and space remains for at least three other components on each side of the band.

Similar consideration of a 1000-transfer distribution gives curve C and more space still for other components.

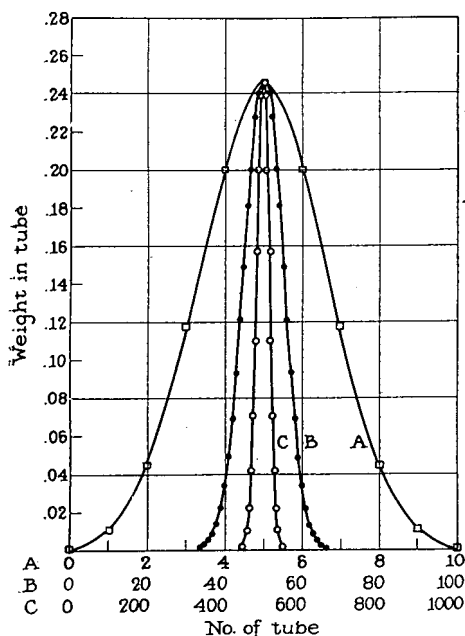A higher number of transfers obviously gives a narrower band with respect to the

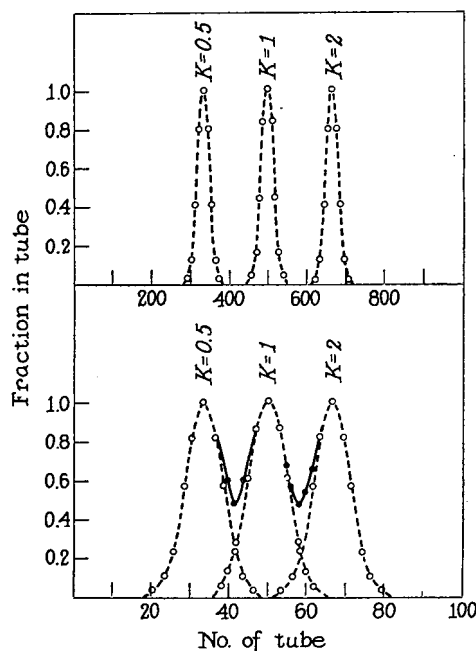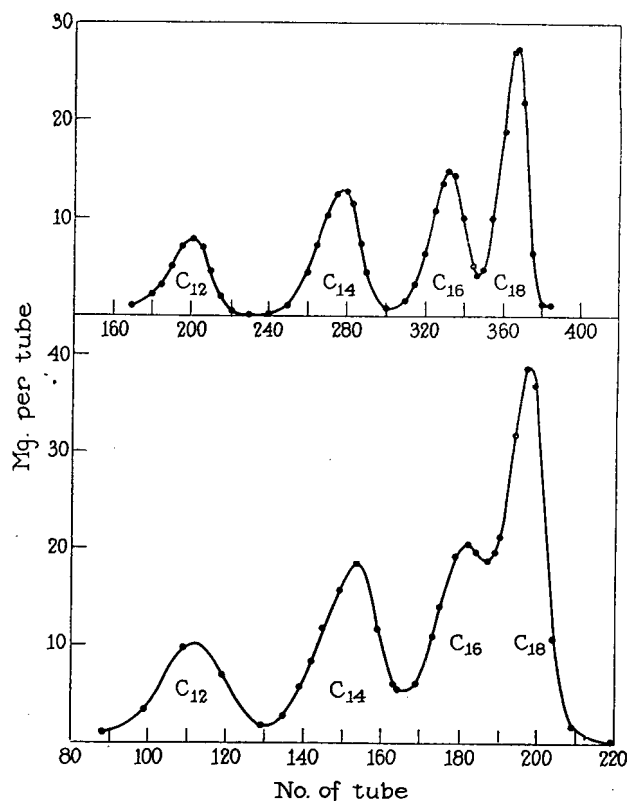**Figure 7. Distribution Patterns for Separation of Artificial Mixture of Fatty Acids**

Lower 220 transfers
Upper 400 transfers

System. Heptane/equal volumes of methanol, formamide, and glacial acetic acid

total solvent used. This is the real basis for the increased selectivity of higher transfers, as the comparative 100-transfer and 1000-transfer distribution of a three-component mixture given in Figure 6 shows. As more transfers are applied, the bands appear to become more sharply defined and further removed from each other.

That this reasoning holds experimentally is proved by actual experiment. Figure 7 shows the effect of doubling the transfers in separating lauric, myristic, palmitic, and stearic acids.

If an infinite number of transfers could actually be applied, each band would be very narrow indeed with respect to the total volume of solvent and would become nearly a line on a pattern no wider than the one above. Moreover, each cell would have vanishingly small capacity unless an infinitely large total volume of solvent were used.

In order to overcome the small capacity of a single cell, the solute could be scattered

Figure 5. Comparative Band Widths

Figure 6. Calculated Distribution Patterns for Three-Component Mixture

Lower 100 transfers
Upper 1000 transfers

at the start of the process in a bank of cells, as in Figure 8. Here it was placed in seven cells initially and carried to 100 transfers. The end result is the summation of seven separate distributions one cell removed- from each other. The sum, curve B, is slightly lower and wider than A, which would be the result of starting with the same amount of solute all in a single cell.

However, if the solute were scattered in a much higher number of cells, as in Figure 9, the band would not appear to "erode" to such a marked extent on migrating through the train and would appear nearly to hold its shape, height, and width. Thus, the ideal behavior proposed for the chromatograph by Wilson (15) has been developed by the ideal stepwise approach.

NATURE OF PARTITION CHROMATOGRAPHY

With this as a background it may be instructive to inquire into the nature of partition chromatography, beginning with experimental observations. We know that irrespective of the way it operates, the method is remarkably efficient for high dilutions of many solutes, as the pattern of Moore and Stein (13), Figure 10, so beautifully demonstrates. We also know that uniform packing, slow flow rates, and relatively linear adsorption isotherms are required for such a result. These conditions parallel the uniform mechanical transfers, state of equilibrium before transfer, and constant partition ratios required for exact mathematical correlation of countercurrent distribution results. In spite of this apparent correlation, it is well to question whether or not such a correlation provides an adequate understanding of partition chromatography. Before attempting an answer to this question, it will be profitable to examine closely the three basic requirements of such a view—i.e., perfect mechanical transfer, constant partition ratios, and equilibrium before each transfer.
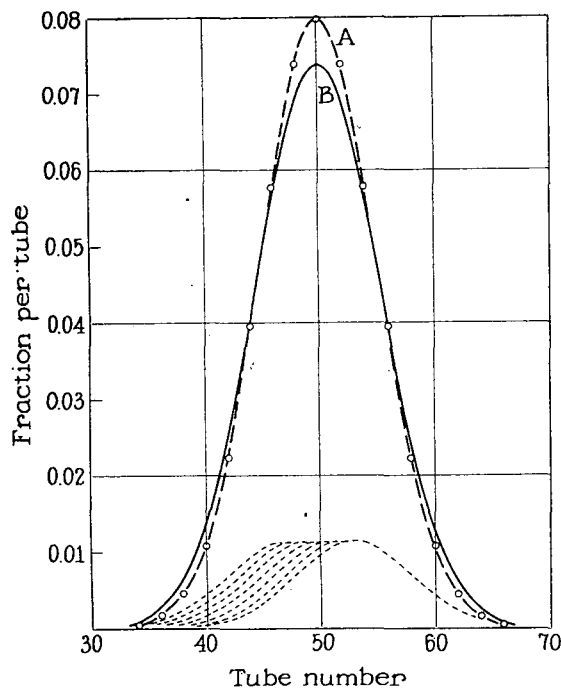
Figure 8. Effect of Scattering Solute Initially

Experience with the stepwise process has shown that perfect mechanical transfer is relatively not so important. An occa-sional error of 15 to 20% made in failing to transfer the upper phase of a single cell (or in transferring some of the lower phase) is not even registered on the shape or position of the final curve when many transfers are applied, nor is a considerable number of

such errors. The normal curve of error takes care of such deviations in a most remarkable way. When such errors become frequent but are of random occurrence, the effect registered is that of making the curve somewhat too broad. Poor packing and nonuniform flow of solvent are known to have a similar and perhaps much greater effect relatively on the operation of a chromatographic column (8), perhaps due to channeling.
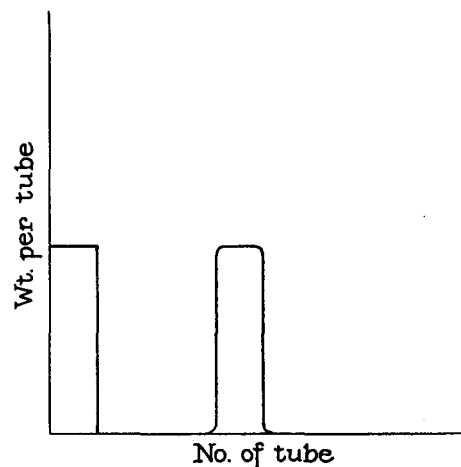
Figure 9.   Hypothetical Band Behavior for Ideal Column

The question of constant partition ratios can be treated most intelligently by expressing the over-all equilibria involved as a partition isotherm, as in Figure 11.

This applies for chromatography as well as for countercurrent distribution. The ideal solute approaches curve A over the operational concentration range. B and C in the case of liquid-liquid extraction are deviations from the ideal caused by the fact that the solute is more or less in a different state of association in the two phases, depending on the concentration. When the stationary phase is a solid (chromatography), B, the familiar adsorption isotherm, is the type of deviation and C is not encountered.

Isotherm A permits a symmetrical distribution curve or withdrawal curve, B permits a steep front and trailing rear, while C permits a slowly rising front and steep rear. Actually, all solutes deviate more or less from A in practical concentrations, but liquid-liquid extraction in general permits concentrations 10- to 100-fold as great as those in partition chromatography before serious deviations occur.

Naturally, the limitations imposed by the isotherm do not hold unless complete equilibrium is reached at each stage throughout the process. There are no stages in a continuous process. Therefore, we can speak only of approach to equilibrium in partition chromatography. But the question can be precisely studied by countercurrent distribution. A cell can be agitated until complete equilibrium is reached and then the transfer made, or the transfer can be made at a desired level of disequilibrium (1). In the first case, the distribution fits the normal curve of error. In the second case, several forms of the curve are obtained. If equilibrium is approached at the same rate from either phase, a symmetrical distribution curve, but too broad for the calculated one, is obtained. The center of the band is not displaced. If approach to equilibrium from either phase is unequal, a curve skewed either to the right or left may be encountered, and the center of the band may be somewhat displaced from the calculated. Strangely enough, too narrow distribution curves have been encountered on a number of occasions, thus giving much better separations than had been anticipated.

A symmetrical curve from a continuous column is by no means an indication that the process approaches equilibrium. On the contrary, apparent symmetry may be caused by disequilibrium, as Martin (8) has suggested. In the stepwise procedure a theoretical equilibrium curve can be calculated and an experimental one wider or narrower than this may then be an indication of disequilibrium. But with the continuous process there is no such yardstick and exactly what is happening is never known. It is always at some stage of disequilibrium and of deviation from its isotherm. Therefore relative rates of approach to equilibrium and small deviations from linearity of the isotherms can be important, if not the deciding factors. Relatively small effects not detectable by measuring the partition ratio can thereby modify the separation greatly in a critical range.

Often with the continuous process it is possible to make calculations of very high numbers of theoretical plates based on the equilibrium values of the partition ratios of the mixture. Too much confidence should not be placed in such a result, because H.E.T.P. values will not be constant with a given column used on a mixture. A solute emerging later in the run may give a band of width indicating one half or less the H.E.T.P. value of an earlier solute (11). An attempt to repeat the process on a different mixture with the same beta values might or might not result in only a small fraction of the efficiency. A narrow band permits the calculation of high numbers of plates but, as has been pointed out, many factors influence the width of the band except in the ideal discontinuous process.
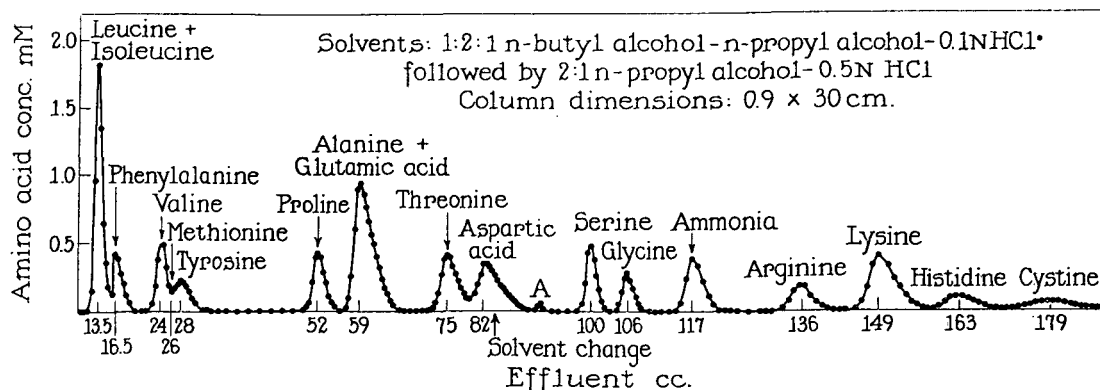

Figure 10.   Separation of Synthetic Mixture of Eighteen Amino Acids by Starch Chromatography

When there is the probability of high numbers of plate equivalents, disequilibrium cannot be dismissed by saying that the column operates at near equilibrium. On this point the stepwise approach is instructive. A 50-transfer distribution will agree with the theory, even though the partition ratio varies from 1.1 at the highest operational ratio to 1.0 at the lowest. But with a 500-transfer distribution, the deviation is apparent as a skewed curve.

Obviously, for transfers numbering in the thousands the small deviations either in partition isotherm or from equilibrium become greater in importance in relation to the importance of the absolute value of the partition ratio, and may be the basic factors producing separations. This reasoning emphasizes the probable differences between the continuous and the discontinuous process, even though many transfers are involved in the latter.
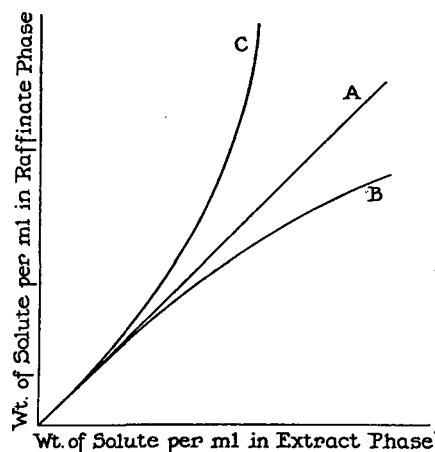

Figure 11.   Types of Partition Isotherms

Partition chromatography appears to be generally accepted as a liquid-liquid extraction process, apparently because of the correlation of the rates of migration of bands with liquid-liquid partition ratios (10). At best this evidence is only circumstantial and probably reflects more the uniform shift in nearly any physical property in a homologous series than the particular property responsible for such an observed effect. The point is analogous to the interpretation of a mixed melting point. Failure to depress may suggest identity, but not necessarily so. On the other hand, a depression offers direct evidence that the two substances are different, just as a migration rate (R_f value) not agreeing with the partition ratio shows that some factor other than liquid-liquid distribution is at least partly responsible for the effect. Moore and Stein (12) first reported such a disagreement with the aromatic amino acids on starch columns. Since then many cases have been reported. The author has found the results of partition chromatography of very little use in selecting systems for countercurrent distribution. Further doubt is thrown on the mechanism by the finding that on starch and paper columns water-miscible solvents give almost the same results as those immiscible with water (2, 12).

Observations bearing on this question are numerous and most of them not really decisive. Actually, partition chromatography always requires an adsorbant active in some degree; otherwise the stationary phase would not be held. On the other hand, where two immiscible liquids are in contact on a column, complete ruling out of the possibility of liquid-liquid extraction is equally impossible, even if direct evidence in favor of it is lacking.

The point is not very important, because there is so much analogy between countercurrent distribution and chromatography. Certainly, the difference between countercurrent distribution and so-called partition chromatography is much greater than that between Tswett chromatography and partition chromatography. In fact, there seems little to be gained by assuming

that liquid-liquid partition plays any significant role in the latter process.

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*3rd Annual Summer Symposium — Separations*

Ion Exchange Separations

EDWARD R. TOMPKINS, *Radiation Laboratory, University of California, Berkeley, Calif.*

This review discusses the properties and laboratory applications of some commercially available ion exchangers, as well as current theories concerning the mechanism of the separation of substances by ion exchange. A brief description of laboratory procedures for equilibrium experiments and for column separations is given. Several theories designed to predict column separations are evaluated. Results of a number of column separations of substances with similar properties are reviewed. This method is unique in its ability to produce extremely pure preparations of members of the lanthanide and actinide rare earth series. It has been used successfully in separating and purifying zirconium and hafnium, the alkaline earth elements, scandium, and many other metallic ions as well as organic substances.

ION exchange resins are solid substances which are insoluble in solvents and solutions usually employed in the laboratory but which ionize in polar solvents. The chief usefulness of these substances in the laboratory depends upon their property of entering into exchange reactions with ions in a contacting solution. They are applicable for separating ions because of the differences in the exchange constants for various ionic species and the ease with which they may be separated from the liquid phase.

The general reaction involving the exchange of monovalent ions (for a cation or anion exchanger) may be expressed by the equation

$$AR + B^{\pm} \rightleftharpoons BR + A^{\pm} \tag{1}$$
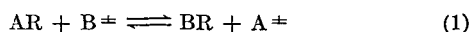
in which R is the exchanger and $A^{\pm}$ and $B^{\pm}$ are ions competing for the available positions on its matrix. For a cation exchanger, R is an anion and A and B are positively charged; for an anion exchanger, R is positively charged and A and B are anions.

PROPERTIES OF EXCHANGE RESINS

Prior to the original preparation of synthetic exchange resins, reported by Adams and Holmes in 1935 (1), exchangers were of limited value for chemical separations. However, because of the rapid development of new types of synthetic exchange resins, a number of very useful products are now available. These resins are cross-linked polymer chains with polar functional groups. Their general structure (6, Figure 1) has been described in detail by Bauman (5, 6). The sources of several typical ion exchangers are shown in Table I. Of these, the strongly acidic cation exchangers and the strongly basic anion exchangers have found the widest application for laboratory separations. They are available in the form of spherical particles, and in some cases, in various mesh sizes. Detailed descriptions of the preparation and properties of these exchangers are given in the literature references cited in Table I.

In their hydrogen form, cation exchangers behave as acids when in contact with ionic solutions; anion exchangers in the

hydroxide form react as bases. As may be seen from the titration curves shown in Figure 1, hydrocarbon cation exchangers with nuclear sulfonic acid groups have acid dissociation constants similar to the constant for sulfuric acid. Likewise, the hydroxide form of the quaternary amine anion exchangers behaves as a strong base. Cation exchangers with other functional groups—e.g., —COOH, —CH₂SO₃H, —OH, etc.—and the hydroxide form of tertiary amine anion exchangers have much lower dissociation constants. In fact, the salts of these weakly acidic and basic exchangers are appreciably hydrolyzed in water (39).

EXCHANGE EQUILIBRIA

The value of the equilibrium constant,

$$K_e = \frac{a_{BR} \times a_A^{\pm}}{a_{AR} \times a_B^{\pm}} \tag{2}$$

in which a represents the activities of the reactants shown in Equation 1, depends upon the hydrated radii of the two competing
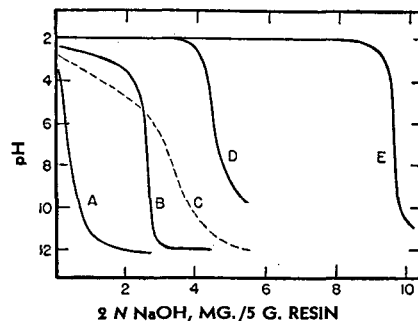

2 N NaOH, MG./5 G. RESIN

Figure 1. Titration Curves of Several Cation Exchanger (88) Functional Groups

A. Phenolic-OH
B. Methylene sulfonic-CH₂SO₃H
C. Carboxyl-COOH
D, E. Nuclear-SO₃H

ions, as demonstrated by Jenny (36), Boyd, Schubert, and Adamson (11), and Kressman and Kitchener (42). Figure 2 demonstrates the relationship between log K and the Debye-Hückel parameter, a^0, calculated from two sets of activity coefficient data (42). Thus the activity coefficients of ions in solutions, which are functions of the hydrated radii of the ions, may be used in estimating the exchange constants (6, 11).

Bauman (6) has applied Donnan's hypothesis to explain the mechanism of this dependence of the exchange equilibria on the activity coefficients. This hypothesis states that the activity of any diffusable electrolyte is the same in both phases at equilibrium. This relationship for cation exchangers may be expressed (6) as

$$\left(\frac{a_B{}^+}{a_A{}^+}\right)_R = \left(\frac{a_B{}^+}{a_A{}^+}\right)_l \tag{3}$$

in which R and l represent the resin and liquid phases, respectively. If the total ionic concentration in both phases is low, the activities of the ions in the two phases are about equal to their concentrations and no appreciable separation occurs. However, the ionic concentration in the resin phase of commercially available exchangers is 2 to 6 molar. Therefore, because the relationships between concentrations and activity coefficients for various ions differ, the ratios of the concentrations of the ions in the two phases will not be equal. This, according to Bauman, is the basis for the separation mechanism of ions of the same valence by ion exchange.

When two ions of similar atomic weight but different valence are involved in the exchange, the ion with the higher charge is selectively adsorbed by the resin phase at low solution concentrations. The exchange constant may be predicted accurately by

the mass law (6, Figure 9). At high solution concentration the resin may favor the ion of lower valence—for example, magnesium selectively replaces sodium from a sulfonic acid resin at low solution concentration, but at high solution concentration the resin favors the sodium ion.
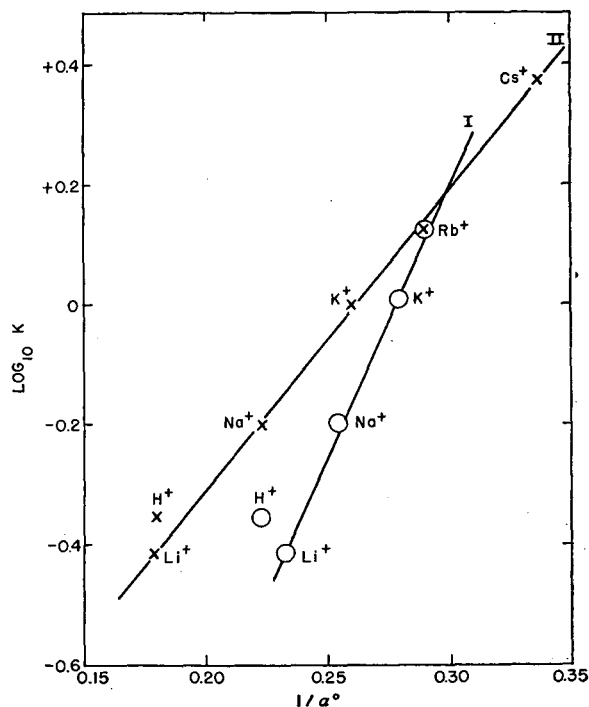

Figure 2. Relationship between Log K and Debye-Hückel Parameter $a^°$ (42)

Calculated from activity coefficient data. I. Stokes and Robinson. II. Harned and Owen

More recently, Bauman (3) has studied the dependence of the separation factor on the degree of cross linkage. If a resin particle is loosely cross-linked, so that it can expand readily and thus increase its pore volume, the difference in concentration between the resin and solution phases will be lower than for highly cross-linked resins. Bauman showed that the percentage of cross linkage of the polymer chains of the exchanger determines the separation factor between two solutes, as would be predicted from the Donnan hypothesis. However, these highly cross-linked exchangers are less applicable in most separations than those with somewhat lower cross linkage, because the rate of exchange decreases with an increase in cross linkage.

The size of many large, highly hydrated ions may exceed the pore diameter of most exchange resins. To enter the resin pores, either a portion of their water shell must be stripped off or the covalent bonds of the resin structure must be distorted. Kressman and Kitchener (42) have postulated a change in the hydration of ions when they enter the resin phase to explain the discrepancy between the ΔH value obtained for an exchange reaction and the value calculated on the basis of coulombic forces.

LABORATORY PROCEDURES

The two types of laboratory techniques in which ion exchangers are customarily employed are equilibrium experiments and column procedures. The experimental techniques and interpretations of results for these applications are discussed below.

Equilibrium Experiments. PREPARATION OF RESIN. The properties of commercially available exchange resins vary somewhat from batch to batch. Therefore, it is desirable to prepare

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Table I. Commercially Available Ion Exchange Resins[a]

Trade Name	Manufacturer	Available Mesh Sizes and Form
Cation Exchangers		
Sulfonated Hydrocarbons (5, 6, 12, 17, 19, 30, 82)		
(Exchange Capacity about 5 Me. per Gram)		
Amberlite IR-120[b]	Rohm and Haas Co.,	20–40, spheres
Amberlite XE-69[b]	Philadelphia	200–325, spheres
Dowex 50[c]	Dow Chemical Co., Midland, Mich.	20–40 to 250–500, spheres
Permutit Q	Permutit Co., New York	16–50, spheres
Duolite C-20[c]	Chemical Process Co., Redwood City, Calif.	20–40, spheres
Sulfonated Phenolformaldehydes (4, 28, 37, 39, 41–43, 56)		
(Exchange Capacities of SO₃H in Range of 2 to 3.5 Me. per Gram)		
Amberlite IR-100[b]	Rohm and Haas	20–40, granular
Zeo-Rex	Permutit	20–50, granular
C-200	Cyanamid	20–40, granular
Duolite C-3[c]	Chemical Process	20–40, granular
Carboxyl Exchangers (35, 49, 92)		
(Exchange Capacity Dependent on pH)		
Amberlite-IRC-50[b]	Rohm and Haas	20–40, spheres
Amberlite-XE-97[b]		200–325, spheres
Duolite CS-100[c]	Chemical Process	20–40
Anion Exchangers		
Quaternary Amines (50, 51, 92)		
Amberlite IRA-400[b]	Rohm and Haas	20–40, spheres
Amberlite XE 67[b]		200–325, spheres
Dowex 2[c]	Dow Chemical Co.	20–40, spheres 200–400, spheres
Other Anion Exchangers, Chiefly Phenolformaldehyde. Tertiary Amines (21, 51, 52, 56, 89)		
Amberlite IR-4[b]	Rohm and Haas	20–40, granular
Amberlite XE-59[b]		200–325
Duolite A-2[c]	Chemical Process	20–40, granular
A-300	Cyanamid	20–40, granular
De-acidite	Permutit	16–50, granular

[a] Additional descriptive literature for most of these resins available from manufacturers.
[b] Available in analytical grade from Eimer and Amend and Fisher Scientific Co.
[c] Available in small quantities for laboratory use from Microchemical Specialties Co., 1834 University Ave., Berkeley, Calif.

a batch of resin large enough to last throughout any series of equilibrium experiments. For most such series, 100 to 500 grams will suffice. A resin with a particle size of 100 mesh or larger is most adaptable for equilibrium studies, as it settles rapidly, permitting an aliquot of the supernatant solution to be withdrawn for analysis.

In order to get rid of fine particles and small bits of foreign matter associated with most commercial resins, they should be stirred with distilled water in a large beaker. After the bulk of the resin has settled, the fines may be poured off with the supernatant water. This process should be repeated until the remaining resin settles completely within a minute.

Usually, it is desirable to have the resin entirely in one form for equilibrium experiments. Even though the label may indicate that it has the desired ion, it will usually contain considerable ionic impurities which are introduced during its manufacture. For this reason, it should be pretreated with a solution of the desired ion before it is used. By stirring the resin in a beaker with a large excess of the conditioning solution having a 6 to 10 molar concentration, it may be largely converted to the desired form. A more complete conversion may be made by separating the solution and resin and again stirring it with another portion of fresh conditioning solution or by a column conditioning as described below. After the conversion is complete, the resin should be washed well with water to remove the adhering conditioning solution. [Ion exchangers which form weak acids and bases should be washed sparingly, because of their tendency to hydrolyze—for instance, Kortschak and Payne (39) found that Amberlite IR-4B was 20% hydrolyzed by passing 20 column volumes of water through the resin in the hydrochloric acid form.] It may then be slurried into a sintered-glass filter which is mounted in a filter flask and dried by drawing air through it with a vacuum. When the particles are sufficiently dry so that they no longer adhere to each other, the resin should be spread in a thin layer in a tray and allowed to remain in contact with the air for several days more. (The hydroxide form of an anion exchanger should be dried in a carbon dioxide–free atmosphere to avoid formation of the carbonate.) If it is stored in a tight bottle, its moisture content will not change appreciably during the series of experiments.

EXPERIMENTAL METHODS. In order to obtain a basis for comparing and interpreting data, it is desirable to determine the moisture content and the equivalent weight of the batch of prepared resin. It is customary to determine moisture by drying the resin at 110° to 115° C. under atmospheric pressure for 48 to 72 hours. Actually, there is a very slow additional loss of weight for a considerable period beyond the 72 hours.

If the ion attached to the exchanger forms an oxide or carbonate of known composition, with a very low vapor pressure, the equivalent weight may be determined by ashing the dried sample from the moisture determination. For exchangers in the hydrogen or hydroxyl form an approximate equivalent weight may be obtained by titrating a known weight of the exchanger with a standard base or acid, respectively, using a glass electrode to determine the end point (6, 28, 37). Gregor and Bregman (28) have shown that a rapid titration will differentiate between strongly and weakly dissociated ions in polyfunctional exchange resins.

Otherwise, the ion on a known weight of the resin may be replaced by an excess of another ion and the change in the quantity of one or both ions in the solution determined after it is separated from the resin. For this purpose it is convenient to pass the conditioning solution through a bed of the resin in a column (84, Figure 1). If an easily titratable ion is used as the conditioning solution, it may be collected in fractions of known volume, each being titrated and compared in concentration to the influent solution. When the concentration of this ion in the effluent solution is equal to that in the influent, the conversion may be considered complete. 'The equivalent weight may then be calculated from the weight of the resin in the column and the decrease in the quantity of the conditioning ion in the solution that was passed through the column.

The technique in equilibrium experiments is similar to the methods used in solubility determinations. Carefully weighed samples of air-dried exchanger are equilibrated with measured volumes of solutions of known compositions. Glass vessels may be used for most of these experiments. Small glass vials with plastic screw caps are very convenient. When the solute being studied is present in very low concentration, its exchange with the glass may cause erratic results. In such cases it is desirable to employ plastic vessels which exhibit no exchange properties, such as molded polystyrene or polyethylene bottles or vials.
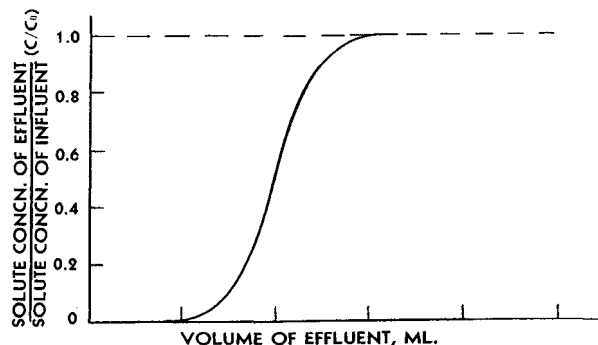

Figure 3. Typical Breakthrough Curve

In most cases only a few minutes are required to reach equilibrium if the contents of the vessel are agitated (6); however, when the original concentration of one or more constituents is very low several hours may be required. If accurate results are desired, the vessels must be thermostated during the equilibration. A wheel, which is provided with clamps for holding the vessels and can be rotated in a constant temperature water bath, is convenient for this purpose. A submerged rack at one side of the water bath may be used to hold the tubes after they are removed from the wheel. In this way constant temperature may be maintained during the withdrawal of aliquots for analyses.

Although it is often desirable to determine the quantity of each solute ion in both phases, it is much more convenient simply to determine their change in concentration in an aliquot of the liquid phase. In case there are only two ions in the system, particularly when the concentration of one is very much smaller than the other, it may be necessary to determine only the change in concentration of the ion in lowest concentration in the liquid phase. In such cases, conditions should be chosen so that there is approximately the same amount of the solute of interest in each of the two phases. This type of experiment may be carried out conveniently by using radioisotopes as indicators. If a beta-emitter is employed and the depth of the solution covering the resin is greater than the range of the beta-particles, the analysis may be performed by counting the radiation coming from the open end of the bottles without separating the phases. The change in concentration of the radioisotope in the liquid phase is determined by comparing each vessel with a standard or blank containing no resin. Ionic constituents present in macroscopic quantities may be determined in an aliquot of the solution by titration, colorimetry, or other analytical methods. In case the quantities of solutes in the solid phase are desired, the resin may be ashed and the ash analyzed, or the ions may be replaced from the resin by an excess of another ion and their quantities determined in the effluent.

INTERPRETATION OF RESULTS. The mass law has been used successfully to interpret the results of equilibrium exchange experiments when the concentration of solutes in the liquid phase is low (11, 22, 28, 34, 37, 42, 43, 69, 85, 88, 90). As the ionic concentration of the solution increases, ionic activities must be used in place of concentrations in expressing the mass law (Equation 2). It has not been possible to determine the activities of the ions in the resin phase. Boyd, Schubert, and Adamson (11) assumed that the resin components form an ideal solid solution when the

ions are singly charged and do not vary too widely in size. Under these conditions the activities of the ions in the solid phase are assumed to be proportional to their mole fractions.

Bauman and Eichhorn (6) applied the Donnan hypothesis to estimate the concentrations of ions in the resin particles. Their calculations were based on the assumptions that the ions are completely dissociated within the pore volume of the resin which was determined from the settled volume of resin in various concentrations of hydrochloric acid. The ionic activities in the resin particles were then calculated from the activity coefficients of solutions of these concentrations. Experimentally, it was shown that the distribution of hydrochloric acid between the resin and solution phases followed that predicted by the Donnan hypothesis at high concentrations but deviated from the hypothesis in the lower concentration range. By taking into account the differences in the hydration of the ions in the two phases, this deviation may be explained (22, 29, 42, 43).

In many cases it may be desirable to follow the distribution of only one solute. Even when separations are being studied, it is sometimes convenient to study the equilibria for the different ions separately. If they are maintained in low concentrations, so that there is a negligible change in the concentration of the major constituents in the solution and resin phases, a very simple equation may be used to express their distribution between the two phases

$$K_d = \frac{\text{concentration of solute in resin}}{\text{concentration of solute in liquid}} = \frac{A_R}{BR} \times \frac{v}{A_l} = \frac{A - A_l}{BR} \times \frac{v}{A_l} \quad (4)$$

where K_d is the distribution coefficient of solute A, A_R and A_l are the fractions of A in the resin and liquid phases, respectively, BR is the weight of the resin, and v is the volume of the solution. Thus, by maintaining a constant solution volume and varying the quantity of resin it has been shown (85) that K_d remains constant over a very wide range of resin to liquid ratios. This type of equilibrium data is valuable in predicting the behavior of a solute on a column (8, 55, 66, 82, 85). If both the resin weight and solution volume are held constant, the effect of varying the concentration of the ion or ions present as the major constituents may be evaluated (11, 69, 85, 88).

APPLICATIONS OF ION EXCHANGE EQUILIBRIUM EXPERIMENTS. Perhaps the most useful application of this procedure is for the determination of physical constants. This has been discussed at length by Schubert (66, 67). By using radioactive tracers and equilibrating known weights of resin with equal volumes of solution of varying concentration of the ion present as a major constituent, the power dependence of its concentration will be reflected in the values of K_d. From this it is possible to determine the valence of the trace constituent in the exchange reaction (11, 66, 67, 85, 88).

Addition of varying quantities of an anion which will form a complex with the trace constituent permits an estimation of the dissociation constant of the complex form the change in K_d (44, 45, 67, 68, 69, 85).

Equilibration may be used in separating ions which differ widely in exchange constants or ionic concentrations. Thus, monovalent ions may be separated readily from trivalent ions of comparable concentrations by equilibrating resin with a solution containing these ions. Likewise, ions having the same valence may be separated by adding an anion which will selectively form a strong complex with one and thus reduce its ionic concentration. This method also may be used to separate ionic constituents from nonionized substances or to eliminate undesired cations or anions and thus to reduce the chance of interferences in the standard analytical procedures. Specific analytical methods which apply to this procedure may be found in reviews by Kunin (46–48) and Rieman (64).

Equilibrium experiments are also useful in determining the factors affecting the separation of very similar ions, such as the rare earths and the alkaline earth elements. By using this technique it is possible to investigate the effect of a large number of variables on the separation factor between two or more ions in a relatively short time. These data can be applied to determining optimum operating conditions for column separations by one of the theories discussed in the next section (55, 66, 85).

Column Separations. EXPERIMENTAL METHODS. The apparatus and techniques employed in making column separations are very simple. Two typical columns have been illustrated (31, Figure 1; 84, Figure 1). In each of these the resin bed rests on a porous disk in a cylindrical tube with a liquid inlet at the top and an outlet below the disk. Many times it is convenient to provide means for maintaining a constant liquid head and for preventing air from being drawn into the column (31, Figure 1). A jacketed column for making column separations at elevated temperatures has been described by Ketelle and Boyd (38).

The resin should be washed free of fine particles and foreign matter by stirring it in a large beaker with distilled water and pouring off the supernatant water and fines after the bulk of the resin has settled. This precaution will avoid clogging of the column, which sometimes causes erratic flow rates. A funnel should be attached to the top of the column with a short length of rubber tubing. The bottom of the column should be attached to a source of distilled water until the air has been displaced from the column and the stem of the funnel. The funnel is then filled by slurrying in the resin which settles, forcing the water from the column up into the funnel. A portion of this water should be removed from the funnel before additional resin is added. This procedure will give a uniform column with the correct degree of packing. In case an exchanger of very fine particle size is used, it may be desirable to permit water to escape from the bottom of the column while it is being filled. This increases the settling rate of the resin and reduces the time necessary to fill the column.

Because exchange resins, as received from the manufacturer, usually contain considerable quantities of ionic impurities, it is desirable to precede any separation run with a conditioning of the bed. This is performed by passing a concentrated (usually 6 to 12 molar) solution, containing the ion desired on the resin bed at the beginning of the separation run, through the column. Sulfuric or hydrochloric acid may be used to convert a cation exchange resin to the hydrogen form. Soluble salts are applicable for converting it to other cationic forms or for converting anion exchangers to various anionic forms. Conversion may be assumed to be complete when there is no detectable difference in concentration between the influent and effluent solutions.

The bed will shrink in volume during the passage of the concentrated solution. In case this solution is followed with water, introduced into the top of the column, the subsequent swelling of the resin bed may break the column. At any rate, the column will be too tightly packed. For this reason the resin bed should be backwashed by introducing water into the bottom of the column and allowing it to escape at the top. It is desirable to have free space in the column above the resin bed to permit the column to expand during backwashing. However, if there is insufficient space in the column, a large funnel may be attached at the top as during the filling of the column with resin. The flow rate during the backwashing should be rapid enough to expand the bed, but not so high that resin is lost from the top of the column. After the column has been allowed to settle it may be washed further by downflow until the conditioning ion cannot be detected in the effluent. It is now ready for the separation run.

Two techniques may be employed for separating ions: (1) break through, in which a solution is passed through a column until one or more of the influent ions appear in the effluent solution; and (2) "chromatographic" elution, in which the solutes are first adsorbed near the top of a column and then eluted with a bulk ion. In the former method, the influent ions replace the ions originally on the exchanger, the latter appearing in the effluent in a concentration equivalent to that of the influent ions. As flow proceeds and the column approaches saturation with the influent ions, their concentrations will increase until they reach the influent concentration, as shown in Figure 3.

Elution or chromatographic separations involve passing a quantity of one or more solute ions, in a solution of low ionic concentration, sufficient to saturate a small, top fraction of the column and following this by another solution of higher ionic concentration. The solute ions are displaced from the top of the column and carried down the column at different rates, depending upon their relative exchange constants. If the correct conditions are chosen, the solutes will separate into distinct bands on the column and be eluted with undetectable amounts of cross

contamination. Elution curves for radioisotopes of several rare earths, as determined by Ketelle and Boyd (*38*), are shown in Figure 4.

THEORETICAL INTERPRETATION. In trying to picture the factors involved in a column separation it is convenient to consider the behavior of a single, "average" ion of one solute.

Let us suppose that this ion, A^+, is entering a column of exchange resin, BR, containing 1 me. of 100-mesh resin and 0.33 ml. of solution in a bed 1 sq. cm. in area and 1 cm. long. The bed will consist of resin particles 0.25 mm. in diameter with a contacting liquid phase which also is interspersed throughout the particles. Randomly distributed throughout the resin particles there will be about 6×10^{20} B^+ ions, each of which is capable of exchanging with ion A^+ should it approach within the right distance for the reaction to occur.
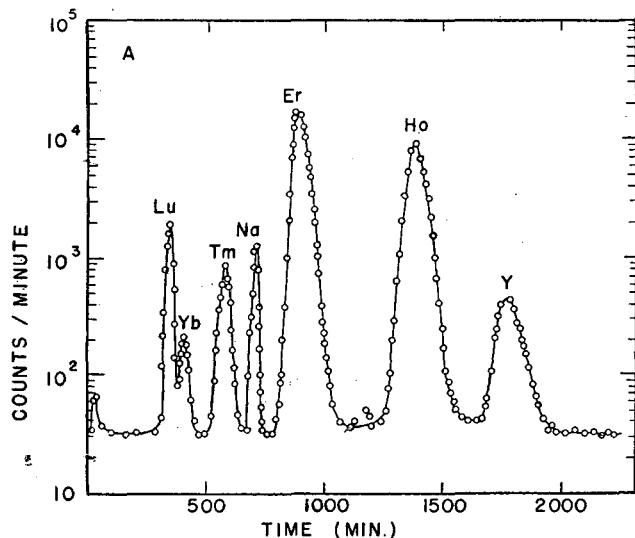

Figure 4. Separation of Rare Earths by Chromatographic Elution after Neutron Activation (*38*)

As ion A^+ enters the column it will be carried downward by the liquid flow through the channels between resin particles. It will also diffuse randomly in all directions. Depending upon the rate of flow (whether laminar or turbulent), it will be moved in various directions to a smaller or larger extent by the liquid molecules surrounding it. When ion A^+ approaches a resin particle it may enter a region of stationary liquid which surrounds the particle. In this case, it has a chance (less than 50%) of diffusing toward the resin particle, or it may diffuse out into the turbulent stream, to be carried further down the column. In this case, depending on the flow rate, it may have passed from the vicinity of the first resin particle with which it had a chance to react. After one or more such encounters, this ion will finally reach the surface of a resin particle and move about until it exchanges with a B^+ ion, taking its place in the resin matrix.

Suppose that a solution 1 molar in B^+ ions is then passed through the column at a rate of 0.33 ml. per minute. Each minute about 2×10^{20} ions of B^+ will pass through the column. If one assumes that the resin particles and solution are distributed uniformly throughout the column, then each particle of resin (whose diameter is 0.025 the column diameter) will be contacted by about $(1/40)^2$ of the solution, or about 1.25×10^{17} ions per minute. Ion A^+ will be replaced, and as it is carried down the column in the liquid stream it may exchange again at a position further down the column. However, under the new conditions, it must compete with the large excess of B^+ ions in the solution phase.

Because of the large number of exchange positions in a resin bed, there may be an inclination to assume, intuitively, that the number of exchanges an "average" ion makes as it passes through 1 cm. of the bed would be very large. However, the reaction must take place between components in a solution and other components which are randomly distributed throughout discrete resin particles, macroscopic in dimensions. In this case, there is not the kind of instantaneous equilibrium found between ions in a solution, since they must diffuse relatively large distances before an exchange reaction is possible. For this reason the "average" ion may not even exchange with each resin particle it passes and

the number of exchanges during its passage through 1 cm. of column bed at a flow rate of 0.33 ml. per minute well may be in the order of 25 or less.

If a large number of A^+ ions are first adsorbed near the top of a column of BR from a very dilute solution and then eluted down the column with a more concentrated solution of B^+ ions, some will exchange more often than others, and thus travel down the column at a slower rate. It is not surprising that, experimentally, one finds that such an elution curve approaches a normalized differential error function (*8*, Figure 1; *14*, Figure 9).

The above discussion indicates a few of the large number of factors which affect column operation and their complicated interrelationships. The size of the resin particles determines the average size of the liquid channels, which in turn determines the amount of turbulence and thus the movement of the ions in the liquid phase as well as the thickness of the stationary liquid film surrounding the particle. The flow rate is also a determining factor of the values of these variables. The resin particles have exchange positions throughout their volume and therefore the particle size also determines the average distance an ion will diffuse through the solid phase before it exchanges. The relative concentrations of the solutes will affect their rates of diffusion through the two phases and determine the average amount of time a solute ion will remain in each phase (which is expressed by the distribution coefficient). When solutes are present in large concentrations, the distribution coefficient will vary throughout the column. In addition to these factors, the temperature affects diffusion rate and the rate of exchange as well as the equilibrium constants for the exchange reactions. The dependence of column length and area is more clear cut, for they are somewhat less interdependent with the other variables.

Because of the large number of variables it has not been possible to express their relationships in mathematically solvable terms and thus to develop a general theory for column separations which is applicable over a wide range of operating conditions. Instead, the attempts have resulted in several theories which explain and predict column separations under limited conditions.

The first theoretical approach was described by Wilson (*91*) and DeVault (*20*) in attempting to explain the distribution of a solute on a chromatographic column. This theory, which has been extended by Offord and Weiss (*57*, *58*) and Glueckauf (*25*–*27*), to describe the separation of several solutes utilized the nature of the adsorption isotherm—i.e., whether linear, convex, or concave. The differential equations used to express the distribution of the solute in the column are based on the further assumptions that equilibrium conditions prevail throughout the column, that diffusion has a negligible effect on solute distribution, and that each solute particle is adsorbed and desorbed a very large number of times during its passage through the column.

These assumptions are not strictly valid. Although this has been recognized by some authors, there has been a tendency to utilize it as an explanation for the failure of the theory to fit the experimentally observed curves rather than as an indication of the need of revising their approach to the problem (*23*). Though this theory is limited in its application to chromatographic separations, its value is even more questionable for ion exchange separations. Qualitatively, it does predict the general forms of the elution curves for the three types of isotherms in chromatographic separations.

Two theories, similar to those used to interpret other processes, have been applied with considerable success for the limited case in which the solute of interest is present in low concentration as compared to the bulk ion. One of these is based on the plate theory which has been developed for distillation and liquid-liquid fractionating columns (*87*). The second utilizes the mathematical approach employed by Furnas (*24*) to explain heat transfer between a bed of solid particles and a gas passing through it.

PLATE THEORY. This theory has been applied very successfully by Martin and Synge (*54*) and Mayer and Tompkins (*55*) for interpreting and predicting the distribution of solute on col-

umns and in the eluate in partition chromatography and ion exchange, respectively. The plate theory is an empirical approach in which the only variables considered are the equilibrium distribution coefficient of the solute between the two phases and the number of theoretical plates in the column. The theoretical plate may be considered as a segment of the column of sufficient length to allow the "average" solute ion to attain equilibrium between the two phases. The success of this theory for interpreting and predicting the degree of separation has been demonstrated (8, Figure 1; 14, Figure 9, 55). For the experiment in the latter reference, conditions were chosen such that separation would be incomplete. The calculated compositions of the various fractions corresponded closely with the experimentally determined values, as shown in Tables II and III. From a preliminary column run of this type, which shows the ratios of the distribution coefficients—i.e., the separation factor—and from which the number of theoretical plates per unit length may be calculated, it is possible to calculate, easily, the dimensions of a column which is required to give any desired degree of separation (55, 66, 82).

Although the plate theory is simple to apply and interpret, it is very limited in its ability to predict the effect of varying the operating conditions on the separation. Furthermore, it does not aid materially in an understanding of the separation process. In spite of these limitations, it is probably the most useful approach for the design of analytical separation procedures.

KINETIC THEORIES. The mass transfer theory was first published in 1941 by Beaton and Furnas (7). Boyd, Adamson, and Myers (10) applied this theory for interpreting the adsorption and desorption of several monovalent ions in trace concentrations. For this purpose the differential equations of Furnas (24) were reformulated using a first-order rate equation which had been found to apply in the description of the adsorption velocity in a single-stage experiment (9). The effects of bed dimension, flow rate, distribution coefficient, particle size, temperature, and rate constants on the shapes of the breakthrough curves were evaluated in terms of the theory.

Thomas' theoretical treatments (76, 77) were formulated on (1) the basis of a bimolecular mechanism in accordance with the

assumption that the exchange process is determined by the rates of opposing second-order reactions, and (2) the basis of diffusion of solute through the solid particle as the rate-controlling step. However, in the latter treatment he considers only the limiting case in which no significant concentration gradient exists within the resin particle. Differential equations were used to express the relationships between the distance from the top of the column (in terms of resin mass), the flow rate, time, solute concentration in each of the two phases, and the pore volume of the solid phase. Solution of these equations in terms of two dimensionless variables gives a family of curves. The experimental breakthrough curves may be fitted to these calculated curves and the values for the constants of the equation determined.

Presumably, the theory then may be employed to predict the results of column runs under varying conditions. Although no very impressive confirmation of its application for this purpose has been published, basically this theory furnishes the most promising approach to an understanding of the mechanism of column separations and as a guide for future experiments.

Vermeulen and Hiester (86) attempted to correlate the theoretical approaches based on the "plate" and mass transfer concepts for the separation of trace components by column elution. They extended the mass transfer equations to include the case of chromatographic elution and developed a simple algebraic relationship between the two theories. On the basis of this extension these authors worked out an engineering design for a radium-barium separation plant based on ion exchange. Unfortunately, no experimental tests of the design, based on this theory, have been reported.

For the most important case, in which two or more solutes in relatively high ionic concentrations are being eluted from a column, no theoretical solution has been suggested. While this is of minor importance in the application of ion exchange to analytical chemistry, such a theory would be very valuable to engineers in designing industrial installations.

FACTORS WHICH AFFECT COLUMN SEPARATIONS. Three general methods have been used to investigate the factors affecting separations: analyses of the elution curves of one or more solutes from a typical separation column operating under varying conditions, equilibrium studies for determining the relationships between various factors and the distribution of the solute between phases, and kinetic studies designed to determine the rate-controlling mechanism under various conditions and its dependence on these variables.

Although the first of these methods is the most direct manner of studying column separations under varying conditions, it is limited in its application by the length of time required for each experiment. Furthermore, the interrelationships between most of the variables are so complicated that such direct studies can give, at best, empirical relationships useful in selecting optimum operating conditions. This was amply demonstrated in the early separation studies of fission products and rare earths (16, 81, 71, 72, 83, 84). However, a certain number of column separation runs are necessary to test theoretically predicted interrelationships which cannot be investigated by other methods.

The equilibrium distribution of the solute between the phases and the constants of the exchange reactions is used in formulating both the plate and kinetic theories of ion exchange separations. The effects of a number of variables on the distribution coefficient may be studied in a comparatively short time.

Results of kinetic studies form the basis for discussions of the kinetic theory and aid in a general understanding of the exchange process. Two general methods have been employed in these studies: measurement of the change in concentration with time of a solute in a solution being stirred with a suspension of exchanger, and the shallow bed technique which consists of passing a solution through a thin section of exchanger and determining the rate of change of the concentration of a solute in the resin. Results of these studies have been reviewed by Thomas (76).

Table II. Cross Contamination

	Eluate, Free Vols.	Observed Ratio of Eu to 61	Fractional Ratios of Eu/61	
			Exptl.[a]	Theoretical
1	6.74	>100	>80	110
2	7.23	8.18	6.7	8.0
3	7.47	2.45	2.0	2.14
4	7.57	1.50	1.22	1.3
5	7.67	0.762	0.62	0.74
6	7.73	0.423	0.34	0.48
7	7.98	0.164	0.133	0.135
8	8.18	0.064	0.052	0.050
9	8.36	0.024	0.020	0.021
10	8.57	0.006	0.005	0.007

[a] Corrected for original ratio of Eu to 61.

Table III. Area under Elution Curve

(Element 61)

Eluate, Free Volumes		Area Units under Exptl. Curve	Fraction of Total Area under Curve	
From	To		Exptl.	Theory
6.0	6.5	4	0.0009	0.0011
6.5	7.0	25	0.0054	0.0054
7.0	7.5	85	0.0185	0.0182
7.5	8.0	215	0.0467	0.0485
8.0	8.5	470	0.1021	0.1027
8.5	9.0	748	0.1625	0.1610
9.0	9.5	927	0.2014	0.1987
9.5	10.0	880	0.1912	0.1899
10.0	10.5	652	0.1417	0.1418
10.5	11.0	370	0.0804	0.0809
11.0	11.5	152	0.0330	0.0352
11.5	12.0	58	0.0126	0.0122
12.0	12.5	13	0.0028	0.0032
12.5	13.0	3	0.0007	0.0007
	Total	4602	1.00	1.00

More recently, studies have been reported by Hale and Reichenberg (30), Juda and Carron (37), Kressman and Kitchener (41), and Adamson and Grossman (2). The results of these studies indicate that, depending on the ionic concentration in the contacting solution, the rate-determining step may be a second-order chemical rate law, diffusion through a liquid film surrounding the resin particles, or diffusion through the resin particles. The first two dependencies have been reported for solution concentrations below 0.1 M, the latter in the case of more concentrated solutions.

In many studies on factors affecting column spearations, particularly those based entirely on column experiments, the interdependence among the various factors has not been taken into account in interpreting the results. However, several dependencies of general interest have been established.

The separation between solutes increases with column length. The plate theory predicts this relationship quantitatively for solutes in low concentrations (in the linear isotherm region).

Decreasing the flow rate increases separation. To calculate the quantitative relationship it is necessary to know the rate-controlling mechanism.

Increasing the temperature increases the separation. The increase in the rate of diffusion is a major factor, although the ratios of K_d values also may vary with temperature.

Decreasing the particle size increases separation. It is obvious that this reduces the distance an ion must diffuse in both the liquid and solid phases.

Increasing the loading of a column—i.e., solute per unit area—above a certain critical value decreases separation. Whenever the ionic concentration of the solute exceeds the value beyond which it affects the K_d, poorer separation will result.

Increasing the exchange capacity of the resin increases the separation if the rate of attainment of equilibrium between the phases is not too adversely affected. For instance, the sulfonated hydrocarbon resins were found much superior to the sulfonated phenolformaldehydes having only one third to one half the capacity.

A number of other variables have been studied for specific separations. Most important of these is the effect of complexing agents on separations (69, 72, 83, 84, 85). These substances not only aid in increasing the separation factor between solutes but reduce the ionic concentration (80), thus permitting larger quantities of solutes to be separated in each run.

EXAMPLES OF COLUMN SEPARATIONS. The technique of separating solutes by eluting them with complexing agents has been applied successfully to a number of substances which had never before been prepared in high purities. It has also been demonstrated to be a much simpler method for other separations which could be accomplished previously only with considerable difficulty. Column separations are particularly valuable for substances in very low concentration.

This technique was developed originally by Tompkins, Khym, and Cohn (84) for separating the fission products, including several rare earths. By its use Marinski, Glendenin, and Coryell (53) separated radioisotopes of element 61 (promethium) from a fission product mixture. Additional work by Tompkins and associates (16, 31, 55, 83, 85), Spedding's group (71, 72), and Ketelle and Boyd (38) has resulted in the development of fairly well standardized methods for separating all the rare earths.

Among other elements which have been separated by this method are zirconium and hafnium by Street and Seaborg (73), radium and barium by Tompkins (81), and scandium from the heavy elements and the rare earths by Harris and Tompkins (32). Kraus and Moore (40) have reported the separation of zirconium from hafnium and niobium from tantalum by eluting the oxalate and fluoride complexes from anion exchanger of the strong base type. The separation of the alkali metals by direct replacement from a sulfonated hydrocarbon resin has been reported by Cohn and Kohn (15) and Beukenkamp and Rieman (8). Other recently reported separations by ion exchange have been reviewed by Kunin (46, 47).

A number of interesting separations of organic compounds by ion exchange elution have been reported. Availability of the new types of exchangers has increased the activity in this field (46). Only a few of these separations are mentioned here.

Amino acid separations have been reported by several investigators recently (13, 59–63, 92). Robinson and Mills (65) studied the separation of fatty acids on anion exchange resins. Harris and Thomas (33) separated the hydrolysis products of ribonucleic acids. Smith and Wender (70) separated xanthine from guanine on a sulfonated phenol-formaldehyde resin. Cohn (14) has reported some excellent separations of ribonucleotides by eluting them from a strongly basic anion exchange resin. The elution curves for these substances (55, Figure 5), like those for inorganic ions, approach the curve of an error function.

Perhaps the most interesting of all the separations that have been made by ion exchange are those of the actinides.

The separation of americium and curium by this method was first demonstrated in 1947 by Cunningham, Tompkins, and Asprey (18). These original separations required considerable time, but now by operating columns of about 20-cm. length at about 85° C., a fairly good separation of these two elements can be obtained in about an hour (78). Column separations were applied in the search for elements 97 and 98 in the bombardment products of alpha-particles on americium and curium, respectively.

In the case of element 97, the major part of the americium was separated by an oxidation cycle. The remaining actinides were next separated from the lanthanide isotopes, formed as fission products during the bombardment, by adsorbing the mixture at the top of a column of sulfonated hydrocarbon exchange resin and eluting the actinides with 12 M hydrochloric acid, which selectively forms complexes with the actinides (74). After evaporation, the actinides were dissolved in dilute acid and again adsorbed at the top of the resin bed. They were eluted with an ammonium citrate–citric acid solution at a pH of 3.5, the americium and curium elution curves being followed by the alpha counts and the curve for 97 by counting its electron capture in a nucleometer. Excellent separations were obtained, as shown by Thompson, Cunnningham, and Seaborg (78). Even though the half-life of this new element, for which the name berkelium has been proposed by its discoverers, is only 4.6 hours, a number of its chemical characteristics have been determined (74).

Much more difficulty was anticipated in the studies designed to establish the presence of element 98 because its half-life was predicted to be even shorter than that of berkelium. Because of the large excess of curium, analyses of the column fractions had to be made on a pulse analyzer which permitted the detection of a small quantity of one alpha-emitter in the presence of much larger quantities of another, in case their energies differed appreciably. Thus, a complete separation was not required to establish the presence of element 98. The experimental method for the column separation was refined and streamlined to such a degree that only about 2 hours were required from the end of bombardment until the first sample was ready for pulse analysis. The exact position at which this new element was expected to appear in the column eluate had been calculated on the basis of the lanthanide elution curves by comparing it to its lanthanide homolog. The experiment had been so carefully planned and was so well performed that this new element was actually discovered in the first attempt (79). Although the half-life of this isotope of element 98 is only about 45 minutes, it has been possible in subsequent experiments to study other properties (75). The number of atoms of element 98 originally formed in the bombardment was on the order of 5000. In spite of this, its elution curve and other behavior on the column were similar to those for macroscopic quantities of the other actinides.

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3rd Annual Summer Symposium — Separations

Analytical Applications of Ion Exchange Separations

JACK SCHUBERT, *Argonne National Laboratory, Chicago, Ill.*

ION exchange techniques offer a remarkably versatile and efficient analytical tool for separating, concentrating, and isolating substances so that a direct gravimetric, volumetric, or radiometric operation will complete the analysis. The indirect value to analytical chemistry is also great because ion exchange can be and has been used for determination of the composition and stability of complex ions, purification of reagent chemicals, and discovery of hitherto unknown inorganic and biochemical substances. Many of these analytical applications were anticipated by the early workers in the field; therefore it is of historical and practical interest to review briefly a few outstanding examples. All the work done before 1935 employed a synthetic inorganic zeolite, which necessarily restricted the versatility and range of application of an analytical ion exchange method.

World War I resulted in the first practical analytical application of an ion exchange reaction. In the nesslerization method

for the determination of ammonia in urine (23) Merck's purified blood charcoal was used to abstract creatinine which otherwise interfered with the analysis. Because this charcoal was no longer obtainable, and no other charcoal preparation was found suitable, Folin and Bell (22) searched for a substitute. They found that a synthetic aluminate silicate discovered about 12 years previously by Gans (26) met their need even better than Merck's charcoal. In principle, the method consists of adsorbing the ammonia on the zeolite as the ammonium ion while the creatinine remains in solution. Subsequently the ammonium is liberated by means of sodium hydroxide, and determined by the Nessler reagent.

About the time Folin and Bell were carrying out their investigation Whitehorn (77), in the course of chemical studies of mental disorders, needed a method for separating amines from other nitrogenous substances present in biological fluids. He found that by the use of inorganic zeolite he could effect a separation of nitrogen bases having a dissociation constant greater than about 5×10^{-9} from weaker nitrogen bases and nonbasic substances. Whitehorn investigated many other important items which he reported in this paper. Considering the time at which it was written, the paper represents an elegant piece of work, well worth reading.

A similar application was made a few years later by Youngberg (82), who used an inorganic cation exchanger for the determination of urea in urine. The ammonium ion was adsorbed from solution while the neutral urea remained in the filtrate where it was subsequently hydrolyzed to ammonia for nesslerization.

Of further historical interest are the ingenious investigations of Günther-Schulze which were reported in 1922 (28, 29). Günther-Schulze, making use of the fact that the uptake of cations by a cation exchanger was a function of the charge on the cation, studied the formation of complex ions in copper salts (28) and the chloride complexes of divalent metals (29). This work shortly led Gustavson (30) to apply cation exchangers for the investigation of complex formation in chromium salts—a problem of especial interest to leather chemists. Several recent accounts of Gustavson's work are available (31).

The availability of high grade synthetic organic ion exchangers has resulted during recent years in a marked acceleration of analytical applications of the ion exchange reactions. Several reviews have been published (39, 40, 53, 56). Most analytical applications thus far have been concerned with the removal of interfering anions—i.e., metathetical reactions. An extensive program along these lines, which is still under active development, was begun by Samuelson about 12 years ago (56). Most of the analytical potentialities of the synthetic organic ion exchange resins were suggested by Adams and Holmes (1) in 1935.

The purpose and plan of this report are to describe certain general procedures and principles utilizing ion exchange reactions and to suggest new possibilities which can be adapted for analytical problems. Many specific applications, other than those involving removal of interfering substances, are cited to illustrate procedures of the widest utility.

MATERIALS AND METHODS

The full extent to which ion exchange reactions could be applied was not realized until the introduction of the synthetic, organic, polymeric, ion exchangers. The several types of cation and anion exchangers now available can be classified by the number and kind of functional groups they possess, such as SO_3H, —COOH, —OH, and—SH in the case of cation exchangers, and —NH_2, —NHR, —NR_2, and the like in the case of anion exchangers. Details concerning the chemical and physical properties of these exchangers and the effect of varying particle size, flow rate, temperature, etc., on separation efficiency can be found in informative articles by Tompkins (70) and Djurfeldt and Samuelson (19). The latter studied various aspects of ion exchange technique primarily as they apply to analytical problems. Bauman (5) has given a concise authoritative treatment of the fundamental properties of ion exchangers.

Naturally, with a wide variety of exchangers from which to choose, the question arises as to which to utilize in a given problem. The writer is of the opinion that for practically all analytical purposes only two resins are required: (1) a cation exchange

resin containing nuclear sulfonic acid groups as the sole exchanging group, such as Dowex 50 or Amberlite IR-120; and (2) a strongly basic anion exchange resin which possesses a quaternary amine-type structure, such as Dowex 2-A or Amberlite IRA-400. In simple solutions other types of exchangers will have more or less greater specificity. However, and this is important, for versatility and in order to impart or acquire a given degree of specificity, it is both preferable and possible to alter the solution composition in such a way as to realize a degree of selectivity which far exceeds that provided by an exchanger as such. For example, one type of cation exchange resin may have a higher selectivity for alkaline earth cations relative to rare earth cations than a sulfonic acid cation exchanger. However, by addition of citric acid and suitable adjustment of pH, the rare earths can be separated from alkaline earths almost completely in nearly a single batch operation by the use of a sulfonic acid resin; the alkaline earths can be kept in a cationic form at a pH below 5 in the presence of citric acid, whereas under the same condition the rare earths are converted to a neutral or anionic, hence unadsorbed, state (61).

Decisions must often be made as to whether a batch or column operation should be employed in an analysis. For quantitative separations and identification of closely related substances it is most always preferable to have small columns permanently set up for use. Furthermore, as was pointed out by Whitehorn (77), column operation minimizes the destruction suffered by easily oxidizable substances. On the other hand, it is necessary to utilize steady-state batch procedures for the highest accuracy when investigating the formation, composition, and stability of complex ions, and measuring activity coefficients in mixed electrolytes. Batch operations also save much time in the measurement of distribution coefficients preparatory to planning optimum conditions for new column separations, or in rapid screening of possible applications to a specific analytical problem.

Table I.   Useful Methods for Effecting-Analytical Separations by Ion Exchange during Adsorption or Elution Steps

Chemical Methods	Physical Methods
1. Natural differences in adsorption affinity because of valence, charge, ionic radii, hydration, rate of uptake	1. Dilution
2. Adjustment of pH	2. Flow rates or contact times
3. Colloid formation	3. Particle size
4. Variation of ionic strength	4. Temperature
5. Complex ion formation	5. Column dimensions
6. Selective precipitation within exchanger	6. Viscosity of solution
7. Modification of adsorption affinity by oxidation or reduction of individual ions	
8. Use of exchanger with high specificity	
9. Variation in solvent—i.e., dielectric constant	

Many types of experimental columns for supporting the exchanger have been devised (57). A type devised by Frizzell (24) is of particular value when it is desired to keep the volume of elutriant to a minimum. It utilizes a reflux type of column similar in principle to a Soxhlet extraction, which involves the re-use of a constant boiling acid eluant.

ION EXCHANGE REACTIONS IN ANALYTICAL CHEMISTRY

General Considerations. Fundamentally, the analytical uses of ion exchange reactions involve separations of individual components with consequent concentration and purification. The separations are effected in either the adsorption or desorption (elution) stage, or both. The extent of separation is dependent on chemical and physical factors, the quantitative and qualitative aspects of which are given by Tompkins (69). Substances are taken up by an ion exchanger by either a true ion exchange reaction, in which case the primary forces governing the relative

The chief service of ion exchange techniques to analytical chemistry is to provide a simple, rapid, and effective tool for separating, concentrating, and isolating substances, so that a direct gravimetric, volumetric, or radiometric operation will complete the analysis. The purpose of this presentation is not to review the literature but to give the fundamental principles underlying the analytical applications of ion exchange. Several applications of the ion exchange technique are given, including the removal of interfering substances, separation of cations from anions, purification of inorganic and biological substances, determination of trace impurities, measurement of the stability of complex ions, determination of activity coefficient, and evaluation of molecular structure. Specific applications are cited.

affinity of the ions are coulombic or van der Waals forces, or by physical adsorption in which the exchanger because of its surface, electrical charge, or both, acts as an adsorbant for coagulated or charged colloidal particles and for precipitates formed within the interstices of an exchanger bed. Substances held by ion exchange are eluted by cationic displacement in the case of cation exchanger–retained material, and by anionic displacement in the case of anion exchanger–held material. The elution of ions is facilitated by agents which form complex ions with the adsorbed substances. Adsorbed colloids are not affected, in general, by cationic or anionic active elutriants, but are easily removed by complex-forming agents. Other physically held materials can be removed by appropriate solvents such as water, pyridine, or alcohol.

Analytical separations are attained by utilizing and enhancing differences in the chemical characteristics of ions, such as basicity and complex constants, as well as in the physical conditions such as flow rates and particle size of the adsorbant. A summary of many of the possible ways in which separation suitable for analytical purposes may be obtained is given in Table I.

SPECIFIC ANALYTICAL USES OF ION EXCHANGE REACTIONS

The examples given in this section illustrate general principles and techniques of the widest utility. Only applications which utilize synthetic organic resins as the ion exchanger are depicted.

Removal of Interfering Substances, Separation of Cations from Anions, and Analysis by Titration of Stoichiometrically Released Hydrogen Ions. ISOLATION OF RADIOELEMENTS FROM URINE. In order to ascertain the amounts of dangerous radioelements which may have accumulated in the body of an exposed individual, it is most convenient to analyze the radioelements excreted in the urine.

An ion exchange method has been developed for quantitatively extracting a trace element from 1 liter of urine and concentrating it in a few milliliters of solution completely free from salts which interfere with standard analytical or radiometric analyses (64). The method is based on the principle that cation exchange reactions follow the law of mass action (7); hence the reaction can be made to proceed in any direction by altering the relative concentration of the reactants and products.

In an ion exchange process for extracting and eluting carrier-free radioactive yttrium from urine, the principal reaction for both adsorption and desorption steps is:

$$Y^{+++} + 3HR \xrightleftharpoons[\text{desorption}]{\text{adsorption}} YR_3 + 3H^+$$
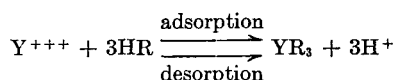
The adsorption of yttrium is made from urine 0.1 M in hydrochloric acid, while the desorption is carried out with 7M hydro-

chloric acid. A detailed flowsheet for the operation is given by Schubert (64).

Acidification of the urine prevents the precipitation of calcium salts, keeps the yttrium in ionic form, and liberates yttrium from any unadsorbable complexes formed with urinary constituents. A solution of 0.4 N hydrochloric acid removes some adsorbed organic matter and other monovalent and divalent cations. Alcohol serves to remove organic matter between runs, which acts as if it coated the resin particles, causing erratic and low adsorption.

Recoveries of 85 to 90% are reported. The method could be improved, particularly by adsorbing the radioelement batchwise and then placing the resin containing yttrium on a previously prepared resin bed.
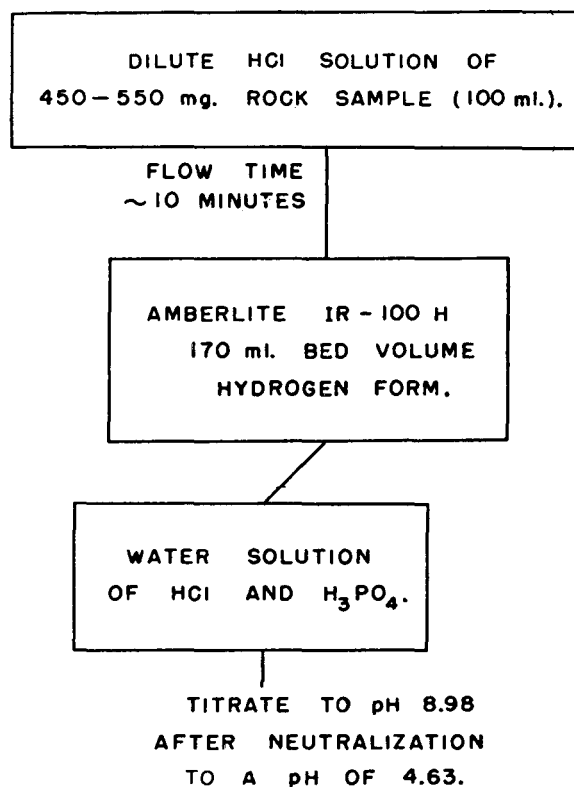

Figure 1. Flow Sheet for Determination of Phosphorus in Phosphate Rock

Constructed from data in (33)

An ion exchange step similar in principle was introduced for the determination of radium in urine (54). A radiochemical determination of rare earths and alkaline earths in 1500-ml. volumes of human urine (72) consists of coprecipitating rare earths and alkaline earths with calcium phosphate from an alkaline solution, separating the phosphoric acid by an ion exchange column, and subsequently separating the alkaline and rare earths from calcium and magnesium by precipitation. Recoveries of lanthanum and yttrium were quantitative; recoveries for barium and strontium exceeded 90%.

DETERMINATION OF TRACES OF COPPER IN MILK. The copper content of raw milk varies from 0.1 to 0.5 p.p.m. The usual analytical methods require a preliminary ashing step. Furthermore, only a small sample of milk can be used, so that the copper concentration is too small for accurate work. The method developed by Cranston and Thompson (17) eliminates preliminary ashing and allows a large (at least 100 ml.) sample to be taken. About 2 hours are required to isolate the copper in a form suitable for polarographic analysis.

COMPOSITION OF ATMOSPHERIC PRECIPITATION. Ions in rain water were collected and concentrated by placing an ion exchange

column before the collection reservoir. Prolonged contact of the rain was thereby prevented and the water could be discarded (*20*).

DETERMINATION OF PHOSPHORUS IN PHOSPHATE ROCK. By using an ion exchange column the analysis is shortened considerably and much less skill is required. The method consists of adsorbing all the cations on a hydrogen-saturated exchanger and liberating the stoichiometrically released hydrogen ions (*33*) (Figure 1). The experimental results when compared with National Bureau of Standards rock samples of known phosphorus pentoxide content had a mean error of less than 0.02%.
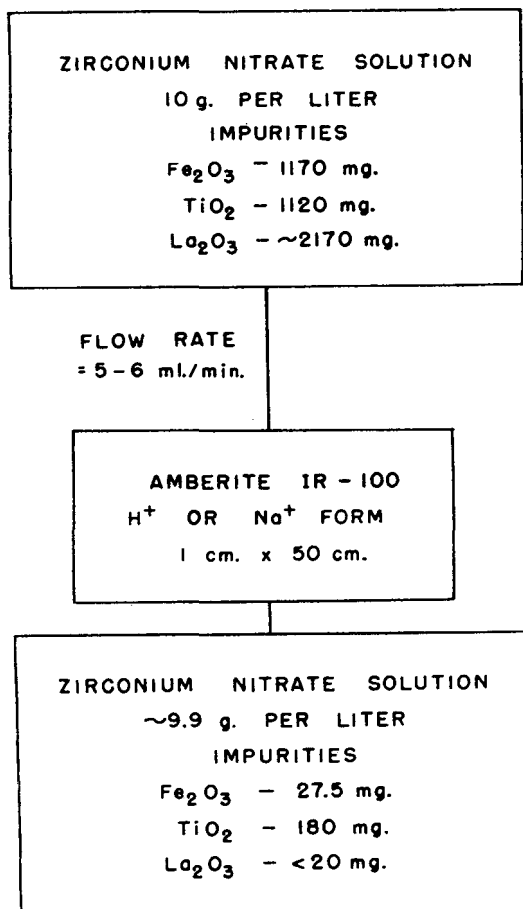
Figure 2. Flow Sheet for Purification of Colloidal Zirconium Nitrate

Constructed from data in (*3*)

DETERMINATION OF TOTAL BASE IN BLOOD. An elegant biological method for the determination of total base in blood serum using the same approach as above, was developed by Polis and Reinhold (*51*). Such a determination gives important information concerning electrolyte balances.

The fundamental reaction is given by the equation:

$$\text{Serum cations} + \text{H}^+\text{R}^- \longrightarrow \text{H}^+ + \text{serum anions}$$
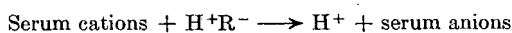
The bicarbonate anions are removed by aeration and the acid effluent is titrated with standard base to the pH of a control sample of serum which had been aerated but not treated with resin. A 0.2-ml. sample of serum is passed through 2 grams of the hydrogen form of a cation exchanger. The average of 126 determinations agreed exactly with the standard electrodialysis method. The ion exchange method takes about an hour to complete, as compared with 12 to 18 hours for the electrodialysis method.

ADDITIONAL COMMENTS. The above methods are capable of being used for removing many other interfering anions such as sulfate and chlorides, depending on the particular analysis. Many such separations together with titrations of released acids have been carried out by Samuelson (*56*). The methods are highly reproducible. The ion exchange columns can be used repeatedly for hundreds of determinations. The use of Dowex 50 or Amberlite IR-120 resins would probably improve the methods because of their greater capacity as well as physical and chemical stability. Anion resins have similar uses. Adams and Holmes (*1*), for example, passed a solution of calcium sulfate through the chloride form of an anion exchanger. The filtrate was found to contain the whole of the calcium as the chloride, but no sulfate ions were detectable.

Purification of Inorganic and Biological Substances, and Isolation, Identification, and Determination of Trace Impurities, New Isotopes, and Compounds. PREPARATION OF CARBONATE-FREE SODIUM HYDROXIDE (*18*). The adsorption affinite of bivalent carbonate is greater than that of monovalent hydroxide for strongly basic anion exchangers. This is the basis for a simple method for preparing the carbonate-free alkali needed for volumetric work and in the preparation of buffer solutions. Amberlite IRA-400 was the resin used.

Rather more than the required amount of alkali is made up, without special precautions, from washed sticks, and a column of the resin which may be initially in the form of its chloride is prepared in the usual way. The capacity of the air-dry resin is 1.4 me. per gram, and a 50-ml. tube two thirds full of the resin would be suitable for preparing 1 liter of 0.1 N sodium hydroxide. The alkali is passed through the resin until the effluent is chloride-free (if necessary), and the tube is then transferred to the neck of the stock bottle. When the rest of the alkali has passed through, the resin column is replaced by a soda lime guard tube, and the carbonate-free sodium hydroxide is ready for standardization.
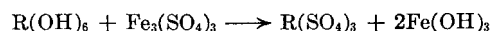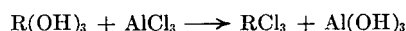
The column is regenerated by the passage of hydrochloric acid, which destroys the carbonate and replaces the hydroxide by chloride.

PURIFICATION AND PREPARATION OF COLLOIDAL SOLUTIONS. The capacity of a cation exchange column for colloidal substances is very low. Solutions of hydrolyzable elements such as zirconium nitrate are usually in the colloidal state, so that cationic impurities are easily removed, as shown in Figure 2 (*3*). The use of an anion exchanger in addition to the cation exchanger would probably enhance the purifications, as has been done with ferric oxide sols and aluminum oxide (*41*).

Many other acidic oxide sols, such as silica, tungstic, or molybdic acid sols, can be prepared and purified in one step in a matter of minutes by treatment with a cation exchanger. Classical purification procedures such as dialysis require hours to effect an equivalent purification. Metal silicates, metal tungstates, etc., when passed through the hydrogen form of a cation exchanger result in the formation of pure silicic acid as illustrated by the equation:

$$\text{Na}_2\text{SiO}_3 + 2\text{HR} \rightleftharpoons \text{H}_2\text{SiO}_3 + 2\text{NaR}$$
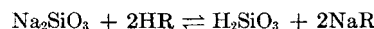
Typical reactions for preparation of sols by alkali-regenerated anion exchangers are illustrated by the following equations (*55*):

$$\text{R(OH)}_3 + \text{AlCl}_3 \longrightarrow \text{RCl}_3 + \text{Al(OH)}_3$$

$$\text{R(OH)}_6 + \text{Fe}_3(\text{SO}_4)_3 \longrightarrow \text{R(SO}_4)_3 + 2\text{Fe(OH)}_3$$

An informative discussion with experimental data on the preparation and purification of hydrous oxide sols by ion exchangers is provided by Ryznar (*55*).

PURIFICATION OF GLUCOSE-1-PHOSPHATE. A method for preparing glucose-1-phosphate reported by McCready and Hassid (*44*) provides a good illustration of the application of ion exchange for working with complex mixtures. In the Hanes method (*32*) for preparing glucose-1-phosphate from starch, the product is usually contaminated with difficultly removable dextrins. The

ion exchange method (44) eliminates the following steps from the Hanes procedure: concentration of large volumes of solution, precipitation of the ester with considerable quantities of alcohol, addition of trichloroacetic acid to precipitate the proteins, and enzymatic hydrolysis of the dextrin impurities.
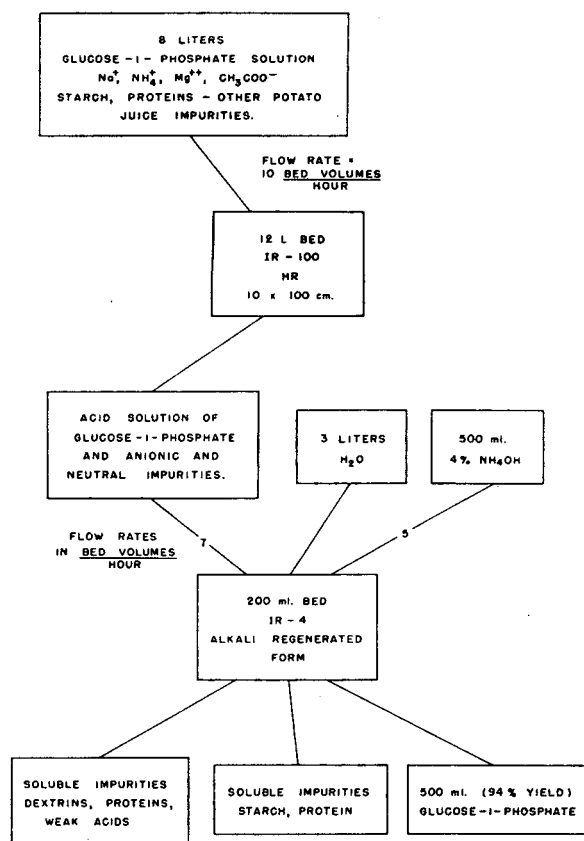

Figure 3. Flow Sheet for Preparation and Purification of Glucose-1-Phosphate

Constructed from data in (44)

A schematic outline of the ion exchange procedure is given in Figure 3. The yield of glucose-1-phosphate, isolated as the crystalline dipotassium salt, was 94%. The product was free of inorganic phosphorus, nitrogen, and dextrins. Considerable success was obtained in the purification of crude preparations of fructose-6-phosphate and fructose-1,6-diphosphate (44).

