ANALYTICAL CHEMISTRY

JULY 1951

What a Reagent Survey told us about you

In a recent widespread survey, you chemists told us a good deal about your likes and dislikes.

You *liked* 'Baker Analyzed' C. P. Chemicals and you ranked them as the No. 1 line of Laboratory Chemicals in *dependability*, in *known quality*, and in *availability*. That was fine praise, and *we liked it.*

Then, some of you told us some things you *didn't* like:

You asked us not to call our chemicals 'C. P.'—but to use the term 'Reagent.'

You felt that 'Baker Analyzed' Labeling could be improved. You wanted the actual analysis on the label, but you wanted it *in type* that could be more easily read. You also wanted the chemical name to appear in *bolder* display.

We welcome your suggestions and we're planning to follow them. Presently, you will begin to see the new 'Baker Analyzed' Reagent label, similar to specimen below.

Of course, the transition will have to be gradual. It will take a long time before all 'Baker Analyzed' Reagents reach you with the new label—for Baker distributors will continue to receive laboratory chemicals labeled both ways until this transition can be completed.

This new label is another contribution to the needs of the laboratory chemist by the makers of Baker Reagents, already first in dependability, first in known quality and first in availability. J. T. Baker Chemical Co., *Executive Offices and Plant:* Phillipsburg, New Jersey.

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Baker Chemicals

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WARNING!

Causes Severe Burns to Skin and Eyes

Avoid contact with skin, eyes, and clothing.
Do not take internally.
When handling, wear goggles or face shield.
While making solutions, add Potassium Hydroxide slowly to surface of solution to avoid violent spattering.
In case of contact, immediately flush skin with plenty of water and wash with vinegar; for eyes, flush with plenty of water for at least 15 minutes and get medical attention.

POISON

Antidote - EXTERNAL: Flood with water, then wash with vinegar. If in eyes, wash with saturated boric acid solution. INTERNAL: Do not use emetics. Give water with large amount of diluted vinegar, lemon or orange juice. Follow with milk or white of eggs beaten with water. CALL A PHYSICIAN.

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KOH PELLETS F. W. 56.104

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Chloride (Cl)	0.008	%
Nitrogen Compounds (as N)	0.0004	%
Phosphate (PO_4)	0.0004	%
Sulfate (SO_4)	0.001	%
Ammonium Hydroxide Precipitate	0.008	%
Heavy Metals (as Ag)	0.0005	%
Iron (Fe)	0.0004	%
Sodium (Na)	0.002	%

J.T. BAKER CHEMICAL CO., PHILLIPSBURG, N.J.

ANALYTICAL CHEMISTRY

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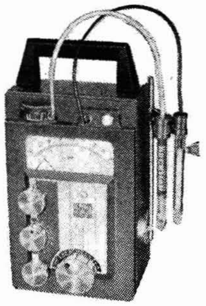
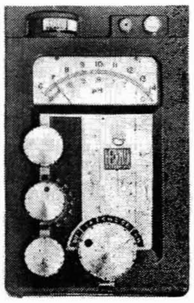
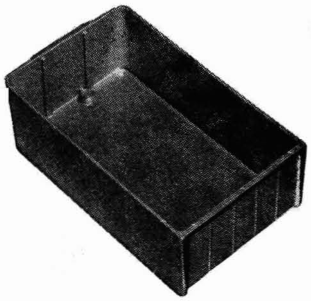


ELECTRODE SUPPORT ROTATES alongside case for maximum convenience in carrying. Instrument can be used in either horizontal position (shown at left) or vertical position (above)—whichever is handier.



CONVENIENT CONTROLS not only centralize all operating functions, but also permit checking amplifier circuits and battery condition without opening case or disturbing battery connections.



RUGGED, COMPACT DESIGN withstands rough field and plant service with negligible maintenance. Solid cast-aluminum case is strong, yet light in weight. Beckman Glass Electrode is virtually unbreakable!

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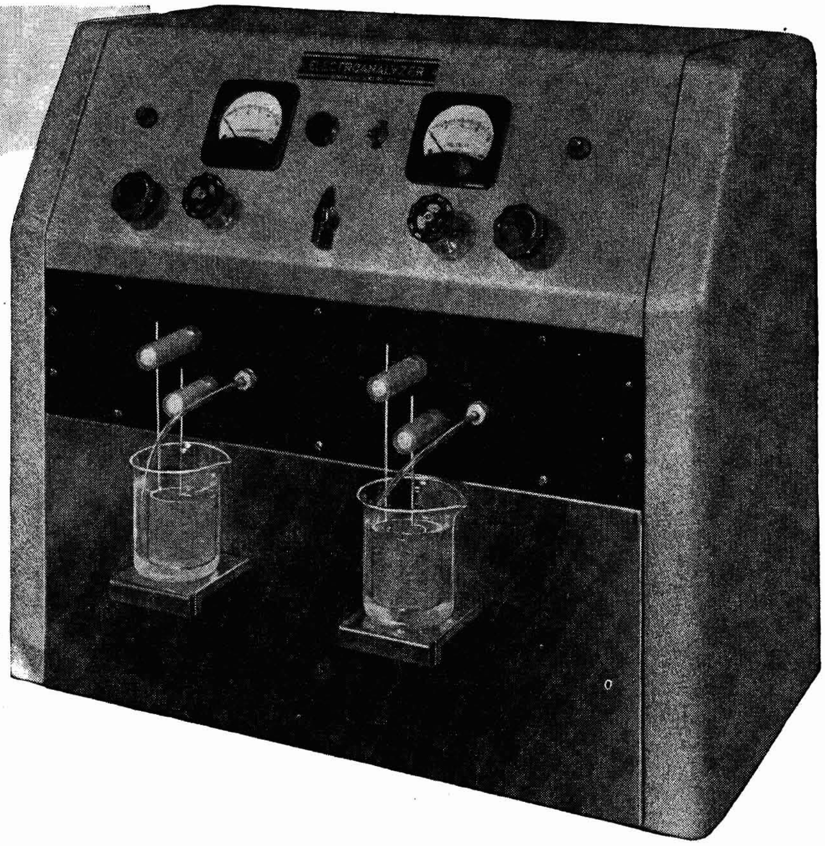

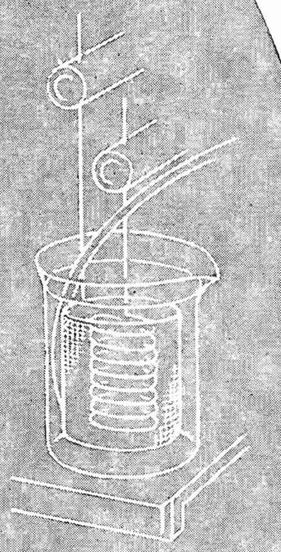

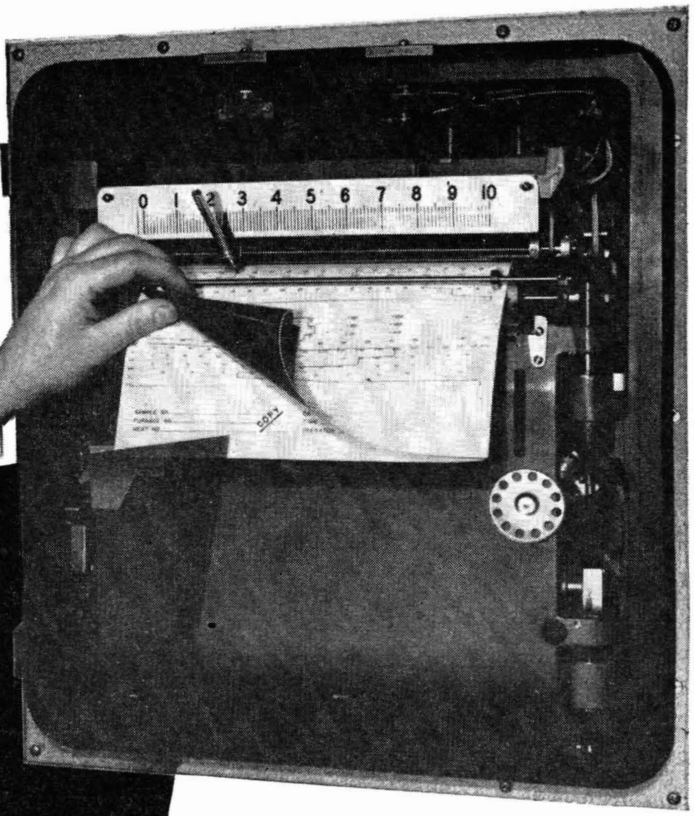

IN 2 MINUTES...

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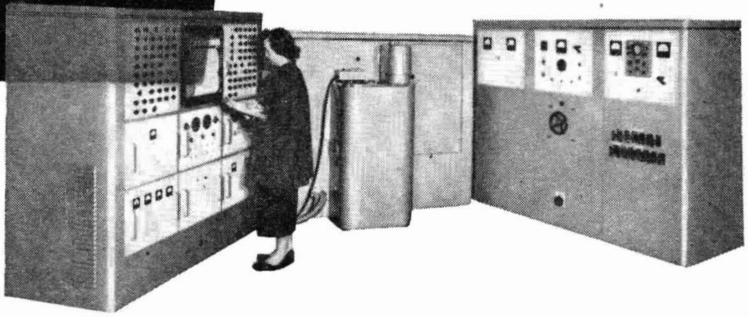

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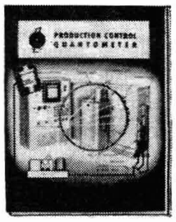

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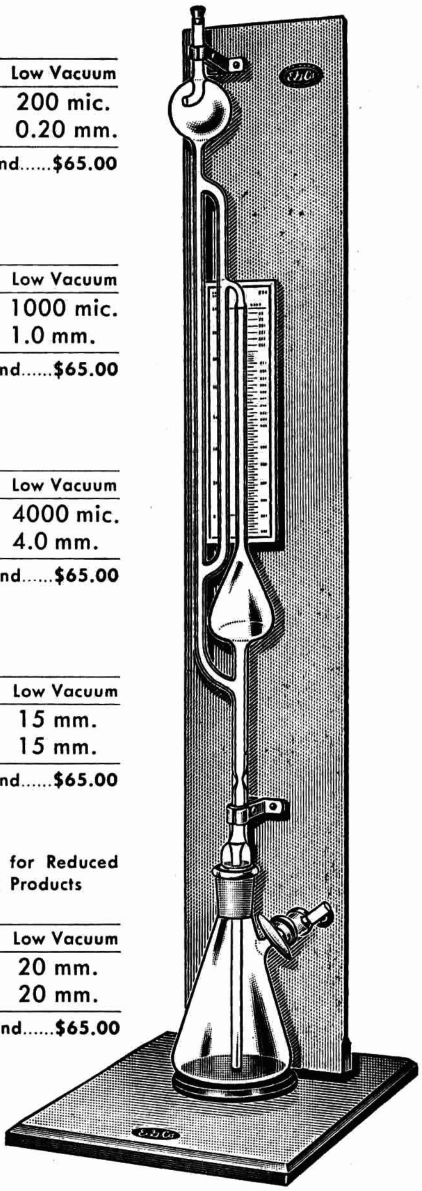

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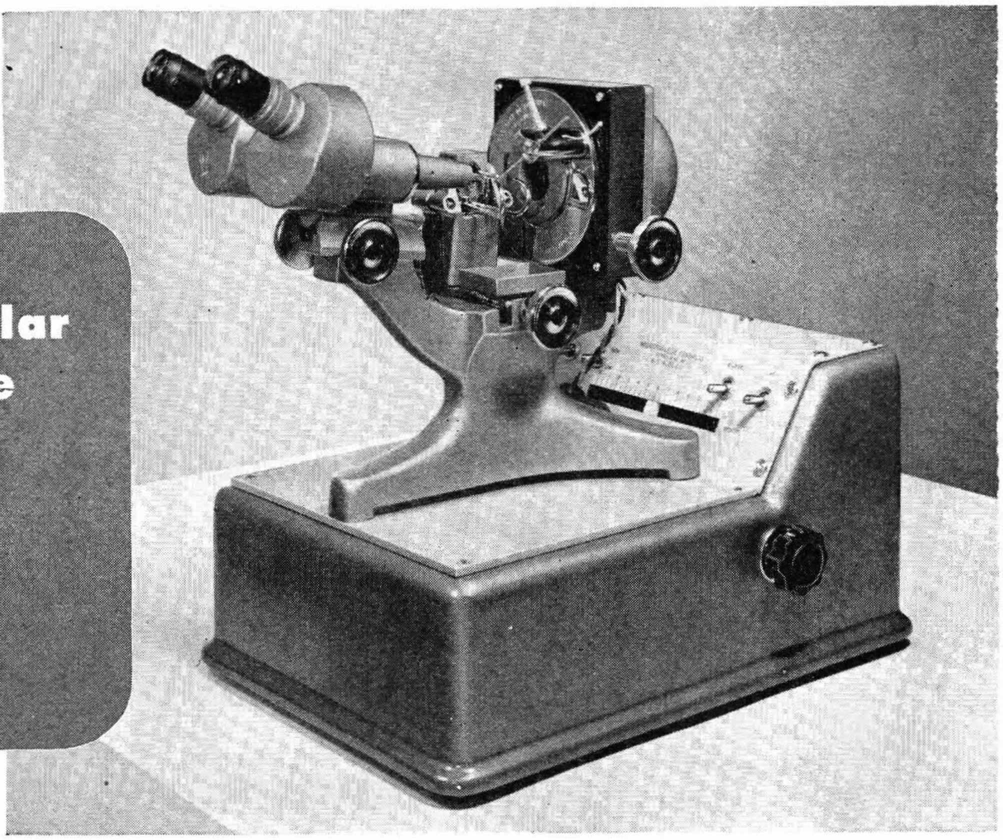

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Extends potential application of any micromanipulator

Micro-probes, scalpels, needles and other tools made to exact specifications under controlled conditions

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Binocular body provides three dimensional vision

The micro-forge is basically a combination of optical and electric forge units. In the improved model, the optical system includes a microscope with inclined binocular body in place of the monocular type. This stereoscopic microscope not only provides three dimensional vision but also shows the image erect. The microscope is equipped with 4X paired objectives and 9X paired wide field eyepieces. These optics provide a magnification of 36X with a large working field. The electrical forge is mounted on an adjustable stage directly in front of the microscope objectives. Two insulated clamps support the cylindrical electrodes connected by a platinum-iridium filament providing temperatures from about 120°F. to 3000°F. Air jets are also mounted on the stage. The lamp housing is set opposite the objective and forge unit. A pivoting spindle for supporting the material is mounted at the periphery of a disc in front of the lamp housing. Both spindle and disc may be rotated about their own axis and the entire assembly adjusted vertically or horizontally. Controls are provided for adjusting the light to the objective. A detailed manual of instructions is furnished with each micro-forge. Accessory equipment including the air pump, rheostats, and transformer is contained in the base. The entire unit is finished in baked-on gray enamel.

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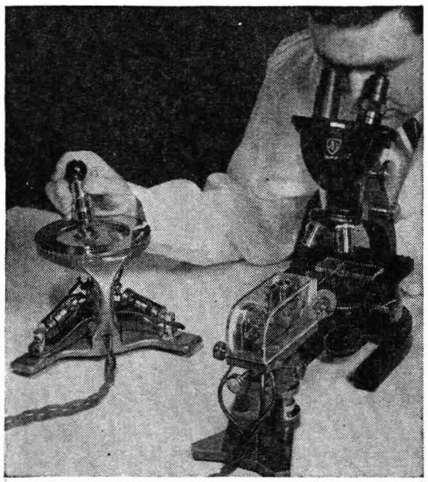

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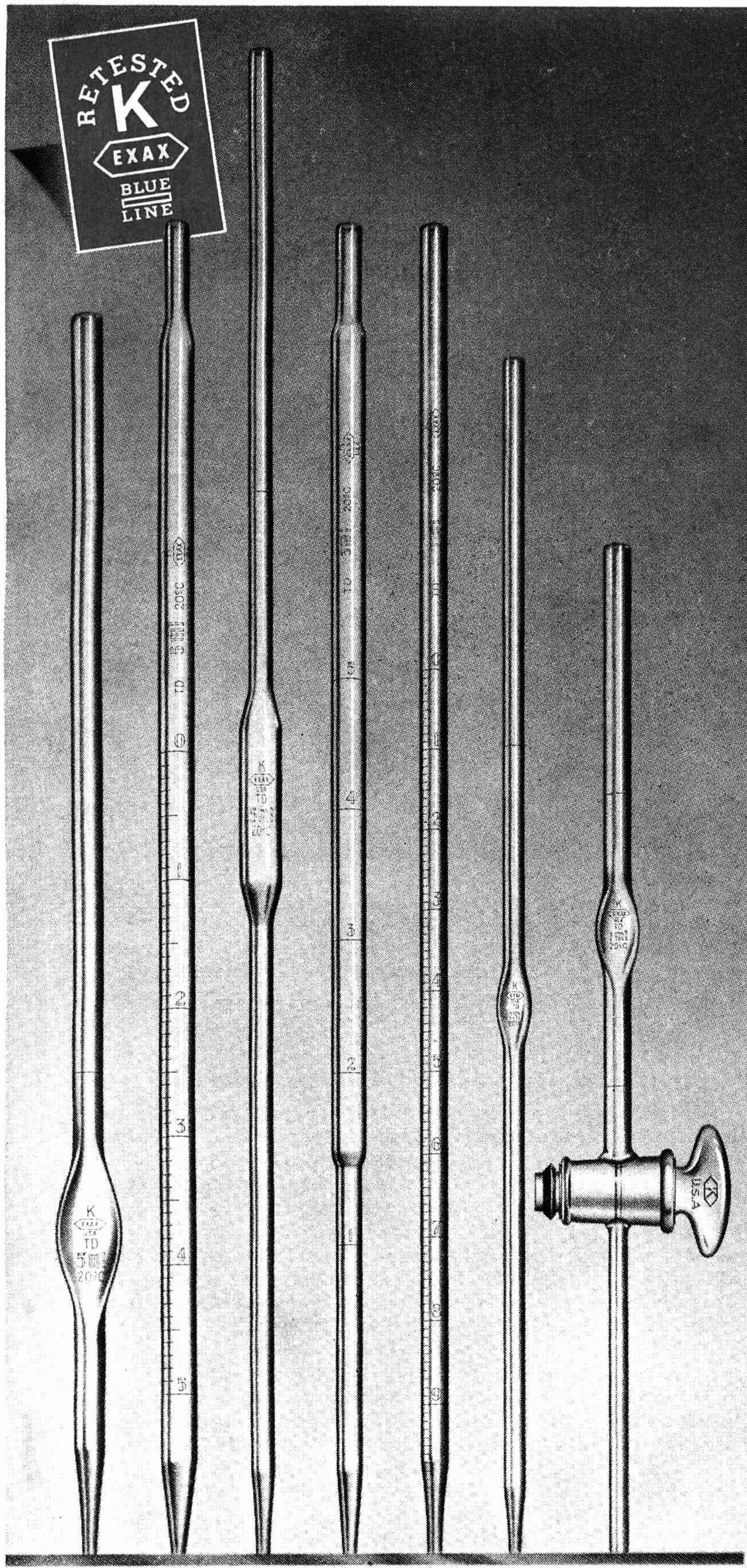
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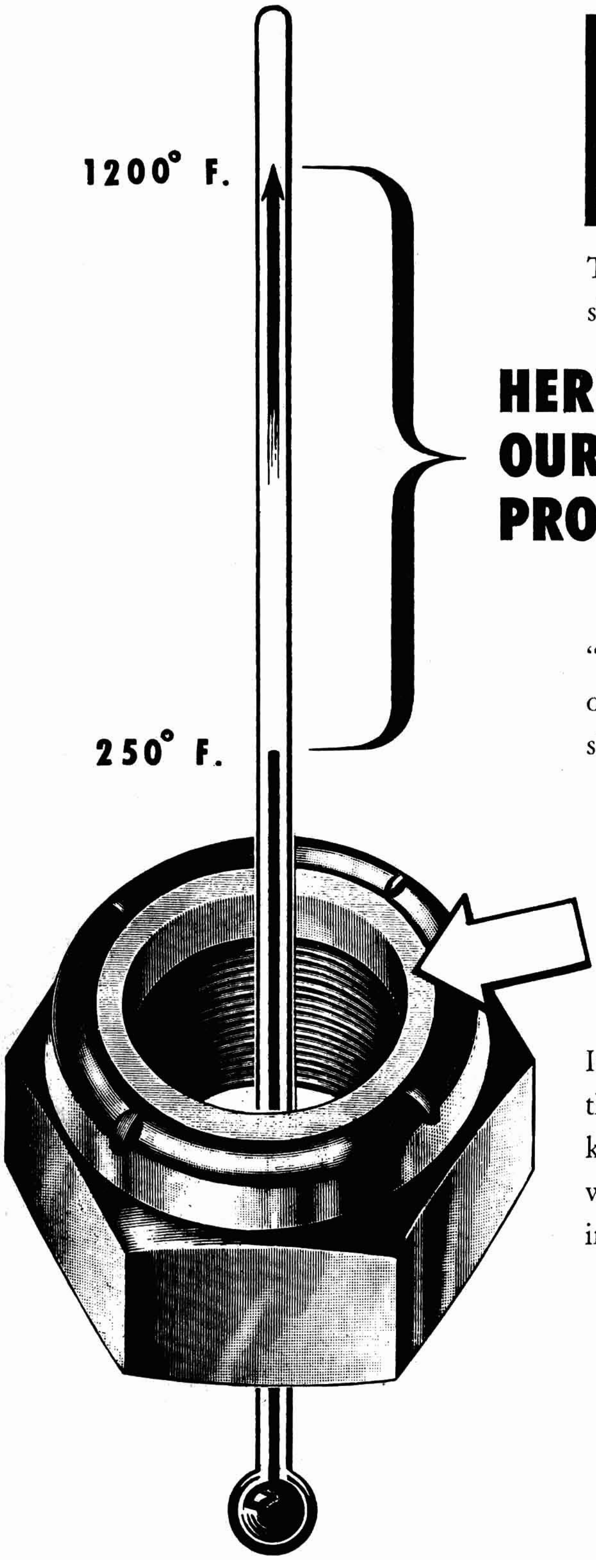
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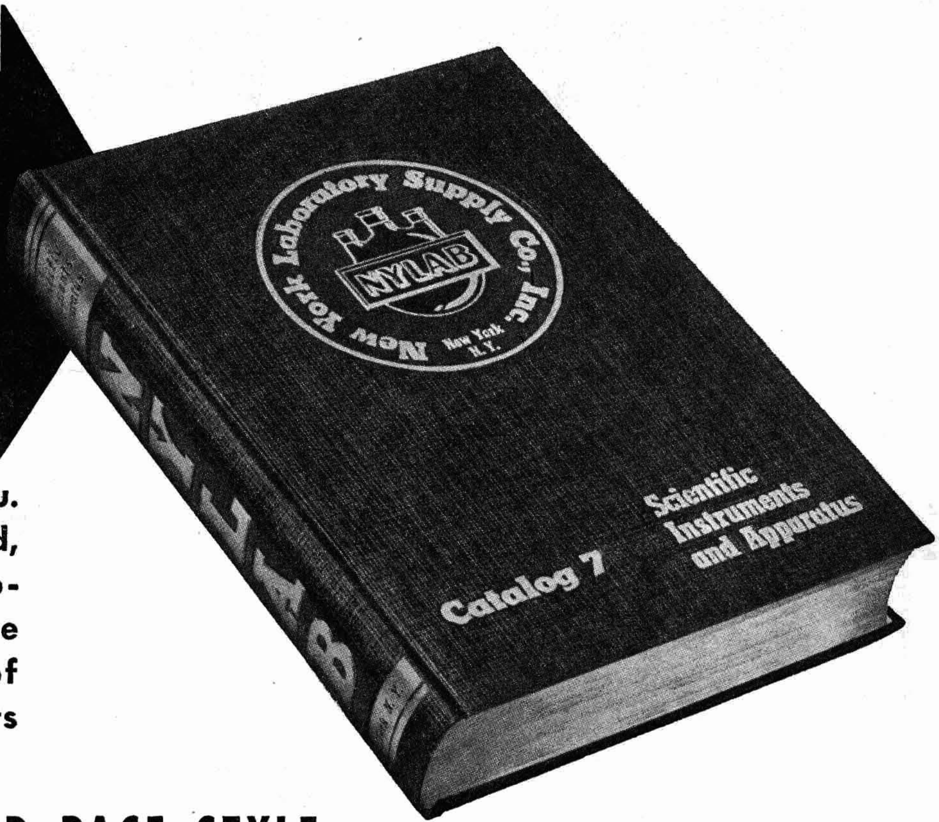
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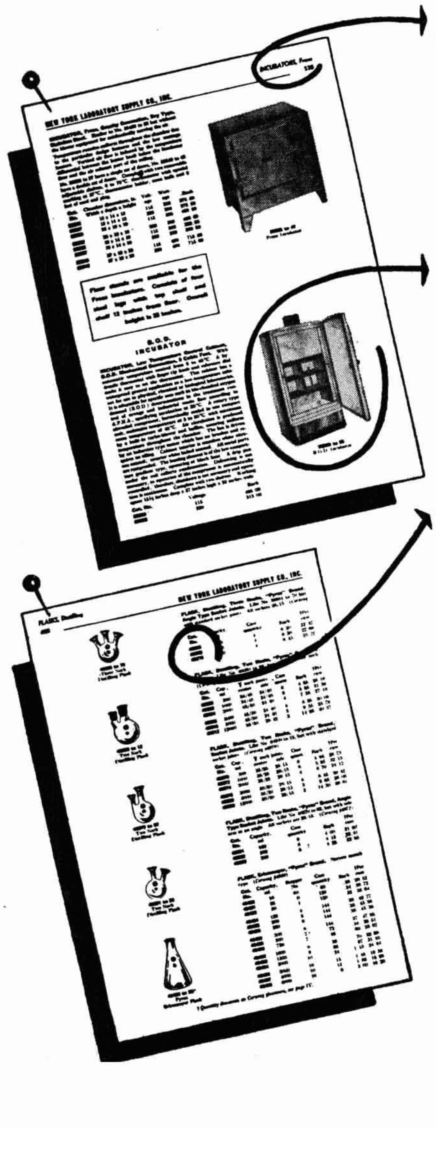

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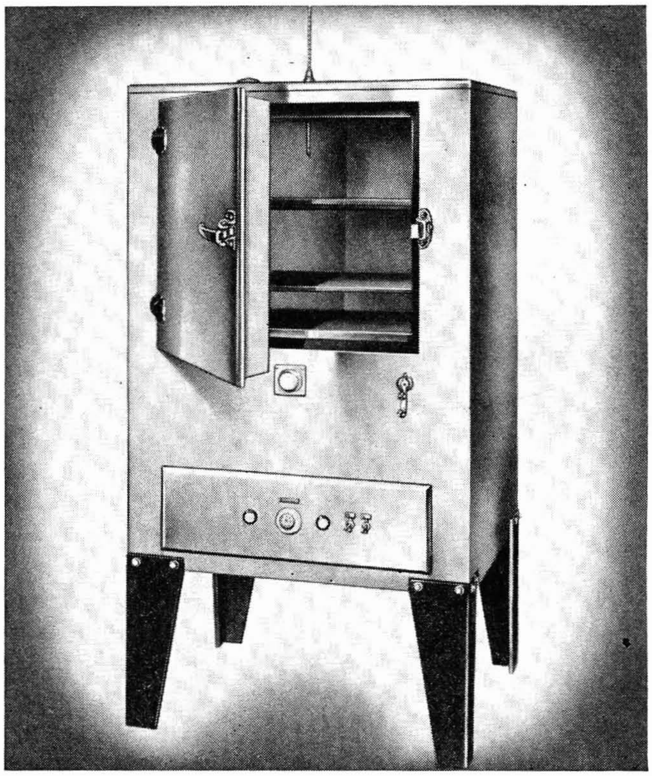

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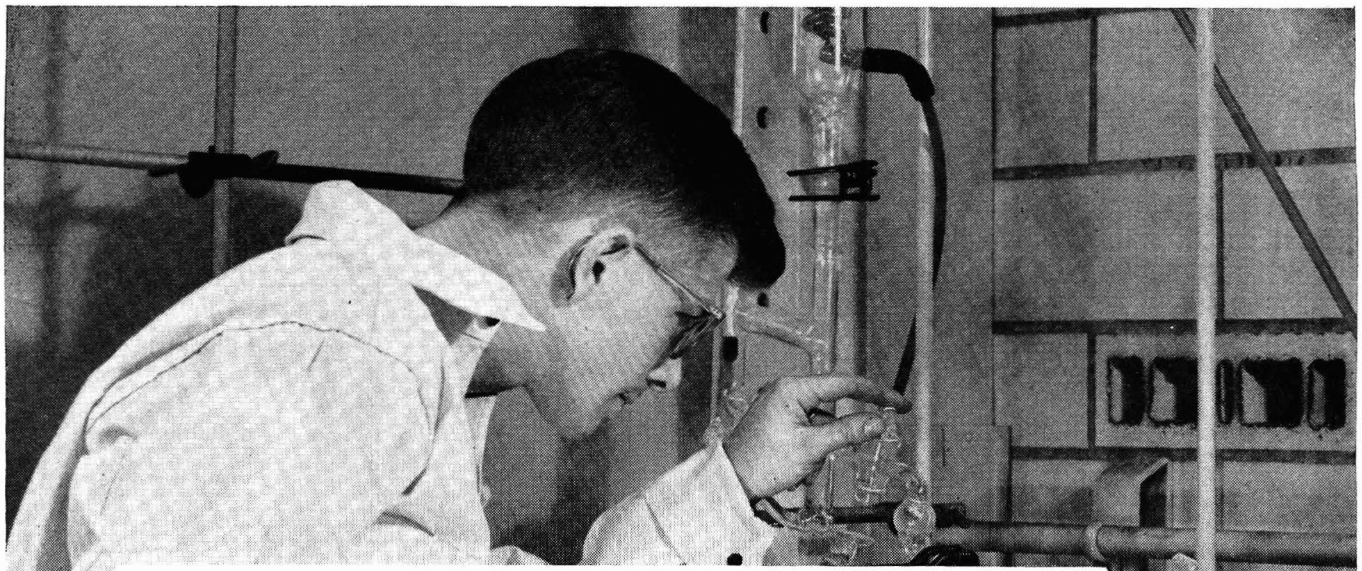

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$CH_3(CH_2)_{15}COOH$

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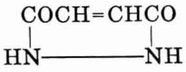
Brake for flora . . .



$$\begin{array}{c}\mathrm{COCH{=}CHCO}\\ |\qquad\qquad |\\ \mathrm{HN{-}{-}{-}{-}{-}NH}\end{array}$$

Maleic Acid Hydrazide (Eastman P6445), with its ability to inhibit growth of plants without killing them, has become the subject of homely philosophizing on topics like the storing of onions without sprouting and the relief of Junior from his grass-cutting chores. Its more formal name is 1,2-dihydro-3,6-pyridazinedione. The most convenient way to acquire a small quantity of it is to order it from us.