In more recent work, ion exchange has been used to help identify the sugar phosphates formed in photosynthesis (9) and to separate phosphate esters formed by the action of yeast enzymes on 6-phosphogluconate (13). In the latter studies pooled phosphate esters were hydrolyzed with alkaline phosphatase and the acids were adsorbed at pH 7 on an anion exchange resin, Amberlite-IRA-400. Elution with 0.1 N hydrochloric acid permitted the separation of gluconate and 2-ketogluconate. A 2-ketonic acid was observed in the eluates.

PURIFICATION OF A NEW ISOTOPE OF NEPTUNIUM. The properties of a new isotope of neptunium, Np[233], were described in a recent report (45). It was prepared from a uranium isotope by bombardment with 15-m.e.v. deuterons. The nuclear reaction involved is:

$$U^{233} (d, 2n) Np^{223}$$
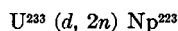
For positive identification, extreme purification of the Np[233] was required, particularly from uranium. Several combinations of separation procedures were employed. One involved the carrying of Np(IV) by a zirconium phosphate precipitate which left most of the U(VI) in solution. The Np[233] was subsequently carried by the lanthanum fluoride precipitate and then extracted from the lanthanum fluoride by extraction with diethyl ether. The final separation of trace amounts of Np from uranium was made by an ion exchange procedure.

A column containing the ion exchange resin, Dowex 50, is used to separate trace amounts of neptunium from uranium. Neptunium as Np(V) is adsorbed on a small amount of resin from a solution of low acid concentration and placed at the top of a column packed with resin and containing 13 M hydrochloric acid. The neptunium is eluted rapidly by passing 13 M hydrochloric acid through the column. The samples for counting are prepared by placing the elutriant dropwise directly on platinum counting plates.

Absorption and alpha-particle data for Np[233] were obtained from neptunium samples purified by the zirconium phosphate, ether extraction, and resin column procedures in that order.

The beautiful and often unique separations and purifications of carrier-free radioisotopes that are attained by ion exchange technique for practically every element in the periodic table are discussed by Tompkins (69) and others (57).

RARE EARTH ANALYSIS. The order with which substances are eluted from an ion exchange column is completely reproducible and is a function, as well, of the chemical properties of the substance in question. Furthermore, the relative distance between the elution peaks is constant and clear-cut under given operational conditions. As a result, new radioelements and isotopes have been discovered, as well as new isomers of complex biochemical compounds. For example, element 61, promethium, was positively identified from the fact that the elution peak of a hitherto unidentified rare earth element immediately preceded element 60 (46). Subsequently several milligrams of promethium were prepared by the ion exchange method. The bombardment of holmium, Ho[165], resulted in the production of three new thulium isotopes. Their chemical identity was made recently by their elution characteristics from a cation exchanger (78).

The chemical similarity of element 97, berkelium, with its anticipated homolog, terbium, atomic number 65, was confirmed by comparison of its elution characteristics and those of its transuranic neighbors from a cation exchanger with the homologous rare earth elements (68).

An excellent demonstration of the power of ion exchange methods as an analytical tool is provided by an investigation of the purity of the rare earth, erbium, carried out by Ketelle and Boyd (36). A 5-mg. sample of spectrographically pure erbium was bombarded by neutrons and subsequently processed on a cation exchanger. Preliminary studies on analysis and identification of neutron-activated elements in blood and animal organs have been made by Wolfe, Dunn, and Tobias (79). Ion exchange data on iron, copper, zinc, and cobalt are presented.

HETEROPOLY ACIDS AND SALTS. Weak acids formed from amphoteric metals easily condense to form anions containing several molecules of acid anhydrides, particularly tungsten, molybdenum, and vanadium oxides. The acid anhydrides condense with other acids, such as phosphoric or silicic acids, to form heteropoly acids as contrasted with the isopoly acids which contain only one type of acid anhydride. The heteropoly acids are complex anions with a second acid furnishing the central atom or central ion (21). The salts are formed generally from solutions of the components acidified to an appropriate pH.

An investigation using the hydrogen form of the high capacity sulfonic acid cation exchange resins was conducted for the purpose of preparing free heteropoly acids from their salts (4). Solutions or suspensions of the salts were passed through a resin column. The original heteropoly salt was reformed from the acid effluent. Most of the reformed salts were purer than the original samples. The solid acids were prepared by evaporation of their solutions. In two cases, new salts of the heteropoly anions were prepared from the acids as well as five new heteropoly acids. No reduction

of the easily reduced heteropoly acids by the cation exchanger was observed.

One example is of particular interest because an insoluble suspension was converted by the cation exchanger (4).

The insoluble salt of $(NH_4)_3H_6[Fe(MoO_4)_6].7-H_2O$ was pulverized and a suspension was passed through the hydrogen form of the cation exchanger (45 × 4 cm. diameter bed). The insoluble particles were completely transposed, during passage through the column, into the free acid and the even more insoluble ammonium form of the resin. The colorless effluent contained no ammonium ion, produced no Tyndall cone, and had a pH of 2.4 at a molarity of approximately 0.003. The addition of ammonium chloride solution produced an immediate precipitate, the crystal form and x-ray pattern of which were identical with those of the parent ammonium salt.

SEPARATIONS OF PURINE AND PYRIMIDINE BASES AND OF NUCLEOTIDES. In the cell nucleus are found the nucleoproteins, which are combinations of nucleic acids and proteins. The nucleic acids are a combination of four nucleotides and therefore constitute a tetranucleotide. A mononucleotide is a molecule containing phosphoric acid, a purine or pyrimidine base, and a carbohydrate or carbohydrate derivative. (The combination of only a sugar and base is called a nucleoside.)

The two purine bases in nucleic acids are adenine and guanine, and there are three pyrimidine bases: uracil, thymine, and cytosine. Cytosine, guanine, and adenine exist as cations in solution at a pH < 4 and hence may be separated from thymine and uracil and from each other by successive elution from a cation exchanger with simple reagents such as hydrochloric acid or sodium chloride (16).

By making use of the different dissociation constants of the bases and nucleotides, Cohn adsorbed mixtures at pH > 6 on an anion exchanger where all the substances are anionic and removed the components by lowering the pH in stepwise fashion (14). Hitherto unknown isomers of adenylic and geranylic acids were discovered by the ion exchange procedure (14) as well as isomeric cytidylic acids (15, 42). Full details concerning the concepts, techniques, and materials employed are given by Cohn (14).

Cohn suggests (14) that because most of the free bases, nucleosides, and nucleotides of nucleic acids can be separated from one another in one column run, the procedure can be used for the quantitative analysis of acid hydrolyzates of nucleic acids in place of the laborious and less accurate precipitation methods. Volkin and Carter (75) recently determined the mononucleotide of spleen ribonucleic acid by ion exchange analysis and found it to be 28% cytidylic acid, 24% adenylic acid, 14% uridylic acid, and 34% geranylic acid. Starting with 50 mg. of ribonucleic acid they recovered 96% (Figure 4).

Fractionation of protein hydrolyzates has been reported (48, 49). Results were the isolation and identification of glucosamine as a constituent of the hydrolysis product of egg albumin. Isolation of hexosamine by conventional procedures is difficult, and unsatisfactory for differentiating one hexosamine from another.

AMINO ACIDS, ALKALOIDS, AND ENZYMES. The applications of ion exchange to the purification and determination of substances such as amino acids, alkaloids, and enzymes are increasing at an ever-accelerating pace. All substances whose charges vary with pH are especially susceptible to treatment by ion exchangers. Methods for the separation, estimation, and preparation of amino acids in protein hydrolyzates were reported several years ago by Block (6) and Cannan (10). The latter used an anion exchanger to raise the pH of a protein hydrolyzate to 6 or 7, at which point the neutral amino acids are dipolar ions with zero net charge,
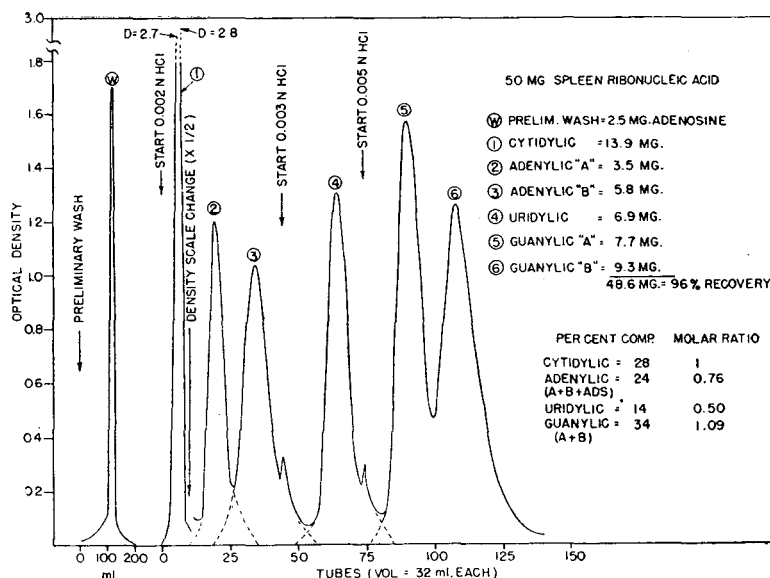

Figure 4. **Separation of Mononucleotides of Spleen Ribonucleic Acid by Anion Exchange (75)**

acidic amino acids are monoanions, and ammonia and basic amino acids (except histidine) are monocations. The chief anions are the dicarboxylic amino acids, aspartic and glutamic acids, and chloride. A large scale analysis of crystalline egg albumin by Cannan's procedure agreed with literature values. A more refined separation of all the amino acids was described by Partridge (50).

The liberation of β-alanine from its hydrochloride is ordinarily very tedious and troublesome. Anion resins are very effective (8) for this purpose, as illustrated by the equation:

$$NH_2CH_2CH_2COOH.HCl \xrightarrow[\text{resin}]{\text{Anion exchange}} NH_2CH_2CH_2COOH$$
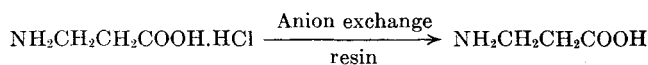
When an aqueous solution of pure β-alanine hydrochloride is passed through a bed of sodium carbonate–regenerated anion exchange resin, the effluent is substantially chloride-free. The yield of chloride-free β-alanine was 93% when pure β-alanine hydrochloride was used or 83 to 88% when crude material was employed (8).

The advances in amino acid preparation and separation by ion exchangers are proceeding so rapidly at this time that further examples would be rendered obsolete in a matter of months. Just recently Stein and Moore (67) worked out excellent separations by the use of either hydrochloric acid or sodium citrate solutions as eluants.

By taking advantage of differences in the isoelectric point it is possible to obtain excellent purification, and if need be, analyses of enzymes.

An example is furnished (43) by a successful ion exchange removal of pectin-methylesterase from pectin-polygalactinonase. Pectin-methylesterase catalyzes the hydrolysis of methyl ester groups and pectin-polygalactinonase catalyzes the hydrolysis of the 1,4 glycosidic linkages of polygalacturonic acids. Because pectin-polygalactinonase always occurs with pectin methylesterase, the results of enzymatic decomposition of the polygalactinonic acid components of pectinic acids are somewhat ambiguous. A cation exchanger was used to remove pectin-methylesterase completely from the other pectinases at a pH of 6.1 and below. Passage through the ion exchange columns took less than an hour.

The interaction of alkaloids with ion exchangers has been treated at length by Applezweig and Nachod (2). The alkaloids in aqueous solution form large cations by combining with hydrogen ions. The adsorbed cations have to be removed from the ex-

change groups by special techniques because the liberated alkaloid bases are sparingly soluble; hence a selective solvent extraction is utilized following an alkaline regenerant, or both steps may be combined by the use of an alkaline organic solvent (2).

An ion exchange analytical procedure for the determination of alkaloids either as salts or as present in plant extracts has been described (34). An ethyl alcohol solution of the alkaloid salt is treated with an anion exchanger. The liberated alkaloid base is titrated in the eluant with 0.1 N hydrochloric acid with a mixture of methyl red and methylene blue as indicator. Agreement with conventional determinations was obtained for solutions of cinchona extract, tincture of ipecacuanha, tincture of opium, and tincture of nux vomica.

Ion Exchangers as Precipitant for Ions. An anion exchanger can be saturated with a given anion for use as a precipitant for specific groups of ions. Gaddis (25), for example, saturated an anion exchanger with hydrogen sulfide and used it as a general precipitant for Group II cations. In similar fashion, strongly basic anion exchangers can be saturated with cyanide, fluoride, oxalate, etc., for precipitating numerous types of cations.

The same principle will probably find use in the future as a means of preparing and purifying organic compounds.

Physical Chemical Measurements. COMPOSITION AND STABILITY OF COMPLEX IONS. A simple, rapid, and effective procedure for the investigation of complex ions is obtained by an equilibrium ion exchange method, particularly when one of the components of the complex is present on the tracer level (58, 63, 65).

Consider the complex ion $(MA)^c$ where M is a cation, A an anion, and c, the net charge on the complex ion, is zero or negative. [The equations for such cases where the complex ion is itself adsorbed or where buffer ions form a complex with the metal have been developed in detail and applied to experimental data (60).] The dissociation constant, K_c, for the complex ion is given by the expression:

$$K_c = \frac{(A^b)^n}{(K_d^0/K_d) - 1}$$

in which b is the charge on the anion, and K_d^0 and K_d are the distribution coefficients of the tracer cation between the exchanger and solution phases, in the absence and presence, respectively, of the specific anion. The distribution coefficient is obtained from mass action expression as mentioned by Tompkins (69) and defined by the equation:

$$K_d = \frac{\% \text{ of tracer in exchanger}}{\% \text{ of tracer in solution}} \times \frac{\text{volume of solution}}{\text{mass of exchanger}} = \frac{\lambda v}{m}$$

in which λ represents the per cent ratio in the equation.

It is possible to measure K_d^0 directly or to derive it from values of K_d by graphical or analytical methods. A good procedure is to plot $1/K_d$ against $(A^b)^n$ and extrapolate the resulting straight line for proper n values to zero concentration of A, as indicated by the relation:

$$1/K_d = \frac{(A^b)^n}{K_d^0 K_c} + \frac{1}{K_d^0}$$

The equations take the simple forms given above because of the use of carrier-free tracers. This means that no corrections for the concentration of anion used to form the complex need be made, and that K_d^0 is independent of changes in tracer concentration. The method allows for the simultaneous determination of the dissociation constants of several metals, as well as effects of graded changes in temperature, dielectic constant, and ionic strength.

Experimentally, the procedures are illustrated by describing the measurement of the dissociation constant of calcium tartrate (60).

To a series of ten flasks containing 75 mg. of the sodium form of Dowex 50 were added 50 ml. of an isotonic veronal buffer at a pH of 7.27. The buffer, already containing tracer Ca[45], was chosen because it is a universal one and contains no anions which form insoluble precipitates with alkaline earths. The total volume of solution in each flask was brought to 100 ml. by addi-

tion of mixtures of isotonic sodium chloride and isotonic sodium tartrate. The volume of sodium tartrate was chosen so that the concentrations of tartrate ion in eight of the flasks varied from 0.009 M to 0.03 M, while two other flasks had no tartrate added. The mixtures were shaken for 3 hours, and a 4.0-ml. aliquot was withdrawn for Ca[45] assay. The blanks and reference solutions consisted of two additional flasks which contained 50 ml. of buffer plus 50 ml. of isotonic sodium chloride but no exchanger.

At a pH of 7.27 tartaric acid is completely dissociated to the divalent tartrate ion, Ta^{--}. A plot of $1/K_d$ versus the first power of the molar concentrate of Ta^{--} gave a straight line which extrapolated to a value of K_d^0 identical with that determined experimentally (Figure 5). The complex is of the 1:1 type— namely, (CaT)—having a dissociation constant of 1.65 ± 0.12 × 10^{-2}, and pK_c of 1.78 ± 0.03. This value is in good agreement with literature values, and probably much more reliable.

The potentialities of the ion exchange method for complex ion studies are yet to be exploited to the fullest in both the inorganic and biochemical fields. There is little doubt that studies in chelated compounds can be expedited to a tremendous extent by application of the ion exchange method.

Measurements by the ion exchange method on the complexes of the rare earths with citric acid at a pH of 2.0 to 3.5 have been reported (71) as well as the association of cerous ion with iodide, bromide, fluoride, sulfite, phosphate, and pyrophosphate ions (47).

ACTIVITIES AND ACTIVITY COEFFICIENTS. In 1931 Vanselow (74) suggested that ion exchanger can be used for the determination of activity coefficients in mixed electrolytes, and applied it to the barium-cadmium exchange reaction on bentonites. Recently the method has been used in conjunction with synthetic cation exchangers and radio tracers for similar measurements (58, 59). For the most accurate and reliable results it is best that a pH-independent cation exchanger be used, and that the exchanging cations have the same valence.
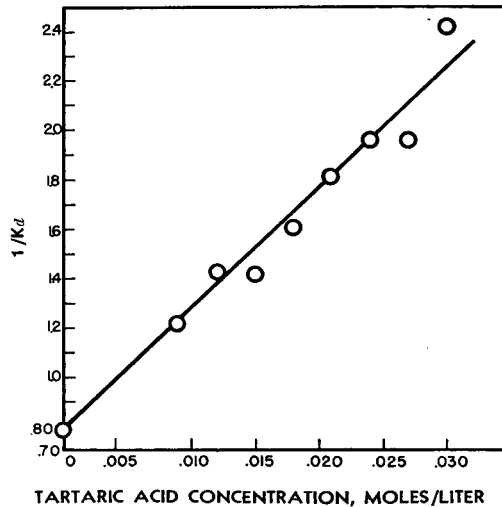
TARTARIC ACID CONCENTRATION, MOLES/LITER

Figure 5. Variation in $1/K_d$ for Adsorption of Calcium as Function of Tartaric Acid Concentration

At ionic strength of 0.16, $t = 25°$, and pH = 7.3. After Schubert and Lindenbaum (60)

The activity coefficients of tracer barium in alkaline earth nitrate solutions have been measured (59). The values obtained are in good agreement with theoretical considerations.

Membranes have been prepared from synthetic cation exchange materials for measuring metal ion activities (81) by taking Amberlite IR-1 and Amberlite IR-100 in the sodium form and mixing with a methyl methacrylate bonding resin. The mixture was molded into disks 2.5 cm. in diameter, in which the particles of the cation exchange material could be clearly discerned scattered throughout the transparent plastic matrix. The disk was

sealed to the base of a glass tube so that the two faces of the disk were exposed. The inside of the tube was filled with salt solution of one concentration and the tube was immersed in a beaker containing the same salt at a different concentration. Potential differences across the membrane were measured. The potentials found followed those computed for the sodium electrode in the Nernst equation. Much work needs to be done along this line.

More recently coherent cation and anion exchange membranes have been prepared (35). These new materials have unusually high specific electric conductivities and exchange capacities. They are available in the hydrogen or sodium form under the name Ionics permionic membrane (Ionics, Inc., 152 Sixth St., Cambridge 42, Mass.), cast in the form of disks, 9 cm. in diameter and 2 to 3 mm. thick.

EXCHANGE AND OXIDATION-REDUCTION REACTIONS. For theoretical and practical reasons it is of importance to ascertain whether exchange of ions among systems such as cobaltous and cobaltic hexamine complexes, ferrous and ferric ions, and the like occurs.

Consider the system of ferric and ferrocyanides investigated with radioiron, Fe^*. If the radioiron is present initially in ferrocyanide, the exchange reaction, if any, can be represented as:

$$Fe^* (CN)_6^{-4} + Fe (CN)_6^{-3} = Fe (CN)_6^{-4} + Fe^* (CN)_6^{-3}$$
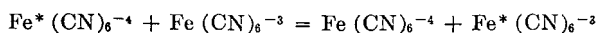
By a suitable separation of the ferricyanide from the ferrocyanide and measuring its concentration of radioiron and the chemical concentration of ferrocyanide, it is possible to calculate the extent of exchange.
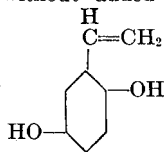
Several methods were used to study this exchange reaction. One of them employed an anion exchanger, Amberlite IR-4, because it was found that the carbonate form preferentially adsorbed ferricyanide ion from water solution (12). The enrichments were about 10 to 20 times greater than either diffusion separation or electrophoretic separation methods, and the reaction time was only 3 to 4 minutes.

The exchange mixture was allowed to trickle through a column 30 cm. long and 1 cm. in diameter filled with 20 to 30 mesh resin at a rate of about 25 ml. per min.$^{-1}$ Two 36-ml. portions of the eluant solution were collected and analyzed, and the per cent exchange was calculated. The resin had previously been tested to see if it would undergo or induce a decomposition or oxidation-reduction reaction with each of the original stock solutions in 30 minutes. No detectable chemical effect of the resin on the solutions could be noted under the exchange conditions. It was found (12) that complete exchange took place, in full agreement with the results of other methods.

Of potential value are the electron exchange polymers prepared and tested by Cassidy (11) and Updegraff and Cassidy (73). The basis of this work was the idea "that it should be possible to prepare polymeric substances capable of reversibly exchanging electrons with the molecules or ions of a contiguous phase."

The behavior is thus analogous to that of the cation exchange polymers, some of which are able to exchange protons for other cations in a contiguous phase. It can now be stated that two of the fundamental particles, the electron and the proton, can be reversibly exchanged between polymeric substances and contiguous phases in much the same manner" (69).

A new compound, vinylhydroquinone, was prepared, and subsequently polymerized without added catalyst. Vinylhydro-

quinone has the formula ... and the polymer may

have structures such as (73):

and
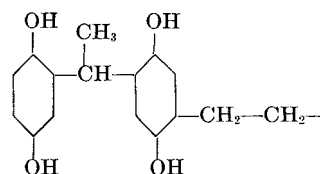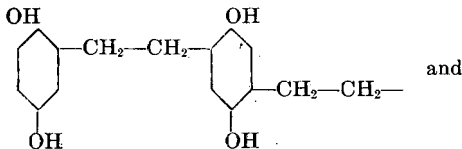
Oxidation of the polymer with bromine or ceric sulfate, for example, results in the development of a pink color, presumably caused by the accumulation of semiquinoid residues, the dismutation of which is hampered by the constraints of the polymer structures.

A number of important chemical and biochemical problems may be attacked by the use of these polymers, such as serving as models for certain biological systems, and as catalysts in organic and other oxidations, similar to coenzymes in action.

DETERMINATION OF MOLECULAR STRUCTURE AND STATE OF SUBSTANCES IN SOLUTION. Ion exchange reactions are a valuable addition to other physical methods for determining the configuration, chemical state, and functional groups of substances in solution. The potential range of utility can only be indicated by certain applied and hypothetical examples.

Table II. Affinity of Large Organic Ions for Phenolsulfonate Resin[a]

Ion	Equilibrium Constant	No. of Atoms in Contact with Surface (Not Counting Hydrogen)	Major Diam., A.
Ammonium	1.00	0	2.4
Tetramethylammonium	3.67	3	4.6
Tetraethylammonium	5.0	6	7.2
Trimethyl-n-amylammonium	8.24	7	9.5
Phenyldimethylethylammonium	25.2	9	8.5
Phenylbenzyldimethylammonium	44.4	14	11.2

[a] After Kressman and Kitchener (38).

Differentiation between cis and trans Stereoisomers. The ability to form complex ions with the alkaline earths is far greater with the cis than with the trans isomer (60)—for example, the reaction of calcium with maleic acid (the cis isomer) to form the complex ion (CaM) gives an association constant of 14.2 as compared with 3.0 for the corresponding fumaric acid complex. The measurements were made in isotonic sodium chloride buffered with veronal at a pH of 7.3.

Identification of Functional Groups. Small differences in the stereochemistry, nature of substituent groups, etc., present in organic compounds, result in relatively large and distinct differences in such properties as complex formation with cations, as, for example, calcium. Obviously, this provides a means for identifying the nature and configuration of functional groups in organic compounds, just as for cis, trans isomers. A systematic study of the effect of substitutents on the stability of calcium and strontium complex ions measured by ion exchange has been made (60). The addition of a single —OH group, for example, to tricarballylic acid to form citric acid results in a fourfold change in the stability of the calcium complex. The calcium complex of succinic acid, $COOH$—CH_2—CH_2—$COOH$, is one and a half times less stable than

$$COOH—CH_2—C—COOH, \text{ itaconic acid}$$
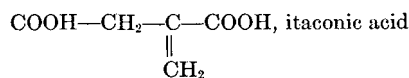
Size of Large Organic Ions and Rate of Uptake. In an interesting paper, Kressman and Kitchener (38) showed that the affinity of some large organic cations such as quaternary ammonium salts and the quinium ion for a cation exchanger increases with increasing size of the ion. This is in contrast to the simple inorganic cations and suggests that van der Waals forces contribute largely to the affinity, the Coulomb forces being less important.

Table III.   Variations in Adsorption of Tracer Cation and Radiocolloid by Organic Cation Exchanger as Expressed by Distribution Coefficient[a]

Solu-tion No.	Soln. Composition as Bulk Electrolyte		Vol. of Soln.	Change in Distribution Coefficient, K_d, as Related to Adsorption Process	
	Nature of bulk electrolyte	Concentration change	Mass of resin, v/m	Cation exchange adsorption, K_d	Radiocolloid adsorption, K_d
1	Noncomplexing salt	Increase	Constant	Decrease	Increase or nearly constant
2	Same as 1	Constant	Decrease	Constant	Decrease proportionately
3	Noncomplexing salt + noncomplexing acid	Constant salt, increasing acid	Constant	Decrease	Increase or nearly constant
4	Same as 3	Constant	Decrease	Constant	Decrease proportionately
5	Noncomplexing salt + noncomplexing acid + complexing agent[b]	Constant	Constant	Decrease	Decrease
6	Same as 5	Constant	Decrease	Constant	Constant

[a] After Schubert and Richter (62).
[b] Assumed that complex forming agent forms anionic complex with tracer.

This is supported by the greater affinity for the resin of the tri-methyl-n-amylammonium ion than of the isomeric tetraethyl-ammonium ion. No physical adsorption was observed.

Qualitatively, if van der Waals forces determine the affinity, the number of atoms in the ion which are able to come within a few Ångström units of the surface should be an index of the interaction strengths. This appears to be the case (Table II).

The saturation capacity in the resin was the same for all the ions, indicating that all the molecular pores within the resin are greater than 6 to 11 A.   The rates of exchange decrease with increasing ionic size.

The equilibrium adsorption of large molecules by an anion exchanger has been found to be a function of ion size (52). A series of aromatic sulfonic acid dyes of different molecular dimensions and sulfuric acid itself was adsorbed on an anion exchanger, De-Acidite B. The rate of uptake was found to increase with decreasing molecular size, while the per cent uptake at equilibrium varied from 0.03 to 100% as the molecular size decreased from 30 to 5 A. with sulfuric acid. These results are consistent with a picture of the resin as an amorphous body containing a network of pores which may vary in size from 10 to 20 A. in diameter, through which all anions must diffuse before adsorption on the exchange sites occurs (52).

The Dow Chemical Company has made available cation and anion resins with different degrees of cross linkages. As a result it becomes possible to effect separations of ions of different sizes, since lower cross linkage permits exchange with larger ions.

Determination of Charge, Valence, and Colloidal States. Data given above have shown how the adsorption of many dipolar ions varies with the pH. This, obviously, affords a means of placing the isoelectric point. In addition, the absence or presence of adsorption may indicate a cationic, anionic, or neutral molecule. For example, an unknown nutritive factor in yeast extract was found to be adsorbed by an anion exchanger, apparently behaving as an acid in so far as uptake and elution were concerned (80). This fact plus other chemical and biochemical properties led to the implication of orotic acid (4-carboxyuracil) as the unknown factor. If adsorbed, the substance may also be a colloid, in which case the nature of the variation of the distribution coefficient with change in solution composition or ratio of solution volume to mass of resin will differentiate between ionic and colloidal uptake (58). The characteristics of colloidal uptake by cation exchangers have been discussed at length (62). The behavior of the distribution coefficient, K_d, in ionic and colloidal systems as a function of ionic strength, complex formation, acidity, etc., is summarized in Table III.

If a substance is ionic we can also determine its valence. This follows from the fact that the valence which an adsorbed ion possesses in the exchanger will be its maximum valence up to and including the tetravalent state (58), and that the equivalent capacity of a resin at a given pH is constant. Thus, in a solution at a pH of 2 to 3, thorium ion has a net charge of about 2 to 3. Yet

the molar capacity of the resin for thorium is one fourth that for sodium, one half that for barium, and three fourths that of lanthanum. It appears that the cations undergo a change of hydration when they pass from the solution to the exchanger phase (37). When cation resins containing both phenolic and sulfonic acids are used, the increase in uptake of simple radio-elements as a function of pH is in the order: trivalent > divalent > monovalent elements.

Methods for determining the state of radioelements in solution have been discussed (58), with suggestions for ascertaining basicity, complex formation, etc. Obviously, the types of properties one can infer from ion exchange reactions are so great that the most effective use depends on the ingenuity, initiative, and judgment of the investigator.

CONCLUDING REMARKS

The use of anion exchangers in analytical chemistry will undoubtedly be accelerated because of the availability of remarkably stable strong basic resins such as Dowex 2-A. Under certain conditions the anion exchanger operates satisfactorily at temperatures up to 125° C., and is stable to organic solvents, acids, and bases (76). Some potential uses can be anticipated from Table IV, in which the equilibrium constants for various anions relative to chloride ion are listed.

Ion exchangers may be expected to function as buffers. This property was utilized by Sperber (66), who placed an anion exchanger in the middle chamber of a three-chamber electrodialysis unit as a buffer in the group separation of the basic, neutral, and acidic amino acids in protein hydrolyzates.

Because chelate structures are highly specific in that they react with only a single species of cation under proper conditions, Gregor (27) prepared a series of exchange resins containing potential chelating groups. One of these chelate resins, a quadridentate diamino, dicarboxyl type, was prepared and seen to form chelate complexes with transition metals. Various separations were effected. Such special resins can be expected to find many novel uses, particularly in unusual analytical problems.

Table IV.   Equilibrium Constants Relative to Chloride on Strongly Basic Anion Exchanger, Dowex 2-A[a]

Anion	Equilibrium Constant	Anion	Equilibrium Constant
Phenate	8.7	OH^-	0.65
I^-	7.3	HCO_3^-	0.53
NO_3^-	3.3	$H_2PO_4^-$	0.34
SO_4^{--}	1.8	Formate	0.22
CN^-	1.3	Acetate	0.18
BrO_3^-	1.01	F^-	0.13
Cl^-	1.0		

[a] From data presented by Wheaton and Bauman (76).

The preparation of optically active ion exchangers would be of special interest. Many applications to organic and biochemical analysis are still lying dormant. Whitehorn (77), for example, tested the uptake of more than fifty organic compounds including amino acids, adrenaline, amines, dyes, etc., and found that many were completely adsorbed in aqueous and nonaqueous solvents. In the near future ion exchange will probably be utilized more and more for the separation and preparation of amino acids, steroids, plant pigments, alkaloids, vitamins, and, of course, pure inorganic chemicals.

An important technique for imparting ion exchange properties to compounds such as hydrocarbons and steroids, for example, is to incorporate acidic or basic groups in the molecule. This approach will surely lead to new and effective means for separating hitherto complex mixtures by ion exchange.

The stoichiometric release of hydrogen ions by the organic cation exchangers suggests a simple rapid means of preparing standard acids. For example, passage of an accurately weighed sample of sodium chloride or sodium sulfate through a bed of acid-regenerated resin will result in an effluent containing equivalent amounts of hydrochloric or sulfuric acid of known normality. The same principle can probably be applied with the strongly basic resins to prepare standard bases.

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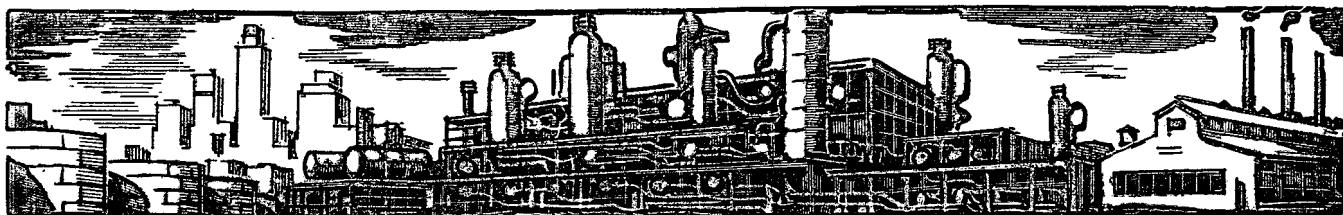
Theory and Practice of Analytical Distillation

ARTHUR ROSE

The Pennsylvania State College, State College, Pa.

A small amount of theory and a great deal of empirical practice form the basis for the very considerable achievements of analytical distillation to date. It is probable that the practical limits are being approached unless there are additional theoretical contributions. These will probably be based on an extension of the Rayleigh equation, with numerical solutions obtained by means of automatic high-speed computing machines. An interim procedure is given for estimating theoretical plates, reflux ratio, charge size, column size, and time required in analytical distillation.

ANALYTICAL distillation is a field in which theory has lagged far behind practice. Applications of distillation in analysis are legion, and include the classical and very difficult work on analysis of petroleum and its products (*3*, *6*).

An equally important but different kind of example is the detection, estimation, and removal of impurities in nearly pure materials (*3*). A host of other examples are cited in recent reviews (*15*, *16*), and range from Engler and A.S.T.M. distillations and microdistillations to superfractionation of barrel quantities. The recent trend has been the combination of distillation with other procedures, including particularly adsorption, optical methods, and specialized chemical analysis. This suggests that the practical limits of fractional distillation have been reached.

Almost all this work has been done with packed laboratory fractionating columns, a great variety of which have been described (*4*).

The original conception of an insulated packed column with a total condenser, and with closely controlled division of the condensate into reflux and product streams, was undoubtedly guided by theory, but most of the ideas were inherent in much older industrial practice and theory. The subsequent development and use of analytical columns have been largely empirical.

Columns have been made taller, and reflux ratios have been raised. Theory has done little more than predict separation for the idealized limiting case of total reflux, confirm the idea that a law of diminishing returns limits the benefits of increased height and reflux ratio, and barely suggest that too great an extension of some factors may give poorer results rather than improvement. Improvement in height of equivalent theoretical plate (H.E.T.P.), throughput, and holdup characteristics of packings has been by trial and error and not through guidance by theory in terms of surface area, free space, and other dimensional and geometric features. It is not yet certain whether small holdup packings are entirely beneficial (*22*). The empirical suggestion (*13*) of an enforced temperature gradient with nonadiabatic column operation has not been analyzed theoretically. The careful analysis of vacuum fractionation (*5*, *25*) has just begun.

The theory that is regularly used in analytical distillation is probably limited to recalling that compounds with closely similar volatilities will be difficult to separate by distillation, and using the Fenske equation (*4*), or its equivalent, to estimate the number of theoretical plates for a particular separation as an aid in choosing the column to be used. There has been some use of the principle that theoretical plates and reflux ratio should have about the same numerical value (*18*).

There has been no use of present theory to determine whether the good practical results already obtained on complicated or difficultly separable mixtures could have been obtained more easily or quickly by some other choice of the apparatus and procedure. In cases where distillation has been discarded or has failed as a method of separation and analysis, there has been no real assurance that some not so obvious choice of apparatus and procedure might have given the desired result.

It is not probable that further empirical work will lead regularly to answers to such questions or to extensive further improvement in over-all results. This is a challenge to the theoretical approach, and at present it seems that some progress along these lines is being made.

For this reason, the remainder of this paper deals with the evaluation and status of batch distillation theory.

ANALYTICAL DISTILLATION AS BATCH DISTILLATION

All analytical distillations are batch distillations, and in these the results are best expressed as a graph of the distillate compositions at any time versus quantity (or per cent) of charge distilled up to that time. The theoretical approach has been to attempt to determine how the shape of such curves is affected by the characteristics of the mixture, the nature of the apparatus, and the operating conditions. The important variables are the relative volatility and composition of the mixture, the theoretical plates in the apparatus, the reflux ratio, the holdup-charge ratio, and indirectly the throughput. The relations are so extremely complex that the mathematical problems have been insuperable, unless extensive simplifying assumptions were made (*2*, *17*).

Most batch distillations involve multiple components, but the multicomponent theoretical case has barely been touched. Young's book (*26*) contains some calculated curves for multicomponent mixtures, but there was no subsequent work until Bowman's (*1*) very recent development of an entirely new scheme for calculating such curves. This is still restricted by the simplifying assumptions of negligible holdup, total reflux, and equal molal flow rates, and there has not been time for experimental confirmation. Even in the simplified form, the calculations are lengthy and generalization is difficult.

An entirely new and as yet undeveloped approach to the calculation of multicomponent batch distillation curves is the use of stepwise plate-by-plate procedures with punched card devices and other automatic computers in the actual numerical calculations (*21*). These do not require extensive simplifying assumptions, and numerical results are obtained easily in quantity, and with freedom from human errors.

The first careful experimental study of ternary batch distillation is still incomplete (*10*). It shows the same improved separation with increasing holdup-charge ratio as did similar binary experiments.

There are two good reasons to continue to attempt to predict the batch distillation behavior of multicomponent systems in terms of their component binaries: the relative simplicity of the

procedure for the binary cases (20, 24), and the considerable number of instances in which experiments have confirmed predictions.

BATCH DISTILLATION OF BINARY MIXTURES

The basis for batch distillation predictions for binary systems is the well known Rayleigh equation (14). In its differential form, it is merely a material balance on the more volatile component before and after removal of a small portion of distillate. Thus, if holdup is negligible,

$$Sx_S = (S - dS)(x_S - dx_S) + x_D dS$$

Upon integration this becomes, in its general form,

$$\log \frac{S_1}{S_2} = \int_{x_{S2}}^{x_{S1}} \frac{dx_S}{x_D - x_S}$$

This provides a way of calculating the quantity remaining undistilled, S_2 (and thus the per cent of charge distilled), corresponding to any desired still and distillate compositions, x_{S2} and x_{D2}, using initial or other known quantities, S_1 and x_{S1}.

The limitations of this equation arise from inability to relate x_D and x_S correctly. The equation is satisfactory for predicting results of simple distillations, because for these cases the $x_D x_S$ relation is merely the usual yx vapor-liquid equilibrium relation. Similarly, the Rayleigh equation may be applied to multicomponent mixtures for cases of simple distillation. The same application may be made for distillation through a column, if total reflux is assumed, so that

$$\frac{x_D}{1 - x_D} = \alpha^n \frac{x_S}{1 - x_S}$$

This gives limiting results that are sometimes far from being achieved, even with what are considered high reflux ratios. The equation has also been found satisfactory for distillation at finite reflux through a column in certain cases where holdup is but a few per cent of initial charge (24), and the $x_D x_S$ relation may be predicted by the McCabe-Thiele procedure (9), the Smoker equation (23), or some equivalent procedure. The reasons for failure of the predictions in other similar cases of small percentage holdup are not yet clear.

A modified and much more complicated form of the Rayleigh equation may be derived for cases of appreciable holdup (17). Unfortunately, the relation between x_D and x_S for such cases cannot be predicted without solution of this modified Rayleigh equation for the previous part of the curve (2). As a result, predictions have not been possible with the integrated forms of the modified equation.

It has, however, been possible to make some progress by numerical solution of unintegrated forms of basic material balance equations for distillation with appreciable holdup. The first successful attempt along this line was a stepwise plate-to-plate calculation of the compositions on each plate in a column at the end of each of a succession of short intervals during the distillation (19). Such calculations were very laborious, but have been shown to be at least in general agreement with experiment. Predictions of batch distillation curves with appreciable holdup have also been made by using a differential analyzer to work out the solution to the unintegrated modified Rayleigh equation (12). This approach seems limited because even the largest analyzers are limited to predictions for seven-plate columns, and must use an approximate vapor-liquid equilibrium relation.

The most hopeful development, relative to predictions of batch distillation results when holdup is appreciable, is the discovery that the stepwise plate-to-plate calculations may be performed on punched card devices (21). The significance of this is better appreciated when it is recognized that the original set of stepwise calculations required approximately 1,200,000 separate arithmetic operations performed as a labor of love of science, comprising approximately 3000 man-hours of toil. The punched

card computer can do the same calculations in about 80 machine-hours at an estimated cost of $500, or about one fifth the cost of the hand calculations.

EFFECT OF HOLDUP

In the interim, while more such calculations are made and compared with experiment, it seems reasonable to make the following statements regarding the effect of holdup in analytical distillations:

Under the normal conditions of low per cent holdup (compared with initial charge) that are commonly used in analytical distillation, the effect of the holdup will either be insignificant, or will cause somewhat sharper separation than predicted for negligible holdup (19, 22).

Under extreme conditions such as very great holdup, very low reflux ratio, and/or very small proportion of a component, results may be very much worse or very much better than predicted on assumption of negligible holdup.

PROCEDURE FOR CHOICE OF COLUMN AND OPERATING PROCEDURE

The following general procedure is suggested for an analyst who is confronted with a new and difficult problem in analytical distillation.

1. Estimate relative volatility
2. Estimate number of theoretical plates
3. Estimate reflux ratio
4. Decide on quantity to be distilled
5. Choose column diameter, packing, and throughput on the basis that holdup must be less than 5% of charge
6. Note time required and column height

The procedure necessarily involves considerable trial and error, particularly for items 4, 5, and 6. The first few trials may well result in impossible or impractical ranges of values for the last items. The relative positions of 4, 5, and 6 are rather arbitrary and might well be changed, if, for instance, minimum time for completion is of major importance.

Relative Volatility. It is most important to have reasonably good information on relative volatility. For closely similar liquids, the relative volatility may be estimated from the boiling points (18).

$$\log \alpha = \frac{H_B - H_A}{2.3 \, (T_B + T_A)}$$

For all other mixtures, any simple practical procedure requires choice of an average mean or effective relative volatility. Such an estimate of relative volatility requires comparison of actual vapor-liquid equilibrium curves. The simplest procedure is to have available a chart with xy curves for various relative volatilities, and to sketch in on this master chart the curve for the mixture under consideration.

A better procedure is to step off on the vapor-liquid diagram the number of theoretical plates, n, at total reflux between 3.6 and 96.4%, and use the value of α that gives the same number of plates in the Fenske equation. This may be expressed by the equation

$$\log \bar{\alpha} = \frac{2 \log 26.8}{n} = \frac{2.86}{n}$$

Thus, if ten plates can be stepped off between 0.964 and 0.036 on the irregular vapor-liquid equilibrium curve

$$\log \bar{\alpha} = 0.286$$
$$\bar{\alpha} = 1.92$$

If 20 plates are stepped off

$$\log \bar{\alpha} = 0.143$$
$$\bar{\alpha} = 1.37$$

An extremely irregular vapor-liquid equilibrium curve may require use of a more complicated procedure for estimation of plates and reflux ratio than is indicated in the following section.

A very great deal of good work is being done on vapor-liquid equilibrium. It behooves analytical chemists concerned with liquid mixtures to maintain close contact with sources of data on azeotropes and vapor-liquid equilibria, methods of correlation, and methods of prediction. The subject is too large for discussion here beyond mention of the information in the latest edition of the "Chemical Engineering Handbook" (11), the publications by Horsley (7) and Lecat (8), and the host of journal articles giving data on specific mixtures.

Choice of Plates and Reflux. The simplest procedure for choice of n and R is by means of the approximate empirical equation (18)

$$n = R = \frac{2.85}{\log_{10}\alpha} = \frac{T_B + T_A}{3(T_B - T_A)} = \bar{n}$$

This approximation results, in the ideal case of a binary mixture with equimolal composition, in a so-called "standard separation" (18) in which the first 40% distilled contains 95 to 98% of the more volatile component. This is a sufficiently sharp separation for analytical distillations.

It is not necessary that n and R have exactly the values computed, for decrease in one may be compensated by increase in the other, to a limited extent (18).

If desired, as in the case of an uncertainty regarding the choice of alpha, a Rayleigh curve may be calculated using the chosen n and R and the actual vapor-liquid equilibrium curve (24). If agreement with the standard separation is not so close as desired, another choice of alpha should be made, and new values of n and R obtained.

Choice of Quantity to Be Distilled. The choice of quantity to be distilled is affected by many factors, some beyond the control of the analyst. If availability of sample or apparatus or need for fractions from the distillation is not a controlling factor, it is suggested that 0.5 liter of sample be considered as a first trial choice of charge to be distilled. Those with semimicro or micro apparatus and experience will tend to a much smaller figure. Whatever is chosen should be considered as a first trial only, subject to revision after choice of packing, column diameter, and throughput.

Choice of Packing and Column Size. The final step in the procedure is the choice of a packing and the column diameter and throughput with which this packing is to be used. This determines column height, holdup, and time for carrying out the distillation, excluding initial equilibration time. The end result must be a column height that is available or can be achieved, a holdup of 5% or less compared with initial charge, and a reasonable time for the distillation.

EXAMPLES OF USE OF PROCEDURE

Suppose that $n = 25$; then R should also be 25. With $C = 500$ ml., H_T must be 25 ml. or less.

The time for distillation (in minutes) will be $t = \dfrac{500 \times R}{r}$, where r is the throughput in milliliters per minute.

For a column 0.5 inch (1.25 cm.) in diameter, a good median of available data gives an H.E.T.P. of 1.6 cm., a throughput of 5 ml. per minute, and a holdup of 0.1 ml. per plate. In this case $t = \dfrac{500 \times 25}{5} = 2500$ minutes $= 40+$ hours; column height $= 25 \times 1.6 = 40$ cm. or about 18 inches; and $H_T = 25 \times 0.1 = 2.5$ ml. or about 0.5%.

For a column 1 inch (2.5 cm.) in diameter, median values of the data give an H.E.T.P. of 2.5 cm., a throughput of 20 ml. per minute, and a holdup of 1.2 ml. per plate. t is now $\dfrac{500 \times 25}{20} = 625$ minutes $\cong 10.5$ hours. Column height $= 25 \times 2.5 = 62.5$ cm. or about 25 inches, while holdup, H_T, is $25 \times 1.2 = 30$ ml. or about 6%. This latter is higher than the limit of 5% previously mentioned.

For a column 2 inches (5 cm.) in diameter, median values give an H.E.T.P. of 7.5 cm., a throughput of 200 ml. per minute, and a holdup of 25 ml. per plate. In this case $t = \dfrac{500 \times 25}{200} = 62.5$ minutes $\cong 1$ hour. Column height $= 7.5 \times 25 = 188$ cm. or

about 75 inches. Holdup, H_T, is $25 \times 25 = 625$ ml. Therefore, the charge is not large enough for the column under study.

In this case the proper choice is obviously the 0.5-inch column. However, serious thought would naturally be given to the possibility of increasing the charge somewhat and using the 1-inch column to achieve the shorter distillation time. The data above are median values intended only as an example and, therefore, do not represent any particular type or kind of packing or column.

The attempts to use this procedure will have varying results. There will obviously be errors due to variation of H.E.T.P., throughput, and holdup with the materials to be distilled. In some cases the procedure will break down for lack of basic data. Other cases may produce the conclusion that processes other than distillation should or must be examined because the separations involved are inherently very difficult or impossible by distillation. In many cases significant results are obtained.

NOMENCLATURE

C = charge to still in batch distillation, ml.
H_A, H_B = heat of vaporization
H_T = total holdup, ml.
n = number of theoretical plates in column and still
$\bar{n}$ = number of theoretical plates that can be stepped off between 3.6% and 96.4% on vapor-liquid equilibrium diagram
R = reflux ratio, liquid rate–distillate rate
r = throughput, ml. per minute
S = quantity of material in still at any time during batch distillation, moles
T_A, T_B = absolute temperature
t = time required to complete distillation, min.
x = mole fraction of more volatile component in liquid
x_D = mole fraction of more volatile component in distillate
x_S = mole fraction of more volatile component in still
y = mole fraction of more volatile component in vapor
α = relative volatility
$\bar{\alpha}$ = mean or average relative volatility

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Separation by Precipitation from Homogeneous Solution

HOBART H. WILLARD

University of Michigan, Ann Arbor, Mich.

When a precipitating ion is added to a solution in which a substance is to be precipitated, the local concentration of the former at the point where the solutions mix often causes coprecipitation of other ions which may remain adsorbed when the solution subsequently becomes uniform. This error is avoided by adding a substance which does not contain the desired precipitating ion as such, so that no immediate precipitation results, and the solution is homogeneous. Heat is then applied and the proper ion is formed by hydrolysis in the solution. If neutralization of an acid solution is required, the hydrolysis of urea to form carbon dioxide and ammonia is a convenient process. If a weak base is thus precipitated in the presence of the proper anion, a dense basic salt is formed. With aluminum, succinate is best; with iron, formate. Errors due to adsorption are therefore greatly decreased and far more effective separations are accomplished. Data for such separations are presented. Oxalate ion is readily formed by the hydrolysis of methyl oxalate, phosphate from triethyl phosphate, sulfate from sulfamic acid or ethyl sulfate. In all cases the crystals are larger and the volume of the precipitate much smaller than is usual, so that filtration and washing are greatly facilitated.

A PRECIPITATION process is usually conducted by adding a suitable reagent to a solution of the substance to be precipitated. Even though the reagent is dilute and is added very slowly with constant stirring, there is an inevitable local concentration of reagent in the region where the two solutions mix. In some cases this has no deleterious effect, but in other cases this local concentration causes more or less of another substance to be precipitated. When the solution subsequently becomes homogeneous on continued stirring, this second substance may not dissolve but may remain adsorbed on the main precipitate. If this local concentration of reagent had not existed, the second substance would not have been precipitated, and if it were adsorbed at all the extent of contamination would have been much less.

This source of error could be avoided if the solution were homogeneous at all times. Such a condition exists when the reagent added does not contain the precipitating ion, but can form this ion, as, for example, by slow hydrolysis, produced by raising the temperature of the solution. A hydroxide or basic salt has been precipitated by various investigators by increasing the pH of the solution without the addition of ammonia. Chancel (1) boiled a solution containing sodium thiosulfate; sulfur dioxide was thus removed. Stock (13) added potassium iodide and iodate; Schirm (12), sodium nitrite and urea; Wynkoop (21), sodium nitrite; Rây and Chattopadhya (11), hexamethylenetetramine; Moser and Singer (9), ammonium nitrite. Moser and Irányi (8) investigated the equilibria resulting from boiling various mixtures of halides and halates and found that for hydrochloric acid and potassium bromate a final concentration of 0.048 N acid resulted, which was suitable for the separation of titanium from aluminum. Moser (7) seems to have been the first to recognize the advantages of this technique, not only in controlling pH but also in yielding denser precipitates especially in an acid solution. He also pointed out the advantage of the slow precipitation which occurred in certain cases. However, he failed to recognize the importance of having present the proper anion to form a dense basic salt. Many of the earlier reactions just mentioned were too rapid to afford the maximum advantages of which this technique is capable. The hydrolysis of urea has, in general, been found the most satisfactory reaction.

In a gradual neutralization process the precipitate is usually a basic salt, inasmuch as its formation begins at a relatively low pH. This is an advantage because this lower pH affords a better separation from other ions. But an even more important property of these basic salts is that when they contain certain anions they are much denser than when other anions are present. This minimizes the error due to adsorption, which is one of the main sources of error in this type of precipitate. In some cases the precipitate appears almost crystalline. The small bulk of such precipitates greatly facilitates their filtration and washing. When one considers the great advantages of this type of precipation—viz., homogeneity with respect to pH, small volume of the precipitate, greatly reduced adsorption, and slow precipitation—it is obvious that the results thus obtained in separations must be far superior to those resulting from the usual procedure.

Table I. Separation of Aluminum from Other Elements

(0.1 gram of aluminum in each experiment)

Other Metal Present, Gram	Metal in Ppt., Mg.			
	1 Pptn. by NH₄OH	1 Pptn. by urea-succinate	2 Pptns. by NH₄OH	2 Pptns. by urea-succinate
Mn 1.0	1.7	0.2	0.02	0
Cu 1.0		0.05		0
Cu 0.05	21.1	..	7.7	..
Ni 1.0	..	1.0	..	0.2
Ni 0.1	..	0.3	..	0
Ni 0.05	0.6	..	0	..
Co 1.0	..	1.2	..	0.1
Co 0.1	..	0.4	..	0
Co 0.05	4.1	..	1.2	..
Zn 1.0	..	1.4	..	0.5
Zn 0.1	..	0.8	..	..
Zn 0.05	21.6	..	10.8	..

The proper anion to give a dense precipitate will vary with different cations. Figure 1 of (20) illustrates this. With aluminum, sulfate, selenate, and succinate are excellent, whereas chloride, nitrate, acetate, and most others are ineffective. For iron and thorium, formate is best; for titanium and gallium, sulfate is excellent. There is some advantage in the use of an organic anion, because the precipitate is easily ignited to the oxide and because the salt formed from the weak acid serves to buffer the solution and cause a more gradual increase in pH.

The hydrolysis of urea has proved a most satisfactory method for increasing the pH of a solution. The basic properties of urea itself are negligible, but a hot solution undergoes hydrolysis to form carbon dioxide and ammonia. At room temperature this hydrolysis is extremely slow, but at 90° to 100° C. it is rapid enough to be useful. The carbon dioxide evolved serves to stir the solution and prevent bumping. The maximum pH which can be attained by this means will depend upon the concentration of ammonium salt in the solution, because there will ultimately be an equilibrium between the ammonia formed by hydrolysis and that lost by volatilization. In the absence of ammonium salts the maximum pH is about 9.3.

Other effective methods of increasing pH are hydrolysis of acid amides such as acetamide, which forms ammonium acetate, and hydrolysis of trichloroacetate salts, which form chloroform and carbonate. Quill and co-workers at Michigan State College (10) have reported excellent results obtained in the separation of lanthanum and praseodymium by the hydrolysis of their trichloroacetates, to form the carbonates; this method of concentrating the praseodymium was far more rapid than the usual recrystallization methods.

The efficiency of precipitation from homogeneous solution is well demonstrated by the separation of aluminum from other ions. Because aluminum is amphoteric, a careful control of pH is more necessary than in the case of iron, for example, where an excess of ammonia may result in a better separation from those ions that form ammonia complexes. Table I shows results obtained in the separation of aluminum from manganese, copper, nickel, cobalt, zinc, and cadmium by the urea-succinate method (19) and by the usual ammonia method. The latter results are from the work of Lundell and others at the National Bureau of Standards and may be considered representative of the best results obtainable by this method. These workers separated aluminum from a maximum of 50 mg. of the other element, whereas in the urea method in most cases twenty times as much was present. Although there is a slight improvement in the separation from manganese and nickel, there is a very great difference in the case of copper, cobalt, and zinc. In fact, the separation of aluminum from zinc by the ammonia method is impossible, whereas the urea method gave fairly good results.

The separation of gallium at pH 4 to 6 as basic sulfate by a similar method gave excellent results (14). In the separation of titanium as basic sulfate at a pH of 1.5 to 2, the hydrolysis of acetamide seemed preferable to that of urea. The separation of titanium from aluminum was less satisfactory than might be expected in view of the considerable difference in the pH values at which they precipitate. The character of the precipitate was greatly affected by the presence of aluminum. The presence of other cations did not have this effect.

The precipitation of stannic tin as basic sulfate at pH 1.5 by the hydrolysis of urea resulted in a denser precipitate, but, unlike the others, it showed such pronounced adsorptive properties that it was of no value as a separation method.

The same anion is not equally effective with different metals. Sulfate is sometimes undesirable, even though it usually gives a dense basic salt. The presence of anions which do not form dense precipitates does not interfere—for example, large amounts of chloride may be present without affecting the physical properties of a basic sulfate or succinate. The proportion of sulfate in a precipitate of basic aluminum sulfate is to some extent a function of the concentration of sulfate ion, but this soon reaches a constant value. However, the proportion of sulfate decreases rapidly as the pH increases, and at the same time the precipitate becomes more flocculent until eventually it becomes practically a hydroxide in composition and appearance (20). The basic succinate of aluminum, for example, is best precipitated at a pH between 4 and 5.

It may be asked: Could not the same result be attained by

adding very dilute ammonia slowly? The answer is "Yes," but to get the same results that can be secured by urea in an hour or two required the addition of 0.002 N ammonia over a period of several days.

The absence of an x-ray diffraction pattern indicates that even the dense precipitates are not crystalline. Under high magnification the particles appear more spherical than of any other shape.

Table II. Separation of Iron from 1 Gram of Other Elements by Precipitation as Basic Formate with Urea

Fe Taken, Gram	Element Added, 1 Gram	Final pH	Element in Ppt., Mg.
0.112	Co	4.0	0.5
0.112	Co	2.3	0
0.672	Co	4.0	1.4
0.672	Co	2.3	0.1
0.672	Ni	4.5	1.4
0.672	Ni	2.6	0.05
0.112	Cu	2.5	1.0
0.672	Cu	2.6	3.0
0.112	Zn	4.0	0.9
0.112	Zn	3.0	0.5
0.112	Cd	6.2	0.1
0.112	Cd	4.0	0

In the precipitation of ferric iron, the succinate ion gave a rather bulky precipitate and the formate gave the best results (18). The precipitate is dense and light brown in color, almost yellow. It shows a pronounced tendency to stick to the beaker, and some of the precipitate cannot be rubbed off with a policeman but must be dissolved off with acid. For that reason it is most effective as a method of removing iron, in order to permit the determination of other metals in the filtrate. This method has been used as an exercise in gravimetric analysis in the introductory course at the University of Michigan with good results. In a ferric solution containing large amounts of chloride, there is a slight reduction to the ferrous form, and it is desirable to add a few drops of hydrogen peroxide at the end of the process to keep the iron in the ferric condition.

Table II shows the results obtained in separating iron from other metals. The separation is better at pH 1.8, but precipitation is not complete until a pH of 2.9 or more is reached. The very small amount of iron remaining in solution at the lower pH suggested a two-stage precipitation process. When a pH of about 1.8 is reached the precipitate is filtered off, and the boiling is then continued until the pH is 3 or more. This very small precipitate cannot carry any appreciable amount of impurity and may be filtered through the same filter if desired. This is much less trouble than the usual method of reprecipitation, and the results are better than those obtained by one precipitation at the higher pH. Although there are no exactly corresponding results for the separations by the ammonia method, it is obvious that the basic formate method gives a much sharper separation.

The separation of thorium from the rare earths by precipitation as dense basic formate at a pH of 5.4 was successful (16). This is important because the usual iodate method leaves much to be desired. One peculiarity of this precipitate is its property of adsorbing completely even very small amounts of silica. So pronounced is this tendency that any precipitate formed in a glass vessel had to be treated with hydrofluoric and sulfuric acids to obtain accurate results.

In addition to basic salts, many other precipitates are formed by neutralizing an acid solution. For many years students at the university have been precipitating calcium oxalate by neutralizing an acid solution by boiling with urea. This has given a much better separation from magnesium and the precipitate is coarser. There are a number of similar processes where this method is applicable.

But the advantages of precipitation from homogeneous solution

are not limited to the neutralization process. The general principle of forming the desired ion by the hydrolysis of an ester greatly extends the field. Sulfate ion can be formed by the hydrolysis of sulfamic acid, or of ethyl or methyl sulfate. It is well known that barium cannot be separated from appreciable amounts of calcium by the addition of sulfate. However, the precipitation of barium by the hydrolysis of sulfamic acid has given an excellent separation and ethyl or methyl sulfate serves the same purpose.

In the separation of thorium from the phosphate present in monazite sand, the precipitation of thorium oxalate by the hydrolysis of methyl oxalate has given a much better separation than the usual method of adding oxalic acid (16). It has also made possible the precipitation of magnesium oxalate (2) from 85% acetic acid solution and of zinc oxalate, too (3). The usual method of adding oxalic acid gives such a gelatinous precipitate that the method is useless, but from homogeneous solution the precipitate is coarse and crystalline.

Table III. Comparison of Phosphoric Acid and Triethylphosphate Methods for Separation of Hafnium and Zirconium

	Weight % Hafnia	
Designation	Phosphoric acid method	Triethylphosphate method
Initial composition	13.0	16.0
Product from step 1	18.0	30.3
Product from step 2	30.0	53.6
Product from step 3	43.0	75.8
Product from step 4	58.0	80.0
Product from step 5	72.0	91.1
Product from step 6	84.0	
Product from step 7	93.3	
Yield of hafnia, %	10.0	23.8

Zirconium can be quantitatively precipitated in strongly acid solution as zirconyl phosphate and thus separated from many other metals. The precipitate is, however, extremely gelatinous and it is impossible to wash it thoroughly. Hafnium phosphate is less soluble than the zirconium salt, and this has been used as a method of concentrating hafnium from its naturally occurring mixture with zirconium. The physical properties of the phosphate made it a poorer method than the difference in solubilities would indicate.

Larsen, Fernelius, and Quill (6) improved the process by adding phosphate and zirconium ions to a solution of sulfuric acid at the proper rate to avoid an excess of either. They obtained a much better precipitate from this approximately homogeneous solution and the concentration of hafnium was greatly facilitated. It seemed that a still denser precipitate would be obtained from a truly homogeneous solution, by the hydrolysis of triethyl or trimethyl phosphate, both of which are completely miscible with water. These esters slowly hydrolyze in a boiling solution of sulfuric acid to yield methyl or ethyl phosphoric acid. To remove the last alkyl group requires a much longer time and is unnecessary, as the properties of zirconium and hafnium alkyl phosphates are about the same as those of the phosphates. The precipitate obtained in this way is crystalline and readily washed. The separation of these elements by this process is considerably better than any previously attained (15). Table III shows a comparison of the results obtained by Larsen, Fernelius, and Quill and by the hydrolysis of triethyl phosphate. In seven steps they obtained a 93.3% hafnia with a yield of 10%. From homogeneous solution in five steps a 91% product was obtained with a yield of 23.8%.

This reaction was applied to the quantitative determination of zirconium by Hahn (17). It was found entirely feasible to determine zirconium by igniting the precipitate to zirconium pyrophosphate, ZrP_2O_7, and to separate it from large amounts of other elements; only antimony, bismuth, cerium, and stannic

ions interfered. The only disadvantage is the 20 hours' heating required to hydrolyze the ester.

A better separation was obtained by the hydrolysis of metaphosphoric acid. The latter forms a soluble complex with zirconium and upon standing at room temperature in 3.6 N sulfuric acid for several hours it is hydrolyzed to orthophosphoric acid and zirconyl phosphate is precipitated in a dense form. This makes possible a separation from all the common ions except stannic, and is applicable to as much as 200 mg. of zirconium.

Another way of accomplishing precipitation from homogeneous solution is to oxidize the reagent gradually from a form in which it causes no precipitate to one in which it causes quantitative precipitation. Gump and Sherwood (5) precipitated zirconyl arsenate in a crystalline form by adding sodium arsenite to a sulfuric acid solution and oxidizing the arsenite to arsenate by nitric acid.

A rather unusual way of precipitating thorium from homogeneous solution was described by Gordon and co-workers (4). When tetrachlorophthalic acid is added to a hot solution of a thorium salt, a gelatinous precipitate is formed immediately. If, however, the solutions are mixed at room temperature, no precipitate forms for several hours. At 70° C. the thorium salt slowly separates in a dense, crystalline form, which is filtered off and ignited to the oxide. The mechanism of this reaction is not clear. It may be due to the increased dissociation with rising temperature of a complex of thorium with hydroxyl ion, or to the reaction of hydrolysis products of thorium salts in the colloidal range with the dissolved acid. The method affords an excellent separation of thorium from the rare earths.

The work on precipitation from homogeneous solution was begun at this university over 20 years ago and is still continuing. The advantages of this method are beginning to be realized, as evidenced by the work of other authors. There are many different ways of applying this principle. Some have been described and others are being investigated. When one considers how frequently precipitation processes are utilized, it is obvious that any improvement in the process is of much value not only to the analytical chemist but also to the chemical engineer who is concerned with industrial applications.

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Precipitation in Homogeneous Solution

Separation and Determination of Barium, Strontium, and Calcium

PHILIP J. ELVING AND ROBERT E. VAN ATTA

Purdue University, Lafayette, Ind., and The Pennsylvania State College, State College, Pa.

Barium, strontium, and calcium can be quantitatively separated as readily filterable sulfate precipitates by digestion of an aqueous methanol solution containing dimethyl sulfate; the sulfate ion needed for precipitation is furnished by hydrolysis of the dimethyl sulfate. The coarseness and ease of filtration increase as the atomic weight of the alkaline earth metal decreases, both strontium and calcium forming rather coarse precipitates. In the separation of barium in 20% methanol, small amounts of strontium interfere but large amounts of calcium do not; moderate amounts of sodium, potassium, and magnesium and large amounts of aluminum, ammonium, and iron do not interfere. Strontium and calcium are precipitated by modified procedures in higher concentrations of methanol; allowable amounts of sodium and potassium decrease as methanol concentration increases. Barium can be precisely determined in synthetic mixtures approximating the composition of barytes samples.

THE customary method of determining barium using relatively dilute solutions of barium and sulfate (*3, 5, 8*), wherein one reagent is added directly to the other at or near the boiling point, may involve several analytical errors, which fall (*11*) into three major categories:

1. Errors due to method of precipitation—e.g., a precipitate of barium sulfate formed by the addition of barium chloride solution to a hot sulfuric acid solution may contain considerable amounts of barium chloride. Even greater error is incurred when the precipitation is carried out in the reverse order (*16*). Although both barium chloride and sulfuric acid are absorbed and coprecipitated with barium sulfate, the reagent present in excess will be entrained to a greater extent. The amount of entrainment occurring is dependent upon the relative concentrations of the reagents, rate and manner of mixing, and temperature.

2. Errors due to the presence of cations other than barium. Coprecipitation of alkali metals (*18*) and certain bivalent and trivalent ions may introduce errors. Coprecipitation of alkali metals occurs especially when sodium or potassium sulfate is used as precipitating agent. Ammonium may also be coprecipitated. Magnesium is only slightly entrained, while calcium may introduce rather large errors due to the slight solubility of calcium sulfate. Ferric ion is usually reduced to the ferrous state, which is entrained to a much lesser extent than the ferric iron or is removed by double precipitation with ammonium hydroxide with subsequent removal of the ammonium salts formed. Aluminum is not greatly entrained, but high concentrations are best avoided. The effect of various cations is: $K^+ > Na^+ > NH_4^+$; $Ca^{++} \gg Mg^{++}$; $Fe^{+++} > Al^{+++}$ (*10*).

3. Errors due to the presence of anions other than sulfate. Coprecipitation of various anions with barium sulfate has been reported as increasing in two different orders: $Fe(CN)_6^{---} < Fe(CN)_6^{----} < I^- < SCN^- < CN^- < Br^- < MnO_4^- < Cl^- < ClO_3^- < NO_2^- < NO_3^-$ (*13*) and $CH_3COO^- < SCN^- < I^- < Br^- < Cl^- < ClO_4^- < Fe(CN)_6^{----} < MnO_4^- < ClO_3^- < NO_3^- < Fe(CN)_6^{----} < BrO_3^-$ (*10*).

Chromate coprecipitates through the formation of mixed crystals with the barium sulfate (*12*). Phosphate is also entrained (*14, 15*). In most cases, entrainment errors due to the presence of anions may be decreased or eliminated by precipitation at or near the boiling point, followed by digestion of the precipitate over a steam bath.

Because of the difficulty of securing accurate results in the precipitation of barium sulfate, investigators (*17, 23*) have proposed empirical correction factors to be applied to the weight of barium sulfate obtained.

Quantitative results are ordinarily much more difficult to obtain in the precipitation of strontium, owing to the solubility of the sulfate formed. In addition to the solubility error, determina-

tion of strontium as the sulfate also includes the possibility of error due to entrainment effects similar to those encountered with barium. The determination of calcium as the sulfate has been discussed (*1*).

The primary purpose of the present investigation was the development of a procedure for the determination of barium which would reduce or eliminate some of the errors mentioned and at the same time produce a readily filterable precipitate; a procedure that would be suitable for the determination of barium in the presence of large amounts of calcium was especially desired. A successful solution was found in the use of the technique of precipitation in homogeneous solutions, whereby the alkaline earth metal sulfate is precipitated in aqueous methanol solution by sulfuric acid formed on hydrolysis of dimethyl sulfate. The separation of strontium and of calcium by the same technique was also investigated.

The use of the technique of precipitation in homogeneous solution through generation of a precipitating or neutralizing agent by hydrolysis has been described by Willard, Gordon, Caley, and co-workers for magnesium (*6*), calcium (*2, 19*), aluminum (*22*), zirconium (*21*), and thorium (*7, 20*). Caley and Elving (*1*) have described the precipitation of calcium as the sulfate in 90% methanol solution. Subsequent to the completion of the experimental work described in this paper, it was learned that Willard and Freund used the hydrolysis of sulfamic acid to generate sulfate ion for the separation of barium and calcium (*4*).

CHEMICALS AND SOLUTIONS

Standard solutions of barium and strontium ions were prepared by dissolving c.p. barium chloride dihydrate or strontium chloride hexahydrate in distilled water; standard calcium solutions were prepared by dissolving purified calcium carbonate (*1*) in hydrochloric acid. The exact concentration of each solution was determined by evaporating a measured volume in a platinum dish with a slight excess of sulfuric acid, igniting to constant weight in an electric muffle at 750° C., and weighing the residual alkaline earth metal sulfate. Samples for the test analyses were prepared from accurately measured volumes of these standard solutions. For the study of the extent of interference, accurately weighed amounts of the c.p. chlorides of the desired cations were dissolved in distilled water; acid solutions were prepared by diluting accurately measured volumes of the desired concentrated acids. Eastman Kodak practical grade (yellow label) or Fisher technical grade dimethyl sulfate was used in all experiments. No unusual difficulty was encountered in the use of dimethyl sulfate. The reagent was kept in a glass-stoppered bottle in a hood and was delivered into the sample solutions by means of a buret kept in the

Table I. Precipitation of Barium as Sulfate in 20% Methanol

Barium Taken, Mg.	Error, Mg.
1.0	-0.1, -0.1
5.0	-0.2, 0.0
10.0	-0.1, +0.1
30.1	0.0, -0.1
65.2	-0.1, -0.2
100.3	0.0, -0.1

Table II. Determination of Barium in Presence of Other Substances

Added Substance Mg.	Barium Mg.	Error Mg.	Added Substance Mg.	Barium Mg.	Error Mg.
50.0 Fe+++	10.0	+0.2	10.0 Sr++	1.0	-0.1
100.0 Fe+++	10.0	-1.2	10.0 Sr++	5.0	+0.2
100.0 Fe+++	10.1	-1.1	1.0 Sr++	10.0	+0.2
100.0 Fe+++	100.3	+0.3	10.0 Sr++	10.1	+1.8
500.0 Fe+++	100.0	-0.4	10.0 Sr++	10.0	+2.8
500.0 Fe+++	100.3	0.0	1.0 Sr++	100.2	+0.1
5.0 K+	10.0	+0.2	5.0 Sr++	100.3	+2.4
50.0 K+	10.0	+0.5	10.0 Sr++	100.2	+3.0
25.0 K+	100.3	0.0	10.0 Sr++	100.3	+4.2
100.0 K+	100.3	+0.5	25.0 NH4+	10.0	0.0
5.0 Na+	10.0	-0.1	500.0 NH4+	10.0	-0.1
50.0 Na+	10.0	+0.1	50.0 NH4+	100.0	-0.2
25.0 Na+	100.0	0.0	100.0 NH4+	100.3	+0.5
100.0 Na+	100.3	+0.5	25.0 HCl	10.0	+0.1
500.0 Al+++	100.3	0.0	100.0 HCl	10.0	-0.5
5.0 Mg++	10.0	0.0	50.0 HCl	100.0	0.0
50.0 Mg++	10.0	+0.4	500.0 HCl	100.0	-0.5
10.0 Mg++	100.0	+0.1	5.0 HNO3	10.0	0.0
50.0 Mg++	100.0	+0.4	10.0 HNO3	10.0	-0.1
500.0 Ca++	1.0	-0.1	25.0 HNO3	10.0	-0.6
500.0 Ca++	5.0	-0.1	50.0 HNO3	10.0	-1.2
25.0 Ca++	10.0	+0.1	100.0 HNO3	10.0	-1.7
50.0 Ca++	10.0	+0.4	10.0 HNO3	100.0	+0.1
10.0 Ca++	100.0	+0.3	50.0 HNO3	100.0	+0.4
10.0 Ca++	100.3	0.0	100.0 HNO3	100.3	-0.1
100.0 Ca++	100.0	-0.1	50.0 H3PO4	10.0	0.0
250.0 Ca++	100.0	0.0	100.0 H3PO4	10.0	-0.2
500.0 Ca++	100.0	+0.8	250.0 H3PO4	100.0	0.0
			500.0 H3PO4	100.0	+0.2

hood. The usual grades of methanol were used. No unpleasant physiological effects were noticed from either the methanol or dimethyl sulfate.

DETERMINATION OF BARIUM

Preliminary Experiments. The excess of dimethyl sulfate necessary for quantitative precipitation in a reasonable time was determined by precipitating 100 mg. of barium with varying excesses of dimethyl sulfate in a 100-ml. solution containing 50 ml. of methanol. The dimethyl sulfate was added in the cold and the solutions were then allowed to digest on the steam bath until complete precipitation occurred. An excess of 75 to 1 (5 ml.) was picked as optimum on consideration of such factors as speed of precipitation, filterability, and ease of washing of the precipitate. In a similar group of experiments, the barium was again precipitated by varying excesses of dimethyl sulfate, but one set of solutions was digested for 1 hour on the steam bath and a second similar set in a 50° C. water bath. Although both baths gave excellent results with a 75 to 1 excess, the steam-bath digestion required 15 to 20 minutes for complete precipitation, while the water-bath digestion required a minimum of 4 hours.

In determining the optimum composition of medium, solutions containing 100 mg. of barium and a varying amount of methanol, ethanol, or 2-propanol were prepared, and the barium was precipitated with a 75 to 1 excess of dimethyl sulfate. The 20% methanol medium was found to produce quantitative results, as well as the most readily filterable precipitate. Although good results were obtained with ethanol and 2-propanol media, considerable creeping was encountered with the precipitates formed in these solutions.

Effect of time of digestion was determined by preparing solutions containing 10 or 100 mg. of barium and 20 ml. of methanol in a total volume of 100 ml., and precipitating with a 75 to 1 excess of dimethyl sulfate, using digestion times of 15 to 60 minutes on the steam bath. Digestion times were considered as beginning with the appearance of heavy precipitation, which usually occurred 15 to 20 minutes after the solutions were mixed and placed on the steam bath. A digestion time of 60 minutes was picked as optimum, owing to ease of filtration of the precipitate formed.

Procedure. Transfer to a 250-ml. beaker the sample solution (75 ml. or less in volume) containing 1 to 100 mg. of barium preferably present as the chloride or nitrate. Add 20 ml. of methanol and dilute to a total volume of 95 to 98 ml. Add to the

cold solution 0.5 ml. of dimethyl sulfate per 10 mg. of barium believed present (minimum volume to be added, 2 ml.) and immediately place the solution on the steam bath; the final volume of the solution should be 100 ml. Allow the solution to digest on the bath for 75 minutes; if appreciable decrease in volume occurs, add methanol to restore the 100-ml. volume. After digestion, filter through a weighed porcelain filtering crucible (Selas No. 3001). Wash the precipitate with 20% methanol, first by decantation and then by stirring up the precipitate in the crucible with a stream of wash liquid. Depending upon the amount of barium present, 20 to 50 ml. of wash liquid are required. Dry the crucible and contents for 15 minutes at 100° to 150° C., then ignite in an electric muffle for 30 to 60 minutes at 750° C., cool in a desiccator, and weigh as barium sulfate. The theoretical factor, $Ba/BaSO_4 = 0.5885$, is used to calculate results.

Separations. Using the above procedure, satisfactory results were obtained for the determination of 1- to 100-mg. amounts of barium in pure barium chloride solutions (Table I). To determine the influence of other ions, precipitations were made in the presence of known amounts of individual foreign cations and acids (Table II). The results given are typical of those obtained for the particular foreign ion specified; only limiting satisfactory results are given with stress placed on situations where interference may occur. Results obtained on complex synthetic samples are shown in Table III; unfortunately, suitable standard samples were not available. However, the samples of Table III have strontium to barium ratios equal to or exceeding those in the synthetic samples used by Kallmann (9) in testing a procedure for the determination of barium in barytes. The content of the other metallic constituents is higher; the silica present in Kallmann's samples was omitted because it was removed in the preliminary separations by the usual acid dehydration procedure. Kallmann's method for barium essentially involved fusion of the sample with potassium carbonate, acid solution of the sample to convert all the elements to the chlorides, and separation-precipitation of the barium as the chloride by the addition of concentrated hydrochloric acid and n-butanol. The results obtained by the dimethyl sulfate procedure are comparable in accuracy to those obtained by the more difficult procedure described by Kallmann, although the latter's procedure would be more advantageous in the presence of appreciable amounts of strontium.

DETERMINATION OF STRONTIUM

Preliminary Experiments. Experiments similar to those described for barium revealed that approximately a 50 to 1 access of dimethyl sulfate was sufficient for the quantitative precipitation of strontium, and that 70% methanol medium produced the best results, as well as a relatively coarse precipitate which was readily filterable. Careful policing of the precipitation beakers was found necessary because of the tendency of a film of strontium sulfate to adhere to the glass walls.

Necessary conditions of digestion were determined by preparing solutions containing varying amounts of strontium and 70 ml. of methanol in a total volume of 100 ml., and precipitating with a 50 to 1 excess of dimethyl sulfate, using digestion times of 45 to 60 minutes on the steam bath followed by 0 to 30 minutes' standing at room temperature. A digestion time of 1 hour on the steam bath plus 15 minutes' standing at room temperature was picked as optimum, owing to the ease of filtration and handling of the precipitates thus digested.

Procedure. Transfer to a 250-ml. beaker the sample solution (25 ml. or less in volume) containing not more than 125 mg. of strontium preferably present as the chloride or nitrate. Add 70 ml. of methanol and dilute with water to a total volume of 95 to 98 ml. Add to the cold solution 0.5 ml. of dimethyl sulfate for each 10 mg. of strontium (2 ml. minimum) and immediately place the solution on the steam bath; add methanol as may be necessary to maintain the volume at 100 ml. Remove after 1 hour on the bath and allow to stand at room temperature for 15 minutes. Filter through a weighed porcelain filtering crucible (Selas No. 3001). Wash the precipitate with 70% methanol, first by decantation and then by stirring up the precipitate in the crucible with a stream of wash liquid. Depending upon the amount of strontium present, 10 to 30 ml. of wash liquid are required. Dry the crucible and its contents for 15 minutes at 100° to 150° C., then ignite in an

Table III. Determination of Barium in Synthetic Mixtures

Composition	Sample, Mg.										
Al+++	50.0	50.0	50.0	10.0	50.0	20.0	20.0	20.0	20.0	50.0	50.0
Fe+++	50.0	50.0	50.0	10.0	50.0	20.0	20.0	20.0	20.0	20.0	50.0
Mg+++	100.0	100.0	100.0	10.0	100.0	50.0	50.0	50.0	50.0	100.0	100.0
Na+	100.0	100.0	100.0	10.0	100.0	50.0	50.0	50.0	50.0	100.0	100.0
K+	100.0	100.0	100.0	10.0	100.0	50.0	50.0	50.0	50.0	100.0	100.0
Ca++	100.0	100.0	100.0	10.0	100.0	50.0	50.0	50.0	50.0	100.0	250.0
Sr++	...	...	5.0	3.0	1.0	1.0	5.0	3.0	1.0	5.0	10.0
Ba++	10.0	100.0	100.3	100.3	92.6	100.3	49.2	49.2	56.4	10.1	10.1
Ba++ Found, Mg.											
	9.8	100.1	102.3	101.8	93.4	101.1	49.8	49.0	46.6	10.3	10.4
	9.9	100.0	102.4	101.7	93.3	100.9	49.7	49.2	46.5	10.1	10.5
Ba++ Error, Mg.											
	-0.2	+0.1	+2.0	+1.5	+0.8	+0.8	+0.6	-0.2	+0.2	+0.2	+0.3
	-0.1	0.0	+2.1	+1.4	+0.7	+0.6	+0.5	0.0	+0.1	0.0	+0.4

electric muffle for 30 to 60 minutes at 750° C., cool in a desiccator, and weigh as the sulfate. The theoretical factor, $Sr/SrSO_4$ = 0.4771, is used to calculate results.