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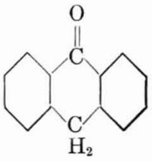

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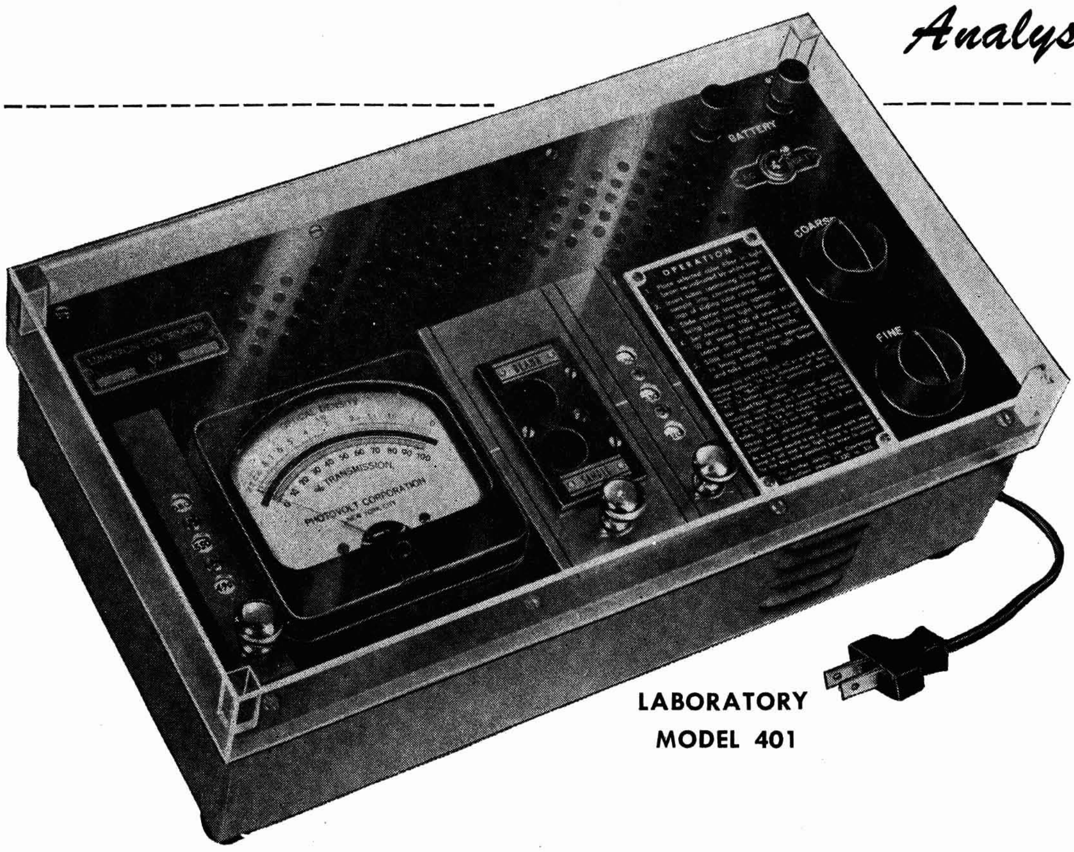

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the analyst's column

The Summer Analytical Symposium held in Washington last month was well attended, and each meeting gives strength to the belief that in such small groups advanced ideas are more easily exchanged, both informally and formally. The work of the National Bureau of Standards on the preparation and analysis of standard samples is little understood, and the papers presented gave a clearer understanding of this standards program. Recent years have seen much progress in the preparations of standards for spectrographic analysis and in the purification of organics for reference standards for physical methods of analysis. Interest in standards for titanium alloys is high at present. This was shown by the questions asked concerning the bureau's plans in this field. To date, the bureau has nothing to offer, but is seriously considering the problem.

ASTM Committee E-3 at its meeting last month in Atlantic City formed a new division called Analysis of Miscellaneous Metals to study the problems involved in the analysis of titanium alloys and suitable reference standards. The Armour Research Foundation of the Illinois Institute of Technology also realized the importance of the subject and sponsored a three-day Symposium on the Analysis and Metallography of Titanium, a report of which is published in this issue.

Our congratulations to H. V. Churchill, who was given an ASTM Award of Merit at the Atlantic City meeting. We have frequently drawn on his talents and experience in our editorial work, and have found his advice always sound and often a source of inspiration.

We are always glad to learn of the activities and viewpoints of analytical chemists in other countries. The following item on physical methods of analysis appeared in the *Manufacturing Chemist* (February 1951), and we believe you will find it interesting:

During the past 25 years physical methods of analysis have been developed at a great pace and their use has spread widely. With this in mind, H. Irving of the Inorganic Chemistry Laboratory, Oxford, recently gave what he called a mid-century review of physical methods of analysis before the

(*Continued on page 19 A*)

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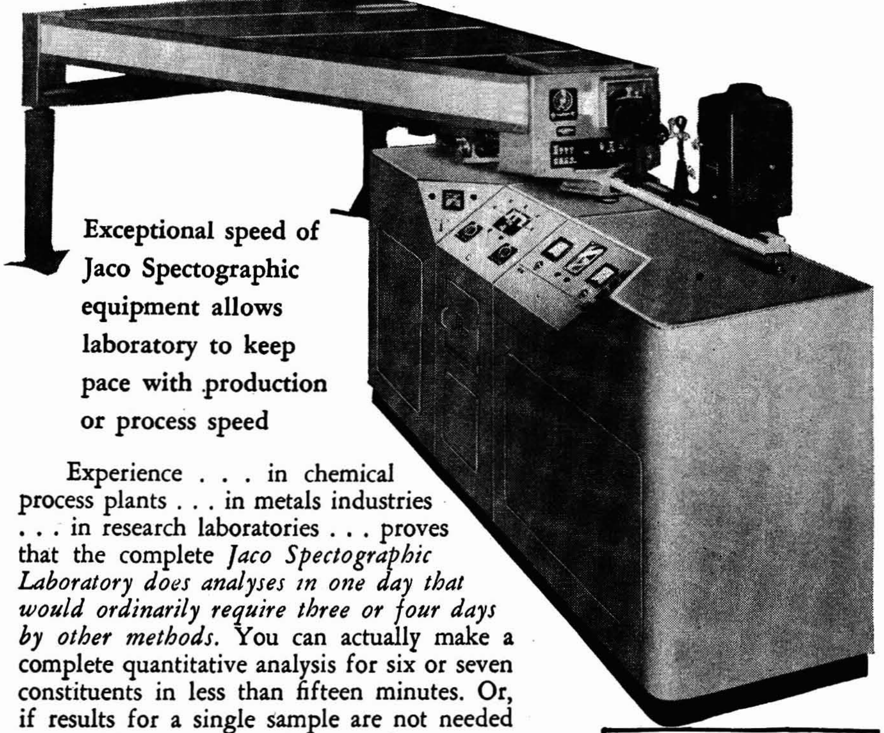

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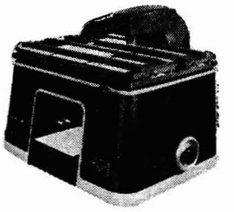

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THE ANALYSTS' COLUMN

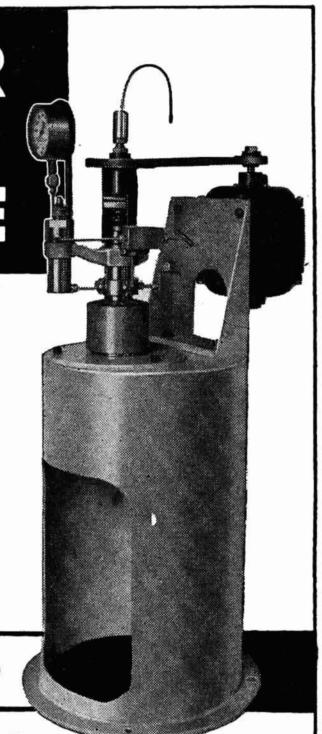
Physical Methods Group of the Society of Public Analysts. He said that it was tempting—but somewhat artificial—to attempt to distinguish between analytical procedures that employ entirely new physical principles and those that have been made possible or at least accessible essentially by virtue of developments in instrumentation. Certainly microwave spectroscopy and high-frequency titrimetry, electron and neutron diffraction, radioactivation analysis, and the various techniques covered by the terms ion exchange and chromatography, belonged essentially to this half-century; but absorption and diffraction of x-rays, mass spectrometry, and infrared or fluorescence spectrography, which had been studied by research and academic chemists for many years, owed their present status and significance in the field of analytical chemistry essentially to profound developments in sources and receivers of energy, and in amplifying and recording devices.

In a necessarily superficial survey of contemporary physical methods of analysis, he traced the influence of such factors as the increasing variety and complexity of analytical problems, the goal or the necessity (as in work with rare, unique or highly radioactive materials) of using ever smaller samples, and the demand for increased productivity—more analyses in less time with less trained staff. In some cases the commercial availability of a good instrument—e.g., the Spekker absorptiometer or the Beckman DU spectrophotometer—had had profound effects in extending the quality, scope, accuracy, and popularity of a wide variety of analytical procedures. In other cases—e.g., the quantometer, automatic recording infrared spectrometers, or mass spectrometers—a single instrument carried out concurrent analyses for a number of constituents in a complex mixture and replaced the traditionally trained analyst by computers and maintenance technicians. When the same type of analysis was being constantly repeated, it might be economically justifiable to build a special instrument based on a more flexible "research laboratory" prototype. A "push-button" polarograph for determining the lead in Ethyl gasoline formed an excellent example of this type of development.

Concluding with a survey of potentiometric methods of analysis, Irving mentioned such topics as cybernetics, economy of effort, and sundry instrumental and mathematical devices for locating the maximum of the potential being measured as a function of titrant volume.

L. T. Hallett

Associate Editor



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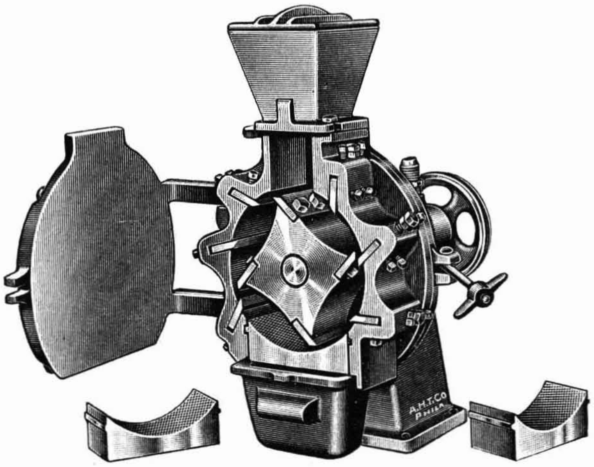

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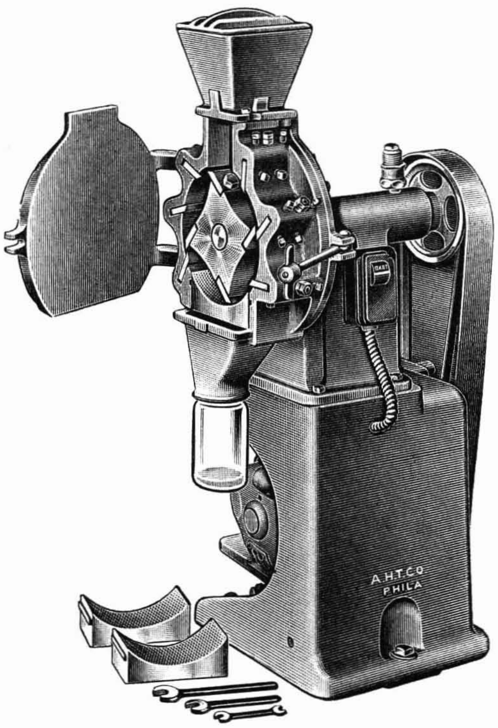

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ANALYTICAL CHEMISTRY

Walter J. Murphy, Editor

Sanity in Statistics

IF LAST month's analytical symposium is any indication, chemists these days are developing a lively interest in statistical methods. Although none of the speakers at the Washington meeting singled out statistics for full-dress review, several gave the topic considerably more than a passing nod. The speakers were not the only ones. A great many of those attending the three-day symposium debated the merits and shortcomings of statistics—earnestly, critically, and at length.

Over the years, statistical methods have had both their energetic partisans and their noisy detractors. To some scientists, statistics is the sun, the moon, and the stars. To others, equally as vocal yet not nearly so numerous, statistics is just so much academic hogwash. Needless to say, the great majority of chemists—those who up until now have managed to remain on the sidelines—are beginning to wonder rather seriously what all the controversy is about.

Today, many of those most skeptical of statistical methods come from the ranks of the disillusioned. Their position is easily understood. Just a few years ago, statistics was heralded as a panacea, a short cut to knowledge, a final answer to the ills of the laboratory. The hope was all too prevalent that somehow—by some magical means—statistics would be able to breathe unheard-of accuracy into half-baked results. Obviously, no self-respecting statistician would have endorsed the extravagant claims that were characteristic of the day. When, inevitably, chemists found that statistics could not live up to its advance billing, many turned their backs. Many still have their backs turned. Others, however, have come to realize that the sins of the past have been the sins of misuse. Statistics has a place in chemistry—a very important place—but its limitations must be recognized and its methods must be intelligently applied. More and more, this is being understood. In fact, one of the most notable features of last month's symposium was its unmistakable evidence that at long last there is evolving a balanced and enlightened approach to statistics on the part of analytical chemists and their laboratory brethren.

In the past, chemists have been all too prone to plug any and all analytical data into standard statistical formulas in the expectation that, with a few turns of the crank, the correct result would necessarily emerge. Many standard textbooks and handbooks, by reprinting simple statistical formulas without even a superficial explanation of their underlying assumptions, have lent tacit support to just such a belief. Experience shows, however, that ready-made formulas applied without an intelligent appreciation of their meaning are worse than useless.

Basically, statistical formulas are designed for the analysis of random errors. In many cases, the significant errors in chemical analysis are not random. Because frequently the extreme results are the ones most nearly correct, the simple calculation of the mean of several chemical determinations may prove grossly misleading. Often it is far better, statisticians say, to report all the raw data—and not just a single calculated result—principally as a means of exposing the caliber of the experimental findings.

In addition, statisticians have a cautioning word about the glib use of formulas for the rejection of results that fall out of line. Even when truly random phenomena are concerned, observations must not be blindly rejected. The mere fact that one set of data may differ markedly from the rest is not, they emphasize, sufficient evidence that such unexpected data may properly be ignored.

William G. Schlecht of the U. S. Geological Survey's Chemical Laboratory has said: "Statistical methods are no substitute for understanding. We should by all means use them when we are ready for them. But before we can study a given analytical method statistically, we must have adequate experience on which to base our study. That requires both a large number of experiments under carefully controlled conditions and a sound theoretical understanding of the process. These must be sweated out for each kind of determination and material. When we do use statistical methods, we must do so responsibly and with a reasonable appreciation of their meaning, plus the extreme skepticism traditionally expected of scientists."

Among chemists there is developing these days a growing awareness that competent statistical analyses may oftentimes require the skill of a professional statistician. The run-of-the-mill chemist who has dabbled briefly in statistics and perhaps is fortified with an elementary knowledge of its jargon, is apt to be hopelessly beyond his depth in dealing with statistical problems. For thoroughgoing statistical work, the chemist must turn to the specialist. Increasingly, chemists are doing just that. Statisticians, in turn, are proving their worth in chemical research not only by their critical appraisal of data but by their competent formulation of experimental procedures. It is a sign of the times that, in more and more laboratories today, the chemically trained statistician has become an essential member of the research team.

Back in 1949, Beverly L. Clarke of Merck & Co., Inc., concluded an address before an analytical symposium with the words: "I urge you not to delay beginning the process of making your organization statistics-conscious. For the longer you delay, the further you will lag behind your bolder rivals who are making more and more extensive use of this youngest and fast-growing accessory technique to chemical analysis." The enthusiastic interest in statistical methods expressed at last month's Washington symposium has made it more than obvious that Dr. Clarke's injunction two years ago did not fall upon deaf ears.

Coulometric Titrations with Externally Generated Reagents

DONALD D. DeFORD, JAMES N. PITTS, AND C. J. JOHNS
Northwestern University, Evanston, Ill.

All coulometric titration procedures described previously have employed internal generation of the titrant. This technique has limited many titrations to the micro range, and has permitted determinations only where the conditions required for satisfactory titration and for satisfactory generation of the reagent were identical. A new type of coulometric titration procedure, in which the titrant is generated in a separate generator cell and subsequently delivered to the titration vessel, involves generation of the reagent by a constant electrolysis current and measurement of the time required for completion of the titration. Satisfactory results in the manual titration of acids with externally generated hydroxyl ion, of bases with externally generated hydrogen ion, and of arsenite with electrolytically generated iodine have been achieved. Precisions and accuracies of the order of ±0.3% are realized. The external generation technique extends the applicability of coulometric titrimetry and offers other significant advantages over the internal generation technique.

THE feasibility of indirect coulometric analyses was first demonstrated by Szebelledy and Somogyi, who applied the method to the determination of thiocyanate (*12*), hydrazine (*13*), and hydroxylamine (*15*). The procedure depended upon the electrolytic generation of bromine from acidified potassium bromide with 100% current efficiency, and the subsequent reaction of the bromine with the substance being determined. This type of analysis has been given the name of coulometric titration (*7*), because the process consists essentially in a titration of the sample with an electrolytically generated reagent. Coulometric titrations extend the range of coulometric analysis to include the determination of substances that cannot themselves be made to undergo quantitative reaction at an electrode, and hence cannot be determined by direct electrolytic methods. Coulometric titrations offer a significant advantage over conventional titrations, because there is no problem of preparing, standardizing, and storing standard solutions. Furthermore, because the titration process is electrical, the possibilities for automatic determinations are greatly enhanced.

The coulometric titrations outlined by Szebelledy and Somogyi employed a chemical coulometer and were extremely precise, but much too slow and cumbersome to be used in routine analyses. A more rapid but less precise technique using electrolytically generated bromine was developed by Sease, Niemann, and Swift (*10*); it employed electrolysis at a constant current for a measured period of time, and used an amperometric method to locate the equivalence point. Myers and Swift (*7*) applied this method to the determination of arsenic by oxidation of arsenic(III) to arsenic(V) with electrolytically generated bromine. From 30 to 1000 micrograms of arsenic were determined with an accuracy of the order of 3 to 10 parts per thousand.

The technique of Myers and Swift has been employed, in slightly modified form, for the coulometric titration of antimony (*1*) and iodine (*16*) with electrolytically generated bromine. Other coulometric titrations involving the use of bromine include the determination of sodium hydroxide (*14*) and the continuous determination of mustard gas in air (*11*).

Other reagents have been described only very recently. Electrolytically generated chlorine (*5*) and iodine (*8*) have been used successfully for the titration of arsenic, and cuprous ion for the titration of chromate and vanadate (*6*). In all these procedures the electrolysis current was electronically regulated (*6*) in order to maintain constant current with a minimum of attention during the titration. Amperometric indication of the equivalence point was employed in all cases.

Unfortunately, coulometric titrations employing amperometric indication cannot be performed with electrolysis currents in excess of about 10 ma. Higher rates of generation induce parasitic currents in the indicator electrodes and make precise location of the equivalence point impossible. As a current of 10 ma. corresponds to a titration rate of about 10^{-4} me. per second, sample sizes cannot exceed about 10^{-1} me. if a reasonable titration time (1000 seconds) is employed. As usual macrotitration procedures are designed for samples of 1 to 5 me., it would be highly desirable to have coulometric methods capable of titrating samples of this size in a reasonable time. Such procedures would require generation rates of 100 to 500 ma. Cooke and Furman (*2*) have recently described a procedure which employs a generation rate of 100 ma. for the titration of ceric sulfate or potassium dichromate by means of electrolytically generated ferrous ion. The equivalence point is located by a potentiometric method employing a platinum-tungsten electrode pair.

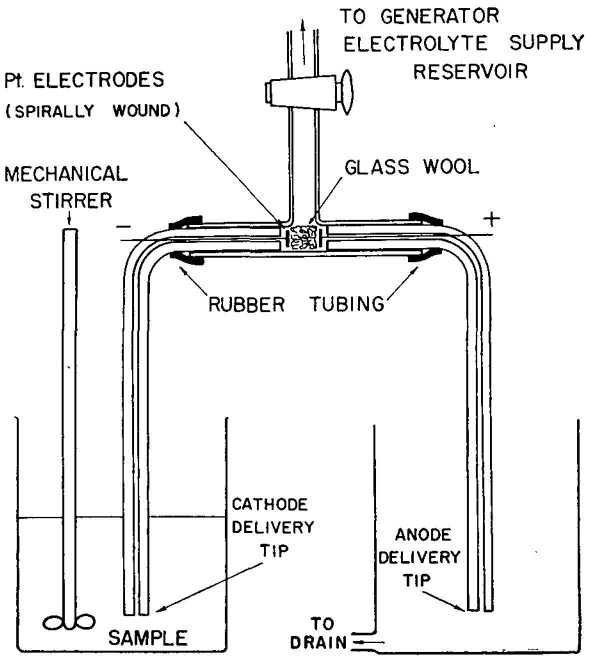

Figure 1. Generator Cell and Titration Assembly

Table I. Acid-Base Titrations

Sample	Taken	Time Calcd.	Time Obsd.	Found	Deviation from Mean	Error
	Me.	*Sec.*	*Sec.*	*Me.*	%	%
HCl	1.208	466.3	467.7	1.212	0.1	+0.3
			467.2	1.210	0.1	+0.2
			467.7	1.212	0.1	+0.3
			466.8	1.209	0.2	0.0
Av.			467.4	1.211	0.1	+0.2
HCl	2.417	933.0	936.3	2.426	0.1	+0.4
			937.0	2.427	0.0	+0.4
			938.4	2.431	0.1	+0.6
Av.			937.2	2.428	0.1	+0.5
NaOH	0.841	324.6	325.1	0.842	0.1	+0.1
			325.5	0.843	0.0	+0.2
			324.6	0.841	0.2	0.0
			326.1	0.845	0.2	+0.5
Av.			325.4	0.843	0.1	+0.2
NaOH	1.682	649.3	653.5	1.693	0.2	+0.7
			650.0	1.684	0.3	+0.1
			651.8	1.689	0.0	+0.4
Av.			651.8	1.689	0.2	+0.4
KHP[a]	1.266	488.7	490.8	1.271	0.0	+0.4
			491.7	1.274	0.2	+0.6
			490.5	1.271	0.0	+0.4
			490.1	1.270	0.1	+0.3
Av.			490.8	1.271	0.1	+0.4

[a] Potassium acid phthalate.

COULOMETRIC TITRATIONS WITH EXTERNALLY GENERATED REAGENTS

In all coulometric titrations that have been described to date, internal generation techniques have been employed—that is, the sample to be titrated was contained in the electrolysis vessel. While this technique is acceptable for many titrations, it fails completely in many others. The internal generation technique requires that the sample itself contain no substances which, under the titration conditions employed, undergo reactions at the electrode at which the reagent is generated. This requirement precludes the titration of acids by electrolytically generated hydroxyl ion in the presence of reducible substances, because these substances, as well as the water that forms the hydroxyl ions, are reduced at the cathode. Examples of similar limitations for many other titrations could be cited.

In order to circumvent these limitations, a new technique has been developed in this laboratory (*4*). The reagent is first generated at a constant current and with 100% current efficiency in a separate electrolysis cell, and is subsequently delivered to the container that holds the sample. This paper presents a summary of results obtained with this method when manual regulation of the current and visual indication of the equivalence point were employed. Titrations of acids and bases by means of externally generated hydrogen and hydroxyl ions, and titrations of tripositive arsenic with electrolytically generated iodine, have been studied. Subsequent publications will deal with automatic coulometric titrations employing the external generation technique.

APPARATUS

Generator Cell. The generator cell employed in these studies is shown in Figure 1.

A solution of a suitable electrolyte—one which, upon electrolysis, will yield the desired titrant—is fed continuously into the top center opening of the generator cell. This influent solution is then divided at the T, so that about equal quantities flow through each of the two arms of the cell. As these portions of solution flow past the electrodes, one in each arm, electrolysis occurs. The products of electrolysis are swept along by the flow of solution through the delivery arms and emerge from the delivery tips. A beaker containing the sample to be titrated is placed beneath the appropriate delivery tip. The generation is continued until an appropriate indicating system in the sample solution shows that the equivalence point has been reached.

The portion of the generator cell between the two electrodes is packed with glass wool in order to prevent mechanical mixing in this area. This simple precaution ensures that the products of electrolysis at each of the electrodes are quickly and quantitatively forced into the respective delivery arms. The spirally wound platinum wire electrodes provide a large surface for reaction as the solution passes through the turns of the spiral. The delivery arms are constructed from 1-mm. capillary tubing and thus have a small holdup volume (about 0.2 ml. each); the products of electrolysis at each electrode are therefore delivered from the cell to the titration beaker with very little delay. A stopcock placed in the line leading to the generator cell permits regulation of the rate of flow of solution into the cell. If necessary, the flow through the delivery tubes can be regulated by placing capillary bore stopcocks in one or both tubes.

Generator System. The simple electrical circuit used in these manual titrations is shown in Figure 2.

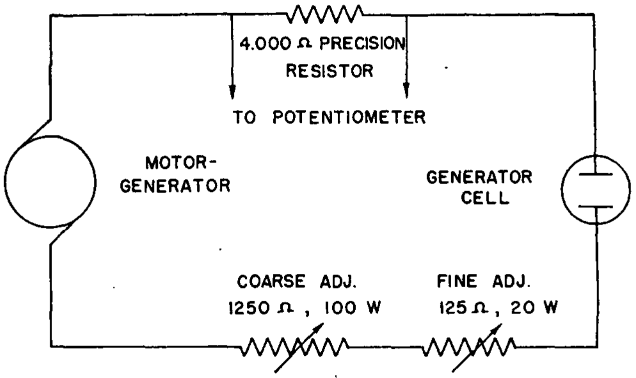

Figure 2. Electrical Circuit for Manual Titrations

A motor generator capable of delivering 260 ma. at 300 volts was used as a source of current. Although a potential of only 6 to 15 volts was required across the electrolysis cell, it was found that the current could be much more readily maintained at the desired value if a high voltage source with large series dropping resistors was employed. The electrolysis current was maintained at 250.0 ± 0.2 ma. for all experiments. The value of the current was determined by potentiometric measurement of the voltage drop across a 4.000-ohm resistor in series with the cell. The current-limiting variable resistors were adjusted during each titration in order to maintain the current at the desired value.

EXPERIMENTAL PROCEDURE AND RESULTS

Acid-Base Titrations. The generator electrolyte employed for all acid-base titrations was a solution approximately 1.0 *M* in sodium sulfate. Because the sodium sulfate occasionally contained appreciable amounts of sodium bisulfate, the solution was adjusted to a pH of 7.0 ± 0.5, when necessary, before use. When this electrolyte is employed, the cathode reaction is

$$2H_2O + 2e \longrightarrow H_2 + 2OH^-$$

and the anode reaction is

$$2H_2O \longrightarrow O_2 + 4H^+ + 4e$$

Acid is thus delivered from the anode arm of the generator cell, and base is delivered from the cathode arm. The gases formed are carried through the delivery arms by the solution flow and emerge at the delivery tips with the other products of the electrode reaction.

Titrations. The flow of generator electrolyte through the cell is adjusted so that about 0.1 ml. per second flows from each delivery tip. The current is turned on and adjusted to the desired generation rate. The beaker containing the solution of sample and indicator is placed beneath the appropriate delivery tip and simultaneously an electric timer is turned on. The solution is stirred vigorously with a mechanical stirrer during the course of the titration. When the equivalence point, indicated by the color change of the indicator, is reached, the stopclock is turned off and the time elapsed is recorded.

Typical results from a series of acid-base titrations are presented in Table I.

The samples of sodium hydroxide were prepared from a sodium hydroxide solution which had been standardized by conventional methods against reagent grade potassium acid phthalate. The hydrochloric acid samples were prepared from a solution of the acid which had been standardized by comparison with the standard sodium hydroxide solution. The potassium acid phthalate samples were prepared by direct weighing of the reagent grade salt. Bromocresol green–methyl red mixed indicator was used in the titration of the hydrochloric acid and sodium hydroiodide solutions, and phenolphthalein was used in the potassium acid phthalate titrations.

Iodometric Titrations. In two series of titrations the generator cell was employed to generate iodine by the electrolysis of 1.0 *M* potassium iodide solution (Table II). The samples employed were solutions of tripositive arsenic prepared by direct weighing of reagent grade arsenic trioxide. The sample solutions were all treated with sodium bicarbonate according to conventional procedures in order to maintain the proper pH for the titration. The apparatus and experimental technique were the same as for the acid-base titrations. Starch was employed as the indicator.

DISCUSSION

It is evident from Tables I and II that the external generation method is capable of excellent precision in both acid-base and iodometric titrations. The finite time that is required for mixing apparently causes a significant delay in indicator response at the equivalence point. This delay is believed to be the primary source of the small but consistent positive error which was observed in nearly all of the determinations. Automatic instruments which anticipate the approach of the end point, thus preventing overtitration, eliminate this systematic error (*3*).

Coulometric titrimetry, employing either the internal or the external generation techniques, offers several significant advantages over conventional titrimetric methods. The need for standard solutions is eliminated. A great range of sample sizes, with little change in apparatus or methods, is permitted. The application of automatic control is greatly facilitated. The method shows promise of great versatility; it has already been demonstrated that hydrogen and hydroxyl ions, chlorine (*5*), bromine (*7, 10–15*), and iodine (*16*), and cuprous (*6*) and ferrous (*2*) ions may be generated with 100% current efficiency for use as reagents in coulometric titrimetry. This list can undoubtedly be extended to provide a suitable reagent for almost all types of titrimetric determinations.

The external generation technique offers several significant advantages which are not possessed by the internal generation technique.

As the generator electrodes are not in contact with the sample solution, there can be no undesired reaction of any of the constituents of the sample at the electrode. Any titration that can be performed by conventional methods may be performed by the coulometric method, if the necessary reagent can be generated electrolytically with 100% current efficiency.

Optimum conditions for generation of the reagent and for performance of the titration can be achieved. As generation and titration are performed in the same solution in the case of internal generation, optimum conditions for one process must sometimes be sacrificed in order to secure satisfactory conditions for the other process. The external generation technique permits the composition of the generator electrolyte to be adjusted to give optimum conditions for the generation of the reagent, and at the same time the composition of the solution containing the sample may be fixed to ensure optimum conditions for the titration.

The technique shows promise of permitting the use of amperometric indication methods even at high generation rates. Amperometric (dead stop) indication furnishes a very precise and convenient method for the location of the equivalence point in many titrations. This method is especially valuable in coulometric titrations, because the response of the indicator system is rapid as compared with the slow attainment of equilibrium often encountered in potentiometric methods. The amperometric method cannot be employed with generation rates in excess of about 10 ma. when internal generation is employed. As the generator electrodes can be completely isolated from the sample solution in the case of external generation, parasitic currents in the indicator system may be largely eliminated. Work now in progress substantiates this conclusion (*9*).

Table II. Iodometric Determination of Arsenic

As Taken *Me.*	Time Calcd. *Sec.*	Time Obsd. *Sec.*	As Found *Me.*	Deviation from Mean %	Error %
1.152	444.7	445.1	1.153	0.1	+0.1
		442.9	1.147	0.4	−0.4
		445.7	1.155	0.3	+0.3
		444.5	1.152	0.0	0.0
Av.		444.5	1.152	0.2	0.0
2.303	889.0	893.6	2.315	0.2	+0.5
		891.0	2.308	0.0	+0.2
		889.3	2.304	0.2	0.0
		889.9	2.306	0.1	+0.1
Av.		891.0	2.308	0.1	+0.2

The necessity of employing a divided titration vessel to separate catholyte from anolyte is eliminated. The simpler titration vessel is more easily cleaned and preparation of the sample for analysis is simplified.

The generator cell may be used to prepare standard solutions to be used in conventional titrimetric methods. By electrolysis of a suitable stock solution for a measured period of time and collection of the electrolytically generated reagent in a suitable vessel, any desired amount of a given reagent may be prepared. The collected reagent may be diluted to known volume, for ready preparation of standard solutions of predetermined concentration with a minimum of effort. The necessity for standardization of reagent solutions is thus eliminated. Solutions of unstable reagents may be readily prepared as needed, thus eliminating storage and frequent restandardization.

Research directed toward the development of improved designs for the generator cell is now in progress. The feasibility of preparing several new reagents by electrolytic generation is also being studied.

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Automatic Coulometric Titrations with Externally Generated Reagents

Applications to Acidimetry and Alkalimetry

DONALD D. DEFORD, CARLTON J. JOHNS, AND JAMES N. PITTS
Northwestern University, Evanston, Ill.

IN PREVIOUS papers (*2*, *3*) the authors outlined the fundamental principles of coulometric titrations with externally generated reagents and presented the results of typical manual titrations. One of the major advantages of coulometric titrations is the ease of making the process completely automatic. The reagent in all coulometric titrations is an electric current, which can readily be regulated, measured, and controlled through the application of conventional electrical circuits.

Many automatic instruments for use with standard solutions of the titrant have been described (*1*, *5*, *9*, *10*, *13*). At least two, one manufactured by the Precision Scientific Co., 3737 Cortland St., Chicago 47, Ill., and the other manufactured by Beckman Instruments, Inc., South Pasadena 15, Calif., are now available commercially. Automatic coulometric analysis by the direct method has been explored by Lingane (*7*) and by Lingane and Small (*8*). In both of these studies the electrolysis electrodes were placed in the solution containing the sample, and the working electrode was operated at a suitable constant potential which permitted only the desired electrolysis reaction to occur. The completion of the electrolysis was indicated by a cessation of the electrolysis current, and the number of coulombs required was determined by means of a coulometer in series with the electrolysis cell.

The only previous work in the field of automatic coulometric titrations is that of Shaffer, Briglio, and Brockman (*12*), who used a continuous automatic titrator for determining the concentration of mustard gas in air. They passed air through the titration assembly at a constant rate and generated bromine electrolytically at a rate that was just sufficient to react with the mustard vapor. The generation current thus provided an instantaneous and continuous measure of the concentration of the mustard vapor in the air. No previous studies on the automatic coulometric titration of discrete samples have been described.

The present paper describes an instrument for the automatic performance of coulometric titrations with externally generated reagents. This instrument employs a constant and carefully regulated electrolysis current. The number of coulombs of electricity required for the titration is then determined from the product of the current and the time. The end point in the titration is detected by means of an ordinary Beckman Model G pH meter, which actuates a relay and thus terminates the titration when the equivalence point pH has been attained.

APPARATUS

Automatic coulometric titrations by means of the constant current technique require an instrument that is capable of maintaining a constant electrolysis current during the titration, detecting the end point, and terminating the titration at this point.

Current Regulator. The complete electrical circuit of the current regulator is shown in the lower half of Figure 1. Its operation is best explained by reference to the simplified semiblock diagram shown in Figure 2.

The regulator is placed in operation by adjustment of resistances R_2, R_9, and R_{12}, so that the desired electrolysis current, indicated either by the meter, M_1, or by the potential drop across the precision resistor, R_{11}, is passing through the generator cell, and so that about one half the maximum plate current is flowing through the 117L7 control tube. Meter M_2 should read about 40 ma. If now the resistance of the generator cell should increase, a momentary decrease in current through the cell, and hence also through resistors R_9, R_{10}, R_{11}, and R_{12}, will result. The decrease in current through these resistors causes a decrease in the input potential to the direct current amplifier. This small decrease in input potential is amplified, and results in a comparatively large decrease in the output potential, which is applied to the grid of the control tube. The decrease in grid potential of this tube causes a reduction in the plate current through the tube. As the plate current of the tube passes through the resistor, R_1, the diminution in plate current results in a diminution of the current passing through this resistor. The lower current through the resistor decreases the potential drop across the resistor and hence makes point *a* more positive. The entire operation thus results in an increase in the potential across the electrolysis cell. The increased potential applied to the cell tends to compensate for the increased resistance and hence maintains the current at a constant value. The operation of the circuit in compensating for changes in the supply voltage follows a similar pattern.

This regulator differs from most current regulators which have been described previously in that the load current is not required to pass through the control tube. This feature is a significant advantage when generation currents in excess of about 100 ma. are being employed. This by-pass regulator permits regulation

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In the final analysis all coulometric titrations employ an electric current as the titrant. Because electric currents are readily susceptible to automatic regulation and control, this type of titration can be performed automatically with comparative ease. An automatic instrument for the performance of coulometric titrations with externally generated reagents has been employed successfully in several acid-base titrations with externally generated hydrogen and hydroxyl ions. The average error for individual determinations is slightly less than ±0.3%. As the entire titration is automatic, and no standard solutions are required, only a few seconds of operator time are required for each titration.

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of generation currents of at least 500 ma. by means of a single tube which has a maximum plate current of about 80 ma.

The values of the circuit components given in Figure 1 are suitable for an electrolysis current in the neighborhood of 250 ma. By appropriate changes in the values of resistors R_1, R_2, R_9, R_{10}, R_{11}, and R_{12}, any desired electrolysis current between 10 and 500 ma. may be secured.

In order to achieve maximum stability and freedom from drift, the direct current amplifier employed in the regulator is battery-operated. The 115-volt direct current was obtained from the laboratory supply, which originated from a bank of storage batteries.

After an initial warm-up period of about 15 minutes, the current drift at a generation rate of 250 ma. has never been observed to exceed 5 parts in 10,000 over a period of 1 hour. The variation in current for a change in supply voltage of ±4 volts or for a change in cell resistance of ±16 ohms is less than 5 parts in 10,000 at a generation rate of 250 ma.

Terminator Circuit. The terminator circuit is shown in the upper half of Figure 1.

The terminator consists essentially of a Beckman Model G pH meter, the output of which is connected to a lamp and scale galvanometer, and a photo relay unit which is actuated by the light beam from the galvanometer.

Two binding posts, connected by internal leads to the terminals of the null point indicating meter, were affixed to the Beckman meter in the manner described by Lingane (*6*). These posts were then connected through the voltage-dividing network, R_{13}–R_{14}–R_{15}, to the galvanometer terminals of a Leeds & Northrup No. 2420c lamp and scale galvanometer. The resistors in the voltage-dividing network were chosen so that the galvanometer index would traverse its full scale as the null meter of the Beckman instrument traversed its full scale. The galvanometer is critically damped to prevent response to erratic fluctuations in the reading of the pH meter. The connection of the voltage-dividing network and galvanometer to the pH meter in no way affects the operation of the pH meter. The zero of the galvanometer was adjusted so that the index was in the center of its scale when the Beckman meter was at the null position. The ground-glass scale of the galvanometer was removed and replaced by a light shield covering half of the opening.

The photo relay unit (G. M. Laboratories photo relay unit, Catalog No. 1222-E) was placed directly in front of the opening in the galvanometer case and was adjusted so that the relay was actuated when the galvanometer index passed the end of the light shield. The photo relay was then connected to a double-pole double-throw power relay which makes and breaks the necessary circuits for starting and stopping the titration.

The direction switch, S_3, is included in the circuit so that the titration may be terminated by movement of the pointer of the Beckman null meter from right to left or from left to right past the null position, whichever is required for the titration. The operation switch, S_5, makes possible preliminary adjustments and preparations for the titration with the generator cell disconnected from the circuit (OFF position). The titration is then begun by throwing this switch to the ON position. The pilot light, P_2, indicates that a titration is either in progress (operation switch on) or will begin as soon as the operation switch is turned on. The reversing switch, S_4, permits the electrodes of the generator cell to be operated at the desired polarity.

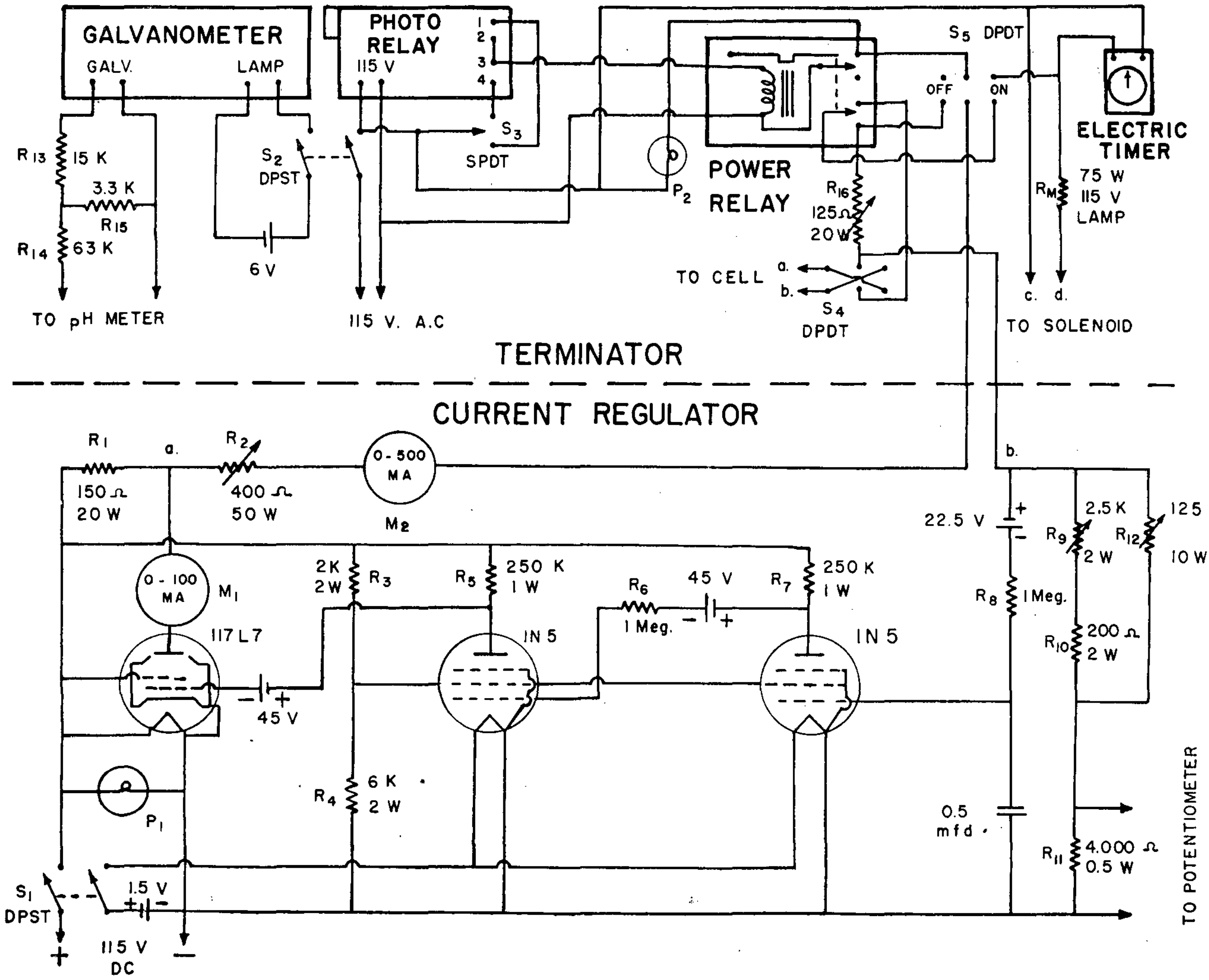

Figure 1. Electrical Circuit of Titration Instrument

The rheostat, R_{16}, is automatically switched into the circuit in place of the generator cell whenever a titration is not in progress. This rheostat is adjusted so that its resistance is the same as the effective resistance of the generator cell. (The effective resistance of the generator cell is defined as the potential applied to the cell divided by the current flowing through the cell.) Because the current regulator drifts badly until it has been in operation long enough for the resistors to come to temperature equilibrium, the rheostat must be provided so that the regulator will continue in operation at all times.

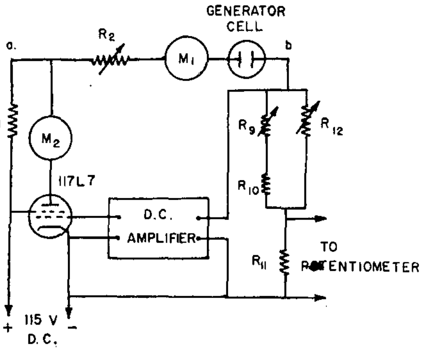

Figure 2. Semiblock Diagram of Current Regulator

The same power relay which controls the electrolysis current also controls the operation of an electric timer and a solenoid valve. The value of the resistance, R_n, in series with the solenoid was selected empirically to provide the maximum current through the solenoid which would not result in overheating.

Titration Assembly. The titration assembly is shown in Figure 3.

The titration vessel was a 400-ml. beaker into which the electrodes of the pH meter, an electric stirrer, and one delivery arm of the generator cell were dipping. The generator cell has been described (*2*, *3*). The generator electrolyte was supplied to the cell by hydrostatic pressure from an overhead stock bottle. A solenoid valve in the supply line permitted solution to flow to the cell during the titration and terminated the flow at the end of the titration. The flush-out tube, which becomes filled with electrolyte when the solenoid valve is opened, was provided to supply a few milliliters of electrolyte to flush all products of electrolysis out of the generator cell at the end of the titration.

The rate of flow of electrolyte through the generator cell was maintained at about 0.2 ml. per second (0.1 ml. per second through each delivery arm). The flow rate was not carefully controlled, as it appeared to have no effect on the results. Very slow flow rates were avoided, because the products of electrolysis must be delivered to the titration beaker without significant delay.

The glass electrode was placed approximately 5 mm. from the delivery tip of the generator cell and in such a position that the rotating liquid in the titration vessel passed from the delivery tip toward the glass electrode. Because an appreciable time is required for the stirrer to accomplish complete mixing, it is essential that the glass electrode be placed very close to the delivery tip if overtitration is to be avoided. There is no danger of error due to incomplete titration; the generator is automatically turned on again if, after mixing is complete, the pH meter indicates that the set equivalence point pH has not been passed.

PROCEDURE

The following procedure was followed in the performance of all titrations.

1. Fill the generator electrolyte reservoir with a solution that is approximately 1.0 *M* in sodium sulfate. Adjust the pH to 7.0 ± 0.5, if necessary, by addition of dilute sodium hydroxide or dilute sulfuric acid.
2. Set the operation switch, S_5, in the OFF position.
3. Adjust the resistance of the rheostat, R_{16}, so that it is equal to the effective resistance of the generator cell.
4. Turn on the power switches, S_1 and S_2.
5. Set the resistance of R_9 at about one half of its maximum value, and adjust rheostats R_2 and R_{12} so that a current of 250 ma. is indicated by M_2 and a current of about 40 ma. is indicated by M_1. Allow 15 minutes for the apparatus to warm up, and then repeat the adjustment of R_2 and R_{12}, if necessary.
6. Adjust R_9 as necessary, so that the potentiometer indicates a current of 250.0 ma. through the precision resistor.
7. Turn on and calibrate the pH meter in the conventional manner as outlined in the manufacturer's instructions.
8. Set the direction switch, S_3, so that control in the desired direction is obtained.
9. Set the reversing switch, S_4, so that the generator electrodes are of the desired polarity.
10. Place the sample, dissolved in about 150 ml. of water, in the titration beaker.
11. Set the drum on the pH meter to read the desired titration exponent—the pH of the equivalence point.
12. Lock the push button on the pH meter down.
13. Turn the stirring motor on.
14. Set the electric timer at zero.
15. Turn the operation switch to the ON position to start the titration.
16. Check the current by means of the potentiometer and, if necessary, repeat operation 6. (If rheostat R_{16} has been set at the proper value, no further adjustment of current will be necessary.)

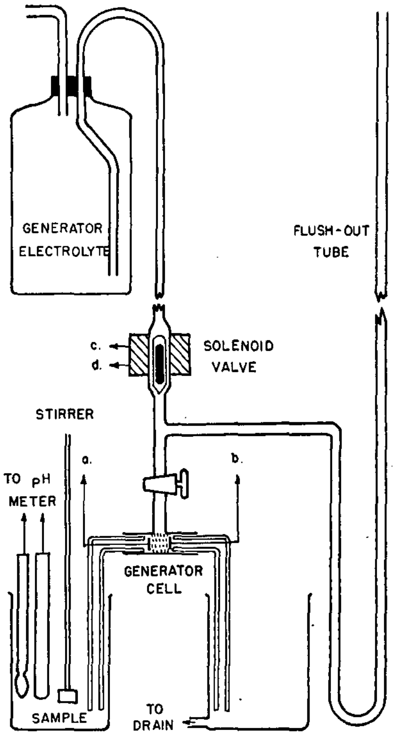

Figure 3. Titration Assembly

17. When the titration has been completed, as indicated by the pilot, P_2, return the operation switch to the OFF position and read the electric timer.
18. Calculate the number of milliequivalents in the sample from the relationship

$$\text{Me.} = \frac{\text{current (amperes)} \times \text{time (seconds)}}{96.5}$$

After the preliminary adjustments have been accomplished, the operations that must be carried out by the analyst for each titration are very few and simple. It is necessary only to place the sample in the titration beaker, return the timer to zero, and start the titration by turning the operation switch on. At the end of the titration the operation switch is returned to the OFF position and the reading of the electric timer is recorded.

RESULTS AND DISCUSSION

The results of several series of typical acid-base titrations are summarized in Table I. The hydrochloric acid and sodium hy-

Table I. Results of Typical Titrations

Sample	Taken	Time Calcd.	Time Observed	Found	Deviation from Mean	Error
	Me.	*Sec.*	*Sec.*	*Me.*	%	%
HCl	0.2444	94.3	94.3	0.2444	0.0	0.0
			94.4	0.2446	0.1	+0.1
			95.1	0.2464	0.9	+0.9
			94.2	0.2440	0.2	−0.2
			94.3	0.2444	0.0	0.0
			93.6	0.2425	0.8	−0.8
Av.			94.3	0.2444	0.3	0.0
HCl	1.222	471.7	473.4	1.226	0.4	+0.3
			469.3	1.216	0.4	−0.5
			472.4	1.224	0.2	+0.2
			470.2	1.218	0.2	−0.3
			471.6	1.222	0.1	0.0
			472.1	1.223	0.2	+0.1
Av.			471.5	1.221	0.2	−0.1
HCl	2.444	943.4	938.0	2.430	0.4	−0.6
			941.1	2.438	0.0	−0.2
			943.5	2.444	0.2	0.0
			939.4	2.434	0.2	−0.4
			941.0	2.438	0.0	−0.2
			945.1	2.448	0.4	+0.2
Av.			941.4	2.439	0.2	−0.2
NaOH	1.268	489.4	485.7	1.258	0.9	−0.8
			489.5	1.268	0.2	0.0
			494.2	1.280	0.8	+0.9
			490.0	1.269	0.1	+0.1
			491.2	1.273	0.2	+0.4
			490.3	1.270	0.0	+0.2
			490.8	1.271	0.1	+0.2
Av.			490.2	1.270	0.3	+0.2
KHP[a]	1.347	520.0	521.5	1.351	...	+0.3
	0.864	333.6	335.0	0.868	...	+0.5
	0.973	375.6	376.2	0.975	...	+0.2
	0.727	280.5	280.9	0.728	...	+0.1
	2.677	1033.4	1032.0	2.673	...	−0.1
	2.086	805.3	805.2	2.086	...	0.0
	2.245	866.7	865.0	2.241	...	−0.2
	2.516	970.9	971.9	2.518	...	−0.1
Av.	...	...	...	...	....	+0.1
Na_2CO_3	0.821	316.9	317.8	0.823	...	+0.2
	0.892	344.3	348.1	0.902	...	+1.1
	1.129	435.8	436.9	1.132	...	+0.3
	0.668	257.8	258.9	0.671	...	+0.4
	0.433	167.9	167.4	0.434	...	+0.2
Av.	...	...	...	...	....	+0.4

[a] Potassium acid phthalate.

droxide samples were aliquots of solutions that had been carefully standardized by conventional procedures. The potassium acid phthalate and the sodium carbonate samples were prepared by direct weighing of the reagent grade salts.

The average deviation of individual results from the mean is of the order of 0.2 to 0.3% for all systems studied. The results of more recent work in this laboratory indicate that precisions much better than this can be obtained with careful work. Hooker (*4*) has recently completed a series of titrations of hydrochloric acid samples in which the average deviation of individual results from the mean is of the order of 0.04 to 0.06%.

With the exception of the determinations of sodium carbonate, positive and negative errors occur in approximately equal numbers, indicating the absence of any systematic error in the method.

The analysis of the sodium carbonate samples was based upon the titration of carbonate with hydrogen ions to form bicarbonate. The errors in the results obtained in this series of determinations are remarkably small in view of the small slope of the titration curve at the equivalence point. The consistent positive error would seem to indicate that the titration was not terminated exactly at the equivalence point. Preliminary titrations of sodium carbonate by conventional methods indicated that the equivalence point occurred at a pH of 8.0; the pH meter was, therefore, adjusted to terminate the titration at this pH. A second series of titrations was performed in which the titration was terminated at pH 8.3, which is the theoretically predicted pH for the equivalence point if values of 4.3×10^{-7} and 5.6×10^{-11} are employed for the acid dissociation constants of carbonic acid. This series of titrations gave results which were consistently low by an average of 1.5%. It would appear that a pH of about 8.1 should be selected as the proper point at which to terminate this particular titration.

CONCLUSIONS

Automatic coulometric titration of acids and bases can be accomplished with a precision and accuracy which are adequate for most determinations. After initial adjustment of the instrument, only a few seconds of the analyst's time are required for each titration.

Work now in progress in this laboratory indicates that the terminator circuit may also be actuated by an amperometric indicator system connected directly to the terminator galvanometer (*11*). Still other indicating devices may be made to actuate the terminator.

By using the current regulator described above in conjunction with a recording pH meter, it should be possible to record titration curves of acids and bases automatically. This matter is now being investigated.

The coulometric titration method appears to be well adapted to continuous automatic titrations, and thus provides a means of obtaining a continuous record of instantaneous concentrations in flow processes. An instrument for the continuous automatic titration of acids in the effluent solution from a chromatographic column, now being tested, generates hydroxyl ion at a rate just sufficient to neutralize the acids as they emerge from the chromatographic column. A recording ammeter in series with the generator cell provides a continuous record of acid concentration in the effluent as a function of time.

The necessity of having a supply of 115-volt direct current for the current regulator described is a distinct disadvantage. Instruments operating directly from 115-volt alternating current are now being tested. Improved terminator circuits which are less bulky and more rugged than the one described are also being tested.