Separations. The procedure described was used for determining strontium in pure strontium chloride solutions; satisfactory results were obtained in the range of 5 to 125 mg. of strontium (Table IV). To determine the influence of other ions, determinations were made in the presence of known amounts of foreign ions; typical results indicative of the extent of interference are given in Table V; the limitation on the data in this table is the same as indicated for Table II. Results obtained on complex synthetic samples are shown in Table VI.

DETERMINATION OF CALCIUM

Preliminary Experiments. Experiments on calcium similar to those described for barium and strontium indicated that a radically modified procedure was necessary because of the very slow rate of hydrolysis of the dimethyl sulfate in the 90% methanol,

which as previously reported (1) was found to be necessary for the quantitative precipitation of calcium. Suitable studies revealed that optimum results were obtained by a two-stage digestion in which (1) the hydrolysis and the bulk of the precipitation were carried out in 40 or 50% methanol solution containing a large amount of dimethyl sulfate during 30 minutes' digestion on the steam bath and (2) the solution diluted to 90% methanol was then allowed to stand at room temperature for 60 minutes. Because 20-mg. amounts of calcium gave only a slight precipitate under such conditions, results are not reported for amounts of calcium less than 50 mg.; with small amounts of calcium (20 mg. or less) the procedure would essentially duplicate that of Caley and Elving (1).

Procedure. Transfer to a 250-ml. beaker the sample solution (10 ml. in volume) containing 50 to 100 mg. of calcium preferably present as the chloride. Add 17 to 25 ml. of methanol and 15 ml. of dimethyl sulfate. Digest on a steam bath for 30 minutes, remove, dilute to 100 ml. with methanol, and allow to stand at room temperature for 60 minutes, then filter through a weighed porcelain filtering crucible. Wash the precipitate with 90% methanol, first by decantation and then by stirring up the precipitate in the crucible with a stream of wash liquid. Depending upon the amount of calcium present, 20 to 50 ml. of wash liquid are required. Dry the crucible and contents for 30 minutes at 100° to 150° C., then ignite in an electric muffle for 30 to 60 minutes at 750° C., cool in a desiccator, and weigh as calcium sulfate. The theoretical factor, $Ca/CaSO_4$ = 0.2944, is used to calculate results.

Separations. The procedure indicated was used for the determination of calcium in pure calcium chloride solutions, and in solutions containing individual foreign ions (Table VII). Results obtained on synthetic mixtures are given in Table VIII.

No extensive experiments were performed on the separation of calcium by precipitation in homogeneous solution and on possible interferences with the method, because the precipitation and

Table IV. Precipitation of Strontium as Sulfate in 70% Methanol

Strontium Taken, Mg.	Error, Mg.
1.0	-0.2, -0.3
2.5	-0.3, -0.2
4.9	0.0, -0.2
10.0	-0.1, -0.1
12.9	-0.2
13.2	0.0
29.9	-0.2, -0.1
65.0	0.0, -0.2
99.8	0.0, +0.1
125.8	0.0
126.5	0.0

Table V. Determination of Strontium in Presence of Other Substances

Added Substance Mg.	Strontium Mg.	Error Mg.	Added Substance Mg.	Strontium Mg.	Error Mg.
30.0 Fe+++	12.7	0.0	25.0 Mg++	99.2	+0.1
100.0 Fe+++	12.7	+0.2	75.0 Mg++	63.6	-0.6
100.0 Fe+++	125.7	+0.4	125.0 Mg++	63.6	-0.1
250.0 Fe+++	125.7	+0.5	250.0 Mg++	63.6	-0.9
1.0 Ca++	1.0	-0.2	250.0 Mg++	49.4	-0.8
5.0 Ca++	1.0	-0.1	250.0 Mg++	99.2	-0.6
5.0 Ca++	0.9	+0.4	250.0 Mg++	125.7	-0.9
5.0 Ca++	4.9	+0.2	10.0 Na+	12.7	+0.1
1.0 Ca++	9.9	+0.1	100.0 Na+	12.8	+0.3
5.0 Ca++	9.6	+0.7	100.0 Na+	25.5	+0.2
5.0 Ca++	96.2	+0.7	100.0 Na+	64.3	+0.2
5.0 Ca++	99.2	+0.8	150.0 Na+	64.3	+0.5
1.0 Ca++	99.2	+0.5	100.0 Na+	125.7	+0.5
50.0 Al+++	12.8	-0.4	10.0 K+	12.7	+0.2
125.0 Al+++	25.5	-1.0	25.0 K+	12.7	+0.1
25.0 Al+++	64.3	-0.1	50.0 K+	63.6	+0.2
75.0 Al+++	64.7	-0.5	100.0 K+	125.7	+0.5
125.0 Al+++	64.3	-0.3	250.0 K+	125.7	+0.6
250.0 Al+++	64.3	+0.3	10.0 NH4+	9.6	+0.1
125.0 Al+++	126.5	-0.2	25.0 NH4+	9.6	+0.2
25.0 Mg++	4.9	-0.4	50.0 NH4+	96.2	+0.3
25.0 Mg++	9.9	-0.6	100.0 NH4+	96.2	+0.4
10.0 Mg++	12.7	+0.2	250.0 NH4+	96.2	+0.7
25.0 Mg++	12.7	-0.3			

Table VI. Determination of Strontium in Synthetic Mixtures

Composition	Sample, Mg.								
	A	B	C	D	E	F	G	H	I
Al+++	100.0	50.0	10.0	20.0	20.0	20.0	20.0	20.0	20.0
Fe+++	100.0	50.0	10.0	30.0	10.0	30.0	30.0	20.0	20.0
Mg++	100.0	50.0	5.0	25.0	25.0	25.0	50.0	25.0	25.0
Na+	100.0	50.0	25.0	50.0	20.0	50.0	50.0	20.0	20.0
K+	100.0	50.0	25.0	50.0	20.0	50.0	50.0	20.0	20.0
Ca++	...	...	...	2.0	2.0	5.0	5.0	5.0	5.0
Sr++	126.5	64.7	13.2	20.4	95.6	20.4	23.9	46.2	95.6
Sr++ Found, Mg.									
	126.2	64.8	13.2	20.4	95.6	20.6	23.4	47.0	96.8
	126.3	64.9	13.3	20.3	95.8	20.5	23.7	46.7	97.1
Sr++ Error, Mg.									
	-0.3	+0.1	0.0	0.0	0.0	+0.2	-0.5	+0.8	+1.2
	-0.2	+0.2	+0.1	-0.1	+0.2	+0.1	-0.2	+0.5	+1.5

Table VII. Determination of Calcium in Concentrated Methanol Solution

Added Substance, Mg.	Calcium, Mg.	Error, Mg.
......	50.7	-0.2, -0.3
......	104.2	0.0, 0.0
500.0 Mg++	104.2	+0.4
200.0 Mg++	104.2	+0.2
5.0 Na+	104.2	+0.8
2.0 Na+	104.2	+0.3
5.0 K+	104.2	+0.4
2.0 K+	104.2	+0.1

separation of calcium as the sulfate in 90% methanol have been thoroughly described (1). The use of the dimethyl sulfate method for calcium seems to offer comparatively little advantage over the method described by Caley and Elving (1) and is in any event restricted to amounts of calcium between 50 and 100 mg.

DISCUSSION

The dimethyl sulfate method of precipitation in homogeneous solution offers four principal advantages for the determination of barium by precipitation as barium sulfate: formation of a relatively coarse precipitate, readily filtered and washed with a minimum amount of creeping; high accuracy and precision over the range of concentrations investigated; considerable freedom from interference due to the presence of foreign anions and cations, especially calcium even when present in large amounts; and saving in analyst's time.

Table VIII. Determination of Calcium in Synthetic Mixtures

Composition, Mg	
Mg^{++}	100.0
Al^{+++}	10.0
Fe^{+++}	10.0
Na^+	2.0
K^+	2.0
Ca^{++}	104.2

	Digestion	
	40% MeOH	50% MeOH
Ca^{++} found, mg.	104.5	104.6
	104.4	104.4
Ca^{++} error, mg.	+0.3	+0.4
	+0.2	+0.2

In the case of the determination of strontium by precipitation as strontium sulfate in 70% methanol solution, the primary consideration is that strontium sulfate cannot be quantitatively precipitated from a water solution, owing to the solubility of the sulfate. In addition, the advantages previously listed for the determination of barium also hold true in the strontium determination, with the minor disadvantage that much more efficient policing of the precipitation beakers must be effected, although the major part of the precipitate is much coarser than that obtained with barium.

Both methods suffer the disadvantage that at least one ion produces appreciable interference with the accurate determination of the desired constituent, strontium in the barium determination and calcium in the strontium determination. Iron, the element most likely to be present in amounts large enough to cause noticeable interference, may be sufficiently removed for the determination of strontium or barium by precipitation with a slight excess of ammonium hydroxide and subsequent filtration, because ammonium ion offers no appreciable interference with either determination. Quantities of barium in the range of 1 to 100 mg. and strontium in the range of 5 to 125 mg. may be accurately determined with a minimum of interference due to other ions, with the exception of those mentioned.

As previously indicated, the dimethyl sulfate method for calcium offers no appreciable advantage over the usual method for precipitating calcium sulfate in methanol solution (1), except that precipitation in homogeneous solution results in a more readily filterable precipitate.

The large allowable concentration of calcium in the barium determination is probably due to the excess sulfuric acid formed, which prevents the precipitation of calcium sulfate.

In the usual sulfuric acid method for the precipitation and determination of barium as barium sulfate, the solutions are mixed at or near the boiling point, with constant stirring during the addition of the precipitant, after which the digestion is carried out. In the dimethyl sulfate method, however, the pre-

cipitant is added to the cold methanol-water solution of the sample from a buret, stirring being unnecessary, and the resultant solution is digested, bringing about the hydrolysis of the dimethyl sulfate and the subsequent precipitation of the desired sulfate. The analyst's time required for precipitation and filtration in the dimethyl sulfate procedure is considerably less than in the conventional method. A total time of about 3 hours is required for determining the amount of alkaline earth metal present in a given solution by the dimethyl sulfate method, 15 to 20 minutes of which are required to perform the actual operations other than ignition and digestion of the sample.

Porous-bottomed porcelain filtering crucibles are recommended for use in filtering off the sulfate precipitates obtained by this method, although Gooch crucibles containing asbestos mats should serve equally well, especially in the case of strontium and calcium sulfates, which are coarser than the barium sulfate. The principal disadvantage of the use of the Gooch crucible in this case lies in the time and care involved in preparing and using such a crucible. The porous-bottomed crucibles used in the present investigation were wiped free of accumulated precipitate and rinsed with distilled water after each determination and before use in the succeeding determination. After three or four successive precipitations, the crucibles were cleaned by drawing concentrated sulfuric acid–potassium dichromate cleaning solution through them, followed by distilled water.

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Electrolytic Separations

Separations by Electroanalysis

S. E. Q. ASHLEY, *General Electric Company, Pittsfield, Mass.*

The purpose of the present symposium is evaluating the utility of important methods of separation by comparing their strength and weaknesses as they now stand in the present knowledge of our science. This cannot be done by a detailed consideration of particular methods of separation, and electrolytic separations are highly specific. The broad aspects of electrolytic separation are discussed here, in an attempt to make the disadvantages and advantages of the technique apparent.

THERE are several ways in which the advantages and disadvantages of electrolytic separation may be presented. An obvious choice is to follow the guidance of Mellon (*15*) who, on page 90 of his text, recommends the following criteria for evaluation separations: the cost of chemicals, apparatus, and laboratory services; the availability of special facilities; the time, skill, and attention required to obtain the requisite degree of accuracy; the general and special applicability of the method; and the efficiency of the separation.

For ease in defining the terms of this discussion, this paper might be called "Separations by Electroanalysis." By electroanalysis is meant (*1*) the use of electrical energy for the precipitation, detection, or determination of elements and compounds in chemical analysis. It is distinguished from other electrical methods of analysis chiefly by the fact that it depends upon the consumption of significant amounts of electrical power, in contrast to potentiometry, conductometric analysis, etc., where the electrical power consumed in the procedure is negligible. Electrophoresis is arbitrarily excepted from treatment here, although it comes within the scope of the definition given.

Definition of the other part of the topic is not so certain. Surprisingly, definitions of "separation" are rare. The dictionary says that a separation is a process of disengaging one thing from another, and because this may be complete, or incomplete in more than one sense, there are four or five kinds of separations possible with electroanalysis:

1. Precipitation of unwanted constituents, leaving the desired constituent(s) in solution—i.e., removal of iron, preliminary to determination of aluminum in ferrous alloys.
2. Precipitation of desired constituent, leaving undesired constituents behind.
    a. "Collection" of a desired constituent from a large mass—i.e., separation of lead or mercury from urine.
    b. Precipitation complete, but precipitate impure—i.e., separation of iron and nickel together on cathode, or lead and manganese on anode.
    c. Precipitation complete or almost so, and ready to be measured—i.e., copper deposited on cathode and weighed; lead deposited on anode and determined colorimetrically, etc.
    d. Coulometric precipitation, where current used to bring about separation is measured.
3. Volatilization of a desired constituent—i.e., formation of hydrides of germanium, arsenic, or antimony by reduction at cathode.
4. Electrosolution.
    a. Separation of inclusion from metals—i.e., dissolving electrode as of steel with controlled potential, inclusions are insoluble and left behind.
    b. "Stripping" to measure coating thickness—i.e., to determine the thickness of electroplating.
5. Electroanalytical "separations" without disengagement or isolation.
    a. Electroreductions—i.e., of iron, titanium, etc., and of nitrates to ammonia.

    b. Coulometric reductions—i.e., of organic compounds to determine structure.
    c. Coulometric titrations—i.e., brominations as carried out by Swift and co-workers.

Mellon (*15*, p. 6) defines a separation as a process by which "the desired constituent, either by itself or associated with certain elements, is isolated by removing it or the interfering elements from the system." Under item 5 are some interesting borderline cases which tax this definition. Although the techniques mentioned under item 5 do not qualify under the definition used, they enable one to reach into the homogeneous phase of a solution and set a constituent apart as surely as if it were isolated in a single phase.

CHEMICALS, APPARATUS, AND LABORATORY SERVICES

Chemicals, apparatus, and laboratory services all are very similar and may be treated as a group. Compared with many modern laboratory methods, the investment in special equipment is very modest, and it is very nearly true to say that everything needed is available as standard equipment in most modern laboratories, with the probable exception of automatic devices for controlling cathode potential. The cost of chemicals is probably below average. Coulomb for coulomb, electrons are cheaper purchased as electricity than as reducing agents, if the electricity is taken off the power supply lines. The sources of electricity are usually primary or secondary cells, rectifiers, or generator sets in order of increasing requirements. Any laboratory can provide itself with one of these supplies by a modest outlay.

Perhaps the most serious problem in the use of electroanalytical methods has been the availability of platinum. High cost of platinum metals and their limited geographical distribution pose serious problems to those on a limited budget or those who must work in "have-not" nations. While platinum still seems to be used almost universally in the United States when required, in other countries (*3*) considerable effort has been directed to the use of stainless steel, anodized aluminum, graphite, and other materials to replace platinum. The mercury cathode, usually employed for other reasons, is a useful substitute (*2*). Schleicher has devoted much time in recent years to the development of internal electrolytic methods as a means of eliminating platinum anodes (*20*). In years past platinum-coated glass, tin, aluminum, the fusible alloy known as Wood's metal, and tantalum have also been proposed as substitutes, among which tantalum seems to be the most useful. The purchase of platinum can, however, be considered as a capital investment which may be recovered by resale. The actual loss of platinum by chemical action is negligible compared with the risks of the metal markets. The

investment in platinum may be minimized by the use of micro-techniques.

SPECIAL FACILITIES

Specialized equipment is available in many forms from manufacturers to cover about every need in electroanalysis except the growing one for work in controlled potential analysis. One or two manufacturers have taken steps to make equipment available in this field, and probably only an increased demand is needed to bring many sorts into the market. Remarks on cost have included other aspects of availability.

TIME, SKILL, AND ATTENTION REQUIRED

In general, it is correct to say that the time, skill, and attention required to obtain the requisite degree of accuracy are not great and manufacturers have dared to bring onto the market equipment with instruction manuals more or less guaranteed to give the user the results he needs. Naturally, a great deal of variation exists in the skill of operators and the ease with which different elements respond to electroanalytical treatment. The separation of iron from aluminum by electrolysis with a mercury cathode is performed countless times daily, but even experienced operators are continually discovering new quirks in the behavior of this system. Separations, as of tin and copper, vary with the amounts of material present, and again the completeness of this separation is a matter of debate by practiced chemists. This lack of reproducibility among operators may be considered one of the disadvantages of electroanalytical separations, although in general it is not a serious drawback.

The time and attention required by electrolytic separations are generally small. In rapid electrolyses with stirring and high current, a precipitation may require only a few minutes. With controlled cathode potential the duration of the analysis may be extended, but it can be made completely automatic in its operation, if the precipitation is measured coulometrically. It is a common practice in industrial laboratories to arrange copper determinations so that they can be started late in the afternoon, be run without supervision overnight, and be ready for final treatment the next morning when work resumes.

APPLICABILITY OF METHOD

The next criterion, suggested by Mellon, is the general and special applicability of the method; this calls for a careful review of the principles involved in its use.

Separations by electroanalysis are based upon the fundamental property that ions of the elements may be reduced (or in some cases oxidized) at critical potentials, and thereby precipitated or dissolved in accordance with the applied energy. This discussion deals entirely with aqueous solutions, and the expression that has been used to measure the potential of an electrode immersed in a solution of its ions is given by the following equation:

$$E = E_0 + \frac{0.058}{n} [\log \text{concn.}]$$

At unit concentration, the last term becomes zero and $E = E_0$. E_0 is known as the standard potential and is usually expressed by reference to the hydrogen electrode, although for practical measurement the calomel or silver chloride electrodes are more convenient.

If the potential of the electrode in a solution of its ions rises slightly above equilibrium value, ions will pass into solution. If the potential drops (becomes more negative toward metal ions), the ions will be discharged. Hence, E is known as the deposition potential. A study of the equation shows that E will increase negatively as the concentration decreases. In other words, the cathode (the negative pole in the electrolysis) will become more negative.

Table I, borrowed from Kolthoff and Sandell (9), shows a

series of deposition potentials with the corresponding electrode reaction. A cathode with a potential slightly below +0.81 volt with respect to hydrogen will be able to discharge silver ions present in unit concentration, but not copper. If the potential is dropped to slightly below +0.345 volt, copper will be discharged at unit concentration and silver at concentrations considerably below the unit value. The effect of deposition potential and concentration on the problem of electrolytic depositions and separations is shown in Figure 1. It brings us to the heart of the problem of electrolytic separations, which makes them unique among electrodeposition processes. It is the continuous change in the composition of the solution during electrolysis which creates such great difficulties for the analytical chemist, compared with the electroplater whose solutions remain virtually constant in concentration.
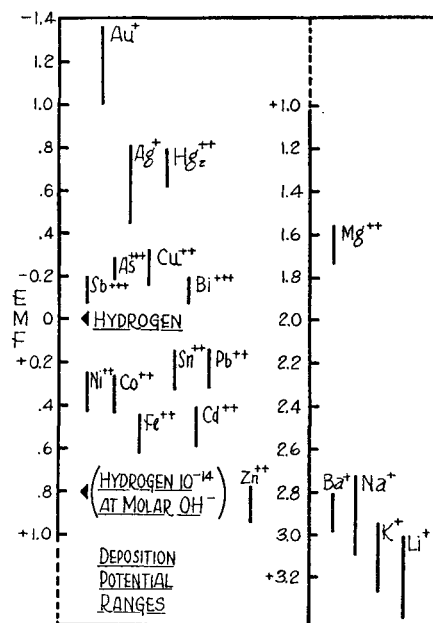

Figure 1. Effect of Deposition Potential and Concentration

In Figure 1 are shown the voltages at which deposition begins for many of the common elements, drawn on a linear vertical scale which is too long to show fully extended. It is divided, therefore, to show a portion on the vertical axis at the left, and the lower end of that linear scale is continued on the axis drawn near the center of the illustration. The upper ends of these short vertical lines show the voltage at which deposition begins at unit molar concentration (more properly expressed in activities), a concentration somewhat greater than is usually encountered in actual analyses for most metals. The range over which the voltage must be decreased (with respect to the hydrogen electrode) to reduce the concentration from unit molar to 10^{-6} molar is expressed by the vertical line. The lower end shows the deposition voltage when the concentration reaches 10^{-6} molar, a convenient practical limit at which the deposition can be considered virtually complete. The concentration has been reduced a million fold during the electrolysis if we can reach this point. However, practical considerations make this goal an ideal one in the majority of actual separations.

Hydrogen Ion Concentration. Another matter of the greatest importance in securing satisfactory electrodepositions is the concentration of hydrogen ion. Silver and copper may be cleanly separated because of their widely different deposition potentials, over the range of their normal concentration ranges. In general, this is true for any element whose deposition ranges do not overlap in the graphical representation or where normal deposition potentials are 0.25 volt apart. In favorable cases where the con-
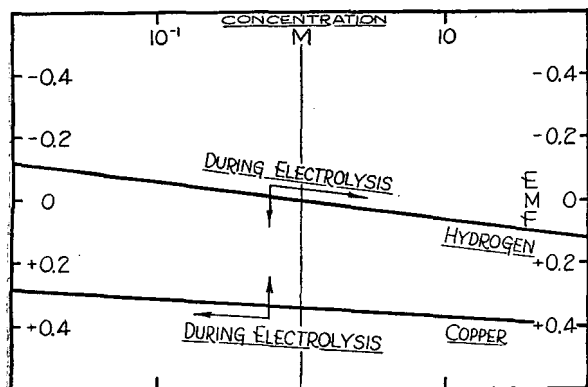
Figure 2. Concentration and Potential Changes during Electrolysis

centration of one ion is low, a difference of 0.1 volt may be large enough.

Hydrogen plays a unique role, in that it is present in a virtually infinite amount. Because we are working exclusively with aqueous media, we must reckon with the dissociation of water. Hydrogen ions are always present from this dissociation as long as we have water or a solution; hence the hydrogen is by definition inexhaustible. Even in solutions which are molar with respect to hydroxyl ion concentration, hydrogen can be discharged at about −0.8 volt, as shown in Figure 1. In a solution in which molar concentrations of silver, copper, hydrogen, and nickel ions exist, silver might first be discharged, then copper, and finally hydrogen as the cathode becomes more negative. However, it is never removed entirely from solution. The only way to cause the nickel to deposit alone is to reduce the concentration of hydrogen until its discharge potential is below that of nickel, and that is what is done in practice by precipitating nickel from a basic ammoniacal solution.
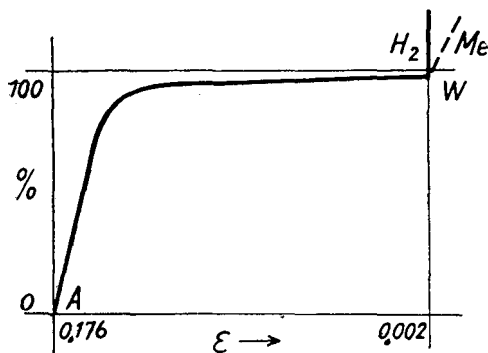
Figure 3. Electrolysis of 0.01 Molar Copper Solution

Meanwhile, at the anode another aspect of the fundamental pattern in the electrolysis of aqueous solutions is taking place. The common anions such as sulfates, perchlorates, fluorides, and nitrates have such a high deposition potential that hydroxyl ions even in low concentration are preferentially discharged according to the reactions:

$$2OH^- \longrightarrow H_2O + O + 2e$$
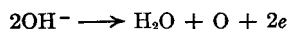
The discharge of the hydroxyl ions leaves an excess of hydrogen ions in the solution, which increase in direct proportion to the coulombs of electricity passing through the solution. Hence, if a solution of copper sulfate slightly under 1 molar and containing an equivalent concentration of hydrogen ion is electrolyzed, the

course of the concentration and potential changes during the electrolysis are shown in Figure 2.

The concentration of copper will decrease and hence shift to the left, and the hydrogen ion concentration will increase in proportion and shift to the right, with the result that the deposition potentials will at some point coincide and copper and hydrogen will be deposited together. The course of an actual electrolysis of a 0.01 molar copper solution is shown in another form of graphical representation borrowed from Schleicher (20, p. 11), Figure 3.

The potential, E, measured with respect to a reference electrode becomes more negative as the electrolysis progresses from left to right. The major proportion of the copper (shown as per cent of total copper on the ordinate) is precipitated in a relatively short space of time over a short voltage range. The remainder of the copper is precipitated until the positive potential drops to the deposition potential of hydrogen. The evolution of hydrogen acts as a buffer at this point.

Table II shows the actual numerical percentages of copper precipitated in the course of the electrolysis. At the voltage where the hydrogen appears, there should be no more than 0.0001% of the original copper left in the solution. The appearance of hydrogen provides a safety valve to permit the easy separation of elements less noble than hydrogen from those that are more noble; hence copper from alkalies, and so on. More elaborate means of controlling the deposition potential are available by the use of internal electrolysis, and by the use of additional reference electrodes within the solution and external circuits for controlling the electrical supply, manually or automatically.

Several secondary factors modify the simple picture of separations at equilibrium conditions as they have been described thus far. The depletion of ions in the neighborhood of the cathode is compensated by the diffusion of ions up to the electrode, and by convection currents set up by the concentration gradient in the neighborhood of the electrode. Stirring the standing electrolytes mechanically has been found to be important not only to speed up the rate of deposition, but also to make possible the use of controlled cathode potential techniques, for it is only under such circumstances that ideal equilibrium conditions can be approached. The evolution of oxygen at the anode which accom-

Table I. Normal Potentials of Metals

Electrode Reaction	E_0, Volts
Li $\rightleftarrows$ Li$^+$ + e	−3.02
K $\rightleftarrows$ K$^+$ + e	−2.92
Na $\rightleftarrows$ Na$^+$ + e	−2.71
Ba $\rightleftarrows$ Ba^{++} + $2e$	−2.8
Mg $\rightleftarrows$ Mg^{++} + $2e$	−1.55
Zn $\rightleftarrows$ Zn^{++} + $2e$	−0.76
Fe $\rightleftarrows$ Fe^{++} + $2e$	−0.44
Cd $\rightleftarrows$ Cd^{++} + $2e$	−0.40
Ni $\rightleftarrows$ Ni^{++} + $2e$	−0.25
Co $\rightleftarrows$ Co^{++} + $2e$	−0.255
Sn $\rightleftarrows$ Sn^{++} + $2e$	−0.14
Pb $\rightleftarrows$ Pb^{++} + $2e$	−0.13
$\frac{1}{2}$H$_2$ $\rightleftarrows$ H$^+$ + $2e$	0.00
Bi $\rightleftarrows$ Bi^{+++} + $3e$	+0.2
Sb $\rightleftarrows$ Sb^{+++} + $3e$	+0.2
As $\rightleftarrows$ As^{+++} + $3e$	+0.3
Cu $\rightleftarrows$ Cu^{++} + $2e$	+0.345
2Hg $\rightleftarrows$ Hg$_2$$^{++}$ + $2e$	+0.80
Ag $\rightleftarrows$ Ag$^+$ + e	+0.81
Pd $\rightleftarrows$ Pd^{++} + $2e$	+0.82
Au $\rightleftarrows$ Au$^+$ + e	+1.5

Table II. Precipitation of Copper

Copper Precipitated, %	Cathode Potential
0	+0.176
90	+0.147
99	+0.118
99.9	+0.089
99.99	+0.060
99.999	+0.031
99.9999	+0.002

panies many electrolyses, and the evolution of hydrogen at the cathode do stir the solution to a moderate degree. However, the circulation is limited, as is evident when the electrodes do not reach the bottom of an unstirred copper solution. The copper is removed from the upper layers, but is practically undeposited from the lower layers without stirring. Heat may sometimes be applied to create convection currents, but temperature changes affect other important factors.
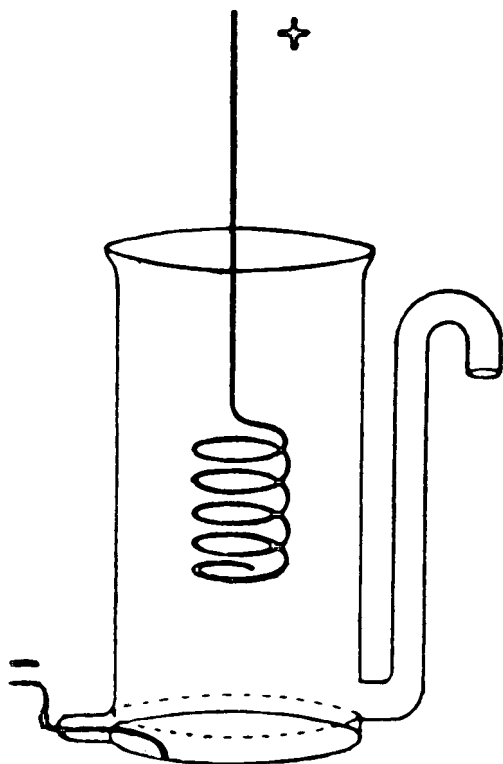

Figure 4. Perkin Cell

Raising the temperature of a solution increases its conductivity and for the same applied voltage may increase the rate of deposition very materially. An increase in temperature may increase the rate of side reactions in the solution and affect the deposition adversely—for instance, from a solution containing nitric acid, it is possible to get excellent deposits of copper on the cathode. However, when the temperature of the solution exceeds 60° C., the oxidation of electrodeposited copper on the cathode by the nitric acid in the solution becomes an important factor and may dissolve the copper as rapidly as it is deposited.

Increasing the temperature will also decrease the overvoltage of hydrogen, iron, nickel, and cobalt. Overvoltage is an excess voltage which must be impressed on an electrode to bring about the deposition of the ion in question over and above the equilibrium voltage which is established by measurement of equilibrium conditions. Overvoltage is very important, as it amounts to almost 0.8 volt for hydrogen on a mercury surface, and consequently permits the deposition in mercury of the more electropositive elements like zinc, even in the presence of relatively large concentrations of hydrogen ion. Platinum covered with platinum black shows no overvoltage to hydrogen. A series of metal surfaces in different conditions will show a progressively greater overvoltage, reaching its maximum with liquid mercury. Iron, nickel, and cobalt are unique among metals in displaying a considerable overvoltage at room temperature. By raising the temperature of an electrolyte to about 90° C. overvoltage can be made to disappear.

Another important means of controlling the deposition of ions

lies in the control that can be exerted over ionic activity by the formation of chemical complexes—for instance, it is not easy in electrolysis to separate considerable quantities of copper and tin present in the same solution. However, McCay (12) has shown that by the use of hydrofluoric acid electrolytes the ionic activity of tin can be so reduced that copper can be cleanly deposited without contamination. Cyanides, oxalates, and tartrates have also been popular for controlling ionic activity, hence the deposition potential making possible the clean separation of one element from another.

Additions are often made to an electrolyte for the purpose of suppressing the discharge of one or another ion at either the cathode or the anode. The addition of nitric acid to solutions from which copper is being deposited serves to prevent the discharge of hydrogen, which tends to cause formation of a loose deposit of copper. The nitrate ion is reduced at the cathode to ammonium ion, and the solution may eventually become alkaline if a "fixed" acid such as sulfuric is not present. When copper and tin are separated from chloride solution by controlled cathode depositions, hydroxylamine hydrochloride is added as an anodic depolarizer to prevent the discharge of chlorine and the consequent attack of the platinum anode. When lead is being determined as the dioxide by deposition on the anode, nitric acid is added in large concentration to the solution to prevent the deposition of lead on the cathode. However, nitrate ion will be reduced at the cathode if hydrogen is the only other cation present in the solution; consequently copper nitrate is often added as a cathode depolarizer. Copper is deposited on the cathode with a consequent improvement in the quality of the lead separation.

It is not always possible to realize theoretical limits in separations. One source of this difficulty may be the occurrence of side reactions which give rise to materials that will attack the cathode (or anode) deposit, making the separation incomplete. Nitrites may be formed in the course of depositing copper from a nitric acid solution. Urea may be added to reduce the nitrites to harmless water and nitrogen.

It is interesting to discover in reviewing the history of electroanalysis, that characteristically the chemists gave very little attention to the electrical phenomena that accompanied the practice of electroanalytical separations. From the time of the invention of electroanalysis by Gibbs in 1864 until Sand started a careful study of the potential of each electrode, almost all the study of analyses was directed to the phenomena within the electrolytic cell. The electricity used for a separation was specified first in terms of kinds of batteries employed, sometimes whether they were fresh or used. Later the gas coulometer came into use to measure current, and finally the importance of voltage became clear from the work of Le Blanc (10) and Freudenberg (5). In 1906 Sand published the first of a series of papers which has opened the way to studying the electroanalytical system as a whole, and the considerable growth of interest in recent years is evidence of recognition of the value implicit in this approach. Mention must first be made of the second important contribution made by O. W. Gibbs—namely, the introduction of the mercury cathode.

MERCURY CATHODE

The mercury electrode was shown to have unique properties as a cathode on which to deposit metals (14). Mercury is one of the more noble and less reactive metals; it forms amalgams with many other metals and possesses a very high overvoltage for hydrogen. Moreover, even when the solubility of certain elements is low in mercury (such as iron) considerable quantities may deposit within the mercury electrode as a separate phase without interfering with its operation. Even when the deposition potential of metals is too high for them to be discharged from aqueous solution in the elementary state, it is often possible to separate them as amalgams because of the lower deposition po-

tential of amalgams. This is particularly true of the alkali and alkaline earth metals. The metals deposited are relatively free of inclusions of electrolyte which are apt to contaminate solid deposits. Because mercury is a liquid, it is free of strains and structural modifications which can shift the potential of an electrode
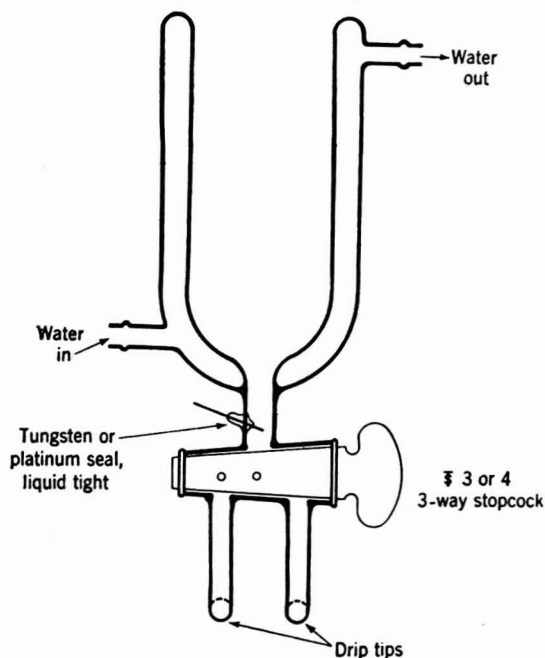

Figure 5. Cell for Mercury Cathode

by a considerable amount. The deposition potentials are actually more nearly reversible. The mercury cathode was studied extensively by E. F. Smith and his co-workers (*21*). It has earned great popularity as a means of removing large amounts of iron or nickel from alloys preparatory to the determination of aluminum, sulfur, and other elements not deposited in the mercury cathode from an acid solution of the alloys.

There are certain serious disadvantages connected with the handling of mercury as an electrode. It does not wet a ceramic container and consequently a globule of mercury is difficult to wash free of electrolyte and to dry without loss after a determination. Typical of the cells used for mercury is the one of fused silica designed by Perkin (Figure 4), from which the electrolyte can be washed by siphoning, and the whole unit placed in an oven to dry.

Hulett (*18*) pointed out that this difficulty could be overcome with an amalgamated platinum crucible and demonstrated high precision analyses of mercury and cadmium compounds. The solubility of platinum in mercury is low, but the mercury wets the crucible and prevents the electrolyte from getting beneath the mercury between it and the container. This idea of Hulett's has been further developed by the use of amalgamated gauze electrodes of platinum or even brass. Sometimes a known weight of mercury is deposited on the electrode simultaneously with the element being determined, such as zinc. Two remaining serious objections to the use of the mercury electrode are its relatively high volatility, which makes appreciable losses by evaporation possible, and the ease with which droplets may be detached. The density of mercury is so great that even minute fragments lost in this way may make a considerable error in a determination.

A more modern sort of mercury cathode designed by Lykken and his co-workers (*8*) appears to have many advantages over its predecessors for compactness and ease of handling. The design

and location of the anode permit high currents to be passed. Losses in weight from the anode are picked up by the cathode and are automatically compensated. The authors discovered an optimum distance between the anode and cathode for the efficient removal of iron from a solution. Increase or decrease of the distance reduced the efficiency. Further developments and studies of this sort should greatly assist more general use of the mercury cathode.

A cell for a mercury cathode, depicted in Figure 5, is designed for the removal of large amounts of metal, say 1 to 5 grams of iron, from a solution in which trace impurities are to be determined. The use of water cooling for such separations has an obvious advantage which does not seem to have been realized until recently, although it has been known for some time that a rise in temperature lowers the overvoltage of hydrogen on mercury. The water-cooled cell naturally permits the use of high currents and vigorous stirring, which tend to raise the temperature of the solution excessively. Vigorous stirring is designed to renew the surface of the mercury as well as to circulate the electrolyte over the cathode surface. The stirring of the mercury keeps the surface free of certain metals (such as platinum, copper, iron, etc.) which, Furman (*6*) reports, have a tendency to lower the overvoltage of hydrogen and hence to make the deposition of certain other metals less complete.
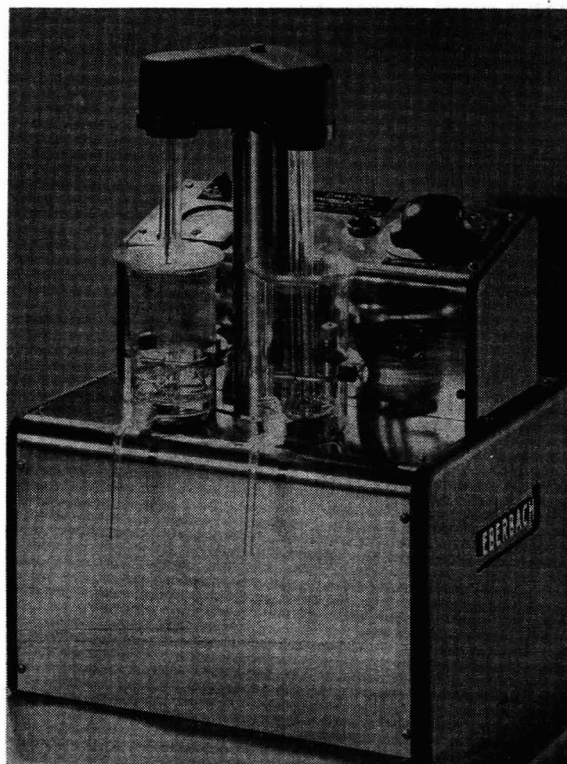

Figure 6. Dyna-Cath Mercury Cathode

The latest advance, recently made at the Battelle Memorial Institute, is an equipment called the Dyna-Cath (Figure 6), marketed by Eberbach and Son Company which sponsored the project. The unit consists of a power supply operating off 60-cycle alternating current lines and supplying to the cells for electrolysis about 16 volts of unfiltered direct current in amounts up to 20 amperes. The mercury cathode holds about 35 ml. of mercury with its surface 8 mm. below the anode. A tube for cooling water is visible just above the anode. The real novelty of this equipment appears to lie in two effects. A magnetic field is imposed on the area between the electrolytes, so that the mercury

and the electrolyte rotate in opposite directions, in effect forming the poles of a direct current motor. Ferromagnetic materials deposited on the surface of the mercury are drawn below the mercury by the magnetic field, causing the surface to be maintained in a fairly clean state.

In recent years advantage has been taken of the reversibility of processes at the mercury electrode, the technique of measuring and controlling deposition potentials, and the laws of Faraday, to devise schemes of coulometric analysis, by which an element like copper is quantitatively deposited in a mercury cathode, with 100% current efficiency under controlled potential. The current required to bring this about is recorded with a coulometer, and the amount of the element that has deposited is easily calculated from its electrochemical equivalent (7). Lingane has successively determined copper and bismuth by this means and has shown that the technique is satisfactory for lead. Even though the deposition potentials of lead and cadmium are only 0.20 volt apart, they can be separated. Lingane has used a silver anode, on which the chloride anion deposits with the formation of silver chloride. The potential of the anode remains virtually constant. The potential of the cathode is controlled automatically. The half-wave potentials observed polarographically can be used to determine the potentials for bringing about these separations.

More recently, Lingane (11) has demonstrated that iodine, bromine, and chlorine can be determined coulometrically at the reversible silver anode, and that separations of iodine from bromine and iodine from chlorine can be made. As has been reported by other investigators, Lingane finds that the bromine-chlorine separation is not satisfactory because of coprecipitation of these two silver halides in certain concentration ranges.

In the earlier types of controlled cathode depositions the course of the analysis must be closely followed with a potentiometer used with a half-cell, in an arrangement of which that shown in a monograph by Diehl is characteristic (4, Figure 1, page 2). Sand's own electrodes were designed so that the outer electrode could then be made cathode or anode, and its potential followed with a calomel, silver chloride, or mercurous sulfate half-cell. The screening was done deliberately to avoid errors in measuring the reversible potential occasioned by stray currents in the solution. The open end of the half-cell is located close to the middle section of the electrode being measured. Stirring is important to maintain close to equilibrium conditions at the electrodes. In controlled potential separations the current falls to a rather small value during the latter part of the analysis; hence the last portion of the element to be removed comes out of the solution slowly. This has probably been an important factor limiting the use of Sand's original method. The automatic devices now becoming available should eliminate this troublesome feature. One of the best of these was described last year by Penther and Pompeo (17).

Possibilities for improving the electrolytic process of analysis seem to lie in further instrumentation. One of the chief difficulties in the successful use of electroanalytical methods lies in the continual change in the composition of the solution during electrolysis. In some instances this is the decomposition of a depolarizer; often it is the change in pH value of the system under electrolysis. It seems reasonable to expect that an automatic titrating device which would maintain the pH at some predetermined level by following it with a glass electrode would be the means of speeding up electrolysis and effecting cleaner separations.

Not only is the hydrogen ion concentration of a solution important, but the presence of other ions in a predetermined state of oxidation may be necessary, as Furman has recently pointed out, where the use of an oxidation-reduction buffer of uranium ions maintains the potential drop at the electrodes in the system automatically, so that certain separations may be conveniently made with a mercury cathode. The antagonistic effects of oxida-

tion at the anode to reduction at the cathode have been demonstrated by *Newton and Furman* (16) by deposition from an ammoniacal copper solution, and by Diehl who has described the interesting effect of tin ions on the deposition of copper. Instrumentally buffering such systems does not appear to be impracticable. While this may seem like a complex sort of system to operate, in instrumentation complexity is often the means toward simplification, as with the introduction of automobiles without clutch pedals, or as Mueller has pointed out, the one-knob superheterodyne radio receiver.

One very simple means of controlling applied potential to a cell is by the application of a limited external potential such as one or more dry cells. Although the total applied voltage may remain the same, the voltage drop at the electrodes may shift in the electrolysis—though, of course, it will never be zero at either electrode, and can never be greater than the applied external voltage. The voltage drop across a cell may be divided into three parts: the voltage drops at each electrode, the voltage drop through the solution sometimes referred to as the *IR* drop, or the current × resistance drop through the solution. This last is small when the electrodes are large, the distances are small, and the electrolytes used are strong, as is almost always the case.

Internal Electrolysis. Another means of controlling the cathode potential is by the use of the technique called internal electrolysis. Briefly, the solution from which a separation is to be made becomes the electrolyte of a battery. A platinum cathode is inserted in the solution and is externally connected by an electric circuit (which may be a simple copper wire) to an electrode of baser metal. The choice of this metal will determine the voltage to be applied to the cathode.

Zinc, magnesium, lead, and mercury amalgams have all been successfully used. The base metal is commonly surrounded by a porous shell (such as an Alundum thimble) containing its own electrolyte—commonly a salt of the base metal. A slight hydrostatic head is maintained to prevent the solution under analysis from entering this chamber.

Internal electrolysis eliminates the use of a platinum anode, and has been extensively investigated for this reason by Schleicher in recent years. One interesting commercial application of this method has been in the analysis of lead cable sheath. Copper and bismuth which are to be determined are deposited together on a platinum electrode from a solution of the cable lead. Pure lead free of copper and bismuth is used as anode and, by this relatively simple device, small amounts of copper and bismuth are cleanly separated from large amounts of lead.

Contamination. The tabulation of processes of electroanalysis at the beginning of this paper shows different degrees of separation. Reference has been made to incomplete separation from incomplete deposition. Separations are also impaired by the presence of unwanted impurities in the material separated. A not unfamiliar type of contamination was reported last year by Mac-Nevin and Tuthill (13) in the separation of rhodium from iridium by controlled cathode potential techniques. After separation it was necessary to reduce the rhodium deposit in hydrogen to remove oxygen from the cathode deposit. This same unexpected occurrence of oxygen on the cathode has been observed with copper and other cathode deposits. Cathode copper may also be contaminated by appreciable amounts of cuprous chloride if chloride ions are present in the solution from which deposition is made.

The contamination of deposits with foreign materials is a serious handicap in electroseparations and one which has not always been thoroughly studied by investigators. It is not enough to assume that because a precipitated metal turns out to have the weight, within experimental error, that was anticipated, the clean-cut separation of the metal has been proved.

Highly specialized separation is possible with electrolytic techniques for those elements forming volatile hydrides— arsenic, germanium, and antimony. Arsenic hydride is formed

at the cathode in an acid solution, germanium is formed in an alkaline solution, and the two may be separated by this difference. Antimony forms unstable stibine, which must be quickly swept from the solution with an auxiliary stream of hydrogen to prevent decomposition. This electrolytic method of producing arsine to detect arsenic has been popular in England for many years.

Separations of an analytical character may be carried out by starting with solid materials as well as solutions. To determine the thickness of a coating or plating of tin, electrosolution methods have been used (7). The piece to be examined is made anode, the time of electrolysis and the current density are correlated to the thickness of the plating to be measured, and the thickness of unknown pieces can thus be measured. The process is often referred to as stripping.

Another type of analysis important in metallurgy is the determination of nonmetallic inclusions in metals by anodic solution of the metal piece. Cementite, iron oxides, aluminum oxide, graphite, silica, and many other nonmetallic materials are left behind when the metal is dissolved. The inclusions are caught on a membrane and subjected to further analytical procedures. The greatest advantage of electrosolution methods for this sort of work lies in the control of oxidation potentials possible at the anode. One electrolyte devised by Klinger contains potassium bromide, potassium iodide, and sodium citrate. The iodide ion serves to prevent the release of oxygen at the anode, and hence the oxidation of such materials as cementite. The citrates serve to hold the iron in a solution which gradually becomes basic. Substances not present in the metal as inclusions may precipitate at the anode—for instance, copper present in the amount of about 0.8% is precipitated completely as cuprous iodide and can be collected with the inclusions from the steel. A further study of how this kind of separation may be applied to other constituents of metals might seem to be worth while.

EFFICIENCY OF SEPARATION

Before reviewing briefly the disadvantages contrasted with the advantages of electroanalytical separations, one should say a word about reliability. Most separations are highly specific, but it is not always easy to duplicate the work reported by other investigators. The behavior of deposits at the electrodes seems to be influenced by many small factors, many of which have not yet been revealed. Electroseparations of zinc, iron, and cobalt are often not very satisfactory, because of the difficulties of reproducing one's own as well as another's results. Copper separations must number hundreds of thousands daily, but even experienced workers (19) at the Bureau of Standards reported a few years ago that the copper depositions were often incomplete. It was finally attributed to the absence of a trace of chloride, formerly present as an impurity in the reagent acids. Quixotic behavior of this kind is apt to be aggravating to a chemist who must depend on reliability.

Disadvantages. Incomplete separations. Nickel and cobalt, copper and silver are so often determined together commercially by electrolytic means that a report for nickel is understood to include cobalt and a report for copper is understood to include silver.

Incomplete separation in the determination of cobalt, cadmium, and even copper. Precipitations are incomplete and small amounts of metal must be separately recovered from the solution.

Only a limited number of elements lend themselves to separation and determination.

Results are not reproducible. Even experienced analysts may have difficulty in getting complete precipitation of iron with a mercury cathode for reasons difficult to assign. Copper sometimes fails to precipitate. Determinations of iron and zinc are so unreliable that they are not often used.

Deposits are impure. Chlorides, oxides, sulfides, and inclusions of electrolyte are all apt to turn up in the deposit.

Advantages. Speed of precipitation. If large electrodes are used, the volume of the solution is kept small, the stirring is

vigorous, and the current is high, precipitation can often be made in less than a half hour.

The solution is not contaminated with impurities. The electric current is the only truly chemically pure reagent that the chemist has.

Small amounts of an element may be determined. Electrodepositions have been successfully applied on a micro scale for many years.

Trace elements may be collected or concentrated. Lead and mercury are commonly determined in urine by electrolysis; copper and other metals may be collected from large volumes of solution by circulating the electrolyte over a small electrode.

Automatic operation without supervision. Analyses are commonly run by allowing the precipitation to occur overnight. Other types of equipment with automatic potential control at the electrodes have been discussed.

Large amounts of material may be handled. It is not uncommon to assay copper by using 5 or 10 grams of the copper sample. When trace elements are to be determined, as in the analysis of the lead cable sheath, large samples of material may be dissolved and the traces precipitated from them by internal electroanalysis.

Use over a wide concentration range. Reference has been made to the determination of copper present in trace quantities and in the assay of copper. There is possibly no method of separation and determination which lends itself to use over such a wide concentration range.

Limited coprecipitation. Large amounts of copper can be separated from small amounts of impurities, even though it is the copper which is precipitated.

Simultaneous separation of two elements. The simultaneous determination of copper and lead in brasses and bronzes is a very common laboratory determination. This is one reason for the great popularity of this determination.

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Separation of Ultramicro Quantities of Elements by Electrodeposition

L. B. ROGERS

Laboratory for Nuclear Science and Engineering, Massachusetts Institute of Technology, Cambridge 39, Mass.

ELECTRODEPOSITION is a promising method for separation and concentration which, unlike coprecipitation, extraction, and ion exchange, has been the subject of comparatively few studies at the submicrogram level. In most studies the investigator has been concerned with the separation of trace amounts of radioactive elements either for studying fundamental electrochemical behavior of a radioactive element existing only in trace amounts or for obtaining a carrier-free preparation of a radioactive nuclide for use as a tracer. However, the radiochemist has also found electrodeposition to be a useful method for preparing films of an element so thin that self-absorption of alpha-particles (24) or of weak beta-radiation (2) is negligible. Although persons working outside the field of radioactivity have shown little interest in the electrodeposition of traces, the techniques for handling submicrogram quantities of elements are useful for concentrating a trace element prior to its analysis or for freeing a solution from traces of impurities.

In any discussion of analysis at the submicrogram level, one must consider both the situation in which the sample consists of a large volume of extremely dilute solution and that in which the sample is a very small volume of moderately concentrated solution. For example, in 100 ml. of water, 1 microgram of silver produces a 10^{-7} M solution, whereas in 0.01 ml. the solution is 10^{-3} M. In view of the fact that a modern text (1) and a recent review (14) on microchemistry failed to mention any technique for carrying out an electrodeposition using less than 0.5 ml. of sample, and a new book on ultramicroanalysis (11) failed to mention electrodeposition as a possible separation method, most of the following discussion is necessarily devoted to studies involving large volumes of dilute solutions. Haissinsky (9), in his excellent review on the electrochemistry of extremely dilute solutions, devoted most of his efforts to the fundamental aspects of the problem; the present paper emphasizes the practical aspects of interest to the analytical chemist.

The practical considerations involved in devising a quantitative electroseparation of submicrogram amounts of elements are discussed.

SOURCES OF ERROR

Contamination. Anyone who has worked on a microgram scale using dithizone or a similar reagent is well aware of the difficulty of avoiding serious contamination of a sample with the same or an interfering element which may be present as an impurity, either in the reagents or on the walls of the equipment with which the solution comes in contact. Obviously, these difficulties become increasingly serious as the amount of element in the sample is decreased. As in work with dithizone, it is necessary to clean every piece of equipment scrupulously, preferably just before it is used. Although doubly or triply distilled water is usually sufficiently pure for rinsing equipment, its use in preparing a solution does not ensure freedom from serious contamination. Almost without exception it has been found necessary to subject solutions of reagents to electrolysis prior to the introduction of the sample. Such a procedure allows one to use ordinary distilled water and to eliminate contamination simultaneously from both the reagent and the solvent.

More spectacular, perhaps, is the fact that dust normally present in laboratory air can be a serious source of contamination (10, 17, 18). Contamination is particularly difficult to avoid if macro amounts of the element in question have in the past been handled in the same room. Frequent mopping of the laboratory floor and wiping of the desks and shelves are necessary, and it is helpful to provide protective covering for the entire electrolytic setup because, for the sake of simplicity, electrolyses are usually carried out in open vessels.

Sorption. Unfortunately, the sources of error which lead to low results are even more numerous and distinctive than those described for positive errors. The most serious and general error arises from sorption, particularly by glass surfaces, because all of a trace element can easily and quickly be removed from a solution by this means. This introduces a serious problem in storing and handling standard solutions of trace concentrations. Furthermore, the sorption process may be sufficiently strong to compete successfully with electrodeposition and thereby to prevent complete deposition. Therefore, it is doubly desirable to coat all containers such as reagent bottles, electrolysis vessels, stirrers, and electrolytic bridges in order to minimize both losses from sorption and positive errors due to contamination. As waxes and lacquers differ in their effectiveness (3, 22), depending upon the ions that are involved, the best coating for a particular situation has to be determined by trial and error. Ceresine wax has been found the most generally applicable coating.

Appreciable sorption may occur at the ends of salt bridges which are plugged with agar, glass wool, or filter paper, but the losses are usually of the order of 5 to 10% and can be corrected for satisfactorily by running appropriate blanks. Fortunately, losses from sorption can be decreased or eliminated if the element is deposited from a solution of a stable complex ion. Thus, in one study with silver the most serious losses were encountered in working with nitrate and perchlorate; small losses, with ammonia; and undetectable losses, with cyanide (8).

Radiocolloid Formation. Like sorption, radiocolloid formation has long plagued the radiochemist. Such formation of insoluble compounds which remain suspended in solution may be considered simply as another type of competing reaction. To date, positive evidence in electrochemical studies for deviations from expected behavior which can be traced to radiocolloid formation is scanty, so one can only point to it as a possible source of difficulty in future studies.

Solubility. If one is interested in the deposition of a compound, such as an oxide, rather than an element, quantitative deposition from extremely dilute solutions may be impossible because of the solubility of the compound. Such a limitation has been noted in studies dealing with the dioxides of manganese (3) and technetium (19). Fortunately, recovery by electrolytic codeposition appears to be feasible.

Even if an element or a compound can be deposited quantitatively on the electrode, one is faced with the problem of minimizing dissolution of the deposit while it is being washed. In handling submicrogram amounts of material, it is not at all unusual for the average depth of a deposit to be less than a monolayer, so that a fraction of a second is enough for most of the

deposit to redissolve unless the required potential is maintained across the electrodes. In the deposition of silver, a relatively noble element, upon platinum electrodes, losses up to 20% were sustained if distilled water (8) or an organic solvent (7) were used as the wash liquid, even if the electrical circuit was not broken during the process. Losses can be decreased somewhat by making the potential of the cathode much more negative immediately before starting to wash (22). In the light of these facts an electrolyte was added to the wash liquid to decrease the losses by facilitating maintenance of a suitable potential. It is important to note, however, that silver, after being deposited quantitatively from a cyanide solution, dissolved to the extent of 5 to 10% when washed with fresh portions of the same cyanide solution, even though control of the potential appeared to be satisfactory. Substitution of sodium nitrate or sodium perchlorate for the sodium cyanide in the wash solution reduced the losses to less than 0.5% (8). These experiments emphasize the desirability of using in the wash solution an electrolyte which has little or no tendency to dissolve the deposit by complex formation.

Assuming that a deposition and washing have been carried out quantitatively, one is then faced with the problem of removing the deposit quantitatively from the electrode prior to the determination of the element by chemical methods. The worst situation is represented by the classical case of polonium deposited on platinum, where complete dissolution of the deposit can be effected only by dissolving the entire electrode. On the other hand, it is not at all unusual to find that 5 to 10% of an element cannot be removed from an "inert" electrode such as platinum even by using solutions of strong complexes combined with reversal of the electrode potential. However, the amount retained by the electrode, in the case of silver deposited upon platinum, is usually decreased by continued use of the electrode (3). This behavior may be the result of removing "loose" electrode material during the process of repeated cleaning, which might, at the same time, decrease the number of pores and cracks in the surface. Alternatively, one may consider that the pores and cracks become saturated with the particular element after a number of electrolyses, so that further deposition (and exchange) is slowed down or prevented. Neither idea by itself appears to be entirely satisfactory as an explanation.

CONTROL OF ELECTRODE POTENTIAL

In recent years analytical chemists have begun to appreciate the fact that electroseparations can be improved by careful selection and control of the electrode potential. Because of the dearth of information on the subject, it was necessary to determine the optimum potential by trial and error until Lingane (15) recently demonstrated the feasibility of using polarographic data obtained with a dropping mercury electrode to obtain data for electrolytic separations to be performed with a mercury cathode. The idea has been extended by others to separations using solid electrodes (8). The fact that polarograms indicate only relative rates of deposition of two or more elements is usually not a serious handicap, but if equilibrium conditions are approached, it appears necessary for best results to consider the relative volumes of the aqueous solution and of the mercury as well as the overvoltage and reversibility of the reactions (20).

Unfortunately, if the electrolysis is to be carried out with a solid electrode and if the amount of deposit is insufficient to form a monolayer, there is no satisfactory method for predicting the potential at which to carry out the electrolysis. A difference of nearly 0.5 volt may be found between the deposition behavior of a fractional monolayer of a deposit and a multilayer "macro" deposit (22). However, a smooth transition in behavior has been observed in one study by examining a series of solutions differing only in the initial concentration of silver ion (3). Likewise, the duration of the electrolysis may be a factor to consider (5, 22). As Haissinsky pointed out (9), there is no real reason for ex-

pecting that predictions based upon the Nernst equation should describe the deposition behavior of a trace upon an inert electrode. Haissinsky and his co-workers (4–6) and others (13, 22) have demonstrated conclusively that the electrode material profoundly affects the extent of deposition at a particular potential. The usefulness of the Nernst equation appears to be limited to providing a reference point from which deviations can be measured in describing the behavior of traces deposited upon solid electrodes (23). Finally, the deposition behavior of a trace element may also be profoundly altered by codeposition of a second element, particularly by "macro" amounts of the latter (20, 21). Thus, the selection of a potential for a large number of possible separations must continue to be determined by trial and error.

Although it is usually possible to maintain the desired potential automatically within a few millivolts by means of specially designed instruments, in exceptional cases regulators may respond too slowly to prevent serious broadening of the limits of control (12). The loss of control appears to occur in a region where gas evolution is just beginning to take place at an appreciable rate. The region of potential at which this phenomenon takes place appears to vary with the previous treatment of the electrode as well as with the potential and the electrode material.

STUDIES USING ULTRAMICRO VOLUMES

During the past 8 months, work at the Massachusetts Institute of Technology has been directed toward the development of a procedure which will allow analyses to be made using a sample of 5μl. made up to a total volume of 10μl. (16). By combining electrolysis at a controlled potential with coulometric measurement of the deposit, it is possible to minimize interfering elements and to determine within about $\pm 10\%$ amounts of silver of the order of 5×10^{-9} gram. The technique can detect amounts slightly less than 10^{-10} gram.

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Role of Extraction in Analytical Chemistry

GEORGE H. MORRISON

U. S. Atomic Energy Commission and Rutgers University, New Brunswick, N. J.

Analytical liquid-liquid extractions fall largely into three classes: inorganic, organometallic, and organic. Laboratory apparatus and general techniques, including batch and continuous procedures, are reviewed. Many inorganic extractions are dependent upon the formation of undissociated complex acids which are soluble in organic solvents. The salting-out effect produced by the presence of cations plays an important role in extraction; in general, the cations of higher valency are more effective. Several simplified theoretical relationships concerning organometallic extractions are presented which emphasize the importance of pH and concentration of reagent in metal extraction. Improved countercurrent distribution instruments permit separation or estimation of closely related organic substances, and are applicable to many complex organic or biochemical problems.

AN EXAMINATION of the development of analytical chemistry during the past few decades reveals an increase in popularity of such fields of analysis as chromatography, ion exchange, and electrodepositions. This trend is easily explained when one considers the increasing need for methods of separating complex materials.

Liquid-liquid solvent extraction has been known for over one hundred years as a method of separation in analytical procedures; however, it is only recently that this technique has gained prominence equaling that of the more important methods. The phenomenon is based upon the fact that if a substance is dissolved in a system of two immiscible or slightly miscible liquids, the substance is distributed between the two layers in a definite manner (*2*). The most important factor in this distribution appears to be the relative concentrations of the solute in both solvents and is usually expressed as the distribution or partition coefficient—i.e., the ratio of the activity or concentration in one phase to that in the other (*29*). In the ideal case, the solute distributes itself between the two liquid phases in the ratio of its solubilities in the two phases. This relationship is in turn fundamentally dependent upon other factors such as the molecular species extracted, the presence of certain salts, and acid concentration.

Figure 1. Batch Microextractor

Although a study of the distribution behavior of pure substances is one approach to the solution of problems in analytical extractions, one should bear in mind the effects produced by the presence of all the components in a complex mixture. Consequently, much of the information obtained so far on analytical extractions has been derived from empirical studies of nonideal solutions.

In analytical chemistry, extraction is applied primarily as a means of separation. By measuring the radioactivity, optical density, or some other physical property of the solute in the organic layer, it is sometimes possible to make use of the organic layer in a direct determination. The more common procedure, however, is to separate the extracted solute from the organic layer, either by evaporating to dryness or by back-extracting the solute into water. Standard analytical procedures may then be applied.

The use of extraction in quantitative analytical work requires that there be a preferential quantitative separation. The problem of extraction, then, consists in determining the conditions which result in extraction of certain elements, and, equally important, determining substances which will not extract under these conditions.

Analytical extractions appear to fall largely into three general classes: inorganic, organometallic, and organic and biochemical. Preparatory to a more detailed treatment of these main types, a discussion of the general techniques and apparatus used in this method of analytical separation follows.

APPARATUS AND GENERAL TECHNIQUES

In laboratory work there are three general types of liquid-liquid extractions. The simplest is batch extraction, which consists of extracting the solute from one immiscible layer into another by simply shaking the two layers until equilibrium is attained. The layers are allowed to settle and are separated. Discontinuous countercurrent distribution extraction, which permits direct application of the binomial expansion in order to interpret the results in a quantitative fashion, is the second general type, and essentially performs many individual extractions rapidly and in sequence. The third type, continuous extraction, makes use of a continuous flow of immiscible solvent through the solution. The spent solvent is purified and recycled by distillation.

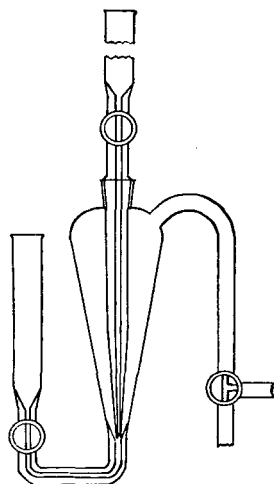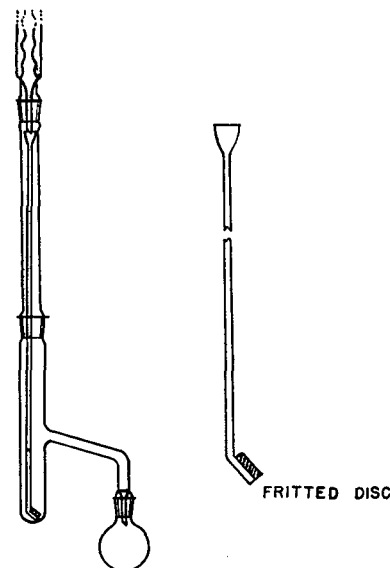Batch extractions may be used to good advantage

Figure 2. Continuous Extractor for Use with Solvent Lighter Than Water

when the distribution coefficient is large, for in such cases a few extractions will effect quantitative separation. The usual apparatus for a batch extraction is a separatory funnel. In extracting from one liquid into a lighter liquid it is necessary, when using a separatory funnel, to remove the heavier liquid from the funnel after each extraction before removing the extracting solvent. Kirk and Danielson (21) avoid this double removal by means of the apparatus shown in Figure 1. This extractor was designed for working with small volumes, but the design could probably be applied to larger volumes.

Discontinuous countercurrent distribution extractors are particularly useful in the separation of substances whose distribution coefficients are of the same order of magnitude and consequently have found greatest application in the field of organic and biochemical separations (33). A series of separatory funnels may be used for this technique; however, certain special devices are more convenient (5, 6).

Continuous extractions are used when the distribution coefficient is relatively small, so that a large number of batch extractions would normally be necessary to effect quantitative separation. Most continuous extraction devices operate on the same general principle, which consists of distilling the extracting solvent from a boiler flask and condensing it and passing it through the solution being extracted. The extracting liquid separates out and flows back into the receiving flask, where it is again evaporated and recycled while the extracted solute remains in the receiving flask. As the extracting solvent passes through the solution fritted glass disks, small orifices, baffles, or stirrers may be used to bring the two immiscible layers in closer contact. Indeed, the efficiency of any continuous extraction apparatus depends greatly upon area of contact developed between the two liquids.

Figure 3. Continuous Extractor for Use with Solvent Heavier Than Water

Figure 2 is a modified tall form of Friedrich extractor designed by Heberling (15) and is used for extraction with a solvent lighter than the solution being stripped. This apparatus is particularly useful for the ether extraction of aqueous solutions of inorganic substances. With solvents heavier than the solution being treated, the extractor in Figure 3 may be used (30). One type of extractor may be converted to the other simply by changing the tube inside the jacket.

An auxiliary technique used with batch extractions to effect quantitative separations of elements is that of washing. The combined organic phases from several extractions of the original aqueous phase contain practically all of the element desired and possibly some of the impurities that have been extracted to a much smaller extent, depending upon their relative distribution coefficients. This combined organic phase, when shaken with one or more small portions of a fresh aqueous phase containing the optimum acid concentration, salting agent, etc., will result in a redistribution of the impurities, as well as the major component, between the two phases. Under optimum conditions most of the element desired will remain in the organic layer; however, the bulk of the impurities will be back-extracted to the fresh aqueous layer. This technique is analogous in many respects to the washing step in a gravimetric precipitation procedure. With the proper conditions most of the impurities can be removed by this washing technique with negligible loss of the main component, thereby resulting in a selective separation.

Many times special organic solvents do not lend themselves to repeated distillations. Certain treatments involving substantial losses may be prohibitive. A simple technique of "stripping" the organic phase of the extracted material may be effected by washing with a fresh aqueous phase containing the proper reagents, thereby causing the extracted material to favor the aqueous portion. Several of these stripping treatments, using relatively small aliquots, should result in quantitative removal of the extract from the organic phase, thereby permitting it to be recycled again. Hixson and Miller (17) suggest the use of this technique in industrial extractions of metals where the cost of organic solvents is a determining factor.

The use of extraction techniques in spot test analysis offers a means of separating an ion from its interferences which might prove valuable in a manner similar to the use of masking agents. West and Carlton (37) have devised an extraction pipet, prepared from a capillary droper pipet. In practice the extraction involves the addition of a few drops of extractant to one or more drops of the test solution. Mixing is accomplished by drawing the liquids into the pipet and then expelling them, repeating the procedure several times, quickly. The organic phase may then be evaporated and analyzed by conventional spot test methods.

INORGANIC EXTRACTIONS

The majority of the extractions of this type involve the extraction of a metal salt from an acid solution into an immiscible organic solvent. High acid concentration has been shown to be a dominant factor in many systems, and in many instances an undissociated complex acid formed by the metal salt and the acid is the species responsible for extraction into the organic phase. In the case of iron, one of the most studied of the extraction systems, the formation of chloroferric acid ($HFeCl_4$), the extracted species, excluding solvation, is particularly favored at an initial hydrochloric acid concentration of 6 formal, using diethyl ether as the extracting solvent (8).

Furman and Morrison (12) have shown that if part of the chloride ion concentration involved in the process of formation of chloroferric acid is supplied as a soluble chloride salt, varying degrees of extraction are effected, depending upon the nature of the cation used. In general, at equal chloride concentrations, the cations of higher valency are more effective, as would be expected according to salting-out theory (7). This effect is illustrated in Tables I and II. In the absence of added hydrochloric acid, using aluminum chloride as a salting agent, the iron does distribute slightly. This effect may be explained by dissociation of the hydrated aluminum ions $[Al(H_2O)_6^{+++}]$ to furnish the needed

Table I. Effect of Ammonium Chloride and Hydrochloric Acid on Ferric Chloride Extraction Using Diethyl Ether

Chloride Concentration, Moles/Liter		Distribution Coefficient, $C_{org.}/C_{aq.}$	% Extracted
NH_4Cl	HCl		
...	5.0	17.6	94.6
2.5	2.5	0.376	26.6
4.9	0.1 [a]	...	...
5.0	...	...	...

[a] 1 mole of HCl present for every mole of Fe.

Table II. Effect of Aluminum Chloride and Hydrochloric Acid on Ferric Chloride Extraction Using Diethyl Ether

Chloride Concentration, Moles/Liter		Distribution Coefficient, $C_{org.}/C_{aq.}$	% Extracted
$AlCl_3$	HCl [a]		
...	5.0	17.6	94.6
2.5	2.5	14.0	93.3
4.9	0.1	0.196	16.4
5.0	...	0.006	0.6
5.0	1.0	33.0	97.1
4.0	2.0	66.1	98.4
3.0	3.0	116.	99.2

[a] Initial HCl concentration of 6 M gives optimum extraction.

protons. At a total chloride ion concentration of 6 molar, various combinations of acid and salt appear to be equally effective in attaining almost complete extraction.

This salting-out effect may be explained in part by the pronounced effect of added salt on the activity of the distributing species. Similarly, one of the primary factors in salting out is a characteristic constancy of binding of a part of the water by some ions, the extent of which is directly proportional to the number of ions. The bound water is probably removed as a shell of oriented water dipoles around the ion and thus becomes unavailable as solvent molecules in which the undissociated chloroferric acid could be dispersed.
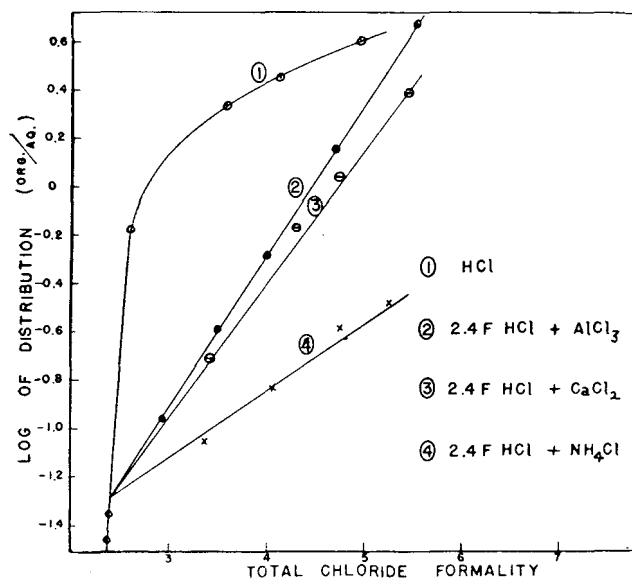
Figure 4. Effect of Salting Agents on Extraction of Molybdenum

① HCl

② 2.4 F HCl + AlCl₃

③ 2.4 F HCl + CaCl₂

④ 2.4 F HCl + NH₄Cl

It has been observed for some time that the distribution ratio of iron between aqueous solutions and an organic layer varies with total iron concentration. Nachtrieb and Fryxell (27) explain this anomaly by suggesting a self-salting-out effect by the iron, which is consistent with the above study. A similar study on the distribution of gallium ($HGaCl_4$) reveals the same effect (28).

Because the analytical chemist is confronted with the separation of inorganic substances present in a particular anionic medium, these inorganic extractions are so arranged in this discussion. In extractions performed in the course of an analytical procedure, relatively large amounts of certain foreign cations, as well as the cation being extracted, act as salting agents and consequently enhance the separation.

Among recent studies on extractions in the chloride system is the extraction of antimonic chloride from hydrochloric acid solutions by Edwards and Voigt (9). Sb^V can be quantitatively separated from Sb^{III} by this method. Garwin and Hixon (13) have succeeded in separating cobalt and nickel by extraction with capryl alcohol from solutions of hydrochloric acid or calcium chloride. An investigation of the effect of salting agents on the extraction of molybdenum from chloride solutions by Morrison and Taylor (26) further substantiates the important role of the higher valent cations. This effect is illustrated in Figure 4.

In the bromide system, conditions for the extraction of bromoauric acid into various organic solvents have been determined by McBryde and Yoe (23), who also studied the behavior of ferric bromide and of the platinum metals. Undoubtedly there are many possibilities for extractions in this system that are not particularly effective in the chloride system.

Extraction from nitrate solutions has resulted in a method for

the removal of cerium (36). The high degree of extraction by butyl phosphate over a wide range of conditions suggests the formation of a compound between the solvent and cerium(IV) nitrate. Templeton, Rothschild, and Hall (35) have investigated the distribution of thorium nitrate between water and certain esters and have proposed an explanation of the nature of the distribution equilibrium. The solubility of uranyl nitrate in ether has been used for years for the separation of uranium from many elements (31). Recently, however, Hecht and Grünwald (16) have used ammonium nitrate as a salting agent to effect complete separation of uranium in the analysis of ores, and Rodden (32) has described a procedure for the continuous extraction of uranyl nitrate using ammonium nitrate.

The insolubility of the perchlorates of the alkali metals in various organic solvents has furnished a convenient method for the separation and determination of potassium (38). Various organic solvents were examined and ethyl acetate appears to be one of the best, the solubility of potassium perchlorate being least and that of sodium perchlorate greatest. The fact that various metal perchlorates are soluble in organic solvents presents many possibilities for future study. Solid extractions have similarly been used to separate calcium and magnesium sulfates (34).
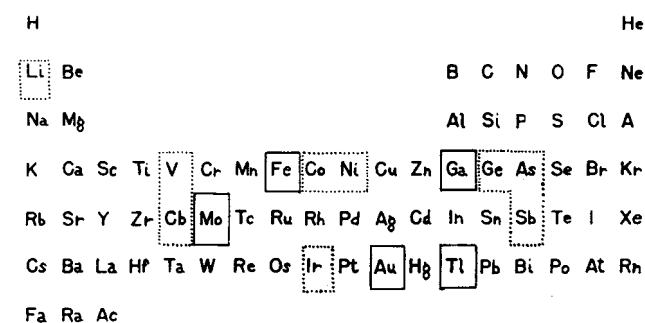
Figure 5. Elements Extracted from Chloride Solutions
Solid blocks. Complete or good extraction
Broken blocks. Fair extraction

A characteristic property of heteropoly acids is their solubility in organic solvents. Thus, the possibility presents itself of effecting inorganic separations by the formation of a complex acid of this type, followed by extraction. A number of elements are capable of forming this type of molecule, and the method developed by Berenblum and Chain (1) for phosphorus, based on
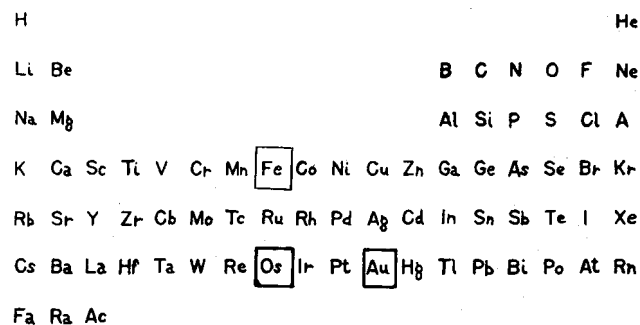

Figure 6. Elements Extracted from Bromide Solutions

H　　　　　　　　　　　　　　　　　　　　　　　　　He

Li Be　　　　　　　　　　　　　　　B C N O F Ne

Na Mg　　　　　　　　　　　　　　Al Si P S Cl A

K Ca Sc Ti V Cr Mn Fe Co Ni Cu Zn Ga Ge As Se Br Kr

Rb Sr Y Zr Cb Mo Tc Ru Rh Pd Ag Cd In Sn Sb Te I Xe

Cs Ba La Hf Ta W Re Os Ir Pt Au Hg Tl Pb Bi Po At Rn

Fa Ra Ac

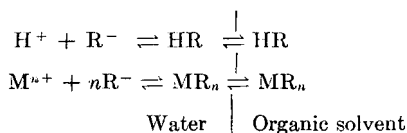Ce Pr Nd Pm Sm Eu Gd Tb Dy Ho Er Tm Yb Lu

Th Pa U Np Pu Am Cm 97 98

Figure 7. Elements Extracted from Nitrate Solutions

the extraction of phosphomolybdic acid, is an example of this class of inorganic extractions.

Figures 5, 6, 7, and 8 indicate most of the elements that have already been extracted into organic solvents under various conditions, using a particular anionic system. By the proper choice of acid concentration, salting agents, organic solvents, valence state, etc., separations may be further effected within any one system.

ORGANOMETALLIC EXTRACTIONS

The separation of metals in the form of organometallic complexes from aqueous solutions is based on the preferential solubility of the chelate compounds in a particular immiscible organic solvent. When, therefore, an aqueous solution of a cation, M^{n+}, is shaken up with a solution of the organic reagent, HR, in a solvent immiscible with water, the following equilibria are in operation:

$$H^+ + R^- \rightleftharpoons HR \rightleftharpoons HR$$

$$M^{n+} + nR^- \rightleftharpoons MR_n \rightleftharpoons MR_n$$

Water | Organic solvent

H　　　　　　　　　　　　　　　　　　　　　　　　　He

Li Be　　　　　　　　　　　　　　　B C N O F Ne

Na Mg　　　　　　　　　　　　　　Al Si P S Cl A

K Ca Sc Ti V Cr Mn Fe Co Ni Cu Zn Ga Ge As Se Br Kr

Rb Sr Y Zr Cb Mo Tc Ru Rh Pd Ag Cd In Sn Sb Te I Xe

Cs Ba La Hf Ta W Re Os Ir Pt Au Hg Tl Pb Bi Po At Rn

Fa Ra Ac

Ce Pr Nd Pm Sm Eu Gd Tb Dy Ho Er Tm Yb Lu

Th Pa U Np Pu Am Cm 97 98

Figure 8. Metal Perchlorates Insoluble in Ethyl Acetate

A very comprehensive quantitative treatment of general partition equilibria by Irving and Williams (20) relates the amount of a metal extracted to the concentration of reagent, the pH of the aqueous phase, and the dissociation constants and partition coefficients of the various molecular species involved. Assuming that the reagent and its metal complex, MR_n, exist in both water and the organic solvent as unassociated molecules, and disregarding solvation, the following four relationships may be used

in deriving a general expression for the extractability—i.e., the ratio of the amount of metal extracted as complex into the organic phase to that remaining in the aqueous phase:

The instability constant of the complex:

$$K_c = \frac{[M^{n+}]_w[R^-]_w}{[MR_n]_w} \tag{2}$$

The Brønsted dissociation constant of the reagent:

$$K_r = \frac{[H^+]^n[R^-]_w}{[HR]_w} \tag{3}$$

Partition coefficients:

$$p_c = \frac{[MR_n]_w}{[MR_n]_o} \tag{4}$$
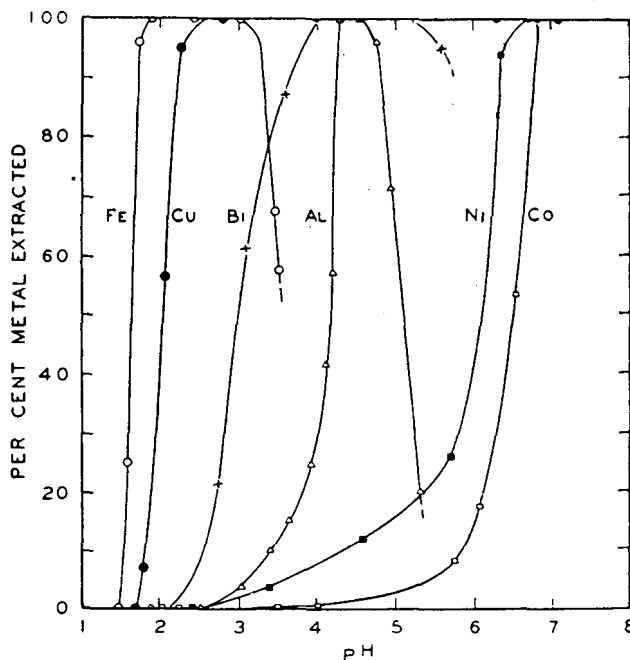
and

$$p_r = \frac{[HR]_w}{[HR]_o} \tag{5}$$

Figure 9. Effect of pH upon Metal Extraction

Subscripts c and r refer to the complex and reagent, and w and o refer to the aqueous and organic phase, respectively. From Equations 2, 3, 4, and 5 the following approximate expression for the extractability, E, is obtained:

$$E = K \left(\frac{[HR]_o}{[H^+]_w}\right)^n \tag{6}$$

where

$$K = \frac{(K_r p_r)^n}{K_c p_c} \tag{7}$$

Kolthoff and Sandell (22) arrive at an expression of this form in a discussion of the extraction of zinc by dithizone, and a theoretical treatment of the cupferrate system by Furman, Mason, and Pekola (11) similarly shows the important role of acidity and concentration of reagent in determining the efficiency of the extraction process for separation purposes. Figure 9, based on the data of Moeller (24), graphically shows this pH dependence of metal extraction in the oxinate system.