ACKNOWLEDGMENT

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Coulometric Titrations with Electrically Generated Ceric Ion

N. HOWELL FURMAN, W. DONALD COOKE, AND C. N. REILLEY
Princeton University, Princeton, N. J.

Because ceric salts are usually prepared by electrolytic oxidation of cerous salts, the application of this process to coulometric analysis seemed possible. This oxidation was found to proceed at essentially 100% efficiency. The resulting ceric ion was used to oxidize samples of ferrous sulfate present in the electrolyzed solution. The electrolytic oxidation was carried out at a constant known current and the time required to reach a potentiometric end point was measured. By employing a current source which was regulated electronically, a controlled current, constant to within 0.01%, was realized. The average error of the coulometric method in the titration of ferrous sulfate was 0.07%. The results indicate that this coulometric process is practical and that it may be extended to other titrations utilizing ceric ion.

THE electrolytic oxidation of cerous salts has long been used as a method for the preparation of ceric salts. It has been shown that such oxidation may proceed at 100% current efficiency (*4*). It therefore seemed advantageous to study the coulometric generation of ceric sulfate and the use of this reagent in analytical oxidations by the process of coulometric titration or in other ways.

The use of chlorine, generated coulometrically, as a strong oxidant has been investigated (*1*). Ceric sulfate is a more powerful oxidant in acidic solutions and is more generally applicable. In this investigation, ceric ion was generated quantitatively at a platinum anode and applied to the coulometric titration of solutions of ferrous ion.

The electrolytic oxidation was carried out at constant current, using an electronic circuit (*3*). In this way, the value of the current could be controlled automatically with high precision. The end point was determined potentiometrically.

As oxygen was found to interfere to a slight extent, the titrations were carried out in an inert atmosphere. A negative error equivalent to about 0.01 ml. of 0.1 *N* ferrous solution was found if air was not excluded. Chloride ion, because it has a lower oxidation potential than ceric sulfate, was found to be anodically oxidized. Large amounts of sodium ion caused a precipitation of a slightly soluble $Na_2SO_4.Ce_2(SO_4)_3.2H_2O$.

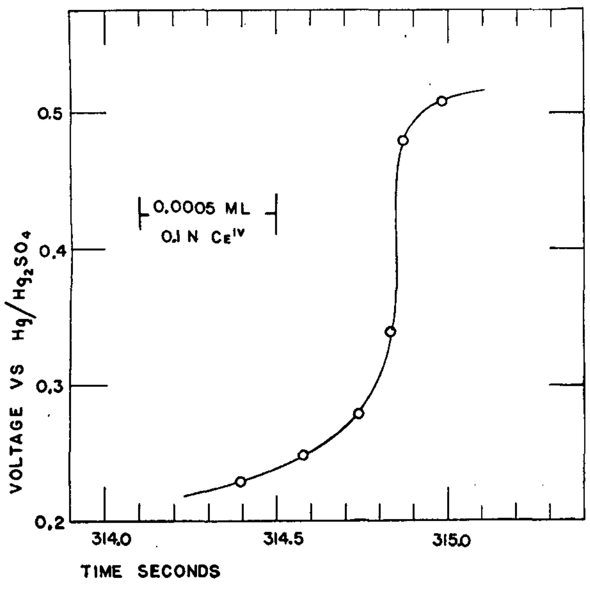

Figure 1. Titration Curve at 25 Milliamperes

The titrations were carried out in a 3 *N* sulfuric acid medium which gave a somewhat sharper and more rapidly attained end point than the 1 *N* concentrations usually used. The end point could be easily determined to within 0.05 second in all instances without plotting the potential curves. This was possible because in coulometric procedures much smaller increments of reagent can be generated in the vicinity of the end point than can be added with the use of a buret. In the titration of 0.1 *N* solutions using a current of 25 ma., amounts of titrating agent can be added which are equivalent to 5×10^{-5} ml. of 0.1 *N* reagent (generation interval, 0.02 second). The addition of such small quantities of reagent would otherwise be extremely difficult in macroprocedures. The potential values near the end point were rapidly attained after the addition of each increment when a sulfuric acid concentration of 3 *N* was used. The precision with which the end point can be obtained is shown in Figure 1.

APPARATUS

Electrical Circuit. The electronic circuit used to maintain the current through the cell has been described (*3*). During a 15-minute run, the value of the current varied less than 0.01%.

Current Measurement. The value of the current was determined by measuring the voltage drop across a standard resistance by means of a potentiometer. A resistance box rated at 0.01% (Otto Woulff, Berlin) was used as the resistance standard. The 10-ohm resistance in this box was checked against a Woulff 10-ohm standard which had a value 10.000. The other resistances in the box were then checked against this 10-ohm value in a manner similar to calibration of a set of weights. A Leeds & Northrup student potentiometer was calibrated at a single point against a new standard Eppley cell, and was subsequently used only in the neighborhood of the calibrated point. This was accomplished by choosing an appropriate value of the resistance over which the voltage drop was to be taken.

Time Measurement. An electric clock (Standard Electric Time Co., Type S-6) employing a synchronous motor was used to time the generation intervals. This clock is equipped with a magnetic clutch which has a start-stop error of about 0.01 second per operation.

Titration Cell. The titration cell used in this work is shown in Figure 2. The various electrodes used were made interchangeable to increase the versatility of the apparatus. The indicator and reference electrodes could be removed for cleaning, as well as the cathode and cathode compartment. The large platinum anode could not be removed from the apparatus, but it was mounted with an interchangeable ground glass joint, so that the electrode could be easily replaced in case of damage. A fifth ground-glass joint was provided, so that the solution could be swept with carbon dioxide. Stirring was accomplished by means of a magnetic stirrer. The mercury-mercuric sulfate (ca. 10% sodium sulfate) electrode was found to be 0.41 volt positive to the saturated calomel electrode (0.66 volt *vs. N* hydrogen electrode).

The platinum anode at which the ceric ion was generated was a 2.5 × 2.5 cm. piece of No. 28 B. and S. foil. A 1 × 2 cm. piece of foil was used as the cathode, but the size of this electrode is unimportant.

The cathode was isolated from the solution that was being titrated in a separate cathode compartment filled with 15% solution of ammonium sulfate. The level of this solution was kept above that of the solution being titrated to prevent diffusion losses. Electrical connection was made through a sintered-glass disk prepared according to the method of Kirk (*2*). This disk should not have too high an electrical resistance, because the heat generated would cause the solution to boil. On the other hand, it should not be so coarse that the catholyte runs out too rapidly. A disk with a resistance of 100 to 250 ohms at 100 ma. was found to be satisfactory.

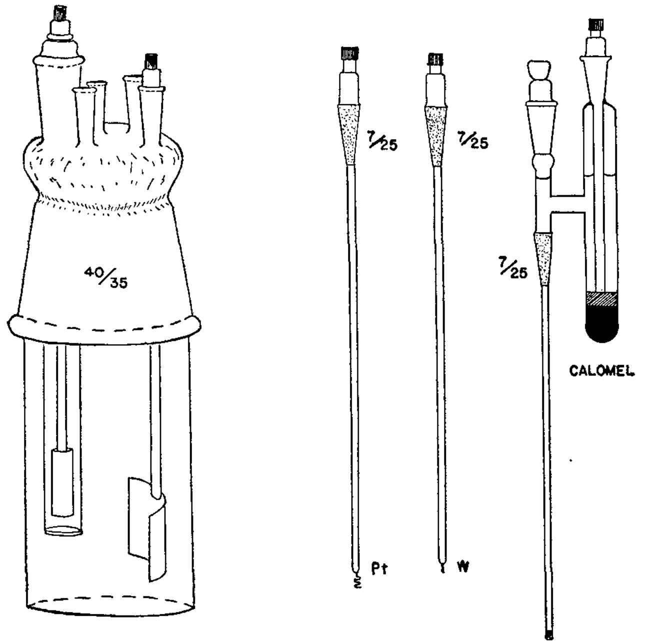

Figure 2. Titration Cells and Replaceable Electrodes

For the potentiometric indication of the end point, a platinum wire indicator electrode was used in conjunction with a calomel or a mercurous sulfate reference electrode. Measurement of the potential across the electrodes was followed with a Beckman Model G pH meter. Other and simpler means could presumably be used for indication.

REAGENTS

Cerous Sulfate Solution. A saturated solution (ca. 12%) of reagent grade cerous sulfate octahydrate (G. F. Smith Chemical Co.).

Standard Ferrous Ammonium Sulfate Solution. A 0.1 *N* solution of ferrous ammonium sulfate was standardized twice daily against a solution of Bureau of Standards potassium dichromate. To increase the accuracy of this titration, the ferrous ammonium sulfate solution was made slightly stronger than the potassium dichromate standard solution. Fifty milliliters of each solution were then pipetted, with the same pipet, into a flask. The excess ferrous ion was titrated potentiometrically (platinum-calomel) using a 5-ml. microburet. A precision of 0.01 ml. or 0.02% was obtained in this fashion.

A 0.02 *N* solution of ferrous ammonium sulfate was prepared by dilution of standardized 0.1 *N* solution. This dilution was carried out in an atmosphere of carbon dioxide, using oxygen-free water. This solution was stored under carbon dioxide and discarded after a few hours.

Table I. Titrations with Ferrous Ion

Fe Taken *Mg.*	Current *Ma.*	Time *Sec.*	Fe Found *Mg.*	Error %
54.70	127.60	741.6	54.76	0.11
	127.59	741.4	54.74	0.07
50.21	127.68	679.9	50.22	0.02
	127.71	678.3	50.13	−0.16
	127.71	679.8	50.24	0.06
	127.54	679.6	50.16	−0.10
27.22	127.56	368.9	27.23	0.04
	127.51	368.6	27.20	−0.07
	127.56	369.0	27.24	0.07
24.88	127.84	336.1	24.86	−0.08
	127.88	335.8	24.85	−0.12
	127.84	336.0	24.86	−0.08
10.800	39.79	469.0	10.798	−0.02
	39.79	468.4	10.785	−0.15
	39.78	469.4	10.808	0.08
	39.78	469.3	10.805	0.05
	39.78	469.0	10.798	−0.02
	39.78	469.3	10.805	0.05
5.376	39.78	233.9	5.385	0.17
	39.76	233.6	5.374	−0.04
	39.76	233.5	5.372	−0.07
	39.76	233.7	5.377	0.02
	39.76	234.1	5.386	0.19
	39.76	233.6	5.374	−0.04

PROCEDURE

Twenty milliliters of saturated cerous sulfate solution and 5 ml. of 18 *N* sulfuric acid were placed in the titration cell, and a rapid stream of carbon dioxide was passed through the solution for a few minutes. Tank gas was used without purification because the error introduced by air oxidation is small. The sample to be titrated was then pipetted into the cell, and the electrolysis begun. The potential of the platinum indicator electrode was followed and the titration carried out as in an ordinary potentiometric titration, except that the oxidant was added electrically. In the vicinity of the end point it was necessary to wait about 5 to 10 seconds for the potential to reach equilibrium. A sharp potential break was obtained and the end point could be easily noted without plotting the potential curves. If care was taken to stop the titration just at the end point, another sample could be pipetted into the cell and titrated without removing the original.

The results of twenty-four titrations with amounts of ferrous ion between 5 and 50 mg. are shown in Table I. The average error of these determinations was 0.07%.

ACKNOWLEDGMENT

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Measurement of Molecular Weight in Organic Solvents

Thermoelectric Method

GUY B. TAYLOR AND MAURICE B. HALL

Experimental Station, E. I. du Pont de Nemours & Co., Inc., Wilmington, Del.

The object of the investigation was to measure molecular weights in organic solvents by a procedure hitherto reported as useful only for water as the solvent. A method was developed for measuring molecular weights with the same precision as advanced ebullioscopic procedures but near room temperature. It is useful for measuring the molecular weights of substances unstable at the boiling points of their solvents, and provides a large extension in the number of useful organic solvents over those having sufficiently stable boiling points for ebullioscopy. Solvents do not require rigorous purification, and in favorable cases a complete measurement may be made with as little as 5 mg. of material.

THE proposal by Hill (*6*) of observing the temperature difference between two different solutions or between a solution and solvent when opposing thermopile junctions are wet with the two in an atmosphere saturated with the solvent vapor was considerably improved by Baldes (*1–3*), who substituted a single couple for the thermopile. The method yields information on osmotic behavior reflected in vapor pressure differences, and hence on the molecular weight of the solute. It appears to have been used exclusively for aqueous systems (*5, 10, 12–15*). For molecular weight measurement where the chamber is presumed to have its atmosphere saturated with the pure solvent vapor, with solvent on one junction of the couple and a solution of the nonvolatile substance under test on the other, the underlying principle is that of the ordinary ebullioscopic method.

The present paper is concerned with an adaptation of this method to organic solvents and use of the modified technique in determining molecular weights. The authors' constructions of fine-wire couples as described by Baldes and Johnson (*3*), comprising tiny circular loops held in a horizontal plane, failed to support organic liquid drops although readily holding water. Exactly the opposite is true of the modified apparatus described here. Couples of the new type readily hold pendent drops of organic liquids but not water.

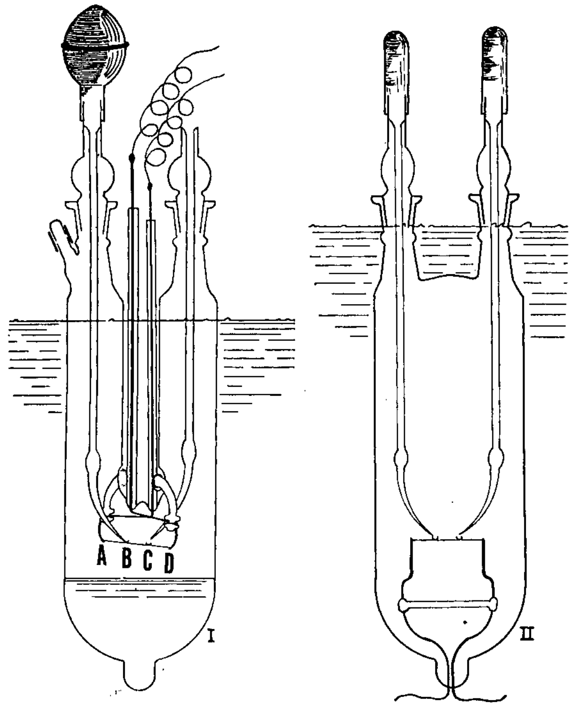

Figure 1. Modified Baldes Apparatus for Molecular Weight

APPARATUS

The two forms of apparatus constructed are shown in Figure 1.

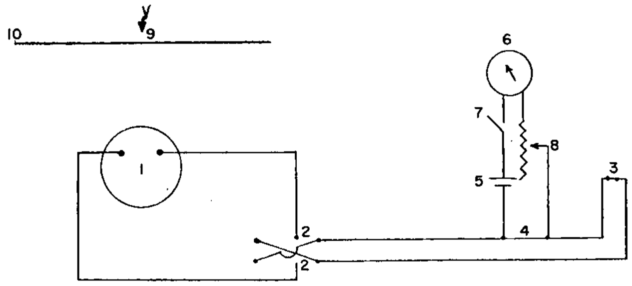

Figure 2. Wiring Diagram for Thermoelectric Method

1. Galvanometer
2. Knives of double-pole double-throw switch
3. Thermocouple in cell
4. Fixed resistance, 0.001 ohm
5. Dry cell battery
6. Milliammeter, 0–5 ma.
7. Switch
8. Variable rheostat
9. Point-o-lite lamp
10. Meter scale marked in mm.

The lead-in wires are of pure No. 18 gage copper and are brought through the walls of the glass cell by flattening short portions and then sealing through Nonex brand glass, which in turn is attached to the Pyrex brand glass of the cell through a graded seal. The thermocouple, supported horizontally from *A* to *D*, is made of 2-mil wire, *B* to *C* constantan, *A* to *B* and *C* to *D* Manganin for cell I and copper for cell II. To make the junctions at *B* and *C* the upper electrode of a spot welder is shaped to fit into stamped-out thin platinum cups about 1 mm. in diameter and the fine wires are held against the bottom of a cup during welding by the flat lower electrode. The wire on either side of both junctions is coated with Teflon tetrafluoroethylene resin (*4*), a chemically inert nonwetting material, to prevent liquid running along the wire. The resin is applied from an aqueous dispersion and subsequently baked at about 300° C.

At the top of the cell are two small, unlubricated ground joints for mounting droppers (capacity 1 ml. or less) equipped with small rubber squeeze bulbs and fine tips, so arranged that by turning the tips may be brought directly over the cups on the junctions and about 5 mm. above them. The cell is mounted in a thermostated water bath capable of control to 0.003° C. Type I was used in a bath at 20° C. when the room was about 25° and hence there was no danger of solvent dew on its exposed part above the water level. Type II was operated at 30° C., but because the part above water level is negligible, it can be operated at any convenient temperature. The lead wires from the bottom of this cell are coated with waterproof resin.

The electrical circuit (Figure 2) is the same as given by Baldes

(*3*) with a Leeds & Northrup high sensitivity galvanometer (Type 2284, resistance 14.3 ohms, rated at 0.05 microvolt per mm. on a scale at 1-meter distance) as the registering instrument for the couple. The resistance of the galvanometer is about equal to that of the rest of the circuit. It was found necessary in practice to mount the galvanometer firmly on a pier free from vibration, and to take considerable care that no extraneous e.m.f. was generated anywhere in the circuit. This latter was accomplished only when all metal except copper was removed from the circuit and all connections (except at the galvanometer itself) were soldered with a solder giving no e.m.f. against copper.

PROCEDURE

Pure solvent is placed in the cell to a level about 1.5 cm. below the horizontal thermocouple wire and both droppers are filled with solvent. The assembled cell is placed in the bath. The lead-in wires are soldered to the circuit with the double-pole, double-throw switch open.

When the cell and contents are at bath temperature, about half an hour after mounting, the droppers are turned with their tips directly over the junctions and several drops of solvent are delivered to each. It is then best to turn the dropper tips away. Alternate drops will hang below the cup and be swept away by the subsequent drop. The size of the drop does not affect observations, even when the drop on one couple is large and pendent and on the other considerably smaller and not pendent. After about 2 minutes readings are taken with the galvanometer by throwing in the switch, first one polarity and then the other. The difference in the two readings is recorded as the blank correction and is to be subtracted from all subsequent observations.

In measurements with organic solvents there is an initial disturbance when putting on the drops, then deflections are steady enough for repeat readings over a period of 5 or 10 minutes, though there probably is always a continuous downdrift with time. In a typical case the deflections were followed to 80% of the initial value in 5 hours on a slightly curved line. If a drop is pendent at the start, it will fall off in 24 hours because of the increase in size. The drop on the solvent junction does not change in visible size during this period.

To calibrate the galvanometer readings in centimeters in terms of microvolts per centimeter, the battery is connected to the test voltage (switch 7, Figure 2) and readings are taken at two or more positions of the milliammeter.

A convenient material with which to determine a calibration constant, k, for any particular lot of solvent is benzil, molecular weight 210. Solutions 1 to 3% by weight are satisfactory. Solvent in one of the droppers is replaced by solution. After 15 minutes, ten or more drops of solution are delivered in succession to its junction and galvanometer observations are made shortly afterward. It is well to repeat the operation. Measurements of unknowns are made following calibration with benzil and in the same way on the same junction as used for calibration. The pool of solvent is sufficiently large to permit calibration and subsequent measurements of several concentrations of unknowns without having to be replaced.

Calculations. All galvanometer readings, S, are centimeter total throw from plus to minus polarity, corrected by the blank obtained with solvent on both junctions

S_1 = cm. for A milliamperes, equivalent to microvolts
S_2 = cm. for benzil solution at concentration b (grams per 100 grams of solvent)
S_3 = cm. for unknown at concentration c
E = A/S_1, microvolts per cm.

$$k = \frac{210\,S_2E}{b}$$

$$\text{Molecular weight} = k\,\frac{c}{S_3E}.$$

DISCUSSION AND RESULTS

Although this adaptation of the thermoelectric method for organic solvents was developed primarily for measuring molecular weights of substances not soluble in water, the use of such solvents is advantageous because they give higher e.m.f. and k values. In Table I are listed theoretical values, k', for a number of solvents based on the ebullioscopic formula

$$\Delta t^\circ = \frac{RT^2}{q} \times \frac{n}{W}$$

where n is moles of solute in W grams of solvent with q calories of latent heat per gram at 30° C. derived from slopes of vapor-pressure plots. In units used in this paper $W = 100$ and $n = E_0/k'$, where E_0 is expressed in microvolts. If the couple gives 40 microvolts per degree, substitution gives $k' = 72900/q$. (This is an approximation influenced by both the quality of the copper and constantan wires and the exact value of resistance 4 in Figure 2 as well as the accuracy of the milliammeter. The resistance is simply a measured length of the circuit proper.)

Experimentally measured constants (k in Table I) with benzil as the solute, averages at several concentrations, are lower than theory because they are based on an assumption never attained in practice, that the vapor pressures of the liquid drops on both junctions are equal to the partial pressure of the solvent in the surrounding atmosphere. In general k/k' approaches unity with increase of vapor pressure of the solvent. Baldes (*1*) gives 0.067° C. for observed Δt° (1 gram of sodium chloride in 100 grams of water) against 0.090° C. theoretical value at 20° C. which makes $k/k' = 0.72$. This result is out of line with the generalization on the trend of the effect of low vapor pressure, but the data of Table I clearly show that all the common organic solvents do extend the range and sensitivity of the thermoelectric method in cases where they can be substituted for water as the solvent because of their higher constants.

Table I. List of k Values for Solvents at 30° C.

Solvent	q	k' (Calcd.)	k (Obsd.)	100 k/k'	Vapor Pressure, Mm.
Benzene	104	700	445	64	120
Toluene	97	750	265	35	37
n-Hexane	88	828	..	..	190
Cyclohexane	93	782	469	60	120
n-Heptane	105	840	392	47	58
Dioxane	122	600	325	47	48
Carbon tetrachloride	51	1425	886	62	143
Chloroform	63	1150	846	73	250
Chlorobenzene	88	830	209	25	15
Pyridine	122	600	220	37	26
Ether	90	810	647	80	650
Acetone	110	565	434	77	283
Methyl ethyl ketone	112	650	395	61	120
Methanol	283	258	..	..	160
Ethanol	222	328	214	65	80
n-Propanol	188	388	..	..	27
Ethyl acetate	97	752	..	..	119
Methyl acetate	105	692	..	..	260
Dimethyl formamide	..	..	63	..	..
Water	580	125	..	..	32

This adaptation of the thermoelectric method has about the same accuracy, sensitivity, and range (extension to high molecular weights) as ebullioscopic procedures employing vapor-pressure thermometers (*9*, *11*). Its advantages over ebullioscopy, for certain cases at least, may be conveniently discussed with three points in mind—the effect of impurities, the signal-registering devices (transducers for a temperature difference), and the apparatus producing that signal.

One prime advantage is a large extension in the number of different solvents that may be employed, as well as the fact that rigorous purification of the solvents is not required. There are few satisfactory solvents that give steady readings at their boiling points with as sensitive an instrument as a vapor-pressure thermometer and they have to be rigorously purified. Purity is not nearly so important with the thermoelectric method, as is shown in the case of benzene. Results are given in Table

II with benzil in C.P. thiophene-free grade, ordinary solvent grade, and the C.P. grade saturated with water at room temperature. A striking example of the negligible effect of minor volatile impurities, such as might result from use of insufficiently dried samples, was an experiment with 95% ethanol as the pool and on both junctions. When the drop on one junction was replaced with 90% ethanol there was a large e.m.f. reverse of the usual polarity, produced instantaneously with a drift back to zero in 15 minutes.

Table II. Data with Benzil in Benzene at 30° C.

Benzil Solution on Junction	C	Benzene in Cell and on Reference Junction, μv. C.P. reagent	 Wet	 Solvent grade
C.P. reagent	0.952	2.03 k = 448	2.05 k = 452	2.01 k = 444
	1.885	3.95 k = 440	3.90 k = 440.	3.94 k = 439
Wet	0.940	2.02 k = 450	2.01 k = 450	.. ..
	1.945	4.08 k = 441	4.08 k = 441	.. ..
Solvent grade	0.978	2.15 k = 461	2.17 k = 465	2.10 k = 450
	1.875	4.04 k = 453	4.00 k = 448	3.96 k = 444

In order to gain the advantage of nearly an order of magnitude in the sensitivity of a vapor-pressure thermometer as a transducer over the classic Beckmann thermometer, considerable elaborations have been required in the apparatus producing the signal (*7*, *9*, *11*) in the items of method of heating at boiling and of jackets to prevent heat losses. Hill and Brown (*7*) report satisfactory determinations of the molecular weight of a polymer as high as 13,000 with concentrations under 7% in methyl ethyl ketone and the especially sensitive ethyl ether thermometer. A calculation will readily show that such a high molecular weight at these concentrations would hardly produce adequate signals with the thermoelectric method when operated as described above.

It was important, therefore, to determine which element—performance of the Baldes cell or sensitivity of e.m.f. registration—governed the upper limit of molecular weight that could be measured with assurance. For amplifying the thermocouple voltages, a breaker-type direct current amplifier, widely applied with thermocouples in infrared spectroscopy, was explored at some length. With the General Motors amplifier supplied by the Perkin-Elmer Corp., results were equivalent to those obtained with the galvanometer, and there may be some advantages in using such an amplifier with multiple cells or for automatic recording. Certainly the necessity for a vibration-free pier is avoided by use of the amplifier. While the noise level of the amplifier itself, as measured with a 10-ohm resistance in place of the thermocouple, was well below the minimum voltage of about 0.03 microvolt reliably measurable with the system employing the galvanometer, its possible advantages for low signal strength were defeated by instability of the signal itself. Presumably the random variations which limit the stability of the system originate in the response of the thermocouples or the shifting of minute temperature gradients in the cell. [Kinsey's paper (*8*) on the use of direct current amplification for the Baldes thermoelectric method appeared over a year after the authors' work was completed.]

Another method of reducing reading error of the galvanometer is the use of elements giving higher e.m.f. than copper-constantan. This idea was explored by substituting silicon for the constantan. Tiny bars of square cross sections were ground from silicon crystals and formed by soldering their copper-plated ends into an inverted V for substitution between *B* and *C*, Figure 1. Satisfactory results were obtained with this couple, but no increase in sensitivity resulted despite a fivefold increase in e.m.f. because of the large increase in the resistance of the circuit. Two or more couples of copper-constantan in series might provide a certain advantage and have been used for aqueous systems (*3*, *5*, *10*, *12–15*).

In some solvent-solute systems, Raoult's law appears to be applicable to considerably higher concentration than would normally be expected. Examples are given in Table III of measurements by both the ebullioscopic (*9*) and thermoelectric methods of a polyterpene resin molecular weight near 1000, and of material with a probable molecular weight around 5000, polyethylene oxide. Here the experimental error is unduly large and obviously an average value of molecular weight at the different concentrations is meaningless. A fair estimate of the molecular weight was obtained by extrapolation of a plot of observed reciprocals of calculated molecular weight against concentration and extrapolation to zero on the concentration axis.

Table III. Ebullioscopic and Thermoelectric Measurements

Ebullioscopic, k = 1290 G./100 cc.	 Cm., v.p. thermometer	 Mol. wt.	Thermoelectric, k = 445 G./100 g.	 μv.	 Mol. wt.
		Polyterpene Resin in Benzene			
0.47	0.61	990	2.27	0.98	1030
1.17	1.62	930	3.49	1.50	1030
1.97	2.77	920	6.00	2.54	1050
2.90	4.03	960	8.35	3.50	1060
4.37	6.08	930			
5.24	7.30	930			
	Av.	940			1040
		Polyethylene Oxide in Benzene			
1.65	0.53	4000	2.46	0.19	5750
3.25	1.06	3950	4.67	0.48	4350
5.33	1.92	3600	7.33	0.88	3700
7.88	3.29	3100	7.75	0.96	3600
	Extrapolated	5300			6000

No specific upper limit of molecular weight for which the technique described is applicable can be set. For mixed sizes of molecules as in all synthetic polymers, the number-average limit is somewhat a function of both polymer and solvent.

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Recording Chlorine Analyzer

J. F. ARBOGAST AND R. H. OSBORN
Hercules Experiment Station, Hercules Powder Co., Wilmington, Del.

Because infrequent spot checks of chlorine concentration in process gases cannot give a complete picture of the condition of chlorination operation, and because the determination of chlorine by chemical methods is time-consuming, an instrument which continuously records chlorine concentrations in a flowing gas stream has been developed. This analyzer has been especially designed to withstand severe corrosive atmospheres, and to give long periods of trouble-free operation. It consists essentially of a photoelectric photometer, the output of which feeds into a recorder reading directly in per cent chlorine concentration, and a gas-handling system to maintain the sample gas at constant temperature and pressure in the optical absorption cell of the photometer. The estimated maximum error of the instrument at 40% chlorine concentration is ±5% of the amount of chlorine present. This instrument should be useful to the chemical process industries for the determination not only of chlorine, but also of other colored gases such as nitrogen dioxide. The analyzer could be modified to handle liquids, making possible continuous colorimetric determinations by adaptation of well-known techniques.