A majority of the organic reagents in general analytical use

have been shown to be rather selective (10); the extraction technique is a very convenient device for effecting further selectivity. As indicated above, adjustment of the pH of the solution to be extracted is of prime importance. The addition of certain masking agents to tie up interfering metals is also a valuable modification, and in some cases alteration of the valence of interfering metals may be resorted to.

Brief mention of several of the more recent studies of the extraction of organometallic complexes follows; this treatment is by no means complete. As regards the oxinate system, Gentry and Sherrington (14) have investigated the pH conditions for the complete extraction of a number of metals from aqueous solutions by means of a chloroform solution of 8-quinolinol (8-hydroxyquinoline). It is shown that the extraction of 8-hydroxyquinolates of the heavy metals is a useful method of purifying solutions of many reagents used in trace analysis.

A comprehensive study of the extraction characteristics of gallium and thallium(III) oxinates by Moeller and Cohen (25) reveals the optimum conditions for their extraction. Gallium can be completely removed; thallium is incompletely extracted from the aqueous layer. Moeller (24) has previously studied the extraction and colorimetric estimation of a number of metal oxinates.

Figure 11. Oxinate Extractions

mixtures that occur in nature, for the isolation of dissolved substances from solutions, and for the removal of soluble impurities from mixtures. The nature of many organic molecules provides for greater applicability of the extractive technique, as predicted by the rules of solubility, and consequently, there are numerous examples of the use of this technique in many varied problems in organic and biochemistry.

As in the case of inorganic extractions, one can resort to modification of organic molecules to form species which distribute more favorably. In some instances, separation may be effected by converting certain functional groups into different forms, thereby producing species which are very soluble in water and insoluble in the organic phase. Thus, carboxylic and sulfonic acids and phenols can be converted to their sodium salts, which are very soluble in water and insoluble in benzene; amines can be converted to hydrochlorides; and aldehydes and ketones may be converted to the bisulfite addition products which are similarly soluble in water and insoluble in certain organic solvents.

Other techniques for improving certain organic extractions involve the use of carriers and complexing agents, as well as salting-out agents, whereby the solubility of many organic substances in water is markedly decreased by the presence of dissolved inorganic salts.

With the advent of improved countercurrent distribution instruments it has become possible to separate and estimate quanti-

Figure 10. Dithizonate Extractions

Recently, Irving et al. (19) investigated the basicity of dithizone in an attempt to shed more light on the nature of the reagent and its role in extraction and demonstrated it to be a monobasic acid, unassociated in dilute solution.

An excellent review by Furman et al. (11) presents the chief analytical properties of the cupferrates with special reference to extraction.

The separation of zirconium and hafnium by means of the preferential extraction of the chelate of the β-diketone, thenoyltrifluoroacetone, into benzene by Huffman and Beaufait (18) illustrates the possibilities of organometallic extractions for the separation of elements of very similar chemical properties. The nature of the extraction equilibrium of this zirconium chelate has been examined in detail by Connick and McVey (3).

Those elements that extract as the dithizonate, oxinate, and cupferrate complexes under various conditions are given in Figures 10, 11, and 12. Other organic reagents that form extractable metallic complexes are dimethylglyoxime, 1-nitroso-2-naphthol, sodium diethyldithiocarbamate, and potassium xanthate, with many more awaiting investigation.

ORGANIC EXTRACTIONS

Solvent extraction has been used in organic chemistry for many years for the separation and isolation of substances from

Figure 12. Cupferrate Extractions
Solid blocks. Complete or good extraction
Broken blocks. Fair extraction

tatively the components of mixtures of closely related substances, such as members of a homologous series and even isomers. Thus, separations can be effected even if the components exhibit closely related partition ratios. This subject has been excellently reviewed by Craig (4).

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3rd Annual Summer Symposium — Separations

THE RARE EARTHS

Separative Extraction of Certain Rare Earth Elements as 5,7-Dichloro-8-quinolinol Chelates

THERALD MOELLER AND DALE E. JACKSON[1]

Noyes Chemical Laboratory, University of Illinois, Urbana, Ill.

Although the 8-quinolinol chelates of the tripositive rare earth elements are not quantitatively extracted into chloroform, extraction of the corresponding 5,7-dichloro-8-quinolinol chelates is complete in controlled pH ranges. Extraction of neodymium and erbium above pH values of 9.4 and 8.3, respectively, shows extraction to be favored by decreased basicity in the rare earth metal ion. Overlaps in the extraction ranges of these two ions indicate that separations among the rare earth elements through extraction of the 5,7-dichloro-8-quinolinol chelates at controlled pH are only fractional in character. Spectrophotometric studies on chloroform solutions of the neodymium and erbium chelates show broad chelate absorptions centering around 4000 A., with sharp characteristic rare earth absorptions at longer wave lengths. Bands at 5740, 5818, and 5872 A. for neodymium and at 5208 and 5245 A. for erbium are of particular importance. Neodymium absorption at 5818 A. and erbium absorption at 5208 A. obey Beer's law in the concentration range 10^{-4} M and are more intense than corresponding absorptions in aqueous solution. Spectrophotometric determination of neodymium in the presence of neighboring rare earth elements is feasible at lower concentrations than in aqueous solutions.

THE tripositive rare earth metal ions show comparatively little tendencies to form complexes with a variety of normally powerful coordinating agents. Although this may be due in part to the relatively large sizes of these cations, it is more probable that their peculiar electronic configurations (in general, $4f^x 5s^2 5p^6$) render the orbital hybridizations essential to complex formation difficult to achieve. Certain chelating groups, notably the β-diketones and 8-quinolinols, however, are capable of overcoming this difficulty through the formation of inner complex compounds. Such compounds, in common with inner complexes in general, are difficultly soluble in water but are soluble in a variety of less polar solvents, among them benzene and chloroform. That separations based upon differences in degree of extraction into such nonaqueous media can be effected is thus a possibility.

Precipitation of certain of the rare earth elements as 8-quinolinol chelates has been suggested for gravimetric determinations (1, 4, 6, 14, 15). Literature reports notwithstanding, it is exceedingly difficult to form such compounds in the three 8-quinolinol to one metal ion stoichiometry predictable from normal valency relations except under very carefully controlled conditions (3, 5). Instead, basic compounds of widely variable

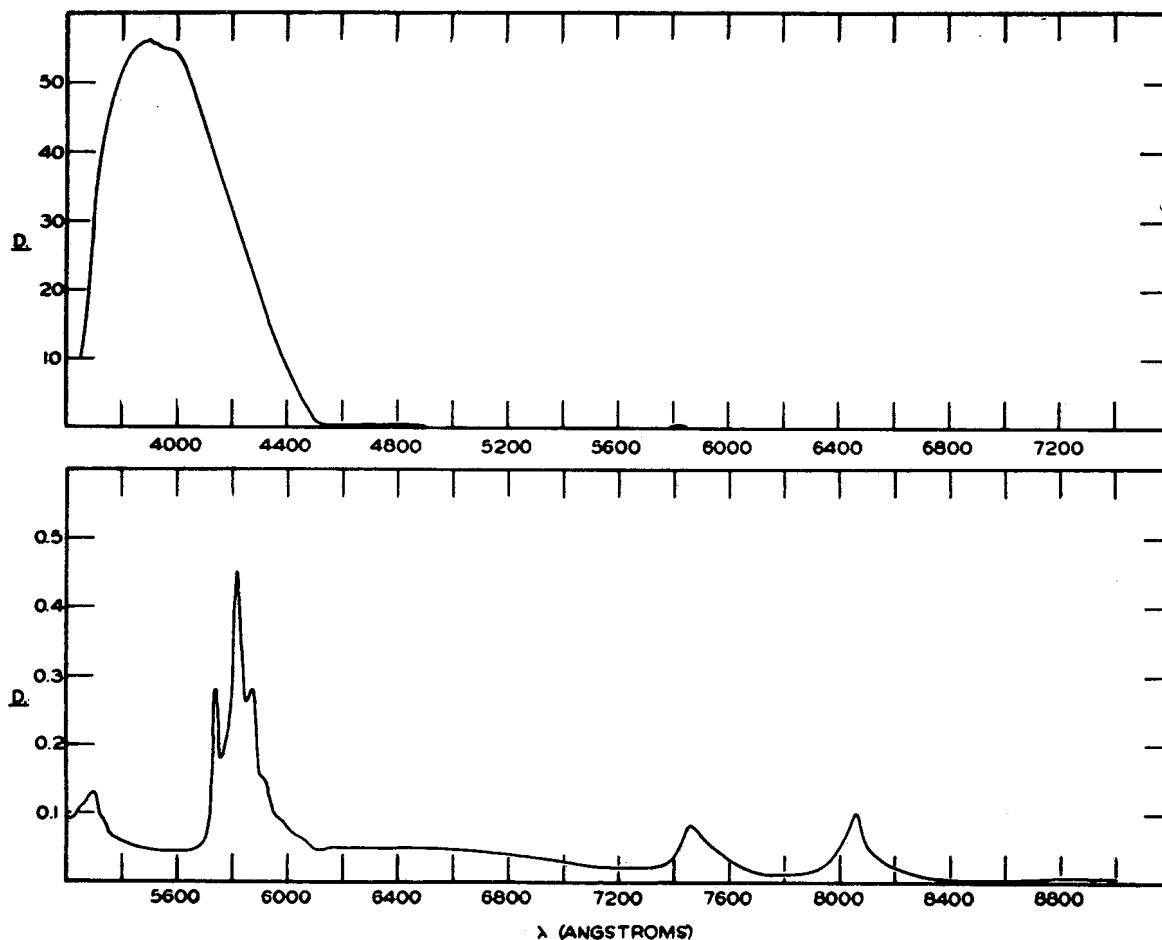[1] Present address, E. I. du Pont de Nemours & Company, Wilmington, Del.

Figure 1. Absorption Spectrum of Chloroform Solution of 5,7-Dichloro-8-quinolinol Chelate of Neodymium

compositions normally result not only with 8-quinolinol itself (*3, 5*) but also with such substituted materials as 8-quinolinol-5-sulfonic acid (*16*).   In extraction experiments, however, where an excess of the chelating agent is present the material taken into the nonaqueous phase has this 3 to 1 stoichiometry (*5*).   Extraction of 8-quinolinol chelates into chloroform is never complete, but extraction of the 5,7-dichloro-8-quinolinol chelates from aqueous solutions of controlled pH values is easily effected.   Inasmuch as 5,7-dichloro-8-quinolinol is a stronger acid than 8-quinolinol, its metal derivatives might be expected to be more ionic and less readily extracted.   The apparent anomaly may be due to the reduced solubilities of the chlorinated chelates and their consequent resistance to hydrolysis which would decrease the extent of extraction.

Greater ease of extraction of the heavier tripositive ions might be expected because of their reduced basicities (*13*).   Under comparable conditions, this should be reflected in extraction of these materials at somewhat lower pH values, although since the basicity differences among the rare earth metal ions are not large, large differences in extraction pH values could not be expected.

Absorption spectra measurements have been found useful in previous extraction studies involving the 8-quinolinols (*2, 7, 10, 11*).   The absorption spectra of chloroform solutions of such chelates in general resemble those of the chelating agents except that bathochromic shifts give broad absorptions centering in the vicinity of 4000 A. (*2, 11, 12*).   Because of a general interest in the absorption spectra of the tripositive rare earth metal ions, it was of interest to determine the effect of chelation upon these

spectra as well.   The strong absorption of the chelating agent in the ultraviolet limits the choice of rare earth ions to those showing inherent absorption in the visible or near infrared.   Furthermore, the broad chelate absorption around 4000 A. prevents study of ions absorbing in this spectral region from this point of view.   Neodymium and erbium ions have sufficient bands at longer wave lengths to permit their use.   These ions have the added advantage of differing basicities (*13*), thus permitting comparative extraction studies as a function of basicity.   This paper concerns the extraction of these two materials into chloroform as 5,7-dichloro-8-quinolinol chelates and with the spectrophotometric characteristics of the resulting nonaqueous solutions.

APPARATUS AND MATERIALS

All absorption spectra measurements were made with a Beckman Model DU quartz spectrophotometer, using 5-cm. cells with quartz windows (*8*).   A Beckman Laboratory Model G pH meter, the glass electrode of which was calibrated frequently against standard buffers, was used for all pH measurements.   The technique employed in absorption measurements was the same as that previously described (*8*).

Purified rare earth materials employed were from the stocks at the University of Illinois.   Weighed quantities of neodymium oxide (ND-34; free from other rare earths) and erbium oxide (ER-1-2S;   98% Er_2O_3, 1% Ho_2O_3 and Tm_2O_3, balance Y_2O_3) were converted to stock solutions by treatment with hydrochloric acid (for neodymium) and perchloric acid (for erbium), evaporation, and appropriate dilution.   Pure 5,7-dichloro-8-quinolinol was prepared by chlorination of 8-quinolinol in glacial acetic acid and subsequent recrystallization variously from acetone, absolute ethyl alcohol, and glacial acetic acid (*5*).   Chloroform

used contained 1% ethyl alcohol by volume as preservative. All other chemicals were of analytical reagent quality.

ABSORPTION SPECTRA OF CHLOROFORM SOLUTIONS OF 5,7-DICHLORO-8-QUINOLINOL CHELATES

Attempts to prepare chloroform solutions of the chelates for absorption spectra studies by direct dissolution of weighed quantities of the precipitated compounds were unsuccessful because of aging effects which reduced solubilities. Solutions were prepared either by extracting aqueous neodymium and erbium salt solutions at suitable pH values with approximately 100% excesses of 5,7-dichloro-8-quinolinol in chloroform, or by adding 100% excesses of the reagent in 3 M hydrochloric acid to the aqueous solutions, adjusting the pH to ensure complete precipitation of the chelates, and extracting with chloroform. Concentrations of the resulting stock solutions were determined by evaporating 500-ml. aliquots to dryness, dissolving the residues in dilute hydrochloric acid, regulating the pH to 5, precipitating with oxalic acid, igniting, and weighing the oxides. Various dilutions were prepared from the stock solutions. Concentrations of solutions studied were 0.0003 to 0.002 M for neodymium and 0.0003 to 0.004 M for erbium.

Absorption spectra were measured over the ranges 3600 to 9000 A. for neodymium and 3200 to 10,000 A. for erbium. The neodymium absorption in the vicinity of 4000 A. could be determined accurately only if a dilute chloroform solution of the reagent was used for comparison. This procedure eliminated all peaks below 4000 A. due to the reagent alone. The entire erbium spectrum was run against chloroform as a comparison liquid.

The absorption spectrum of a 0.00119 M chloroform solution of the neodymium chelate is shown in Figure 1, two ordinates being employed to emphasize the intensity of the chelate absorption (centering at approximately 3800 A.) in comparison with the much weaker characteristic neodymium absorption at longer wave lengths. Comparison of this spectrum with that of an aqueous neodymium chloride solution (8) indicates clearly the masking by the chelate absorption of all neodymium peaks at wave lengths less than approximately 4800 to 5000 A. General bathochromic shifts in the longer wave-length neodymium bands are also apparent, but the fact that in this region the spectrum of the complex and that of the neodymium ion are very similar to each other indicates that in complex formation the 4f electrons are not involved (9). Of particular interest is the marked intensification of the band found normally at 5745 A. and its resolution into three bands centering at 5740, 5818, and 5872 A., respectively. Absorption at 5818 A. is some eleven times that at 5745 A. for an equivalent amount of neodymium in aqueous solution. At the same time, the very intense 7420 and 7975 A. bands of the neodymium ion are much less affected. The same effects are observed in aqueous solutions in the presence of strongly chelating ions such as ethylenediamine tetraacetate and tartrate (9). Particular electronic transitions within the 4f level appear to be most affected when chelate structures form.

The absorption spectrum of a 0.00328 M chloroform solution of the erbium chelate is shown in Figure 2. Again strong absorption due to the complex centers in the 4000 A. region (at approximately 3950 to 4000 A.), but a sharp peak at 5208 A.
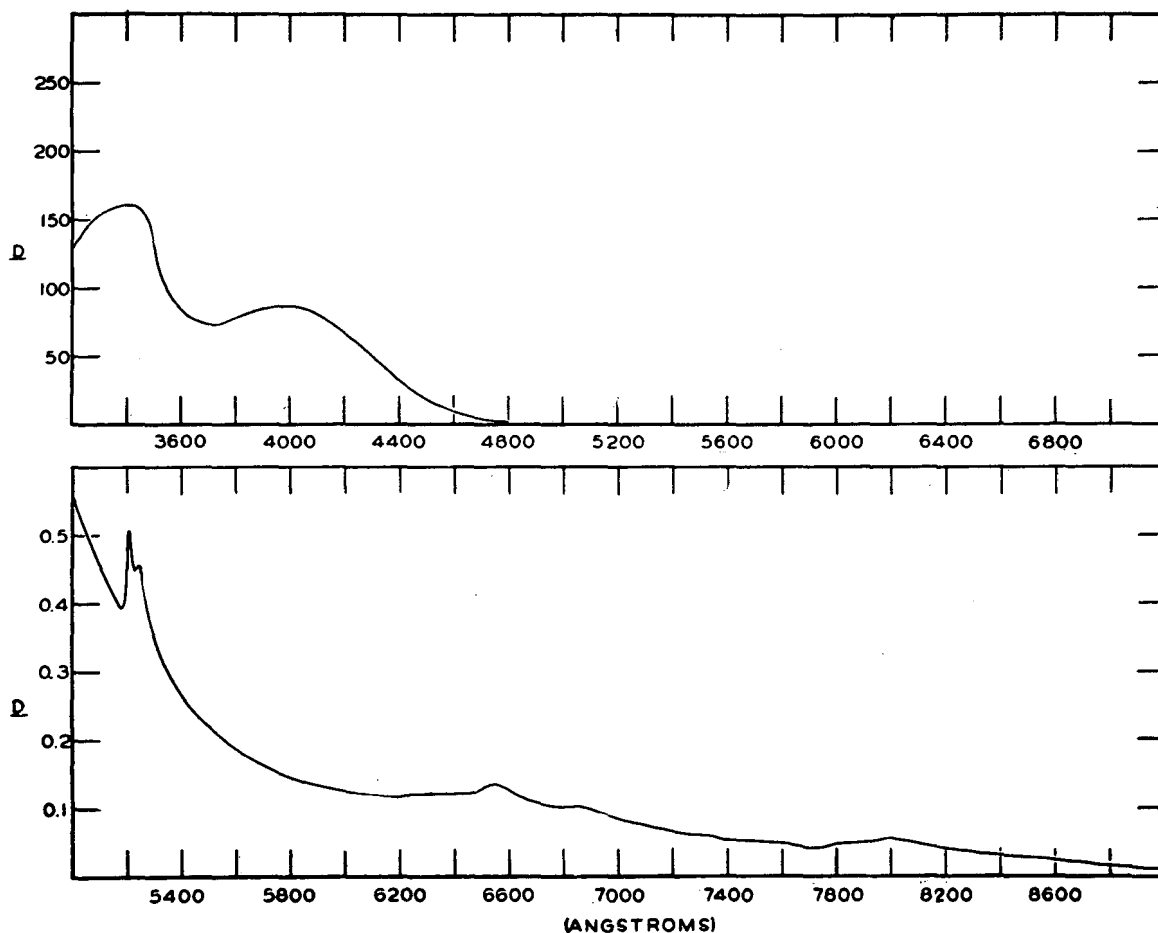

Figure 2. Absorption Spectrum of Chloroform Solution of 5,7-Dichloro-8-quinolinol Chelate of Erbium

and a lesser one at 5245 A. appear on the long wave-length side of this major absorption. Comparison of this spectrum with that of an aqueous erbium perchlorate solution (8) shows these peaks to be, in all probability, the 5200 and 5228 A. peaks, again slightly displaced. These absorptions are again more intense than those for comparable erbium concentrations in aqueous solutions. The transitions responsible for these peaks appear to be influenced by chelate formation in the same fashion as the transitions responsible for the 5745 A. neodymium absorption. All erbium peaks at lower wave lengths are masked by the broad chelate absorption.
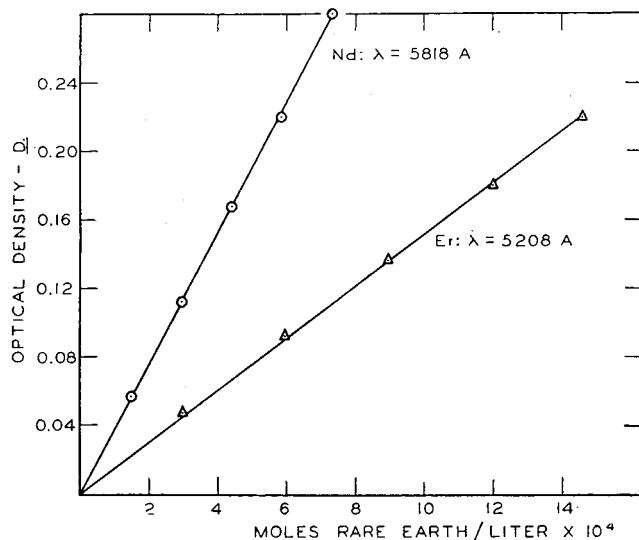
Figure 3. Beer's Law Adherence of Chloroform Solutions of 5,7-Dichloro-8-quinolinol Chelates of Neodymium and Erbium

The effects of concentration on absorption by the neodymium chelate at 5818 A. and by the erbium chelate at 5208 A. are shown in Figure 3. Beer's law is obeyed up to concentrations of at least 7×10^{-4} M for neodymium solutions and 15×10^{-4} M for erbium solutions. Molecular extinctions for neodymium and erbium at these wave lengths average to 76.3 and 30.9, respectively, compared with values of 6.66 and 1.96 for aqueous solutions of neodymium chloride and erbium perchlorate, respectively.

EXTRACTION OF NEODYMIUM AND ERBIUM INTO CHLOROFORM AS 5,7-DICHLORO-8-QUINOLINOL CHELATES

Extraction of chelates of this type into nonaqueous media is dependent upon such factors as temperature, relative quantities of the reactants, and pH of the aqueous phase (2, 7, 10, 11). Of these, temperature appears to have the least influence providing major variations are avoided. In these studies, temperature variations never exceeded 5° to 10° C. Successful extraction, regardless of the technique employed, depended upon the presence of excess reagent, and as a uniform procedure a 100% excess was used. This indicates the inherent instabilities of the chelates. Extractions as functions of pH were then studied under these conditions, the quantity of material extracted in each case being determined spectrophotometrically. Two extraction techniques were investigated: first, a liquid-liquid technique in which the aqueous phase after being buffered to an appropriate pH was extracted by shaking with several portions of a 0.02 M chloroform solution of the reagent, and second, a precipitation technique in which the aqueous phase was treated with the reagent dissolved in 3 M hydrochloric acid, the pH adjusted, and extraction effected with chloroform. Although both

variations gave essentially identical results, the precipitation procedure is easier to handle experimentally and reduces the possibility of basic salt formation. The pH adjustment was made with aqueous ammonia in both variations. The resulting systems, although not highly buffered, were reproducible. Reproducible results were not obtainable with potassium hydroxide, possibly because of basic compound formation.

The effects of pH upon per cent extraction are shown for neodymium in Figure 4 and for erbium in Figure 5. Below pH 5 to 6, there is no extraction. With neodymium, extraction begins at pH 6.1 and is complete above pH 9.4. With erbium, true incidence of extraction is difficult to detect because of difficulty in finding the rather weak erbium absorption peak, but from the data in Figure 5, it is apparently around pH 5. Erbium extraction is complete above pH 8.3. The differences between neodymium and erbium, although not large, are significant. Reduced basicity and enhanced tendency toward complex formation permit extraction of erbium at lower pH values. It may be assumed logically that the extraction of ions of the elements lying between neodymium and erbium in atomic numbers will occur within the pH range 8.3 to 9.4, that the extraction of ions more basic than the neodymium ion will occur at pH values above 9.4, and that the extraction of ions less basic than the erbium ion will occur at pH values below 8.3.
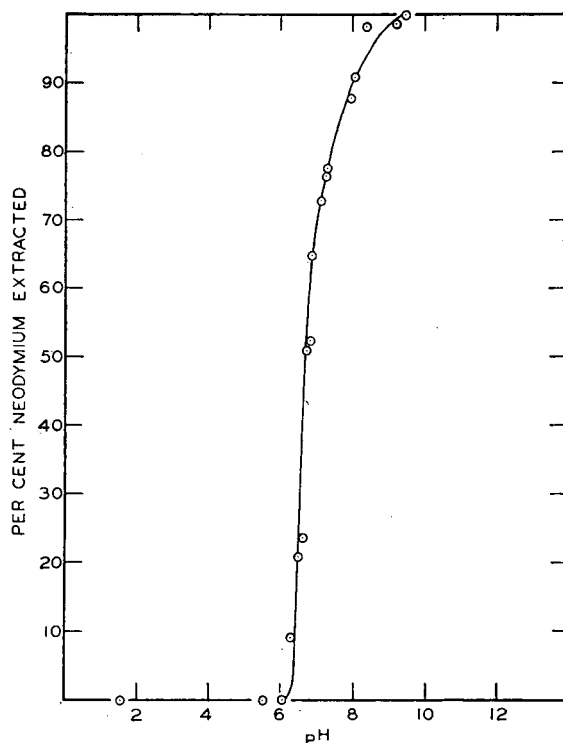

Figure 4. pH Dependence of Extraction of Neodymium Chelate into Chloroform

The overlap in extraction ranges indicated in Figures 4 and 5 shows clearly that separations of the rare earth metal ions by extraction of the 5,7-dichloro-8-quinolinol chelates on anything but fractional bases are impractical. This is particularly true of adjacent members in the rare earth series, but as in all basicity procedure (13) better separation involving more widely separated members could be expected. The practicality of such a procedure is limited still further by the reduced solubilities of chelates in nonaqueous media. However, because the extraction of many other ions at pH values below those at which the rare
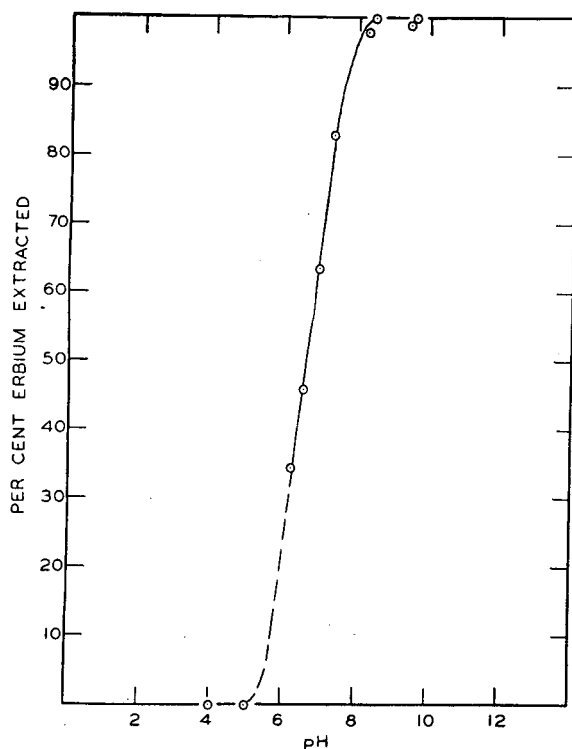
Figure 5. pH Dependence of Extraction of Erbium Chelate into Chloroform

earth metal ions extract is readily effected, separations of such materials from the lanthanides are practical.

An obvious method of approach to the study of these extractions at much lower concentration levels involves use of the intense but nonselective chelate absorption in the 4000 A. region. Experimental difficulties are greater because of the absorption in this region of any extractable chelate, and this approach was not considered practical in the current study.

SPECTROPHOTOMETRIC DETERMINATION OF NEODYMIUM AS THE 5,7-DICHLORO-8-QUINOLINOL CHELATE

Spectrophotometric determinations using aqueous salt solutions are limited to macroscopic quantities of the rare earth metal ions because of the low intrinsic intensities of the absorption peaks (8). The enhanced absorption characteristics of the 5,7-dichloro-8-quinolinol chelates and the adherence of these absorptions to Beer's law at concentrations of the order of 10^{-4} M suggest spectrophotometric determinations involving these chelates at much lower concentration levels than are possible in aqueous solutions. Results obtained with neodymium confirm these views.

A number of synthetic and natural neodymium-containing mixtures were converted to ca. 0.1 M aqueous chloride solutions and analyzed spectrophotometrically (8). Small aliquots were taken in such volumes that the optical densities of the final chloroform extracts would be in the range 0.1 to 0.2 (3 to 6 $\times$ 10^{-4} M in neodymium). These were diluted to 25 ml., treated with 100% excesses of 5,7-dichloro-8-quinolinol in 3 M hydrochloric acid, and precipitated with 0.2 M aqueous ammonia in the presence of ammonium acetate. When the precipitates became permanently yellow in color, the pH was raised to 9.5 with 15 M ammonia and the suspensions were extracted with 100-ml. volumes of chloroform. The extracts were then analyzed for neodymium, using the 5818 A. absorption band.

Table I. Representative Spectrophotometric Analyses for Neodymium as 5,7-Dichloro-8-quinolinol Chelate

No.	Materials Present	Neodymium Present, Mole/Liter	Neodymium Found, Mole/Liter
M-1	Nd, Y, etc.	0.0378	0.0378
			0.0381
M-2	Nd, La, etc.	0.0321	0.0325
			0.0320
			0.0320
ND-69	Nd, Pr, etc.	0.0577	0.0577
			0.0579
			0.0574
ND-70	Nd, Pr, etc.	0.0695	0.0694
			0.0692

Data summarized in Table I indicate the method to be accurate. That these results are calculated from data obtained for solutions of the order of 10^{-4} M in neodymium is important.

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[End of Symposium]

Spectrochemical Determination of Iron, Magnesium, and Manganese in Titanium Metal

MAURICE J. PETERSON, *Bureau of Mines, College Park, Md.*

A spectrochemical method for the determination of iron, manganese, and magnesium in titanium metal is described. A sulfuric acid solution of the metal is placed in a porous cup electrode, and excitation is by means of a controlled Multisource unit. Average deviations from chemical values are approximately ±8% for iron and manganese in the concentration ranges 0.08 to 0.5% and 0.02 to 0.2%, respectively. Average deviation for magnesium is ±6% in the range of 0.05 to 0.7%. The method has been useful for testing sample lots.

TITANIUM metal promises to become an important constructional and engineering material, owing to its unique combination of desirable properties, such as high strength, lightness, high melting point, and corrosion resistance. Moreover, there is an abundant supply of raw material.

In connection with the Bureau of Mines physical metallurgy program on the study of titanium and its alloys, a spectrochemical method of analysis of high-purity titanium has been applied to determination of iron, magnesium, and manganese. This investigation is part of a continuing program of development of new and improved methods of analysis and evaluation of minerals, mineral products, metals, and alloys conducted by the Physical and Chemical Section of the Eastern Experiment Station, College Park, Md.

Table I. Data for Preparing Standard Samples

Sample	Per Cent Added			Final Per Cent		
	Fe	Mn	Mg	Fe	Mn	Mg
1064	None	None	None	0.10	...	0.01
1064-A	None	None	0.05	0.10	...	0.06
1064-B	None	None	0.15	0.10	...	0.16
1064-C	None	None	0.35	0.10	...	0.36
1064-D	None	None	0.70	0.10	...	0.71
1001	None	None	None	0.098	0.023	0.42
1001-A	0.05	0.05	None	0.148	0.073	0.42
1001-B	0.15	0.15	None	0.248	0.173	0.42
1001-C	0.35	0.35	None	0.448	0.373	0.42

Table II. Lines Employed for Analyzing Titanium

Element	Element Line	Internal Standard Line	Concn. Range	Index[a]
Iron	Fe II 2599.40	Ti II 2572.65	0.08–0.5	0.42
Manganese	Mn II 2593.73	Ti II 2572.65	0.02–0.2	0.10
Magnesium	Mg II 2795.53	Ti II 2841.94	0.05–0.7	0.12

[a] Index is concentration at which intensities of analytical line and internal standard line are equal.

Essentially, the techniques are those recently described by Feldman (*3*, *4*) for the analysis of solutions by the porous cup electrode method. Gassman and O'Neill (*5*) have successfully applied the method to determination of phosphorus and metals in lubricating oils. Keirs and Englis (*7*) have described a similar procedure which utilizes a glass reservoir, one end of which is drawn to a pointed capillary. A carbon electrode is attached to the capillary, and liquid is fed into the spark through a small channel in the carbon. Recently Colin and Gardner (*2*) have adapted this procedure to determination of alumina in steel.

Conventional methods of spectrographic analysis, such as the sparking of self-electrodes or Petrey disk samples, are not applicable because it is not feasible to prepare a cast sample. At the temperature required for melting (3140° F.), titanium is very reactive; melting must be done under an inert atmosphere.

PREPARATION OF SAMPLES

Samples of the metal submitted for analysis were either in the form of powder (approximately 60 mesh) made by the reduction of titanic chloride with magnesium, or sheets made by consolidating this powder by the process of sheath rolling (*8*).

Small turnings were cut from the flat surfaces of the sheath rolled samples, using a carbide-tipped cutter in the tool post of a lathe. Care was taken to discard the first 0.025 inch of metal removed from the surface, inasmuch as tests had shown that iron contaminates the surface as a result of the sheath rolling. Five hundred milligrams of powder or turnings were dissolved in 22 ml. of 25% sulfuric acid with the aid of heat. Boiling should be avoided, as it may cause precipitation of the titanium. When solution was complete, 10 drops of concentrated nitric acid were added to oxidize the titanium to the Ti^{++++} condition. The solution was again heated to remove excess oxides of nitrogen and allowed to cool. Three grams of tartaric acid were then added to stabilize the titanium. Finally, the solutions were made up to a final volume of 25 ml. Solutions carefully prepared in this manner have shown no evidence of precipitation after several months.

PREPARATION OF STANDARDS

Two samples of chemically analyzed metal were used as starting material for the preparation of a series of standards. Standard sample 1064 contained 0.01% magnesium, a value much less than that to be expected in the samples submitted for spectrochemical analysis. Standard sample 1001, containing 0.098%
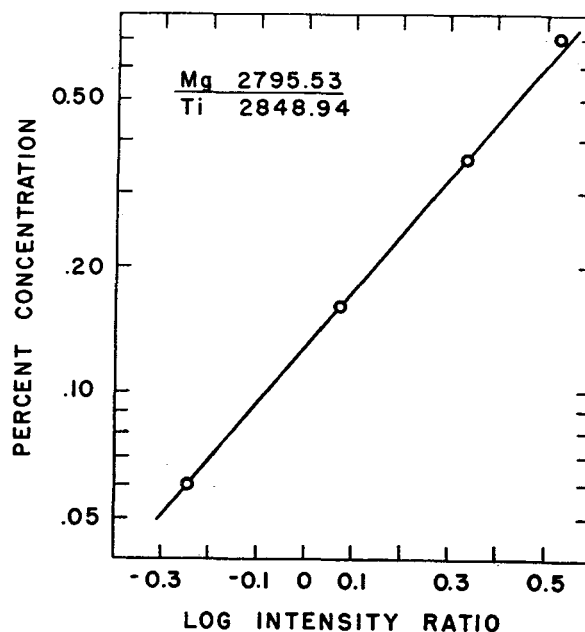

Figure 1. Working Curve for Magnesium

Table III. Titanium Lines Used for Calibrating Emulsion

Ti I	2541.92	Ti I	2632.42
Ti I	2555.99^a	Ti I	2661.97
Ti	2572.65^a	Ti II	2713.76
Ti II	2581.72	Ti I	2727.42
Ti I	2599.92	Ti I	2736.68
Ti I	2605.15	Ti II	2786.00
Ti I	2611.29	Ti II	2856.62
Ti I	2619.94		

^{a} Classified by Russell (9, 10), as lines of the spark spectrum of titanium.

Table IV. Analyses of Different Solutions of Same Sample

Solution	Mg, %	Fe, %	Mn, %
A	0.29	0.092	0.029
B	0.30	0.091	0.029
C	0.30	0.095	0.030
D	0.31	0.098	0.028

Each result is average of 2 determinations.

iron and 0.023% manganese, served as starting material for these two elements. Five hundred milligram portions of each of these samples were weighed and treated as described under sample preparation. Before making up to final volume, measured amounts of iron and manganese in 25% sulfuric acid were added to three of the 1001 samples. In like manner, magnesium was added to four of the 1064 solutions. In each instance, the amount added was calculated as per cent of the weight of titanium. The percentages of the three elements added are summarized in Table I.

The line pairs used and the concentration ranges are listed in Table II.

Chemical values of samples later submitted for analysis extended the ranges for iron and manganese to 0.08 and 0.02%, respectively.

PROCEDURE AND DISCUSSION

The sample electrodes are prearced at 5 amperes for 5 seconds with a direct current arc before use. This makes them porous and assures more uniform feeding of the liquid through the graphite.

The upper electrode is filled by means of a glass pipet with a rubber bulb. Care must be taken to expel the liquid while the pipet tip is touching the bottom of the electrode cavity; otherwise, bubbles may form in the solution, causing it to spatter during sparking.

With the type of discharge used, it is necessary to connect the sample electrode to the negative terminal of the Multisource. Otherwise the porous cup electrode becomes too hot and the liquid boils over.

After the electrode is filled and the gap adjusted the Multisource power is turned on for 5 seconds with the shutter closed. This is followed by a waiting period of approximately 15 seconds to allow the liquid to seep through the graphite. The lower electrode is replaced with one having a freshly prepared tip, and after a 3-second prespark, the shutter is opened for 3 seconds to record the spectrogram for the magnesium determination. The 3-second prespark volatilizes any excess liquid that may have seeped through the graphite. After the plate holder is racked and the counter electrode replaced, the same sample electrode is presparked again for 3 seconds, followed by a 30-second sparking to record the spectrogram for the iron and manganese determinations. It is important to replace the counter electrode with one having a freshly prepared tip for each exposure, as the formation of titanium dioxide on the tip will cause erratic results.

Each plate is calibrated by means of the group of titanium lines listed in Table III, the relative intensities of which were determined from calibrations made with a direct current iron arc and step sector.

Densitometer readings of the selected titanium lines are taken from one of the sample spectrograms exposed for 30 seconds. The data are treated in the usual manner by converting log-intensity ratios to concentration by means of the analytical curves shown in Figures 1 and 2. No background corrections are necessary. Averages of duplicate determinations are reported for each element. Two control standards are exposed in duplicate on each plate.

The equipment and operating conditions used are listed as follows:

Spectrograph, grating, Eagle mounting (1), 5.5 A. per mm. Slit width 100 microns. Grating aperture 1.25 inches. Region 2445 to 3095 A., second order.

Condensing lens, quartz, spherical, f_D = 25-cm. image of discharge focused on grating.

Upper electrode, high-purity graphite, 0.25 inch in diameter, 1.125 inches long. Hole drilled with No. 30 twist drill to within 1 mm. of flat bottom. Electrode held in spark stand with open end up.

Lower electrode, high-purity graphite, 0.125 inch in diameter, pointed in pencil sharpener.

Gap, 2 mm.

Spark stand, Bausch & Lomb spring-clamp type. Tips wrapped with platinum foil.

Power, Multisource unit (6) condenser discharge oscillating. Capacitance 2 μf. Inductance 50 μh. Resistance 0.4 ohm. Phase angle 95°. Output potential 940 volts. Charge vs. discharge 180°.

Exposure, 3 seconds for magnesium, 30 seconds for iron and manganese.

Photographic plate, Eastman type III-0.

Development, 5 minutes at 65° F., Eastman Formula DK-50, continuous agitation.

Densitometer, Baird nonrecording.

PRECISION AND ACCURACY

As a check on the precision of the method, 29 single determinations using the same solution were made for iron and manganese and 25 determinations for magnesium. Exposures were made on four plates and the per cent standard deviations were calculated. These were 7.6, 6.7, and 6.8%, respectively, for iron, manganese, and magnesium.
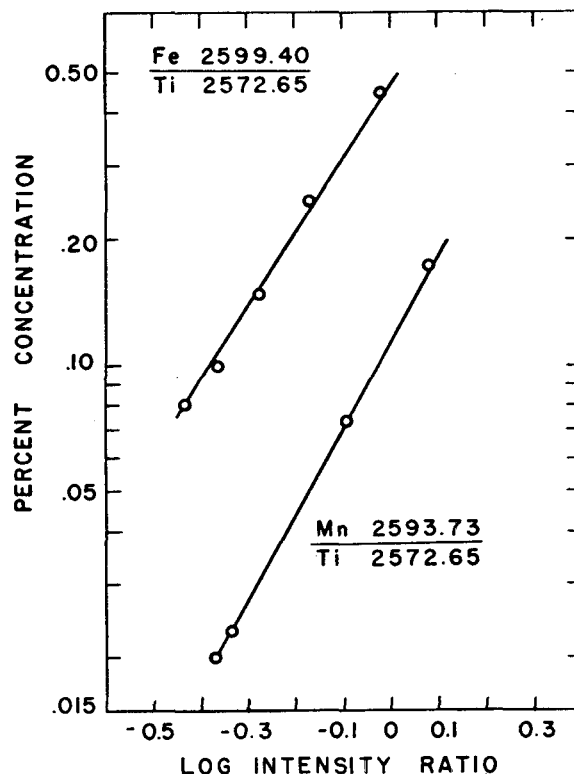
Figure 2. Working Curve for Iron and Manganese

To check for possible segregation, analyses were made on different solutions of the same sample. Results are as shown in Table IV.

Deviations between the results of wet-chemical and spectro-chemical determinations are summarized in Table V.

Table V.   Accuracy of Results

Element	No. of Detns.	Concn. Range	% Av. Deviation
Iron	17	0.080–0.13	7.8
Manganese	20	0.020–0.040	8.2
Magnesium	22	0.27 –0.50	5.6

The average deviations of approximately 8% for iron and manganese and 5.6% for magnesium are considered adequate for routine testing of sample lots.

Because there is considerable heating of the sample electrode when the Multisource is used, exposures must be of relatively short duration to avoid spattering of the solution. A spark stand equipped with water-cooled electrode holders would minimize heating of the sample electrode. The precision could probably be improved by using a conventional high voltage spark source, because this would allow one to use longer exposure periods, a slower optical system, and a slower emulsion. Use of a sample electrode with a truncated cone bottom similar to that described by Scribner and Ballinger for the analysis of bronzes (11) would also probably improve the precision of the method.

ACKNOWLEDGMENT

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Division, and under the immediate supervision of Howard F. Carl, chief, Physical and Chemical Section.

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Spectrochemical Analysis of Radioactive Solutions

CYRUS FELDMAN, Chemistry Division, Oak Ridge National Laboratory, Oak Ridge, Tenn., MYRON B. HAWKINS, Radioisotope Applications Company, Berkeley, Calif., MARVIN MURRAY, Chemistry Division, Oak Ridge National Laboratory, Oak Ridge, Tenn., AND DONALD R. WARD, Isotopes Division, U. S. Atomic Energy Commission, Oak Ridge, Tenn.

A description is given of a chamber designed to permit electrodes for spectrochemical analysis to be loaded outside the spectrographic laboratory, excited with spark or other intermittent excitation, and disposed of with a minimum risk to personnel. If strippable films are used to protect the most heavily exposed surfaces, residual radiation levels of ∼2 mr. per hour at contact on the chamber parts can easily be attained for samples customarily encountered.

IN ANALYZING any type of material spectrochemically, one naturally attempts to attain the maximum accuracy, precision, sensitivity, and speed. In analyzing radioactive materials, however, the main consideration is safety, and the following factors must be considered first:

Protection of operators from α, β, and γ radiation (shielding). Protection of operators from contact with radioactive materials. Minimization of number of handling and transfer operations prior to excitation of sample. Prevention of air contamination, especially during excitation of sample. Safe and rapid disposal of used electrodes. Safe, rapid, and complete decontamination of auxiliary apparatus.

The general interests of safety and efficiency are usually served best by standardizing techniques as much as possible. When the samples are radioactive, safety and efficiency also affect the choice of excitation technique and sample form.

CHOICE OF EXCITATION TECHNIQUE

Because the discharges used in spectrochemical analysis are disruptive, they must be conducted within an enclosed chamber in order to provide shielding and prevent contamination of the air. It must be possible to decontaminate such a chamber quickly and safely, in order both to safeguard personnel and to have the chamber available for re-use as soon as possible.

The effectiveness and dispatch with which a surface can be decontaminated tend to vary inversely with its area. The minimum permissible internal area of a chamber is dictated largely by the size and power rating of the discharge taking place within it. If the discharge continuously liberates large amounts of heat and vapor, as is the case with the direct current arc, the chamber must have a volume large enough to prevent overheating. This is a matter both of convenience of handling and of possible spectral line interferences from chamber materials which might be volatilized into the discharge if the chamber walls were too close to the arc. The use of spark techniques, however, lowers the temperature within the chamber, and makes it possible to adopt two measures which greatly simplify the decontamination problem:

The size of the chamber cavity may be greatly reduced, thus decreasing the contaminated area.
The area exposed to contamination may be coated before exposure with a strippable film. After exposure, this film may be removed and the contamination eliminated. This technique can be used only with spark excitation, because the film materials available cannot withstand the temperatures prevailing in an arc chamber.

Almost all of the radioactive materials analyzed in the authors' laboratory occur in solution form. Because this laboratory's nonradioactive solutions are usually analyzed by either the copper spark method (1, 3), or the porous cup method (2),
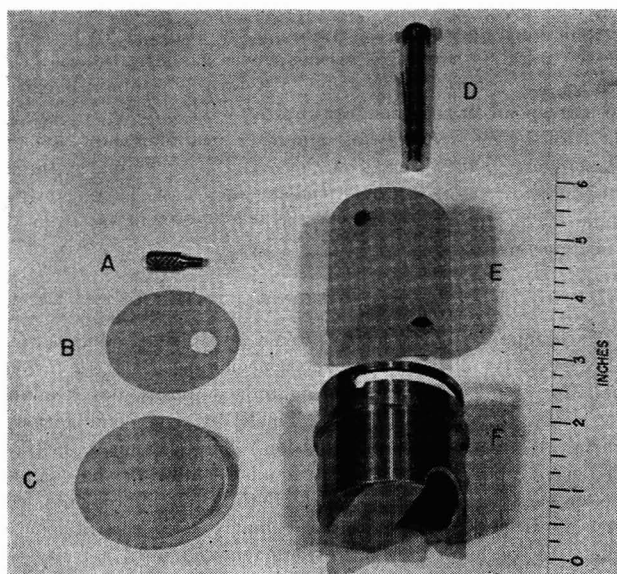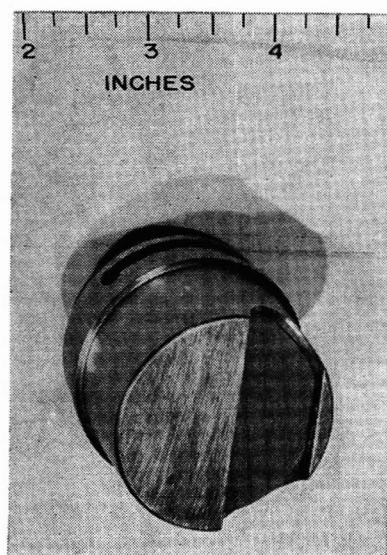
Figure 1. Components of Cassette Assembly

slipping out of the tube. A copper electrode in its tube is shown in Figure 1, *D*.

The loaded tube is then inserted into a stainless steel–lined hole in the Fluorothene (plastic polymer of chlorotrifluoroethylene) rotor, *E*, and pushed through until the end of the copper electrode emerges into the hemicylindrical cavity hollowed out in the end surface of the rotor. This entire assembly is then inserted into the stainless steel cassette, *F*, and secured by inserting the threaded turning pin, *A*, through the slot in the cassette and screwing it into the tapped hole shown on the outside curved surface of the rotor. The completed assembly is shown in Figure 2.
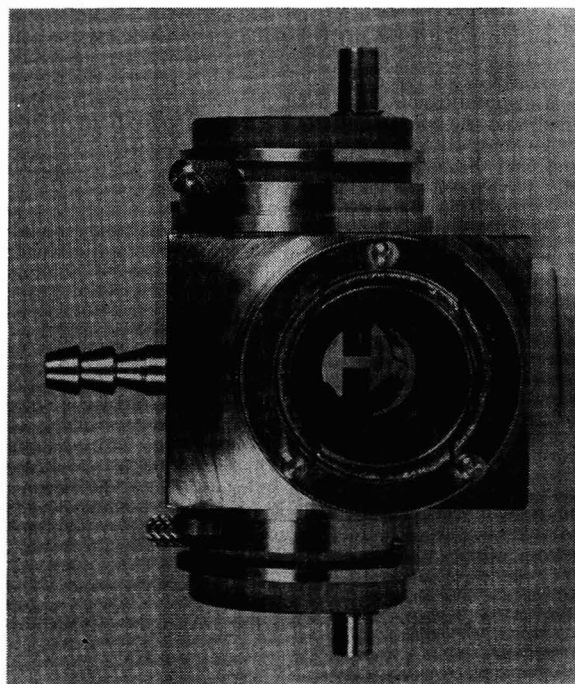

Figure 4. Spark Chamber Assembled

it appeared that the most serviceable protection chamber would be one built expressly for spark excitation of solutions by either of these methods.

A chamber has been developed which permits the sample to be carried to the laboratory, excited, and disposed of without exposure of operators to dangerous levels of radiation or airborne contamination. It can be decontaminated in 2 to 3 minutes, with negligible risk to the operator.

The chamber consists essentially of two cassette assemblies and a chamber block. The cassette assemblies contain the electrodes, and can be closed in such a way as to protect the operator against radiation or contaminated dust coming from the sample.

ASSEMBLY AND OPERATION OF CHAMBER

When the copper spark method is to be used, the order of operations is as follows (see Figure 1): A copper rod 0.25 inch in diameter, machined as described in (*1, 3*), is inserted part-way into a closely fitting stainless steel tube. A long U-shaped cut has been made in the wall of the tube, and the metal tongue thus formed is bent into the form of a wave ($\sim$) of very low amplitude. The resulting spring action prevents the electrode from

The cassette is then closed by turning the rotor until the pin reaches the end of its slot. Figure 3 shows the cassette assembly when closed.

Two such assemblies are prepared and sent to the laboratory submitting the sample. They are then opened as shown in Figure 2 and placed on a suitable support. The radioactive solution is deposited on the end of the electrodes by a remote-control pipet, and dried to a residue by means of an infrared lamp. If Cocoon protective coatings are used (manufactured by the R. M. Hollingshead Company, Camden, N. J.), care should be taken to avoid overheating. A sheet of metal or cardboard, containing a 0.375-inch hole, may be placed over the cassette assembly in such a way that the end of the electrode is the only portion of the assembly exposed to the rays of the lamp.

When the liquid has evaporated, the cassettes are closed again, carried to the spectrographic laboratory, and inserted into either end of the vertical hole passing through the stainless steel chamber block. They are correctly oriented and held in place by their rims and a suitable pair of indexing and retaining screws. The block is provided with windows consisting of glass or fused quartz disks held in suitable recesses by spring clips. It is supported on the optical bench as shown in Figure 5.

Once the cassettes are in place, the chamber cavity is created by rotating the rotors within the cassettes by means of the turning pins. Figure 4 shows the appearance of the chamber after this has been done. The two cassette assemblies come together at the center of the block, completely filling it except for the cylindrical cavity surround-

Figure 2. Cassette Assembly Open

Figure 3. Cassette Assembly Closed

ing the electrode gap. The surface of this cavity, most of which is on the rotors, is the only surface directly exposed to contamination.

The steel sleeves lining the hole in the rotor through which the electrode tube is thrust project 5 to 10 mm. from the outside end surface of the rotors; excitation is provided by clamping the electrical leads to this projecting portion (see Figure 5). The insulation furnished by the body of the rotor has proved sufficient to permit the use of an A.R.L. spark source (peak voltage ~35 kv.). The spark gap is given its final adjustment with the aid of a projected shadow image, and the exposure is made. The electrical leads are then disconnected, and the rotors are turned to the closed position, thus covering the greatest part of the contaminated area. The entire chamber, still containing the cassettes, is then removed from the supporting yoke and carried to the laboratory for disposal of electrodes and decontamination.

To dispose of the electrodes, each cassette assembly is removed, still closed, from the chamber block. It is then inverted over a disposable container, such as a wide-mouthed bottle, and opened, and the contaminated electrode is pushed out of its tube from behind, into the bottle. The cassette assembly is then closed, and the bottle is capped and discarded. After both electrodes have been disposed of, the cassette assemblies and the chamber block are ready for decontamination.

If the porous graphite cup technique is to be used, the porous cup electrode is first dipped open side down into a dilute solution of Zapon until most of the side surface, but none of the end, or sparking surface, has been coated (*2*, Figure 1, *B*). This prevents corrosion of the electrode tube by any acid solutions which may be inserted into the porous cup electrode. (Alternatively, parts coming in contact with corrosive solutions may be made of tantalum or platinum.) The porous cup electrode is then inserted into an electrode tube open end first, until the sparking surface projects about 0.25 inch from the end of the tube. This is used as the upper electrode. A graphite rod 0.25 in diameter is used as the lower electrode. The chamber is assembled as above, and the sample solution is inserted into the porous cup from outside the chamber (*2*, Figure 1, *A*). Subsequent disposal and decontamination are accomplished as with the copper spark techniques.

Table I. Transmission of Radiation through Shielding[a]

Type of Radiation	% Transmitted	
	Through cassette walls (3 mm. of stainless steel)	Through chamber block walls (10 mm. of stainless steel)
α	None	None
β (up to 4 m.e.v.)	None	None
γ (0.5 m.e.v.)	83	54
γ (1.0 m.e.v.)	87	64
γ (2.0 m.e.v.)	90	72

[a] Data supplied by F. Western.

Chambers now in use provide at least 2300 mg. per sq. cm. of shielding in all directions, so that once the cassette assemblies have been closed, after evaporation of the residue, the operator is completely protected from α and β radiation. Protection against γ radiation, however, is comparatively slight, even after the cassettes have been inserted into the chamber block (see Table I).

AVOIDANCE OF AIR CONTAMINATION

The breathing in of radioactive solid particles may be particularly dangerous because of the extremely high level of radiation in the immediate neighborhood of such a particle (*5*). It is therefore urgent that the vapors created by the excitation of radioactive samples be kept under control.

In order to prevent the escape of radioactive vapors into the room, a partial vacuum is maintained in the chamber. No attempt is made to have the chamber vacuum-tight; clearances of 0.2 to 0.3 mm. are purposely left between chamber block and cassette, cassette and rotor, etc. The air which thus leaks into the chamber is drawn off through a small outlet drilled through the body of the block near the rear (glass) window (see Figure 4). The current of the air seeping into the chamber makes the escape of radioactive vapors into the room virtually impossible. Air samples taken during the sparking of residues which read ~5 roentgen per hour at a distance of 3 inches when unshielded have shown no activity above background (measurements made by

P. E. Brown and co-workers). Before entering the vacuum line, the air emerging from the outlet passes through 10 inches of cotton wadding and a gas washer whose gas inlet tube is fitted with a coarse fritted glass disk. The scrubbing liquid is chosen to correspond to the chemical nature of the radioactive species. Tests of the gas stream before and after scrubbing show that this step removes 90 to 99.8% of the activity remaining in the air stream after passage through the cotton. Tests have shown no radioactivity to be present in the condensate or oil from the vacuum pump.

DECONTAMINATION OF CHAMBER

Technique. It has always proved possible to reduce surface activity of the chamber parts to a negligible level [≈2 mr. per hour for (β plus γ) activity or ≈30 decompositions per minute for α activity at a distance of 1 inch] by some combination of chemical treatment and abrasion. The chemical methods of decontamination have involved disassembly of the chamber below the surface of a chemical bath whose ingredients were chosen, if possible, to form a complex with the radioactive chemical species. The baths were renewed until activity was down to the level mentioned.

Chemical decontamination methods have several disadvantages, however.

Their effect on β- and γ-active substances, especially on porous surfaces, tends to follow a law of diminishing returns. Surfaces contaminated with radioactive isotopes of elements amenable to chemical treatment, such as the alkalies, alkaline earths, common metals, etc., may require several hours for decontamination; the last traces of the more stubborn elements, such as tungsten, columbium, etc., may yield to nothing short of sandpaper.

Their effect on some α-active substances, such as plutonium and americium, is both slow and incomplete. Prolonged abrasion of the surface is always necessary, thus increasing the danger to the operator.

The use of drastic chemical agents is limited by the nature of the material of the chamber. Although the use of Fluorothene (polymerized monochlorotrifluoroethylene) in constructing the rotors makes them proof against any combination of chemical reagents (*4*), the stainless steel parts are particularly susceptible to attack by hydrochloric acid and alkalies.

In view of the difficulties connected with chemical decontamination methods, it appeared that the problem might be solved more effectively by avoiding contamination of the surface in the first place.

Attempts were first made to precoat parts to be exposed to contamination with a layer of Carbowax 1540 or Carbowax 4000
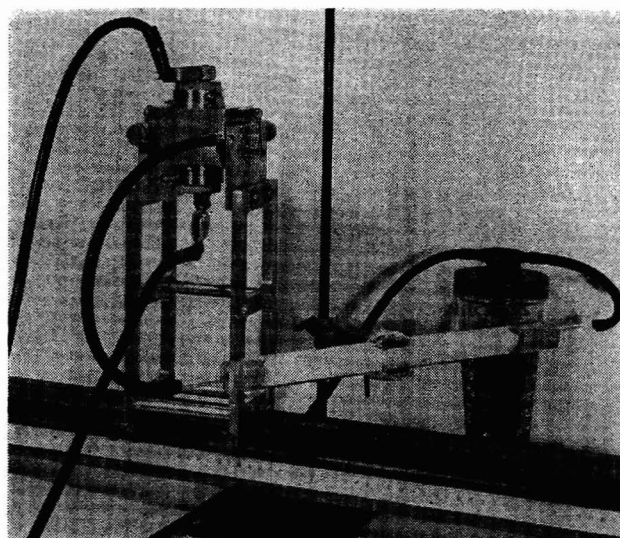

Figure 5. Spark Chamber and Filters in Operating Position

(water-soluble polyethylene glycols). After exposure, this coating was removed by immersing the parts in a bath of warm complexing agent and flushing this away with warm water. This procedure considerably decreased the amount of activity deposited on the chamber parts themselves, but some chemical and abrasive treatment was still necessary for surfaces contaminated with plutonium, americium, or large amounts of β- and γ-active substances.

The most successful coating agent found so far has been Cocoon, a liquid which, when spread on a surface, dries rapidly to give an elastic, strippable film. The coating may be applied either by dipping or by cementing suitably shaped pieces of the dried film to the surface to be protected.

Table II. Effectiveness of Decontamination with Strippable Coating[a]

Sample No.	Residual Activity on Part before Coating	Activity on Coating Part after Spectrographic Exposure, before Removal of Coating	Activity on Part after Removal of Coating
1	<1	400	4.0
2	<1	250	2.5
3	<1	150	2.5
4	<1	100	1.5
5	<1	50	1
6	<1	47	<1
7	<1	15	<1
8	<1	12.5	<1

[a] Measurements by Amanda Estepp.

The surfaces coated are usually the internal surface of the rotor and both flat surfaces of the cassette, including the edges which form a part of the cylindrical cavity. When plutonium or americium contamination is expected, the conical surfaces between the cylindrical cavity and the windows (seen foreshortened in Figure 4) are also coated with the liquid.

The specially shaped pieces used in coating the rotor and the cassette are prepared as follows:

Cocoon is sprayed onto a smooth surface to form a layer approximately 0.015 inch (0.3 mm.) thick, and allowed to dry for approximately 30 minutes. It is then stripped from the surface. The pieces are next stamped out of this sheet with the aid of suitably shaped cutting dies. Stamped pieces for the rotor and cassette, respectively, are shown in Figure 1, B and C.

When needed, the coatings are cemented to the rotors and cassettes with a mixture consisting of 1 part of Cocoon and 4 parts of acetone. This procedure readies the chamber for use much more quickly than would be possible if the coating were applied by dipping, inasmuch as the exposed coating surfaces do not have to be dried, and no trimming is required. Figure 1, E and F, shows coatings on the rotor and cassette, partly peeled away.

If such coatings are used, clearances between the parts involved must, of course, be correspondingly increased.

When the exposure has been completed and the electrodes have been removed, the chamber is disassembled under the surface of a complexing solution to prevent contamination of the air by radioactive dust. The film is immediately peeled away from the surface with forceps and discarded. The part is then flushed with fresh water and allowed to dry.

Results. Table II gives the results of recent measurements made on rotors and cassettes with the aid of a Zeus ionization meter. All parts were dry when measured, and the instrument geometry was the same for all measurements. All readings are given in milliroentgens per hour; the activity in each case was a combination of β and γ.

After porous cup exposures of solutions containing ≈ 1 mg. per ml. of plutonium (specific activity $= 1.3 \times 10^8$ decompositions per minute per mg.), the face of the rotor has been found to have as few as 30 counts per minute of α activity after removal of the coating.

ACKNOWLEDGMENT

The authors wish to thank L. B. Rogers for suggesting the development of a new chamber, and for his advice and encouragement in connection with the development of the present model.

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Iridium in Perchloric, Phosphoric, and Nitric Acid Mixtures

A Spectrophotometric Study

GILBERT H. AYRES AND QUENTIN QUICK[1], The University of Texas, Austin, Tex.

THE determination of iridium is usually accomplished by reduction with zinc, or by precipitation as the hydrous dioxide followed by reduction with hydrogen, and weighing as metal (23, pages 732-5). The method is tedious, and subject to numerous possible sources of error. The uses of iridium in jewelry, dental alloys, electrical equipment, and corrosion-resistant chemical ware, and as a catalyst indicate the need for an accurate, rapid method for its determination. Although several color reactions of iridium in solution have been reported (5, 6, 14, 16, 20, 21, 24, 25), apparently few have been studied for application to colorimetric determination. This paper reports an investigation resulting in the development of a spectrophotometric method for the measurement of iridium, based upon the

[1] Present address, Carbide and Carbon Chemicals Corporation, South Charleston, W. Va.

purple color produced by heating solutions of iridium(IV) chloro complex with mixed perchloric, phosphoric, and nitric acids.

The color produced when iridium(IV) solutions are heated with sulfuric acid appears to have been reported first in 1883 by Lecoq de Boisbaudran (15); he found that heating iridium(IV) chloride to fumes with sulfuric acid, followed by dilution with boiling water, gave solutions which were usually green, but sometimes blue or violet. More recently, various authors have reported the formation of blue or violet solutions by heating iridium(IV) compounds with a mixture of fuming sulfuric and fuming nitric acids (20, 24). Scott (23, page 655) cites this reaction as a method for the detection of nitrate in the presence of nitrite. In the authors' experience the reaction is not specific for nitrate; the same characteristic color can be produced by many other

A spectrophotometric method has been developed for the measurement of iridium, based upon the purple color produced when solutions of iridium(IV) are heated with a mixture of perchloric, phosphoric, and nitric acids. The system has been studied thoroughly to establish the conditions required to produce the colored component in its greatest intensity, stability, and reproducibility. The optimum concentration range for the procedure used is about 10 to 75 p.p.m. of iridium; the maximum accuracy of the photometric process is about 0.5% relative error for a precision of 0.2% absolute transmittancy.

Of the other Group VIII metals, palladium is the only one that interferes slightly in the direct determination of iridium. Palladium and iridium can be determined in the same solution by measuring the transmittancies at 415 and 564 mμ, and solving simultaneous equations. The color system has been studied in an endeavor to ascertain the nature of the reaction that occurs. In the purple solutions, the iridium is still in the oxidation state +4; hence the color formation is not an oxidation process. There is some evidence that the colored component consists of large aggregates.

reagents. Miller and Lowe (19) used the reaction with mixed sulfuric and nitric acids as a test for iridium; Miller (18) modified the method by substituting ammonium nitrate for the nitric acid. The authors' findings were that the color developed by the use of sulfuric and nitric acids was poorly reproducible, and rather unstable with time. Noyes and Bray (20) reported the formation of a deep purple solution when iridium(IV) chloride was treated with perchloric and nitric acids and heated to strong fuming, and they used the color reaction for estimating iridium. In the authors' laboratory, similar tests with the same reagents did not give a deep purple solution, but instead a rose-colored solution of spectral characteristics entirely different from those of the deep purple solution obtained by using sulfuric and nitric acids.

Mixtures of phosphoric, sulfuric, and nitric acids were tested for developing the iridium color. The system was studied with respect to total acid concentration, acid ratios, order of addition of reagents, temperature of development, and the intensity and stability of the color produced. After the color had been formed in concentrated acids, dilution with water or with dilute sulfuric acid caused the color to fade considerably. Sandell (22) has reported the destruction of the purple color by addition of water. Because the viscous solutions in concentrated sulfuric and phosphoric acids are also inconvenient to handle in transfer, a search was made for more suitable means of color development.

A similar study was made of iridium solutions treated with hot mixtures of nitric and phosphoric acids. The same purple color was produced, but the color intensity was low and not reproducible.

When the iridium solution was treated with a 1 to 1 mixture of perchloric and phosphoric acids and heated to 150° C., the color was developed to an intensity not previously obtained. Dilution with water did not destroy the color, which was reproducible and stable. The formation of an insoluble compound with rhodium was prevented by the addition of a small amount of nitric acid. Accordingly, the perchloric-phosphoric-nitric acid mixture, hereafter designated as "mixed acid," was adopted for further study.

REAGENTS

Iridium(IV) chloride and iridium metal were obtained from Eimer and Amend. Spectrographic examination of iridium(IV) chloride showed lines due to chromium, copper, platinum, rhodium, and zinc. Similar examination of the iridium metal showed it to be free from contamination; hence the metal was used for the preparation of standard solutions of iridium by the method described below. The iridium(IV) chloride was used for some comparative studies in which the small amounts of impurities would not interfere.

Standard solutions of the other Group VIII metals were used in the study of interferences. Osmium, in solution as chloroosmate, was prepared from c.p. osmium tetroxide as described by Ayres and Wells (2); ruthenium(III and/or IV) solution was prepared by dissolving the metal in alkaline hypochlorite (13), followed by acidification with hydrochloric acid and boiling; the

solution was standardized gravimetrically. Rhodium(III) solution was prepared from the metal by fusion with potassium acid sulfate and sodium chloride, using a modification of the procedure described by Bouvet (4). Solutions of palladium(II), platinum-(IV), and cobalt(II) were prepared from their c.p. chlorides. Nickel(II) solution was made from the sulfate, and iron(III) from ferric ammonium sulfate.

c.p. perchloric acid was used in the form of 70 to 72% solution; U.S.P. orthophosphoric acid, 85%, and c.p. nitric acid were used. All other reagents were also of the highest purity readily available.

APPARATUS

A Beckman Model DU quartz spectrophotometer was used for making all transmittancy measurements, in matched Corex cells having a 1.001-cm. light path. The instrument was operated at constant sensitivity, using slit widths of the order of 0.02 to 0.1 mm., corresponding to band widths of about 1 to 4 millimicrons. Spectrographic examinations of the iridium(IV) chloride and iridium metal, and also the residue from evaporation of some of the standard solution, were made with a 1.5-meter Applied Research Laboratories spectrograph and associated equipment.

EXPERIMENTAL

Preparation of Iridium Solution from the Metal. Iridium metal was attacked by the procedure of Beamish and Russell (3). A weighed amount (416 mg.) of the metal was fused with sodium peroxide in a silver crucible, and the dissolved melt was acidified with nitric acid; no undissolved iridium could be detected (9, 12). After boiling with sodium bromate, sodium bicarbonate was added to adjust the pH to 6; a blue-black precipitate of hydrous iridium dioxide separated, and was filtered off and washed; the filtrate gave only a faint test for iridium. The precipitate was dissolved in hydrochloric acid; upon dilution, silver chloride (from attack of the crucible used in making the fusion) separated and was removed. The filtrate and washings were diluted to 416 ml.; assuming complete attack and recovery of the iridium, this solution should contain 1 gram of iridium per liter (1000 p.p.m.).

Gravimetric Standardization of Iridium Solution. Hydrolytic precipitation, described in the previous paragraph, was used for separation of the iridium. Triplicate aliquots of the stock solution were boiled with sodium bromate, then adjusted to a pH of 6 by addition of sodium bicarbonate; the precipitate of hydrous iridium dioxide was filtered off, ignited, reduced by hydrogen, and weighed (8). The precision was poor, and the residues were heavier than corresponded to the amount of iridium taken, owing to material adsorbed on the hydrous oxide precipitate. Consequently, the residues were leached with 1 to 1 hydrochloric acid, dried, and weighed again; some loss in weight had occurred. The metal was refluxed with aqua regia for 2 days, and the dried residue was again weighed; no further loss in weight had occurred.

Results of the analyses are shown in Table I. The concentration of the stock solution was found to be 968 p.p.m. of iridium, indicating a loss, for the entire procedure of preparation and analysis of the solution, of 3.2% of the iridium metal originally taken. The residue from evaporation of a portion of the standard solution was examined spectrographically for impurities; of the heavy metals other than iridium, only the two most persistent lines of silver and of copper were found as spectral lines of weak intensity.

Table I. Gravimetric Analysis of Iridium Solution

Aliquot No.	Volume Taken, Ml.	Weight of Ppt., Mg.	
		Before leaching with HCl	After leaching with HCl
1	25.00	26.60	24.31
2	25.00	26.82	24.15
3	25.00	26.21	24.15
		Av.	24.20
		Av. deviation	0.3%

Concentration of solution $\dfrac{24.20 \times 1000}{25.00} = 968$ p.p.m.

Development of Color. A measured volume of the stock iridium solution was treated with mixed acid and heated at 110° C. for 1 hour, to expel most of the more volatile constituents. The temperature was then raised to 150° C.; during heating at this temperature a color transition from amber to deep purple suddenly occurred (over a period of about 20 seconds), the color appearing from 10 to 30 minutes after the temperature was raised. After cooling, the mixture was diluted to known volume with 1% nitric acid. Blanks were prepared in the same manner. Data for the spectral curves were obtained by measuring the transmittancy at frequent wave-length intervals over the range 300 to 800 mμ; the solutions had a transmittancy maximum at 430 mμ and a minimum at 564 mμ. For subsequent study of the effects of the various factors on the color system, transmittancy measurements were made at 564 mμ on solutions containing 32.5 p.p.m. of iridium; as is shown below, this concentration is near the middle of the optimum concentration range.

Table II. Effect of Varying Acid Ratios on Color Intensity

Volume % of H₃PO₄ in HClO₄	% Transmittancy of 32.5 P.P.M. of Iridium at 564 mμ, at Time Intervals Indicated				
	10 min.	2 hr.	14 hr.	44 hr.	64 hr.
70	37.9	38.0	38.2	38.3	38.4
60	36.7	36.7	36.7	36.7	36.8
55	36.5	..	..	..	..
52	36.3	..	..	..	..
50	36.2	36.2	36.3	36.4	36.5
48	36.5	..	..	..	..
45	38.0	..	..	..	..
40	42.0	42.0	42.1	42.2	42.2

Rate of Color Development. When the iridium mixed-acid system was heated to 150° C., purple color suddenly formed in from 10 to 30 minutes. Measurements of transmittancy against time of heating after this initial color development showed that the transmittancy of the system decreased slightly, reaching a stable minimum within about 4 minutes. To ensure a safe margin, 7 minutes (after purple color appeared) at 150° C. were chosen for the developing condition in the final procedure. No significant change in transmittancy occurred over a period of 64 hours. At lower temperatures the solutions developed to the full color intensity, but a longer period of heating was required. Prolonged heating at much higher temperatures caused considerable fading of the color; on cooling, the color partially returned, but not fully to its previous intensity.

Optimum Ratio of Acids. Preliminary tests had shown that the amount of nitric acid in the mixed-acid reagent was without influence on the intensity of purple color produced; hence, only the ratio of perchloric to phosphoric acid was considered in this study. The data of Table II show that maximum color (minimum transmittancy) was produced by the use of perchloric acid and phosphoric acid in a 1 to 1 ratio by volume. This ratio was adopted for future use, the mixed-acid reagent consisting of 50 parts (by volume) of 72% perchloric acid, 50 parts of 85% phosphoric acid, and 5 parts of concentrated nitric acid. Table II also shows that no essential transmittancy change occurred over a period of 64 hours.

Effect of Total Acid. In the preliminary experiments it was found that when the color-developed samples were diluted with water, significant differences in color intensity resulted if the total acidity was different in the diluted samples. Table III

shows that the lowest transmittancy was obtained when the total acid in the final solution was 50% by volume—e.g., 25 ml. of mixed acid used, finally diluted to 50 ml. However, the high viscosity of such solutions made them somewhat inconvenient to handle in making transfers. Solutions having a final acidity of 20% by volume showed almost as low transmittancy as those containing 50%, and were much easier to manipulate.
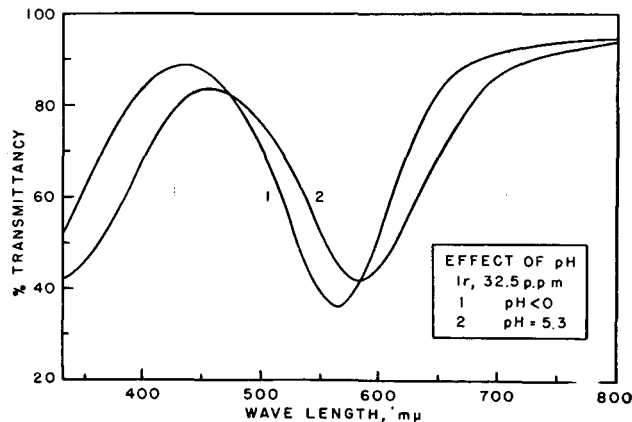

Figure 1. Effect of pH on Transmittancy of Iridium in Mixed Acid

When the purple solutions were nearly neutralized with sodium hydroxide, a color transformation occurred. At a pH of about 3 the purple color began changing to blue, and the change was complete at a pH of about 5.2. The spectral characteristics of the blue solution were somewhat different from those of the purple solution, as shown in Figure 1. The effects were to shift the entire spectral curve about 20 mμ toward longer wave lengths, to widen the curves around the inflection points, and to increase the transmittancy of the minimum.

Temperature Coefficient of Transmittancy. Over the temperature range of 15° to 35° C. the transmittancy increased linearly with increasing temperature at a rate of 0.07% absolute transmittancy per degree; the change was completely reversible. Laboratory temperatures at which the solutions were measured were generally in the range of 24° to 27° C.; this temperature variation will account for differences of 0.2% (absolute) in transmittancy.

Table III. Effect of Total Acid Concentration on Color Intensity

% Mixed Acid in Final Solution	% Transmittancy of 32.5 P.P.M. of Iridium at 564 mμ, at Time Intervals Indicated				
	2 hr.	14 hr.	20 hr.	40 hr.	64 hr.
10	37.1	37.7	..	38.0	38.1
20	36.4	36.4	..	36.5	36.7
50	36.1	36.0	35.9	35.7	35.9

Standardized Procedure. On the basis of the previous findings, the following standardized procedure was adopted:

Measured aliquots of the stock solution, to give a final concentration ranging from 6 to 100 p.p.m. of iridium, were treated with 10 ml. of mixed acid. After preliminary heating at 110° C. for 1 hour, the temperature was raised to 150° C. and held at that temperature for 7 minutes after the purple color developed. The mixture was cooled and made up to 50.0 ml. with 1% nitric acid, and the transmittancy was measured at room temperature.

Transmittancy versus wave-length curves for several concentrations are shown in Figure 2.

Reproducibility. A statistical treatment was made of the results of the transmittancy determination of 46 samples containing 32.5 p.p.m. of iridium, developed by the above procedure.

Data for this evaluation were collected over a period of about 2 months; all analysis errors, from the time of sampling on, were included, and no results were rejected. The results approached a normal distribution, with but a slight skewness toward high transmittancy. The standard deviation (σ) of the 46 determinations was $0.21 \pm 0.02\%$ absolute transmittancy.

Effect of Other Group VIII Metals. All the other Group VIII metals were examined as possible interferences. Solutions of the metal ions were treated by the standardized procedure described previously; in each case the final concentration was 200 p.p.m. as metal. Solutions of iron, cobalt, nickel, and platinum underwent no apparent change; rhodium and palladium were precipitated by heating with mixed-acid reagent, but redissolved when the samples were diluted to volume with 1% nitric acid. Ruthenium solution became much darker red-brown, then changed to green and finally to colorless as the ruthenium tetroxide was volatilized. Osmium (chloro-osmate) was decomposed and volatilized as the tetroxide.
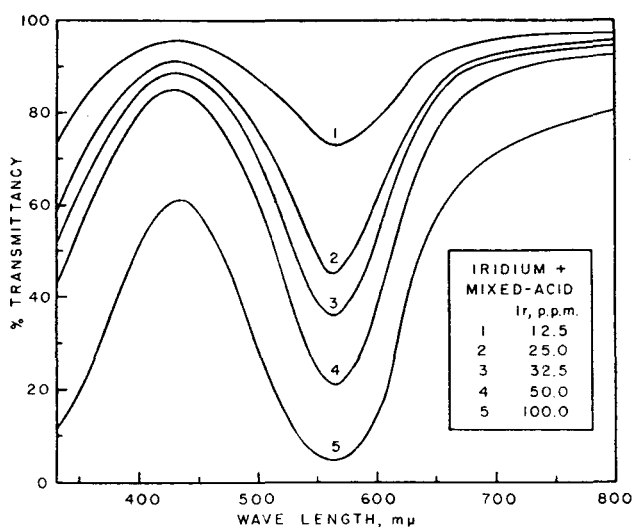
Figure 2. Spectral Curves for Iridium in Mixed Acid

Spectral curves for the mixed-acid systems of iron, cobalt, nickel, rhodium, palladium, platinum, and iridium are shown in Figure 3. At concentrations of 200 p.p.m. of metal, all the solutions except palladium had practically 100% transmittancy at 564 mμ, the iridium minimum; hence, no interference would be expected (except in the case of palladium) unless the other metals were present in excessively large amounts relative to the iridium content. Solutions containing 32.5 p.p.m. of iridium and 200 p.p.m. of a second metal (iron, cobalt, nickel, rhodium, or platinum) had transmittancies not significantly different from the transmittancy of a solution of the same concentration of iridium alone. The tolerance of the iridium system for palladium was determined by measuring the transmittancies of solutions containing 32.5 p.p.m. of iridium and varying amounts of palladium; the tolerance was taken as the largest amount of palladium that would give a transmittancy not more than 0.5% (2.5 σ) absolute different from that of iridium alone. On this basis, the iridium system can tolerate up to 25 p.p.m. of palladium, or about 80% of the amount of iridium present.

It is pointed out in the discussion that the purple iridium color can be produced by the use of a wide variety of acids; therefore, the effect of anions, similar to that of cations, was not studied.