THE chemical methods for determining chlorine concentration in process gases are laborious, and they yield only spot checks on the condition of a chlorination operation. Spot checks can indicate, only very ineffectively, fluctuating chlorine concentrations which often accompany erratic operation. A device that would continuously record chlorine concentration would obviously be of considerable value from the standpoint of process savings. It would enable the operator to adjust chlorine feed rate to suit the demands of the reaction, and thus avoid unnecessary waste.

A number of instruments based on the measurement of the optical absorption of gases and vapors have been described (*3–5*, *7–9*). Most of these were designed to detect small concentrations of the gas, and for one reason or another it was felt that none could easily be adapted to the reliable measurement of large concentrations of chlorine under corrosive plant conditions. Accordingly, an experimental instrument, capable of continuously analyzing and recording chlorine concentrations between 0 and 100%, was designed and built in the authors' laboratory. The analyzer, which is described in this paper, has been especially designed to withstand severe corrosive atmospheres, and to give long periods of trouble-free operation. One of the instruments, built according to the design, has been in continuous operation on a plant chlorinator for over two years.

PRINCIPLE OF OPERATION

In the search for a means of determining chlorine quantitatively in a manner suitable for automatic recording, consideration was given to a number of methods based on physical properties such as density, electrical properties, and refractive index. However, such methods necessarily involve more or less complete removal of interfering gases.

Ideally, it would be desirable to use a method based on a unique property of chlorine not shared by any of the other gases present in the reaction. One such property is that of color. Chlorine is a greenish-yellow gas, while other gases normally present in process gas are colorless. Hence, an instrument based on photometric analysis was designed.

In essence, the chlorine analyzer consists of a tungsten lamp, a violet filter, a lens to collimate the filtered beam from the lamp, a glass-windowed absorption cell through which the process gas is continuously passed, and a measuring photocell to receive the collimated light beam after its passage through the absorption cell. A balancing photocell, which receives reflected light from a partially transmitting mirror placed in the main beam, provides a means of minimizing the effect of voltage fluctuations in the lamp supply. A specially designed recorder unit measures the photocell output, which varies inversely with the chlorine concentration. A gas-handling system provides a flow of filtered gas at constant pressure and temperature to the absorption cell.

PHOTOMETER UNIT

The photometer unit is shown in Figures 1 and 2. The entire unit is enclosed in a light-tight case which also affords some measure of protection against corrosion.

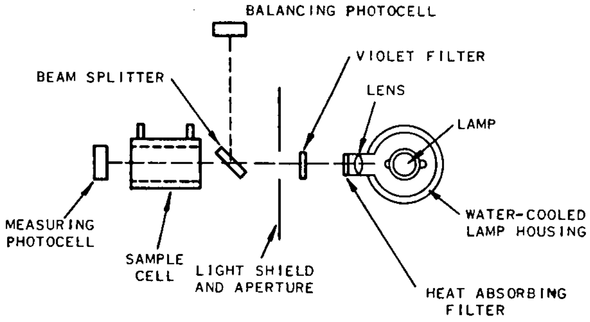

Figure 1. Optical System of Chlorine Analyzer

Light Source. The light source is a 200-watt, 120-volt, General Electric projection lamp with a Type 2CC8 filament and medium prefocused base. The lamp and socket are mounted in a water-cooled housing consisting of two concentric copper pipes silver-soldered together on a mounting plate. A cover is provided to prevent leakage of stray light. A Lucite rod, 0.375 inch in diameter, which is connected to the lamp housing at one end, and to a small warning reflector on the instrument case at the other end, indicates lamp burnout.

Lens. A lens 40 mm. in diameter and of 50-mm. focal length is mounted in a holder which, in turn, is silver-soldered to the lamp housing, and focuses the lamp filament on the photocells approximately 12 inches away.

Originally, a General Electric Type H-4 mercury lamp, equipped with a filter which transmitted only the 4358 and 4046 A. lines, was used as a source of radiation. Insufficient intensity and instability in the arcs of some lamps prompted the change to an incandescent source.

Filters. A Corning No. 3966 Aklo filter is mounted in the lens holder to reduce heat radiation. A Corning No. 5113 violet filter, having a peak transmittance at 407 mμ is mounted in a holder directly in front of the lamp housing. The maximum absorption of chlorine gas occurs at 332 mμ. However, the energy output of a tungsten lamp at this wave length is very low. Hence, a wave length was chosen where the lamp energy is adequate, and where chlorine still absorbs strongly.

A light shield is built into the filter holder to protect the photo-

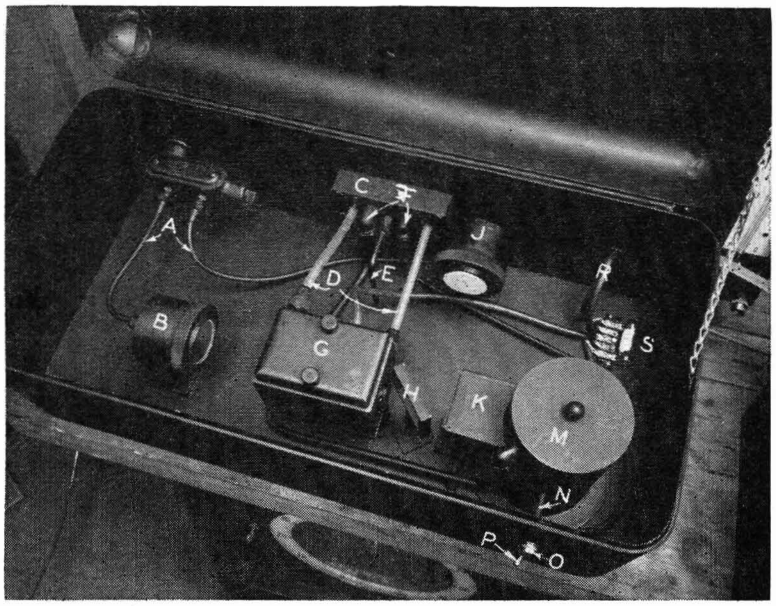

Figure 2. Photometer Unit

A.	Photocell leads	*J.*	Balancing photocell
B.	Measuring photocell	*K.*	Filter holder and light shield
C.	Haveg terminal block	*M.*	Lamp housing
D.	Process gas lines	*N.*	Lucite rod
E.	Air inlet	*O.*	Warning light
F.	Water lines	*P.*	Power switch
G.	Sample cell	*R.*	Power leads
H.	Beam splitter	*S.*	Series resistor

cells from stray light emanating from various positions of the optical system, and contains a limiting aperture for the light beam.

Beam Splitter. A beam splitter, consisting of a semitransparent mirror prepared by evaporating chromium on a piece of optical glass, is mounted at an angle of 45° to the main beam. The chromium film is protected from corrosion by another piece of optical glass cemented over it. The glasses are firmly mounted in a brass holder. This device reflects approximately 40% of the light to the balancing photocell, and transmits 40% through the absorption cell to the measuring photocell.

Absorption Cell. The absorption cell is machined from a solid block of impregnated Karbate supplied by the National Carbon Co., and is provided with removable windows. Its inside dimensions are approximately 100 mm. in length by 40 mm. in diameter. The windows are borosilicate glass disks of fair optical quality, mounted in the Karbate block with Tygon gaskets. It has been found necessary, in plant operation, to clean these windows about once a month. The absorption cell is mounted on a platform which centers the light beam through the windows.

Photocells. The photocells used in this photometer are General Electric, Type 8PV2FAA, hermetically sealed, barrier-layer cells with standard octal bases. They are mounted in brass holders which are positioned in such a manner that the light beam is centered on the active portion of the photocell. This type of cell is designed for use in corrosive atmospheres, and with reasonable care should last indefinitely.

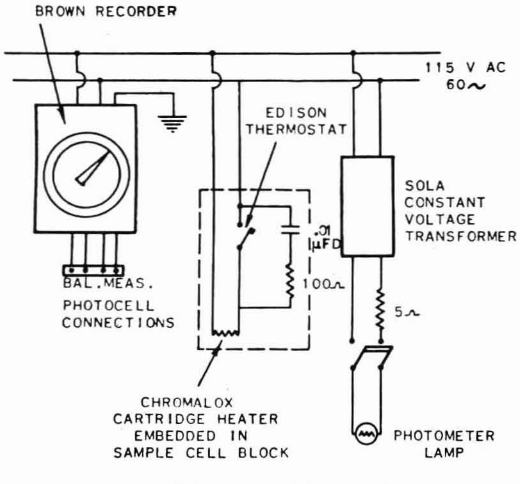

Figure 3. Schematic Wiring Diagram

ELECTRICAL AND RECORDING SYSTEMS

The power-supply circuits for the chlorine analyzer are shown in Figure 3.

A Sola, Catalog No. 30807, 115-volt, 250-watt, constant-voltage transformer supplies current to the lamp. A 5-ohm resistor is placed in series with the lamp to decrease the voltage across it. By operating the lamp at reduced voltage, the lamp life is extended from a rated 50 hours to about 250 hours.

The absorption cell block is heated to a temperature of 45° C. by means of a 30-watt, 115-volt, Chromalox cartridge heater, which is controlled by an Edison, Catalog No. 31-1A, 30-watt, 110-volt, glass-enclosed thermostat. A 100-ohm resistor in series with a 0.01-mfd. condenser is wired across the thermostat contacts in order to reduce arcing. The heater and thermostat are embedded in the sample cell block to provide good heat transfer.

The photocell circuit is a modification of that due to Brice (*1*). The Brice circuit is of the null current balancing type employing two photocells.

The modified circuit (Figure 4) uses the Brown recorder standardizing rheostats, 1 and 2, across the measuring photocell. The recorder slide-wire, 3, and the variable resistor, 4, are connected across the balancing photocell. Resistor 4 serves to expand the scale, so that when the absorption cell contains pure chlorine, the recorder may be adjusted to read 100%. Variable resistor 5 provides a zero adjustment which permits the standardizing rheostats to balance the recorder at zero on the scale when the cell contains no chlorine. Variable resistor 6 shunts the Brown recorder slide-wire. It may be adjusted to make the recorder read almost directly in chlorine concentration over part of the scale. The deviation from linearity may be made negligible over the range from 0 to 60% by proper adjustment.

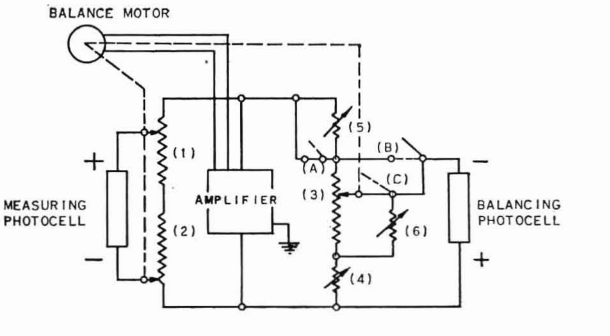

Figure 4. Detail of Recorder Balancing Circuit

A, B, C.	Push-button standardizing switches
1, 2.	Standardizing rheostats, 70 ohms total
3.	Slide wire, 42-ohm Helipot
4.	10-ohm Helipot
5.	5-ohm Helipot
6.	50-ohm Helipot

The standardizing rheostats, 1 and 2 in Figure 4, are an integral part of the recorder. They are coupled to the balancing motor by means of a push-button friction clutch arrangement during the interval when standardization takes place. The standardizing switches are also mechanically connected to the push-button assembly. When the standardizing button is pushed, the balance motor engages the standardizing rheostats, and the standardizing switches are actuated. Switch *A*, normally closed, is open during standardization, so that variable resistor 5 is in series with slide-wire 3. Switch *B*, normally open, is closed, and switch *C*, normally closed, is open during standardization, disconnecting the slide-wire contact, and connecting the negative terminal of the balancing photocell and the upper end of shunt 6 to the upper end of the slide-wire. A single standardization at the beginning of each 8-hour shift is sufficient for satisfactory operation of the instrument.

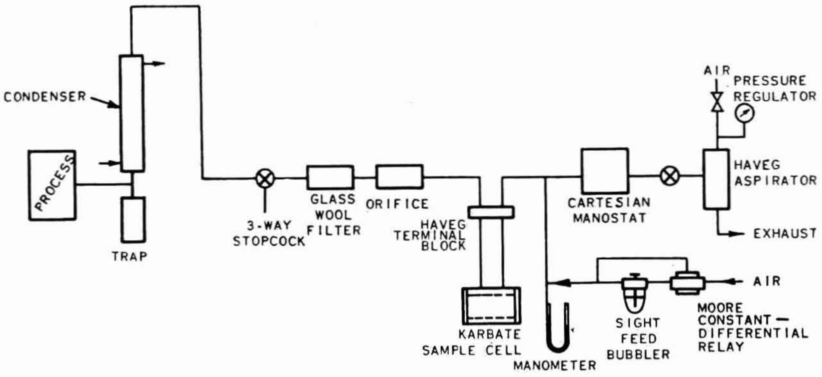

Figure 5. Flow Diagram of Gas-Handling System

A modified Brown Electronik, potentiometer-type, circular chart recorder is connected to the photometer as shown in Figure 3. It contains an amplifier unit that converts a direct current signal to alternating current, amplifies the signal, and causes it to drive a balancing motor. The balancing motor is mechanically coupled to the slide-wire contactor, recorder pen, and indicator pointer. Any electrical unbalance detected by the amplifier causes the balancing motor to move in such a direction as to position the slide-wire contactor at the point of electrical balance. Because the photocells work at relatively low light intensities, a high-gain amplifier, having a sensitivity of 1 microvolt, was supplied with the recorder used in this work.

GAS-HANDLING SYSTEM

The gas-handling system is designed to deliver a stream of process gas containing chlorine to the analyzer at constant temperature and pressure. In addition, a three-way stopcock is provided for flushing the sample cell with air during the period of standardization. The flow diagram of Figure 5 indicates the details of this system.

An air-driven Haveg aspirator, designed by the Schutte and Koerting Co., is used to pull the gas from the process through the cell, and exhaust it to the atmosphere. Any convenient pressure can be chosen for the gas in the absorption cell. Pressures close to atmospheric are somewhat easier to handle instrumentally. Therefore, the pressure has been fixed at approximately 460 mm. of mercury absolute. The adjustment for this pressure is made by varying the air flow through the aspirator.

Initially, the gas is passed through a condenser maintained at the proper temperature to prevent condensation in the absorption cell. The gas is next passed through a three-way stopcock, open to the process for normal operation, and open to the atmosphere to allow air to flush the cell during standardization. A glass wool filter, inserted in the gas line, minimizes the deposition of dirt on the sample cell windows. Next, the gas flows through a restricting orifice which protects the sample cell against excessive pressures that might build up in the process.

The gas finally enters the Karbate sample cell through a Haveg terminal block mounted on the back of the photometer case. It is raised to a temperature of 45° C. by first passing it through several return-bend passages drilled in the Karbate block.

Both the accuracy and precision of the instrument depend largely on the degree to which constant temperature and pressure are realized. Constant pressure is achieved by the use of a laboratory model Cartesian manostat (*2*) redesigned to withstand contact with chlorine (Figure 6). This manostat was manufactured by the Emil Greiner Co. In the redesign, all-glass construction has been substituted for metal, Teflon is used as an orifice seat instead of rubber, and the mercury ordinarily used has been replaced by highly chlorinated dimethylpentane—a liquid compound which will not undergo appreciable physical change during long exposure to chlorine.

A mercury manometer is used to set the manostat at a given pressure, and serves to check its operation. The setting is ordinarily made once each day. An air-purge system, utilizing a Moore constant-differential relay, serves to bleed air slowly into that leg of the manometer which is connected to the system. In this manner the mercury is protected from corrosion. The manometer is located downstream from the sample cell to prevent purge air from mixing with process gas in the cell.

CALIBRATION

The instrument is calibrated by introducing pure chlorine into the sample cell, and varying the pressure from several millimeters of mercury to the operating pressure of 460 mm. of mercury. The sample cell is maintained at an operating temperature of 45° C. The recorder reading at 460 mm. of mercury corresponds to 100% chlorine.

In Figure 7 is shown a typical calibration curve. From 0 to 60% concentration, there is a one-to-one correspondence between recorder readings and per cent chlorine concentration. Deviation from linearity occurs between 60 and 100%, but this is outside the normal operating range. By properly adjusting the value of resistor 6 (Figure 4), a better correspondence between chlorine concentrations and recorder readings can be obtained in the upper range of concentrations. However, the correspondence in the lower range is then sacrificed.

The instrument calibration may be checked periodically by introducing pure chlorine into the gas-handling system through the air-inlet of the three-way stopcock.

The calibration has been found to remain fairly constant during the lifetime of a lamp, and even from lamp to lamp.

It is estimated that the maximum error from all sources, at a

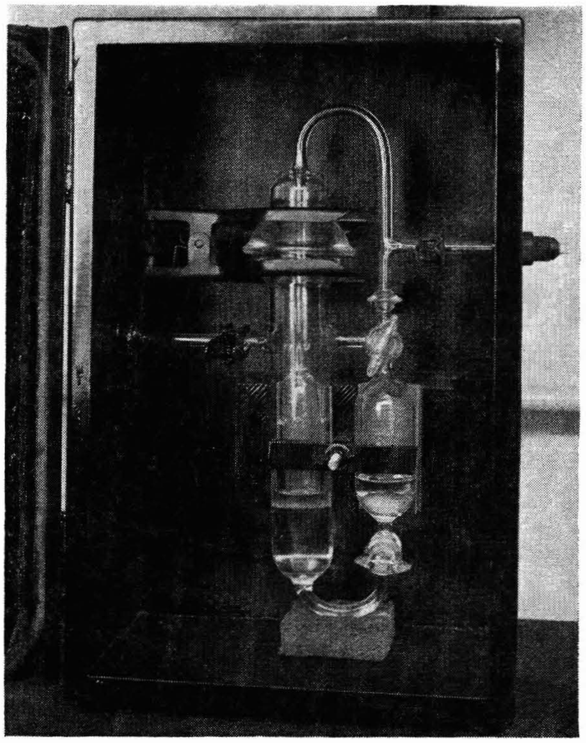

Figure 6. Cartesian Manostat

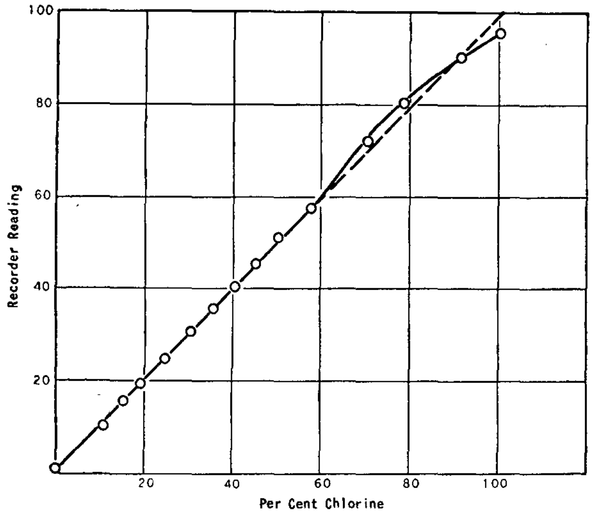

Figure 7. Calibration Curve

concentration of 40% chlorine, is no greater than ±5% of the amount of chlorine present.

PROTECTION FROM CORROSION

Extremely corrosive plant conditions prompted special precautions for the protection of the various components of the analyzer. The recorder, constant-voltage transformer, and photometer are primarily protected by maintaining the cases surrounding the units at positive air pressures. An air-failure warning device is employed for added protection. The units comprising the analyzer are housed in a wooden enclosure near the process control panel. This enclosure, too, is maintained at a positive air pressure.

Experience has shown that the recorder is the portion of the analyzer most vulnerable to corrosion. A number of steps have been taken to reduce the possibility of instrument failure from this cause. In addition to placing the recorder case under positive air pressure, all electrical components of the measuring circuit, including those outside the recorder, are coated with a Parlon (chlorinated rubber) lacquer. The amplifier components are sprayed with a protective coating (tropicalized) by the Brown Instrument Co.

Saran tubing (0.375-inch) and fittings are used to connect the components of the gas-handling system. In the construction of the analyzer, Teflon, Tygon, Karbate, chlorinated dimethylpentane, glass, Haveg, and Parlon, all chlorine-resistant materials, are used.

DISCUSSION

Although the apparatus described in this paper was designed for the analysis of gaseous chlorine mixed with colorless gases, it should be equally useful in the analysis of other colored gases, such as nitrogen dioxide.

With suitable modification of the sample-handling equipment, the instrument could be adapted to liquids. Then, by proper choice of filters, a large variety of chemical colorimetric determinations could be carried out in continuous processes. Continuous recording of color, per se, would also be possible by rearranging the optical system. Such a rearrangement would comprise removing the violet filter from the main beam (Figure 1), locating the sample cell between the lamp and the beam splitter, and placing appropriate tristimulus filters directly in front of the two photocells (*6*).

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Infrared Analysis of Pharmaceutical Products

Acetylsalicylic Acid, Phenacetin, and Caffeine, and Combinations of These with Codeine or Thenylpyramine

T. V. PARKE, A. M. RIBLEY, E. E. KENNEDY, and W. W. HILTY
Eli Lilly and Co., Indianapolis, Ind.

ACETYLSALICYLIC acid, phenacetin (acetophenetidin), and caffeine can be determined simultaneously in pharmaceutical products even in the presence of codeine phosphate or thenylpyramine hydrochloride [*N*,*N*-dimethyl-*N*′(2-thenyl)-*N*′-(2-pyridyl)-ethylenediamine hydrochloride] without separation and with a minimum of mutual interference by infrared spectrophotometry. Determination of these components is not complicated by the addition of codeine phosphate or thenylpyramine hydrochloride to the mixture.

Previously described chemical methods for the analysis of mixtures of acetylsalicylic acid, phenacetin, and caffeine (*1–3*, *9*) have required extensive extraction procedures for the separation of the individual or a pair of components prior to their final estimation. Apparently any one or any combination of these chemical methods has not given sufficiently good precision to warrant adoption as a general method of analysis by the National Formulary, which recognizes these mixtures as official preparations.

A method has been developed (*4*) which utilizes ultraviolet absorption characteristics of phenacetin and caffeine for their simultaneous determination and for determination of the acetylsalicylic acid separately.

Washburn and Krueger (*7*) describe a method using infrared absorption, in which considerable preparation of sample is required and calculations must be made by successive approximations because of mutual interference of the components. These authors have also published a method for analysis of combinations of these three components with thenylpyramine hydrochloride, in which the thenylpyramine is separated and determined as the reineckate (*8*). The present method has the great specificity inherent in infrared absorption analyses, accuracy equivalent to

A method is described for analysis of pharmaceutical products containing acetylsalicylic acid, phenacetin (acetophenetidin), and caffeine, which is applicable to mixtures containing codeine or thenylpyramine. Acetylsalicylic acid, phenacetin, and caffeine are determined simultaneously by infrared absorption in the 5- to 7-micron region by direct solution in chloroform. Relative freedom from mutual interference permits direct calculation of results. Codeine is determined by infrared absorption at 10.62 microns following extraction into carbon disulfide. Thenylpyramine is determined by an ultraviolet procedure. Average deviation of analysis of weighed samples was less than 2% for all components. The methods are rapid and suitable for routine control analysis of these mixtures.

the method of Washburn and Krueger, and a considerable advantage in time required for performance of the analysis. Neither codeine phosphate nor thenylpyramine hydrochloride causes any interference at the wave lengths used.

EXPERIMENTAL

Spectra have been obtained with a Baird infrared recording spectrophotometer Model A equipped with rock salt prism. The slit cam of this instrument has been altered to give slightly wider slits than originally provided. Repeatability in per cent transmittance recording is about ±0.2% and the resolution is slightly reduced. The cell path lengths are measured by the interference method (*6*) or by direct measurement with a microscope. No attempt was made to match the sample and reference cells precisely.

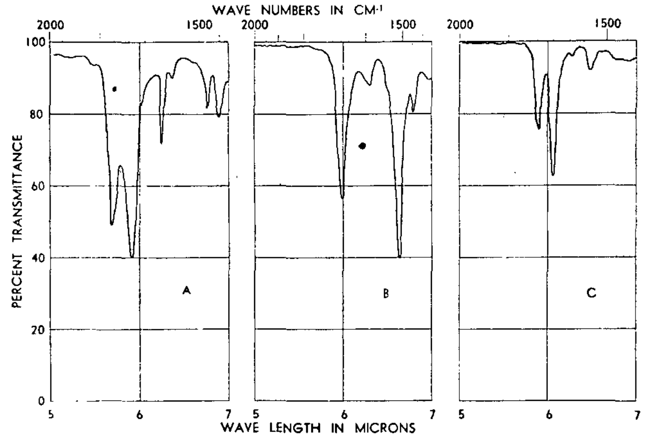

Figure 1. Infrared Absorption Spectra

A. 908 mg. of acetylsalicylic acid in 50 ml. of $CHCl_3$
B. 642 mg. of phenacetin in 50 ml. of $CHCl_3$
C. 130 mg. of caffeine in 50 ml. of $CHCl_3$
Sample cell path length 0.0097 cm. Chloroform in reference cell

Infrared absorption spectra of acetylsalicylic acid, phenacetin, and caffeine in chloroform solutions (Figure 1) show strong bands in the 5- to 7-micron region. Water vapor bands always present in this region do not appear in the double-beam spectrophotometer record and sufficient energy is transmitted to give accurate quantitative results. Concentrations of solutes in Figure 1 were chosen equivalent to the contents of four tablets, each containing 3.5 grains (227 mg.) of acetylsalicylic acid, 2.5 grains (162 mg.) of phenacetin, and 0.5 grain (32.4 mg.) of caffeine dissolved in 50 ml. of chloroform.

Figure 2 shows the infrared spectrum of a mixture of the above quantities with a blank curve or "base-line" of chloroform versus chloroform. Each measured absorbance (optical density) is corrected for the absorbance of the blank at the selected wave length. Each corrected absorbance, A, should be divided by the cell path length, b, in centimeters in order to reduce all observations to absorbance per unit path length, A/b.

Factors to correct A/b for interference by other components and for conversion of A/b to milligrams of component per tablet or capsule are determined as outlined below. These factors will vary considerably from one instrument to another, depending on the resolution and response characteristics of the spectrophotometer, and might vary somewhat with time for a given instrument. The factors calculated for the instrument in these laboratories are intended to illustrate their magnitude. Individual calibration of each instrument is essential. The factors can be readily checked by analysis of a weighed sample from a powdered mixture containing exact theoretical quantities of each component. Although experience has shown these factors to remain valid for several months, such analysis requires little time and can be carried out at regular intervals.

Diluents present in the tablets and powders analyzed have been shown experimentally to exhibit no interference in the 5- to 7-micron region. While tablets or powders of other manufacturers may contain other diluents, it is unlikely that these will be present in quantities sufficient to cause appreciable interference. This point should be checked by adding weighed amounts of all diluents equivalent to that present in four tablets to 50 ml. of chloroform and recording the infrared absorption in the 5- to 7-micron region.

The absorbance of acetylsalicylic acid at about 5.67 microns obeys Beer-Bouguert's law beyond the concentration range encountered in commercial products and a conversion factor can be calculated which multiplied by A/b at 5.67 microns gives the amount of acetylsalicylic acid in milligrams per tablet. The acetylsalicylic acid factor for this instrument is 6.90.

Phenacetin exhibits a strong, narrow absorption band at about 6.62 microns with but very slight interference from the other components. The absorbance of this band is linear with concentrations for a wide range on either side of the theoretical quantity of 648 mg. in 50 ml., but deviates considerably at very low and high concentrations. Phenacetin was accordingly calibrated across this concentration range. The interference of the other components at 6.62 microns can be corrected for by subtraction of a small constant correction from the A/b value. For the authors' instrument A/b at 6.62 microns is about 44.0 for the theoretical mixture containing 648 mg. per 50 ml. plus the proper proportions of the other components; the correction to be subtracted is 2.5 and the factor for conversion to milligrams per tablet is 3.90.

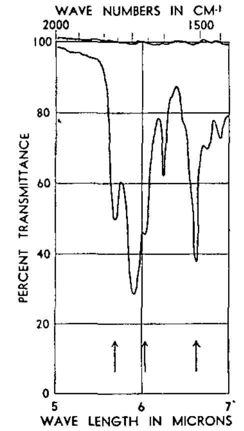

Figure 2. Infrared Spectrum

Lower. 908 mg. of acetylsalicylic acid, 642 mg. of phenacetin, and 130 mg. of caffeine in 50 ml. of $CHCl_3$. Sample cell path length 0.0097 cm. Chloroform in reference cell. *Upper.* Blank curve with chloroform in both cells

Caffeine absorbance is measured at the maximum, about 6.04 microns. Both acetylsalicylic acid and phenacetin show considerable absorption at this wave length. The phenacetin interference at this wave length is a point on the side of a rather strong band. It was found inadequate to calculate the interference factors from the spectra of the individual components, as those factors proved erroneous when all three substances were present in the same solution. Rather the factors for interference were calculated for each component by weighing mixtures containing theoretical quantities of two components and first 10% more, then 10% less than the theoretical quantity of the third. This permitted calculation of the factor for conversion to milligrams of caffeine per tablet. The A/b at 6.04 microns is corrected by subtracting the sum of the acetylsalicylic acid correction factor times the number of milligrams of acetylsalicylic acid per tablet as calculated above, plus the phenacetin correction factor times the calculated number of milligrams of phenacetin per tablet. The corrected A/b multiplied by the caffeine conversion factor gives the milligrams per tablet. With this instrument the correction factors at 6.04 microns for acetylsalicylic acid and phenacetin are 0.026 and 0.070, respectively, and the caffeine conversion factor is 1.77. It is necessary to determine the correction factors as well as the conversion factors for the instrument to be used.

Figure 3 shows the absorption in the region 5 to 7 microns of 100 mg. of thenylpyramine hydrochloride per 50 ml. of chloroform. No interference is found for acetylsalicylic acid, phenacetin, or caffeine. Codeine phosphate has low solubility in chloroform, and Figure 3 shows no interference from a suspension of 260 mg. in 50 ml. of chloroform.

The foregoing method of calibration is felt to be entirely adequate, because the factors have been shown experimentally to remain constant beyond the concentration limits to be expected in a commercial lot of this preparation.

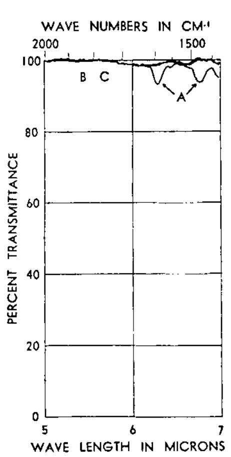

Figure 3. Infrared Spectra

A. 100 mg. of thenylpyramine hydrochloride in 50 ml. of CHCl$_3$
B. 260 mg. of codeine phosphate suspended in 50 ml. of CHCl$_3$
C. Chloroform blank
Sample cell path length 0.0097 cm. Chloroform in reference cell

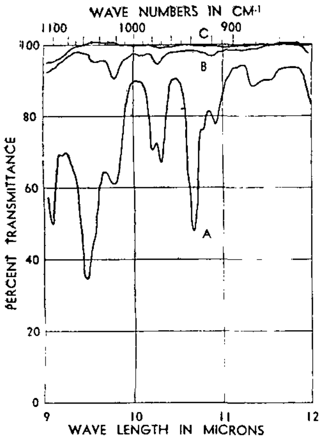

Figure 4. Infrared Spectra

A. CS$_2$ extract prepared by described procedure from 388.8 mg. of codeine phosphate, 2.724 grams of acetylsalicylic acid, 778 mg. of phenacetin, and 389 mg. of caffeine
B. CS$_2$ extract prepared by described procedure from 2.724 grams of acetylsalicylic acid, 778 mg. of phenacetin, and 389 mg. of caffeine
C. CS$_2$ blank
Sample cell path length 0.075 cm. CS$_2$ in reference cell

Codeine phosphate is determined on a separate sample of the mixture. The powdered sample is shaken with water to dissolve the codeine phosphate. An aliquot of the filtrate from this extraction is made alkaline and the free codeine base is partitioned into carbon disulfide. This is not an exhaustive extraction, but rather an equilibrium distribution of the codeine between the aqueous and nonaqueous phases. Extensive series of analyses have shown that this equilibrium distribution gives adequately quantitative results, if the relative volumes of aqueous and nonaqueous phases are held constant and excess alkali has been added to the aqueous phase. The absorption spectrum of this carbon disulfide solution run against a carbon disulfide reference in the region 9 to 12 microns is shown in Figure 4. Curve *A* is the absorption of codeine extracted from the mixture, curve *B* is absorption of the other components extracted from the mixture in the absence of codeine, and curve *C* is the carbon disulfide blank. Pharmaceutical preparations containing acetylsalicylic acid, phenacetin, caffeine, and codeine phosphate are made with several dosages of codeine phosphate for the same dosage of the other components. Typical are products containing 3.5 grains (227 mg.) of acetylsalicylic acid, 2.5 grains (162 mg.) of phenacetin, 0.5 grain (32.4 mg.) of caffeine, and either 1 grain (64.8), 0.5 grain (32.4 mg.), 0.25 grain (16.2 mg.), or 0.125 grain (8.1 mg.) of codeine phosphate per tablet or capsule.

The absorbance of the codeine band at 10.62 microns is linear with the amount of codeine phosphate in the tablet or capsule through the 0.5-grain (32.4-mg.) dosage. With the procedure described the codeine absorbance of the 1-grain (64.8-mg.) dosage is less than theoretical, possibly because of saturation of the carbon disulfide phase in the partition extraction. Consequently, in the procedure described below powder equivalent to twelve tablets or capsules is extracted for all dosages except the 1-grain (65-mg.) dosage, where the equivalent of six tablets or capsules is used. A factor for conversion of A/b values for the codeine absorption at 10.62 microns can be determined from weighed samples of codeine phosphate to which the proper amounts of acetylsalicylic acid, phenacetin, and caffeine have been added. These samples should be carried through the extraction procedures outlined below. The conversion factor for codeine with this instrument is 7.5. No correction for the slight interference of the other components at 10.62 microns is necessary, because analysis of weighed mixtures has shown absorbance of the codeine band linear within 1% with concentration over the range 0.125 to 0.5 grain per tablet. This interference appears to be greatly diminished when codeine is present or is otherwise self-correcting.

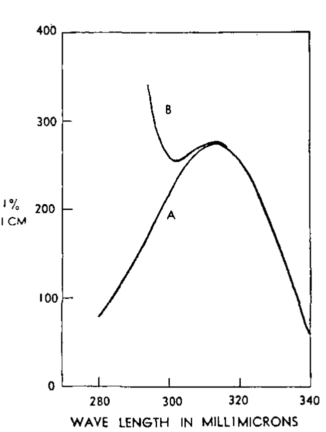

Figure 5. Ultraviolet Absorption Spectra

A. 25 mg. of thenylpyramine hydrochloride per liter in 0.1 N HCl
B. Acidified water solution prepared by described procedure from 25 mg. of thenylpyramine hydrochloride, 227 mg. of acetylsalicylic acid, 162 mg. of phenacetin, and 32.4 mg. of caffeine

Thenylpyramine hydrochloride can be determined by a simple and rapid ultraviolet absorption procedure adapted from a method published by Martin and Harrisson (*5*). A separate sample is weighed from the powdered tablets or contents of capsules, the thenylpyramine hydrochloride is dissolved from the sample with water, and the water extract is diluted with approximately 0.1 N hydrochloric acid. Figure 5, *A*, illustrates the strong absorption band in the ultraviolet of thenylpyramine hydrochloride in dilute hydrochloric acid. The amounts of the other three components dissolved by the volume of water used interfered very little at this band.

Curve *B* shows the absorption of thenylpyramine hydrochloride when dissolved in the presence of acetylsalicylic acid, phenacetin, and caffeine by this procedure. The $a^{1\%}_{1\,\mathrm{cm.}}$ for thenylpyramine hydrochloride at 313 mμ in approximately 0.1 N hydrochloric acid was found to be 276. The $a^{1\%}_{1\,\mathrm{cm.}}$ for thenylpyramine hydrochloride when 25 mg. were dissolved in the presence of 227 mg. of acetylsalicylic acid, 162 mg. of phenacetin, and 32.4 mg. of caffeine was found to be 278. The latter figure was used in calculating the thenylpyramine hydro-

Table I. Analyses of Weighed Mixtures

Weighed per Tablet or Capsule, Mg.			Found per Tablet or Capsule, Mg.		
Acetylsalicylic acid	Phenacetin	Caffeine	Acetylsalicylic acid	Phenacetin	Caffeine
250	171	35.8	252	166	36.0
227	160	31.8	226	159	32.6
252	156	28.3	254	158	29.2
232	176	31.2	237	174	32.2
222	151	37.9	224	152	36.4
259	167	32.0	260	166	31.4
227	160	32.5	231	162	33.0
214	170	34.2	216	172	33.8
221	184	36.0	223	181	36.4
227	160	32.5	226	160	32.0
227	160	25.0	228	164	24.8
227	160	40.0	229	162	39.9
227	145	32.5	224	144	33.1
227	175	32.5	226	172	33.6
227	160	32.5	225	158	32.7
227	160	32.5	225	161	31.8

Table II. Analyses of Production Samples

(Mg. found per tablet or capsule)

Acetylsalicylic Acid (Theoretical 227 Mg.)	Phenacetin (Theoretical 162 Mg.)	Caffeine (Theoretical 32.4 Mg.)
241	160	32.7
233	163	30.6
238	165	32.0
231	159	30.6
232	166	30.4
222	160	31.8
229	160	30.1
228	160	30.4
226	165	32.4
239	162	30.4
230	160	31.0

chloride, because all preparations assayed had this same ratio for the four components.

PROCEDURES

Mixtures of Acetylsalicylic Acid, Phenacetin, and Caffeine. Twenty tablets of approximate theoretical composition, 3.5 grains (227 mg.) of acetylsalicylic acid, 2.5 grains (162 mg.) of phenacetin, and 0.5 grain (32.4 mg.) of caffeine, are weighed and an average weight per tablet is determined. The tablets are ground in a mortar to a fine powder. An amount of powder equivalent to four tablets is weighed, transferred to a volumetric flask, and made up to 50 ml. with chloroform. The suspension must be vigorously shaken to dissolve all soluble components. The suspension may be filtered to remove insoluble components, but it is not necessary, as the suspended particles do not interfere with the analysis. A portion of the solution is transferred to a rock salt cell of about 0.1-mm. path length. The spectrum for the unknown is recorded from 5 to 7 microns, using chloroform as the comparison solvent. A blank curve of chloroform measured against chloroform is recorded on the same chart.

At each selected wave length, values of per cent transmittance for the blank and sample curves are noted, and absorbance for each is calculated. The blank absorbance is subtracted from that of the sample and the corrected absorbance is divided by the cell path length to give A/b.

1. Mg. per tablet of acetylsalicylic acid = A/b (5.67μ) × factor for acetylsalicylic acid
2. Mg. per tablet of phenacetin = [A/b (6.62μ) − constant correction] × factor for phenacetin
3. Mg. per tablet of caffeine = [A/b (6.04μ) − acetylsalicylic acid correction factor × mg. of acetylsalicylic acid per tablet − phenacetin correction factor × mg. of phenacetin per tablet] × factor for caffeine

Mixtures of Acetylsalicylic Acid, Phenacetin, Caffeine, and Codeine Phosphate. Acetylsalicylic acid, phenacetin, and caffeine can be determined in preparations containing the above components by the procedure described above. (Some difficulty has been experienced in filling the infrared cells with solutions having suspended codeine phosphate. If the suspension clogs the filling channels, it may be filtered before use.)

Codeine phosphate dissolved or suspended in the solution does not absorb in the 5- to 7-micron region.

For determination of codeine phosphate, an amount of the powder prepared above equivalent to twelve tablets or capsules for 0.125-grain, 0.25-grain, and 0.5-grain dosages or equivalent to six tablets or capsules of 1-grain dosage is weighed and transferred to a 50-ml. glass-stoppered Erlenmeyer flask. Twenty milliliters of distilled water are added and the suspension is shaken vigorously for several minutes. The suspension is filtered, 10 ml. of the filtrate are transferred to a 50-ml. glass-stoppered Erlenmeyer flask, 15 ml. of carbon disulfide are added, and the solution is made alkaline with 0.5 ml. of 50% sodium hydroxide. It is essential that these volumes be held constant. Codeine is extracted into the carbon disulfide by vigorous shaking for several minutes. When the layers have separated, a few milliliters of the carbon disulfide layer are removed by a dropper or pipet and dried by shaking with 1 gram of anhydrous sodium sulfate in a small glass-stoppered flask. Care must be exercised to avoid appreciable evaporation of the volatile carbon disulfide during these operations. The solution is then transferred to a rock salt cell of path length about 1 mm. and the spectrum is recorded from 10 to 11 microns, using carbon disulfide in the reference solvent cell. A blank curve with solvent in both cells is also recorded. The absorbance of the peak at 10.62 microns is corrected for absorbance of the blank at this wave length and the corrected absorbance is divided by the cell path length to give A/b.

Mg. of codeine phosphate per tablet or capsule of 0.125, 0.25, and 0.5-grain dosage = A/b (10.62μ) × factor for codeine phosphate

Mg. of codeine phosphate per tablet or capsule of 1-grain dosage = A/b (10.62μ) × 2 × factor for codeine phosphate

Mixtures of Acetylsalicylic Acid, Phenacetin, Caffeine, and Thenylpyramine Hydrochloride. Assay of acetylsalicylic acid, phenacetin, and caffeine is carried out exactly as described above.

For determination of the thenylpyramine hydrochloride, an amount of the powder prepared for the assay of the other three components equivalent to 25 mg. of thenylpyramine hydrochloride is weighed and transferred to a 50-ml. volumetric flask with distilled water and made up to volume. The mixture is thoroughly shaken, the suspension is filtered, and 5 ml. of the filtrate are diluted to 100 ml. with approximately 0.1 N hydrochloric acid. The absorbance of this solution at 313 mμ is determined in 1-cm. cells in a Beckman spectrophotometer and the amount of thenylpyramine hydrochloride is calculated from the following formula:

$$\text{Mg. of thenylpyramine hydrochloride} = \frac{\text{absorbance at 313 m}\mu}{278 \times 10^{-4}}$$

Table III. Analyses of Weighed Mixtures of Acetylsalicylic Acid, Phenacetin, Caffeine, and Codeine Phosphate

Codeine Phosphate, Mg.		Codeine Phosphate, Mg.	
Weighed	Found	Weighed	Found
8.1	7.9	32.4	32.8
8.1	8.1	32.4	32.3
8.1	8.3	32.4	32.1
16.2	16.6	32.4	32.1
16.2	15.6	32.4	32.2
16.2	16.2	32.4	32.8
16.2	16.5	64.8	64.6
16.2	16.2	64.8	65.4
16.2	16.1	64.8	64.5
16.2	16.1		

Table IV. Analyses of Production Samples

Acetylsalicylic Acid Found (Theory 227 Mg.)	Phenacetin Found (Theory 162 Mg.)	Caffeine Found (Theory 32.4 Mg.)	Codeine Phosphate, Mg.	
			Theory	Found
240	170	33.3	8.1	8.2
232	170	34.5	8.1	8.7
237	162	32.5	16.2	16.8
228	166	33.3	16.2	16.9
227	156	33.1	16.2	17.2
226	162	32.7	16.2	16.3
237	166	32.5	16.2	16.6
223	158	33.3	32.4	31.3
233	163	32.7	32.4	33.1
234	160	32.7	32.4	33.4
240	159	32.5	32.4	32.9
227	155	30.7	32.4	33.6
226	168	31.9	32.4	30.8
232	161	33.5	64.8	63.6
226	163	33.0	64.8	63.2
229	166	33.7	64.8	62.3

Table V. Analyses of Weighed Samples

Amount Weighed, Mg. per Capsule				Amount Found, Mg. per Capsule			
Acetylsalicylic acid	Phenacetin	Caffeine	Thenylpyramine HCl	Acetylsalicylic acid	Phenacetin	Caffeine	Thenylpyramine HCl
228	154	33.5	25.0	222	153	35.0	24.9
218	162	35.2	31.6	222	162	36.1	31.5
229	152	33.0	37.2	232	153	33.8	36.4
236	162	33.0	37.5	240	164	32.6	36.8
232	167	34.5	24.4	236	165	35.7	24.8
226	154	33.0	27.6	224	151	33.4	27.8
222	166	34.0	25.6	223	161	33.4	25.9

Table VI. Analyses of Production Samples

(Amount found, mg. per capsule)

Acetylsalicylic Acid (Theoretical 227 Mg.)	Phenacetin (Theoretical 162 Mg.)	Caffeine (Theoretical 32.4 Mg.)	Thenylpyramine HCl (Theoretical 25 Mg.)
225	163	32.8	23.6
224	164	33.1	26.4
222	157	33.0	26.6
222	155	32.8	25.2
222	160	32.6	25.6
226	167	32.8	25.9

RESULTS

Mixtures of Acetylsalicylic Acid, Phenacetin, and Caffeine. Table I gives the results of analyses of sixteen weighed mixtures and Table II lists the results of eleven production samples of tablets and filled capsules. Average deviations of the results on known samples were 0.88% for acetylsalicylic acid, 1.19% for phenacetin, and 1.84% for caffeine. Maximum observed deviations for each component were +2.1, −2.9, and −3.7%, respectively. Although these deviations are somewhat greater than those observed in some of the methods described in the literature, the precision of analysis is believed to be adequate for the rapid routine control of commercial samples.

The time required for performance of this method is about 30 minutes per sample, including preliminary weighings, preparations of the sample, and calculations of results. Where several samples can be prepared and assayed concurrently, the time required per sample is accordingly reduced.

Mixtures of Acetylsalicylic Acid, Phenacetin, Caffeine, and Codeine. Table III gives the results of analyses of nineteen weighed samples of codeine phosphate to which appropriate quantities of acetylsalicylic acid, phenacetin, and caffeine had been added. These samples were assayed for codeine only, because the procedure for analysis of the other components is identical to the procedure used for the analyses listed in Table I. Table IV lists the results of analyses on sixteen production samples of tablets and filled capsules. Average deviation of codeine assay on weighed samples was 1.1% and maximum observed deviation was −3.7%. The complete analysis for these four components requires about 1 hour per sample. This includes all weighings, sample preparation, extractions, and calculations.

Mixtures of Acetylsalicylic Acid, Phenacetin, Caffeine, and Thenylpyramine Hydrochloride. Table V gives the results of determinations made on seven mixtures containing weighed amounts of the four components. The average deviations from amounts weighed were 1.9% for acetylsalicylic acid, 0.6% for phenacetin, 1.6% for caffeine, and 0.8% for thenylpyramine hydrochloride. Greatest observed deviations were +1.8, +1.2, −3.3, and −1.1%, respectively. Table VI gives results of analyses on six production lots of capsules. About 1 hour per sample is required for the complete analysis of this mixture, including all weighings, preparation of samples, and calculation of results.

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Spectrophotometric Determination of Aspirin, Phenacetin, and Caffeine in Mixtures

MARIE JONES AND R. L. THATCHER
The Squibb Institute for Medical Research, New Brunswick, N. J.

MIXTURES containing aspirin, phenacetin, and caffeine have been produced by pharmaceutical manufacturers for over 25 years. From time to time, there have appeared in the literature various assay procedures for the three constitutents, but none has been widely accepted for routine analytical work. This may be attributed to the fact that most of these methods are excessively time-consuming and show poor recovery or erratic results.

The method of the Association of Official Agricultural Chemists (*1*), involving the hydrolysis of phenacetin, is a lengthy procedure which introduces considerable possibility of error. The Holt method (*4*) has been found unsatisfactory by many workers because of its incomplete separations and erratic results. A method by Green (*3*), proposing a determination of phenacetin by ethoxy content, the usual bromination assay for aspirin, and determination of caffeine by difference, seems to give better recovery than the previous methods, but is still unsatisfactory for caffeine and requires elaborate apparatus for the ethoxy determination. A modification of the A.O.A.C. method by Wilson and Hilty (*8*) retains many of the undesirable features of the original procedure. In 1948 Green, Corbin, and Powers (*2*) discussed a spectrophotometric method for caffeine in the presence of phenacetin. The Holt procedure was used for the separation of aspirin and phenacetin, which were then determined chemically.

In December 1949 a method was published (7) describing the simultaneous determination of the three components by means of infrared spectrometry. Although no separations are needed, the preliminary procedure involves extraction of the materials with chloroform from an aqueous suspension, and subsequent evaporation of the chloroform solution. The method is said to require 4 hours, and reproducibility is claimed to be within ±2%. A second infrared method by Parke *et al.* (6) describes a more rapid, simultaneous method for aspirin, phenacetin, and caffeine, and includes procedures for these mixtures in combination with codeine phosphate and thenylpyramine hydrochloride. These methods are applicable where an infrared spectrophotometer is available. A tentative spectrophotometric method for the simultaneous assay of the three materials, based on ultraviolet absorption, has recently been published (5). It has been the authors' experience that methods for determining three materials in one solution do not usually show satisfactory precision, particularly when one of the substances is present in relatively low concentration.

In the method presented here, the three materials are determined spectrophotometrically on the basis of their ultraviolet absorption. Caffeine and phenacetin are determined together in chloroform solution after the removal of aspirin with sodium bicarbonate. The aspirin–sodium bicarbonate solution is acidified, and the aspirin is extracted and determined spectrophotometrically in chloroform. The absorption spectra are such that after removal of aspirin, the phenacetin and caffeine may be determined spectrophotometrically by the method of multicomponent analysis.

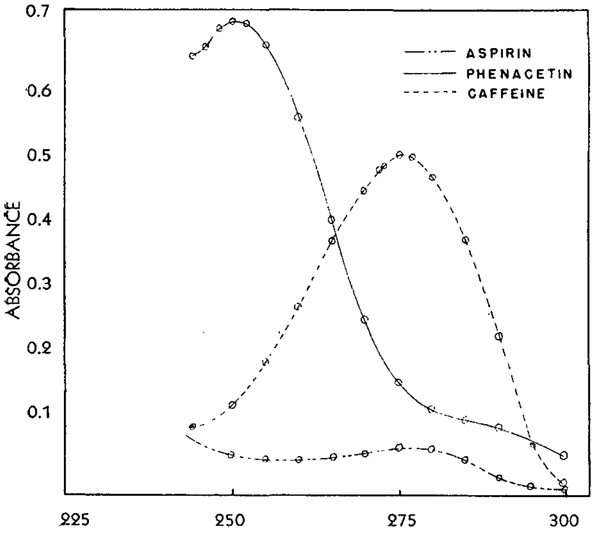

Figure 1

Aspirin was found to have an absorption maximum at 277, caffeine at 275, and phenacetin at 250 mμ (Figure 1). The $E^{1\,\text{mg./l.}}_{1\,\text{cm.}}$ values were calculated from standard solutions, and the values for caffeine and phenacetin were used to develop simultaneous equations for the determination of these materials.

Known mixtures, prepared to contain 220 mg. of aspirin, 160 mg. of phenacetin, and 32 mg. of caffeine, were assayed in the manner described. These proportions correspond to those usually found in tablets. Results indicated an accuracy of ±2% for phenacetin and aspirin and ±5% for caffeine. The entire procedure can be completed in about 2 hours.

METHOD

Reagents. U.S.P. chloroform.

Sodium bicarbonate solution, 4%.

Methods heretofore available for the determination of aspirin, phenacetin, and caffeine in pharmaceutical products have failed to show satisfactory precision or reasonable simplicity. A simple, reliable control procedure for the assay of these constituents, based on the ultraviolet absorption of the three materials, has been devised. A single separation of aspirin from caffeine and phenacetin is the only preparatory procedure required. Absorption measurements are made on the Beckman spectrophotometer and results calculated on the basis of previous standardization. The method requires about 2 hours' working time and precision is ±2% for aspirin and phenacetin and ±5% for caffeine. The operations are simple and can be performed by any trained technician without other special apparatus.

Sulfuric acid, 10%.

U.S.P. diluted hydrochloric acid.

Standardization. Prepare standard solutions in chloroform to contain 50 to 120 mg. per liter of aspirin, 6 to 10 mg. per liter of phenacetin, and 4 to 9 mg. of caffeine. Measure absorbancy on the Beckman spectrophotometer at the following wave lengths: caffeine at 275 and 250 mμ, phenacetin at 275 and 250 mμ, and aspirin at 277 mμ.

Use a constant slit width for all standardization and subsequent assay work. Correct for optical mismatch by alternating the sample and blank solutions in the cells. Check the absorbancies three times and average the readings. These precautions are particularly important in determining values for caffeine and phenacetin. Calculate the $E^{1\,\text{mg./l.}}_{1\,\text{cm.}}$ values for each component. These values, once determined, are used in setting up equations for calculations. Because of slight differences in instruments, it is recommended that standard values be determined in each laboratory.

Procedure. Weigh accurately an amount of powdered tablets or mixture equivalent to about 220 mg. of aspirin, 160 mg. of phenacetin, and 32 mg. of caffeine. For other materials adjust the concentrations so that absorbancy measurements fall between 0.15 and 0.80. Transfer the material into a 250-ml. separatory funnel with 80 ml. of chloroform. Extract the chloroform solution with two 40-ml. portions of chilled 4% sodium bicarbonate solution, to which 2 drops of diluted hydrochloric acid have been added, and then extract with one 20-ml. portion of water. Allow the layers to separate completely each time. Wash the combined aqueous extracts with three 25-ml. portions of chloroform and add to the original chloroform solution. Before proceeding, acidify the sodium bicarbonate solution as directed below to eliminate the possibility of hydrolysis of the aspirin. Filter the combined chloroform extracts through filter paper which has been washed with chloroform in order to remove traces of water into a 250-ml. volumetric flask. Dilute to volume with chloroform and prepare a second dilution of 2 to 200 ml. Measure the absorbance at 250 and 275 mμ on the Beckman spectrophotometer. Check each reading three times, alternate sample and blank in the cells, and repeat. For each value average the six readings. Substitute in the equation below.

Acidify the sodium bicarbonate extracts, using 25 ml. of 10% sulfuric acid. Add the acid very slowly in 5-ml. portions and rotate the funnel gently until the pressure becomes negligible before mixing vigorously. After acidification the pH should be between 1 and 2. Extract the acidified solution with eight 50-ml. portions of chloroform, filtering through a previously chloroform-washed paper into a 500-ml. volumetric flask. Dilute to volume and then dilute 20 to 100-ml. with chloroform. Measure the absorbancy at 277 mμ in the same manner as before and calculate the aspirin content.

Calculation. For caffeine and phenacetin:

	Experimental Values
$E_a = E^{1\,\text{mg./l.}}_{1\,\text{cm.}}$ for caffeine at 250 mμ	0.0131
$E_b = E^{1\,\text{mg./l.}}_{1\,\text{cm.}}$ for phenacetin at 250 mμ	0.0702
$E_c = E^{1\,\text{mg./l.}}_{1\,\text{cm.}}$ for caffeine at 275 mμ	0.0485
$E_d = E^{1\,\text{mg./l.}}_{1\,\text{cm.}}$ for phenacetin at 275 mμ	0.0159

E_m = absorbancy of mixture at 250 mμ
E_n = absorbancy of mixture at 275 mμ
x = mg. of caffeine per liter
y = mg. of phenacetin per liter

$$xE_a + yE_b = E_m$$
$$xE_c + yE_d = E_n$$

Solving for x and y and substituting standard values, the following equations are obtained:

$$x = 21.96\ E_n - 4.97\ E_m$$
$$y = 15.17\ E_m - 4.10\ E_n$$

Therefore

$$\text{Mg. of caffeine in sample} = \frac{[(21.96\ E_n) - (4.97\ E_m)] \times 200 \times 250}{1000 \times 2}$$

$$\text{Mg. of phenacetin in sample} = \frac{[(15.17\ E_m) - (4.10\ E_n)] \times 200 \times 250}{1000 \times 2}$$

For aspirin:

$$E_{1\ \text{cm.}}^{1\ \text{mg./l.}} = 0.00682 \text{ (experimental value)}$$

$$\text{Mg. of aspirin in sample} = \frac{\text{absorb. at 277 m}\mu \times 500 \times 100}{E_{1\ \text{cm.}}^{1\ \text{mg./l.}} \times 20 \times 1000}$$

or

$$\text{Mg. of aspirin in sample} = \frac{\text{absorb. at 277 m}\mu \times 2.5}{E_{1\ \text{cm.}}^{1\ \text{mg./l.}}}$$

DISCUSSION

Considerable work was done using the Holt procedure as a basis for spectrophotometric work. In this method aspirin and most of the phenacetin are extracted with ether from an acid suspension of the mixture. The caffeine and remaining phenacetin are then extracted from the acid with chloroform. The spectrophotometric assays were performed on two solutions, one containing aspirin and most of the phenacetin, and the other containing caffeine and a small amount of phenacetin. The separation was satisfactory, inasmuch as it separated the two components aspirin and caffeine, which have absorption maxima at about the same wave length. Because ether is not a satisfactory solvent for spectrophotometric work, the aspirin and phenacetin solution was evaporated to dryness and the residue was dissolved in alcohol for the absorbancy measurements.