Simultaneous Determination of Iridium and Palladium. The spectral curves for iridium and palladium are favorable for the determination of both of these elements in the same solution, by measuring the transmittancy of the mixture at 564 mμ (the iridium minimum) and at 415 mμ (the palladium minimum),
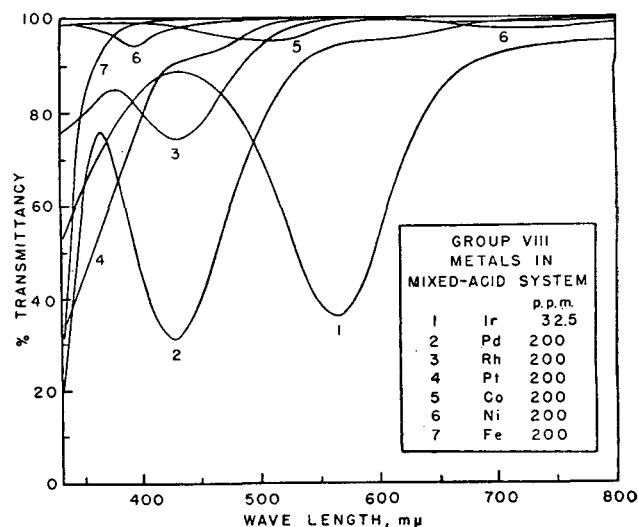

Figure 3.   Spectral Curves for Group VIII Metals in Mixed Acid

Table IV.   Simultaneous Determination of Iridium and Palladium

Sample No.	Iridium, P.P.M.			Palladium, P.P.M.		
	Taken	Found	Diff., %	Taken	Found	Diff., %
1	32.5	32.2	0.92	80	77	3.8[a]
2	20.0	20.1	0.50	50	49	2.0
3	40.0	40.0	0.00	100	98	2.0
4	50.0	50.7	1.40	150	153	2.0
5	70.0	69.7	0.43	200	202	1.0
		Av.	0.65			1.8

[a] Not included in average.

and applying the method of simultaneous equations (26). Iridium up to at least 100 p.p.m., and palladium up to at least 200 p.p.m., were proved to follow Beer's law. Table IV shows the results of five determinations on mixtures containing both iridium and palladium.

Study of Color Reaction. A few attempts were made to separate the colored component from the solution. No colored material could be extracted by ether, chloroform, carbon tetrachloride, amyl alcohol, or amyl acetate. The colored component was not adsorbed by silica gel; basic absorbants could not be used on account of the high acid concentration of the solutions; ion exchange resins were not tried.

All the methods previously cited for the production of the purple color involved reagents and conditions conducive to oxidation, suggesting that the iridium in the purple solutions was in an oxidation state higher than the iridium +4 from which it was prepared. The purple color was discharged by reducing agents such as iron(II) chloride, tin(II) chloride, phenylhydrazine, and sodium thiosulfate, but not by arsenite or oxalate, nor by active metals such as iron, zinc, or magnesium. From the reduced solutions, the purple color was restored to its original intensity and spectral characteristics by the addition, in the cold, of oxidizing agents such as sodium hypochlorite, potassium periodate, potassium bromate, and cerium(IV) sulfate, but not by bromine water.

The above behavior suggested the possibility of establishing the electron change associated with the color change. Freshly prepared standard solutions of iron(II) chloride were titrated by purple solutions of known iridium concentration until the purple color of excess iridium was just detectable. The experiments were repeated, using tin(II) chloride as the standard reductant. In each case the weight relations of the reactants corresponded to a gain of one electron per atom of iridium. The titrations of iron(II) chloride by the purple iridium solutions

were repeated potentiometrically; the electrochemical equivalence point occurred at 0.82 volt (referred to hydrogen electrode = 0). Although these experiments established the electron change in the reaction, they furnished no information as to the actual oxidation number of the iridium in either the oxidized or reduced state.

The oxidation number of the iridium in the purple solutions could be established by any change which would give a different, well-recognized oxidation state (either higher or lower) by a reaction in which the stoichiometric relations between oxidant and reductant could be determined. The most obvious case would seem to be reduction to metallic iridium. Although active metals, such as zinc and magnesium, are reputed to reduce iridium compounds to the metal, the authors were unable to effect reduction of the purple solutions with these metals; they merely dissolved in the acid present without affecting the color of the solutions.

An alternative method of deducing the oxidation state of iridium in the purple solutions is by comparison with a reaction of iridium of known oxidation number, such as the titration of iridium +4 by iron(II). Solutions of iron(II) chloride were titrated potentiometrically with solutions of iridium(IV) chloride of known iridium content. The weight relations established the reaction as involving a gain of one electron per iridium atom, which was the same electron change that had been found in the titration of the purple solutions. It appears, therefore, that in the purple solutions the iridium is in the oxidation state +4.

Attempts were made to obtain cathodic or anodic polarographic waves with the purple solutions, and also with the blue solutions obtained by partial neutralization of the acid. No polarographic waves could be detected.

It has long been known that iridium(IV) chloride forms an indigo-blue precipitate of hydrous iridium dioxide or iridium(IV) hydroxide when boiled with an aqueous solution of alkali carbonate (17). Samples of this precipitate were prepared by adding iridium(IV) chloride to excess sodium carbonate, and boiling for 2 minutes. The hydrous oxide settled out as an indigo-blue precipitate, but the supernatant liquid was blue in color. The spectral transmittancy curve for this solution had the maximum and the minimum transmittancy at the same wave length as, and was otherwise qualitatively similar to, the curve of the blue solution obtained by nearly neutralizing the purple mixed-acid samples. The hydrous iridium dioxide precipitate was dissolved in the cold by the following acids: sulfuric, nitric, phosphoric, perchloric, formic, acetic, oxalic, and tartaric; in each case a purple solution was obtained. Hydrochloric acid was singularly different in its action on the hydrous oxide precipitate; a large excess of acid was required for the dissolution, and the resulting solution was blue.

The hydrous iridium dioxide precipitate was soluble in mixed-acid reagent (perchloric, phosphoric, and nitric acids) in the cold giving a purple solution of spectral characteristics qualitatively identical with solutions developed from iridium(IV) solution by the standardized procedure described previously. In potentiometric titrations using iron(II) chloride, solutions from the two different methods of preparation showed almost identical electrochemical equivalence voltages, and the weight relations corresponded in each case to a gain of one electron per atom of iridium.

In discussing iridium dioxide, Friend (7) mentions that the compound can be obtained in colloidal form as a violet material. The authors found that the purple system formed by iridium and mixed acid, as well as the blue samples formed by partial neutralization of the purple solutions, showed some Tyndall effect and contained particles rendered visible in an ultramicroscope; the colored materials were retained by collodion membranes unless they were extremely thin, whereupon the colored material passed through very slowly. Iridium(IV) chloride solutions readily diffused through the collodion membranes.

DISCUSSION

Range and Accuracy. For constructing the calibration curve, transmittancy measurements were made at 564 mμ on solutions of iridium content from 6 to 100 p.p.m.; each point for the curve was established by taking the average of many replicate determinations. The iridium mixed-acid system showed excellent agreement with Beer's law over the concentration range studied. The calibration curve shown in Figure 4 is plotted in the form of per cent absorptancy (100 − % transmittancy) against logarithm of concentration; the maximum slope of the curve occurs at about 32 p.p.m. of iridium, and corresponds to a relative analysis error (of the photometric process) of 2.7% per 1% absolute photometric error, as expected from Beer's law (1). For a photometric reading error of 0.2% absolute transmittancy (the standard deviation of the photometric measurement), the maximum relative accuracy is therefore 0.5% of the concentration. In the range of 10 to 75 p.p.m. of iridium, the relative analysis error does not exceed 4% per 1% absolute photometric error, or 0.8% relative error on the concentration measured. The range can be extended upward, with an increase in accuracy, by the method of measuring transmittance ratios (1, 11)—that is, by using a standard iridium solution instead of the customary blank solution.

Color Reaction. The methods of formation of purple iridium solutions reported in the literature and the methods investigated in the earlier part of this study strongly indicated that the purple color was due to an oxidation state of iridium higher than the +4 state from which the solutions were prepared. However, the studies on acidification of hydrous iridium dioxide, to produce a purple color identical with that developed by the strong oxidizing systems, indicated that oxidation was not necessary for production of the color; the purple color was formed when hydrous iridium dioxide was treated with acids such as acetic, formic, oxalic, and cold dilute perchloric, which do not have oxidizing properties. In fact, some of these reagents are active reducing agents, and hence could not increase the oxidation number of the iridium in the solution obtained from the hydrous dioxide.

In the experiments involving titration with iron(II), it was established that the reaction involved a gain of one electron per atom of iridium, whether the oxidizing system was iridium(IV) chloride, or the purple solution developed by treatment of iridium(IV) with mixed acid, or the purple solution produced from hydrous iridium dioxide by treatment with nonoxidizing acid. It is concluded, therefore, that in the purple solutions the
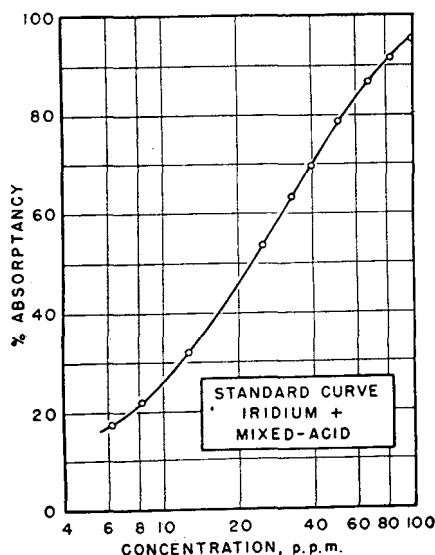

Figure 4.   Calibration Curve for Iridium in Mixed Acid at 564 mμ

iridium is in an oxidation state of +4, and that some change other than oxidation is the cause of the color formation.

The fact that identical purple solutions can be formed by treatment of iridium(IV) chloride (or chloro complex), or of hydrous iridium dioxide, by such a wide variety of acids makes it seem improbable that the color is due to any specific complex of iridium(IV) with the anion of the acid. The existence of large aggregates is indicated by the fact that the colored material exhibits some Tyndall effect, and passes through collodion membranes only very slowly. It is possible that some kind of polymer might form through iridium-oxygen bridges, in a manner similar to the formation of chromium-oxygen bridges when solutions of chromic salts are aged or boiled, with a resulting color change from violet to green (10). Further studies of the color reaction are contemplated.

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Infrared Determination of Ortho and Meta Isomers in p-Cresol

Freezing Points of Pure Cresols

O. E. KNAPP AND H. S. MOE, The Sherwin-Williams Company, Chicago, Ill.,

AND

R. B. BERNSTEIN, Illinois Institute of Technology, Chicago, Ill.

An infrared spectrophotometric procedure for the determination of low concentrations of o- and m-cresol in p-cresol is described. The absorption bands at 13.37 and 12.92μ characteristic of the ortho and meta isomers are used for the determination. With a 0.027-mm. absorption cell, the accuracy of the analyses was ±0.3% o- and ±0.5% m-cresol. An account of the method of preparation and purification of the three isomers is given. Freezing-point data for the pure compounds are given.

DETERMINATION of the concentrations of o- and m-cresol in samples of impure p-cresol is of practical interest, as is a detailed development of a suitable instrumental procedure, inasmuch as no precise chemical method is known. A rapid infrared spectrophotometric method suitable for use in the low range of concentrations has been developed, based on the early infrared studies of the cresols by Whiffen and Thompson (3). These authors indicated the possibility of infrared analysis of mixtures of isomeric cresols. The present paper outlines the details of a practical procedure for the determination of isomeric impurities in p-cresol. Special consideration is given to the problem of obtaining pure standards, which has not been adequately stressed in previous reports on cresol analysis.

Reliable data on the freezing points of the individual pure cresols were sought. Obviously, the freezing point of pure p-

cresol was of particular interest; therefore, all values reported were obtained while observing the best conventions, including a carefully standardized precision-type thermometer. Seeding was found to be essential and was employed in every case. It was necessary to guard against contamination of samples by moisture. For this reason, all transfers were conducted under a bell jar in an atmosphere of dry nitrogen.

The presence of water in cresols, even in small quantities, produces a significant lowering of the freezing point. For example, with p-cresol containing approximately 3% o-cresol, an increment of 0.1% in water content produced a freezing point depression of 0.37° C., over the range 0.05 to 0.8% water. Standards containing not over 0.1% water were deemed to be satisfactory. Water determinations were made according to the Karl Fischer method.

Table I. Summary of Analytical Data

Mixture	Wt. Cresol, G.	A, Ortho	% Ortho Calcd.	% Ortho Taken	Δ%, Ortho	A, Meta	% Meta Calcd.	% Meta Taken	Δ%, Meta
1	1.13	0.002 0.002	0.3 0.3	0.0	+0.3 +0.3	0.012 0.010	3.1 2.6	2.05	+1.0 +0.6
2	1.18	0.023 0.024	3.0 3.1	3.05	-0.1 0.0	0.006 0.010	1.5 2.45	1.75	-0.2 +0.7
3	1.28	0.010 0.010 0.013	1.2 1.2 1.55	1.45	-0.3 -0.3 +0.1	0.000 0.002 0.000	0.0 0.45 0.0	0.45	-0.5 0.0 -0.5
4	1.21	0.023 0.023	2.9 2.9	3.05	-0.2 -0.2	0.011 0.006	2.6 1.45	1.75	+0.8 -0.3
5	0.95	0.058 0.055	9.35 8.85	8.95	+0.4 -0.1	0.000 0.000	0.0 0.0	0.0	0.0 0.0
6	1.07	0.034 0.040 0.034 0.036	4.9 5.7 4.9 5.15	4.9	0.0 +0.8 0.0 +0.2	0.031 0.029 0.032 0.033	8.4 7.85 8.65 8.95	8.45	-0.1 -0.6 +0.2 +0.5
7	1.14	0.11 0.11	1.5 1.5	1.4	+0.1 +0.1	0.015 0.015	3.8 3.8	3.55	+0.2 +0.2
8	1.26	0.025 0.025 0.029	3.0 3.0 3.5	3.2	-0.2 -0.2 +0.3	0.007 0.008 0.007	1.6 1.85 1.6	1.5	+0.1 +0.3 +0.1
9	1.00	0.071 0.073 0.072	10.9 11.2 11.0	11.1	-0.2 +0.1 -0.1	0.017 0.018 0.021	4.9 5.2 6.1	5.6	-0.7 -0.4 +0.5
10	1.00	0.060	9.2	9.4	-0.2	0.036	10.5	11.9	-1.4
11	1.02	0.031	4.65	5.7	-1.0	0.049	13.9	15.2	-1.3
12	1.02	0.096	14.4	14.9	-0.5	0.043	12.2	12.6	-0.4
13	1.03	0.041 0.042	6.1 6.2	5.7	+0.4 +0.5	0.019 0.021	5.35 5.9	5.3	+0.1 +0.6
14	1.02	0.040 0.041	6.0 6.15	5.4	+0.6 +0.7	0.030 0.030	8.5 8.5	8.0	+0.5 +0.5
15	1.05	0.060	8.7	8.3	+0.4	0.023	6.35	5.7	+0.7
16	0.99	0.082	12.7	12.4	+0.3	0.045	13.2	11.9	+1.3
Av. Deviation					±0.3				±0.5

STANDARDS

p-Cresol. PREPARATION 1. Nitration-grade toluene was sulfonated with concentrated sulfuric acid and the resulting toluenesulfonic acid mixture, in the form of the sodium salt, was subjected to alkali fusion. The crude product obtained was purified by a succession of distillations and recrystallizations. The preparation in its final form had a freezing point of 34.3° C. and a water content of 0.05%.

PREPARATION 2. *p*-Toluidine was diazotized and allowed to undergo a modified Sandmeyer reaction. The crude product was separated, treated with barium carbonate, and then purified by fractional distillation. This preparation had a freezing point of 33.3° C. and a water content of 0.09%.

PREPARATION 2A. *p*-Cresol (preparation 2) was recrystallized four times. The crystallization yield was about 50%. The freezing point of this preparation was 34.0° C. and the water content was 0.06%. (The highest freezing point reached as a result of repeated recrystallizations and fractionations was 34.6° C.)

o-Cresol. Paragon (Matheson Company) *o*-cresol (practical, freezing point 30.0° C.) was recrystallized three times. The remaining crystals were distilled at atmospheric pressure, and the intermediate cut was retained. The freezing point of the refined product was 30.7° C., and the water content was 0.08%.

m-Cresol. Paragon (Matheson Company) *m*-cresol (practical, freezing point 9.3° C.) was recrystallized three times in a water bath held at 7° to 8° C. The remaining crystals were distilled at atmospheric pressure, and an intermediate cut was taken. The freezing point of the refined product was 11.3° C., and the water content was 0.10%.

Cyclohexane. Paragon (Matheson Company) cyclohexane was used without further purification as the solvent for the infrared studies.

APPARATUS AND PROCEDURE

A Perkin-Elmer Model 12C spectrophotometer with sodium chloride optics was employed. The thickness of the matched absorption cells was 0.027 mm., determined by the method of interference fringes (*2*). A continuous slit drive was used; the average slit width was about 0.25 mm. This rather low slit width was used for better resolution of the ortho and meta bands. The

absorption bands chosen for the analysis were those suggested by Whiffen and Thompson (*3*) which appeared at 13.37 and 12.92μ for *o*- and *m*-cresol, respectively. These were the bands used by Friedel *et al.* (*1*) in the analysis of mixtures of phenols and cresols and presumably those used by Woolfolk *et al.* (*4*) in their study of complex mixtures containing cresols.

In the present work the base line chosen to represent 100% transmission was the absorption curve for a standard solution of pure *p*-cresol in cyclohexane. A series of synthetic mixtures was prepared to cover the desired range of concentrations. The infrared absorption spectrum for each solution was obtained over the range from 12 to 14μ. A blank determination on the cyclohexane showed no interference in this region. Figure 1 shows a recorded transmission curve. On the recorded chart, 1 cm. corresponds to about 0.01 microvolt output from the thermocouple. The zero transmission base line is not shown.

The following was adopted as a standard working procedure for the analysis of all samples of mixed cresols:

Approximately 1 gram of total cresol was weighed out into a tared weighing bottle of approximately 15-ml. capacity. Cyclohexane (10 ml.) was then pipetted directly into the weighing bottle. After stirring thoroughly, a portion of the solution was transferred to a small glass-stoppered (℥) bottle for storage. The percentage of *o*- and *m*-cresol in the sample is given by the following expressions, obtained from calibration data:

$$\% \text{ ortho} = 1.53 \times A/W \times 100 \qquad (1)$$
$$\% \text{ meta} = 2.90 \times A/W \times 100 \qquad (2)$$

where the A's represent, respectively, the absorbancies of the 13.37μ (ortho) and 12.92μ (meta) bands, and W is the weight of the sample in grams.

A - 100 % P-CRESOL #2 (100 % BASE LINE)
B -   4.9 % ORTHO-, 8.5 % META-CRESOL
C - 14.9 % ORTHO-, 12.6 % META-CRESOL

ALL SOLUTIONS APPROXIMATELY 0.8M
TOTAL CRESOL IN CYCLOHEXANE

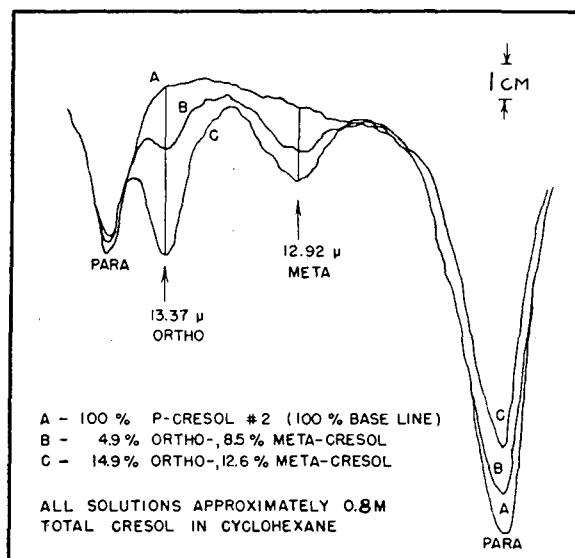13.37 μ ORTHO   12.92 μ META   PARA   1 CM

Figure 1. Infrared Transmission Curve for Cresol Solutions

Table I summarizes the data for sixteen synthetic mixtures. The columns give, successively, the weight of total cresol taken, the average absorbancy of the ortho band taken from several successive wave-length scans, the calculated percentage of *o*-cresol, the actual percentage of ortho- taken, and the difference between

calculated and known percentages of ortho-; the remaining columns give the corresponding data for the meta isomer. Where several observed values are given for a particular mixture, they represent the results of repeated determinations made at other times over a period of several weeks.

DISCUSSION

The largest source of error in the determination is the uncertainty in absorbancy due to the noise-to-signal ratio. The noise level was variable but generally amounted to about ± 1 mm. (0.001 microvolt) or less on the recorder chart, corresponding to approximately 0.5% of the total deflection. For o-cresol at 5% concentration, this corresponds to $\pm 0.4\%$ error; for m-cresol at the same concentration, the anticipated error would be $\pm 0.8\%$. The average deviation of all the results is $\pm 0.3\%$ ortho and $\pm 0.5\%$ meta. These values are somewhat more favorable than the calculated errors, probably because two or more successive wave-length scans were always averaged for each determination.

Samples of purified p-cresol prepared in the different ways previously outlined were compared on the basis of their spectra in the region 12 to 14μ; these were found to be indistinguishable at concentrations of about 1 M.

The results of this study show that an accuracy of approximately $\pm 0.3\%$ for o- and $\pm 0.5\%$ for m-cresol is possible in the low concentration region with the infrared spectrophotometric method described. With the use of absorption cells of greater thickness and a split-beam type spectrophotometer, a considerable improvement in precision should be attainable. Unfortunately, these were not available. The present method does not appear suitable as an analytical technique when the purity of the p-cresol is above 99%. Preliminary experiments have indicated that the freezing point depression offers a more sensitive analytical method for total impurities in the region from 0 to 2% impurity.

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High Frequency Titrations

Mercurimetric Determination of Chloride

W. J. BLAEDEL AND H. V. MALMSTADT
University of Wisconsin, Madison, Wis.

Chloride may be determined in acidic solution by direct titration with 0.01 M mercuric nitrate using the high frequency titrimeter with a precision corresponding to about 0.03 ml. of mercuric nitrate. The end point agrees well with the equivalence point over a considerable range of conditions, allowing a simpler procedure than is possible when chemical indicators are used to establish the end point. For this titration, the high frequency titrimeter appears superior to the potentiometric or conductometric methods for establishing the end point.

CHLORIDE may be determined volumetrically by titration with standard mercuric nitrate according to the reaction:

$$Hg^{++} + 2Cl^- \longrightarrow HgCl_2 \qquad (1)$$

As stated by Kolthoff and Sandell (3), this determination is of considerable practical importance because it allows direct determination of chloride in acid medium even at great dilutions. Inasmuch as there do not exist many such methods, it seems worth while to attempt improvement of the mercurimetric procedure.

Any of several substances may be used as indicators for the mercurimetric titration of chloride. Perhaps the most careful investigation of the procedure is that by Roberts (6), in which 1,5-diphenylcarbohydrazide is used as an indicator. The difficulty with this indicator (and with others) is that the end point is considerably different from the equivalence point and that large blanks are therefore required. The blank—which is as high as 0.5 ml. of 0.01 M mercuric nitrate in some instances (1, 6)—is highly dependent on the conditions of the titration, such as: mercuric chloride concentration at the end point; indicator concentration; acidity; and ionic strength. Close adherence to carefully selected conditions is necessary for accuracy, and this makes for some inflexibility and inconvenience in titration procedure. Particularly troublesome is the dependence of the blank on the amount of sought-for substance—i.e., chloride.

Kolthoff and Sandell (3) recommend use of sodium nitroprus-

side as an indicator, but unpublished work (1) has shown this inferior to 1,5-diphenylcarbohydrazide. Among other things, nitroprusside is unstable, decomposing to cyanide, which reacts with mercuric ion. Potassium iodate and potassium periodate are superior to sodium nitroprusside, but inferior to 1,5-diphenylcarbohydrazide (1).

These difficulties are great enough to prevent widespread use of the mercurimetric procedure. Many of the difficulties are due primarily to inadequacy of the available chemical indicators. By use of an instrumental method to establish the end point, these difficulties may be circumvented.

In this paper, a comparison is made among the potentiometric, conductometric, and high frequency methods of establishing the end point for the mercurimetric determination of chloride. The limiting conditions, together with the relative advantages, of the high frequency procedure are given.

COMPARISON OF POTENTIOMETRIC, CONDUCTOMETRIC, AND HIGH FREQUENCY TITRATION PROCEDURES

No extensive study has been made of the possibility of establishing the end point potentiometrically for the mercurimetric titration of chloride. The prospects for doing so do not seem good. Silver–silver chloride or calomel electrodes are not stable in solutions containing mercuric ion (1, 4). Müller and Aarflot (5) claim
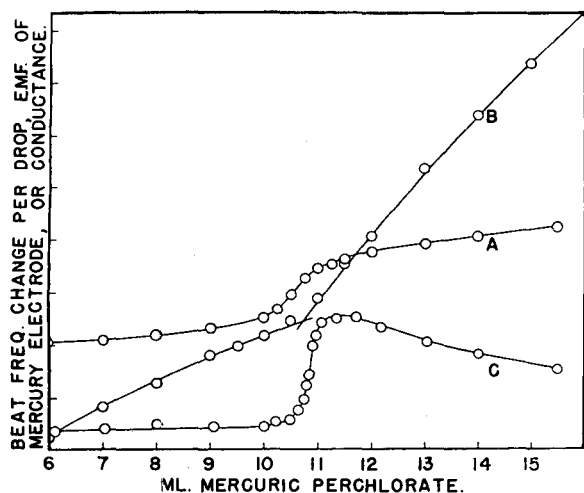
Figure 1. Comparison of Potentiometric, Conductometric, and High Frequency Titration Procedures in Mercurimetric Determination of Chloride

Conditions: 20 ml. of 0.01 M sodium chloride titrated with 0.00920 M mercuric perchlorate in end point volume of 80 ml. End points: Theoretical, 10.86 ml.; potentiometric, 10.65 ml. at 375 mv.; conductometric, 10.70 ml. at 0.00325 reciprocal ohms; high frequency, 10.84 ml.
Scale: One ordinate scale unit equals 100 cycles/sec., or 100 mv., or 0.0003 reciprocal ohms

that chloride may be titrated potentiometrically with mercuric perchlorate, using mercury and normal calomel electrodes, but details of the procedure are not given.

It was not possible to reproduce the work of Müller and Aarflot in this laboratory. By adding metallic mercury to solutions of mercuric perchlorate containing chloride, mercurous chloride was always formed. This was true whether chloride was present in low concentration or in excess of the mercuric perchlorate and also whether the solution was only slightly acid (pH 3 to 4), or highly acid (pH 1). The same results were obtained with mercuric nitrate instead of mercuric perchlorate. This work, in agreement with the standard potentials involved, showed the mercury electrode to be unstable in solutions containing mercuric ion because of the reaction:

$$HgCl_2 + Hg \longrightarrow Hg_2Cl_2 \qquad (2)$$
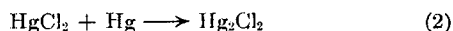
However, consideration of the stoichiometry of this reaction also showed that it caused no stoichiometrical error in the mercurimetric titration of chloride. Within experimental error, this was verified by titrating 20 ml. of standard 0.01 M sodium chloride with a standard solution containing 0.00920 M mercuric perchlorate and 0.005 M perchloric acid to prevent hydrolysis and precipitation of basic mercuric salts. The end point volume was about 80 ml. The end point for these dilute solutions, as shown in curve A, Figure 1, was not good. In addition, the potential did not reach equilibrium rapidly in the region of the end point. In this titration, the calomel half-cell was isolated from the titrated solution by means of a bridge containing 0.1 M perchloric acid to prevent contamination of the solution by chloride. The potentiometric titration is apparently not a good one.

The mercurimetric titration of chloride does not appear to have been performed conductometrically, although this is theoretically possible. A conductometric titration was performed under the same conditions as described

in the potentiometric case. In obtaining the data, an Industrial Instruments bridge (Model RC-1B) was used, and the titration vessel was thermostated at $23° \pm 0.1° C$.

Inspection of the conductometric titration curve (curve B, Figure 1) shows that the end point is not sharp. Three factors contribute to this lack of sharpness:

1. The presence of perchloric acid in the standard mercuric nitrate diminishes the difference in slopes before and after the equivalence point.
2. Curvature in the wings of the titration curve makes for difficulty in locating the equivalence point. Although the end point of curve B, Figure 1, agrees reasonably with the theoretical, the curve could have been just as validly drawn to give an end point differing from this by 0.1 to 0.2 ml. In cases such as this, the spacing of points and personal judgment influence location of the end point greatly.
3. Curvature in the region of the equivalence point, due to formation of mercurous chloride ions, spreads out the end point. This cannot be serious, however, since the high frequency end point is subject to the same error but is quite sharp.

The high frequency curve—curve C, Figure 1—for the same titration as described for the potentiometric case, possesses a sharper end point than the potentiometric or conductometric curves and appears superior as far as the mercurimetric titration of chloride is concerned. The factors which cause spreading of the conductometric end point are minimized by use of the differential titration procedure (2). In the following paragraphs the details and limiting conditions for the high frequency titration are presented.

TITRATION CONDITIONS

Reagents. Mercuric nitrate (0.01 M) was prepared by dissolving the reagent grade salt in water with excess acid to give a concentration between 0.004 and 0.006 M in nitric acid. Excess acid was required to prevent hydrolysis and precipitation of basic mercuric salts. This mercuric nitrate solution was standardized as 0.01086 M with 0.01000 M potassium thiocyanate prepared from Acculute solution. Standard 0.01000 M sodium chloride was also prepared from Acculute solution and checked against the thiocyanate solution by titrating both against equal portions of a 0.03 M silver nitrate solution. All concentrations checked within 0.1%.

Titration Procedure. In all the following titrations, various aliquots of the standard sodium chloride solution were titrated with the standard mercuric nitrate solution. The titrations took place at room temperature (20° to 25° C.), and the end point volumes fell between 70 and 80 ml. The differential titration procedure using the 30-mc. titrimeter was followed in all titrations (2). All titration curves obtained were similar to curve C, Figure 1, although in some cases where larger amounts of acid or interferences were present, the magnitude of the change at the end point was reduced. Results of all titrations performed are summarized in Table I.

There are limitations to the use of the high frequency titrimeter; the principal one is that titrations are restricted to a certain concentration range for adequate sensitivity (2). For the 30-mc. titrimeter, this range corresponds to 0.003 to 0.02 M sodium chloride or 0.0007 to 0.004 M hydrochloric acid. All de-

Table I. Effect of Varying Conditions on End Point in Mercurimetric Determination of Chloride

Detn.	Vol. 0.01000 M NaCl Used, Ml.	HNO₃ Concn. at End Point, M	HgCl₂ Concn. at End Point, M	Vol. 0.01086 M Hg(NO₃)₂ Used, Ml. Observed	Theoretical	Error
1	5.00	0.0002	0.0004	2.30	2.30	0.00
2	5.00	0.0015	0.0004	2.27	2.30	−0.03
3	5.00	0.0030	0.0004	2.33	2.30	+0.03
4	1.00	0.00004	0.0016	0.47	0.46	+0.01
5	5.00	0.0002	0.0016	2.30	2.30	0.00
6	5.00	0.0015	0.0016	2.31	2.30	+0.01
7	5.00	0.0030	0.0016	2.33	2.30	+0.03
8	5.00	0.0015	0.0032	2.31	2.30	+0.01
9	5.00	0.0015	0.0064	2.25	2.30	−0.05
10	5.00	0.0015	0.020	?ᵃ	2.30	?ᵃ
11	10.00	0.0004	0.0008	4.45	4.60	−0.04
12	20.00	0.0007	0.0016	9.25	9.20	+0.05
13	25.00	0.0009	0.0020	11.52	11.51	+0.01
14	50.00	0.0018	0.0040	22.97	23.01	−0.04

ᵃ Indefinite end point.

terminations in Table I fell within this range, except 1 and 4, where potassium nitrate was added as an inert electrolyte to make the sensitivity adequate.

Effect of Acidity on the End Point. Within the range of conditions which could be studied, acidity has a negligible effect on the end point, as shown in determinations 1 to 3. This is not the case where chemical indicators are used to establish the end point. Acidities lower than that in determination 1 could not be studied conveniently, for this acidity resulted from the nitric acid introduced with the standard mercuric nitrate solution. Higher acidities were obtained by adding required amounts of 0.0100 M nitric acid to the samples before titration. In these determinations, the mercuric chloride present at the end point corresponded to that formed in titrating the sodium chloride sample; no mercuric chloride was added.

It was not possible to study directly the effects of low acidity for larger sample sizes because of the appreciable amounts of acid added with the standard mercuric nitrate solution. However, end point concentrations of mercuric chloride corresponding to larger samples of sodium chloride—i.e., 20 ml.—were achieved by adding reagent grade mercuric chloride as 0.100 M solution in determinations 4 to 7. Acidities corresponding to much more than 0.003 M nitric acid could not be studied, for these exceeded the optimum concentration range for good sensitivity of the titrimeter (2).

It is apparent that the end point acidity may lie anywhere between 0.00004 M and 0.003 M without causing error in this titration. The upper limit is set by inability of the 30-mc. titrimeter to handle higher concentrations. When a titrimeter of higher frequency becomes available, larger acidities may be tolerable. Below 0.00004 M, there is an indication, obtained by titration of samples even smaller than that in determination 4, that results are high—i.e., too large a volume of mercuric nitrate is required. This is probably due to hydrolysis of mercuric ion at such low acidity.

Effect of Mercuric Chloride Concentration on End Point. When indicators are used to establish the end point, the sample size has an effect on the size of the blank, owing to the formation of mercurous chloride ions (1, 3). In the high frequency titration, this causes no discrepancy between the observed and theoretical end points, as shown by determinations 2, 6, and 8 to 10. However, the end point inflection was spread out increasingly, until, for determination 10, the end point could no longer be located precisely. (This does not detract from the method; the mercuric chloride concentration of determination 10 would never be achieved by titrating with 0.01 M mercuric nitrate.)

Effect of Sample Size on the End Point. To check the conclusions of the two preceding sections, different sized samples of sodium chloride standard solution were titrated with the mercuric nitrate, as shown in determinations 1 and 11 to 14. No excess nitric acid or mercuric chloride was added; the concentrations of these two substances corresponded to the concentrations added with the standard solutions and the concentrations formed in the titration. These data confirm the agreement between end and equivalence points over a wide range of conditions.

Interferences. Theoretically, any cation may interfere which complexes or precipitates chloride ion with the same order of efficiency as mercuric ion. Also, any anion may interfere which complexes or precipitates mercuric ion with the same order of efficiency as chloride ion.

The possible interferences of several kinds of ions were studied by adding them in roughly equivalent quantities to identical 25-ml. aliquots of a 0.01000 M sodium chloride solution and titrating these aliquots with standard 0.01086 M mercuric nitrate. Results are shown in Table II.

The anions studied were phosphate, acetate, oxalate, borate, fluoride, and cyanide. Of these, none caused appreciable error in acidic solutions except cyanide. In cyanide a single, sharp end point was observed, corresponding approximately to the sum of chloride and cyanide. However, the sharpness of the end point was slightly decreased by all these anions except phosphate. Iodide, bromide, and thiocyanate are known to bind mercuric ion even more effectively than chloride; these were not studied.

The cations studied were cupric, ferric, and plumbous. Table II shows that none of these cations interfered under conditions of these experiments. Silver ion was not studied as it is known to bind chloride even more effectively than mercuric ion.

This study of interferences is not complete, but it is indicative. As the ratio of interfering ions to chloride increases, the error undoubtedly becomes appreciable. This is probably particularly

true in lead, which forms an undissociated chloride, and also in oxalate, which precipitates mercuric ion. The limiting ratios for negligible interferences were not studied; these would probably depend on sample size and acidity.

In any intended application of the method, all potential interferences should be studied before use of the method. There are usually too many considerations involved to predict safely whether or not a particular substance will interfere.

Table II. Interferences in the Mercurimetric Determination of Chloride

[In all determinations 25.00 ml. of 0.01000 N NaCl containing the interfering substance was titrated with 0.01086 M Hg(NO₃)₂]

Interfering Ion		Moles Interfering Ion/Mole Chloride	Titration, Ml. Standard Hg(NO₃)₂ Reqd.
Type	Mode of addition		
None	....	None	11.50
Phosphate	H₃PO₄	0.5	11.53
Acetate	HOAc	1.0	11.49
Oxalate	H₂C₂O₄	0.5	11.48
Borate	H₃BO₃	1.0	11.53
Fluoride	KF	2.0	11.50
Cyanide	KCN	1.0	22.3
Cupric	Cu(NO₃)₂	0.5	11.53
Ferric	Fe(NO₃)₃	0.5	11.50
Plumbous	Pb(NO₃)₂	0.5	11.48

CONCLUSIONS

Table I shows it is possible to determine chloride directly by high frequency titration with a precision corresponding to 0.03 ml. of 0.01 M mercuric nitrate. There is no appreciable bias on the results. Accurate results are obtained over a wide variety of conditions when the 30-mc. high frequency titrimeter is used. Nitric acid concentration may range from 0.00004 to 0.003 M at the end point. Sample size has no effect on accuracy, as long as the mercuric chloride concentration formed at the end point does not exceed 0.006 M; above this concentration, the sharpness of the end point decreases. No variable blank corrections are needed. Interferences do not appear to be many.

For the mercurimetric titration of chloride, the high frequency titrimeter appears to be superior to the conductometric or potentiometric methods for establishing the end point. This procedure illustrates how the high frequency titrimeter may be used to simplify existing titration procedures.

It must be stated unequivocally that the mercurimetric determination of chloride is inferior to the argentimetric determination, providing a precipitate is not objectionable, since the end point is considerably sharper for the latter procedure (2).

The effect of temperature on the end point could not be systematically studied without inconvenience. However, the end point is not critically dependent on temperature, for the titrations in Table I were carried out at room temperature, which varied from 20° to 25° C.

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High-Frequency Titrations

A 350-Megacycle Titrimeter

W. J. BLAEDEL AND H. V. MALMSTADT, *University of Wisconsin, Madison, Wis.*

A stable and sensitive high-frequency titrimeter using quarter-wave-length concentric-line oscillators and operating at 350 Mc. per second is described. All the basic types of titrations have been performed with it, and it is possible to carry out titrations with a considerable quantity of foreign electrolyte present. Precise and accurate titration curves are presented.

RECENTLY there have been described high-frequency titrimeters which measure frequency changes in the course of a titration (1, 7). The titration vessel is placed in the tuning circuit of a high-frequency oscillator, and as the composition of the solution changes, the frequency of the oscillator changes. A plot of frequency against volume of standard solution gives a titration curve much like that for a conductometric titration. The value of such an instrument to the analytical chemist is obvious, for neither indicator nor electrodes nor physical contact of any sort with the solution are necessary to perceive the end point in a titration.

A stable, sensitive titrimeter using the simple Clapp (2) oscillator, and operating at 30 megacycles, has been described in detail (1). Briefly, this titrimeter consists of two oscillators, one of which is loaded with the titration vessel, the other unloaded. The output frequencies of the two oscillators are mixed and a continuous indication of the beat (difference) frequency is obtained on a conventional frequency meter. Because the frequency of the unloaded oscillator remains constant, the beat frequency is a measure of the change in frequency of the oscillator which is loaded with the titration vessel.

Many different kinds of titrations may be precisely performed using the 30-Mc. titrimeter, but the instrument possesses one serious fault which makes it difficult or impossible to perform many useful titrations: The sensitivity of the instrument drops off very rapidly when the electrolyte concentration in the titration vessel rises above a maximum value. For the 30-Mc. instrument, the maximum tolerable electrolyte concentration is rather low, and corresponds to about 0.06 M sodium chloride (1). Although many kinds of titrations may be successfully performed below this limit, others may not, and it is a definite disadvantage to be restricted to so low a total electrolyte concentration.

Considerations recently presented (1) show that the maximum tolerable electrolyte concentration is directly proportional to frequency. It follows, therefore, that the frequency of the titrimeter must be increased if the maximum tolerable electrolyte concentration is to be increased. From these considerations, a titrimeter operating at about 350 Mc. per second would have a maximum tolerable electrolyte concentration corresponding to 0.7 M sodium chloride or its equivalent. With such a titrimeter, it would be possible to carry out most titrations even with large amounts of foreign electrolyte present.

In this paper, the construction, properties, and use of such a 350-Mc. titrimeter are described, and typical titration curves are given. Quarter-wave-length concentric-line oscillators are used. The sensitivity and stability are sufficient to carry out most titrations, even when a considerable quantity of foreign electrolyte is present.

DESCRIPTION OF 350-MEGACYCLE TITRIMETER

Quarter Wave-Length Concentric-Line Oscillators. It was believed necessary to maintain the same high stability at 350 Mc. per second as found with the 30-Mc. titrimeter, which possessed a stability of 5 cycles per second—i.e., a stability of 2 to 10^7. A survey of the electronics literature for very stable and simple oscillators operating at 300 to 500 Mc. per second was not encouraging. A quarter-wave-length concentric-line oscillator seemed the best of several kinds described (6), even though it was stated to possess a frequency stability of only 1 to 10^5. However, it appeared possible to improve this stability with better mechanical construction and certain other circuit changes. This proved to be the case.

The complete assembly of the oscillators and lines is shown in Figure 1. Figure 2 is a schematic diagram of one of the oscillators. The construction of the oscillators and lines is described in considerable detail in the following paragraphs for two reasons: (1) Extreme care in layout of parts and mechanical construction is essential. Reproduction of this equipment might be very difficult or unsuccessful without these details. (2) No dependence may be placed upon the literature of electronics, for there is
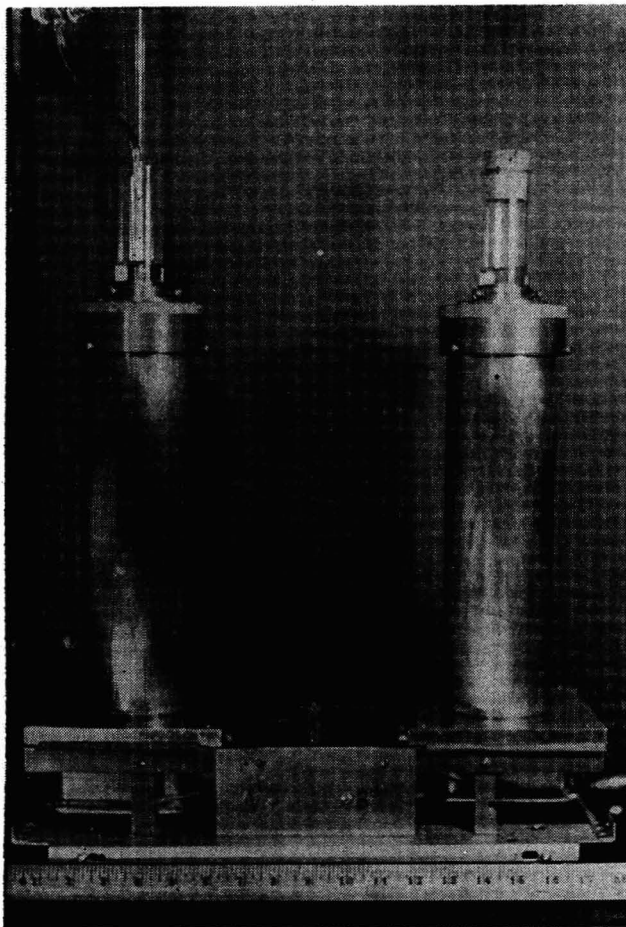

Figure 1. Assembled 350-Megacycle Titrimeter

no description available of a simple 300- to 500-Mc. oscillator with the requisite stability.

The quarter-wave-length line oscillator shown in Figure 2 consists of a brass cylinder, A, and a coaxial Invar rod, C. D and E are the input and output coupling loops, respectively.

A was made from brass tubing (0.125-inch wall, 3.5 inches in outside diameter, and 12 inches long). The lower edge of the cylinder was machined with a No. 20 thread to screw into the square, brass plate base, B ($6 \times 6 \times 0.5$ inch), to a depth of 0.25 inch. The lower edge of the cylinder was beveled slightly (see Figure 2), so that the inner edge dug firmly into the base, B, to make good high-frequency electrical contact.
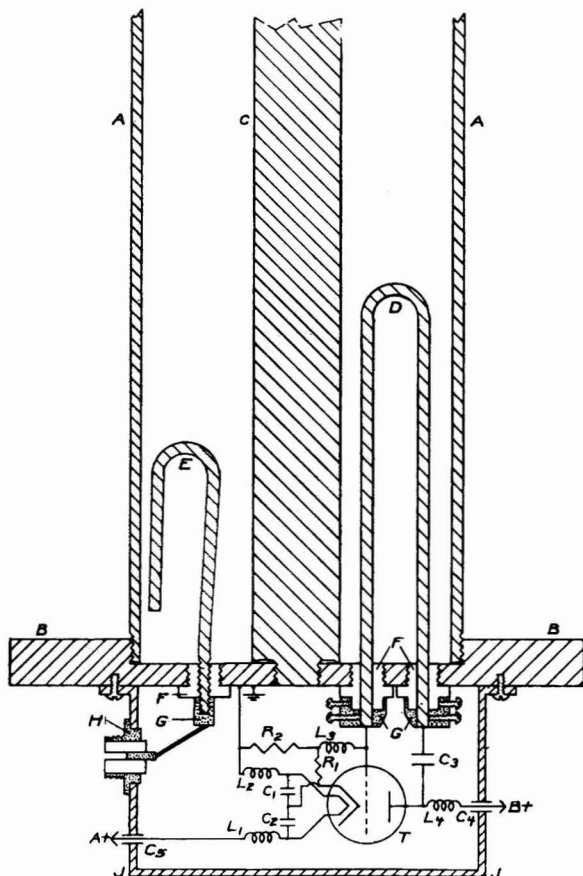
Figure 2. Schematic Diagram of 350-Megacycle Titrimeter

$A, B, C, D, E, F, G, H, J$.   See text
A^-.   6-volt high capacity storage battery
B^+.   B batteries (225 volts)
C_1, C_2.   56 $\mu\mu f$. ceramic condensers, zero temperature coefficient
C_3.   200 $\mu\mu f$ "silver mica" condenser
C_4, C_5.   55 $\mu\mu f$ chassis lead-out condensers
L_1, L_2.   4 turns, No. 18 stranded wire, cellulose acetate yarn wrap, $1/4$ inch diameter closely wound
L_3, L_4.   6 turns, No. 22 copper wire on $3/8$ ceramic former, wire diameter spacing between turns
R_1.   750-ohm resistor
R_2.   12,000-ohm resistor
T.   955 tube

C was an Invar rod ($29/32$ inch in diameter $\times$ 8.25 inches), threaded into B to a depth of 0.25 inch with a $1/2$-20 thread, so that it was coaxial with A. The lower end of the rod was also beveled to give good contact with the base. It was the length of this rod which determined the frequency of oscillation, and for high-frequency stability it was necessary to keep the length invariant. Invar was used because of its low temperature coefficient of expansion. In order to obtain high "Q" and high stability, the ratio of the inner diameter of A to the diameter C was chosen to be about 3.6; C, B, loops D and E, and the inner surface of A were all silver plated (6). To prevent radiation loss from the line, the cylinder was extended about one eighth of a wave length above the top of the rod.

The hairpin-shaped input coupling loop, D, was made from Invar rod (0.125 inch in diameter) and was $9/16$ inch wide and 4 inches long. Without the feed-back resistor, R_1, the length of
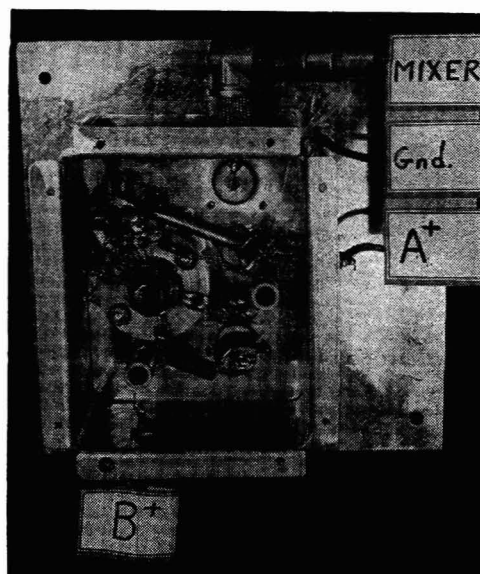
Figure 3.   Oscillator

this loop required to avoid parasitic oscillations was critical. With the equipment shown in Figure 2, but without R_1, parasitic oscillations could not be eliminated by varying the length of loop from 3 to 4 inches. Use of the feed-back resistor, R_1, eliminated parasitic oscillations, but no study was made to determine over what limits the loop length could be varied without reintroduction of the parasitics.

E was the output coupling loop (also made from $1/8$ inch rod) which fed some of the high-frequency energy to the mixer unit. The size of this loop was obtained by trial and error. A straight rod and small loops were first used, but these did not couple a sufficiently large signal into the mixer unit. A satisfactory loop was of the shape shown in Figures 2 and 4. The height was 2.375 inches from B to the top of the loop. Because this loop proved successful, no further study was made to determine size limits or other possible configurations.

Loops D and E passed through porcelain insulators, F, which were screwed into B. The insulators had $7/16$-14 threads. Porcelain was used rather than polystyrene because polystyrene was susceptible to deformation by heat when soldering leads. However, polystyrene would probably have worked as well if excessive heat had not been applied.

Brass fittings, G, held the loops firmly in place and provided soldering points for leads to the oscillator circuit (see Figure 3 also). J was a shielded aluminum chassis ($3 \times 3.5 \times 2.5$ inches deep) which was screwed to the bottom side of B. The output to the mixer was taken through the coaxial junction, H (Amphenol 83-1R), which was connected with a very short lead to output loop E. The other parts of the oscillator are shown in the schematic diagram, Figure 2, and their general lay-out in Figure 3. Figure 4 shows the resonant line with the cylinder removed.

A 6-volt high-capacity storage battery was used for the filaments of both oscillators, and B batteries (225 volts) were used for the plate supply.

The cap for holding the titration vessel in the top of the quarter-wave-length line is shown in Figures 1 and 4. Dimensions were not critical, but good mechanical construction was necessary to hold the titration vessel firmly in place and to allow no movement during titration. The titration vessel (a test tube, 8 inches $\times$ 1.5-inch diameter) slip-fitted into a split collar attached to the cap, and could be easily inserted or removed by loosening or tightening a setscrew. The cap was threaded to fit a No. 32 thread on the top end of the brass cylinder (A, Figure 2). This arrangement allowed precise positioning of the titration vessel in the high-frequency field, so that any desired beat frequency or sensitivity could be obtained, as described later. Both of the concentric lines were equipped with such caps.

Mixer. The mixer unit that was first used was a small crystal unit similar in design to the one described with the 30 Mc. per second titrimeter (1). Although this mixer gave beat frequencies and isolated the oscillators sufficiently, it possessed a nonlinear characteristic—that is, the beat frequency output from the mixer,

as measured on a frequency meter, was not strictly proportional to the actual difference in frequencies of the two oscillators. The cause of this was undetermined. It was actually possible to use this unit, but it caused some scattering of points used to determine the titration curves. Consequently, a different mixer was used.

It was expedient to use the duo-diode mixer contained in a war surplus radio altimeter, APN-1 (4). The unit was removed from the altimeter and kept intact, except that a coaxial junction was used to replace the coupling loop and lead which ordinarily coupled into the transmitter of the altimeter. It was thereby possible to couple both oscillators of the titrimeter into the mixer with the usual coaxial leads. This unit worked very well. The isolation of oscillators was good, and "pulling" of the beat frequency was noted only below 500 cycles.

Frequency Meter. A simple, four-tube, direct-reading frequency meter was used. The frequency was read directly on a milliammeter (4 inches square, 0 to 1 mil full scale). Three sensitivities were available, corresponding to 2500, 5000, and 50,000 cycles per second for full scale deflection, and meter response was linear with frequency for these three ranges. This meter and its power supply were constructed with some modifications from a war surplus crystal duplicator (Majestic Radio and Television).

The circuit diagram of this frequency meter is not given here. A more compact and versatile circuit is being built and will be described in a future publication. The circuit diagram of the mixer is not given; at present a project is under way to construct a simple and compact unit that will work well at frequencies even higher than 350 Mc. per second.

PROCEDURE FOR PERFORMANCE OF TITRATIONS

The titration tube containing the solution to be titrated was inserted and fixed firmly in position by tightening the setscrew on the holder cap. The position of the titration tube was adjusted so that the bottom of the tube was a predetermined distance from the top of the Invar rod, depending on the sensitivity desired. Reference marks on the side of the tube were used to indicate this distance. The volume of solution used was always sufficient to keep the level above the top of the holder cap (about 100 ml.). The solution was stirred with a small, motor-driven stirrer, which could be extended as far as 2 inches into the concentric line without introducing noticeable fluctuations in the beat frequency.
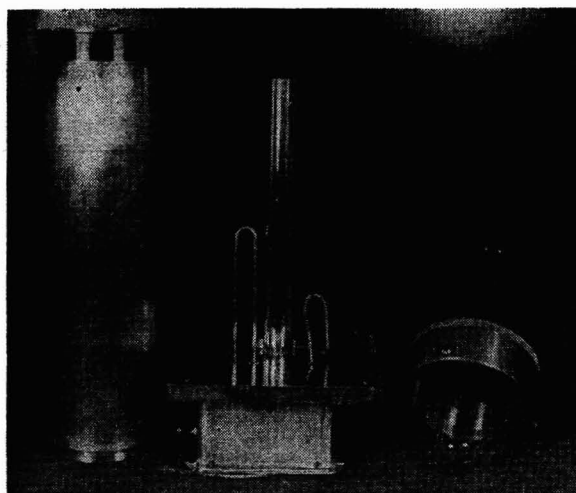
Figure 4. Concentric-Line Oscillator with Outer Cylinder and Vessel Holder Removed

The cap on the reference oscillator was adjusted for a beat frequency such that the frequency meter needle fell at the far left end of the scale, using minimum frequency meter sensitivity. Then, using the medium or fine sensitivity, the reference oscillator was further adjusted to have a higher or lower frequency than the titration oscillator, depending on the titration performed, and so the meter needle always traveled from left to right at the start of a titration. The beat frequency was always kept above

500 cycles per second when titrating, so that "pulling" would not occur.

It was common practice to run through a titration rapidly with the meter set on coarse range. It was possible to locate the end point roughly with this method by watching the meter and observing when the frequency change per unit volume of standard solution underwent an abrupt change. Another equal aliquot of solution was then titrated carefully in the region of the end point. The frequency meter was set on either fine or medium sensitivity, and the frequency changes were precisely read and recorded as a function of volume of standard solution added.

For some titrations it was possible to use the differential procedure described in connection with the 30-Mc. titrimeter (1). However, when a large quantity of foreign electrolyte was present the frequency changes per drop of standard solution were usually not large enough to be precisely read. In order to be consistent, one method of carrying out titrations with the 350-Mc. titrimeter was adopted.

This method consisted of adding the standard solution in 0.5-ml. increments over a range of several milliliters on both sides of the end point, and recording the change in beat frequency after each addition on the medium sensitivity scale of the frequency meter. (The fine sensitivity scale was used only for differential titrations.) Commonly, the total frequency change in this region was greater than 5000 cycles, corresponding to full scale deflection on medium sensitivity. In such cases, the frequency meter was reset as the needle approached full scale by turning the holder cap on the reference oscillator so as to bring the meter needle back to the far left of the scale. Several such resettings were sometimes required in the course of a titration. Titration curves similar in form to those for conductometric titrations were plotted by adding each successive beat frequency change to the total before it and plotting total frequency change against volume of standard solution (see Figures 7 to 9, inclusive).

Curves from data taken in this way were extremely smooth; errors due to occasional and rare fluctuations, caused by jarring the instrument, were for the most part eliminated, as were errors due to drifts occurring during temperature equilibration. Inspection of the curves in Figures 7 to 9 shows that the segments of the titration curves have little curvature. This indicates that the sensitivity of the instrument remained constant through the region over which the data was taken. The reason for this was twofold: (1) There was considerable foreign electrolyte present in most of the titrations. (2) The data were taken only in the region about the end point. Both factors combined to maintain fairly constant ionic concentration (and therefore constant sensitivity).

CHARACTERISTICS OF TITRIMETER

Stability. After 10 to 20 minutes were allowed for warming up, it was found that the two oscillators beating together gave a beat frequency which had an average fluctuation of 50 cycles when operating at 350 Mc. per second. This represented a relative stability of about 1 to 10^7. The time required for warming up was usually 15 to 20 minutes.

After the solution had reached the equilibrium temperature of the titrimeter, the beat frequency drifted negligibly. This indicated that the dimensions of the frequency-determining resonant lines remained constant and that the amount of energy absorbed by the solution was so small that it did not heat appreciably. It was noted that, even after the instrument had warmed up, there were very slow drifts of beat frequency for a short time after insertion of a sample, probably due to temperature changes of the solution. These caused no difficulty in the titration procedure described above.

Sensitivity. A quantitative study was made of the dependence of sensitivity on concentration. To do this, the change in frequency was observed on adding standard hydrochloric acid into

hydrochloric acid solutions of known concentration. The same was done for sodium chloride.

In Figures 5 and 6 beat frequency is plotted as a function of concentration of the electrolyte in the titration vessel. These plots show that the frequency changes with concentration only within certain concentration ranges, depending on the nature of the electrolyte. This is in accord with the theoretical considerations recently described (*1*, *3*).

As stated previously, the sensitivity could be varied simply by changing the distance between the bottom of the titration vessel and the top of the quarter-wave-length Invar rod. The adjustment of this distance was easy and provided an excellent means of selecting any desired sensitivity. The sensitivity curves for three different distances are given in Figures 5 and 6. It was noted that decreasing the distance from 1 to 0.75 inch tripled the sensitivity.
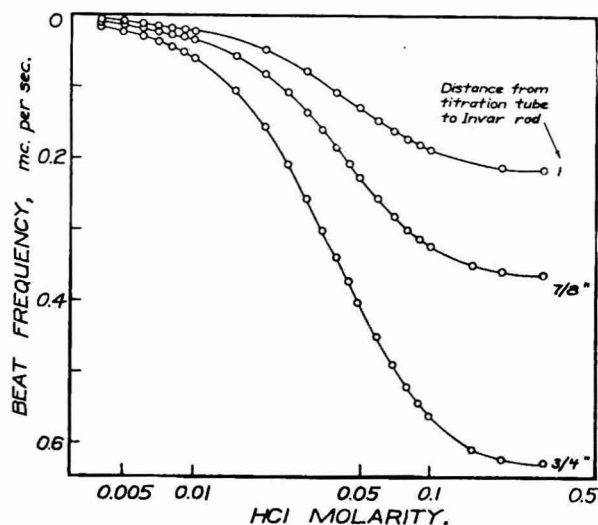
Figure 5.   Sensitivity Curves for Hydrochloric Acid
Solutions

It was not possible to obtain a beat frequency at a distance of 0.625 inch or less, even though the oscillators remained in oscillation. Although the reason for this was not definitely established, it was believed due to setting in of a parasitic oscillation. It was considered likely that certain changes in design would have enabled a decrease in the distance between the titration tube and Invar rod with an attendant increase in sensitivity. These changes were not attempted for two reasons: (1) The attainable sensitivity was amply sufficient to carry out most titrations, even with a considerable quantity of foreign electrolyte present. (2) The changes required a completely different design and construction.

TITRATIONS PERFORMED

It was found that the 350-Mc. titrimeter could be used to determine end points in titrations based on acid-base, precipitation, soluble complex formation, and redox reactions. In all cases, observed end points agreed excellently with calculated equivalence points based on other accepted methods of titration. In the following paragraphs there are discussed only typical titration curves which illustrate certain characteristics or potentialities of the titrimeter. All titrations were carried out at sensitivities between the 1-inch and 0.75-inch position (see Figures 5 and 6).

Titration of Silver Nitrate with Standard Sodium Chloride. Figure 7, *A*, shows the titration of 25 ml. of 0.1 *M* silver nitrate with 0.1 *M* sodium chloride in an end-point volume of about 125 ml. Sodium nitrate was present as a foreign electrolyte, the

total electrolyte concentration consisting of 25 mole % silver nitrate and 75 mole % of *sodium nitrate* at the beginning of the titration. In this case, the total electrolyte concentration at the end *point* was less than 0.1 *M*, and the addition of 0.1 *M* sodium chloride after the end point caused an increase in concentration and a reversal in the titration curve.
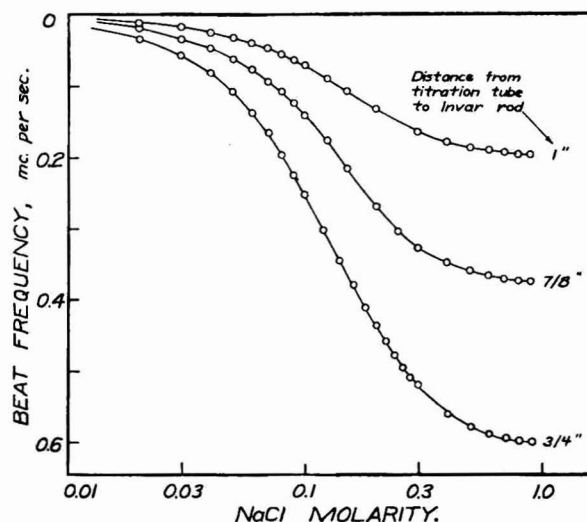

Figure 6.   Sensitivity Curves for Sodium Chloride
Solutions

Figure 7, *B*, shows the titration of silver nitrate with 0.1 *M* sodium chloride when the total concentration of electrolyte consisted of 10 mole % of silver nitrate and 90 mole % of sodium nitrate at the beginning of the titration. The total concentration at the end point was about 0.2 *M*. The addition of 0.1 *M* sodium chloride after the end point thus caused a dilution and no reversal was observed. However, because of the preciseness of obtaining the beat frequency changes, a sharp and accurate end point was obtained. The presence of the precipitate did not affect the frequency stability.

Standard sodium chloride and silver nitrate solutions were prepared from Acculute solutions, and were checked against each
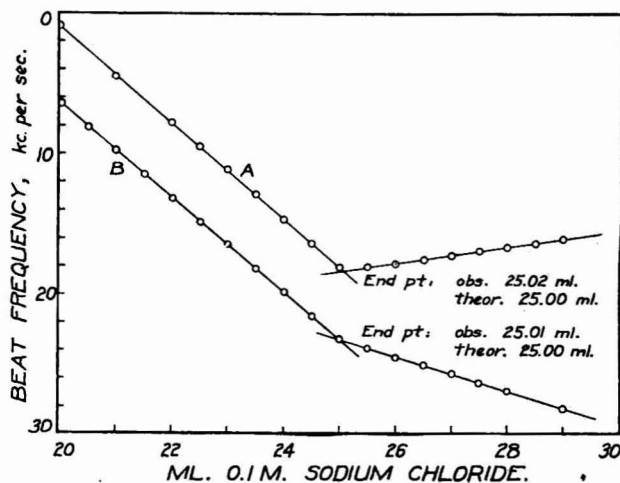

Figure 7.   Titration of Silver Nitrate with Standard
Sodium Chloride

A.   25 ml. of 0.1 *M* silver nitrat etitrated with 0.1 *M* sodium chloride
in presence of 75 ml. of 0.1 *M* sodium nitrate
B.   25 ml. of 0.1 *M* silver nitrate titrated with 0.1 *M* sodium chloride in presence of 22.5 ml. of 1.0 *M* sodium nitrate

other using the Mohr (chromate indicator) method. On the curves of Figure 7 are indicated the theoretical equivalence points calculated from the standard concentrations. Agreement of observed with calculated end points is excellent. These titrations show that a considerable quantity of foreign electrolyte is tolerable during a titration; this is not the case in conductometric titrations.

Titration of Mercuric Nitrate with Potassium Thiocyanate. Figure 8 shows the titration of 25 ml. of 0.05430 M mercuric nitrate with standard 0.1 M potassium thiocyanate in an endpoint volume of about 125 ml. This curve is plotted on an enlarged scale to illustrate the precision of the measurements, and to show how small are the deviations of the experimental points from the best straight lines through them.

To prepare standard mercuric nitrate solution, reagent grade, red mercuric oxide was dissolved in an excess of nitric acid. This solution was standardized against 0.1 M Acculute potassium thiocyanate solution, using ferric alum as an indicator. The theoretical end point on Figure 8 was calculated from these standard concentrations. There is excellent agreement of the observed and calculated end points.

Titration of Oxalic Acid with Thorium Nitrate. In Figure 9 is given the curve for the titration of 25 ml. of 0.04972 M oxalic acid with standard 0.02466 M thorium nitrate in an end-point volume of 125 ml. The oxalic acid was weighed out as a primary standard and checked against Acculute potassium permanganate. The thorium nitrate was prepared from Baker's reagent grade thorium nitrate and standardized gravimetrically (5). The theoretical end point calculated from the standard concentrations is annotated on Figure 9 and agrees well with the observed end point.

characteristics of the instrument supports the theory of high-frequency titrations advanced earlier by the authors.

The existing titrimeter is considered an experimental model, for there appear to be many possibilities for improvement of this first instrument of the concentric-line type. An improved design is under construction in this laboratory, and a long-range study is planned to obtain maximum stability and sensitivity with this type of titrimeter. With increased stability and sensitivity, it might be possible to titrate small quantities of a sought-for constituent in the presence of considerable quantities of foreign electrolytes.
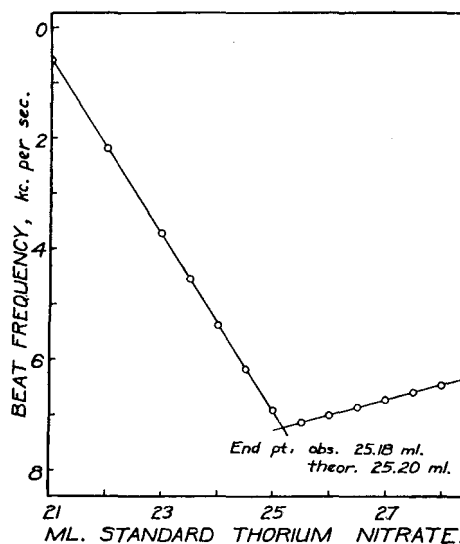

Figure 9. Titration of Oxalic Acid with Thorium Nitrate

25 ml. of 0.04972 M oxalic acid titrated with 0.02466 M thorium nitrate

To date, the indications are that stable and sensitive high-frequency titrimeters may be built and used in titrations to give an accuracy comparable to that of good gravimetric methods—i.e., 0.1%. These instruments are neither inexpensive nor simple to build. Once built, however, they are simple to use and very easy to maintain. If and when some of the potentialities of the high-frequency titrimeter are definitely proved and illustrated, it may become apparent that the time and expense of construction are more than compensated by the new methods of analysis made possible by this instrument.

Figure 8. Titration of Mercuric Nitrate with Standard Potassium Thiocyanate

25 ml. of 0.05430 M mercuric nitrate titrated with 0.1 M potassium thiocyanate

This titration illustrates how the 350-Mc. titrimeter may be used to devise new procedures in volumetric analysis. A simple and relatively rapid method for the determination of thorium based upon the oxalate titration is being worked out.

CONCLUSIONS

The 350-Mc. titrimeter is a stable and sensitive instrument, and may be used for most titrations, even when considerable quantities of foreign electrolytes are present. A study of the

ACKNOWLEDGMENT

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Measurement of Large Partition Coefficients by Interchange Extraction

CALVIN GOLUMBIC AND SOL WELLER

Research and Development Branch, Office of Synthetic Liquid Fuels, Bruceton, Pa.

A satisfactory method for measuring large (or small) partition coefficients is described. The method is essentially a means of increasing the concentration of solute in the denser (or lighter) phase until measurable values are obtained. The technique by which this can be accomplished is termed "interchange extraction." The method was subjected to precise mathematical analysis, which led to the development of an equation relating the partition coefficient to the number of extraction stages. The equation was tested by the experimental determination of the partition coefficients of o-phenylphenol in two systems.

THE partition coefficient of a compound is usually a readily measurable quantity that is useful as a supplementary constant for identification purposes (1), for devising isolation schemes (4), and, when the compound in question has an acidic or basic function, for calculation of acid or base strength (3). Partition coefficient, k, is usually defined by the expression

$$\frac{\text{concentration of solute in lighter phase}}{\text{concentration of solute in denser phase}}$$

It may be measured in two ways: by determining the concentration of solute in one phase before and after equilibration, and by measuring the concentration of the solute in each phase after equilibration. Both methods are usually inadequate when the partition coefficient is very large or very small (>100 or <0.01). Under these circumstances, the first method may be modified by successive extraction of the phase in which the solute predominates with fresh portions of the other phase in order to magnify the decrease in concentration of the solute (5). As this alteration in technique still entails measurement of a relatively small difference between large numbers, a suitable modification of the second method is desirable. Such a procedure has been developed and is described in this report. It is a technique of "interchange extraction," whereby the concentration of the solute in the phase containing the lesser amount of solute is raised to an accurately measurable range.

Interchange extraction involves the following operations:

The solute is dissolved in the phase of preferential solubility, which is then equilibrated with the other phase in a separatory funnel. After stratification of layers, the denser phase is drawn off into a second separatory funnel. Fresh lighter solvent is added to the second separatory funnel and fresh heavier solvent to the first funnel; both are shaken. This operation completes the first stage. For the next stage, the lower phase of the second separatory funnel is transferred to a beaker and replaced by the denser phase of the first funnel. The liquid layer in the beaker is then poured into the first funnel, and both funnels are shaken. This step completes the second stage. The process consists, therefore, of stepwise interchange of the heavier phase, according to the scheme shown below:

Solute .

L phase	⇌	L phase
H phase		H phase
I		II
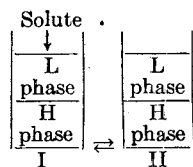
It is noteworthy that this technique of extraction could be carried out in a Craig countercurrent distribution instrument (2), provided every other upper tube of the instrument contained identical solutions of the solute at the start.

At the conclusion of a large number of stages, the quantity of solute in the phase of preferential solubility in each funnel is determined by any convenient method. The partition coefficient is then calculated by Equation 2, the development of which is given in the following section.

THEORY OF INTERCHANGE EXTRACTION

Let $k' = $ (weight of solute in upper layer)/(weight of solute in lower layer); $r = $ (volume of upper layer)/(volume of lower layer); $k' = k\,r;\ n = $ number of stages (interchanges of lower layer); $m_0 = $ weight of total solute present; and $m = $ weight of solute in any layer. Solute is present originally only in funnel I, funnel II being solute-free. The distribution of solute (expressed in units of weight fraction of total solute present, m/m_0) before interchange ($n = 0$) and after the first two stages ($n = 1$ and 2, respectively) is shown in the following scheme. In each instance, the indicated distributions are those that exist after equilibration of layers. It is assumed that the partition coefficient is independent of concentration.

n	Funnel I	Funnel II
0	$k'/(k'+1)$ $1/(k'+1)$	0 0
1	$k'^2/(k'+1)^2$ $k'/(k'+1)^2$	$k'/(k'+1)^2$ $1/(k'+1)^2$
2	$(k'^3+k')/(k'+1)^3$ $(k'^2+1)/(k'+1)^3$	$2k'^2/(k'+1)^3$ $2k'/(k'+1)^3$

For concreteness, the discussion may be limited to the case where the partition coefficient is very large. The phase of preferential solubility is then the upper layer, and attention may be directed particularly to the solute content of the upper layer of funnel II.

Table I. Partition Coefficients and Ionization Constant of o-Phenylphenol

System	n	r	k	pKa
Cyclohexane-water	9	0.333	87	..
Cyclohexane–phosphate buffer, pH 6.65	9	0.333	270	9.7

In stages 3, 4, and 5, for example, the fractions of total solute found in the upper layer of funnel II (m_{IIu}/m_0) are $(3k'^3 + k')/(k'+1)^4$, $(4k'^4 + 4k'^2)/(k'+1)^5$, and $(5k'^5 + 10k'^3 + k')/(k'+1)^6$, respectively. For n stages of extraction, the value of this fraction is found to be of the form

$$\frac{(nk'^n + y_n k'^{n-2} + \text{terms of the order of } k'^{n-4} \text{ and smaller})}{(k'+1)^{n+1}} \quad (1)$$

Because large values of k' are being considered, the third and higher terms in the numerator may be neglected in comparison with the first two. The coefficient y_n satisfies the difference

equation, $y_{n+2} = n^2 + y_n$, the solution of which is $y_n = n/3 - n^2/2 + n^3/6$. To a good approximation, therefore,

$$\frac{m_{IIu}}{m_0} = \frac{nk'^n + (n/3 - n^2/2 + n^3/6)k'^{n-2}}{(k' + 1)^{n+1}} \quad (2)$$

The value of k' is easily determined from Equation 2 by successive approximations; a first approximation is $k' = n/(m_{IIu}/m_0) - 1$. Both m_{IIu} and m_{Iu} are determined at the end of the multistage extraction; m_0 is best taken as $m_{IIu} + m_{Iu}$, or, if very precise values are desired, the small amounts of solute present in the lower layers of both funnels may be calculated, using an approximate value of k', and included in m_0. The value of k is obtained from the relation $k = k'/r$.

The preceding discussion has explicitly treated the case where the partition coefficient is very large. If the partition coefficient is very small, exactly analogous considerations are involved, except that in this case the lower rather than the upper layer of each funnel should be analyzed.

MEASUREMENTS WITH o-PHENYLPHENOL

The interchange extraction technique was tested by measuring the partition coefficients of o-phenylphenol for distribution in the systems, cyclohexane-water and cyclohexane-0.5 M phosphate buffer of pH 6.65. The initial concentration of solute in the cyclohexane was 0.5 mg. per ml. The ratio of cyclohexane to aqueous phase was 1 to 3. The extractions were carried out in centrifuge separatory funnels equipped with capillary outlets; the funnels were centrifuged to clarify layers at the end of each

stage. After nine stages, the concentration of o-phenylphenol in each cyclohexane layer was determined by measuring its optical density at 280 mμ with the Cary recording spectrophotometer. Partition coefficients were then calculated by means of Equation 2. The results of these measurements are presented in Table I. The partition coefficient in the cylohexane-buffer system is much higher than the partition ratio in the cyclohexane-water system because of the salting-out effect of the buffer. Both ratios are about 10 to 20% lower than those previously obtained by the less precise, successive extraction technique (5). From the partition coefficient at pH 6.65 and from the previously determined partition ratio at pH 12.54 (3), the value of pKa was calculated (Table I). This value agrees with that obtained earlier (5) within 0.1 pK unit.

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Determination of Aromatics and Olefins in Wide Boiling Petroleum Fractions

A. E. SPAKOWSKI, ALBERT EVANS AND R. R. HIBBARD

National Advisory Committee for Aeronautics, Lewis Flight Propulsion Laboratory, Cleveland, Ohio

A method is described for the analysis of wide boiling petroleum fractions with end points below 600° F. Chromatography is used to split the sample into four fractions: nonaromatic, intermediate, pure aromatic, and a pure aromatic "wash." The per cent aromatics in the intermediate fraction is determined by specific dispersion and the total aromatics in the sample is the sum of those found in the intermediate and final two fractions. Total olefins plus aromatics are determined by sulfonation and olefins by difference. Accuracies of 1% are attained with analysis times of less than 8 hours.

IN ORDER to understand more fully the effect of fuel variables in aircraft propulsion systems, it is often necessary to determine the concentration of olefin and aromatic hydrocarbons in petroleum products. The most recent turbojet fuel specifications (AN-F-58a) call for a wide boiling fuel with 5- to 7-pound Reid vapor pressure and a 600° F. end point. Aromatics up to 25% and olefins equivalent to a 30 bromine number are permitted. A review of the literature showed the following general methods which might be applied to fuels of the AN-F-58a type.

The first of these is the A.S.T.M. procedure in which olefins and aromatics are absorbed by a mixture of sulfuric acid and phosphorus pentoxide, olefins are calculated from bromine number, and aromatics are obtained by difference (2). The concentrations of paraffins and cycloparaffins can also be estimated from the older A.S.T.M. method, using refractivity intercept and the density of the raffinate from the sulfonation (1). Occasionally inaccurate results will be obtained by the use of this A.S.T.M. procedure. Its greatest weakness appears to be in the calculation of the per cent olefins from bromine number and the molecular weight where the average molecular weight of the olefins

and not of the total sample is required. The molecular weight is estimated from the 50% boiling point of the total sample in the A.S.T.M. procedure and substantial errors often result in the calculation of the per cent olefins. Errors in per cent olefins are also reflected as equal errors of opposite sign in the determination of the per cent aromatics by A.S.T.M. procedure. Although the approved method for the analysis of AN-F-58a fuels is the A.S.T.M. procedure, these fuels may have bromine numbers above the value of 20, which is the maximum permitted in the scope of the method.

The A.S.T.M. silica gel method (3) applies to fuels containing less than 1% olefins and therefore does not cover the AN-F-58a specifications.

Another general method relies on chromatography alone to split samples into paraffin and cycloparaffin, olefin, and aromatic fractions. Mair (14) and Dinneen (7) have proposed this type of analytical separation. Both have shown its effectiveness on relatively simple blends and Dinneen has also given data on shale oil naphthas (7). However, it has been the authors' experience that, while good separations are obtained on multicomponent

blends of pure hydrocarbons, an olefin plateau is not obtained in the chromatographic fractionation of the complex type fuels when small amounts (10% or less) of olefins are present. Thus this method is not universally applicable to fuels meeting the AN-F-58a specifications.

Grosse and Wackher developed a method for the determination of aromatic hydrocarbons in fuels based on the measurement of the specific dispersion of the sample (8). The relative uncertainty of the method on turbojet-type fuels lies in the inaccuracy of the olefin determination and in not knowing the specific dispersion of the aromatics present in the fuel.

Conrad has developed a rapid method for the determination of aromatic compounds in fuels of the gasoline and kerosene range, based on chromatography and ultraviolet stimulated fluorescence (6). Limited experience has shown this method to be less reliable as the complexity of the aromatics and the olefinic content increases, as is the case with AN-F-58a fuels. Provision is not made to obtain fractions of saturates or aromatics on which further studies can be made.

While the procedure of Kurtz et al. (10) is recommended for the analysis of samples having end points no higher than 437° F., it is probable that the method could be modified to include the 600° F. end point fuels. The method requires a fractional distillation and the determination in each fraction of the volume per cent absorbed by sulfuric acid–phosphorus pentoxide, bromine number, and specific dispersion. The determination of the per cent olefins by the nitrogen tetroxide method may also be required on some fractions. Apart from the uncertainty as to whether the method could be extended to fuels of higher end point, the principal objection to this procedure is the necessity of running a fractional distillation which requires about 24 hours and the relatively large number of determinations which must be made on the many distillation fractions.

A method which has been in satisfactory use at this laboratory for over a year uses chromatography to separate a nonaromatic fraction, an intermediate fraction, and a pure aromatic fraction. To make the separation more plainly seen, Parasheen is used (6). The per cent aromatics in the intermediate fraction is then determined by the specific dispersion method of Grosse and Wackher (8). Although high precision cannot be obtained in the analysis of wide boiling fuels by the above dispersion method, the inaccuracies are confined to only a small part (about 10%) of the whole fuel and the error in the analysis of the total fuel is only about 10% of what it might have been had the aromatics in the total sample been determined by the same method. The per cent olefins are obtained by the difference between the total olefins and aromatics from the A.S.T.M. sulfonation (2) and the aromatics as determined by the proposed procedure. An aromatic fraction is also obtained which can be further characterized, if desired, and paraffins and cycloparaffins can be determined on the sulfonation raffinate (1).

This method for determining aromatics and olefins in jet-type fuels is described herein and supporting data on multicomponent blends are given. Some results on typical turbojet-type fuels are also included.

APPARATUS AND MATERIALS

A borosilicate glass absorption column (3), without the stopcock and ground-glass joint at the bottom.

Activated silica gel, 28 to 200 mesh. Through-200-mesh gel may also be used with similar results, but with longer analysis times (Davison Chemical Corporation, Baltimore, Md.).

Graduated mixing cylinders in 100-, 25-, and 10-ml. sizes.
Stoddard solvent bottles.
Refractometer capable of measuring n_F-n_C values to 0.0002.
Mercury arc ultraviolet lamp, such as Model 16200, manufactured by the Hanovia Chemical and Mfg. Co., Newark, N. J.