Erratic results were obtained for some time by this method, particularly for aspirin. During evaporation on the steam bath a decomposition of aspirin in the aspirin-phenacetin-ether solution was noted, which may have been due to heat or condensation of moisture during the evaporation. The authors were unable to eliminate both conditions by evaporations under vacuum or by a stream of air, and the method was abandoned.

However, results indicated that the spectrophotometric method was valid and needed only a simpler and more reliable extraction procedure. Results for the three constituents ranged from 90 to 103% of theory, with occasional wider deviations for the aspirin.

The method of Wilson and Hilty was investigated, in which the three materials are extracted from an acid solution with chloroform, and the aspirin is then separated with sodium bicarbonate solution. The method was modified, omitting the preliminary acid solution (which proved unnecessary), and including a subsequent acidification of the sodium bicarbonate–aspirin solution followed by a chloroform extraction of the aspirin. Two chloroform solutions were thus prepared, one containing the phenacetin and caffeine, and another containing the aspirin. Results indicated good accuracy.

In the standardization procedure, the deviation of the E value from the average seemed to be of greater significance than what is usually encountered in spectrophotometric work, particularly at extremely high or low concentrations. In solutions of a single solute very slight deviations in the constant introduced only an insignificant error. However, with two materials in solution, such errors are magnified, as the calculation for each material is affected by the accuracy of its own constant and also by the accuracy of the constant of the associated material. In this assay, slight changes in the $E_{1\ \text{cm.}}^{1\ \text{mg./l.}}$ value for phenacetin at 275 mμ introduce a significant error into the caffeine result. The phenacetin result is not so critically affected by small errors in the $E_{1\ \text{cm.}}^{1\ \text{mg./l.}}$ value at its own maximum wave length, or at that of caffeine. Aspirin, although it has comparatively low absorption, is not critically affected by small errors in the $E_{1\ \text{cm.}}^{1\ \text{mg./l.}}$ value, because it is determined alone.

For these reasons the $E_{1\ \text{cm.}}^{1\ \text{mg./l.}}$ values were determined with all possible precision. The method described under experimental details was found to give satisfactory results. For each material, $E_{1\ \text{cm.}}^{1\ \text{mg./l.}}$ values were determined over a concentration range which would give suitable absorbancy measurements: aspirin from 50 to 120 mg. per liter, phenacetin from 4 to 10 mg. per liter, and caffeine from 4 to 10 mg. per liter. A graph of absorbancy versus concentration indicated apparent conformity with the Beer-Lambert law in all cases.

An error in absorbancy of ±0.002 at 275 mμ will introduce an error of 3 to 3.5% in the caffeine assay, but an error of only 0.1% in the phenacetin assay. The same error in absorbancy at 250 mμ produces an error of 0.7 to 0.9% for caffeine, and 0.4 and 0.5% for phenacetin. A similar error in reading for aspirin at 277 mμ gives a 0.3% difference in result.

The caffeine assay might appear unreliable, in view of these facts. However, in actual practice, when all absorbancy measurements were made with the suggested precautions, the actual caffeine results including all errors did not deviate more than ±5% from theory. The values obtained were well within this limitation, ranging from 96 to 103% of theory.

Table I. Assay of Commercial Samples of Aspirin, Phenacetin, and Caffeine Tablets

Manufacturer	Sample	Aspirin	Phenacetin	Caffeine
A	1	98.3	101.0	99.7
	2	98.3	99.3	96.3
	3	99.9 99.3	99.3 101.6	97.5 96.5
B	1	97.9	98.0	89.8
C	1	99.0	110.0	99.0
D	1	..	97.7	95.7

To determine the reason for the relatively large percentage error in caffeine assays resulting from small errors in absorbancy measurements, known mixtures were prepared to contain 30, 100, and 200 mg. of caffeine. When results were calculated it was found that small errors in absorbancy measurements produced negligible error in the mixtures containing 100 and 200 mg. of caffeine, and errors of 2 to 3% in the mixture containing 30 mg. of caffeine. Apparently the relatively low concentration of caffeine in the usual mixture is the reason for the greater percentage error for this material.

Samples of tablets from outside manufacturers were obtained and assayed by the foregoing procedure (Table I).

Anhydrous caffeine has been used in standardization work, and mixtures of this type are usually labeled on the basis of anhydrous materials, although some mixtures on the market may be labeled on the basis of hydrated caffeine. This appears to be true in the case of manufacturer B, and would account for the low caffeine result obtained in this case.

This method has been used in the authors' laboratories for the routine assay of tablets containing aspirin, phenacetin, and caffeine for about a year, with satisfactory results.

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Analysis of Aluminum and Aluminum Alloys Using Pin Samples

Direct-Reading Spectrochemical Methods

R. W. CALLON AND L. P. CHARETTE
Aluminium Laboratories, Ltd., Arvida, Quebec, Canada

The development of direct-reading spectrochemical methods using an ARL research model quantometer with high precision source for the quantitative analysis of aluminum and aluminum alloys was undertaken in order to obtain more rapid and accurate, as well as cheaper, methods than those using photographic methods. Analytical methods were developed utilizing pin samples 0.25 inch in diameter, which provide improved precision and accuracy, coefficients of variation of the order of 1% for elements greater than 5%, and coefficients of variation of 1 to 2% for elements in the range 1 to 4%, with satisfactory precision for lower percentage elements. Satisfactory limits of detection were obtained for all trace elements which are of interest; in general, these limits are better than those obtained previously by photographic methods. By making minor modifications to the instrument, including the use of a two-position, water-cooled electrode stand, the rapidity with which analyses can be made is approximately doubled over the most efficient photographic methods previously used.

THE principles and advantages of direct-reading spectrometers, utilizing photomultiplier tubes instead of a photographic emulsion as the recording medium for the analysis of metallic samples, have been discussed (*1-5, 8*). As it was felt that this type of instrument would be useful in some of the analytical laboratories of the Aluminum Co. of Canada, Ltd., and other companies of the Aluminium, Ltd., group, experimental tests were run in 1947 on the two spectrometers commercially available at that time. At the end of these tests it was decided that the ARL research model quantometer would be more suitable for the work.

REQUIREMENTS

Adaptability to Development Work. In such work it is a distinct advantage to be able to experiment rapidly with an almost unlimited number of spectral lines, as very little information has been published on direct-reading methods for the analysis of aluminum and its alloys.

Flexibility. The instrument had to be sufficiently flexible to allow development and routine work to be carried out during alternate shifts.

Accuracy. The instrument had to provide the highest possible accuracy, so that elements of the order of 10% or higher might be determined satisfactorily.

Efficiency in Routine Analysis. The instrument had to be capable of analyzing daily 1000 or more samples of commercial purity aluminum plus several hundred alloy samples.

Reliability. The instrument had to be designed so as to facilitate diagnosis and repair in case of failure, as it had to carry a large portion of the analytical load.

The ARL research model quantometer and high precision source unit (*6*) which were installed in the analytical laboratory of the Arvida Works of the Aluminum Co. of Canada, Ltd., are shown in Figure 1. In this particular laboratory, 1000 to 1300 commercially pure aluminum samples and 100 or more alloy samples are analyzed daily for seven to eleven elements. The recording of results is simplified in that, for a large percentage of the aluminum samples of commercial purity, only two to four elements are actually recorded, the rest being controlled at an insignificantly low level. The instrument was calibrated quickly for the analysis of commercial purity aluminum, so that it began to pay for itself within a few weeks of the completion of the installation. Attention was then directed to the development of methods for the analysis of alloys, where the accuracy requirements are more critical.

The following high percentage elements were of particular interest to this plant: silicon (4 to 14%), copper (3 to 8%), magnesium (1 to 10%), nickel (1 to 3%), iron (0.5 to 4%), and manganese (1 to 2%). It was felt that, if a satisfactory compromise between the experimental conditions could be reached for these percentages, satisfactory values would be obtained for elements present in lower percentage.

CHOICE OF SAMPLE FORM

At the outset it was realized that in order to limit the scope of the program a choice of sample form was necessary. In the past two pin samples 0.25 inch in diameter were used for all routine spectrochemical work, whereas most American workers in the aluminum field have preferred a disk sample versus a graphite rod.

Advantages of Two-Pin System. A lower limit of detection is obtained for most elements.

An average result for two samples can be obtained by using one electrode from each. This technique has been used to improve the control of certain casting operations and to facilitate calibration from a limited number of standard samples.

An appreciable saving results from the elimination of the graphite rod. In Canada the cost of high purity graphite is between 1 and 2 cents per exposure, which amounts to around $8000 a year for the Arvida Works laboratory.

Unless the graphite rods are carefully selected, significant errors can be introduced from variations in their thermal and/or electrical conductivity.

In some cases at least, it is easier to obtain samples free from porosity.

Interfering effects from molecular spectra of carbon compounds are avoided.

Advantages of Disk Type of Sample. Accurate alignment of the electrodes is easier. However, little difficulty has been experienced on this score when using pin samples in the two-position, water-cooled electrode stand discussed below.

Repeat analyses can be made more rapidly on disk-type samples when it is satisfactory to use the same machined surface.

It has been stated that the graphite counter electrode reduces oxidation and metallurgical effects.

Fabricated materials are more readily compared to standards when using a counter graphite system. This factor is not of particular importance in a reduction plant.

Less difficulty is experienced with surface oxidation effects.

Accuracy, however, is usually the main consideration and, in general, the same over-all accuracy has been claimed in the literature for both types of samples when using photographic methods. Similar data are not available for direct-reading spectrometers. Difficulties associated with the preparation of standard samples will vary with the problem.

After due consideration, the use of pin electrodes was continued, partly for the reasons given above, partly because all the company's laboratories were equipped with accessories for this type of sample, and partly because of the availability of a suitable range of standards in that form.

Precautions. The most important precautions that must be observed when using pin electrodes are:

The samples should be free from porosity. This can be accomplished by using book-type steel molds with a controlled rate of cooling along the length of the sample. Samples cast by suction in graphite, borosilicate glass, copper, or steel tubes have not been found, in general, to be as satisfactory. Solid ejector-type molds are very useful in certain cases, as the diameter of the sample is more easily controlled.

They must be free from fins, for accurate alignment, and of uniform diameter. Samples are controlled at 0.250 ± 0.005 inch.

They must be free from either real or apparent segregation along their length. A few elements such as lead, bismuth, and possibly magnesium, at high percentages, have been known to give difficulty in this respect.

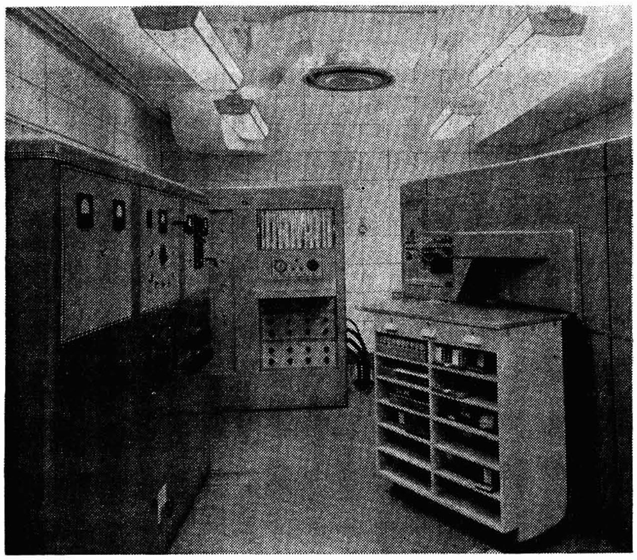

Figure 1. ARL Research Model Quantometer and High Precision Source Unit Installed in Arvida Works Laboratory

Table I. Variables to Be Studied in Development of Alloy Procedures

A	Internal standard line
B	Spectral line o. alloying element
C	Primary or secondary voltage of spark source
D	Inductance in series with analytical gap
E	Duration of prespark period
F	Duration of exposure
G	Type and diameter of sample
H	Electrode spacing
I	Optical variables and portion of analytical gap utilized

Table II. Reproducibility for Silicon (12%) in Aluminum

	12% Level					
	Al 2568 A.		Al 3066 A.		Al 3944 A.	
Si, A.	cv[a]	df[b]	cv	df	cv	df
2516	1.5	100	1.7	100	2.0	100
2882	1.8	100	2.0	100	2.4	100
2988	0.9	200	1.0	300	1.2	100

[a] Coefficient of variation, defined as ratio of standard deviation to amount present, expressed as a percentage.

[b] Degrees of freedom.

Experimental conditions

Inductance	720 μh.	Prespark	4 seconds
Primary voltage	160 volts	Exposure (approx.)	25 seconds
Spark gap	2 mm.		

In certain cases the samples should be exposed within a few hours of machining.

The surface must be smooth and clean-cut, the lathe tools being arranged so that no center tip remains. The electrodes should have a reproducible chamfer of approximately 1/64 inch.

The machined surface must not come into contact with the analyst's fingers, as this will cause sodium contamination and promote oxide formation.

The electrode surfaces must be accurately aligned, with a constant separation. This point is discussed in dealing with electrode stands.

DEVELOPMENT OF ALLOY METHODS

The parameters which were considered to be the most important in the development of a method when using the ARL high precision source unit are listed in Table I.

Arbitrary restrictions were made for some of these variables from visual observations of typical spark discharges. Factors considered were steadiness of discharge, tendency to spark to the sides of the electrodes, tendency to flame outward, and evenness of etch. In general, the spark became less steady after a total discharge period of 30 to 35 seconds, thus limiting factors (E) and (F).

As the optimum electrode diameter will depend, to some extent, on the electrical conditions and as samples 0.25 inch in diameter had been found most suitable for photographic work, this diameter was chosen, thus eliminating (G). At a later date some limited tests using different diameters were made for silicon at the 12% level; maximum reproducibility was obtained, fortunately, with the samples 0.25 inch in diameter.

As some leeway was desired for the over-all exposure level, the grating aperture was left at 80% of full aperture. With this setting the gap length utilized was slightly more than 1.9 mm. of the central portion of the discharge. The entrance slit was set at 50 microns and all receiver slits at 100 microns. As other optical variables such as the focal length of the external lens were arbitrarily fixed, factor (I) was eliminated.

Even with these limitations, a large number of tests were required in order to determine optimum conditions. Fortunately, some combinations of the other parameters were also discarded on the basis of visible or audible unsteadiness of the spark discharge. By studying simultaneously as many lines of aluminum and an alloying element as possible and restricting other parameters to around three to four levels, the scope of the experiment required for each element was kept within reasonable bounds. The best combinations of parameters, as determined from these precision tests, were then checked more thoroughly in order to arrive at optimum conditions. A large number of coefficients of variation must be calculated in this work. This may be simplified greatly by the use of IBM machines which, unfortunately, were not available during the greater part of this program.

In the course of this investigation some interesting phenomena were observed in the study of a 12% silicon alloy, as the results were different from those observed by other workers using a point to plane electrode system. For example, it has been reported (7) that, when a disk sample versus a graphite electrode was used, there was a linear relationship between the primary voltage and the intensity of Al 2568 A. and that highest accuracy was obtained with the line pair Al 2568 A.–Si 2882 A. with next best results obtained with Al 2568 A.–Si 2516 A. In that work an inductance of 360 μh., a primary voltage of around 250 volts, and an analytical gap of 3 mm. were used. When using pin samples the results were different, as shown in Figure 2. For comparison purposes, two inductance values and three aluminum lines are shown for both aluminum of commercial purity and a 12% silicon alloy. A linear relationship was not obtained for an inductance of 360 μh., but was obtained for 720 μh., the inductance that eventually was found to give the most precise results. It does not necessarily follow, however, that a linear relationship is required for the highest precision. With regard to precision, the best results obtained from combinations of the following silicon and aluminum lines

Si	2217, 2435, 2507, 2516, 2882, 2988, 4552 A.
Al	2373, 2568, 2652, 3066, 3093, 3944 A.

are given in Table II. Al 2568 A. and 3066 A. were both satisfactory as the internal standard line, whereas Si 2988 A. gave decidedly superior results.

Si 2516 A. gave approximately the same reproducibility in counts as Si 2988 A. but had a less favorable analytical slope. Si 2882 A. gave relatively poor results. The best results were obtained with different source conditions, the spark gap being 2 mm., inductance 720 μh., and primary voltage 160 volts.

Variation in the prespark period from 0 to 10 seconds had little effect on the coefficients of variation, but with total sparking periods of over 30 seconds the spark discharge tended to become irregular and the coefficients of variation to increase. Because during the first few seconds the number of counts was relatively high and was above the recommended rate of operation of the counters, a prespark of 4 seconds and an exposure of around 25 seconds were chosen.

In more recent work 700 routine casts of 12% silicon alloy were analyzed in duplicate on the quantometer in parallel with the chemical laboratory, over a period of 4 weeks. In such parallel analyses there are a number of sources of error which are not included in precision tests such as those reported in Table II.

Setting-up errors. These include both the error in making sensitivity and tab adjustments and errors in determining the exact calibration curve at levels other than those of the standards.

Drift of the instrument between standardizations.

Bias due to incorrect values assigned to the standard samples. This may include variation in the metallurgical structure between the standards and routine samples.

Variation in real or apparent composition in different sections of the standard.

Sampling error, in both chemical and spectrochemical samples.

Extraneous element effects.

Errors in chemical analysis.

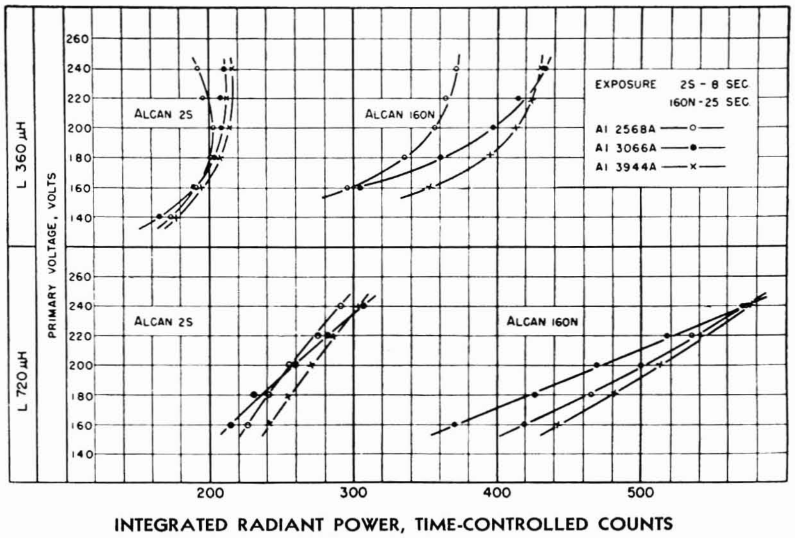

Figure 2. Integrated Radiant Power of Aluminum Lines *vs.* Primary Voltage

The first five sources of error can be minimized to a point at which they are negligible in comparison to the others, assuming, of course, that maximum care is exercised at all stages of the analytical procedure. The sixth error, variation in the percentage of other elements, can be important in this alloy if sodium is present. An increase in the sodium content causes an apparent increase in the percentage of silicon. As the range of sodium values encountered is usually narrow, and a suitable correction can be applied if wide variations exist, this leaves only errors in chemical analysis and the inherent error of the quantometric analysis.

The results obtained in parallel determinations of silicon are summarized in Table III. In general, the duplicate analysis was obtained about 4 hours after the original analysis, the instrument having been standardized every hour.

Table III. Comparison of Chemical and Quantometric Values for Silicon in Alcan 160N Alloy

(12% Si)

	Coefficient of Variation, %	Bias, % Si
Quantometer reproducibility	0.9	...
Av. of duplicate quantometric values *vs.* original chemical value	2.4	0.071
Av. of duplicate quantometric values *vs.* checked chemical value[a]	1.3	0.024
First quantometric value *vs.* checked chemical value[a]	1.4	0.027
No. of determinations	700	
Internal standard line, A.	Al 3066	

[a] Chemical values checked whenever they differed by more than 0.20% from average quantometric values.

Thus, the coefficient of variation included setting-up errors and instrument drift error as well as the quantometric error. The coefficient of variation of 0.9%, as computed from the duplicate quantometric values, agreed very well with the results of the rapid reproducibility tests, showing that the standardizaton errors were negligible. (Coefficient of variation = $\frac{\bar{\omega}}{1.128} \times \frac{100}{\%\ \text{Si}}$ where $\bar{\omega}$ is the average difference between duplicate values.) The coefficient of variation of 2.4% between the chemical value and the average of the quantometric results was only fair, but was reduced to 1.3% by checking chemical values that appeared out of line. Finally, the coefficient of variation was calculated, assuming that only the first quantometric value was available. This gave a value of 1.4% of the amount present. As the last two values still included most of the normal chemical error of routine control work and a small bias, this showed that the results of rapid precision tests could be approached in long-term routine analysis.

All these results for silicon were obtained using a regular steel book-type mold without a controlled rate of cooling along the length of the electrode. As this type gives some porosity, and as the largest deviations in the quantometer results are obtained for samples showing porosity, it is expected that still lower coefficients of variation will be obtained using samples from a newer type of mold which eliminates this source of error.

Some points of interest were observed in the analysis of "high copper" alloys. As shown in Figure 3, rather surprising shapes were obtained for the analytical curves, an inflection point being observed at copper contents above 12%. No practical disadvantage resulted, however, as all commercial alloys have less than 10% copper. Figure 4 shows the variation in integrated radiant power for both aluminum and copper with increasing percentages of copper when time-controlled exposures are used. This explains at least qualitatively the shapes of the curves shown in Figure 3.

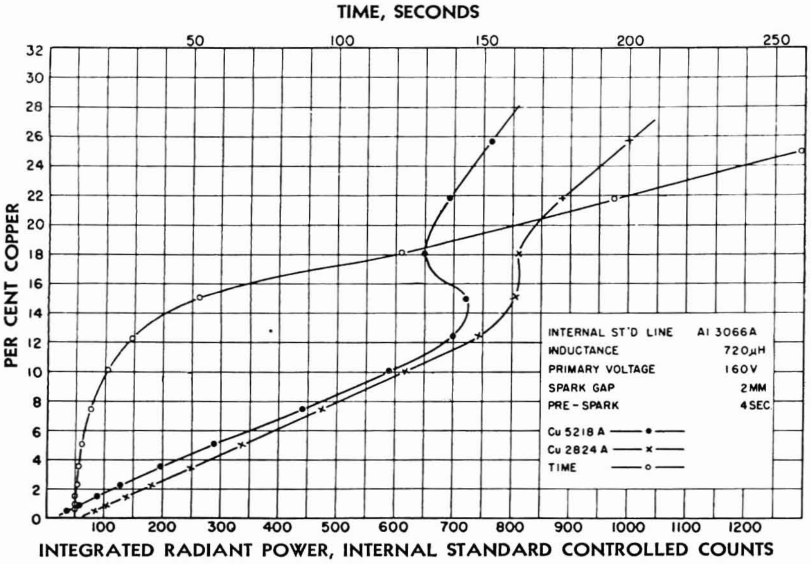

Figure 3. Analytical Curves for Copper in Aluminum

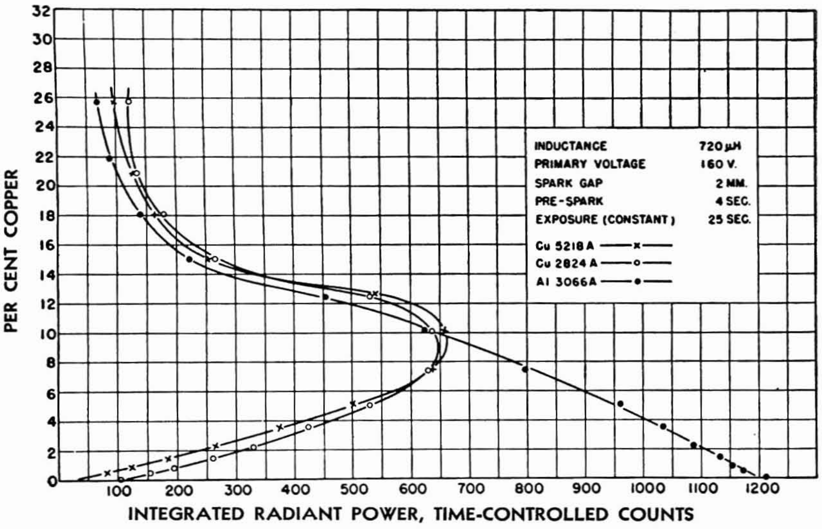

Figure 4. Variation in Aluminum and Copper Integrated Radiant Power *vs.* Copper Content

Table IV. Reproducibility for Copper (5.0% and 7.5%) in Aluminum

	5.0% Level				7.5% Level			
	Al 2568 A.		Al 3066 A.		Al 2568 A.		Al 3066 A.	
Cu, A.	cv	df	cv	df	cv	df	cv	df
2824	0.9	108	1.0	108	0.95	212	0.95	212
5153	0.9	108	1.0	108	1.3	104	1.1	104
5218	0.8	108	0.9	108	1.1	104	1.1	104

Experimental conditions

Inductance	720 μh.	Prespark	4 seconds
Primary voltage	160 volts	Exposure (approx.)	25 seconds
Spark gap	2 mm.		

Table V. Reproducibility for Magnesium (5.5% and 9.5%) in Aluminum

	5.5% Level				9.5% Level			
	Al 2568 A.		Al 3066 A.		Al 2568 A.		Al 3066 A.	
Mg, A.	cv	df	cv	df	cv	df	cv	df
5184	1.6	100	1.7	100	1.7	160	1.9	160
5528	1.1	100	1.2	100	1.2	160	1.2	213

Experimental conditions

Inductance	720 μh.	Prespark	4 seconds
Primary voltage	160 volts	Exposure (approx.)	25 seconds
Spark gap	2 mm.		

Here again, extended tests were run to determine the best combination of the variables, which was found to coincide with that for silicon. The best results from the reproducibility tests using these conditions and the following spectral lines

Cu 2192, 2247, 2824, 5106, 5153, 5218, 5782 A.
Al 2568, 3066, 3093, 3944 A.

are shown in Table IV. Cu 2824 A. gives more reproducible results as the percentage is increased, and it is probable that this line would be preferable when determining high percentages of copper.

As the same source conditions were found suitable for both copper and silicon, these conditions were tested for magnesium using combinations of the following lines:

Mg 2780, 2791, 2803, 2852, 2929, 3332, 3337, 3832, 3838, 4481, 5173, 5184, 5528 A.
Al 2568, 3066, 3944 A.

As shown in Table V, satisfactory results were obtained for some line pairs; so no other source conditions were tested.

The radiant powers of both aluminum and magnesium lines for samples having high percentages of magnesium varied considerably, rising to a maximum in about 5 seconds and then dropping to 30 to 40% of the peak radiant power in about 10 seconds. In order to maintain uniform exposure conditions, a 4-second prespark was used, even though this resulted in a high counting rate during the initial part of the exposure. Although this might have resulted in some jamming of the electromechanical counters, no difficulty of this nature was experienced.

This work was extended to iron, manganese, and nickel using the same source conditions and the following spectral lines:

Fe 2396, 2599, 3735, 3820 A.
Mn 2576, 2594, 2606, 2673, 2795, 2801, 2933, 2949, 3460, 4031, 5341 A.

Ni 2254, 2265, 2270, 2287, 2438, 2473, 2633, 3134, 3415, 3434, 3493, 3515, 3525, 3858, 3975, 3994, 4402, 4459, 4714, 5477 A.

Al 2568, 3066, 3093, 3944 A.

As shown in Table VI, satisfactory coefficients of variation were obtained for certain line pairs. Better values might possibly have been obtained using other source conditions, but the need for uniformity ruled out any further investigations.

Comparing the results obtained in Tables II, IV, V, and VI it may be seen that, when using the best spectrum line for each element, Al 2568 A. was significantly better than Al 3066 A. for nickel, while the reverse was true for manganese. No significant differences were obtained for the other elements. As there was negligible difference in the over-all reproducibility, the final choice of the internal standard line was determined by a number of secondary factors which favored Al 3066 A.—for example, the results of reproducibility tests for commercially pure samples obtained with Al 3066 A. as internal standard line were better than those obtained with Al 2568 A. Similarly, it was found that accidental misalignment of the spectrometer optics and extraneous elements had less effect on the analytical results when Al 3066 A. was used.

ANALYSIS OF LOWER PERCENTAGE ELEMENTS

While the lines chosen from the above work are satisfactory with regard to reproducibility at higher percentages, they are not necessarily satisfactory for the determination of these elements at low percentages. Table VII gives data on the limit of detection and precision for lines considered to be satisfactory for low percentages of these and other elements of interest.