Isopropyl alcohol, c.p. grade. If the sample is suspected to contain aromatics of high molecular weight, Carbitol used as the eluent will desorb these aromatics more completely.

Acidified calcium chloride solution, 450 grams per liter plus 20 ml. of concentrated hydrochloric acid.

Parasheen (Paraflow Sales Department, Chemical Products, Enjay Company, 26 Broadway, New York 4, N. Y.).

PROCEDURE

The column, thoroughly cleaned and dried, was filled with silica gel and packed following the A.S.T.M. method (3). A 100-ml. sample containing 2 drops of Parasheen was introduced into the reservoir and allowed to percolate into the gel. To ensure the complete transfer of the sample, the flask was rinsed with 2 or 3 ml. of eluent (isopropyl alcohol) and the rinse was added to the reservoir immediately after all the first portion of the sample had been adsorbed on the silica gel. When the rinse was completely adsorbed, the reservoir was filled with eluent and an air pressure of 3 to 10 pounds per square inch was applied to maintain the desired rate of descent (7 to 13 mm. per minute). Additional eluent was added when necessary, so as to keep the gel covered. In samples where the aromatic content was under 10%, 90 ml. of sample were taken and 10 ml. of pure isopropyl benzene were added.

When the sample was about to issue from the bottom of the column, a glass-stoppered 100-ml. graduated mixing cylinder was placed under the column to receive the nonaromatic fraction. These receivers were packed in ice to reduce evaporation losses of the volatile components. As the column was not equipped with a ground-glass joint to accommodate this type of receiver, a tight seal was maintained by allowing the weight of the column to rest directly on the receiver with a little glass wool serving as a gasket. This connection was not air-tight and therefore provided the necessary vent while keeping evaporation losses small.

As the fractionation progressed, the leading edge of the aromatic portion was located in the column by shining ultraviolet light thereon in a darkened room (or in a suitable dark box). The Parasheen tracer allowed this boundary to be followed easily. Although the boundary was found to be sharp for sample having low olefin content (5% or less), it became less distinct as olefin concentration increased.
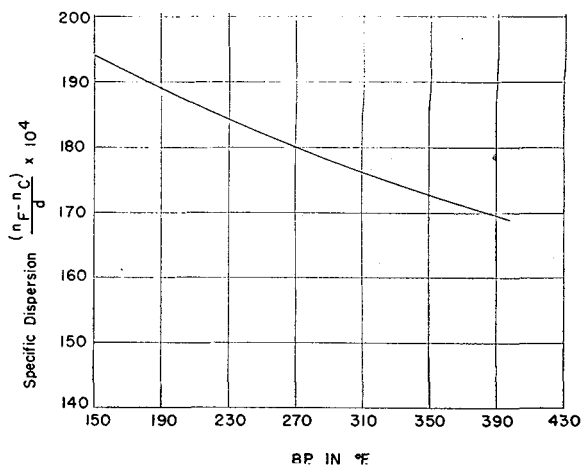

Figure 1. **Specific Dispersion of Alkylbenzenes as a Function of A.S.T.M. 50% Boiling Point**

When the boundary approached to within 5 cm. of the column tip, the cylinder receiving the nonaromatic fraction was replaced by a 10-ml. graduate. A 10-ml. intermediate fraction was then taken, which contained sample on either side of the break point. The receivers were again changed and the major aromatic fraction up to 2 cm. of the alcohol-aromatic boundary, which was always visible, was removed. A final 10-ml. fraction, including the remaining aromatics mixed with alcohol, was collected in a Stoddard solvent bottle and the alcohol was removed by washing with acidified calcium chloride solution until the volume of the aromatics remained constant (usually three washings). The washing was accomplished by adding calcium chloride solution to the solvent bottle so that the level of the liquid was in the graduated neck, shaking the mixture into an emulsified condition, and centrifuging until the mixture separated into two layers. The spent calcium chloride solution was removed by inverting the bottle, carefully loosening the stopper, and permitting the water solution to drain, leaving the aromatics in the bottle. Recovery of the total sample was found to be 98% or better. The losses were assumed to be low boiling paraffins.

Table I. Composition of Test Blends

Blend	Paraffin-Cycloparaffin, Vol. %	Olefin, Vol. %	Aromatic, Vol. %
1	75	0	25
2	70	5	25
3	65	10	25
4	55	20	25
5	70	20	10
6	75	20	5
7	80	20	0
8	100	0	0
9	90	5	5
10	80	10	10

Table II. Composition of Stocks

Paraffin-Cycloparaffin Stock	Vol. %	Aromatic Stock	Vol. %	Olefin Stock	Vol. %
n-Heptane	12.5	Benzene	15.0	1-Octene	33.3
n-Decane	12.5	Toluene	15.0	Diisobutylene	33.3
Iso-octane	25.0	Xylenes	20.0	Cyclohexene	33.4
Cyclohexane	12.5	Methylnaphthalene (1, 2)	25.0		
Methylcyclohexane	12.5	Tetralin	25.0		
Decalin	25.0				
	100.0		100.0		100.0

To calculate the volume per cent aromatics present in the sample it is only necessary to determine the aromatics in the intermediate fraction, because the subsequent cuts are pure aromatics. The method employed is based on the measurement of the specific dispersion of the cut on an ordinary Abbe refractometer. Laboratories not equipped to measure specific dispersion may find it possible to calculate this value from the 50% boiling point, density, and refractive index using the method of Lipkin and Martin (11). The weight per cent of aromatics in the cut is given by the equation of Grosse and Wackher (8):

$$\text{Weight \% aromatics} = \frac{\delta_{cut} - 0.16 \times \text{bromine No.} - 99}{\delta_{arom.} - 99} \times 100$$

where $\delta = \frac{n_F - n_C}{d} \times 10^4$

The specific dispersion of the aromatics present in the cut can be obtained from the graph in Figure 1 if the A.S.T.M. 50% boiling point of the original sample is known (8). In cases where isopropyl benzene was added, the specific dispersion of the aromatics was taken as 172.0 (15). The bromine number is found by the A.S.T.M. method (2).

The volume per cent aromatics in the intermediate fraction can be calculated using the equation

$$\text{Volume \% aromatics} = \text{weight \% aromatics} \times \frac{d_{cut}}{d_{aromatics}}$$

The density of the aromatics, being chosen as 0.870 gram per ml., represents an average of a series of typical single-ring aromatics present in fuels. The total volume per cent of aromatics in the sample is equal to the sum of the aromatics in the intermediate cut plus that in the aromatic fraction and wash.

In the cases where the sample contained less than 10% aromatics, and 10 ml. of isopropyl benzene were added, the volume per cent of aromatics was corrected by the equation

$$(\text{Volume \% aromatics} - 10) \frac{10}{9} = \text{volume \% aromatics in sample}$$

The olefins plus aromatics are determined on the original sample by the standard A.S.T.M. sulfonation method (2) and the olefins are obtained by the difference between this value and that of the aromatics above.

If desired, the paraffins and cycloparaffins can be computed from the sulfonation raffinate (1, 9, 13). The naphthalenes can be determined from the major aromatic fraction and wash by the ultraviolet spectrophotometric method of Cleaves and Carver (5) and the average number of rings per molecule by the method of Lipkin and Martin (12).

RESULTS

To prove the accuracy of the method, ten blends of paraffins, cycloparaffins, olefins, and aromatics covering the range of AN-F-58a specifications were analyzed by the above procedure. The stocks used for the blending were mixtures of pure hydrocarbons representing the following types: straight- and branched-chain paraffins; cycloparaffins; straight- and branched-chain olefins, cyclo-olefins; and single- and double-ring aromatics. The boiling range was from 71° to 305° C. Table II shows the composition of the stocks which were used. The paraffin stock was found to contain less than 0.1% aromatics by the ultraviolet method of Cleaves (4). A slow chromatographic fractionation through 200-mesh silica gel of a blend of 45.0 ml. of aromatic stock and 5.0 ml. of certified iso-octane (2,2,4-trimethylpentane) indicated that the aromatic stock contained less than 0.3% of nonaromatic components. Each of the olefins showed less than 0.1% aromatics by the ultraviolet method (4) and each had a bromine number that was within 2% of the calculated value. The compositions of the test blends are given in Table I; samples contained from 0 to 20% olefins and 0 to 25% aromatics, representing the specification limits.

The results of the test blend analyses are given in Table III. The average absolute errors for aromatics and olefins are ±0.3%. In Table IV the results from three jet-type fuels are listed. Fuel A is a refinery-supplied fuel which meets AN-F-58a specifications and had a bromine number of 13.8. To this fuel was added 8% of No. 3 furnace oil to give B and 8% of No. 3 furnace oil plus 13% of hydroformate bottoms to give C. The No. 3 furnace oil and the hydroformate bottoms were analyzed by a slow percolation through <200-mesh silica gel. The former was found to have 29.3% aromatics and the latter 97.3% aromatics.

Table III. Results of Blend Analysis

	Aromatics, Vol. %			Olefins, Vol. %		
Blend	True	Found	Error	True	Found	Error
1	25.0	24.6	−0.4	0.0	0.2	+0.2
2	25.0	25.0	0.0	5.0	4.6	−0.4
3	25.0	24.7	−0.3	10.0	10.0	0.0
4	25.0	25.4	+0.4	20.0	19.6	−0.4
5	10.0	10.2	+0.2	20.0	20.2	+0.2
6	5.0	4.9	−0.1	20.0	20.3	+0.3
7	0.0	0.8	+0.8	20.0	19.6	−0.4
8	0.0	0.0	0.0	0.0	0.0	0.0
9	5.0	5.2	+0.2	5.0	5.5	+0.5
10	10.0	10.3	+0.3	10.0	10.0	0.0
Av. error			±0.3			±0.3

Table IV. Results of Refinery Fuel Analysis

Fuel	Aromatics, Vol. % Theoretical	Found	Error	Olefins, Vol. % Theoretical	Found	Error	A.S.T.M. Procedure, % Aromatics	Olefins
A	(18.2)	18.2	...	(7.2)	7.2	...	14	11.5
B	19.1	19.8	+0.7	6.6	6.2	−0.4	14.5	11.5
C	29.4	30.3	+0.9	5.7	5.4	−0.3	24	12

Both were free of olefins and because of this, the aromatic determinations were believed good. Also listed in Table IV are the percentages of aromatic and olefin found in these three fuels, using the A.S.T.M. sulfonation and bromine number technique. While the sums of the aromatics and olefins are the same as are obtained by the proposed method, the olefins average 5.5% higher and the aromatics 5.5% lower. These differences are largely due to inaccuracies in the molecular weights of olefins estimated by the A.S.T.M. procedure. These molecular weights were estimated at from 134 to 155 for these fuels, where fractional distillation followed by bromination of the fractions showed

the true average molecular weight of the olefins to be very close to 90.

The theoretical values given in Table IV for fuels B and C are calculated from the determined percentages of olefins and aromatics for A and the above analyses of heavy components that were added to form them. The agreement between the analyzed and calculated values shows the method to be consistent at least for fuels containing heavy components.

Fuel A was also analyzed in another laboratory using fractional distillation prior to the determination of aromatics and olefins in each fraction; 18.2% aromatics and 9.0% olefins were found by this more time-consuming method, a satisfactory agreement with the results shown above.

SUMMARY

A chromatographic procedure for the analysis of aromatics and olefins in wide boiling petroleum fractions although not tested on all types of refinery samples, has been shown to give accuracies on the order of 1% for an analysis time of less than 8 hours. An added advantage of this method is that only four fractions are taken, and analytical data are required on but one to determine the aromatics in the fuel.

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Polarographic Determination of Cobalt as Trioxalatocobaltate(III)

I. M. KOLTHOFF AND JAMES I. WATTERS[1]

University of Minnesota, Minneapolis, Minn.

A new polarographic method for the determination of cobalt, in the presence of a large excess of nickel, copper, and iron as well as most other elements, is described. Cobalt is oxidized to trioxalatocobaltate(III) by lead dioxide in a slightly acidic oxalate solution. The polarographic wave for the stepwise reduction to cobalt(II) occurs before the waves due to oxalato complexes of most other metals. The height of this wave is directly proportional to the concentration of cobalt. Vanadium, chromium, and manganese, which yield interfering waves, are selectively reduced with hydroxylammonium ion.

THE authors have recently reported (11) a polarographic method for determining cobalt by transforming cobalt(II) into the rose-colored amminocobalt(III) complex ion in ammoniacal solution. In this method, large amounts of copper as well as manganese and iron interfere. Souchay and Faucherre (7) have recently reported a similar method for cobalt in which Trilon B [(ethylenedinitrilo)tetraacetic acid] is used as the complexing ion. They separate iron, which interferes, with pyridine.

The complex trioxalatocobaltate(III) ion and the salt $K_3Co(C_2O_4)_3.3.5 H_2O$ were prepared by Sörensen (6) through oxidation of slightly acidic solutions containing cobalt and oxalate slowly by oxygen of the air or more rapidly by other oxidizing agents such as lead dioxide, barium peroxide, and sodium peroxide. Vranek (10) studied the photolysis of the green complex ion in solution by potentiometric and spectrophotometric methods. Cartledge and Nichols (2) developed a spectrophotometric method for cobalt as the oxalato complex. At the selected wave length, chromium, iron, and nickel have low extinction coefficients for which corrections can be made, whereas copper must be separated because its extinction coefficient is rather large. The present polarographic procedure has the advantage that all inter-

[1] Present address, Department of Chemistry, Ohio State University, Columbus, Ohio.

fering ions are rapidly reduced by addition of a little hydroxylammonium ion. Cartledge and Nichols were able to titrate the complex potentiometrically with iron(II) but the potential was poorly defined before the end point, while in a back-titration with dichromate there was an induced oxidation of oxalate. It will be shown in a subsequent paper that the direct amperometric titration with iron(II) can be easily performed using a dropping mercury indicator electrode.

APPARATUS

The manual apparatus (3), in which currents are measured by the potential fall across a standard 10,000-ohm resistance, was used. Similar results have been obtained with automatic instruments. The capillary had a drop time of 4.30 seconds and delivered 1.042 mg. of mercury per second in a solution 1 M in potassium oxalate, 0.2 M in ammonium acetate, and 0.35 M in acetic acid at the potential of the saturated calomel electrode. The capillary characteristic, $m^{2/3} t^{1/6}$, was 1.311 mg.$^{2/3}$ sec.$^{-1/2}$. The polarograph cell was a tall 100-ml. Berzelius beaker without spout equipped with a No. 11 rubber stopper having holes to receive the electrodes and nitrogen tube. The saturated calomel electrode was equipped with an agar salt bridge 1 cm. in diameter which could be immersed directly in the solution in the cell.

A thermostatically controlled water bath was used to maintain all solutions at a constant temperature of 25.0° ± 0.1° C.
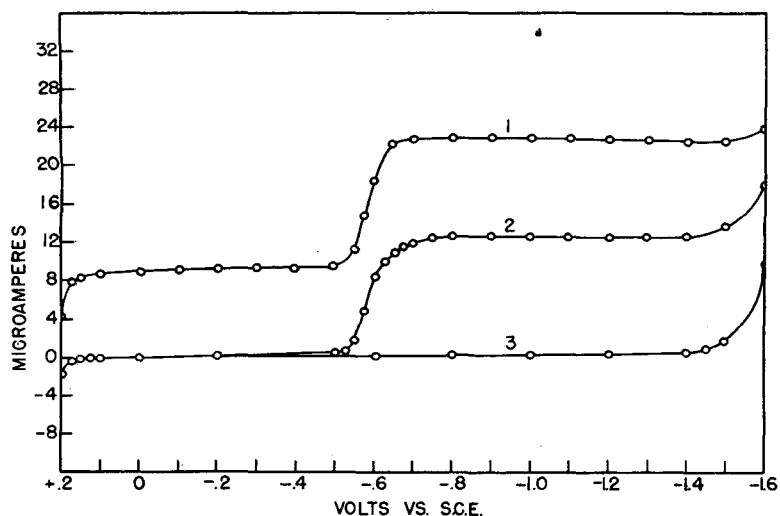
Figure 1. Characteristics of Trioxalatocobaltate Wave

1. 5 millimolar cobalt, employing general procedure but oxygen removed. Support-
ing electrolyte, 1 M potassium oxalate, 0.2 M ammonium acelate, 0.35 M acetic acid,
0.02% gelatin. pH = 5.0
2. As 1, without cobalt
3. As 1, but untreated with lead dioxide

REAGENTS

Standard Cobalt(II) Solution, 0.1 M. Dissolve 29.105 grams
of cobalt(II) nitrate hexahydrate in water containing 10 ml. of
of 1 N nitric acid and dilute to 1 liter. The molarity was verified
by the gravimetric pyrophosphate method.

Potassium Oxalate, 2 M. Dissolve 184 grams of potassium
oxalate monohydrate in 400 ml. of hot water, cool, and dilute to
exactly 500 ml.

Acetic Acid (1 + 1). Mix equal volumes of glacial acetic acid
and water.

Hydroxylammonium Chloride, 20%. Dissolve 1 gram of
analytical reagent in 5 ml. of water. The solution, which is stable
for several days, can be added to the cell by a medicine dropper.

Gelatin, 5%. Dissolve 1 gram of gelatin in 19 grams of hot
water. Warm gently before using. (Gum arabic is more satis-
factory than gelatin.)

Gum Arabic, 5%. Dissolve 1 gram of gum arabic in 19 grams
of hot water. The solution is stable for several days.

PROCEDURE

The sample to be determined should contain 2 to 60 mg. of co-
balt and no more than about 0.6 gram of iron in aqueous solution
of not more than 25-ml. volume. The cobalt may be in the form
of nitrate, sulfate, or perchlorate. Neutralize by adding dilute
sodium hydroxide until a permanent turbidity or precipitate is
just observed. To this solution add 4 ml. of acetic acid solution
(1 + 1), 10 ml. of 2 M ammonium acetate, and 50 ml. of 2 M po-
tassium oxalate. Dilute to exactly 100 ml. and mix well.

Transfer approximately 75 ml. of the solution to a 125-ml.
Erlenmeyer flask, add 1 gram of lead dioxide (manganese-free),
and shake at frequent intervals for 5 minutes. If the green color
is very intense, add 0.5 gram more of lead dioxide. Filter
through a quantitative filter paper such as Whatman No. 42, re-
turning the first portion to the unfiltered solution. The funnel
stem should be filled with the liquid to ensure rapid filtration.

If interfering ions such as vanadate, chromate, cerium(IV), or
trioxalatomanganate(III) are present, continue according to the
next paragraph. If they are absent, collect a suitable volume of
the filtrate in a dry polarograph cell or one previously rinsed with
small volumes of the filtrate. Add 3 drops (0.10 ml.) of 5% gum
arabic or gelatin for each 25 ml. of solution and rapidly pass nitro-
gen through the solution for 3 minutes. Insert the saturated
calomel anode and the dropping mercury electrode and measure
the diffusion current at 0.0 to −0.1 volt vs. the saturated calomel
electrode in the absence of other complex-forming metal ions, at
−0.1 volt vs. the saturated calomel electrode in the presence of
much nickel, or at −0.04 volt vs. the saturated calomel electrode
in the presence of much iron. To determine the residual current,
transfer the 25-ml. portion of the solution which was not oxidized
to a polarograph cell and proceed in the same manner.

In the presence of vanadium, cerium, chromium, and/or man-
ganese, which interfere, add the maximum suppressor and re-

ducing agent to the dry cell in which the filtrate is
to be collected. Add 3 drops of 5% gum arabic or
gelatin, and for each 20 mg. of total content of
manganese, chromium, and cerium or for each 6
mg. of vanadium in the sample add 1 drop of hy-
droxylammonium chloride solution, allowing 0.5 to
1 drop in excess. Bubble nitrogen through the fil-
trate in the cell during the filtration process to
hasten mixing. Collect approximately 25 ml. of
the filtrate. Pass nitrogen through the cell an addi-
tional 3 minutes. Without interruption, insert the
saturated calomel anode and capillary, and con-
tinue as indicated in the previous paragraph. If
the contents of chromium, vanadium, and man-
ganese are not known, no appreciable error will
result from adding an amount of hydroxyl-
ammonium chloride known to be an excess.

In the presence of much iron, there is a slight
decomposition of trioxalatocobaltate by hydroxyl-
ammonium chloride. This can be corrected for by
making a second current measurement after an
equal interval of time. Add the difference between
this and the first measurement to the first meas-
urement.

CHARACTERISTICS OF THE
POLAROGRAPHIC WAVE

A typical current voltage curve obtained for
the reduction of trioxalatocobaltate(III) to the
divalent state is illustrated by curve 1, Figure 1.

The solution was 5 millimolar in trioxalatocobaltate(III).
This solution and the others (Figure 1), unless otherwise indi-
cated, contained as the supporting electrolyte, 1 M potassium
oxalate, 0.2 M ammonium acetate, and 0.35 M acetic acid. The
pH was approximately 5.0. The solution was made oxygen-free
by bubbling nitrogen through it for 15 minutes. Only 1 drop of
gelatin per 25 ml., corresponding to 0.02%, was used. Curve 2
was obtained by the same procedure but without cobalt, while
curve 3 gives the current-voltage curve of 3.5 millimolar dioxalato-
cobaltate(II) in the same medium. (Lead dioxide was omitted.)
The first wave in curve 1 beginning at +0.2 volt versus the satu-
rated calomel electrode (S.C.E.) is due to the reduction of tri-
oxalatocobaltate(III) to dioxalatocobaltate(II). The wave with
a half-wave potential of −0.58 volt (S.C.E.) is due to the re-
duction of lead(II) introduced as lead oxide. The terminal sup-
porting electrolyte wave starts at about −1.5 volts (S.C.E.).

Because the first wave occurs at the same potential as does the
anodic wave due to oxidation of the mercury in curve 2, it is
evident that the half-wave potential corresponds to the latter
process. In the presence of a large excess of nickel, the cobalt
wave separates slightly from the anodic dissolution wave. That
the wave is irreversible is shown by the fact that the portion of the
cobalt wave which, in the presence of much nickel, separates
from the anodic mercury wave, has a slope of 0.032 volt for the
log $i/(i_d - i)$ versus potential plot as compared to the theoretical
slope of 0.059 volt for a one-electron transfer. No anodic oxida-
tion wave is obtained with a similar solution containing the cobalt
in the divalent state.

OPTIMUM CONCENTRATION OF SUPPORTING ELECTROLYTE

Most metal ions form slightly soluble oxalates which redis-
solve as oxalato complexes when an excess of oxalate is added.
Accordingly, a large concentration of oxalate is required if other
metals are present.

The pH is of importance because hydrogen ions are consumed
during the oxidation with lead dioxide, and increasing the acidity
causes other metal waves, particularly that of iron(III), to shift
to more positive potentials. Although the oxidation is quantita-
tive in as little as 2.5 millimolar excess oxalate ion, increasing the
potassium oxalate concentration improves the shape of the wave
and shifts the wave to more positive potentials. Both effects
contribute to the attainment of the diffusion current at lower
applied negative potentials. The slight reduction of trioxalato-
cobaltate(III) by hydroxylammonium ion (added to reduce inter-
fering ions) is practically eliminated when the oxalate ion concen-

tration is increased from 0.1 to 1 molar. A final concentration of 1 molar potassium oxalate was found adequate to retain large amounts of other metals in solution and also to produce good cobalt(III) reduction waves.

The effect of acidity was studied by varying the amount of acetic acid (1 + 1) added from none to 8 ml. in a final volume of 100 ml. Without acetic acid, the color after oxidation was only a pale green and the diffusion current was only 0.73 μa, showing that only about 8% of the cobalt was oxidized. From colorimetric and polarographic measurements, it was found that using from 1 to 8 ml. of acetic acid (1 + 1) yielded complete oxidation. With 6 or 8 ml. of acetic acid the diffusion current was not reached before −0.1 volt (S. C. E.). The detrimental effects of higher hydrogen ion concentrations than required for the oxidation are presumably due to the decrease in the oxalate ion concentration through association to form hydrogen oxalate ions. Factors which tend to decrease the oxalate ion concentration shift the wave to more negative potentials. A volume of 4 ml. of acid, yielding a final pH of about 5.2, was considered optimum.
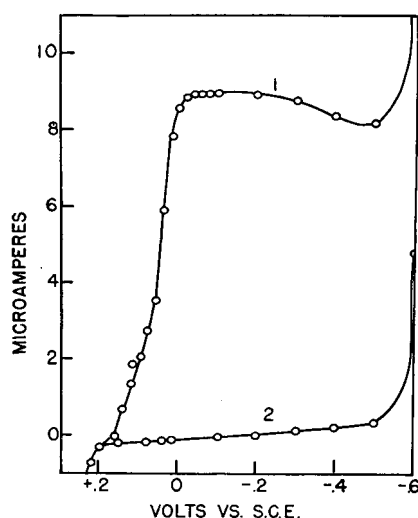
Figure 2. Cobalt(III) Wave in Presence of Much Nickel

1. 0.005 M in cobalt and 0.1 M in nickel
2. As 1, without cobalt

The effect of oxygen dissolved from air was studied by measuring the diffusion current in the region of +0.2 to −0.2 volt without bubbling nitrogen and after bubbling nitrogen through the solutions for 3 and 20 minutes, respectively. From these experiments it was found that most of the oxygen was removed, so that it did not affect the wave height at −0.1 volt (S. C. E.), provided nitrogen was bubbled through the solution for 3 minutes. Without this treatment the contribution of oxygen amounted to 0.70 microampere at −0.1 volt (S. C. E.) in the blank and to 0.38 in the 5 millimolar cobalt(III) solution. The 3-minute nitrogen bubbling served the additional purpose of mixing the gelatin which was added after filtration.

With no maximum suppressor present the galvanometer oscillations were irregular and the diffusion current was too small at the crest of the wave where maxima are usually obtained. These difficulties were eliminated if the solution contained 0.02% gelatin. Because foaming resulted when the gelatin was added before the oxidation, it was found more practical to add 5% gelatin dropwise after filtering. The effect of this dilution amounts to less than the instrumental error.

As shown in Figure 3, the presence of 0.01 to 0.06% gelatin was without effect on the magnitude of the diffusion current at 0.0 to −0.1 volt (S. C. E.). However, the presence of gelatin caused he current to decrease in the region from −0.1 to −0.45 volt

(S. C. E.). Increasing the concentration of gelatin increased the effect. A similar effect was observed in the cathodic tripyrophosphatomanganate(III) wave at positive potentials using tylose to suppress the maximum (4). After this work was completed, a similar concentration of gum arabic was found to be as effective as gelatin and did not cause an appreciable current decrease in the region between −0.1 and −0.45 volt (S. C. E.).

PROPORTIONALITY BETWEEN DIFFUSION CURRENT AND CONCENTRATION OF COBALT

The diffusion currents measured at 0.0 and − 0.1 volt (S. C. E.), for various concentrations of the green cobalt(III) complex prepared according to the procedure, are given in Table I. The diffusion current measured at either potential is, within an experimental error of 1%, proportional to the cobalt concentration throughout the investigated range of 0.5 to 10 millimolar cobalt. From the mean diffusion current of 1.81 μa. per millimolar concentration of cobalt, the diffusion current constant was found to be 1.38 μa. per millimolar concentration per unit capillary characteristic. Using a capillary with a much faster drop time of 2.16 seconds, the value of diffusion current constant was calculated to be 1.39.

That photolysis was negligible was shown by the fact that the diffusion current of the 5 millimolar cobalt solution remained practically unchanged after 20 minutes' exposure to indirect sunlight.

EFFECT OF OTHER ELEMENTS

No coprecipitation phenomena interfere in the presence of nickel, inasmuch as 100 ml. of 1 M potassium oxalate can retain about 2 grams of nickel in solution as the rich blue colored dioxalatonickelate(II) complex, according to Vosburgh, Israel, and Birch (8, 9). A series of synthetic samples was prepared from nickel nitrate and the standard cobalt solution corresponding to 0.5 to 10% of cobalt in 0.6 gram of nickel. No nickel wave was obtained before the lead wave, as shown in Figure 2. At about −0.05 volt (S. C. E.) all results for cobalt were accurate within ±1%, with a mean diffusion current of 1.80 μa. per millimolar concentration of cobalt compared to the observed mean of 1.81 without nickel added. The only noticeable effect of nickel was to cause some separation of the anodic mercury dissolution wave and the cobalt reduction wave, presumably due to the removal of oxalate ions through complex formation with nickel.

The phase diagrams of the dioxalate complexes of zinc, magnesium, and copper were studied for solutions of the less soluble sodium oxalate by Britton and Jarrett (1), who observed solubilities of about 19, 34, and 7 millimolar, respectively. Copper, which is present in many alloys, forms a rich blue colored complex in the final solutions, and when its concentration reaches

Table I. Proportionality between Concentration of Cobalt and Diffusion Current

(No other metal in sample)

Final Millimolar Concn. of Cobalt	Apparent Diffusion Current at E_c 0.0 and −0.1 volt, μa.	Diffusion Current $(i_{app.} - i_r)$, μa.	True Diffusion Current per Millimolar Concn.[a], μa.	Deviation from Average, %
0.00	−0.06 −0.02	... ...	... ...	... ...
0.50	−0.84 −0.88	0.90 0.90	1.80₇ 1.80₇	−0.4 −0.4
1.00	1.76 1.80	1.82 1.82	1.82₇ 1.82₇	+0.7 +0.7
5.00	8.99 9.02	9.05 9.04	1.81₇ 1.81₅	−0.2 −0.1
10.00	17.89 18.01	17.95 18.03	1.80₂ 1.81	−0.7 −0.1
			Av. 1.81₄	

[a] Corrected for dilution due to addition of gelatin.

about 10 millimolar in copper, part of the copper occasionally precipitates as rich blue colored needles of $K_2Cu(C_2O_4)_2$. These needles readily redissolve when the solution is warmed, to form a rather stable supersaturated solution. Diffusion currents were measured using samples yielding a final concentration of ·0.05 M copper and 0.5 to 10 millimolar cobalt. Some precipitate formed, but the solutions remained rich blue in color. A steady diffusion current for cobalt was obtained from +0.15 to −0.15 volt (S. C. E.), after which the wave due to copper started and increased rapidly. The wave heights were the same, within −1%, as in the absence of copper, showing that no measurable amount of cobalt was lost through precipitation with the copper and that copper did not interfere. Similar concentrations of cadmium and zinc did not yield precipitates and did not influence the cobalt wave.

Table II. Current Voltage Measurements for Cobalt-Free Samples Containing Iron as Ferric Nitrate

(Absence of oxygen)

Ec (S.C.E.), Volt	ir Blank, No Iron, μa.	ir, Sample, μa.		
		0.10g. Fe	0.28g. Fe	0.56g. Fe
0.10	−0.15	−0.15	−0.15	−0.15
0.06	−0.13	−0.13	−0.13	−0.13
0.00	−0.07	−0.06	−0.06	−0.04
−0.02	−0.03	−0.03	−0.03	−0.02
−0.04	−0.01	−0.01	0.00	0.00
−0.06	0.00	0.00	+0.06	+0.06
−0.08	0.00	+0.02	0.19	0.40
−0.09	0.00	0.05	0.40	0.95
−0.11	0.00	0.42		
−0.14	0.00	1.64		
−0.16	0.00	3.23		

Preliminary experiments showed that the wave due to the reduction of trioxalatoferrate(III) might interfere, because it was shifted to more positive potentials when the concentration of potassium oxalate was too low, or the acidity was too high. This interference of iron was eliminated at a potassium oxalate concentration of 1 molar and at a pH of about 5.2, as in the procedure. It was also found that in the presence of much iron, the amount of gelatin should be increased to 3 drops to avoid irregular readings. The current voltage measurements were obtained using samples containing only 0.10, 0.28, and 0.56 gram of iron as ferric nitrate (Table II). The iron was without effect at voltages of −0.04 volt and more positive, but contributed appreciable current at more negative voltages. If the current measurements are made at a potential of −0.04 volt (S. C. E.) the residual current may be taken as zero over a large range of concentrations of iron. Samples containing 5 ml. of 1 M ferric nitrate and 0.5 to 10 ml. of 0.1 M cobalt nitrate, corresponding to 0.3-gram samples of metallic iron, were analyzed by the polarographic procedure. The waves, which were similar to those obtained with nickel present, had a half-wave potential of +0.07 volt (S. C. E.) and the diffusion currents were attained at +0.02 volt (S. C. E.). The diffusion currents, corrected for residual current, were perfectly constant from +0.02 to −0.06 volt (S. C. E.) and the current increased rapidly at potentials more negative than −0.06 volt (S. C. E.). The calculated diffusion current constants were all within ±1% of the value obtained in the absence of iron. There was no appreciable loss of trioxalatocobalt(III) in 0.5 hour due to photolysis of trioxalatoferrate(III) with as much as 0.6 gram of iron present.

Manganese, if present, is oxidized by lead dioxide to the cherry red trioxalatomanganate(III) which is reduced at the same potentials as trioxalatocobaltate(III). The diffusion current constant was found to be essentially the same as that of trioxalatocobaltate (III). This red complex is fairly rapidly reduced by the excess of oxalate. Using a 1 millimolar solution ,of manganese, the diffusion current decreased from 1.84 to 1.68 μa. in 6 minutes. The solution was colorless after about 90 minutes. When the manganese(III) solution was made alkaline, the manganese was precipitated as dioxide. However, part of the green cobalt com-

plex was lost during this reaction, presumably through its reduction by the reaction

$$Co^{III} + Mn^{III} \longrightarrow Mn^{IV} + Co^{II}$$
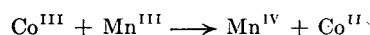
Some cobalt may also coprecipitate with the manganese dioxide. It was found that 10 drops of hydroxylammonium chloride completely eliminated the manganese(III) diffusion current in 100 ml. of 10 millimolar trioxalatomanganate(III). Thus each drop of hydroxylammonium chloride instantly reduces 5.5 mg. of manganese, corresponding to 22 mg. in the original sample.

VOLTS VS. S.C.E.
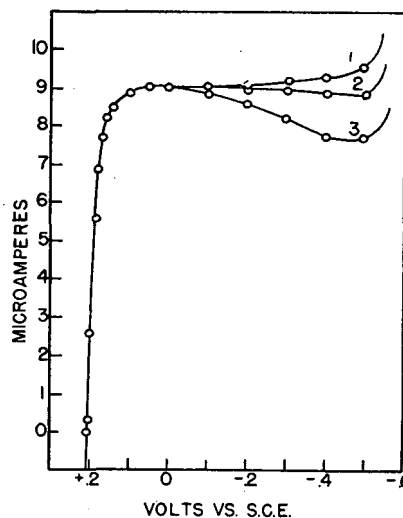
Figure 3. Effect of Gelation on Cobalt(III) Wave

Solutions 0.005 M in cobalt, 1 M in potassium oxalate, 0.2 M in ammonium acelate, 0.35 M in acetic acid
1. 0.02% in gelatin
2. 0.04% in gelatin
3. 0.06% in gelatin

Experiments were performed on the simultaneous determination of cobalt and manganese by first measuring the sum of their currents and then measuring the wave due to cobalt alone after addition of the reducing agent. The error amounted to about −3% for cobalt, presumably because of induced reduction of the green cobalt complex during the decomposition of the cherry red manganese complex. The decomposition of the manganese reduces the accuracy for the determination of manganese by about the same value.

One drop of hydroxylammonium chloride did not reduce the diffusion current due to either 1 or 5 millimolar cobalt from the initial values of 1.80 and 9.02 microamperes in 5 minutes. When 4 drops of hydroxylammonium chloride were used, the currents decreased to 1.79 and 8.90 μa., respectively. The reduction of the cobalt(III) complex thus amounted to less than 1% after correcting for dilution. The presence of 1 M trioxalatoferrate(III) in the final solution (corresponding to a 0.6-gram iron sample) did not seriously increase the reduction of the cobalt(III) complex by hydroxylammonium chloride. Thus, 10 minutes after addition of 5 drops of reducing agent to 25 ml. of solution, which was 1 M in iron, the current due to 1 millimolar cobalt(III) complex decreased from 1.80 to 1.74 μa., while the current due to 10 millimolar cobalt(III) complex decreased from 9.02 to 8.90 μa. The oxalate ion concentration must be kept rather large, or reduction of trioxalatocobaltate(III) may occur.

To study the effect of chromium a sample containing 5 ml. of 0.1 M chromium(III) nitrate was treated according to the polarographic procedure and a diffusion current of 4.07 μa. was measured at −0.04 volt (S. C. E.). By obtaining polarograms of potassium dichromate in the same supporting electrolyte, it was

Table III. Proportionality between True Diffusion Current and Concentration of Cobalt

(Using a simulated 0.45-g. Al alloy sample containing chromium, vanadium, and manganese as well as other metals)

| Cobalt Taken, Mg. | Final Molar Concn. of Cobalt | Apparent Diffusion Current at −0.1 V., μa. | True Diffusion Current, μa. | | % Error | |
			Corrd. for dilution and decomp. in 5 min.	Per millimolar concn. corrd. for dilution and decomp.	Decomp. not corrd.[a]	Decomp. corrd.
2.95	5×10^{-4}	0.90	0.91	1.82	+0.9	+0.9
2.95	5×10^{-4}	0.90	0.91	1.82	+0.9	+0.9
5.89	1×10^{-3}	1.76	1.81$_2$	1.82$_2$	−1.2	+0.4
11.79	2×10^{-3}	3.49	3.59$_4$	1.79$_7$	−2.1	−0.4
29.47	5×10^{-3}	8.90	9.05	1.81	+0.3	−0.1

[a] Using value 1.804 microamperes per millimolar concentration in presence of 0.6 g. of nickel.

found that about 5% of the chromium had been oxidized during the lead dioxide oxidation procedure. When 1 drop of hydroxylammonium chloride was added for each 6 mg. of chromium finally as dichromate, the current was immediately decreased to 0.00 μa. the value obtained for a blank.

In analogous experiments using samples containing vanadyl ion, the blue color of vanadyl ion was observed to change to the yellow of vanadate during the oxidation with lead dioxide. Polarographic experiments showed that vanadyl ion is quantitatively oxidized to vanadate. Thus vanadium interferes seriously. One drop of hydroxylammonium chloride solution was sufficient to reduce each 6 mg. of vanadium in about 2 to 3 minutes, and to eliminate the interference.

Molybdenum and uranium do not interfere. Calcium precipitates as the oxalate and appreciable amounts of cobalt are coprecipitated. Iodide interferes as a result of its oxidation to iodine during the procedure and of its anodic depolarization wave at fairly negative potentials. Bromide is not oxidized by the lead dioxide, but its depolarization wave interferes below −0.1 volt (S. C. E.). Chloride, as a result of its depolarizing effect on mercury, shifts the cobalt(III) wave to more negative potentials. Therefore, large concentrations of chloride should be avoided, especially in the presence of much iron. Chloride ion, in concentrations of 10 millimolar, or less, does not interfere, because it produces only a negligible decrease in the residual current at −0.05 volt (S. C. E.).

In Table III are given the results using simulated samples corresponding to 0.45 gram of a composite alloy containing about 11% iron, 22% nickel, 25% cadmium, 14% copper, 6% manganese, 6% chromium, 2% vanadium, and 0.6 to 6% cobalt. Seven drops of hydroxylammonium chloride were put in the cell in which the filtrate was collected and the timer was started when

half the filtrate had been collected. The error due to decomposition of cobalt(III) amounted to less than 2%.

A preliminary separation of chromium, vanadium, and cerium from cobalt and manganese with pyridine as described by the authors (5) was also studied. No cobalt was lost and only sufficient reducing agent to reduce the manganese was required.

SUMMARY

Cobalt is oxidized to the emerald green trioxalatocobaltate(III) with lead dioxide in slightly acidic oxalate solution. The polarographic wave for the reduction of the complex is obtained immediately following the anodic dissolution potential of mercury. Copper, nickel, tin, zinc, and iron which form soluble oxalate complexes are reduced after the cobalt and do not interfere. Uranium and molybdenum form anions which yield no interfering waves. However, manganese which is oxidized to the cherry red trioxalatomanganate(III), vanadium which is oxidized to vanadate, and chromium which is partially oxidized to chromate, yield waves in the same potential range. Their interference is eliminated through reduction by hydroxylammonium ion which does not appreciably reduce the green cobalt(III) complex. The method is applicable to the determination of cobalt in a large variety of alloys.

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Oxidation of Chromium(III) with Potassium Ferrate(VI)

J. M. SCHREYER, G. W. THOMPSON[1], AND L. T. OCKERMAN[2], *University of Kentucky, Lexington, Ky.*

THIS paper reports results of a continuation in the development of methods for the analysis of samples of potassium ferrate(VI).

The authors' previous paper (1) presented data relative to methods of analysis based on the oxidation of arsenite with the ferrate(VI) ion. A method involving an estimation of the total iron present in the compound (potassium ferrate) was reported also. The arsenite-cerate method was not recommended for the analysis of solutions of potassium ferrate(VI) which are highly decomposed and contain large quantities of hydrous ferric oxide, be-

cause the o-phenanthroline end point is obscured by the color of excess ferric ions.

The total iron method appears unsuited for the general analysis of solutions because of its restriction to highly alkaline solutions during the removal of the hydrous ferric oxide.

The chromite method, as developed in this laboratory, is based upon the oxidation of chromite in strongly alkaline solution with the ferrate(VI) ion as shown in the following equation.

$$Cr(OH)_4^- + FeO_4^{--} + 3H_2O \longrightarrow$$
$$Fe(OH)_3(H_2O)_3 + CrO_4^{--} + OH^-$$
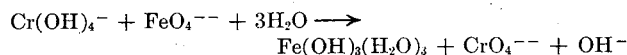
This method, in contrast to the previously reported arsenite-

[1] Present address, Richfield Oil Corporation, Box 22, Cuyama, Calif.
[2] Deceased April 11, 1950.

An additional method of analysis of potassium ferrate(VI) is described, based on the oxidizing property of the ferrate(VI) ion in alkaline solution.

cerate method, is applicable to the analysis of solutions containing low concentration of the ferrate(VI) ion.

A weighed sample of potassium ferrate, or an aliquot of a solution containing the ferrate(VI) ion, is added to an excess of alkaline chromite solution. The chromate(VI) solution produced by the oxidation is acidified and the resulting dichromate is titrated with a standard solution of ferrous ions.

Table I. Effect of Alkalinity of Chromite Solutions on Determination of Percentage of Potassium Ferrate

Sample No.	Average % K_2FeO_4	Alkalinity [OH^-]
1	49.70	3.8
	49.93	4.5
	50.58	5.5
	50.71	6.3
	50.69	7.0
2	69.69	4.2
	69.53	5.0
	69.74	5.9
	70.29	6.0
	70.96	6.5
	70.97	7.4
	70.99	8.9

Table II. Comparison of Methods for Analysis of Potassium Ferrate

Sample No.	Potassium Ferrate, %	
	Arsenite-cerate method	Chromite method
1	73.76	73.94
	73.80	73.96
2	80.33	80.38
	80.38	80.36
3	86.20	86.25
	86.26	86.26
	...	86.19
	94.40	94.41
	94.45	94.49
	94.50	94.55
	94.41[a]	94.56
	94.29	94.61
	94.55	...

[a] Values previously reported (1).

DEVELOPMENT OF METHODS

Investigation to determine the optimum alkalinity of the chromite solution used in the determination of potassium ferrate(VI) showed higher percentages of potassium ferrate in those determinations conducted in the more alkaline solutions. The analyses reported in Table I were carried out by the chromite method described in this paper.

For samples of potassium ferrate in a state of high purity, erratic results were sometimes noted in cases where chromite solutions 5 to 8 molar in hydroxyl ions were used. Consistent results were obtained by using chromite solutions 11 to 12 molar in hydroxyl ions. The greater the alkalinity of the chromite solution, the longer the time necessary for the oxidation by the ferrate(VI) because of the lessened solubility of solid potassium ferrate. Sodium hydroxide, instead of potassium hydroxide, is used because of the greater solubility of potassium ferrate in alkaline solution prepared from sodium hydroxide. This difficulty is not encountered in the case of analysis of solutions of the ferrate(VI) ion.

As a method of reference for the chromite method, potassium ferrate samples used were analyzed by the arsenite-cerate method

(1) which has been shown to give values in good agreement with an independent method of analysis based on the amount of iron present in the compound potassium ferrate.

Chromic Chloride Stock Solution. Add 25 grams of chromic chloride hexahydrate to 150 ml. of distilled water.

Saturated Sodium Hydroxide Solution, Free of Reducing Agent. Saturate 500 ml. of distilled water with sodium hydroxide and add 0.05 gram of potassium ferrate by boiling. Destroy the excess potassium ferrate by boiling.

Sulfuric acid solution, 1 to 5 sulfuric acid.

Sulfuric Acid–Phosphoric Acid Mixture. To 240 ml. of distilled water, add 60 ml. of concentrated sulfuric acid and 150 ml. 85% phosphoric acid.

Standard dichromate solution, approximately 0.085 N.

Ferrous ammonium sulfate solution, approximately 0.085 N.

Sodium Diphenylamine Sulfonate Solution. Dissolve 0.32 gram of barium diphenylamine sulfonate in 100 ml. of water and add 0.5 gram of sodium sulfate.

ANALYTICAL PROCEDURE

Procedure for Chromite Method. Add 20 ml. of saturated sodium hydroxide solution, free from reducing agents, to 3 to 5 ml. of chromic chloride solution and 5 ml. of distilled water. Cool to room temperature. Prepare a fresh solution immediately prior to each analysis.

ANALYSIS OF SOLID SAMPLES. Weigh a sample, containing approximately 0.15 to 0.20 gram of potassium ferrate into a flask containing the alkaline chromite solution. Add the potassium ferrate sample carefully and do not allow it to strike the sides of the flask. Swirl the liquid rapidly until dissolution of the potassium ferrate is complete. Complete dissolution may require considerable shaking, depending on particle size, and premature addition of acid will give erratic results. Add 150 ml. of distilled water, and acidify with 60 to 70 ml. of 1 to 5 sulfuric acid and 15 ml. of sulfuric-phosphoric acid mixture. Titrate immediately with standard ferrous solution using 5 to 6 drops of sodium diphenylamine sulfonate indicator. The ferrous solution must be standardized against the standard dichromate solution immediately prior to use. The end point is marked by a change from purple to light green. If the end point is overstepped, a known volume of the standard dichromate solution may be added and the end point again approached cautiously. A correction should then be made to account for the ferrous solution equivalent to the added dichromate.

From the known titer of the ferrous solution and the volume used, calculate the per cent potassium ferrate as follows:

$$\text{Per cent } K_2FeO_4 = \frac{(\text{ml. of } Fe^{++} \times N\ Fe^{++}) \times K_2FeO_4}{3000 \times \text{wt. of sample}} \times 100$$

ANALYSIS OF SOLUTIONS. Using a 5-ml. pipet, introduce a 5-ml. aliquot of a solution containing the ferrate(VI) ion into a flask containing the alkaline chromite solution. Add the aliquot carefully and do not allow it to strike the sides of the flask. Swirl the liquid in the flask. Analyze in the manner described above.

From the known titer of the ferrous solution and the volume used, calculate the concentration of potassium ferrate as follows:

$$K_2FeO_4 \text{ (mole/liter)} = \frac{(\text{ml. of } Fe^{++} + N\ Fe^{++})(1000)}{(3000)(5)}$$

DISCUSSION OF RESULTS

The results of analyses made by the chromite method were in good agreement with those obtained by the arsenite-cerate method. The validity of the arsenite-cerate method has previously been demonstrated by comparison with data obtained by an independent method of analysis.

The chromite method is particularly suitable for the analysis of dilute solutions of ferrate(VI) ion. This direct method is also recommended for routine analyses because of ease of manipulation.

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Photometric Determination of Phenols

Application to Blending of New Lubricating Oils

ROBERT E. SNYDER AND RALPH O. CLARK

Gulf Research & Development Company, Pittsburgh 30, Pa.

THE use of additive agents in lubricating oils to decrease the deterioration of the oil by inhibiting oxidation is widespread throughout the petroleum industry. A class of organic compounds commonly employed for this purpose is the alkyl-substituted phenols. These substances are effective in low concentrations, and are difficult to estimate quantitatively when dissolved in a mineral oil.

A review of the literature reveals that there is no lack of qualitative tests for phenols. Only a limited number, however, are applicable for the detection of phenolic material in lubricants, because the reactions are either specific for certain types of phenols, or are inhibited by the solvents used for extraction purposes. These limitations, in addition to those imposed by a quantitative procedure, materially restrict the organic agents and analytical techniques that are of practical value.

Included among the methods that have been applied quantitatively, with limited success, are those of Gibbs (5), in which the phenol is condensed with a substituted quinone chlorimide to form a highly colored indophenol, of Graham (6), whereby nitrosophenols are derived from phenols and Millon's reagent (8), and of Folin and Denis (4), who utilized the blue complex formed when a mixture of phosphotungstic and phosphomolybdic acids is treated with a phenolic compound.

Houghton and Pelly (7) have modified the original indophenol reaction of Gibbs, and Stoughton (13) has introduced several improvements into the nitrosophenol procedure. Lykken, Treseder, and Zahn (9) have, in turn, improved the utility of the latter method by extending it on a quantitative basis to a greater variety of sample types.

None of these investigators has considered the "molybdenum blue" reaction between phenols and phosphomolybdic acid in ammoniacal solution (11). The test, although similar to the Folin-Denis procedure, merits consideration in preference to the latter for the following reasons: The reagent is readily available, phosphomolybdic acid is soluble in water and numerous organic solvents, and it has a practical range of sensitivity. A colorimetric method is rarely encountered that cannot be applied because of excessive sensitivity; it is this feature of the Folin-Denis procedure, however, that renders it impractical for the detection or determination of substituted phenols in mineral oils. Distinction of a "phenol-free" lubricant from one that may contain several tenths of 1% phenolic material is virtually impossible because of the similarity in color intensity of the test solutions. The depth of color produced with phosphomolybdic acid, however, is markedly different in such instances. Paradoxically, the lower sensitivity of this reagent enables an analyst to detect with certainty the inhibited sample, and to measure quantitatively small differences in phenol concentration.

The method presented has been applied successfully for the determination of the amount of phenol added in blending lubricating oils. It is not applicable quantitatively to base oils of unknown nature or to uncharacterized phenols. These limitations are inherent in any colorimetric reaction of the compounds (1, 7, 9, 10, 13) and are not specific for the phosphomolybdic acid test.

APPARATUS AND REAGENTS

Apparatus. The only special equipment required is a spectrophotometer, or a photoelectric colorimeter fitted with a filter having maximum transmittancy between 680 and 720 mμ.

Reagents. Phosphomolybdic acid, made by dissolving 1.2 grams of the analytical reagent grade acid in 100 ml. of n-amyl alcohol, filtering the solution, and storing it in a glass-stoppered amber colored bottle. The solution should be prepared daily.

Ammonium hydroxide. A mixture of 25 ml. of concentrated ammonium hydroxide (specific gravity 0.90), 50 ml. of ethylene glycol, and 50 ml. of n-amyl alcohol.

Table I. Sensitivity of Phenols to Phosphomolybdic Acid

Compound	Sensitivity, Micrograms	Concn. Limit, Parts/1000
Phenol	0.31	0.031
p-tert-Butylphenol	0.15	0.015
Di-tert-butylphenol	0.58	0.058
2,4,6-Tri-tert-butylphenol	1.18	0.118
p-Cresol	0.06	0.006
2,4,6-Trimethylphenol	0.01	0.001
2-tert-Butyl-4-methylphenol	0.13	0.013

EXPERIMENTAL

A positive color reaction has been obtained with all phenols that have been tested with phosphomolybdic acid. The sensitivity of the reaction, other factors remaining constant, is dependent upon the reactivity of the hydroxyl group as affected by substituent groups, particularly a methyl group in the para position. In general, cresylic-type compounds are more reactive with heteropoly acids, and can be detected at extremely high dilution ratios, whereas phenols possessing steric hindrance usually have a somewhat higher limit of detectability. Illustrative of these characteristics are the data in Table I determined by a spot test technique similar to that described by Feigl (3).

Compounds of mixed functionality, such as salicylic acid, are in general insensitive to phosphomolybdic acid. This is not considered a serious limitation of the method, because the concentration of such substances can usually be estimated on the

The use of phenolic compounds as addition agents in lubricating oils for inhibition of oxidation is widespread throughout the petroleum industry. Existing photometric methods for the determination of phenols have utilized an extraction procedure prior to the development of color. In the proposed test, the oil is treated directly with a n-amyl alcohol solution of phosphomolybdic acid, and the "molybdenum blue" complex is developed and extracted simultaneously with an ammoniacal solution of ethylene glycol–amyl alcohol. This colorimetric reaction has been applied successfully for the quantitative estimation of numerous phenols in the blending of lubricating oil stocks with a mean error of ±5%. Attention is directed to limitations of the method as a control in the compounding of new lubricating oils, and the wide variance in the sensitivity of response of phenols as a function of constitution and structure. Additional factors are discussed that affect the formation and stability of the color and the over-all performance of the method.
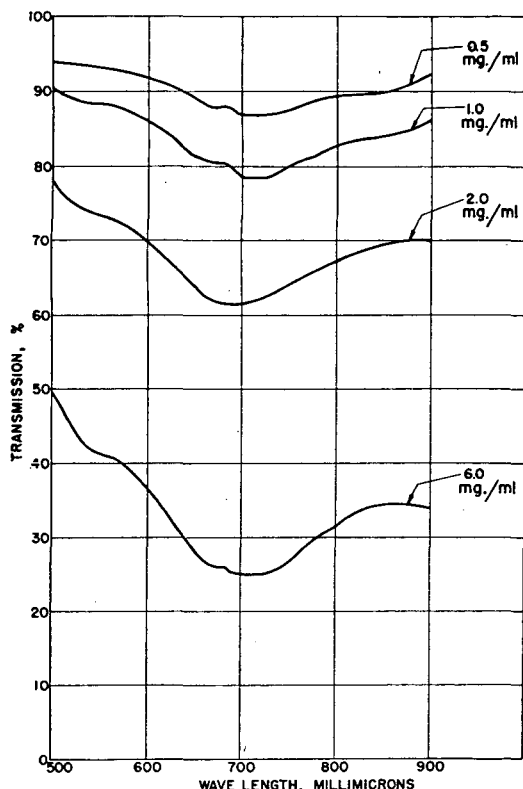
Figure 1. Spectral Characteristics of Colored Complex vs. Concentration of o-Cresol

Table II. Analysis of Oil Blends for Added Phenol

Oil Base	% Mesitol		% Butylcresol	
	Found	Added	Found	Added
Coastal	0.09	0.10	0.09	0.09
	0.10		0.09	
	0.20	0.20	0.20	0.20
West Texas	0.30	0.30	0.30	0.31
	0.31		0.32	
	0.55	0.50	..	..
	0.53			

basis of an equivalent reaction of a substituent group of the molecule.

Procedure. The sensitivity of the phenolic compound to be determined can affect significantly the size of sample to be taken for analysis. For this reason the amount of oil specified below may have to be varied in certain instances to maintain the density of the colored solution within practical working limits.

The size of sample indicated is weighed accurately into a 30-ml. separatory funnel.

Phenol Content, %	Sample Size, Grams
0.0 to 0.4	5
0.3 to 0.6	3
0.5 to 1.0	2

Four milliliters of the phosphomolybdic acid reagent are pipetted into the funnel, and after mixing, 8 ml. of the ammonium hydroxide solution are introduced from a measuring pipet. The liquids are mixed by swirling, 2 ml. of a saturated solution of potassium chloride are added from a pipet (the salt materially hastens separation of emulsified oil), and the color is developed by vigorous shaking for 15 to 20 seconds. A portion of the lower colored liquid is transferred into a glass-stoppered 1-cm. absorption cell, and the transmittance is measured at 700 mμ against a similar solution prepared from the uninhibited or base oil exactly 10 minutes after the addition of the ammonia solution.

The analytical results shown in Table II demonstrate the applicability of the procedure. These data represent consecutive

analyses obtained with two different base oils blended to contain known amounts of each of two phenols, 2,4,6-trimethylphenol and 2-tert-butyl-4-methylphenol.

The method has been applied with equal success on a control basis to a variety of phenols in new transformer and turbine oils and automotive lubricants. In general, duplicate analyses can be completed in an elapsed time of 25 minutes, including the time required for preparation of the blank or reference solution.

Calibration Procedure. A working curve showing the relation between optical density and phenol content should be constructed with oils containing the same phenolic compound that is to be determined, photometric measurements being referred to an extract of the original oil.

DISCUSSION

Effect of Phenol Concentration and Time. The relation between the adsorbancy of the final colored solution and the concentration of a phenol, using for illustration o-cresol, is represented graphically in Figure 1. Experience gained in application of the method to a variety of related compounds indicates that slightly better results are obtained if the optical density of the test solution lies within the range of 0.05 to 0.6. Concentrations corresponding to an optical density of less than 0.05 are subject to increasing absolute errors of measurement, and those equivalent to an optical density greater than 0.6 tend to deviate from Beer's law. The weight of oil recommended in the procedure has been based on this condition and on the assumption that the concentration of inhibitor to be determined is within the range usually employed in industrial lubricants. Variations in this latter condition will necessitate an adjustment of the suggested sample size.
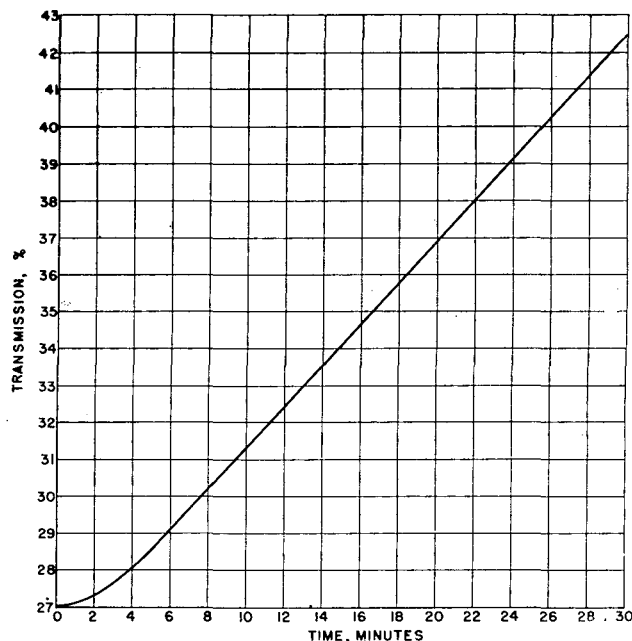
Figure 2. Effect of Time on Intensity of Color Produced with Mesitol

The linear relationship between transmittancy and time, using mesitol as an example, is shown in Figure 2. The slope of the curve is independent of concentration, time, and in all cases studied, of the nature of the phenolic material. This behavior of the system can be employed to advantage where for some reason the density of the colored solution has been measured at a time interval that varies from the standard or normal procedure. Such a practice should be used with reservation and with the understanding that contamination of the test sample might alter

Table III. Effect of Base Stock and Method of Refining on Color Intensity

Sample Description	Opacity of Color Relative to Opacity of Reagents
Acid-treated West Texas Oil A	1.07
Furfural-extracted mid-continent oil B	1.17
Mixture of acid-treated West Texas oil A and furfural-extracted mid-continent oil C	8.33
Alchlor-processed Ordovician oil D	1.50

Table IV. Effect of Repeated Extraction by Caustic

Base Oil H	Opacity of Color Relative to Opacity of Reagents	
	Oil after extraction	KOH extract
After 1 extraction	1.38	1.00
After 2 extractions	1.25	1.00
After 3 extractions	1.16	1.00
After 4 extractions	1.11	1.00
After 5 extractions	1.04	1.00
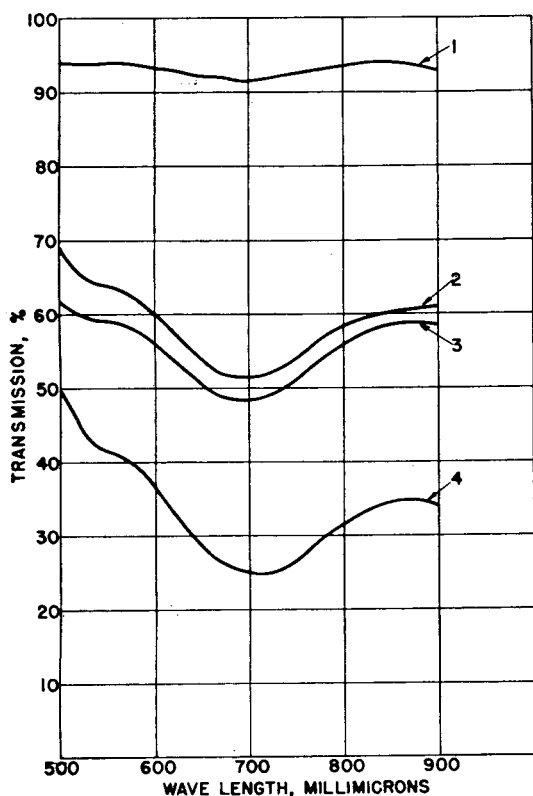
Figure 3. Spectral Characteristics of Colored Complex Produced by Various Phenols

1. p-Benzylphenol, 1.0 mg./ml.
2. Mesitol, 0.16 mg./ml.
3. Resorcinol, 0.33 mg./ml.
4. o-Cresol, 6.0 mg./ml.

the fading characteristics of the complex and introduce cumulative errors that could have been minimized had the regular procedure been followed.

Spectral Characteristics. The spectral transmittance curves presented in Figure 3 demonstrate that the absorption characteristics of the reduction product of phosphomolybdic acid are independent of the constitution of the phenol. Data for molybdenum blue produced by reduction of ammonium phosphomolybdate with various inorganic, as well as organic, reagents show maximum absorption in the region 700 to 710 mμ (2, 12). This indicates that the oxidized form of the phenol is not a constituent part of the colored complex and that the same complex is produced in all these reactions. Figure 3 also illustrates quantitative differences in sensitivity of the compounds. These data, to-

gether with the values listed in Table I for the limit of concentration of several homologs, support the statement that the extinction coefficient of a system is dependent on both the composition and structure of the phenolic compound.

Interference. The procedure that has been described was designed to function primarily as a control on the amount of a phenol added in a blending process, positive interference being eliminated by the use of an extract of the base oil as a reference solution. If, however, interference of this sort could be compensated for more simply, or reduced to a nominal level by the choice of a suitable material for adjustment of the null position of the measuring instrument, the method would have much greater flexibility. With this thought in mind, a study was made to determine the effect of an oil on the color intensity produced with an inhibited sample of the same oil. Briefly, the experiment consisted of blending each of ten oils of widely different composition with 0.2, 0.4, and 0.6% of three different alkylated phenols and determining the transmittancy of the resulting colored solution when measured against an extract of the uninhibited sample, and the latter when only the reagent blank was employed. The correlated data demonstrated that oils refined from different stocks or by different refining methods vary widely in the amount of material that is reactive with phosphomolybdic acid, and that the sensitivity of response of a given phenol to the reagent is affected in an unpredictable manner. Rather than present all the experimental results, a limited amount was selected at random and tabulated in Table III and plotted graphically in Figure 4. These data substantiate the statement that unless both the reference and test oils are identical in character, the experimentally determined value will not be a true measure of the added phenol concentration, and that compensation for this variable by any alternative method will lead only to an erroneous result.

Supplemental data (Table IV) support the belief that the constituents of an oil reactive with phosphomolybdic acid are essentially nonphenolic in character. Various methods were tried to remove or to inactivate these diverse substances but with little success except upon repeated extraction with a caustic solution (Table IV), an obviously impractical procedure except in the case of the highly hindered phenols (Table V).

Table V. Effect of Caustic Extraction Prior to Color Development

	Opacity of Color Relative to Opacity of Reagents	
	Original oil	KOH extract
Base oil G	2.00	1.00
Base oil G + 0.2% 2,6-di-tert-butyl-4-methylphenol	2.99	1.00
Kerosene B	1.43	1.12
Kerosene C	1.62	1.29

The effect of an oil on color intensity can frequently be overcome by extraction of the phenolic additive prior to color development. The procedure is limited, however, to phenols soluble in alkali and to samples not containing naturally occurring phenolic material (Table V). The latter limitation is generally not restrictive except in the case of lower boiling distillates—e.g., gasolines, naphtha, etc.—whereas steric hindrance is exhibited by numerous alkylated phenols currently employed as antioxidants for industrial lubricants. These latter compounds may be, depending upon the nature of substituent groups, only partially soluble or completely insoluble in caustic. In either instance, an extractive procedure cannot be employed for analytical purposes without prior knowledge of the sample, and must, in many cases, be supplemented by an alternative method. Development of color in situ eliminates these undesirable features, and in addition, materially shortens the time for analysis without introducing subsequent variable factors.

Sensitivity. It is impossible to predict the effect that will be produced on a colorimetric reaction by a change in composition of the solution medium. There is an effect on the colorimetric response of phenolic material when oil is a constituent part of the color system. Consequently, the sensitivity values listed in Table I have little significance except in an essentially aqueous
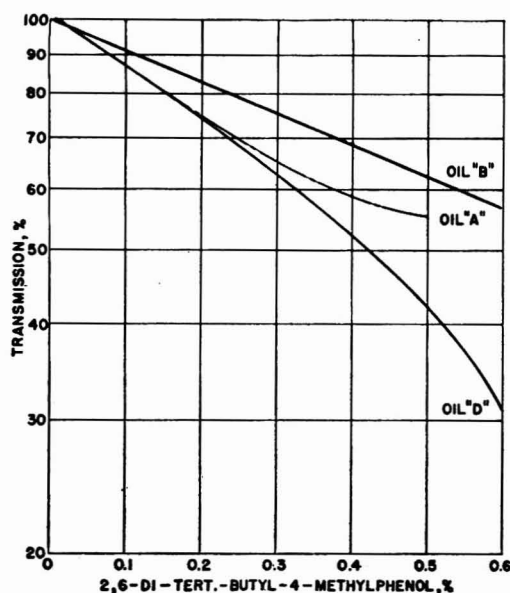

Figure 4. Effect of Base Oil on Sensitivity of Response of Phenols

solvent. These values can, however, be related to the lowest practical working limit of the phosphomolybdic acid procedure if they are expressed as a concentration in terms of milligrams of phenol per milliliter of oil. While the order of magnitude of these figures is somewhat greater than for other tests that might be employed, no difficulty has been experienced because of the lack of sensitivity.

Accuracy. The reliability and precision of the method are typified by the data in Table II. Analyses performed periodically for the purpose of checking the technique of new operators or evaluating the performance of different stock bases show a mean average error of $\pm 5\%$. The reproducibility of results is somewhat better; deviation of a single determination from the mean seldom exceeds $\pm 3\%$.

SUMMARY

An earlier version of the phosphomolybdic acid method was based on extraction of phenols from mineral oils with 95% ethyl alcohol. This procedure consumes considerable time in multiple extraction, centrifuging, and separation of the alcoholic extracts. Moreover, it is mandatory that the extraction be carried out in a precise manner, as the success of the determination is contingent on this step of the procedure. Consequently, the analysis is tedious and exacting to perform, and the resulting data are frequently in doubt. With the proposed procedure of simultaneous extraction and color development, complete solution of the reagent with the oil is effected, and the composition of the ammonium hydroxide solution assures an adequate concentration of ammonia in both the oil and nonoil layers for development of the molybdenum blue complex. And because the colored component is practically insoluble in oil, simplicity, sensitivity, and accuracy are achieved simultaneously.

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Seagoing Photoelectric Colorimeter

WM. L. FORD[1], *Woods Hole Oceanographic Institution, Woods Hole, Mass.*

PHOTOELECTRIC colorimeters have come to be widely accepted in analytical work because of their objectivity and speed. However, most existing instruments are adversely affected by the vibration, motion, and high humidity of work at sea. A successful seagoing colorimeter must be unaffected by these conditions. It must, furthermore, have greater sensitivity than visual comparative methods and a large range to accommodate wide differences of color intensity, such as are encountered between the determinations of phosphate phosphorus and nitrate nitrogen in sea water. These requirements have been met in the colorimeter herein described. For convenience the instrument has been named the electric eye photometer.

[1] Present address, Naval Research Establishment, H.M.C.S. Stadacona, Halifax, Nova Scotia, Canada.

An electric eye tube (electron-ray tube) which is unaffected by vibration and rolling is used in place of the conventional galvanometer to provide an indication of the balance point. Absorption cell lengths up to a maximum of 26 cm. may be used, thus permitting determinations over an unusually wide range of concentrations. In general, accuracy is limited by the analytical method rather than by the instrument. The sensitivity is about 0.5% of the scale range.

The principle employed consists of balancing a beam of light which has been partially absorbed in passing through the colored solution against a second beam which is sent through an adjustable aperture. Each beam impinges on a phototube, the pair of which activate an electron-ray tube to provide an indication of balance. The balance point is attained by adjustment of the

A photoelectric colorimeter is described which has operated successfully during the past two years at sea under conditions of vibration, motion, and high humidity. Absorption cell lengths up to 26 cm. are employed to accommodate the wide variations of color intensity encountered in chemical determinations of sea water. The sensitivity is about 0.5% of the scale range and the accuracy is in general determined by the analytical method rather than the instrument.

variable aperture, the position of which gives a measure of the light absorbed and hence of the concentration of the solution. Because light absorption by a colored solution is usually governed by Beers' law, a logarithmic aperture is employed in order that the scale readings will bear a linear relationship to concentration.

OPTICAL-MECHANICAL DESIGN

The instrument may be conveniently described under the headings of optical-mechanical components and electrical components. The optical-mechanical part of the colorimeter consists of the following basic units: a source of collimated uniform light, a color filter unit, an aperture and scale-mechanism for measuring the relative amount of light being absorbed (the extinction coefficient), an absorption cell, and a phototube assembly. Figures 1 and 2 illustrate the relation of these components to one another.
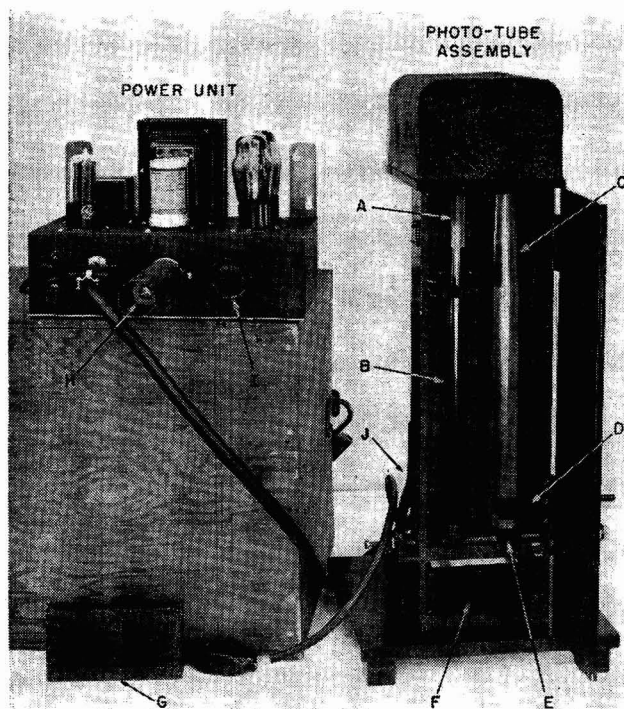
Figure 1. Seagoing Photoelectric Colorimeter

A.	Plunger	F.	Mirror
B.	Absorption cell	G.	Light filters and holder
C.	Lucite rod	H.	Electron ray tube (electric eye)
D.	Spring clip	I.	Dark balance control
E.	Aperture and scale mechanism	J.	Light source (rear)

The light system contains no prisms or lenses, yet provides a light beam which is adequately collimated and of uniform intensity.

As shown in Figure 2, the light from a 100-watt projection bulb located at the center of curvature of a semicylindrical flat-white surface is reflected through a black tunnel to the color filters and thence is directed by a mirror through the aperture mechanism to the absorption cell. Direct light from the bulb is prevented from reaching the absorption cell by a blind.
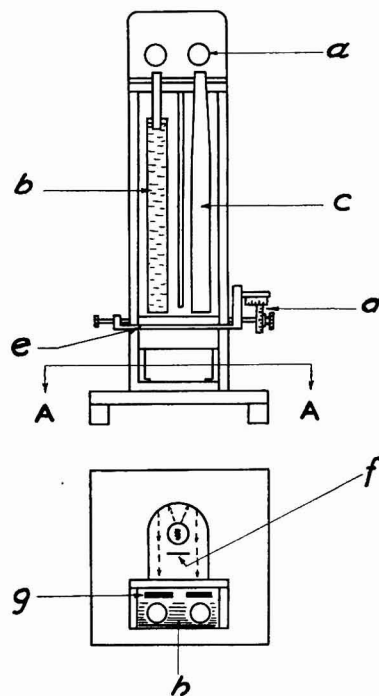
Figure 2. Diagram of Photoelectric Colorimeter

Showing light system (section A-A) and 26-cm. absorption cell,

a.	No. 926 phototubes	e.	Aperture mechanism
b.	Absorption cell	f.	Blind
c.	Lucite rod	g.	Light filters
d.	Vernier scale	h.	Mirror

The color filter unit uses two filters, each 2 × 2 inches (5 × 5 cm.), which do not require careful matching.

The aperture and scale mechanism is shown in Figure 3. Light which passes through the left aperture is partially absorbed by the solution in the tube above, the remainder impinging on a phototube at the top. Light which passes through the logarithmic aperture on the right travels through a Lucite rod directly to a second phototube at the top. The amount of light passing the logarithmic aperture is adjusted by means of the vernier-operated wedge until the electron-ray tube indicates equality of the light beams reaching the two phototubes. The reading of the vernier then is a measure of the light absorbed by the solution, and therefore the concentration of the substance under investigation.

The logarithmic aperture is made photographically. A large-scale accurately made drawing of the aperture is photographed and positives of the desired size are produced on a lantern slide. Opaqueness of the logarithmic aperture is ensured by applying Kodak opaque, taking care not to overlap the edge of the aperture. The slide is cut to fit a recess in the base plate of the aperture mechanism. If the gelatin surface becomes scratched or otherwise damaged, the aperture is easily replaced. The method is both inexpensive and precise.

Refraction of the light beam at the surface of the solution in the absorption cell is avoided by the use of a glass plunger which is mounted under the head of the colorimeter and extends below the liquid surface.

ELECTRICAL COMPONENTS

The circuit diagram used for the colorimeter is given in Figure 4.

In the electrical design there were three important specifications to be met:

1. The equipment was to be operated at sea with inherent vibration and movement of a ship, which dictated the use of an indicator unaffected by motion.
2. Components would have to withstand high humidity and salt-carrying air.
3. The equipment had to be unaffected by line voltage variations in the order of 10 to 20%.

To satisfy the first condition, an electron-ray tube was chosen as being most adaptable. This tube is capable of showing

voltage changes (hence light unbalance) in the order of a few millivolts by utilizing a ray of electrons striking a target situated within the glass envelope. The angle of shadow provides a balance indicator using no moving parts and hence is unaffected by vibration and rolling.

The second factor (the most troublesome) was overcome by the use of well constructed and sealed parts, careful placement of parts, and spraying the wiring and components with a fungus- and moisture-proofing compound such as General Electric Company Glyptal No. 1202 gray.

The third condition was solved by the use of voltage-regulating glow tubes which place a fixed voltage on the sensitive circuit elements. Tests indicate that supply voltages varying from 105 to 130 volts produce no appreciable errors in the operation of the instrument.

No. 926 phototubes are used because of their satisfactory response to the visible light spectrum. The pair of phototubes must be selected so that they will have similar cathode emission characteristics. The Type 38 tube should have low grid current characteristics.

The electronic assembly is divided in two convenient parts— a phototube head mounted on top of the optical-mechanical assembly (see Figure 1) and a power unit which also contains the electron-ray tube.
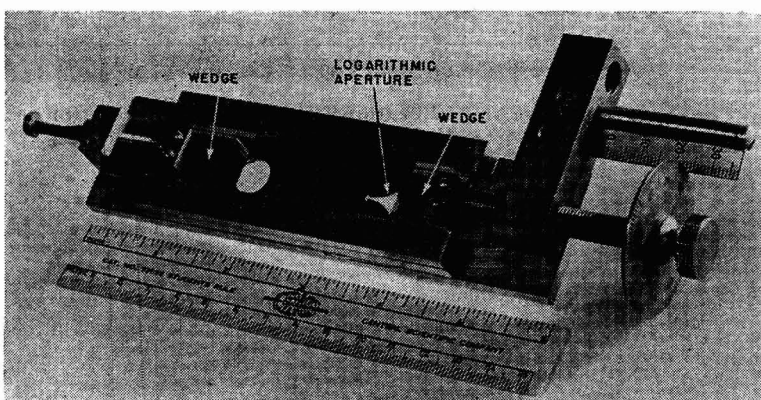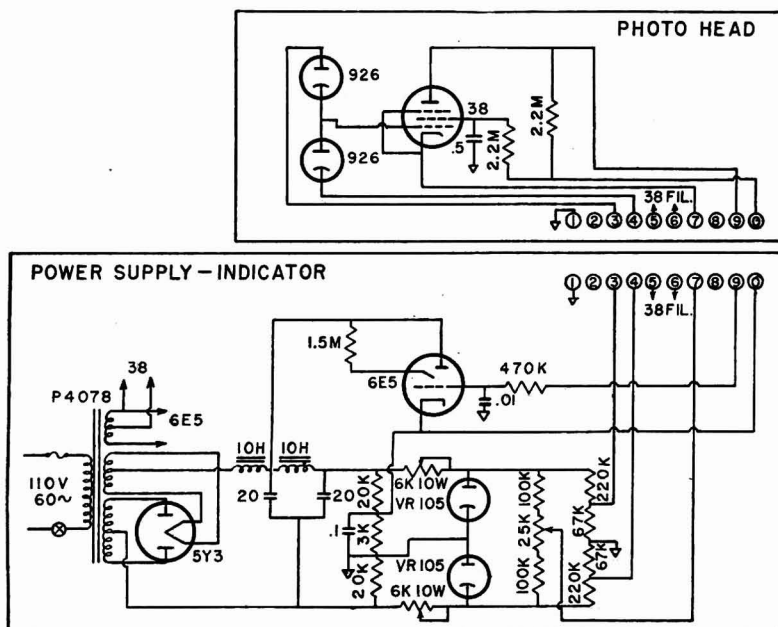
Table I. Calibration Phosphate Phosphorus

(Using 9-cm. absorption cell and red filter with transmittance peak at 645 mμ)

Concn. of P, μg Atom	Direct Reading	R^a	F^b	Deviation from Mean, %
Distilled water	470			
Blank 1	478			
0.50	558	79	0.00633	5.0
0.75	595	116	0.00646	3.0
1.00	622	143	0.00700	0.6
1.50	686	207	(0.00725)	(8.9)
2.00	772	293	0.00684	2.7
2.50	855	376	0.00665	0.2
Blank 2	480			
Distilled water	470			
		Mean	0.00666	(omitting 1.50)

^{a} Corrected reading, direct reading minus average reading for blanks.
^{b} Factor for converting R to concn. of phosphorus.

OPERATION OF INSTRUMENT

The power unit is turned on some 10 minutes in advance to attain warm-up stability. With the light source off and the door of the colorimeter closed tightly so that no light reaches the phototubes, an adjustment called the "dark balance" is made by adjusting the control, I in Figure 1 (25-kv.-ohm potentiometer in Figure 3), to obtain an arbitrary balance of the phototubes, indicated by a narrow slit on the electron-ray tube.

In the next step a reading with distilled water is obtained. The appropriate light filters for the analysis in question are placed in their holder, the absorption cell is filled with distilled water and placed in the instrument, the door is closed, and the light source is turned on. The vernier is adjusted until the electron-ray tube returns to the same narrow slit obtained in the dark balance, and the reading is noted. The light is then turned off to check the dark balance reading, which should remain unchanged. From time to time during a series of measurements the distilled water reading is repeated to determine the presence or absence of drift in the balance point.

The third step is to run a reagent blank to measure the color originating from the reagents. This is usually done both at the beginning and end of a series of analyses. The procedure is identical to that in step 2.

In the fourth step, the unknown solution to which reagents have been added is placed in the absorption cell and a reading is obtained as described above.

In calibrating the instrument the same procedure is used, but with solutions of known concentration. Once a calibration curve has been obtained, it is necessary only to make check runs from time to time at one or two concentrations.

Because, in nearly all cases, the calibration curve is a straight line over a wide range, the concentration of the unknown is obtained directly by multiplying the corrected reading by a factor which is the reciprocal of the slope of the curve. The corrected reading is obtained by subtracting the value for the reagent blank from the direct reading. These operations are illustrated in Table I, which is a typical set of calibration data for the phosphate phosphorus determination.

Certain precautions are to be observed. The outside of the absorption cell must be dry and clean, especially the bottom. Its orientation in the colorimeter must always be the same, to avoid errors from inequality of light transmittance through the different parts of the bottom. It is essential that the level of solution in the cell be high enough to cover the end of the plunger, which must also be free of air bubbles that sometimes tend to collect.

Figure 3. Aperture and Scale Mechanism

Figure 4. Schematic Circuit Diagram of Photoelectric Colorimeter

It has been indicated that any length of absorption cell up to a maximum of 26 cm. may be used. In practice, the three lengths, 26, 9, and 1.5 cm., have accommodated all analyses so far encountered. The 26-cm. cell is made from a Nessler tube of about 1-inch (2.5-cm.) outside diameter cut to a length of 28 cm.; 26 cm. is the length of the light absorption path between the bottom of the tube and the plunger when the tube is in place. The tube need not have an optically flat bottom (but must be oriented in the same way for all readings).

The 9-cm. cell is also made from a Nessler tube as described above, but cut to an over-all length of about 11 cm. When this cell is used, a spacer of Lucite rod is fitted into the lower part of the left-hand chamber as illustrated in Figure 5, A. It conducts the light beam up-ward to the 9-cm. cell located between the Lucite rod and the plunger. The rod has protective brass rings at each end.

The 1.5-cm. cell is square in cross section and 3 cm. high. With the colorimeter in a horizontal position (see Figure 5, B), the 1.5-cm. cell is placed between the glass plunger and a Lucite rod which conducts the light beam from the aperture mechanism. Access to the 1.5-cm. cell is through a small sliding hatch in the door of the colorimeter. The 3-cm. height of the cell provides sufficient depth of solution to avoid interference of the light path by the surface.

Color filters are used which have a narrow spectral band and a transmittance peak at the same wave length as the absorption peak of the solution. For this purpose the so-called monochromatic filter glass combinations are useful. The importance of these considerations is seen in the case of the colorimetric determinations of phosphate in sea water. It has been pointed out by Harvey (1945) and others (1–3) that in this analysis a greenish tinge sometimes develops in what is normally a blue solution. If a color filter is used which has a narrow spectral band covering the absorption peak for the phosphomolybdic complex at 645 mμ, the danger of interference by other absorption bands is greatly reduced.

SOME EXPERIMENTAL RESULTS

The instrument has been used on a routine basis at sea for the colorimetric determination of the following constituents of sea water: phosphate phosphorus, nitrate nitrogen, silicate silicon, and reducible iron. Calibration data for phosphate and reducible iron are presented, as illustrative of experimental results.

The iron was determined by a method (2) in which ferrous iron combines with 1,1'-bipyridine to give a stable red coordination compound. Because of the reproducibility of the method, the calibration data give an indication of the accuracy to be expected from routine operation of the colorimeter. Results of runs using absorption cells 26, 9, and 1.5 cm. in length are given in Figure 6.
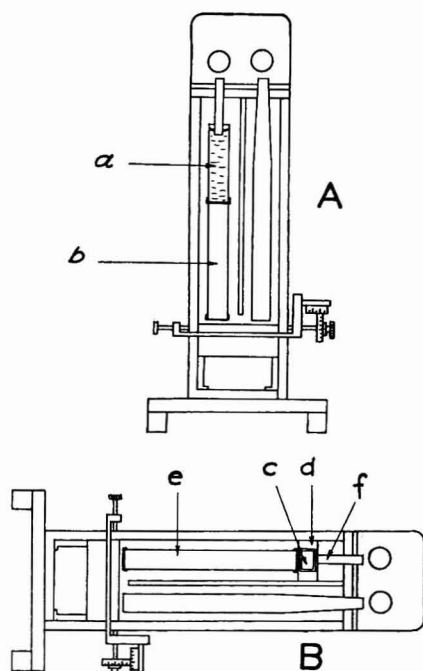
Figure 5.   Photoelectric Colorimeter

A.   Front view
   a.   9-Cm. absorption cell
   b.   Supporting Lucite rod
B.   Plan view showing colorimeter in position
   for use with 1.5-cm. absorption cell
   c.   1.5-Cm. absorption cell
   d.   Cell holder
   e.   Lucite rod
   f.   Glass plunger
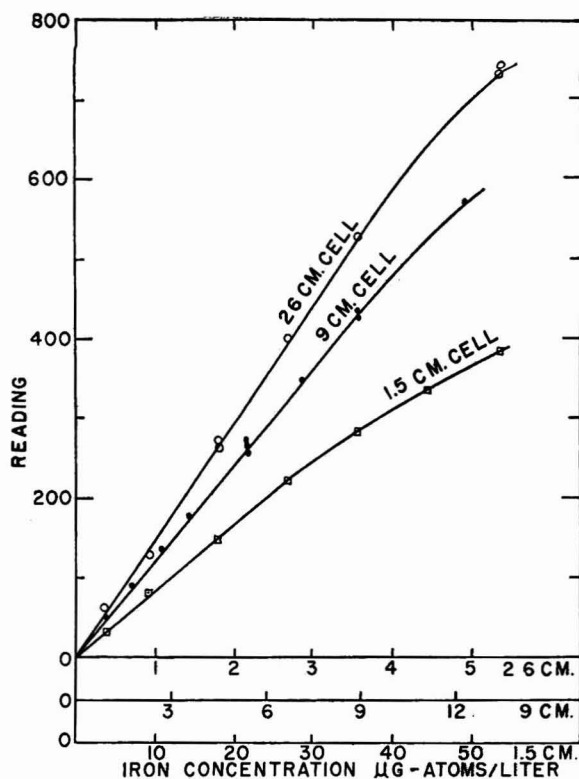
Figure 6.   Calibration Curves for Determination of Reducible Iron in Sea Water

The data for the 26-cm. cell are the result of two runs 7 days apart. Beers' law is obeyed up to a concentration of 3.5 microgram-atoms per liter, but the usable range extends to 5.5 microgram-atoms per liter. For the 9-cm. cell, results of three runs extending over 10 days are given. The curve is linear up to
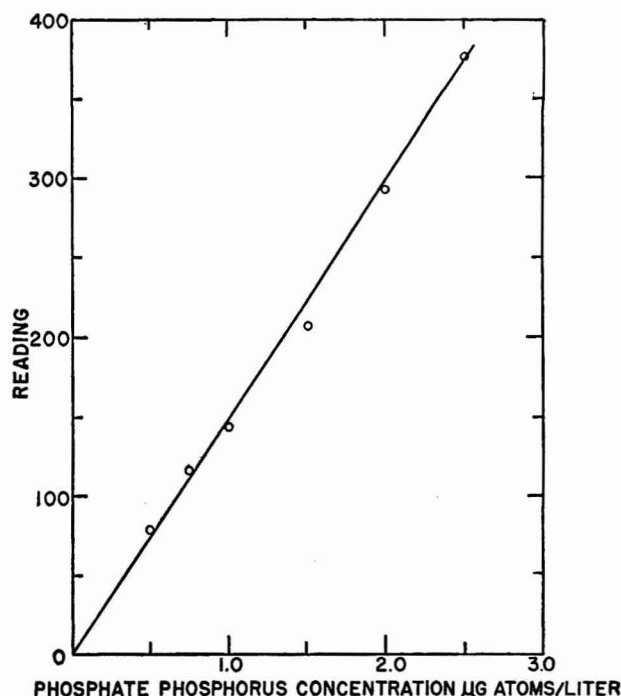

Figure 7.   Calibration Curve for Determination of Phosphate Phosphorus in Sea Water

9-cm. absorption cell

9 microgram-atoms per liter. A single series of data is given for the 1.5-cm. cell. Its curve is linear to 30 microgram-atoms per liter, but has a usable range to at least 60 microgram-atoms per liter. These figures indicate the wide range of concentration that may be measured by the instrument.

The absolute accuracy decreases with decreasing length of cell, but the percentage error for any given concentration is about the same for all three cases—for example, at a scale reading of about 300 the percentage error is approximately ±3%.

The phosphates were run by the ceruleomolybdate method of Denigés as applied to sea water by Atkins (1), with the modification that samples were analyzed in the colorimeter within 5 to 10 minutes after the stannous chloride had been added. It has been found that the maximum color is developed in that time.

The results of a typical calibration are presented in Table I. The corresponding calibration curve is given in Figure 7. The curve is linear to 2.5 microgram-atoms per liter. The points are distributed within ±0.05 microgram-atoms per liter of the curve with the exception of one at concentration 1.5 microgram-atoms per liter. This figure for the margin of error is substantiated by numerous other calibration runs.

The electric eye photometer, in common with other photoelectric colorimeters, has certain advantages over visual comparators. Errors due to eye fatigue and color blindness are eliminated. Eye fatigue becomes especially important as a source of error when visual colorimeters, which employ an eyepiece, are used at sea.

In such analyses as that for phosphate in sea water where the color is transitory, it is important to determine the optimum time after the addition of reagents to take the reading. This may be done with the present instrument, as the rate of fading of the color may be measured.

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Apparatus for Turbidimetric Study of Polymerization Activators

T. W. SARGE, *Saran Development Laboratory, The Dow Chemical Company, Midland, Mich.*

THE principal object of the present exposition is to describe a simplified turbidimeter and to present experimental data relating particularly to the polymerization of monomer-insoluble polymers, as those of vinylidene chloride. Obviously, the principle upon which the study is founded is not new: the development of haze, and eventually of opacity, produced by the formation of colloidal particles which first scatter and then eventually, almost completely, obstruct the path of transmitted light. The instrument first devised by Jackson for measurement of water turbidity was later converted to a turbidimeter for sulfur analysis (3) and more recently modifications of technique and apparatus permit the study of solids showing haze, such as plastic films (1, 2).

Polymer chemistry presents an intermediate field for the application of turbidimetry, or viewed somewhat differently, polymerization processes may be studied by dynamic turbidimetry, whereas the applications previously mentioned involve static concentration (in liquid) or static form (in solid). Expressed more specifically, it appears possible to obtain in situ relative quantitative data on polymerization phenomena, such as polymerization induction time, polymerization rates, influence of inhibitors and catalysts (by effect on induction time and rate polymerization), and the effect of concentration of reagents, inhibitors, catalysts, and other additaments.

DESCRIPTION OF APPARATUS

An extremely simple apparatus was designed to enable assembly from readily available parts. Figure 1 shows all the essential cooperative parts, while Figure 2 indicates the over-all size.

A simple turbidimeter for the measurement of dynamic polymerization phenomena is described. By graphical analysis of the direct data, it is possible to obtain P_i, the induction time of polymerization, as well as dI/dt, the slope or change of intensity which is proportional to the rate of polymerization at the interval examined. By an extension of the data, a simple but workable equation relates the over-all rate of polymerization as determined by actual bottle or semiplant polymerizations to the turbidimetric data as follows:

Rate of polymerization (observed) =
$$k \times 1/P_1 \times dI/dt \ (T, \text{catalyst})$$

Data are presented for the vinylidene and vinyl-type monomer which form monomer insoluble polymers, but it is also shown that if a precipitant is added to the original monomer, polymers that are normally soluble in monomer may likewise be examined. Direct application to problems of monomer purity, catalyst concentration, effect of inhibitors, influence of comonomers on polymerization rate, etc., are discussed, and it is suggested that the apparatus may generally be used to study emulsion stability, and reactions where concentration, time, temperature, and cloudiness are factors.

Not obvious from the sketch or photograph are the following facts: The 1-ounce (30-ml.) square specimen bottles receive heat by radiation from two sides and the bottom only of the circulating liquid bath, the two sides in the light path being open. Regulation of the voltage is a necessity, because of constant fluctuations during increased and decreased loads; however, the light intensity itself may have an arbitrary value, provided it remains constant. The total light path is 12 inches (30 cm.), with the specimen located at the center. The Worner light source is also provided with a slot for receiving filters, as is the cross-shaped attachment. Water with corrosion inhibitor, such as radiator rust inhibitor, glycol, or glycerol, provides suitable permanent bath liquid. The temperature differential between the contents of the specimen bottle and the bath is 1° to 1.5° C., the specimen being lower. Observation of the specimen shows a continual circulation, due to convection currents arising from the hot and cold walls of the square bottle.

TEST PROCEDURE

The composition of the test sample is the only determining factor in the length of time required to prepare the sample for turbidimetric examination. The sample is quickly transferred to the 1-ounce bottle and ordinarily not more than 25 ml. (from 25 to 28 grams) should be used, and the volume or weight should thereafter be maintained constant. Bakelite caps, lined with
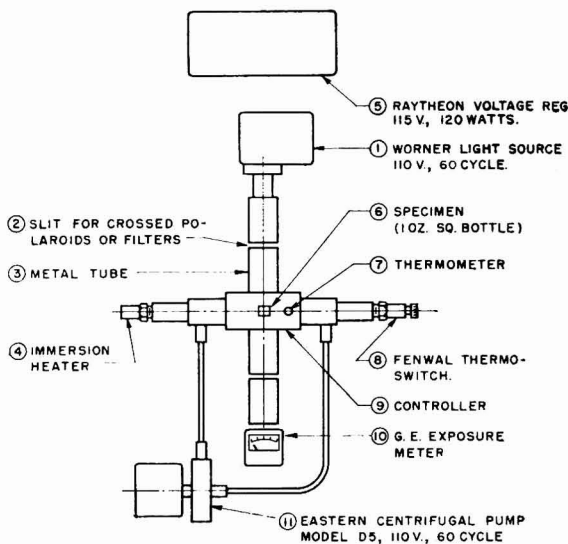
Figure 1. Turbidimeter
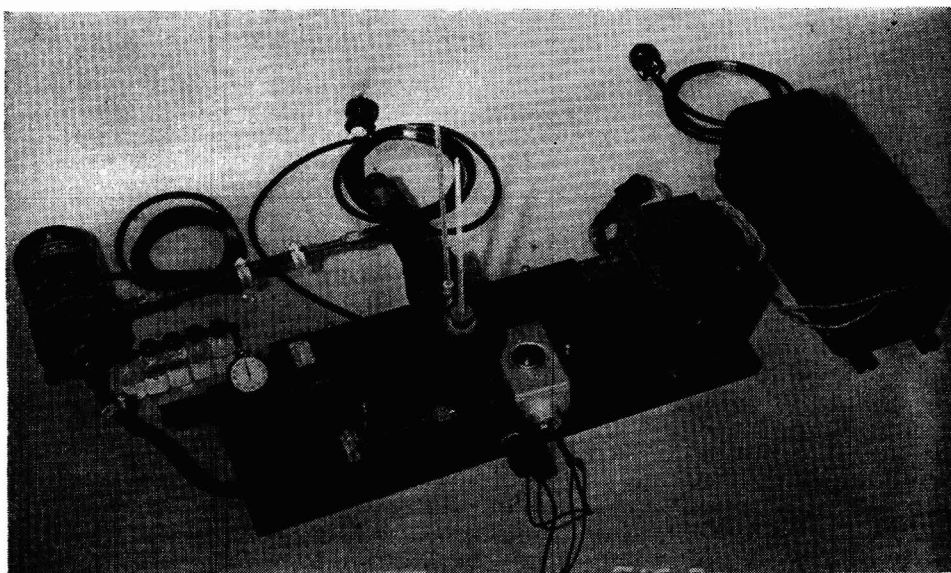
Figure 2. Photograph of Turbidimeter

Table I. Polymerization of Inhibited Vinylidene Chloride (25 Ml.) at 50° C.

Reagent	Volume, Ml.	Turbidity Rate $(-dI/dt)$, Foot-Candles/ Min.	Induction Time, Min.
CH_3COCl	1	0.84	30
	3	1.11	10
	5	1.0	8
$(CH_3CO)_2O$	1	0.88	13
	3	1.0	8
	5	1.06	5

Figure 3. Turbidity Effect during Mass Quiescent Polymerization of Vinylidene Chloride at 46° C.

plastic film or aluminum-faced paper or cork, form satisfactory seals, even for highly volatile monomeric compositions. In the present work, 1-mil (0.001-inch) saran film was also found satisfactory as a seal on glass threads. It is advisable to rub off fingerprints and dust particles with lens paper from the faces of the square bottle which are to be exposed to the light path. The cleaned, sealed, and stoppered bottle is now ready for insertion into the specimen slot.

DATA AND DISCUSSION

The only data which need be taken are time, in minutes or seconds, and foot-candle readings under constant temperature conditions. Graphical analysis of the data permits one to arrive at quantitative or semiquantitative results regarding the progress of polymerization.

In a typical application, it was desired to compare the polymerization behavior of vinylidene chloride monomer uninhibited uncatalyzed, uninhibited catalyzed with benzoyl peroxide, inhibited uncatalyzed, and inhibited catalyzed with benzoyl peroxide. The comparisons are shown in Figure 3. Disregarding the initial light intensity value (as representing only the initial clarity), it can be seen from the curves that the induction of polymerization, P_i, and the slope, dI/dt, which is
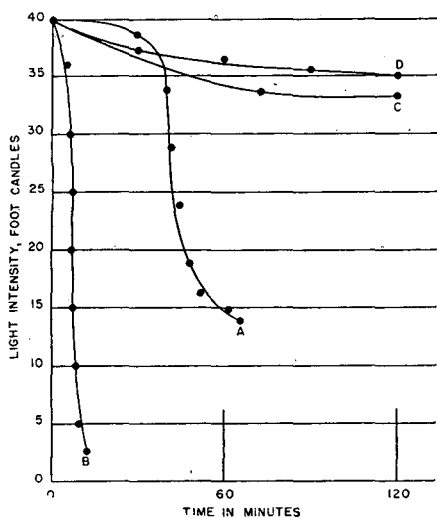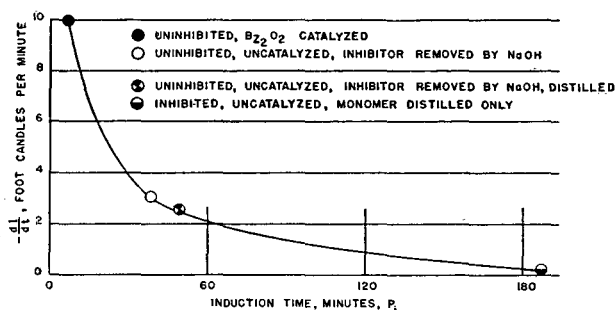
Figure 4.   Figure 3 Idealized

Figure 5.   Intensity Change vs. Induction Time of
Vinylidene Chloride at 46° C.

agents for initiating polymerization of inhibited vinylidene chloride monomer, the data represented in Figures 6 and 7 were obtained. The effect of increased concentration of acetyl chloride on the induction time and rate of turbidity development is easily seen in Figure 6, while Figure 7 shows the limiting effect of increased acetyl chloride concentration per se.   Similarly, Figures 8 and 9 show these relationships for acetic anhydride.   A summary of the observed data is given in Table I.

It is clear from the table that the turbidity rates (which should be proportional to the rate of polymerization in the early stages) are substantially equal to 1.0, and that the increase in concentration of the reagents affects, measurably, only the induction time of polymerization.   This is, of course, obvious also on inspection of the curves of Figures 6 and 8.   Data for adipyl chloride, not shown in the figures, give essentially the same results, with the exception of induction time which is even longer
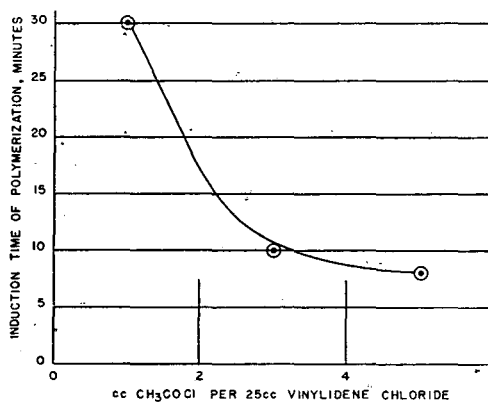
Figure 7.   Effect of Increased Acetyl Chloride
Concentration

proportional to the rate of polymerization, are easily obtained,— i.e., for curves A and B of Figure 3, P_i values are 38 and 6.5 minutes, respectively, and dI/dt are −2 and −10, respectively. The negative values for the slope of I vs. t merely indicate the decrease in transmitted light intensity as polymerization progresses.

An idealized or corrected graph of the curves in Figure 3 would perhaps be more suitable and is easily drawn by starting from a common value of I (initial) as in Figure 4.

A series of P_i and dI/dt values, plotted in Figure 5, shows for different methods of activation the inverse relationship $dI/dt \propto 1/P_i$ or $dI/dt = k/P_i$.   Also evident from this graph is the effect of various washing or purification treatments on monomer reactivity.

In an effort to determine satisfactory

Figure 6.   Turbidity Effect during Mass Quiescent Polymerization of Vinylidene Chloride at 46° C.
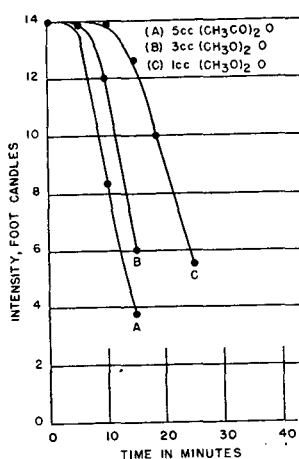

Figure 8.   Turbidity Effect during Mass Quiescent Polymerization of Vinylidene Chloride at 50° C.

—i.e., 30 minutes for 5 ml. It would seem, therefore, that short-chain reagents are more effective than long-chain or aromatic compounds of the same class.   This is further substantiated by the fact that 5 ml. of benzoyl chloride show no reactivity at 168 hours under the same polymerization conditions.

Because it appears that further additions (or an increase in concentration) of the reagents merely modify induction time, it is interesting to examine the question as to whether mere thermal polymerization follows the induction period or whether the rate of polymerization is also altered.   Table II shows the values as compared with Table I.

The trend of the data in Tables I and II was confirmed by actual bottle polymerizations, which gave the results shown in Table III.

It can therefore be concluded that the polymerization which takes place in the presence of acetic anhydride is not merely thermally catalyzed, but appears also to be slightly activated.

One manner of utilizing the turbidimetric data, P_i and dI/dt,

Table II. Polymerization of Uninhibited Vinylidene Chloride at 50° C.

Reagent	Volume	Turbidity Rate $(-dI/dt)$, Foot-Candles/ Min.	Induction Time, Min.
None	None	2.00	38

Table III. Polymerization

Monomer	% $(CH_3CO)_2O$	50° C. Av. Polymerization Rate, % per Hour
Vinylidene chloride, uninhibited	None	0.28
Vinylidene chloride, inhibited	1	0.53

is to attempt a correlation with observed rates of polymerization, as those given in Table III. For example,

$$\text{Rate of polymerization (observed)} = k \times \frac{1}{P_i} \times \frac{dI}{dt} \quad (1)$$

In order to evaluate k, the data from Tables I and III for inhibited vinylidene chloride monomer are employed, giving

$$0.53 = k \times 1/10.5 \times 0.94 \quad (2)$$

or
$$k = 5.23$$

If now we wish to estimate the probable polymerization rate of uninhibited vinylidene chloride monomer at the same temperature, we substitute in Equation 1 the values from Table II and Equation 2, giving

$$\text{Rate}_x = (5.23)\,(1/38)\,(2) = 0.275 \quad (3)$$

which approximates the observed 0.28.

In another example, it was desired to examine the "dampening" effect of vinyl chloride monomer on the polymerization rate of vinylidene chloride monomer. Figure 10 shows the data graphically.

Although there is little difference in the induction time of polymerization, there is a large difference in apparent rate of polymerization. The graphical data show, therefore, that such a turbidity test could be used advantageously to detect monomer ratios after calibration against known mixtures.

The previous examples relate to systems wherein the polymer formed is insoluble in its own monomer. In order to examine the possible utility of this turbidimetric method in monomer-soluble systems, the polymerization of inhibited styrene was examined after choosing a diluent in which polystyrene is insoluble.
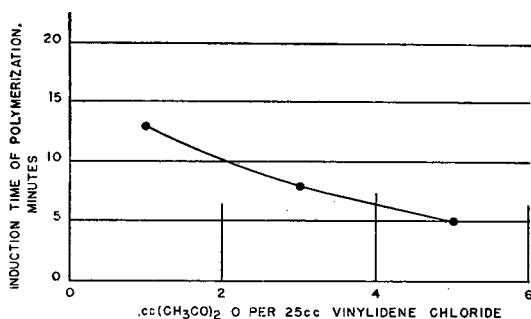
Figure 9. Effect of Increased Acetic Anhydride Concentration

The turbidimetric data are given in Figure 11. It can be seen in general that styrene polymerizes much more sluggishly than vinylidene chloride at 50° C. On the other hand, the activity of benzoyl chloride is now noticeable and is perhaps due to the compatibility of styrene and benzoyl chloride.

An attempt to study the mass polymerization of styrene,
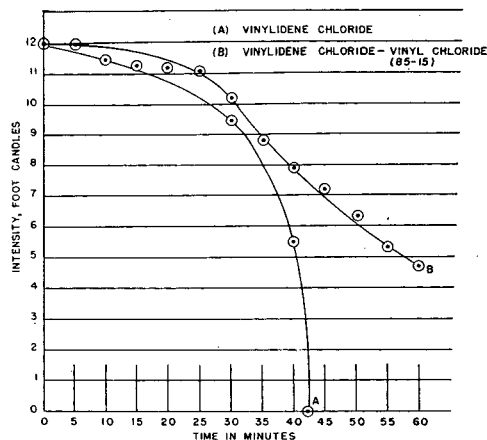
Figure 10. Effect of Vinyl Chloride Monomer on Polymerization Rate of Vinylidene Chloride Monomer
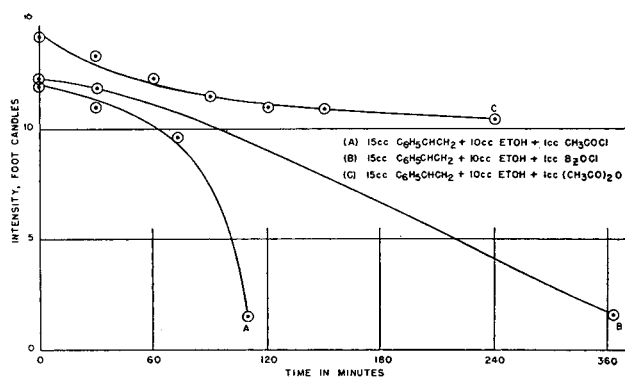
Figure 11. Turbidimetric Analysis of Styrene Polymerization at 50° C.

using parallel and crossed polaroids, in the presence of acetyl chloride but no peroxide catalyst showed no results. It is likely that higher temperatures would be more satisfactory for this study.

OTHER APPLICATIONS

Although no significant results have as yet been obtained, the apparatus and technique described appear to suggest possible utility in studying the following phenomena:

Rapid control test for monomer purity (or monomeric compositions after calibration against knowns).
Evaluation of polymerization catalyst efficiency.
Evaluation of polymerization inhibitor efficiency.
Evaluation of various pre- or posttreatments to monomer, catalysts, etc.
Emulsion stability in the presence of possible precipitants.
General precipitation or cloud occurrence or disappearance where concentration, time, temperature, and light intensity are variables.

Obviously, the apparatus described would be even more usefu when rendered automatic so as to record light intensities photometrically and to record the data graphically against time.

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Autopneumatic Apparatus for Measuring Stress Relaxation

C. S. WILKINSON, JR., AND S. D. GEHMAN, *The Goodyear Tire and Rubber Company, Akron 16, Ohio*

An apparatus for measuring stress relaxation in rubber under compression is described. Expansion of a Sylphon bellows by air pressure compresses small cylindrical test pieces. As stress in the samples decreases owing to relaxation, air is automatically released through an ordinary tire valve, thus maintaining the force at a magnitude just sufficient to keep the sample at a constant compressive strain. The force, which is a function of the air pressure within the bellows, is calculated from readings indicated by an accurate Bourdon-type gage directly connected to the bellows. The amount of compression is indicated by a dial micrometer connected to one end of the bellows. The apparatus is compact, simple, and completely self-contained. Reliability of results is improved by use of test pieces of low shape factor, recesses in platens for ends of samples, and cyclic preloading of samples before starting the test. Accuracy of the instrument was checked by comparing results with those obtained using a resistance wire strain gage. Experiments upon GR-S and Hevea compounds showed that the rate of stress relaxation was not appreciably affected by the degree of compression over a fairly wide range. Over the range from −20° to 212° F. somewhat greater rates of stress relaxation were observed for extreme high and low than for intermediate temperatures. The effect of temperature upon initial stress was also observed. Tests were made upon compounds of several types of GR-S and Hevea to determine the effect of cure upon the rate of stress relaxation. In all instances longer cures gave lower rates of relaxation. Examples illustrate the usefulness of the apparatus in comparing particular gasket-type compounds. Extensive tests were made to study possible correlation between stress relaxation results and compression set results. For some compounds, such a correlation may exist.

THE value of observations of stress decay in strained rubber as a means of studying molecular flow processes and the scission of molecular bonds has been demonstrated by Tobolsky and co-workers (7, 8, 10–12), who have published a number of interesting papers describing experimental methods developed for this purpose. Stress decay in rubber bands in tension was shown by them to behave in a manner that could be reasonably well accounted for by theoretical considerations based on Eyring's concepts of reaction rate processes.

Recently, attention has been directed toward the stress relaxation of rubber under compression. Interest is primarily due to demands upon compounds to be used as material for gaskets and mountings over a wide range of temperature. Several instruments have been designed to indicate the progressive decrease in the load required to maintain a constant compressive deformation of a sample under test.

Blow and Fletcher (2) described a simple beam-type apparatus in which a sliding weight was shifted to obtain a balance at the time of observation. Between observations, a constant compression of the test piece was maintained by means of a stop at the end of the beam. Results were plotted as stress *vs.* time on linear scales.

Beatty and Juve (1) have recently published extensive work using this type of apparatus.

Macdonald and Ushakoff (6) designed an apparatus capable of recording stress decay of samples in compression, tension, or shear. They pointed out, however, that results of the three were similar, and that compression was to be preferred for the sake of simplicity. A high degree of accuracy and reproducibility was claimed. Their results were plotted as the ratio of stress to initial stress (0.01 hour) *vs.* log time. Labbe and Phillips (5) elaborated on the above apparatus, adapting it to operation at very low temperatures and incorporating a system for changing the amount of compression while the test was in progress. By this means, they were able to get a measure of a sample's recovery properties. Their method of plotting results was the same as that of Macdonald and Ushakoff.

Morris, James, and Seegman (9) used an instrument designed by Morris for an extensive study of the effect of various accelerators in nitrile gasket compounds. Stress decay measurements were made at 194° F. and 30% compression, extending over 14 days' time. Interesting comparisons were made with results from other types of tests upon the same stocks. Their instrument was unique in that air pressure was used to apply the compressing load, and an air gage was used to indicate the force. Results were plotted both as stress *vs.* time and as the per cent decrease from 1 hour stress *vs.* time, all scales being linear.
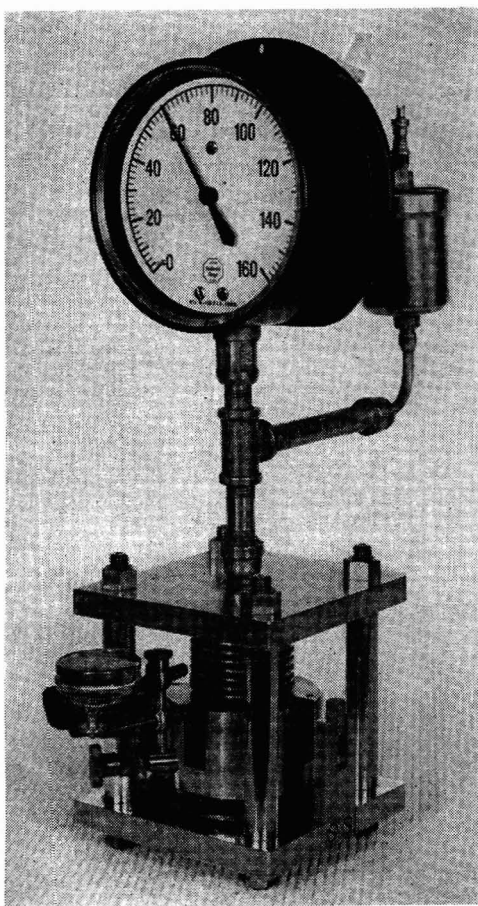

Figure 1. Apparatus

The apparatus herein described incorporates a novel means for the automatic adjustment of the compression load to correspond to the decay of stress in the rubber. Data here presented are intended primarily to illustrate possibilities of the instrument and the general stress relaxation characteristics of typical polymer compounds rather than the development of specifically useful types of gasket compounds.

DESCRIPTION OF APPARATUS

The apparatus, shown in Figures 1 and 2, is comparatively simple to make, easy to operate, accurate, and self-contained. This last feature is especially valuable when it is desired to use it at different temperatures, necessitating transfer of the instrument from oven to refrigerator, etc. Its relatively small size is also advantageous in such situations.

Air pressure is used to furnish the compressive force, and an ordinary tire valve serves to adjust this pressure continuously and automatically to the exact amount necessary just to equal the decreasing stress within the sample. A Sylphon bellows takes the place of the more conventional cylinder and piston, thus allowing considerable simplification in design. An air gage connected to the bellows indicates the pressure at all times. Readings of this gage are taken at intervals throughout the duration of the test. A universal-type micrometer dial gage, shown in Figure 1 but not in Figure 2, gives the compression of the sample at any time. A "hole attachment" is used to transmit motion of the bellows to the gage.

The principle of operation may be explained by referring to Figure 2. Air is introduced through the inlet valve to expand the bellows downward against the test pieces. They are thus compressed until the balancing valve makes contact with the height adjustment cross bar. This contact opens the valve, releasing air and arresting any further expansion of the bellows. A ceramic porous plug smooths out the cycling operation by retarding the air flow through the valve. When a balance between stress in the sample and pressure in the bellows has been attained, the valve closes. But the balance is upset as the stress decays within the sample; the bellows expands, opening the valve. Air pressure is released until a new balance is reached and the valve closes. This cycling continues throughout the test.

Motion of the bellows in opening and closing the valve is so slight, less than 0.001 inch, that the sample compression may be regarded as essentially constant.

All joints in the apparatus are soldered. Leakage with good valves is so small as to be negligible, less than 1 pound per square inch in 2 or 3 days. No correction for leakage is required as long as the stress relaxation rate exceeds the leakage.

Test pieces are cylinders 0.5 inch in diameter by 0.5 inch high. Three, four, or six pieces may be arranged in shallow recesses in the platens, the number depending on the stiffness of the stock. By using several pieces, each having a small shape factor (4), end effects are minimized.

Samples may be molded to size or cut from a vulcanized slab with a rotating cutter.

COMPOUNDS USED

Formulas for compounds used in this work are given in Table I.

EXPERIMENTAL PROCEDURE

Samples to be tested are prepared by lightly buffing their ends with Crocus cloth. Their height is measured with a micrometer and the necessary deflection for the desired percentage of compression is calculated from this dimension. They are then placed in the apparatus and the whole assembly is put into the oven or low temperature cabinet for 2 hours in an unstressed state.

At the end of this conditioning period air is pumped into the bellows, using an ordinary tire pump, until the micrometer dial gage indicates the correct deflection. The cross bar is then carefully adjusted to make contact with the automatic balancing valve.
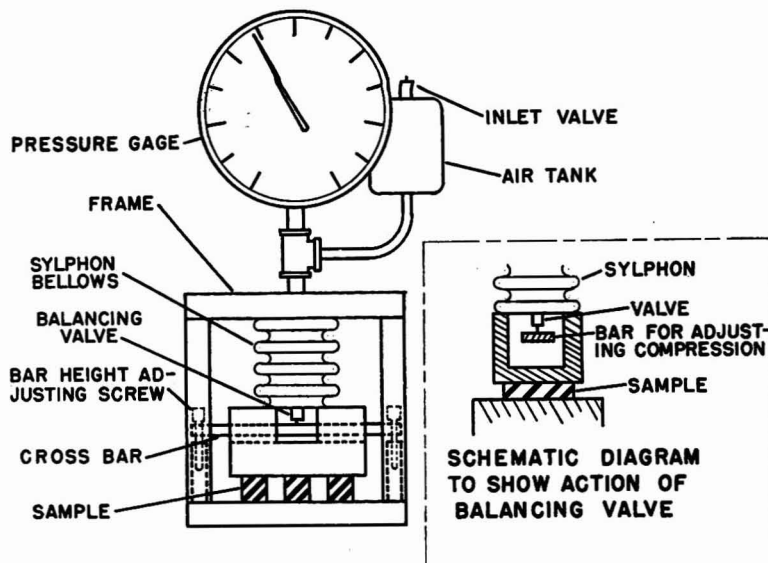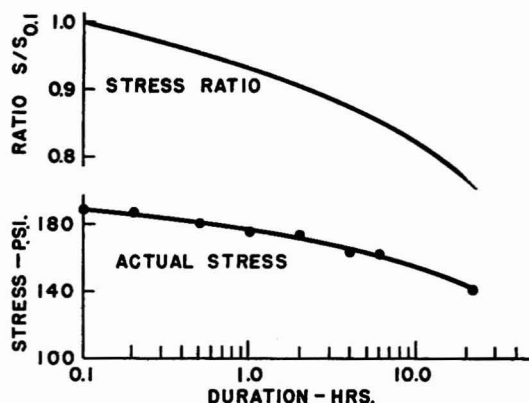

Figure 2. Diagram of Apparatus

Figure 3. Typical Curves for Tread Stock

GR-S redox R11X349-15.   Cure 35/275
Compression 30%.   Test temperature 158° F.

Before starting the test the bellows is alternately exhausted and refilled three times at 1-minute intervals. This type of prestressing has been found advantageous in obtaining reproducible results in compression-type tests (4) and performs this same useful function for stress relaxation tests. However, it reduces markedly the relatively large transient relaxation usually observed at the start of a test with the initial loading.

The first reading of the air gage is taken 6 minutes after the start of the test, and subsequent readings are taken at appropriate intervals. At the termination of the test the samples are removed from the apparatus and allowed to recover for 0.5 hour. Their height is then measured again with the micrometer for calculation of set.

Typical curves are shown in Figure 3. The actual stress curve is based upon calculations which take into account air pressure, cross-section area of the bellows, stiffness of the bellows, and cross-section area of the samples. The equation used is:

$$S = \frac{aP - bx + c}{\frac{\pi}{4} d^2 N}$$

where

S = stress, pounds per square inch
a = cross-section area of bellows, square inches
P = gage pressure, pounds per square inch
b = spring constant of bellows, pounds per inch
x = amount of compression, inches
c = dead weight of coupling system, pounds

d = diameter of a test piece, inches
N = number of test pieces being used

Here a, b, and c are constants for any particular apparatus. For any group of experiments x, d, and N are usually constants. In this case the equation may be simplified to:

$$S = \frac{aP + C}{K}$$

where C and K are constants for the fixed conditions.

For example, with the present apparatus and three test pieces 0.5 inch in diameter, and 0.5 inch high, compressed 30%, the equation becomes:

$$S = \frac{2.14P - 10.66}{0.59}$$

As a numerical example: The 0.1-hour reading of the pressure gage was 56.7 pounds per square inch for the compound used in obtaining data for the curve shown in Figure 3. Substituting this value for P in the above equation gives:

$$S = \frac{(2.14)(56.7) - 10.66}{0.59}$$

$$= 187.6 \text{ pounds per square inch}$$

Alternatively, for definite testing conditions, the gage dial may be graduated to read directly the stress in the test pieces.

The stress ratio curve is obtained by dividing the stress at any
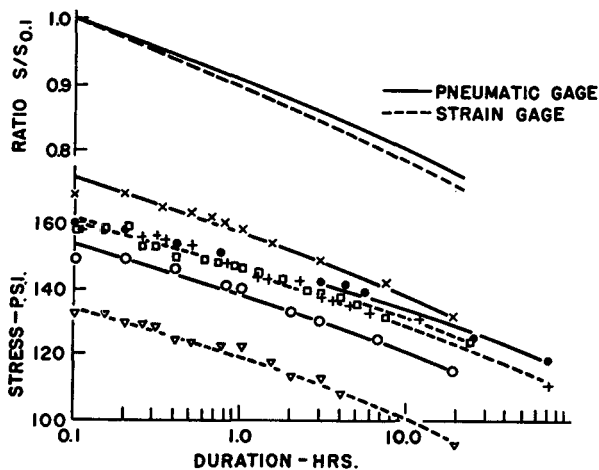
Figure 4. Comparison of Pneumatic Gage with Resistance Wire Strain Gage

GR-S tread R11X374-2.   Cure 100/275

time by the stress at 0.1 hour. This arbitrary choice of initial stress time differs from that of both Ushakoff and Macdonald and Morris, James, and Seegman. A few later experiments at 212° F. indicated that the initial time of 1 hour used by Morris *et al.* may be the more useful.
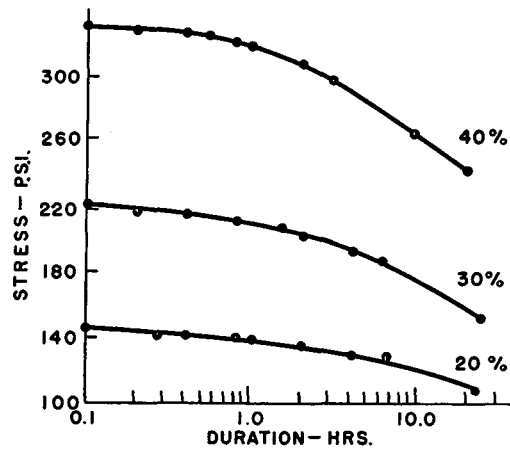
Figure 5. Effect of Amount of Compression

GR-S tread R11X400-6
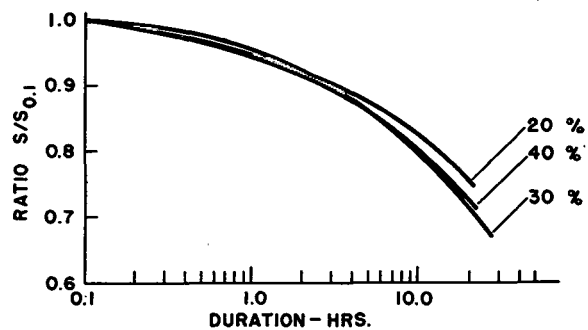Test temperature 158° F.   Cure 20/275

Figure 6. Effect of Amount of Compression

GR-S tread R11X400-6
Test temperature 158° F.   Cure 20/275

For convenience semilogarithmic paper is generally used in plotting results. Short-term tests extending over a few hours or several days are best plotted in this way. When tests extend over several weeks, curves are more descriptive when exhibited on linear graph paper.

COMPARISON WITH RESISTANCE WIRE STRAIN GAGE

Stress relaxation tests were made using a Baldwin Southwark resistance wire strain gage incorporated into the apparatus on a stiff spring as in the apparatus of Macdonald and Ushakoff (*6*). This gage was one arm of a conventional Wheatstone bridge circuit. The initial load was applied by means of the bellows as before, but brass spacers were immediately inserted to maintain a constant deflection and all air was then released. A check upon the pneumatic system by a more familiar method was thus made possible.

Comparisons were obtained for 30% compressions at 158° F. The stress relaxation curves for three tests using the pneumatic method and three tests using the strain gage method are shown in the lower part of Figure 4. Points from the

Table I.   Compound Formulas Used[a]

Materials	R607D489	R36X17- 1	R36X17- 5	R36X17- 6	R11X349- 15	R11X349- 16	R11X400-6[b]
GR-S	100	100					100
GR-S redox					100		
GR-S-10						100	
Smoked sheet			100	100			
Sulfur	2	2	3	3	2.5	2.5	2.5
Captax[c]	1.5	1.5	1	1	1.5	1.5	1.5
DOTG[d]					0.35	0.35	0.35
Zinc oxide	5	5	3	3	5	5	5
Stearic acid	2	2	4	4	2	2	2
Softener[e]	3	3			3	3	3
Pine tar			3.75	3.75			
Anax[f]	1	1			1	1	1
EPC black	50			50	50	50	
HAF black							30

[a] BJ93 and BJ94 were supplied without formulations by C. K. Chatten, chairman of A.S.T.M. Section on Relaxation of Rubber in Compression.
[b] R11X374-2 (Figure 4) same as R607D489, except polymer was obtained from a different run.
[c] Mercaptobenzothiazole.
[d] Di-*o*-tolylguanidine.
[e] Paraflux.
[f] Phenyl-2-naphthylamine.

three curves by each method were averaged to use in calculating the two ratio curves shown in the upper part of the figure. New samples were of necessity used for each test, which introduced some variation.

OPERATIONAL VARIABLES

Two variations in conditions of operation have been investigated: the effect of the amount of compression and the effect of the temperature of testing.

Figures 5 and 6 show results obtained from samples cut from the same vulcanized slab and tested at three different compressions. Although the actual stress curves have different shapes, when the data are plotted as ratio curves, they are similar. These results indicate that the degree of compression over a considerable range has little influence upon the rate of stress decay.
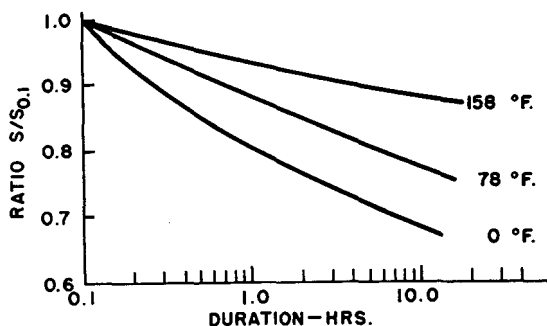
Figure 7.   Effect of Test Temperature

GR-S gum R36X17-1
Compression 30%.   Cure 100/275

The effect of the temperature at which the samples are tested was studied using GR-S gum and treat compounds. Figure 7 shows results from the gum compound. The lowest temperature curve indicates high initial stress, which decays rapidly during the early part of the test. This behavior is in agreement with that found in low temperature torsion flex tests (3), where the greatest rate of creep is found at about this temperature. At the higher temperatures the decrease in stress during the early period of the test is much less severe. The ratio of stress decay curves shows that the rate of stress decay increases regularly as the temperature decreases.
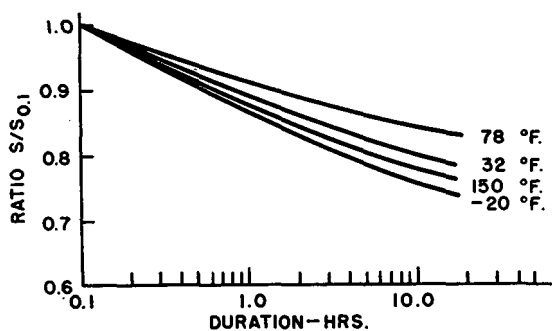

Figure 8.   Effect of Test Temperature

GR-S tread R607D489
Compression 30%.   Cure 100/275

Results for the tread compound, tested over a wider range of temperatures, are similar with one exception. As shown in Figure 8, the rate of stress decay goes through a minimum at 78° F., being greater at both lower and higher temperatures.

Figure 9 shows an interesting outcome incidental to this study. Here the initial stresses for a series of tests on Hevea and GR-S gum compounds are plotted against temperature. The Hevea compound shows a practically proportional increase in stress with
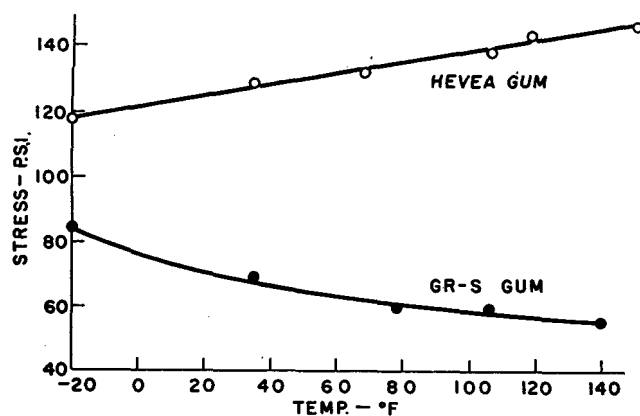

Figure 9.   Effect of Temperature on Initial Stress
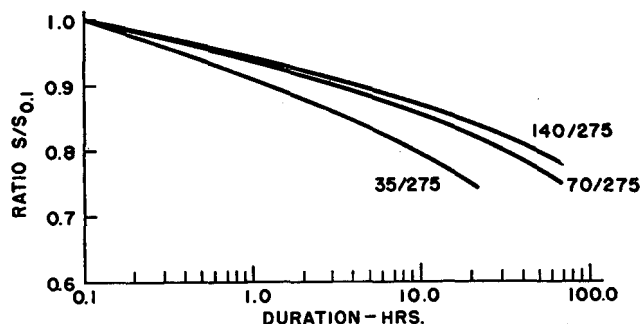
Compression 30%

Figure 10.   Effect of Cure

Hevea tread   R36X17-6
Compression 30%.   Test temperature 158° F.

Table II.   Correlation with Type B Compression Set

| | BJ93 | | BJ94 | |
Temp., °F	Set, %	Decay at 20 hours, %	Set, %	Decay at 20 hours, %
86	7	8	9	6
158	9	6	43	15
212	29	7	72	42

rise in temperature, as might be expected from the Joule effect. The GR-S acts oppositely, probably because of higher internal friction at lower temperatures.

EFFECT OF CURE

Hevea and GR-S tread compounds were tested at 158° F. to determine to what extent stress relaxation is affected by amount of cure. The duration of these runs was generally 22 hours, although in several instances longer times were used. Figures 10
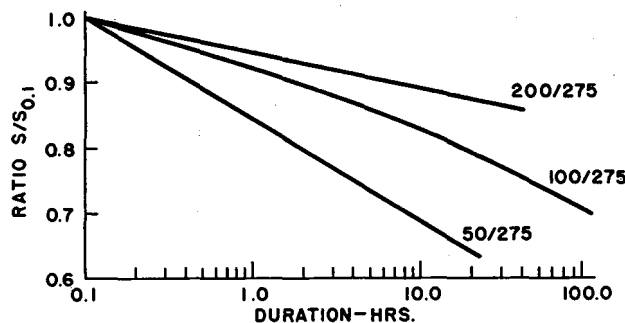

Figure 11.   Effect of Cure

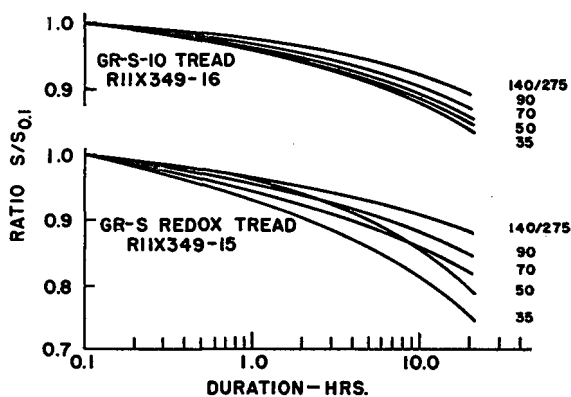GR-S tread R607D489.   Compression 30%.   Test temperature 158° F.

Figure 12.   Effect of Cure

Compression 30%.   Test temperature 158° F.

and 11 show results from these experiments. In all cases longer cures gave lower rates of relaxation. Figure 12 shows results of similar tests on GR-S-10 and Redox tread compounds.

COMPARISON OF COMPOUNDS

Usefulness of the apparatus in comparing particular compounds may be illustrated by referring to Figures 13 and 14. The stress curves show that at all three temperatures BJ94 has a much higher initial stress. Under constant compression of 40%, however, the samples at higher temperatures soon begin to fail rapidly. BJ93, on the other hand, although having a lower
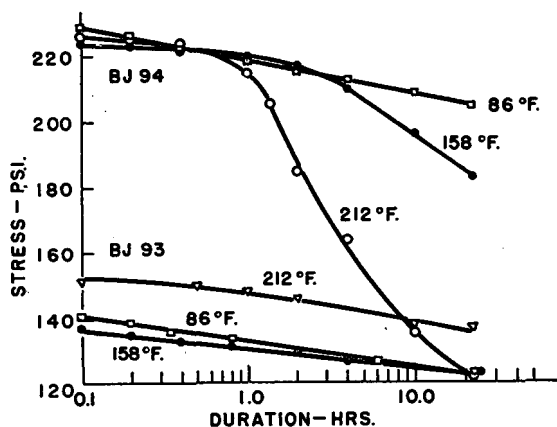

Figure 13.   Comparison of Compounds
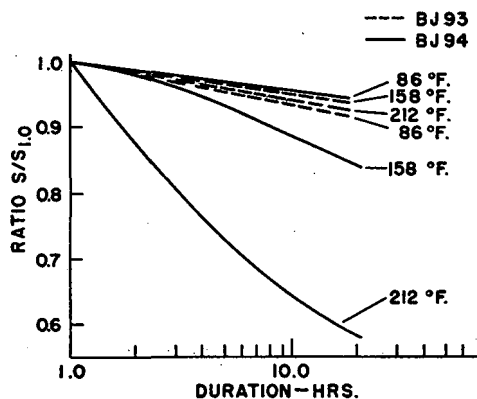
Compression 40%

Figure 14.   Comparison of Compounds

Compression 40%

initial stress, maintains it well at all temperatures. The ratio curves emphasize this fact. Only at the lowest temperature does BJ94 compare favorably with BJ93.

In connection with this experiment extensive measurements of compression set were made, upon both test pieces used in the stress relaxation apparatus and samples run concurrently between polished plates. An idea of the degree of correlation between compression set and stress relaxation may be obtained from Table II, which was prepared from averaged results of seventeen tests.

A considerable amount of correlation exists for BJ94 but none for BJ93. A possible explanation of this widely different behavior may be based upon knowledge of other types of experiments. It is theorized that at elevated temperatures strained rubber is constantly undergoing scission and formation of bonds. For each bond broken there is a corresponding decrease in stress; but when a bond is formed, there is no change in stress because the new bond is formed in an unstrained state. In the stress relaxation test, primarily, scission of bonds is being measured. But in the compression set test combined effects due to both scission and formation of bonds are being measured, and possibly effects due to delayed elasticity.

Applying this to the results here shown it may be said that in the case of BJ93 the rate of scission is practically unaffected by these temperatures, but the formation of bonds is increased at higher temperatures. In the case of BJ94 both bond scission and bond formation are accelerated by increasing the temperature.

CONCLUSIONS

The results of these experiments may be summarized in the four following conclusions:

The rate of stress relaxation is independent of the amount of compression over a considerable range. It is affected by the test temperature; therefore, the test temperature should approximate the temperature at which the product is to be used. The rate of stress relaxation decreases with increase in cure. It cannot be predicted from results of compression set tests, although for some compounds some degree of correlation exists.

ACKNOWLEDGMENT

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Potentiometric, Amperometric, and Polarographic Methods for Microanalysis

THOMAS D. PARKS[1] AND LOUIS LYKKEN

Shell Development Company, Emeryville, Calif.

A review is given of various practical methods for the microdetermination of common constituents in petroleum products by potentiometric, amperometric, and polarographic means. A brief description or mention is included of the equipment used in these methods, together with typical applications to microanalysis. Methods are outlined for the determination of acidity, basicity, saponification number, and halogens by potentiometric titration; sulfate ion, halogens, silver, lead, iron, and copper by amperometric titration; and lead, aluminum, and sodium by polarographic analysis.

MANY investigators have recognized the value of electrometric methods in the determination of small amounts of material (3, 6, 9, 10, 22, 29, 30). Benedetti-Pichler, for example, points out the general advantages of a potentiometric end point in microanalysis when dealing with colored or very dilute solutions (3). Stock (29) recently reviewed microchemical applications of potentiometry with emphasis on special apparatus used for very small volumes (drop-scale analysis). Polarographic methods are inherently suited to microchemical work because they utilize dilute solutions (10^{-6} to 10^{-2} molar). Majer has described various cells for the polarographic examination of very small volumes of solution (21). Amperometric titrations, either at a dropping mercury or a rotating platinum electrode, are useful in the analysis of small volumes of dilute solutions (28).
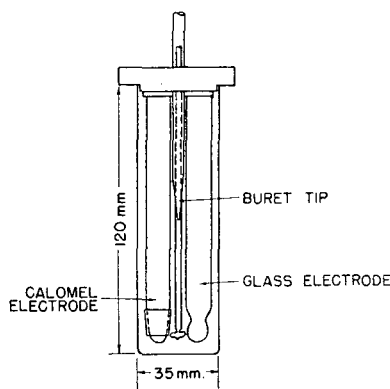

Figure 1. Cell for Micropotentiometric Titration

Potentiometric, amperometric, and polarographic methods are closely related in their fundamental reactions, together forming a powerful tool for microanalysis. In general, they are rapid and sensitive methods which often permit the separation or simultaneous determination of ions which are very similar chemically. Representative procedures are outlined below to illustrate the microdetermination of various constituents in petroleum products.

POTENTIOMETRIC TITRATIONS

Reduced-scale potentiometric titration methods are described for representative analyses carried out in these laboratories.

[1] Present address, Stanford Research Institute, Stanford, Calif.

The titrations are made in the cell illustrated in Figure 1, which can be used with a variety of electrode combinations and which permits titration in 10 ml. or less of solution (19).

Acidity and Basicity. The potentiometric methods for the determination of acidity and basicity have two advantages over visual color-indicator methods: Dark colored oils give no difficulty and both strong and weak acids can be determined in one titration. The titration medium consists of equal volumes of c.p. benzene and c.p. isopropyl alcohol, containing 0.5% water (1). An outline of the procedure is given below; the detailed procedure and typical curves obtained are similar to those of the American Society for Testing Materials (1).

The total acid and strong acid numbers are determined on 10- to 50-mg. samples in a 10-ml. volume, titrating with 0.02 N alcoholic potassium hydroxide. The total base and strong base number are similarly determined, except that the sample is titrated with 0.02 N alcoholic hydrochloric acid. In both cases, the buret used has graduations every 0.02 ml. and a blank test is made.

Saponification Number. A reduced-scale procedure for saponification number, adapted from the A.S.T.M. procedure (2), is used for 50-mg. samples of used oils. The saponification rack is equipped with water-cooled finger condensers (2) which fit the small potentiometric titration cell (Figure 1) described above. The oil samples are refluxed for 110 to 120 minutes in a known amount of potassium hydroxide dissolved in a benzene-isopropyl alcohol medium. After cooling, the excess potassium hydroxide is titrated immediately with alcoholic 0.02 N hydrochloric acid by the potentiometric method (above). A blank test is made under the same conditions, omitting the sample.

Halogens. The potentiometric determination of halide ions with silver nitrate solution is used after the microcombustion of organic materials in a quartz tube (27) or after solution or leaching of inorganic materials, especially when more than one of the halogens are present. The apparatus used for the titration is the same as that used for acid-base titrations, except that a silver electrode is used as indicator electrode and a glass electrode is used as reference electrode (20). The silver electrode is conditioned before use by polishing with emery cloth and titrating 3 drops of 10% potassium iodide with approximately 0.1 N silver nitrate. The solution (10 ml.) containing 0.02 to 0.2 ml. of halide ion is acidified with nitric acid, 0.5 gram of barium nitrate is added, and the solution is titrated with small increments of 0.01 N silver nitrate. In titrating with silver nitrate, breaks for iodide, bromide, and chloride ions are easily distinguished from each other when present in comparable amounts (see Figure 2).

Discussion. While it is possible to use more classical microequipment (3) for these potentiometric titrations, it has been found advantageous to use scaled-down cells and procedures (27) based on the common macromethods because this permits ready comparison with results obtained by macro means and permits use of regular electrodes. The potentiometric titration of halides is a longer procedure than the amperometric titration (14), but it permits ready identification of the halides present.

AMPEROMETRIC TITRATIONS

Amperometric titrations are carried out in a cell having a fixed potential between a reference electrode and an indicator electrode. The current produced at the indicator electrode is used to measure the increase or decrease of an electroactive ion and the current is plotted against the reagent volume to obtain a graphical end point. The dropping-mercury electrode was first used as an indicator in amperometric titrations as a logical development of polarography (6); more recently, a rotating-platinum electrode was introduced (17). Together, the platinum and mercury electrodes permit the determination of a wide range of anions and cations. Where applicable, amperometric titrations are much more rapid than potentiometric titrations; the platinum electrode is more useful than the dropping-mercury electrode for titrations carried out at a positive potential, because of oxidation of mercurous ions formed by solution of the mercury.
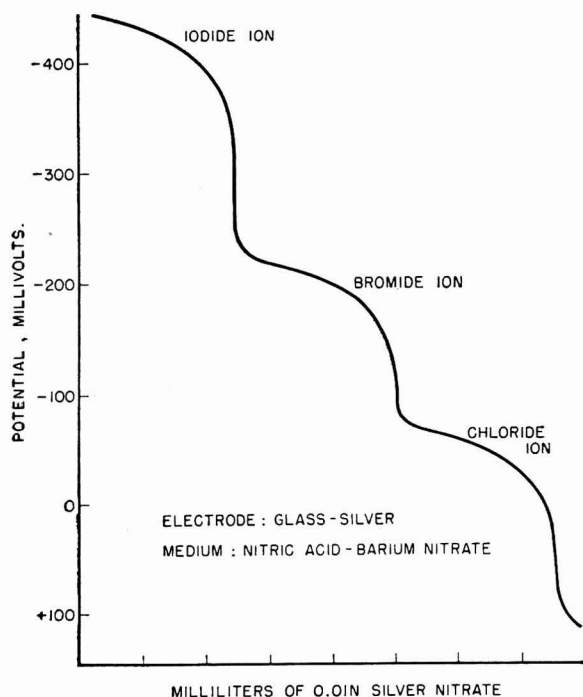

Figure 2. Potentiometric Titration of Small Amounts of Halide Ions with Silver Nitrate

The apparatus required for amperometric titrations is simple. The indicator electrode is a piece of platinum wire sealed into 6-mm. soft-glass tubing to form an electrode 5 to 10 mm. long. The reference electrode is generally a saturated calomel–salt bridge combination or a mercury pool. The Fisher Scientific Company Electropode is convenient for application of a fixed potential and measurement of the current produced at the indicator electrode. A schematic diagram of the rotating-platinum electrode apparatus is shown in Figure 3. The apparatus for titrations at a dropping-mercury electrode differs in that provision is made in the cell for the capillary electrode and for purging with nitrogen.

Amperometric methods, using the rotating-platinum electrode, are outlined below for the determination of halide, silver, lead, copper, and iron ions. Sulfate ion is determined using the dropping-mercury electrode in an air-free solution.

Halogens. Amperometric titrations are used in the microanalysis of organic halogen compounds after combustion (27) or after leaching or fusion of inorganic residues. Generally, it is possible to determine bromide ion amperometrically in the presence of chloride ion and iodide ion in the presence of bromide ion and chloride ion (15) but, when more than one halogen is present, the potentiometric method is preferred.

In the amperometric method, 25 ml. of solution, containing 0.02 to 0.2 me. of halide ion, are acidified with nitric acid and 25 ml. of acetone and 0.5 ml. of 1% gelatin solution are added. The solution is titrated amperometrically with 0.01 N silver nitrate, using a zero applied potential. For smaller amounts of halogen (less than 0.02 me.), the volume is reduced to 5 to 10 ml., 10 to 15 ml. of acetone are added, and the solution is then titrated with 0.001 N silver nitrate.

Sulfate Ion. The procedure for the microdetermination of sulfate ion is similar to that described by Kolthoff and Pan (13). It is particularly useful for the determination of sulfate ion in the presence of organic matter—e.g., sulfonates.

The sulfate ion is titrated amperometrically with 0.01 M lead nitrate solution (in the presence of isopropyl alcohol and a saturated solution of lead sulfate in 0.1 M potassium nitrate), using a dropping-mercury electrode in place of the rotating-platinum anode and an applied potential of −1.2 volts.

Silver. The amperometric method for the determination of silver is applicable to oils which contain aluminum, barium, calcium, copper, iron, lead, magnesium, tin, and zinc, as well as chlorine, bromine, sulfur, and phosphorus (26). Milligram quantities of silver are determined with an accuracy of 1%. An ammoniacal solution of silver ions is titrated amperometrically with 0.01 N potassium iodide solution, using the rotating-platinum anode and an applied potential of −0.23 volt.

Copper and Iron. Kolthoff and May titrated very dilute solutions of dichromate ion with ferrous ion at a rotating-platinum anode and suggested the possibility of the reverse titration of ferrous ion with dichromate solution (11). Under the conditions used for the titration (25), ferrous ions are oxidized at the rotating anode to produce a current. When dichromate solution is added, a diminution of current is found which gives a typical amperometric end point. Cuprous ions are not titrated directly but are used to produce an equivalent amount of ferrous ions before titration. As little as 100 micrograms of copper and 20 micrograms of iron are determined with an accuracy of 1%.
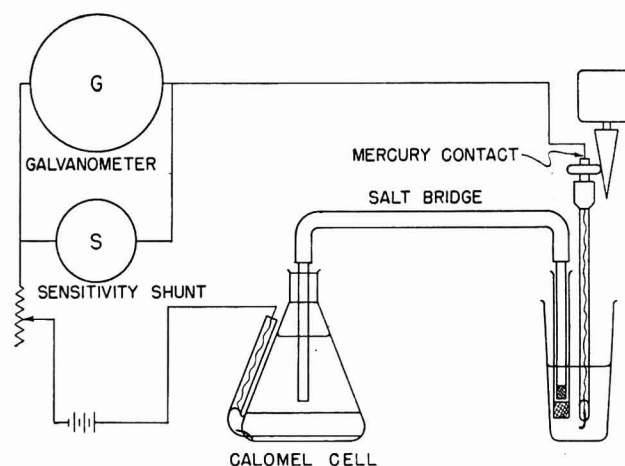

Figure 3. Amperometric Titration Assembly

In the procedure for the determination of copper and iron, the metals are obtained in acid solution and the solution is passed through a silver reductor to give ferrous and cuprous ions. One aliquot of the solution is received under ferric alum and titrated with dichromate solution using a rotating-platinum anode at a potential of +1.0 volt to measure the total iron and copper in the sample; another aliquot is purged with air to oxidize the cuprous ion preferentially and the remaining ferrous ion is titrated as before; the copper is calculated by difference.

Lead. Small amounts of lead are determined by an indirect amperometric procedure.

The lead is precipitated as lead chromate and, after solution of the precipitate, the dichromate ion associated with the lead is

titrated with 0.01 N ferrous ammonium sulfate solution, using an applied potential of +1.0 volt. The method is particularly useful for the determination of lead in engine deposits containing large amounts of calcium. The apparatus used for the precipitation, filtration, and solution of the lead chromate is similar to that of Gordon and Burdett (4).

Discussion. Five minutes are usually required to complete an amperometric titration at a rotating-platinum electrode, but this time is often reduced to 1 or 2 minutes per titration in a series of similar samples. Titrations using a dropping-mercury indicator electrode require 15 to 20 minutes, in any sequence. This increase in time is due to the nitrogen purge which is necessary between each addition of reagent to stir the solution and to remove dissolved oxygen.

The reduction of silver ion at a rotating-platinum electrode is used as the basis for a number of amperometric methods. In addition to the procedures given above for silver and chloride ions, methods have been reported for bromide and iodide ions (14), cyanide ion (16), mercaptans (8), sulfide ions (5), and disulfides (12). Alcohol or acetone is usually added to suppress the solubility of the silver salts when titrations are made with 0.01 N or 0.001 N silver nitrate solutions.

Oxidation of ferrous ions using a rotating-platinum anode at a potential of +1.0 volt is the basis for several titrations. Iron and copper are determined in the presence of aluminum, barium, calcium, lead, magnesium, potassium, silicon, phosphorus, and zinc (25); lead is determined by indirect titration of lead chromate.

POLAROGRAPHIC METHODS

The value of polarographic methods in microanalysis was recognized early by many workers in the field. The apparatus, techniques, and applications are summarized by Heyrovský (6), who points out that as little as 0.005 ml. of solution can be analyzed by the polarographic method. In general, however, polarographic cells utilizing 5 to 10 ml. of solution give sufficient sensitivity for microanalysis. A utilized cell assembly is used which employs interchangeable cells with standard-taper joints (18).

A polarographic method is often chosen for the microdetermination of a metal or organic compound even when other micromethods are available. The choice of method used depends on many factors, including the number of replicate analyses, the time per determination by each method, the equipment available, and the accuracy required. When the amount of material for analysis is limited—e.g., samples from engine deposits or corrosion strips—a microbalance is used to weigh the sample for the determination. On the other hand, trace amounts of metals in used lubricating oils are determined on the residue from a large sample.

Of the large number of metals which can be determined by the polarograph, three typical procedures are outlined below.

Lead (10) and sodium (31) are determined directly by measuring the diffusion wave of the metal ion in solution. Lead gives a well defined wave and generally requires little sample preparation; on the other hand, the procedure for sodium is difficult because it is necessary to remove many interfering metal ions and because it is difficult to obtain a good electrolyte. Aluminum is determined by an indirect method (24); the procedure illustrates a means of circumventing poor polarographic characteristics of an ion by using a secondary reaction in the determination. In this case, the aluminum is determined by measuring the decrease in wave height of a standard 8-quinolinol (oxine) solution upon the addition of the unknown aluminum solution.

For the determination of lead in organic samples, the organic material is removed by wet oxidation, the precipitated lead sulfate is dissolved in 1 N hydrochloric acid, and the lead ion is determined polarographically using a potential range of −0.2 to −0.6 volt.

In the procedure for the determination of sodium, most of the interfering elements are removed by means of the mercury cathode (7, 23), and the remainder are removed by treatment with

ammonium carbonate and ethyl alcohol. The sodium is then determined polarographically using tetraethylammonium hydroxide as the supporting electrolyte (31).

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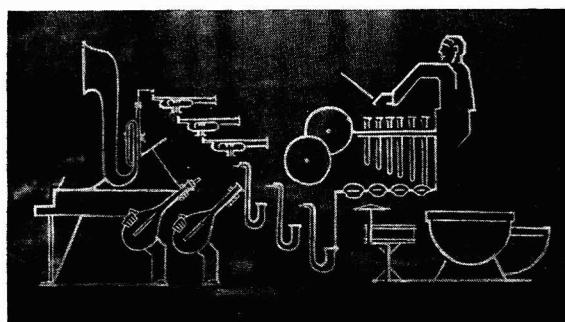
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THE ORCHESTRA

Determination of Tryptophan with p-Dimethylaminobenzaldehyde

Elimination of Interference by Chloride and Bisulfite Ions

JOSEPH R. SPIES

Allergen Research Division, Bureau of Agricultural and Industrial Chemistry, U. S. Department of Agriculture, Washington 25, D. C.

IN A collaborative study on chemical tests for amino acids in protein hydrolyzates Lesuk (1) reported that chloride ions increase the intensity of the color obtained with tryptophan when determined by a method previously described by Spies and Chambers (2). Lesuk also observed that chloride ions increase the requirement of sodium nitrite to give maximum color. These observations were confirmed in this laboratory.

The purpose of this paper is to show the magnitude of the increase in color caused by chloride ions, and the amount of sodium nitrite required to produce maximum color in the presence of chloride ions, and to describe a simple method for eliminating this interfering effect. It was observed in the present study that sodium bisulfite, sometimes used to stabilize protein hydrolyzates, decreases the color (about 10%) obtained with tryptophan and p-dimethylaminobenzaldehyde and also increases the sodium nitrite required to produce maximum color. The interference by both chloride and bisulfite ions was eliminated by treating tryptophan-containing solutions with silver sulfate. After complete precipitation of interfering ions, the insoluble silver salts were removed by centrifuging and the supernatant solutions were analyzed for tryptophan (2).

APPARATUS, REAGENTS, AND METHODS

Apparatus, reagents, and methods for the determination of tryptophan have been described (2). The following reagents were also used. Silver sulfate was reagent grade, free from nitrates. Hydrochloric acid was twice distilled, constant boiling acid. Sodium chloride was Merck's reagent grade as used for biological work. Metasodium bisulfite was a commercial reagent grade. Commercially available amino acids of best quality were used.

Procedure T (use of silver sulfate to remove interfering effect of chloride and bisulfite ions). To 10 ml. of the chloride- or bisulfite-containing solution also containing 50 to 100 micrograms of tryptophan per ml. in a 25-ml., glass-stoppered Erlenmeyer flask was added 1.0 gram of pulverized silver sulfate. The suspension was shaken frequently for 20 to 30 minutes until precipitation of silver chloride or silver sulfite was complete, as indicated by rapid settling of the precipitate. The suspension was then centrifuged using a capped 12-ml. centrifuge tube. One milliliter of the supernatant solution was used directly for tryptophan analysis by Procedure F (2). Confirmatory test for the presence of sufficient sodium nitrite to develop maximum color was made by determining that no appreciable change in transmittancy occurred within 15 minutes following addition of a second equal amount of sodium nitrite to the colored solution.

Application of Procedure T to Determination of Tryptophan in Presence of Other Amino Acids. To a 125-ml. glass-stoppered Erlenmeyer flask containing 20 mg. each of arginine, lysine, histidine (a weight of the monochloride of these three amino acids equivalent to 20 mg. of the free amino acid was used), tyrosine, alanine, serine, threonine, glutamic acid, aspartic acid, phenylalanine, proline, hydroxyproline, glycine, methionine, and 5 mg. of cystine were added 50 ml. of a water solution containing 100 micrograms of tryptophan per ml. The suspension was shaken until all but a trace of insoluble matter dissolved and the clear solution was decanted (Solution A). Solution A contained approximately 5.7 mg. per ml. of the combined amino acids. Ten milliliters of Solution A were added to 100 mg. of sodium chloride or to 100 mg. of sodium chloride and 5 mg. of metasodium bisulfite and these salts were dissolved. To the solution was then added 1 gram of powdered silver sulfate and the suspension was shaken vigorously and continuously for 5 minutes. The suspension was centrifuged for 3 minutes in a capped 12-ml. centrifuge tube. The supernatant solution was clear when sodium chloride was used, but slightly opalescent when both sodium chloride and sodium bisulfite were used. The slight opalescence of the latter solution caused no interference because it cleared completely in the subsequent tryptophan analysis.

The supernatant solution was decanted (Solution B) and tryptophan analysis by Procedure F (2), as described below, was started within 15 minutes after addition of silver sulfate to Solution A. To 30 mg. of p-dimethylaminobenzaldehyde in a 25-ml. glass-stoppered Erlenmeyer flask were added 9.0 ml. of 21.4 N sulfuric acid. To this solution was added 1.0 ml. of Solution B, and after mixing and cooling to 25° C. the flask was stored at 25° for 1 hour in the dark. Then 0.1 ml. of 0.04% sodium nitrite solution was added and the flask was shaken. Transmittancy was determined after 30 minutes' standing. To the colored solution was added another 0.1 ml. of 0.04% sodium nitrite and transmittancy was determined after 15 minutes.

The same procedure was followed when 0.06 and 0.08% sodium nitrite solutions were used. Slightly lower transmittancies were obtained after the second addition of 0.04% sodium nitrite, but not after addition of the 0.06 or 0.08% solutions, indicating that 0.1 ml. of the latter concentrations was sufficient for maximum color development. The standard curves used to convert transmittancy to weight of tryptophan were prepared using the same concentration of sodium nitrite used in corresponding tests.

A blank solution containing 9.0 ml. of 21.4 N sulfuric acid, 1.0 ml. of water, and 0.1 ml. of sodium nitrite solution was used in determining transmittancies of tryptophan solutions both alone and in the presence of the other amino acids. The validity of this procedure was shown by determining the relative indicated tryptophan contents of a colored solution when transmittancies were determined with four blank solutions in which the only variable was the composition of the 1.0 ml. of solution added to the 9.0 ml. of 21.4 N acid.

The relative tryptophan-recovery values were 100, 97.9, 100 and 99.7% when the compositions of the added 1.0 ml. of solution were: (1) water, (2) a water solution containing the same amount of tryptophan used in the test, (3) a water solution containing 5.7 mg. of the mixed amino acids as described above but no tryptophan, and (4) 30 mg. of p-dimethylaminobenzaldehyde plus a water solution containing 5.7 mg. of the mixed amino acids but no tryptophan, respectively. It is apparent that tryptophan in the blank is the only amino acid causing any appreciable adventitious color under the conditions of these tests.

RESULTS

The effect of chloride ions on the relative intensity of the tryptophan–p-dimethylaminobenzaldehyde color is shown in Figure 1, in which the indicated tryptophan contents of solutions containing varying concentrations of hydrochloric acid are plotted against the log of the molar ratio of hydrochloric acid to tryptophan. The average recovery of tryptophan in solutions containing molar ratios of from 10 to 200 of hydrochloric acid to

tryptophan was 99.1%. The indicated tryptophan then increased with increase in chloride ions from 104.3 to 113.5% for molar ratios from 400 to 6400 of hydrochloric acid to tryptophan. The hydrochloric acid concentration of solutions (containing 50 micrograms of tryptophan per ml.) tested to obtain results shown in the graph were 0.0025, 0.0062, 0.012, 0.025, 0.049, 0.98, 0.20, 0.39, 0.78, and 1.56 N, which corresponded to molar ratios of hydrochloric acid to tryptophan of 10, 25, 50, 100, 200, 400, 800, 1600, 3200, and 6400, respectively.

The numbers in parentheses in Figure 1 show the approximate ratio obtained by dividing the quantity of sodium nitrite required to develop maximum color in the presence of chloride ions by that required when no chloride ions were present. It is apparent that the amount of sodium nitrite required to give maximum color was not increased with solutions containing molar ratios up to 100, but it gradually increased to a maximum of threefold to ninefold when the molar ratio was 6400. Recoveries of tryptophan from five solutions, containing 50 micrograms of tryptophan per ml. and in addition (1) 1.1% hydrochloric acid (0.3 N), (2) 1.1% hydrochloric acid and 0.05% sodium bisulfite, (3) 0.05% sodium bisulfite, (4) 1% sodium chloride, and (5) 1% sodium chloride and 0.05% sodium bisulfite, were 99.6, 96.7, 100.1, 99.4, and 97.0%, respectively, when analyzed by Procedure T as shown in Table I. Excess silver sulfate had no effect on the tryptophan determination because, as shown in Table I, the recovery of tryptophan from solutions saturated with silver sulfate was 100.8%. The requirement of sodium nitrite to develop maximum color was the same with tryptophan solutions treated with silver sulfate as for those not requiring this reagent.

Elimination of interference by chloride and bisulfite ions in the determination of tryptophan in the presence of other amino acids was also effected by use of Procedure T. In this application of Procedure T the colorimetric tests were set up within 15 minutes after adding the silver sulfate to the solution to be analyzed because slight loss (about 3% in 3 hours) of tryptophan occurred on standing. Slightly more sodium nitrite was required to develop maximum color in tests when the other amino acids were present than when tryptophan was determined alone. Results of analysis of a solution containing 100 micrograms of tryptophan per ml. and a total of 5.7 mg. per ml. of the fifteen different amino acids, and which in addition contained 1% sodium chloride and 0.05% sodium bisulfite, are shown in Table II. Recoveries of tryptophan were from 98.8 to 100% when two 0.1-ml. portions of an 0.04% solution of sodium nitrite or single 0.1-ml. portions of 0.06 or 0.08% solutions of sodium nitrite were used to develop the color of test solutions; 0.04% is the normal requirement with tryptophan alone.

DISCUSSION

The method described for elimination of interference by chloride and bisulfite ions in the determination of tryptophan in the presence of other amino acids is probably typical of most applications likely to be encountered in practice. However, this application should be regarded as illustrative and subject to slight adaptive modification or judged inapplicable, depending on the presence of unknown interferers in the solution to be analyzed.

Several considerations regarding the use of p-dimethylaminobenzaldehyde in the determination of tryptophan have been discussed (2, 3). The destructive effect of nitrites and undoubtedly other oxidizing agents on the tryptophan-p-dimethylaminobenzaldehyde

Table I.   Elimination of Interference by Chloride, Bisulfite, and Mixed Chloride and Bisulfite Ions in Tryptophan Determination by Procedure T

| No. of Detns. | Additional Components of Solutions Containing 50γ of Tryptophan per Ml. | | | | Av. Tryptophan Recovered | Σd/N | Gain or Loss |
	Hydrogen chloride %	Sodium chloride %	Sodium bisulfite %	Silver Sulfate G.	%	%	%
5	0	0	0	0	100.0	±0.4	...
4	0	0	0	1	100.8	±0.3	±0.8
5	1.1	0	0	1	99.6	±0.3	−0.4
2	1.1	0	0.05	1	96.7	±0.3	−3.3
4	0	0	0.05	1	100.1	±0.3	+0.1
2	0	1.0	0	1	99.4	±0.0	−0.6
2	0	1.0	0.05	1	97.0	±0.3	−3.0

Table II.   Determination of Tryptophan in the Presence of Amino Acids, Chloride, and Bisulfite Ions by Procedure T

| Additional Components of Solutions Containing 100 γ of Tryptophan per Ml. | | | Concentration of Sodium Nitrite Used % | Av. Tryptophan Recovered[a] % | Difference % |
Mixed amino acids Mg./Ml.	Sodium chloride %	Sodium bisulfite %			
5.7	1.0	0.0	0.04[b]	99.1	−0.9
5.7	1.0	0.0	0.06[c]	98.8	−1.2
5.7	1.0	0.0	0.08[c]	98.9	−1.1
5.7	1.0	0.05	0.04[b]	100.0	0.0
5.7	1.0	0.05	0.06[c]	99.9	−0.1
5.7	1.0	0.05	0.08[c]	100.0	0.0

[a] Average of duplicate determinations. Average deviation was less than ±0.5%.
[b] Two 0.1-ml. quantities of 0.04% sodium nitrite reacting for 30 and 15 minutes, respectively, were required to give maximum color.
[c] One 0.1-ml. quantity of this concentration of sodium nitrite reacting for 30 minutes gave maximum color.

color when present before condensation of tryptophan and p-dimethylaminobenzaldehyde (Reaction I) is complete has been shown (2). The development of color (Reaction II) is an oxidative reaction; therefore if traces of reducing agents are present the quantity of sodium nitrite required to produce maximum color may be greater than that required for tryptophan alone (2, 3). Thus in the analysis of alkaline hydrolyzates of proteins 0.1 ml. of 0.07% sodium nitrite solution was used
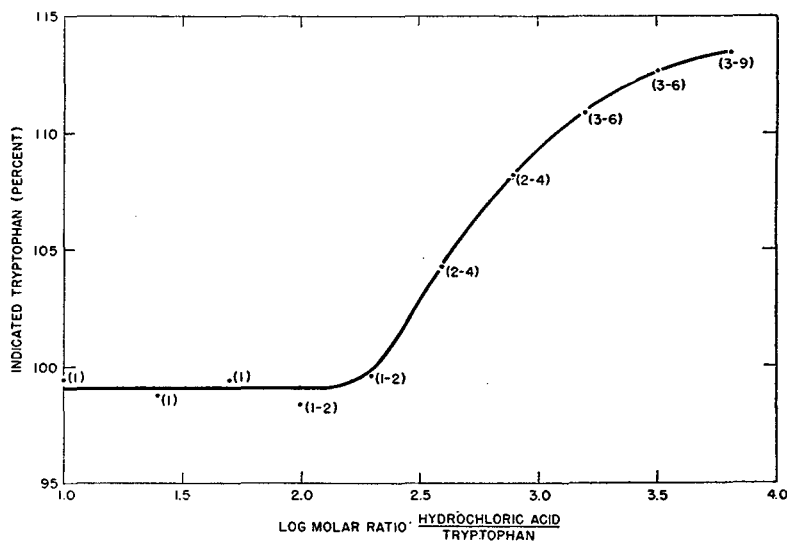
Figure 1.   Effect of Chloride Ions on Color Reaction of p-Dimethylaminobenzaldehyde and Tryptophan

19 N sulfuric acid
Procedure G (2)

Numbers in parentheses show ratios of sodium nitrite required for maximum color with and without chloride ions

per test instead of the 0.04% used for tryptophan alone (*3*). Also in the determination of tryptophan in unhydrolyzed proteins the optimum concentration of sodium nitrite to develop maximum color varied with different proteins from 0.03 to 0.06% (*3*). A large excess of sodium nitrite over that required to develop maximum color, however, should be avoided because the quality of the color is thereby affected and, as shown in Table IV (*2*), slightly less than maximal color is obtained when color is developed with even a relatively small excess of sodium nitrite in a single addition. For example, in the present work minimum transmittancies of 14.1, 14.9, and 15.0% were obtained when the same tryptophan solution was analyzed by Procedure F and transmittancies were determined 30 and 15 minutes after addition of two successive 0.1-ml. portions of 0.04, 0.06, and 0.08% sodium nitrite solutions, respectively. However, excellent recoveries of tryptophan were obtained when the standard

curve was prepared using the same concentration of sodium nitrite as was used on test solutions. Thus as shown in Table II, equally good recoveries of tryptophan were obtained when two 0.1-ml. portions of 0.04% or single 0.1-ml. portions of 0.06 or 0.08% sodium nitrite solution were used to develop the color of corresponding test and standard solutions.

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Rapid Test for Fluoride Ion

W. R. CRANDALL, *M. Ewing Fox Co., Inc., New York, N. Y.*

I N ORDER to prepare industrial casein solutions of relatively low viscosity, sufficiently resistant at room temperature to the continued action of water and alkali, sodium fluoride is often added for the purpose of decomposing calcium compounds naturally present in commercial casein.

A qualitative test based upon a known reaction of alkali fluorides with hydrated alumina was devised and successfully used to control the excess of fluoride required for this purpose. The test was afterward found to be generally applicable and responsive to one drop of 0.01% sodium fluoride solution, or its fluoride equivalent, without interference by sodium caseinate or low concentrations of the more common anions, except oxalate ion.

Initially the reaction forms AlF_6^{---} and OH^-, and it must also be assumed that in the presence of sodium or potassium ion, precipitation of a fluoaluminate may occur, inasmuch as precipitation of potassium fluoaluminate (K_3AlF_6) and of sodium and potassium basic fluoaluminates was observed by Craig (*1, 3*) under similar conditions.

$$Al(OH)_3 + 6F^- = AlF_6^{---} + 3OH^-$$
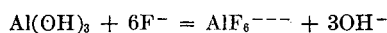
Though for convenience aluminum hydroxide may be indicated as the reacting substance, precipitated and dried basic sulfate and basic acetate were also observed to react promptly. Perhaps all basic salts of aluminum react in the same manner if not too strongly dehydrated; for even kiln-dried industrial clays reacted with 0.02% sodium fluoride solution. Pyrophyllite, a nonhydrous silicate, was inert.

Similarly, the reaction of basic aluminum sulfate with potassium fluoride was applied by Craig to the alkalimetric titration of basic sulfate in aluminum sulfate solutions, and the method was afterward developed by Scott (*1, 2*).

PRELIMINARY OBSERVATIONS

An alkalimetric titration of fluoride on the same principle was demonstrated, with only partial success. To neutral solutions containing up to 0.2% sodium fluoride not less than 25% excess of 0.08 M aluminum sulfate was added, and titrated back to pH 7 at room temperature with 0.2 N sodium hydroxide. The designated excess was necessary to ensure rapid reaction. It can be assumed that the precision attained (about ±2%) would have been improved by titrating at the boiling point, but the method was abandoned as unsuitable upon observing large positive errors caused by phosphate ion and precipitated calcium fluoride.

Equilibrium values of pH were observed at room temperature for aluminum hydroxide and clay, respectively, and are represented graphically by Figure 1. Sodium fluoride in known concentration was added to distilled water containing a large indefinite excess of suspended solid, and allowed to stand for 3 days at 19° to 24° C. with occasional agitation. Observations of pH reproducible to ±0.05 unit were made by means of a direct-reading glass electrode instrument, calibrated with standard buffer solutions at pH 4 and 8.
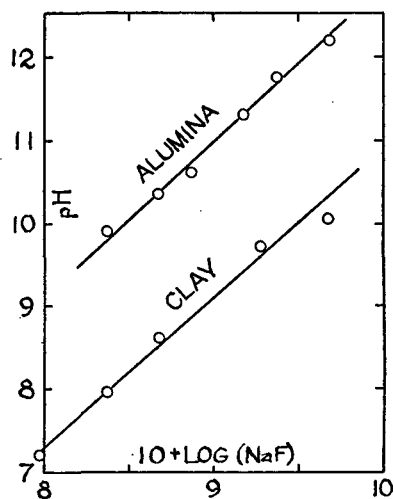

Figure 1. Relation of Equilibrium pH to Molal Concentration of Sodium Fluoride

Aluminum hydroxide, substantially anion-free, was prepared from amalgamated commercially pure aluminum and distilled water. Suspensions, respectively, 0.0476, 0.152, and 0.476 M in sodium fluoride attained constant pH values in 19 to 24 hours; the initial change could be observed in a few seconds. At the end of 48 hours these mixtures, which had approached equilibrium from the acid side, were diluted with an equal volume of water and observed again at the end of another 24 hours, during which period equilibrium had been approached from the alkaline side.

The clay was a commercial wet-classified kaolin substantially free of water-soluble matter. Its suspensions attained constant

values of pH in 3 to 4 days; but in this instance the equilibrium was not tested by dilution.

REAGENT AND INDICATORS

For reasons of convenience both reagent and indicators were incorporated in slips of filter paper. Indicator papers made by drying alcoholic dye solutions on qualitative filter paper were found to be somewhat more quickly reactive than the equivalent commercial indicator papers containing size. The preferred indicators, methyl red, bromocresol purple, bromothymol blue, and thymol blue, were chosen for their sensitiveness—i.e., the visibility of the color contrast. Methyl orange and phenolphthalein proved relatively insensitive, and are not recommended.

Aluminum acetate paper was prepared by dipping filter paper in a cold solution of 1% ammonium alum and 1% sodium acetate, blotting, dipping in boiling 0.2% sodium acetate solution, and drying at room temperature. Paper so prepared remains sensitive for at least a year.

PROCEDURE

On a glass surface a slip of dry indicator paper is laid, and across it a slip of dry aluminum acetate paper. To the intersection a drop of solution is applied, previously brought within the middle or lower pH range of the chosen indicator—e.g., 6 to 7.5 if bromothymol blue is to be used. In the absence of interfering substances, one drop of solution containing 0.01% or more of sodium fluoride (or its fluoride equivalent) regularly causes a perceptible color contrast between the covered and uncovered parts of the paper, provided the test is made within the pH range 6 to 8.

Outside this range the sensitivity is reduced, as must be expected from the mathematical relation of pH to ion concentration; but unbuffered or slightly buffered solutions containing 0.1% of sodium fluoride gave satisfactory positive results throughout the pH range 4 to 9 with appropriately chosen indicators.

INTERFERENCE BY ANIONS

In the presence of 0.25% sodium phosphates at pH 7, 0.1% sodium fluoride solution regularly gave a positive result, but not when the phosphate was increased to 0.5%. Interference by the buffer function of the salt must be assumed. That in this instance the formation of aluminum phosphate did not contribute to the effect was shown by soaking aluminum acetate paper in neutral phosphate solution before making the test. Paper thus treated and imperfectly washed with water reacted normally thereafter with 0.01% fluoride solution.

False positive results were obtained with 0.1% ammonium oxalate solution. Aluminum acetate paper wetted with oxalate solution and washed with water was thereafter insensitive to fluoride ion, but not if washed with dilute calcium chloride followed by water—observations which suggest the formation of an aluminum oxalate decomposable by calcium ion.

As a test for interference by other anions, 1% salt solutions were prepared, neutralized approximately, and tested with and without the addition of sodium fluoride, 0.1% of the weight of solution. The following substances interfered slightly or not at all: sodium borate, thiosulfate, nitrate, nitrite, acetate, chloride, chlorate, sulfate, sulfite, and citrate; potassium iodide, iodate, bromide, phthalate, and ferrocyanide; and ammonium tartrate.

ACKNOWLEDGMENT

The assistance of Judith Passikoff is gratefully acknowledged.

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Test for Microdetection of Parathion in Orange and Lemon Oils

F. A. GUNTHER AND R. C. BLINN
University of California Citrus Experiment Station, Riverside, Calif.

A QUICK method for the detection of the presence of the insecticide, O,O-diethyl O-p-nitrophenyl thiophosphate (parathion) in microquantities of vegetable material should find numerous applications. Such a method has been developed for use with orange and lemon oils. The procedure here presented is a micro adaptation of the basic analytical method proposed by Averell and Norris (1), which is based upon the reduction of the nitro to the amino group with subsequent diazotization and coupling with N-1-naphthylethylenediamine to afford a magenta color.

PROCEDURE

Reagents. Ethyl alcohol, 95%. Hydrochloric acid, concentrated. Zinc dust. Sodium nitrite solution, 0.25%. Ammonium sulfamate solution, 2.5%. N-1-Naphthylethylenediamine dihydrochloride solution, 1.0%.

Procedure. One drop of the orange or lemon oil is placed in a 7 × 50 mm. test tube; then 2 drops each of ethyl alcohol and water, 1 drop of concentrated hydrochloric acid, and a trace (about 0.1 gram) of zinc dust are added. After being heated in a water bath for 5 minutes, the mixture is filtered into a 10 × 70 mm. centrifuge tube through a wisp of cotton in a 15-mm. funnel, and the test tube is then washed with 2 successive drops of water. To the filtered solution is added 1 drop of a 0.25% solution of sodium nitrite, followed in 5 minutes by 1 drop of a 2.5% solution of ammonium sulfamate, then after 2 minutes with 2 drops of a 1% solution of N-1-naphthylethylenediamine dihydrochloride. A magenta color developing within 10 minutes indicates that parathion is present. It is suggested that a sample of similar oil known to be free of parathion be run simultaneously for comparison (cf. 2, 3).

DISCUSSION

With this procedure it is possible to detect parathion in these citrus oils in a concentration as low as 25 p.p.m. in 1 drop of oil, which is approximately 1 microgram of the insecticide per drop. Because this represents a value of about 0.5 p.p.m. of parathion in the fresh peel of the fruit, the 25 p.p.m. limit of the oil is not so high as it may first appear. By using 2 drops of oil, parathion in a concentration of 12 p.p.m. in the oil can be detected. The use of much larger quantities of the oil, however, increases interference with color interpretation and thus obviates this micro adaptation. It must be kept in mind that, even when compared with a proper check sample, the development of the characteristic magenta color in this test does not prove the presence of parathion. Many other nitro compounds and amines respond similarly.

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Elimination of Interferences in Determination of DDT Residues

L. B. NORTON AND BARBARA SCHMALZRIEDT, *Cornell University, Ithaca, N. Y.*

CERTAIN crops give interfering colors in the Schechter (*3*) colorimetric method for determining DDT residues. Cauliflower curds and alfalfa give colors sufficient to mask small quantities of DDT, and even to make a reading impossible on the extract from a large sample. A sulfuric acid treatment such as that used in the analysis of DDT in milk (*3*) will remove these interferences. However, this procedure requires a change of solvents, tends toward low recoveries, and is somewhat unpleasant and tedious to use. A direct removal of the interfering material from the benzene extract by selective adsorbants was attempted, and gave satisfactory results.

Preliminary tests with alumina, magnesia, and Attapulgus clay–Celite mixtures (*1*) as adsorbants all gave promising results. Alumina was chosen as the best of these because of more consistent DDT recovery, ease of regeneration of the adsorbant, and superior physical properties. All the data reported here were obtained with alumina.

PROCEDURE

A slurry of alumina (General Chemical Company aluminum oxide, ignited powder, reagent, Code 1236, mean particle diameter approximately 100 microns) in benzene was poured into a column 1 inch (2.5 cm.) in diameter and 18 inches long, containing a small plug of cotton. A bed of adsorbant about 2 inches deep was usually sufficient. As soon as the level of benzene had reached the top of the adsorbant bed, a 5- to 50-ml. aliquot of the benzene strip solution was passed through, and was followed by approximately 50 ml. of benzene added in small portions, to carry through all unadsorbed material. After being passed through the column, the benzene solution was carried through the usual Schechter procedure. The interferences from both cauliflower curds and alfalfa were completely eliminated, the absorption spectrum of the final solution being identical with that obtained with pure DDT.

The physical state of the alumina was such that the benzene passed through the column at a convenient rate without pressure or suction. It was therefore possible to set up several columns at once to save time. The alumina was recovered by driving off the benzene with gentle heating and then igniting for several hours in a muffle furnace at dull red heat. It could be used again without further treatment.

RECOVERY OF DDT

Known quantities of DDT were added to the benzene strippings from untreated alfalfa and these solutions were carried through the procedure described. The results are presented in Table I.

A series of samples of cauliflower leaves had been run without any preliminary treatment. As a check on the possibility that small fragments of curd might have been included and might have contributed some interference, aliquots of some of the same strip solutions were treated with alumina and analyzed again. There was evidence of interference in only one sample, so that the rest of the samples furnished useful recovery data on residues from actual field treatments. The results are presented in Table II.

The deviations in Table I were considered within the experimental error, especially because test tubes were used as absorption cells in the photometric readings. The 64% drop of the fourth sample in Table II was considered due to interference in the first analysis rather than to incomplete recovery in the second, in view of the full recoveries in all other samples. The slight tendency toward high values was very probably due to concentration of some strip solutions by evaporation, inasmuch as the samples were stored for several weeks between the analyses in bottles closed with corks covered with tinfoil.

It was concluded that the alumina treatment would remove the interferences without causing significant loss of DDT. Similar

Table I. Recovery of DDT from Alfalfa Strippings after Alumina Treatment

DDT Added, γ	DDT Found, γ	% Deviation
79	83	+5
	81	+2
90	93	+3
	91	+1
	86	−4
	93	+3
113	114	+1
	117	+4
157	161	+2
	159	+1

Table II. Recovery of DDT from Aliquots of Strippings from Cauliflower Leaves with and without Alumina Treatment

DDT Found in Aliquot, γ		% Deviation
Without alumina	With alumina	
108	115	+ 6
93	99	+ 6
108	108	0
11	4	− 64
32	32	0
58	65	+12
93	100	+ 8
4	4	0

tests with DDD or TDE [1,1-dichloro-2,2-bis(*p*-chlorophenyl)-ethane] indicated that it would also come through the alumina without significant loss.

BENZENE INTERFERENCE

A reddish-brown interfering color results if the last traces of benzene are not removed before the nitration step of the Schechter colorimetric procedure. Alfalfa is particularly susceptible to this interference because of the large quantity of extracted material, which holds the last traces of benzene tenaciously on evaporation. Only part of this extracted material is removed by alumina. The addition of alcohol to the residue as suggested by Schechter *et al.* (*4*) is not satisfactory in this case because alcohol forms a gelatinous mass which is extremely slow to dry at room temperature. Heating was not considered because serious losses of DDT have resulted in this laboratory from heating dry extracts even on the steam bath.

It was found that chloroform would not form a gelatinous mixture, and that it would yield a film type of deposit. Although not so efficient in removing benzene under normal conditions, it was much more satisfactory with alfalfa extracts. The procedure finally adopted to remove all interferences from alfalfa strip solutions was a treatment with alumina, evaporation of the benzene, two evaporations with chloroform, and finally exposure of the residue to the air for at least a day.

A transfer to carbon tetrachloride and passage through a column of Celite–sulfuric acid as recently described by Davidow (*2*) may offer a better method of treatment for such voluminous extracts, although it has not as yet been tried on alfalfa by the authors. The alumina treatment appears at its best as a rapid and convenient method for removing direct interferences where secondary effects are not serious.

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Measurement of Density of Hydrocarbon Liquids by the Pycnometer

H. M. SMITH AND COOPERATORS, *Bureau of Mines, Bartlesville, Okla.*

ONE of the most important physical properties of a hydrocarbon or hydrocarbon mixture is its density. It is one of the criteria upon which the identification and purity of individual hydrocarbons are based, and it is also of importance in a number of calculated properties, such as specific dispersion, refractivity intercept, and specific refraction, and in the calculation of kinematic and absolute viscosities from each other.

As hydrocarbon research develops more precise methods of estimating the quantities of a given component, the necessity for more accurate physical properties becomes very urgent. Not only must these properties be determined accurately, but they must also have excellent precision within a given laboratory (repeatability), and between laboratories (reproducibility); the method should also be capable of relatively rapid application.

Research Division IV on Hydrocarbon Analysis, a subcommittee of Technical Committee D2 of the American Society for Testing Materials, has been working for a number of years on the development of analytical methods for hydrocarbon groups in petroleum products, particularly of the distillate class. In connection with developmental work on methods by this committee, the need for accurate methods of determining density and refractive index frequently arose and, therefore, Section D of Research Division IV was established to study methods for determination of density and refractive index. One of the first duties of this committee was to develop or standardize a method for determining density which would be accurate to at least 0.0002 gram per ml.
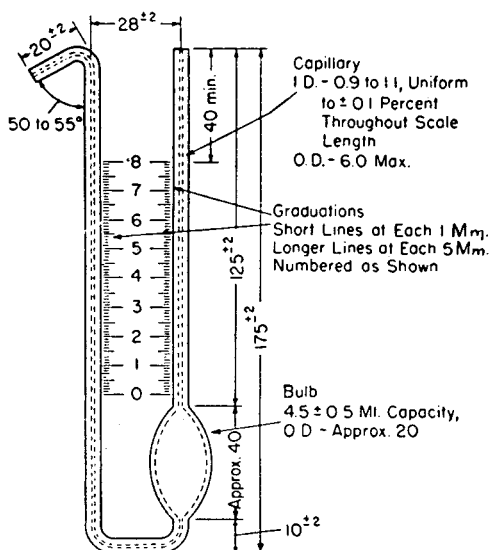

Figure 1. Open-Arm Bicapillary Pycnometer

All dimensions in millimeters. Material, borosilicate glass. Weight, 30 grams max. Graduation lines extend around entire circumference of pycnometer at integral numbers half-way around at half divisions

Table II. Cooperative Data Obtained with A.S.T.M. Bicapillary Pycnometer for Toluene

	Commercial Toluene			
Laboratory	Av. density	No. of detns.	Av. Deviation	
A	0.8654	3	0[a]	+1[b]
C	0.8653	3	0	0
D	0.8654	2	1	+1
E	0.8652	1	..	-1
F	0.8652	2	0	-1
G	0.8652	2	0	-1
H	0.8652	2	1	-1
I	0.8652	2	1	-1
J	0.8653	3	0	0
Av. of all results	0.8653	20	1	..
Maximum dev. of lab. av.	..	..		±1

a Average deviation × 10⁴ of laboratory's results from that laboratory's average density.
b Deviation × 10⁴ of laboratory's average from over-all average.

Among the methods considered was a pycnometer method, developed by Lipkin *et al.* (*2*). According to the authors, this method gave results, within a given laboratory, having a precision of ±0.0001 gram per ml. and a probable accuracy of the same magnitude.

In the use of these pycometers it was felt that the types of compound which would be most susceptible to error probably would be those that are relatively volatile, inasmuch as this instrument relies upon an open capillary to control diffusion of the lighter materials. Therefore a series of cooperative tests was arranged among ten laboratories, using the U-shaped open-arm bicapillary pycnometer, shown in Figure 1. For comparative purposes, the Bingham pycnometer, which is a standard instrument used by many laboratories, and the fifth-place Chain-o-matic specific gravity balance were concurrently tested.

The test materials selected were: (1) pure "isopentane" (2-methylbutane), which was selected primarily to give an indication of the accuracy that might be expected; (2) a 12-pound Reid vapor pressure gasoline, which would give not only indication as to the repeatability and reproducibility of a sample within given laboratories and between laboratories, but also an indication of accuracy. This latter feature was possible because the density of this gasoline was especially determined at the National Bureau of Standards, so that a value accurate to 0.0001 gram per ml. was known. In addition, the densities of several samples of relatively pure aromatic compounds were determined. These compounds were not so volatile as the two previous samples, but gave indications of repeatability and reproducibility in a somewhat higher boiling range.

Tables I and II show the deviations obtained in some of these cooperative tests. These tables substantiate the results reported by Lipkin *et al.*, in that, except for laboratory D, the average deviation of each laboratory's results from its mean value was

Table I. Cooperative Data Obtained with A.S.T.M. Bicapillary Pycnometer for Isopentene and Gasoline

	Isopentane			12-Pound Reid Vapor Pressure Gasoline			
Lab.	Av. density	No. of detns.	Av. deviation	Av. density	No. of detns.	Av. deviation	
A	0.6197	4	1[a] +1[b]	0.6615	4	1[a] +1[b]	+2[c]
B	0.6196	3	0 0	0.6611	4	0 -3	-2
C	0.6199	3	0 +3	0.6616	4	1 +2	+3
D	0.6196	5	2 0	0.6614	4	2 0	+1
E	0.6197	3	0 +1	0.6615	3	1 +1	+2
F	0.6197	3	0 +1	0.6614	3	0 0	+1
G	0.6195	2	1 -1	0.6615	3	1 +1	+2
H	0.6197	3	1 +1	0.6615	3	1 +1	+2
I	0.6194	6	1 -2	0.6612	4	1 -2	-1
J	0.6198	3	0 +2	0.6614	3	0 0	+1
Av. of all results	0.6196	35	1 ..	0.6614	35	1 ..	+1
Max. dev. of lab. av.		..	+3			.. -3	+3

a Average deviation × 10⁴ of laboratory's results from that laboratory's average density.
b Deviation × 10⁴ of laboratory's average from over-all average.
c Deviation × 10⁴ of laboratory's average from value furnished by National Bureau of Standards, 0.6613.

±0.0001 gram per ml. or less for both isopentane and the 12-pound gasoline. It is also true that the individual determinations (not shown in table) of a given laboratory did not deviate from each other in most instances more than their average deviation from the over-all average. For example, out of 35 individual determinations on the 12-pound gasoline, 30 deviated from the laboratory average by either 1 or 0 in the fourth decimal place, four had a deviation of 2, and in only one was a deviation of 3 in the fourth decimal place reported. Similar conclusions apply also to the tests made with isopentane and the commercial toluene.

With regard to reproducibility between different laboratories, the results seem to indicate that a value of ±0.0002 is satisfactorily established, inasmuch as only one out of ten laboratories cooperating reported a value higher than this. Here again, out of 35 determinations on the 12-pound gasoline, 29 had a deviation of 2 or less in the fourth decimal place, 6 a deviation of 3, and none was higher. Similar observations can be made on the data obtained with isopentane and commercial toluene.

It was the committee's opinion that if 90% of the laboratories could achieve this degree of repeatability and reproducibility, it could with safety indicate those limits as being applicable to the method.

Regarding accuracy, A.P.I. Research Project 44 tables give the density of pure isopentane as 0.61967. The average value shown in Table I for the 10 laboratories is 0.6196. This would indicate that the accuracy was of the same order of magnitude as the repeatability, or 0.0001 gram per ml., especially as the deviations of the individual determinations were of comparable values. This is further borne out by the average value of 0.6614 obtained for the 12-pound vapor pressure gasoline as determined by the cooperating laboratories, compared to the National Bureau of Standards value of 0.6613. This again confirms the opinion that the accuracy of these data is comparable with the precision.

Cooperative data for the Bingham pycnometer indicated similar precision and accuracy. This device, however, requires simple accessory equipment for easy cleaning and a hypodermic syringe for convenient filling. The data obtained with the fifth-place Chain-o-matic specific gravity balance, when used under carefully controlled conditions by laboratories which were familiar with its use, indicated that it was also capable of excellent accuracy and precision. However, as this instrument is not commonly found in most petroleum laboratories, its standardization by the committee was not considered. Based on the results of the cooperative testing, part of which is reported in Tables I and II, the committee has standardized the U-shaped bicapillary pycnometer, described by Lipkin et al., and it is now an A.S.T.M. standard method (1). It also has an American Standards Association designation (1).

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Determination of Relative Specific Surface of Zinc Oxide Pigments

WARREN W. EWING AND RICHARD N. RHODA

Lehigh University, Bethlehem, Pa.

VARIOUS methods have been devised for determining the surface area of finely divided solids, but the agreement among methods as to the values of such areas is not good. The disagreement may be attributed to fundamental weaknesses in the method or to the fact that different area characteristics are measured. The microscopic method is an example of fundamental weakness; here there is a large degree of uncertainty as to whether the operator is measuring the distance between the actual edges of a crystal or an optical illusion due to refraction rings, poor resolution, etc.

Area characteristics are governed by the use to which the solid is subjected. If the solid is to be used as a catalyst in a gas phase reaction, the Brunauer-Emmett-Teller gas adsorption method using an adsorbate of a nature similar to the gas adsorbed by the catalyst is indicated. But if the solid is to be used in a liquid medium as in the compounding of paints, rubber, etc., a method involving the adsorption of an adsorbate in a liquid might give a truer picture of the characteristic area pertinent to such a system. If an absolute value of a surface area is desired, the method of Harkins and Jura (6) is available.

Harkins and Gans (5) have studied the adsorption of oleic acid on titanium oxide from a benzene solution. Ewing (2) has shown that the specific surfaces of various zinc oxides can be determined by adsorbing methyl stearate and glycol dipalmitate from benzene solutions. Smith and Fuzek (7) determined the surface area of nickel and platinum catalysts by adsorbing fatty acids from organic solvents.

The presence of water interferes seriously with adsorption from organic solvents, and the necessity of carefully drying both pigments and solvents makes the procedure tedious. The method presented here for determining the surface areas of pigments by adsorption from aqueous solutions eliminates the tedious drying procedures, thus shortening the time of operation and making the method adaptable to practical application. The area obtained by this method should be the characteristic area desired for pigments dispersed in liquid media.

EXPERIMENTAL

The zinc oxide pigments were obtained from the New Jersey Zinc Company of Pennsylvania. Quantities of the samples were placed in large evaporating dishes and washed with several portions of carbon dioxide–free water by stirring and decanting the liquid. The slurries were dried in an oven at 100° C.; the pigments were then pulverized by crushing the lumps with the fingers or by gently grinding in a mortar. Electron micrographs and electron diffraction patterns of representative samples (1) showed negligible conversion of the surface of the oxide to carbonate in washing. The washing apparently removed foreign material from the pigments; in some cases the data for the washed samples gave surface values which were much nearer the values expected from the electron microscope data. Electron micrographs of the pigments before and after washing showed no apparent change in the surface area due to the washing.

Table I. Comparison of Adsorption Method with Electron Microscope and Nitrogen Adsorption Method for Specific Surface

| Type | Sample No. | Daxad Adsorbed per Gram ZnO, G. | Specific Surface, S, Sq. Meters/Gram | | |
			From solution	Electron microscope	Nitrogen BET
USP 512	1	0.00300	2.6	2.6	3.5
XX 601	2	0.00347	3.0	3.3	2.9
FGS 8	3	0.00372	3.2	3.2	3.7
XX 78	4	0.00416	3.6	3.7	3.9
XX 101	5	0.00462	4.0	4.0	3.5
USP 12	6	0.00486	4.2	4.3	4.2
Kadox 72	7	0.00578	5.0	5.0	5.8
Kadox 15	8	0.01030	8.9	8.9	7.9

The dispersing agent used was Daxad No. 11, sodium sulfate-free (Dewey and Almy Chemical Company, Cambridge B, Mass.), a polymerized sodium salt of a sulfonic acid of the alkyl-aryl type. It was used because exhaustive studies of zinc oxide slurries in dilute solutions of one hundred dispersing agents showed that this agent caused the zinc oxide to settle to the smallest volume. Several other surface-active agents gave the same degree of dispersion, so that the choice of Daxad was more or less fortuitous.

For adsorption work samples of the dry washed pigment were weighed into 75-ml. borosilicate glass centrifuge tubes by difference. In general, 10.000-gram samples were used. Various concentrations of 50-ml. samples of aqueous solutions of the surface-active agent were added from a calibrated pipet, and the tubes were stoppered and manually shaken, and then rotated end over end at 80 r.p.m. for a specified time. Figure 1 shows that complete equilibrium will occur in 8 hours; it was convenient to roll the samples 17 hours. The samples were removed from the rolls and centrifuged till clear at a maximum relative centrifugal force of 1350 (2000 r.p.m. on the authors' centrifuge). This step involved 1 to 4 hours, depending upon the pigment studied. Clear samples of the solution were withdrawn for analysis.

The solutions of the surface-active agents were analyzed before and after adsorption on the pigments by means of a Zeiss interferometer. The calibration curve of interferometer readings vs. concentration was a straight line in the region of concentrations studied, and passed through the origin. The concentrations of the solutions used in calibrating the instrument were determined by drying known volumes of the solutions of 100° C. under a jet of air to constant weight.
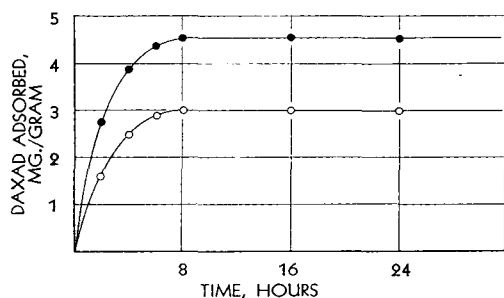
Figure 1. Adsorption as Function of Time

O Sample 4
● Sample 8

Eight samples of one pigment were studied at one time, using seven initial concentrations of the adsorbate and a blank in distilled water. The interferometer reading for the blank was subtracted from the other readings and in most cases was small enough to be neglected. This blank represented the small solubility of the pigment in water. All determinations were performed at room temperature.

RESULTS

Experimental results are tabulated in Table I.

Brubaker (1) determined the diameters of the various zinc oxides used in this investigation from electron microscope measurements. Specific surfaces were calculated from the formula

$$S = 6/\rho d_3$$

where ρ is the density of the zinc oxide and $d_3 = \Sigma n d^3/\Sigma n d^2$ (4). The density, 5.655 grams per ml., was determined by a method of the authors (3). These specific surface data are tabulated in column 5. Column 6 lists specific surface data as determined by C. W. Siller of the New Jersey Zinc Company by the nitrogen adsorption method (BET). Column 4 lists the specific surface values obtained from Daxad adsorption data. The values are relative and are obtained by the following procedure.
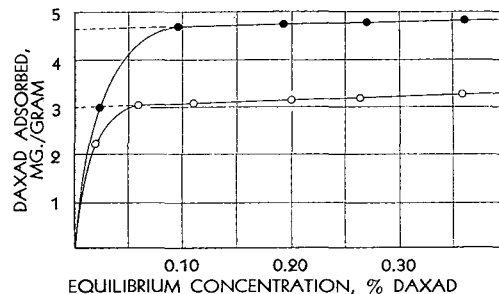
Figure 2. Typical Adsorption Isotherms for Zinc Oxides

O Sample 1
● Sample 6

Typical adsorption isotherms are shown in Figure 2 for the adsorption of the surface-active agent on two different zinc oxide pigments. These isotherms are of the type which indicate that a monomolecular layer of adsorbate is adsorbed and the reversibility of the curves on desorption indicates that the adsorption is of a physical nature. If it is assumed that the flat region of the curve indicates a monomolecular layer, the deviation from the horizontal might be assumed to be a crowding effect due to the increase in concentration of the solution. In order to obtain corresponding conditions for the various pigments, the curves have been extrapolated to zero concentration and the intercepts have been assumed to give relative functions of the surface area of the pigments. Sufficient data concerning the molecular weight of the Daxad and the cross-sectional area of the adsorbed Daxad molecule are not available for calculating directly the specific surfaces of the zinc oxides from the weight of Daxad adsorbed. However, relative specific surfaces may be evaluated by plotting the weight of the Daxad adsorbed against the specific surfaces of the zinc oxide as determined by other methods.
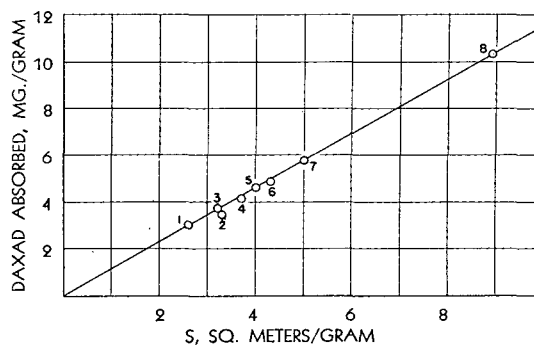
Figure 3. Relative Specific Surface of Zinc Oxide Pigments

For these pigments the electron microscope data give a better correlation than does the nitrogen adsorption method. Consequently, the weight of the Daxad adsorbed per gram of zinc oxide has been plotted against the specific surface from the electron microscope data in Figure 3. The solid line is a straight line drawn through the origin and the data for sample 8, the

sample having the largest specific surface. It is drawn through the origin because for zero surface there should be zero adsorption. The slope of this line indicates that 1 mg. of adsorbed Daxad covers 0.864 square meter of zinc oxide surface. From this value and the extrapolated value of the weight of Daxad adsorbed per gram of pigment the specific surfaces of the various zinc oxides have been calculated (column 4). This straight line indicates that the electron microscope and this adsorption method are measuring the same surface characteristics and the deviations indicate that both methods give an accuracy of 0.1 square meter per gram of zinc oxide unless both methods have a corresponding error for any one pigment. An exception should be noted in the case of pigment 2. This is an acicular zinc oxide and the highly irregular shapes revealed by the electron microscope make evaluation of their dimension difficult. The authors feel that in this case the adsorption method gives the better value.

The weight of Daxad adsorbed plotted against the specific surface as determined from electron microscope data gives a straight line. When a similar plot is made against the specific surface data determined by BET nitrogen adsorption, erratic behavior results. These different behaviors might be explained by assuming that the nitrogen adsorption method is measuring a different surface characteristic than is measured by the other two methods.

DISCUSSION

This study indicates that the specific surfaces of zinc oxide pigments can be determined by the adsorption of a surface-active wetting agent from aqueous solution. As an analytical method it is less tedious than the usual methods. For routine analytical work the procedure can be shortened to a determination of three points on the flat portion of the curve (Figure 1). If an interferometer is not available, equally precise results can be obtained by gravimetric methods, using a semimicrobalance and following the procedure suggested by Ewing (2).

The accuracy of the method depends upon the accuracy of the determination of the concentration differences and upon the

reproducibility of the attainment of either a monomolecular adsorbed layer or some function of it. The interferometer is a precise instrument; actual readings consist of drum readings where one unit = 0.000256% solids, or in the ordinary runs of 50 ml., one unit = 0.128 mg. of Daxad. This corresponds to 0.11 square meter of surface per gram of sample. The interferometer can be read easily to ±0.5 unit on the drum (usually by averaging ten different readings), and the precision is therefore more than adequate for this type of determination. In working with solutions of high concentration—0.30% in the case of Daxad —the interference patterns are difficult to match, and on the authors' instrument a mismatch of patterns gives a constant difference of 20 drum units. This introduces a serious error and can be eliminated by the use of less concentrated solutions and some degree of care in removing samples from the centrifuged tubes. The reproducibility of the adsorbed film was investigated by ten consecutive determinations of the specific surface of sample 6; all gave results that were in agreement within the experimental error. Maximum value was 4.4, minimum value 4.1, average value 4.2, and average deviation ±0.05 square meter per gram.

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Volumetric Determination of Sulfate Ion

Using Barium Ion and a Standard Disodium Dihydrogen Ethylenediamine Tetraacetate Solution

J. R. MUNGER[1], R. W. NIPPLER[2], AND R. S. INGOLS
Engineering Experiment Station, Georgia Institute of Technology, Atlanta, Ga.

SEVERAL volumetric procedures for determining sulfate ion concentration are described in the literature, but each appears to have flaws, either because of time-consuming steps or because of inaccuracies in the values obtained with low sulfate ion concentrations. Thus, sulfate ion concentrations (1) can be determined with benzidine hydrochloride, but the determination involves a filtration step and a blank correction for low sulfate ion concentrations. Barium chromate (4) can be double-precipitated with barium sulfate and the sulfate ion determined by subtraction of the excess chromate ion from the known amount added, but the precipitate must be removed by filtration before the titration step is possible and a calibration curve must be drawn to obtain accurate results. The internal indicator, disodium tetrahydroxyquinone (1), can be used for the titration of the sulfate directly with standard barium chloride solution, but because of the relatively slow formation of the barium sulfate precipitate at low sulfate ion concentrations, the technique is limited to use with

high sulfate ion concentrations such as those normally found in boiler water.

Schwarzenbach (3, 10–12) recently published a series of articles on the formation of soluble organic complexes with divalent and monovalent metallic ions, in which the divalent metal ion concentrations are reduced to values which are useful for analytical and industrial purposes. His technique (3, 10) for determining hardness in water has been readily accepted, and confirming articles indicating success in its use have been published (2, 5–7, 9). Two of the confirming articles give complete and slightly modified procedures and data (2, 6).

From the original literature, it is evident that the disodium salt of ethylenediamine tetraacetic acid (Versenate) can be used for determining the concentration of the barium ion while using the dye, Eriochromeschwarz T, as the indicator. It should then be possible to add a standard barium chloride solution to a sample being analyzed for sulfate ion concentration and to determine the excess barium ion. Because the standard barium ion solution is added to the sample in excess in the first step, it is possible to

[1] Present address, Red Stone Arsenal, Huntsville, Ala.
[2] Present address, Georgia State Board of Health, Rome, Ga.

Table I. Recovery of Sulfate Ions Using Versenate Titration of Excess Barium Ions

Sulfate Added	Sulfate Recovered	Error		Reproducibility (Standard Deviation)
P.p.m.	P.p.m.	P.p.m.	%	P.p.m.
5.3	6.4	1.1	20	±0.7
10.6	12.9	2.3	20	±0.8
21.1	22.7	1.6	8	±1.4
52.8	52.2	0.6	1	±0.5
106	105	1	1	±1
158	157	1	0.7	±3.0
211	211	0	0	±3.4

Table II. Analysis of Natural Waters by Versenate Sulfate Ion Concentration[a]

Sample No.	Direct	Amount Added	Amount Recovered	Difference	Deviation
	P.p.m.	P.p.m.	P.p.m.	P.p.m.	P.p.m.
1	5.0	20.3	25.9	5.6	+0.6
2	5.4	20.3	25.9	5.6	+0.2
3	9.6	20.3	30.1	9.8	+0.2
4	19.1	21.4	40.6	19.2	+0.1
5	8.0	40.5	49.6	9.1	+1.1
6	8.0	60.8	70.9	10.1	+2.1

[a] All values are average of at least six determinations.

precipitate the barium sulfate completely even at very low sulfate ion concentrations before making the titration for the excess barium ion. It is not necessary to remove the precipitate of barium sulfate before making the titration for the excess barium ion, so that this titration step can be started very shortly after beginning the procedure.

The major usefulness of this procedure will be found only in a laboratory also using the Versenate procedure for determining the total hardness, because the value of the combined calcium and magnesium ion concentrations is required for calculating the sulfate ion concentration.

TECHNIQUE

Reagents. Standard Versenate solution, 0.02 N. The reagent that includes magnesium chloride may be used (6).

Buffer solution, 8.25 grams of ammonium chloride and 113 ml. of concentrated reagent ammonium hydroxide in 1 liter pH 10.0 when 10 ml. are added to 50 ml. of sample.

Barium chloride solution, 0.020 N.

Calcium chloride solution, 0.020 N, from calcium carbonate as described in (1). This is the primary standard for the Versenate, barium, and magnesium chloride solutions.

Magnesium chloride solution, 0.02 N.

Standard hydrochloric acid solution, 0.020 N.

Indicator, Eriochromeschwartz T, 0.4% in alcohol (8).

Procedure. Determine hardness with Versenate as described by Biedermann and Schwarzenbach (3, 10) and modified by Diehl, Goetz, and Hach (6). Determine alkalinity with the standard hydrochloric acid solution (not the usual sulfuric acid solution). To a third aliquot of 50 ml. of sample, add standard acid equivalent to the alkalinity (or slightly more), in order to destroy carbonates. Boil the sample and add 5 or 10 ml. of the standard barium chloride solution (depending on the estimated sulfate ion concentration), and allow the mixture to boil for a few seconds. Cool the flask, add 10 ml. of buffer and 5 drops of indicator, then titrate with the standard Versenate solution. The first end point may not be used, because its accuracy will be poor even when the standard solution containing some magnesium ion is used (6). The addition of a small amount of standard magnesium ion solution and a second end point with extra Versenate solution will give good accuracy, because the indicator is more sensitive to the magnesium ion. In order to minimize the end-point error, it is recommended that one approach the same color change used for the determination of the hardness.

Calculations. The sulfate ion can be calculated by the formula:

$$(H + B + M - T) \times 48 \, \frac{1000}{s} = \text{p.p.m. of sulfate}$$

where H is milliequivalents of Versenate required for total hardness, B is milliequivalents of barium chloride solution added, M is milliequivalents of magnesium ion solution used to sharpen the end point. T is the total milliequivalents of Versenate used for the

titration of barium ion plus magnesium ion, and s is milliliters of sample used.

RESULTS

A number of waters with known sulfate ion concentrations were prepared and analyzed with the Versenate technique as outlined above and the results were compared with the theoretical values. The results of this comparison, as shown in Table I, indicate that the technique gives an agreement within approximately 1 part per hundred at the higher concentrations used. A study of the time involved showed that six samples were analyzed in an hour by the Versenate method, and that the results obtained included data on total hardness, alkalinity, and sulfate ion concentration. The accuracy of the Versenate increased as the amount of sulfate ions increased, but reasonable recovery was obtained with concentrations as low as 5 p.p.m. This accuracy was checked in natural waters by the addition of a known increment to a second aliquot; the results from this study, which are presented in Table II, show a good agreement in the values obtained first directly and then by difference from the increment.

The Versenate technique is not completely free of interference. In order to use it in the presence of copper, manganese, cobalt, and nickel ions, the modifications given by Diehl, Goetz, and Hach (6) for total hardness should be used. For concentrations of copper up to 10 p.p.m., Betz and Noll (2) recommend a different buffer system; they indicate that manganese up to 2 p.p.m. does not interfere with the accuracy of the test, although it does change the color of the indicator when enough is used. The modifications have been checked and found to work for the sulfate ion determination.

DISCUSSION

The over-all accuracy of this technique depends on the accuracy of the preliminary hardness titration as well as the final titration after addition of the barium chloride solution. In both titrations, an adequate concentration of dye is essential. Although it is not necessary for the usual determination of hardness, it has been found that the titration for determining the total hardness can be made more accurate by the incorporation of the back-titration with magnesium chloride as recommended for the final titration with barium.

Back-titration of the sample with magnesium chloride is recommended because the color change for the initial end point when using the barium ion alone is slow in forming, and can easily be passed. Upon addition of the magnesium chloride, the wine-red color is restored, and the final end point can be reached quickly and accurately. As might be expected from the data in the articles by Schwarzenbach, the magnesium chloride gave a much sharper end point than did calcium chloride in the back-titration.

The addition of more indicator does not sharpen the end point. The addition of a small amount of sodium chloride as recommended in the turbidimetric determination of sulfates (13) does not sharpen the end point nor increase the rate of precipitation but tends to reduce the reproducibility of the results. Previous workers (2, 6) and the authors have found that sodium chloride does not interfere in the calcium and magnesium ion determinations, so that the cause of these poor results is not understood.

If a sample is known to have a large sulfate ion concentration, the range of the technique can be extended by the addition of a larger portion of barium chloride, or a smaller aliquot of sample may be used. If a large number of samples at high sulfate ion concentrations are to be analyzed, the concentrations of the reagents may be adjusted as necessary.

ACKNOWLEDGMENT

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Determination of Acetyl in Pectin

E. L. PIPPEN, R. M. MCCREADY, AND H. S. OWENS, *Western Regional Research Laboratory, Albany, Calif.*

DURING a study of pectin acetates at this laboratory, a simple method for the analysis of acetyl in pectin was desired. Although successful methods (*3, 4, 6*) have been described for the determination of acetyl in pectin, the method presented here requires few operations, is economical of materials, and is rapid and accurate.

The method is a modification of Clark's (*2*) procedure, devised to overcome the inconsistencies obtained when hot alkali is used for the saponification. The authors' experience has agreed with that of Lüdtke and Felser (*5*), who have shown that acids, other than acetic, are formed when pectin is heated in alkali.

APPARATUS

The apparatus is identical to that described by Clark (*2*) except for the distilling flask and condenser, which were modified slightly (Figure 1).

MATERIALS

The pectin acetates analyzed were prepared by acetylation of commercial citrus pectin by the procedure of Carson and Maclay (*1*). Results for pectin are expressed on a moisture- and ash-free basis. The purity of other substances analyzed was established by their melting points, saponification equivalents, and specific rotations, where applicable.

PROCEDURE

An accurately weighed 0.5-gram sample of the pectin acetate was placed in a 250-ml. Erlenmeyer flask and 25 ml. of 0.125 N sodium hydroxide were added. The flask was stoppered and the contents were stirred until all the pectin was dissolved. The flask was then set aside at room temperature for at least 1 hour. (As a routine procedure, samples were permitted to stand in alkali overnight.) The contents of the flask were diluted to 50.0 ml. and a 20.0-ml. aliquot was withdrawn and placed in the distilling flask. This was followed by a 20-ml. aliquot of Clark's (*2*) magnesium sulfate–sulfuric acid solution and an ebullition tube. After the steam inlet tube was set in place, the rubber tubing was closed with the screw clamp and distillation was carried out by

heating the distilling flask with a flame until the volume of liquid in the distilling flask was about 15 to 20 ml. Steam was then permitted to enter through the steam inlet tube by loosening the screw clamp. The rates of steam inlet and application of heat to the distilling flask were adjusted so that the volume of liquid in the distilling flask remained at about 15 to 20 ml. (Keeping the volume of liquid in the distilling flask low ensures a quantitative recovery of the acetic acid in a 100-ml. distillate volume.) Distillation was thus carried out until a distillate of 100 ml. was collected, which was titrated with 0.05 N sodium hydroxide to an end point with phenol red as the indicator. A blank determination was carried out by distilling, as described above, a mixture of 20 ml. of the magnesium sulfate–sulfuric acid solution and 20 ml. of distilled water. Titration of the distillate from the blank run usually requires 0.1 ml.
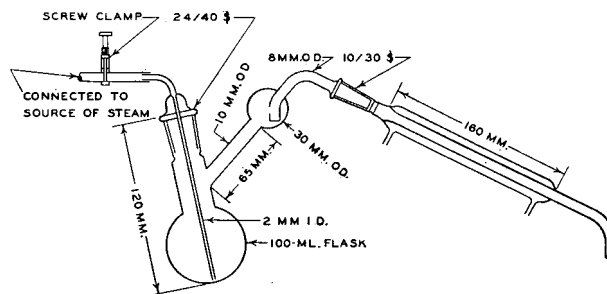

Figure 1.   Diagram of Distilling Flask and Condenser

Calculation. Net ml. of NaOH = (total ml. of NaOH required to titrate distillate) − (total ml. of NaOH required to titrate distillate of blank run)

$$\% \text{ acetyl} = \frac{(\text{net ml. of NaOH}) \ (\text{normality of NaOH}) \times (0.043) \ (100)}{\text{weight of sample, grams, in 20.0-ml. aliquot}}$$

RESULTS

On duplicate analyses on pectin, reproducibility of results within 0.1% or better was consistently obtained. Further experiments to determine the accuracy and scope of the method were conducted. Comparison with the method of Henglein and Vollmert (*4*) (Table I) shows that these two methods are in excellent agreement for the analyses of pectin acetates. When substances other than pectin acetates were analyzed (Table II), results for glucose and galactose pentaacetates were higher than the theoretical acetyl values. While the results of only two analyses of galactose and glucose pentaacetates are presented, other analyses of these compounds gave results which were consistently 1 to 2% higher than the theoretical values. In the analysis of glucose, as well as the acetates mentioned above, the apparent acetyl content generally increased in direct proportion to the time of saponification. Consequently, the method, as described in this paper, is unsuitable for acetates of these sugars and presumably for ace-

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Table I.   Comparison of Authors' with Henglein and Vollmert (4) Method

Substance Analyzed	Acetyl Found, %	
	Method of Henglein and Vollmert	Modification of Clark's method
Pectin acetate 13	2.5	2.56, 2.57
Pectin acetate 12	2.9	3.01, 2.97
Citrus pectin	0.3	0.29, 0.30

Table II.   Acetyl in Substances Other than Pectin

Substance Analyzed	Acetyl, %	
	Found	Calculated
Arabitol pentaacetate	59.3, 59.3	59.5
Galactose pentaacetate	55.2, 56.4	55.1
Glucose pentaacetate	55.7, 57.2	55.1

tates of other simple sugars. The high results obtained for these compounds are probably due to the formation of acids, other than acetic, which are sufficiently volatile to enable them to appear in the distillate. On the other hand, consistent results were obtained on duplicate analyses of pectin acetates, for which the time of saponification was varied by as much as 1 to 20 hours. Thus, if any acids, other than acetic, are formed under the conditions specified, they are not sufficiently volatile to interfere with the method herein described for the analysis of pectin acetates. Arabitol pentaacetate served as a suitable standard and the analysis of it gave consistent results which were close to, but never exceeded, the theoretical acetyl value. Thus the method is suitable for arabitol and pectin acetates and would presumably be useful for other o-acetyl compounds which are readily saponified by dilute alkali near 20° C. and do not give rise to acetic acid by side reactions or to volatile acids other than acetic acid.

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Determination of Chloride in Water—Addendum

Preparation and Effect of Mercuric Nitrate Reagent

FRANK E. CLARKE, *U. S. Naval Engineering Experiment Station, Annapolis, Md.*

IN A previous article (*1*), the author described an improved method for determining chloride ion by titration with mercuric nitrate solution in the presence of diphenylcarbazone–bromophenol blue indicator and controlled pH. The instructions for preparing reagents were given briefly, assuming that they would be made in accordance with accepted laboratory practice. This prescribes acidification of the mercuric nitrate solution to prevent hydrolysis.

There has been some concern that acidification of the mercuric nitrate might affect the accuracy of the chloride determination, which is influenced by pH. This note provides more information on the preparation of the mercuric nitrate reagent and shows that its acidification does not affect accuracy significantly.

PREPARATION OF MERCURIC NITRATE SOLUTION

Mercuric nitrate does not dissolve readily in distilled water. Even in preparing 0.025 N solution, a large proportion of the crystals will remain undissolved and hydrolysis products may precipitate. The solubility is affected somewhat by the degree of hydration of the mercuric nitrate crystals.

It is common laboratory practice to dissolve the mercuric nitrate residue by adding concentrated nitric acid slowly, while stirring vigorously. This procedure usually consumes more than the minimum effective quantity of acid. It is better practice to dissolve the crystals directly in a small quantity of acidic water, and then to dilute the solution to volume. The quantity of mercuric nitrate required to make 1 liter of 0.1 N solution can be dissolved in 100 ml. of water containing 1.0 to 1.5 ml. of concentrated nitric acid. The quantity required for a 0.025 N solution can be dissolved in 25 to 50 ml. of water containing 0.25 to 0.40 ml. of concentrated nitric acid. When prepared in this manner, either directly or by dilution from 0.1 N stock, the 0.025 N mercuric nitrate solution will have a pH of 2.25 to 2.50. It will be clear and remain clear for long periods of storage. Sediment which forms in storage can be filtered off, but the solution must be restandardized.

EFFECT OF MERCURIC NITRATE ACIDITY ON CHLORIDE DETERMINATION

At the optimum pH, the mercury-diphenylcarbazone color complex forms after all the chloride ion is combined as weakly ionized mercuric chloride. In weakly acid solutions the color complex will form in the presence of a large excess of chloride ion. In strongly acid solutions the tendency to form the complex is reduced, so that a large excess of mercuric ion is required to develop the color. Between these two extremes there is a reasonably wide pH region (3.0 to 3.5) in which excellent accuracy can be obtained at all chloride concentrations. It is most convenient to establish the optimum pH by adding nitric acid to the chloride solution before titrating it with mercuric nitrate (*1*). Because the mercuric nitrate solution contains some nitric acid, there is a slight increase in acidity of the chloride solution during the titration—for example, titration of 2 mg. of chloride ion in 100 ml. of solution will require 2.26 ml. of 0.025 N mercuric nitrate and reduce the pH from approximately 3.3 to 3.25. Titration of the maximum quantity of chloride ion recommended in (*1*) will require 22.6 ml. of 0.025 N mercuric nitrate solution and reduce the pH to approximately 3.05.

The acid error in milliliters of mercuric nitrate solution consumed, and therewith milligrams of chloride, depends on the deviation from the optimum pH. It is essentially independent of the chloride concentration. The acid error as percentage of chloride varies inversely with the total quantity of chloride present. It therefore is most significant in low chloride concentrations. Fortunately, these require small mercuric nitrate titrations, which yield insignificant pH reductions. At higher chloride concentrations, where larger quantities of mercuric nitrate yield greater pH changes, the lower percentage errors balance out the effects and maintain good accuracy. The pH-error graph in (*1*) was based on a 20 p.p.m. solution of chloride ion (2 mg.), which is a concentration frequently encountered in water work. It would not be applicable to chloride ranges far above or far below that concentration. The data in Table III (*1*) were obtained by first adjusting the chloride solution in accordance with the recommended procedure and then titrating with acidified mercuric nitrate solution. No correction was made for the additional acid introduced with that reagent. The data show that this procedure is adequate for all normal analytical work.

If extreme accuracy is desired, as in microanalysis, corrections can be made for indicator sensitivity and for excess acid introduced with the titrating solution. The indicator correction is determined by making a blank titration on chloride-free water containing the total quantities of indicator and acid which will exist in the sample at the end of its titration. The effect of excess acid is overcome by neutralizing most of the excess before adding the indicator. Slightly less than the required amount of mercuric nitrate solution is run into the untreated chloride sample. The diphenylcarbazone–bromophenol blue indicator is then added, the pH of the solution is adjusted, and the titration is completed. These refinements are not required for most analytical work.

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38. Potassium Permanganate, KMnO₄

Contributed by WALTER C. McCRONE

Armour Research Foundation,
Illinois Institute of Technology, Chicago 16, Ill.

THIS description represents the use of an infrared eyepiece for the determination of optical properties for a strongly absorbing compound. Potassium permanganate is completely transparent at 10,000 A., or more accurately perhaps in some wavelength range utilized by the 1-P-25 infrared image tube (2). Excellent crystals of potassium permanganate can be obtained from water either in a beaker or on a microscope slide.

These data were obtained with much greater ease through use of a trick to change the crystal habit so that a principal view was shown directly. Gelatin is absorbed on the 100 face of potassium permanganate, so that thin plates lying on that face can be crystallized from a dilute aqueous gelatin solution.
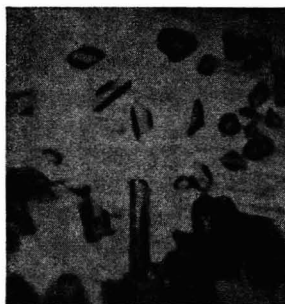

Figure 1. Crystals of Potassium Permanganate from Water

Observed through 1-P-25 infrared image tube

CRYSTAL MORPHOLOGY

Crystal System. Orthorhombic.

Form and Habit. Prisms from water slightly elongated parallel to c. The prisms are closed by the brachydome, {011}. When crystallized from dilute aqueous gelatin thin 100 plates are formed.

Axial Ratio. $a:b:c = 0.813 : 1 : 0.630$.

Interfacial Angles (Polar). $011 \wedge 01\bar{1} = 76° 54'$; $110 \wedge 1\bar{1}0 = 78° 12'$.

X-RAY DIFFRACTION DATA

Space Group. V_h^{16} (1).

Cell Dimensions. $a = 7.394$ A., $b = 9.098$ A., $c = 5.730$ A.; $a = 9.10$ A., $b = 5.60$ A., $c = 7.40$ A. (1).

Formula Weights per Cell. 4.

Formula Weight. 158.03.

Density. 2.703; 2.745 (x-ray).

Principal Lines

d	I/I₁	d	I/I₁
5.72	0.21	1.73	0.18
4.54	0.50	1.71	0.15
3.85	0.21	1.66	0.15
3.70	0.35	1.63	Very weak
3.54	0.90	1.59	0.12
3.42	0.35	1.53	Very weak
3.20	1.00	1.50	Very weak
2.93	0.82	1.48	Very weak
2.86	0.54	1.46	0.12
2.55	0.37	1.44	0.12
2.42	Very weak	1.41	0.12
2.34	Very weak	1.38	0.13
2.28	0.09	1.35	Very weak
2.18	0.65	1.32	Very weak
1.98	Very weak	1.30	0.12
1.91	0.12	1.24	Very weak
1.84	0.22	1.19	Very weak
1.81	0.22	1.16	Very weak
1.75	0.07	1.14	Very weak

OPTICAL PROPERTIES

Refractive Indexes (red light; 25° C.) $\alpha = 1.80 \pm 0.02$; $\gamma = 1.85 \pm 0.02$. These two refractive indexes were obtained on very thin plates lying on 100 crystallized on a microscope slide from water containing about 1% gelatin. Even these very thin crystals showed very strong absorption and observation of the Becke line was extremely difficult. No attempt was made to measure β, and the above values of α and γ are thought to be ±0.01 but may be ±0.02.

Refractive Indexes (10,000 A.; 25° C.) $\alpha = 1.765 \pm 0.005$; $\beta = 1.78 \pm 0.01$ (calculated from α, γ, $2V$, and sign); $\gamma = 1.81 \pm 0.01$. The refractive indexes at 10,000 A. were determined using ordinary immersion liquids and an infrared eyepiece (2). The refractive indexes of the liquids at 10,000 A. were determined using an infrared eyepiece with an Abbe refractometer. It is worth noting that these liquids (Cargille) show almost no change in refractive index from 5893 to 10,000 A.

Optic Axial Angles (10,000 A.; 25° C.). $2V = 80°$.

Optic Axial Plane. 100.

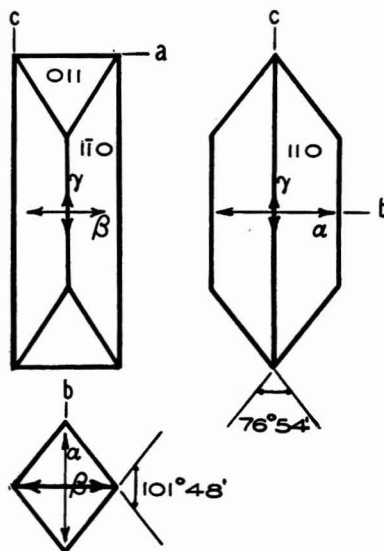Sign of Double Refraction. Positive.

Acute Bisectrix. c.

Figure 2. Orthographic Projection of Typical Crystal of Potassium Permanganate

PLEOCHROISM. Although potassium permanganate shows very strong absorption in all orientations, it is possible to see that absorption is strongest for light vibration parallel to c on very thin crystals.

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(2) Perrine and McCrone, *Frontier*, 12, No. 211 (1949).

CONTRIBUTIONS of crystallographic data for this section should be sent to Walter C. McCrone, supervisor, Analytical Section, Armour Research Foundation of the Illinois Institute of Technology, Chicago, Ill.

CORRECTION. In the paper on phenylacetic acid [ANAL. CHEM., 22, 1338 (1950)], the name of Donald G. Grabar was misspelled.

Book Reviews

Manual of Standardized Procedures for Spectrophotometric Chemistry. *Harold J. Fister.* 1st ed. 500 pages. Standard Scientific Supply Corp., 34 West Fourth St., New York 12, N. Y., 1950. Price, $30.

This new work might better be entitled "Directions for Selected Absorptiometric Clinical Methods." The objective of the author was "to collate under one cover a selection of methods adequate

for the needs of the clinical laboratory and to present them in such a manner that they may be readily followed by those with a minimum of experience in the use of the spectrophotometer." The manual is intended for routine work.

More than 200 specific methods are included for some 70 desired constituents. Although organic constituents predominate, the list includes the following inorganic examples: Bi, Br, Ca, Cl, CO, CO_2, Cu, Fe, Hg, I, K, Mg, N, Na, NH_3, P, Pb, S, SO_4. For many constituents more than one method is given, each of which may apply to more than one substance. Thus, for uric acid one finds (1) the cyanide-urea method, applied to plasma or serum, to whole blood, and to urine, and (2) the glycerol-silicate method, applied to plasma or serum, and to urine.

In general, the material for each procedure is arranged consistently under the following headings: principle of method, sample, special apparatus, reagents, technic (spelled correctly, the reviewer believes), calibration procedure, alternate instrumental procedures, selected bibliography of original references, blank space for notes, a calibration curve, and a coordinate ruled page for recording meter readings.

Both the operating directions and the calibration curve are for the author's Coleman Universal spectrophotometer, using 13-mm. square cells. The procedures are not limited, of course, to this instrument. The alternative techniques included are for filter photometers equipped with a linear scale (Sheard-Sanford type) or with a logarithmic scale (Klett-Summerson type). The author advises each operator to calibrate his own instrument, for obviously it might range in spectral band width at least from the three-filter photometer of the Fisher Company to the very narrow-slit Beckman DU spectrophotometer.

The appendix includes a conversion table for density-meter reading values, and also a list of values for the normal amounts of the various constituents covered by the methods.

The reviewer is not competent to decide whether the methods selected from the biochemical literature are the best available for the purpose intended. They are written in a very clear and concise way, with all the individual reagents and steps in the procedures numbered and well separated for easy reading. Any trained Lundell determinator should be able to follow the directions readily. Because each method is a complete unit and the binding is loose-leaf form, any given procedure may be easily replaced as improvements occur.   M. G. MELLON

The Theory and Practice of Semimicro Qualitative Analysis.
G. B. Heisig. 2nd ed. 356 pages. W. B. Saunders Co., West Washington Square, Philadelphia 5, Pa., 1950. Price, $3.50.

The author states in the preface of this work that it was designed for the use of students who have had a thorough course in general inorganic chemistry and was intended to serve as a basis for a two-quarter or two-semester course in qualitative analysis. It is the opinion of the reviewer that the author has succeeded in his purpose.

Like many other textbooks in qualitative analysis, the material in this work is divided into a theoretical and an experimental section. The experimental section of the text is exceedingly well organized and the procedures presented are clearly stated and are of such nature as to provide excellent illustrative material for the study of the principles of ionic theory and chemical equilibrium. Very little use of organic reagents and "spot" tests is made. This will appeal to those who consider the study of the procedures of qualitative analysis not simply as an end in itself but also as a means of reviewing and extending the students' knowledge of the principles of general chemistry.

The theoretical section is adequate, but is not so well organized or so clearly written as are the experimental procedures. In most cases the author has adapted modern points of view, but in a few instances the discussion is not up to date, notably in the

definition of oxidation-reduction reactions in terms of loss and gain of electrons, and in his use of "valence" and "oxidation state" as synonymous terms. Also the author brings in the now outdated terms of "principal" and "auxiliary" valence used by Werner in his original coordination theory. The author's treatment of ion-dipole bonds and of covalent bonds in complex formation is misleading and is not entirely correct in its implications.

The book is well designed and printed. There are a number of useful tables in the appendix and an adequate index is provided. Altogether, the book is a good text and will serve admirably for the purpose for which it was written.   HARRY H. SISLER

NEW BOOKS

Condensed Chemical Dictionary. 4th ed. *Francis M. Turner*, editorial director. xxix + 726 pages. Reinhold Publishing Corp., 330 West 42nd St., New York 18, N. Y. $10.

G. E. Manual of Instrument Transformers. Operation Principles and Application Information. 76 pages. Bulletin **GET-97A.** General Electric Co., Schenectady, N. Y., 1950. $1.

Industrial Instrumentation. *Donald P. Eckman.* vi + 396 pages. John Wiley & Sons, Inc., 440 Fourth Ave., New York 16, N. Y. $5.

Physico-Chemical Constants of Pure Organic Compounds. *J. Timmermans.* viii + 693 pages. Elsevier Publishing Co., Inc., 250 Fifth Ave., New York, N. Y. $12.50.

Scientist's Ready Reckoner. *W. Roman.* viii + 142 pages. Dr. W. Junk, 13, Van Stolkweg, The Hague, The Netherlands. $3.95.

United States Pharmacopeia. 14th rev. ed. lv + 1067 + 4 pages. Mack Printing Co., Easton, Pa. $9.

CORRECTION. In the review paper on "Light Absorption Spectrometry" [Mellon, M. G., ANAL. CHEM., 22, 2 (1950)], in the first line on page 5, the word "absorbency" was incorrectly used instead of "absorptancy." The phrase should have read: "absorptancy (1 − transmittancy) is plotted against the logarithm of the concentration." This error crept into the text after the author had read and approved the text.

The Analyst's Calendar

International Congress on Analytical Chemistry

Considerable progress has been made in connection with arrangements for the International Congress on Analytical Chemistry, to be held at Oxford, England, beginning September 4, 1952. The technical sessions will be held in one of the main university buildings, and accommodations will be made available in the colleges as well as in hotels. Excursions and visits will be planned to take place during the week end of the congress.

It is expected that a meeting of the board of Section V, Analytical Chemistry, International Union of Pure and Applied Chemistry, will be held in Oxford during the congress. Sir Ian Heilbron is honorary president and C. J. van Nieuwenburg is president of this section. R. C. Chirnside, Research Laboratories, General Electric Co., Ltd., Wembley, England, is honorary secretary of the congress.

Fourth Symposium on Analytical Chemistry. Louisiana State University, Baton Rouge, La., January 29 to February 1, 1951

Pittsburgh Conference on Analytical Chemistry and Applied Spectroscopy. William Penn Hotel, Pittsburgh, Pa., March 5 to 7, 1951

Fourth Annual Summer Symposium. Washington, D. C., June 14 to 16, 1951

Device for Introduction of Solid Reagents. Harry M. Andersen and Robert P. Zelinski, De Paul University, Chicago, Ill.

IN A series of pyrolysis experiments recently carried out in this laboratory it was necessary to introduce a solid charge at a slow, constant rate into a tube furnace for periods up to 8 hours. This was accomplished with the device described here.

As shown in Figures 1 and 2, the apparatus consisted essentially of an aluminum hopper, under which was located a slowly rotating, horizontal aluminum disk, $\frac{1}{16}$ inch thick and 5 inches in diameter, with a ring of 40 holes of 0.189-inch diameter around its edge. This disk rested on a fixed, circular, aluminum plate, 0.25 inch thick and 6 inches in diameter, and was covered by a Lucite plate, 0.25 inch thick and 6 inches in diameter, to which the hopper was secured by means of a bronze flange. The Lucite and aluminum plates, between which the disk rotated, were separated from each other by slightly more than the disk's thickness by means of a spacing ring and gasket paper. They were sturdily fastened around their circumference with machine screws tapped into the aluminum plate.

The perforated aluminum disk was rotated by means of a 0.25-inch brass shaft passing through a rubber-sealed bearing in the lower aluminum plate. As the ring of small holes in the disk passed under the hopper, the holes were filled with the solid material contained therein; after rotating 90° the holes passed over an exit port in the lower aluminum plate. This exit port connected directly with the upper end of the vertical pyrolysis tube.

In order to prevent bridging of the solid in the hopper and consequent failure of the material to fill the holes in the disk, it was necessary to insert a simple, slowly rotating agitator in the hopper. This agitator was supported by a rubber-sealed bearing in the Lucite cover of the hopper. Gasket paper was used between all the parts of the assembly to effect seals.

As shown in the diagram, gears and shafts were fitted to both the rotating disk and the hopper agitator, so that both could be driven from a common source. The power source was a small,

fixed-speed, gear-head motor with a shaft speed of approximately 0.5 r.p.m. and the ability to exert 36 inch-pounds of torque at this speed. The rotating disk was driven at this same speed and the agitator at only a very slightly higher speed. By using a fixed-speed motor, the rate of delivery could be adjusted by changing the gear ratio to the disk or by constructing disks having different numbers and sizes of holes. In practice, the latter method was found more expedient. Obviously, it is possible to obtain widely different delivery rates by this method.

Into the exit port in the aluminum plate there was tightly threaded a piece of aluminum pipe, 1 inch in diameter, 0.125 inch in wall thickness, and 1 inch long. Suitable connection was made from here to the pyrolysis tube.
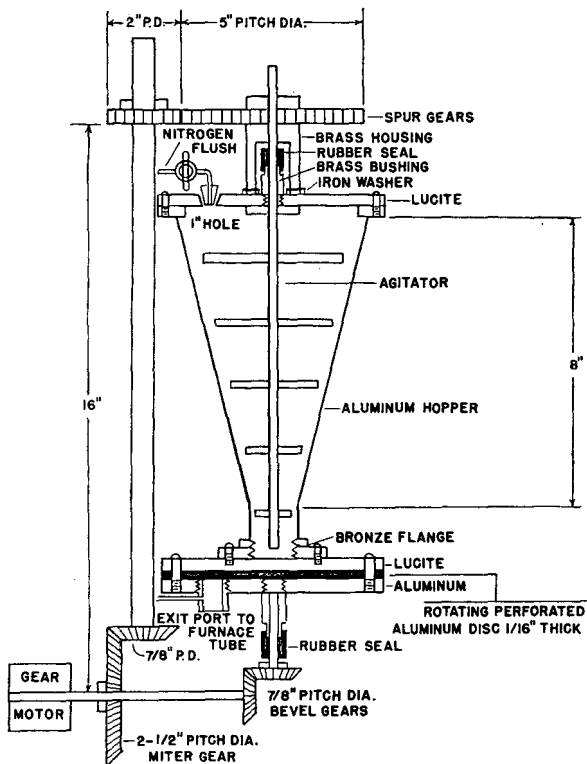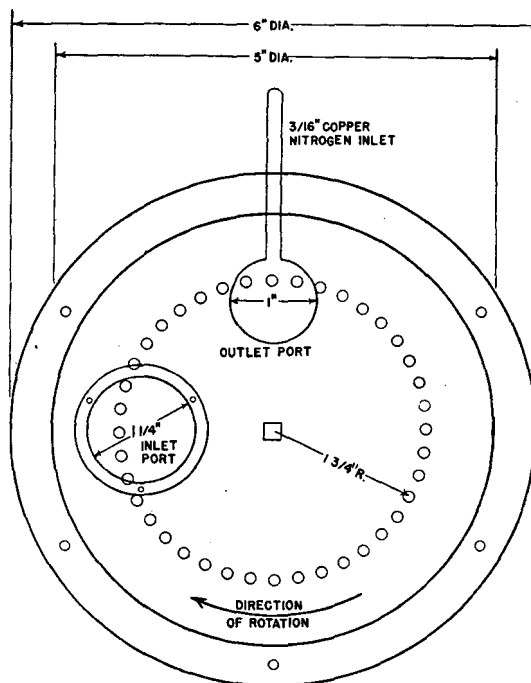
Figure 2. Top View of Rotating Disk Assembly with Hopper Removed

The specifications in the drawings are those for the disk actually used in most of the experiments here, which delivered approximately 0.5 gram per minute of a typical organic compound, at a rate constant to within 1%. The delivery rate will vary with the density and granular size of the solid. Using a disk having smaller holes, and reducing the speed of the disk by changing the gear ratio, feed rates as low as 0.040 gram per minute and constant to within 1% were achieved.

To overcome the tendency of the material to stick in holes rather than fall out the exit port, the undersides of the holes were slightly beveled, and directly over the exit port a solenoid and cylindrical iron slug were mounted. The solenoid was activated by a pulse of current seventy times a minute, so that the slug was repeatedly lifted and allowed to fall upon a bolt in the Lucite plate. The slight jarring resulting therefrom caused the material to drop from each hole as it passed over the exit port. The pulse of current was derived from an electronic timer originally designed to operate the solenoid valve of a partial take-off still head which happened to be available. Any simple repeating switch, such as that used for operating blinking display signs, should be suitable. With a more freely flowing material than that used, both the hopper agitator and the vibrating device might be unnecessary.

The entire assembly was so mounted that it could be conveni-

Figure 1. Apparatus for Introducing Solids into Furnace

ently removed from the motor and weighed before and after a run to determine the amount of material charged. Aluminum and Lucite were favored in the construction to reduce the tare weight.

Versatile Laboratory Concentration Device.
L. C. Craig, J. D. Gregory, and Werner Hausmann, Rockefeller Institute for Medical Research, New York, N. Y.

IN BOTH chromatography and countercurrent distribution the problem of rapid quantitative recovery of solute from relatively large volumes of dilute solution is encountered. The apparatus shown schematically in the diagram overcomes many of the difficulties.

to vacuum
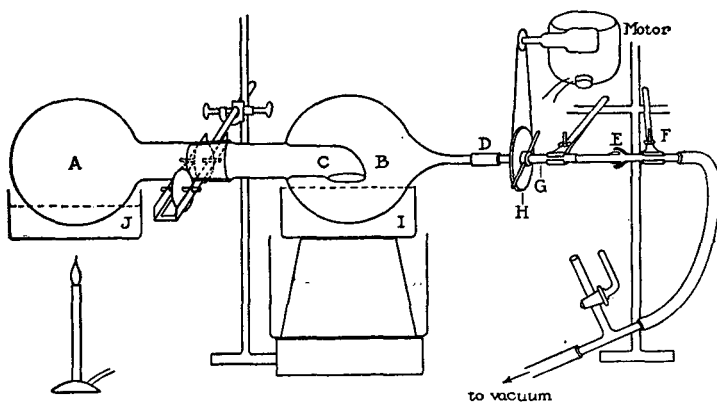
The solution to be concentrated is placed in a round-bottomed flask, A. B is a bulb which is at least as large as or larger than A and has an inlet tube, C, whose width and opening are not smaller than the standard taper connecting A and C. The other opening in B is a 7-mm. glass tube which is located opposite and in line with C. The smaller opening is connected by a short piece of rubber tubing, D, to a 7-mm. glass tube approximately 15 cm. in length which has a standard ball joint (2/5), E, at its further end. The other part, F, of the joint is held stationary by a clamp attached to a ring stand and connects to the vacuum pump through a rubber tube.

The glass tube which connects D and E passes through a cork borer, G, which is supported by a clamp attached to the ring stand to serve as a bearing. The tube also passes through a rubber stopper which is forced into a hole in the center of the wooden pulley, H, and thus is made to grip the tube tightly. The pulley is turned by a leather belt and a smaller pulley attached to an electric motor which has a reduction gear (20 to 1 ratio) and an appropriate slide-wire resistor. Flask A and bulb B are supported by two small wheels with solid rubber tires.

For operation, joint E is well greased with a heavy stopcock lubricant and evacuation is begun. The motor is then started and the speed is so adjusted that the steady rotation of A and B does not greatly disturb the surface of the liquids in either vessel.

B serves as the condenser. It may be cooled by the ice and water contained in the flat pan, I. Ice is added to the pan and the maximum surface of B is cooled because it is rotating constantly. Heat at any desired temperature is supplied to A by water in pan J.

Because A rotates steadily, a film of the liquid is constantly being pulled up on the upper inside wall and a relatively large heated surface is thereby furnished for vaporization. Thus distillation takes place rapidly without ebullition as in molecular distillation [Hickman, K. C. D., *Ind. Eng. Chem.*, 29, 968 (1937)] and there is little or no tendency for bumping when pressure and temperature are properly adjusted. Even salt solutions have often been quietly brought to dryness. The familiar capillary leak or boiling stone is completely unnecessary. For solutes of poor stability, the level of the warm water in J can be reduced

as the solution in A decreases; thus, *overheating of the dry residue* is avoided. Moreover, if evaporation at a low temperature is desired, dry ice and acetone can be placed in I and a high vacuum can be supplied with an oil pump. The apparatus then becomes a convenient freeze-dry assembly.

Device for Filtering Solutions into Reagent Bottles.
C. W. Fleetwood, North Dakota Agricultural College, Fargo, N. D.

SOME procedures for the preparation of standard potassium permanganate (*1, 2*) state that the solution is to be filtered into the reagent bottle. Filtering of most mixtures without the aid of suction or pressure is a waste of time, yet no suggestion is given to aid in following the procedures. If the mouths of reagent bottles were large, or if all laboratories were equipped with bell jars large enough to cover bottles of various sizes, the process would be simple. Thought was given to the construction of a simple, inexpensive device which would be applicable.

The filter device illustrated was constructed of borosilicate glass tubing, a borosilicate glass crucible with fritted disk, and two rubber stoppers. A fritted disk may be used instead of the sintered-glass crucible. This size of apparatus may be used for filtering solutions into reagent bottles with mouth openings of 1 to 5 cm. Changing the dimensions of various parts will give devices of different sizes and capacities. The principles employed by Rothman (*3*) may be used to construct a filter device for filtering into reagent bottles, but such a device would be more susceptible to breakage than the one illustrated.

The device is attached to a suction line containing a 3-way stopcock which can be used as a vent to stop filtration, and to isolate the system from the pump while venting it. The lower stopper is set on the reagent bottle and at the same time the tube leading to the solution to be filtered is placed in the solution to the required depth. The suction line is opened by closing the vent on the stopcock and pressure on the bottom stopper seals the glass-to-rubber junction.

The formation of a vacuum within the system causes the solution to feed automatically. Once filtering has begun, the system requires no attention, providing there is no possible backup of

water from the vacuum line trap. Filtering may be stopped by venting the vacuum line or by placing both hands on the shoulder of the bottle and pushing with the thumbs on the bottom stopper.

In filtering mixtures which contain suspended precipitates that clog or are difficult to remove from the filter plate, the plate should be covered with an asbestos mat. To prevent contamination of the solution by the top rubber stopper, a ground-glass joint construction can be used at that point.

The device has been in use in this laboratory for 2 years and has been a very practical time saver in filtering large volumes of reagents, as well as in filtering potassium permanganate into reagent bottles.

LITERATURE CITED

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(3) Rothman, S., ANAL. CHEM., 22, 367 (1950).