The limit of detection is defined here as the percentage at which the integrated radiant power, expressed in counts, of the spectral line plus the total background—i.e., spectral background and dark current or electrical noise—is 10% higher than that of the total background alone. These limits of detection depend on source conditions, ratio of sensitivity to total background obtained with a given mutiplier tube, the percentage range covered with a given number of counts, and the width of the receiver slit, in this case 100 microns.

The positioning of receivers plays an important part in the final selection of lines and was one of the main reasons for picking the line which is listed first for each element for most analyses. With this receiver arrangement, it is very simple to change from commercially pure metal to alloy analysis. A satisfactory limit of detection is obtained for each element when the high precision type of spark discharge is used.

The limits of detection are, in general, conservative estimates, because a criterion of 10% above total background is higher than is really necessary, and standards were not available at very low percentages in a number of cases; consequently, no values below 0.0001% have been reported.

At various times reproducibility checks have been made for each of the minor elements. Typical coefficients of variation are also shown in Table VII. The values given for some of the low percentages are abnormally high because the data were not recorded to a sufficient number of decimals. While there is considerable difference between the elements—relatively large deviations usually being caused by a poor choice of line—they are all satisfactory from the practical viewpoint.

Table VI. Reproducibility for Iron (3.5%), Nickel (2.8%), and Manganese (1.3%) in Aluminum

	Coefficients of Variation												
	Iron, 3.5%					Nickel, 2.8%			Manganese, 1.3%			
Al, A.	df	2396 A.	2599 A.	3735 A.	3820 A.	df	3134 A.	3858 A.	df	2673 A.	2933 A.	3460 A.
2568	150	2.4	2.1	2.0	1.9	100	1.9	1.6	120	1.8	1.6	1.6
3066	150	2.3	2.0	2.1	2.2	100	2.4	1.9	120	1.4	1.2	1.1

Experimental conditions
Inductance 720 μh.
Primary voltage 160 volts
Spark gap 2 mm.
Prespark 4 seconds
Exposure (approx.) 25 seconds

Table VII. Limit of Detection and Reproducibility for Low Percentage Elements in Aluminum

Element	λ, A.	Limit of Detection, %	Coefficient of Variation % level	cv[a], %
Be	2349	0.0001	0.002	3.2
			0.02	5.1
	3130	0.0001	0.002	4
			0.02	5.5
Bi	3068	0.003	0.010	4.3
			0.049	1.8
Cr	4254	0.0007	0.005	3
			0.038	2.1
Cu	3274	0.0004	0.010	5
			0.045	2.7
	3248	0.0003	0.010	4
			0.045	3.1
Fe	3735	0.002	0.10	2
			0.45	1.5
Mg	5184	0.003	0.042	1.5
	2852	0.0001	0.001	6.6
			0.042	4.1
Mn	2933	0.003	0.006	4
			0.047	1.8
	2594	0.0004	0.006	3.2
			0.049	1.5
Na	5890	0.0001	0.005	4
Ni	3858	0.010	0.04	5
	3415	0.0008	0.006	4.5
			0.035	3.0
Pb	4058	0.002	0.005	6
Si	2516	0.0008	0.10	1.9
			0.23	1.5
	2882	0.0007	0.095	2.6
			0.25	1.9
Sn	3175	0.005	0.013	7.2
Ti	3685	0.001	0.005	3
			0.04	1.5
	3349	0.0002	0.005	4.6
			0.042	2.1
V	4379	0.001	0.015	2
Zn	3345	0.002	0.005	7
			0.05	1.5
Zr	3392	0.0001	0.005	1.5

[a] Coefficient of variation using 48 degrees of freedom.

Experimental conditions. Internal standard line Al 3066 A. for all elements except for Bi 3068 A. (Al 2568 A.)
Inductance 720 μh.
Primary voltage 160 volts
Spark gap 2 mm.
Prespark 1 second
Exposure 8.5 ± 0.5 seconds
Receiver slit 100 microns

INSTRUMENTAL MODIFICATIONS FOR ROUTINE ANALYSIS

As the instrument had to be capable of carrying a large analytical load, some changes were necessary in order to achieve the desired rate of analysis. First, the exposure time for analysis of metal of commercial purity was cut to approximately 8.5 seconds with 1-second prespark. The coefficients of variation given in Table VII were all obtained using these exposure conditions. In order to prevent jamming of the counters, a maximum recording cycle of 300 counts instead of 600 was used. A second reset tab was added to each tape in order to cut the reset time from a maximum of 10 to 5 seconds. When analyzing alloy samples, the second tab is removed from the internal standard line tape and appropriate alloying line recorders. This arrangement can be improved by adding a switching system, so that in one position the second tab will not actuate the reset mechanism. Filters were installed on all receivers, so that a greater range of light intensities could be covered without a major change in the attenuator settings, which in

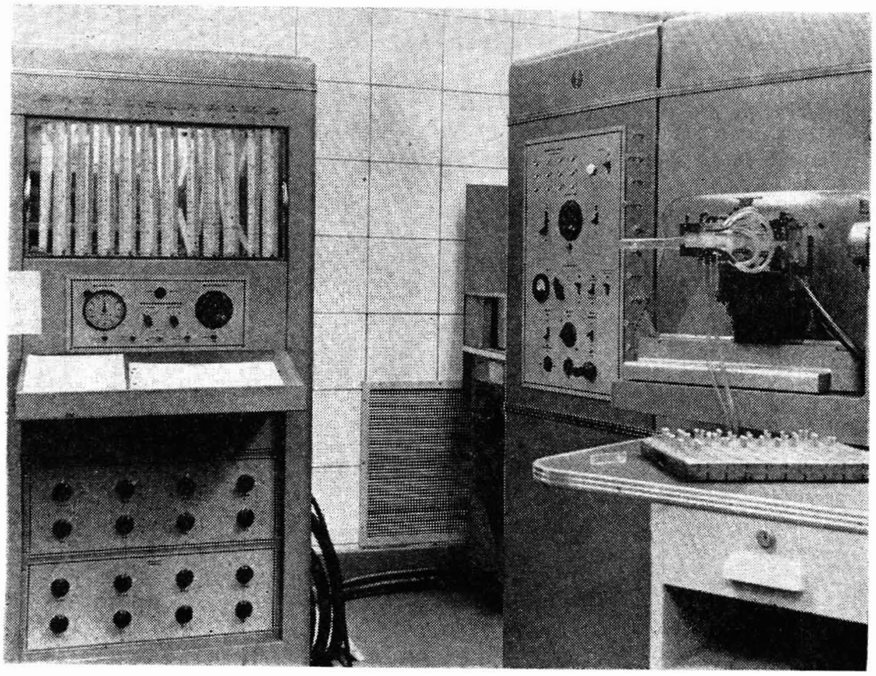

Figure 5. Two-Position Electrode Stand

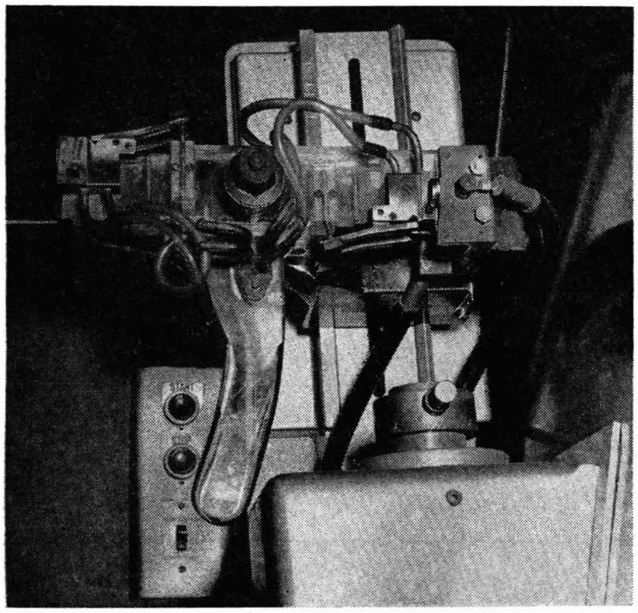

Figure 6. Plan View of Two-Position Electrode Stand

turn would cause a change in the fatiguing characteristics of the multiplier tubes. For example, one can determine from 0.01 to 3% iron without any appreciable change in attenuator settings and still obtain accurate results at all percentages in this range.

The major change made was the addition of a more suitable electrode stand to permit rapid exchange of samples. In photographic work the authors have used a rotating 3-position electrode stand, so that one can simultaneously load one pair of electrodes, prespark a second, and expose a third pair. While this has operated satisfactorily, it was not precise enough mechanically for direct reading work and did not give maximum utilization of the light available, in that the electrodes were horizontal; it also lacked water cooling. For these reasons a water-cooled, two-position stand was constructed, as shown in Figure 5. A typical set of analytical scales as used for routine analysis can also be seen in this photograph.

The plan view of the electrode stand is shown in Figure 6.

The base is an aluminum casting; the horizontal arm, which rotates on ball bearings, is of polystyrene, as are the handle and various insulating spacers. The vee-blocks are of brass, drilled for cooling water, and have spring clamps attached for holding pin electrodes. Replaceable wear plates are affixed to the vee-blocks; fixed rollers (ball-bearing) guide the assembly to correct height in the sparking position. Means are provided for adjusting both the swinging arm and the electrical contact assembly vertically and horizontally for alignment of the image of the spark gap on the grating. Water leads are of transparent Tygon tubing, and are grounded near the center of the moving assembly to obviate any possibility of electrical shock through the water. The resistance from each vee-block to ground is about 1.5 megohms with tap water flowing through the leads. A Lucite hood (not shown) over most of the stand prevents the operator from accidentally touching high-voltage components and protects the discharge from air currents. Both polystyrene and steel spacers have been used for setting the electrode gap; the former are preferred.

Very accurate alignment is necessary with this type of stand, because standards may be run in one position and routine samples in the other. Maximum tolerances of ±0.001 inch were specified for the positioning of the samples. Even so, some asymmetry was observed. Careful adjustment and equalization of the resistance to ground in the two water connections did not completely eliminate this trouble. Another difficulty was unevenness in the spark etch. Air jets provided some improvement, but of a variable nature. The problem was satisfactorily solved by cementing small glass or plastic plates in the cavities behind the electrodes. These apparently altered the electrical field so as to equalize the discharge and thereby provide a uniform etch on the electrodes. This also improved the symmetry to a satisfactory level for analysis of commercially pure aluminum samples and some alloys. Only one side of the stand is used for alloys containing high percentage elements.

This stand has been used to analyze around 1,000,000 samples and has not shown any signs of wear, except for the sliding contacts which are readily replaceable.

As a check on the uniformity of the results obtained with this stand, standard samples were analyzed as routine samples each day for several weeks. No significant differences, using around 200 degrees of freedom, were obtained between the averages of the coefficients of variation calculated for each side of the stand and those obtained when all the results were grouped together—i.e., the bias was negligible in all cases.

With these changes the analysts have been able to analyze commercially pure metal and pot-room samples for up to 10 or 11 elements, recording elements that are 0.01% or greater, and some elements to 0.001%, at the rate of around 1100 to 1300 samples in an 8-hour shift. For example, at a peak period in 1949, 1380 samples were analyzed in an 8-hour period, an average of 2.9 samples per minute. An operating rate of 3.5 samples per minute is often attained for small groups of, say, 50 to 100 samples. This has resulted in large savings in the laboratory, as the number of analysts required to handle this work is one half of that required previously when the analysis was done by photographic methods; Moreover, the results are more accurate than those obtained previously.

The change-over from commercially pure metal to alloy analysis is done rapidly by the shifting of one or two receivers and/or the insertion of one or more filters.

CONCLUSION

Satisfactory precision, an adequate limit of detection for all elements of interest, and a satisfactory rate of analysis can be obtained when pin electrodes are used with the ARL research model quantometer and high precision source unit.

In the future, considerable improvement can be expected in both the ease and precision of analysis. The research-type instrument will be superseded by semifixed slit instruments in most fabricating plants, but it will still be preferable for research work, in plants where the analytical work changes rapidly and where a large number of samples must be analyzed. A satisfactory compromise can be reached in certain cases by the use of a hybrid instrument—i.e., one in which the lower rear bridge is removed and a relatively large number of semifixed receiver slits and multiplier tubes are inserted in its place.

ACKNOWLEDGMENT

It is a pleasure to acknowledge the work of other members of the laboratories who have done most of the experimental work. This applies particularly to R. H. Black and W. D. Russell of the staff and H. M. Parkhurst of the Arvida Works technical staff.

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High-Frequency Titration

A Bridge Method

JAMES L. HALL AND JOHN A. GIBSON, JR.
West Virginia University, Morgantown, W. Va.

Wider investigation of the possibilities of high-frequency titrimetry has been hampered by the small number of analytical chemists having the time or electronic know-how to construct their own apparatus, lack of agreement on selection of the best frequency and concentration for a given reaction, and uncertainty as to the nature of the quantities measured by various types of apparatus. These objections may be largely overcome by the bridge method described here. Aside from the very simple glass titration cell, this apparatus was assembled entirely from standard, commercially available parts. It has very good stability, sensitivity, and flexibility, as demonstrated by its use in a number of well-known analytical reactions. The availability and simplicity of operation of the apparatus should enable many analysts to apply it to their problems, and the capacitance and conductance data reported here should lead to a better understanding of the theoretical aspects of the method.

SEVERAL varieties of apparatus have been described recently for use of high frequency for the indication of chemical end points. The literature on this subject has been adequately reviewed by Jensen and Parrack (*4*), West, Burkhalter, and Broussard (*6*), and Blaedel and Malmstadt (*2*). The types of apparatus reported to date introduce a cell into one or more components of the tank circuit of a vacuum tube oscillator and measure the effect of changes within the cell on one or more parameters of the oscillating circuit—for example, Jensen and Parrack (*4*) measured the effect on the plate current of the oscillating tube. Anderson, Bettis, and Revinson (*1*) measured the effect on the grid current of the tube, and West, Burkhalter, and Broussard (*6*) measured the shift in frequency of the oscillating circuit. The authors have tried modifications of some of these schemes, but found that they lacked sensitivity, stability, or the flexibility desired.

The present paper reports the use of an impedance-measuring circuit for direct determination of changes in the components of admittance, susceptance, and conductance, in a cell in which a reaction is being carried out. The admittance, Y, is defined by the relation

$$Y = G + jB$$

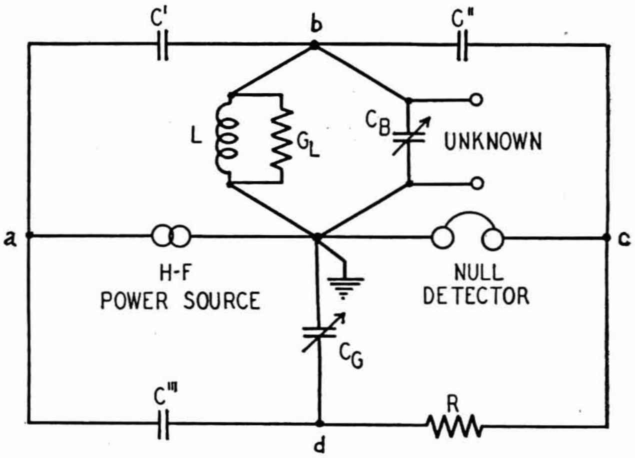

Figure 1. Basic Diagram of Twin-T

where G represents the conductance, B represents the susceptance, and j is the operator. The susceptance is obtained from the capacitance, C_B, by the relation

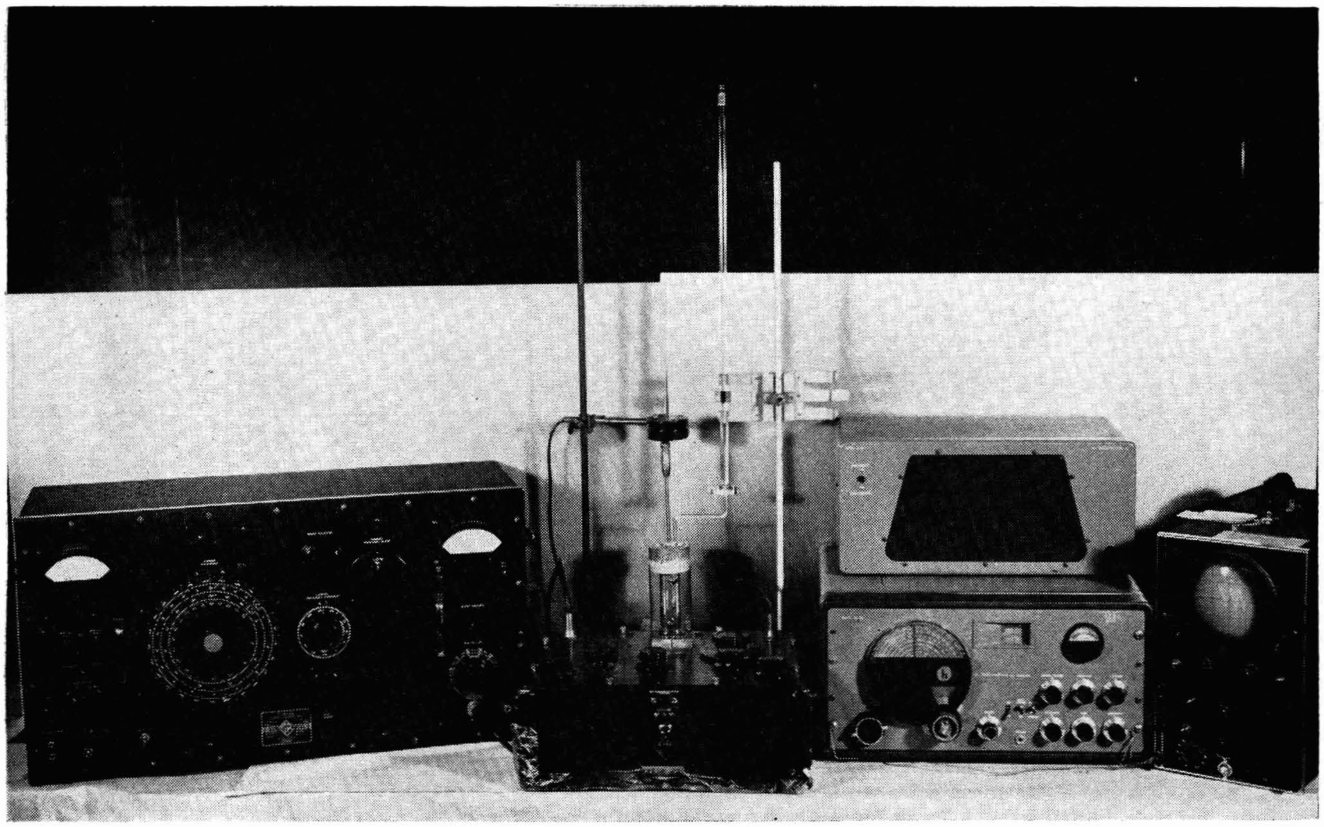

Figure 2. Complete Apparatus

$$B = \omega C_B$$

where ω is frequency in radians per second. The quantities read from the bridge are capacitance differences, ΔC, and conductance differences, ΔG.

DESCRIPTION OF APPARATUS

Except for the cell, the entire apparatus was assembled from commercially obtained components.

The bridge was a General Radio Type 821-A Twin-T impedance-measuring circuit (*5*). The high-frequency oscillator was a General Radio Type 805-C standard signal generator. The detector unit consisted of a Hallicrafters SX-42 receiver with a Du Mont Type 208 oscillograph for visual indication and a speaker for audio indication of the null point. All final balances were made using the beat frequency oscillator of the receiver in place of the internal modulation of the signal generator. For use of the bridge, the manufacturer's directions were carefully followed. It was possible to make measurements at any frequency from the lower limit of the receiver, 0.54 Mc., to the upper limit of the bridge, 30 Mc.

A simplified schematic diagram of the bridge is shown in Figure 1; Figure 2 is a photograph of the entire apparatus. The circuit consists of two T networks connected so that they furnish parallel transmission paths, *a-b-c* and *a-d-c*, from the high-frequency oscillator to the detector. A null balance is obtained—that is, there is zero energy transfer from the generator to the detector, when the transfer impedances of the two T networks are made equal and opposite (*3*). The setting of the capacitor, C_B, determines the susceptive balance. The capacitor dial is calibrated in micromicrofarads. The value of the conductance is given by

$$G = \omega^2 C'C''R \frac{\Delta C_G}{C'''} = K\omega^2 \Delta C_G$$

and the dial C_G is calibrated directly in conductance for frequencies of 1, 3, 10, and 30 Mc. For other frequencies, the dial reading is multiplied by the ratio of the squares of the working and direct-reading frequencies. For example, if the direct-reading frequency is 10 Mc. and the operating frequency is 6 Mc., the dial readings are multiplied by $(6)^2/(10)^2$ or 0.36.

A photograph of the face of the bridge is shown in Figure 3.

The cell was constructed in this laboratory.

Figure 3. General Radio Twin-T Impedance-Measuring Circuit

It consists of a borosilicate glass tube 25 by 110 mm., on which were mounted two copper bands 22 mm. wide with a space of 25 mm. between them. The bands were kept in position by being attached to an insulating strip. Copper wires about 20 cm. long were soldered to the bands and were connected to banana plugs, which were mounted on an insulating strip in such a way as to plug directly into the unknown terminals of the bridge. To prevent moisture and dust from affecting the copper bands or the glass between them, the cell was mounted within a larger borosilicate glass tube by means of a plastic tape and wax seal. The connecting wires were sealed through this outside tube. Several shielding arrangements were tried with the cell, but entirely satisfactory results were obtained without shielding. A photograph of the cell is shown in Figure 4.

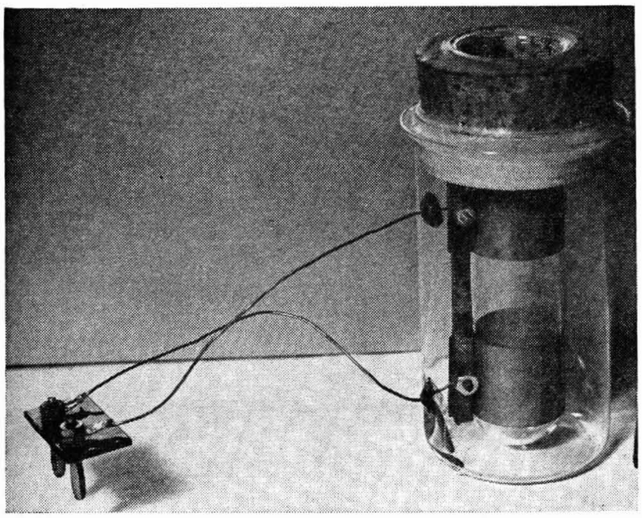

Figure 4. Cell

A motor-driven glass stirrer was placed in the cell with a paddle midway between the two copper bands. The operation of the stirrer changed the initial conductance and capacitance readings slightly, but had no effect on the shape of the curves or the value of the end points.

METHOD OF OPERATION

Because about 80 ml. were required to fill the cell to above the top of the upper metal band, it was necessary to start each titration with that volume. For the results reported here 8 ml. of the solution to be titrated at the concentration specified were placed in the cell and diluted with 72 ml. of distilled water. Dilution of the initial solution at this point also tended to minimize effects due to reduction of the concentration of certain ions during the progress of the titration. The bridge was brought to balance at the selected frequency without the cell, and then was rebalanced with the cell connected, both before and after filling.

In all cases the filled cell gave an increase in capacitance and conductance over that given by the empty cell. For the higher frequencies and higher concentrations the increase in conductance was greater than the range of the calibrated conductance dial, but except for the combination of concentration above about 1 *M* and frequency above about 15 Mc., the bridge could be balanced by the use of the auxiliary conductance knobs. For these higher concentrations and frequencies the actual conductance increase may be measured by placing an auxiliary capacitor in series with the cell, but the calculations are tedious; as the results are not of immediate interest, they are not reported here.

The data recorded are the differences between the capacitance and conductance readings of the balanced bridge with the cell, initial solution, and stirrer in position, and the corresponding balances after addition of the successive increments of the second solution. The operation of the bridge is simple and quick. Only about 15 seconds are required to rebalance the bridge after each addition of the second solution. The capacitance and conductance differences are recorded in micromicrofarads and micromhos, respectively. The balance points were exceedingly sharp and could be reproduced within the precision of the reading of the calibration marks on the dials.

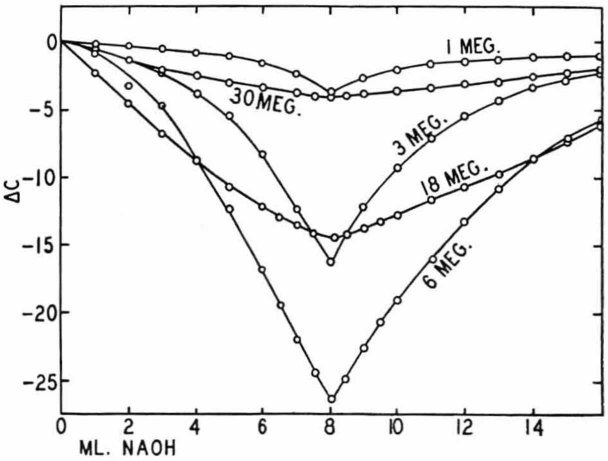

Figure 5. Effect of Frequency

Titration of 0.1 *N* hydrochloric acid with 0.1 *N* sodium hydroxide. Capacity changes

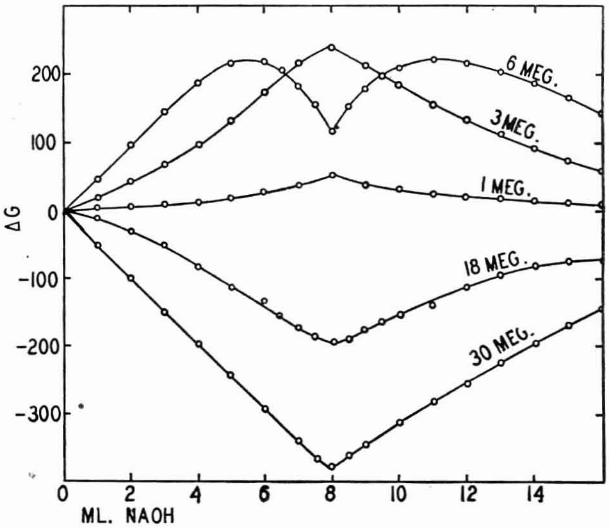

Figure 6. Effect of Frequency

Titration of 0.1 *N* hydrochloric acid with 0.1 *N* sodium hydroxide. Conductance changes. Numerical values at 18 and 30 Mc. divided by 10 before plotting

EXPERIMENTAL RESULTS

The apparatus has been tested by carrying out titrations involving several well-known analytical reactions.

Acid-Base Reactions. EFFECT OF FREQUENCY. For each titration 8.0 ml. of 0.1 *N* hydrochloric acid diluted to 80 ml. in the cell were titrated with approximately 0.1 *N* sodium hydroxide. This reaction was carried out at more than fifteen frequencies, the results of five of which are shown in Figures 5 and 6.

The end points agree with indicator-determined end points within the precision of the buret readings. In all cases the capacitance of the cell decreases to the end point and then increases, the curves being approximately symmetrical about the end point. As the frequency is increased from 1 to 6 Mc. the

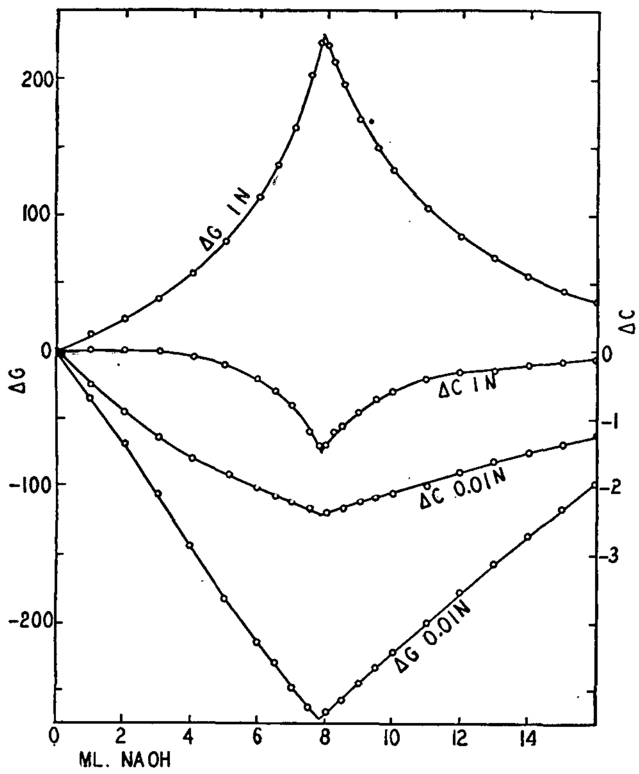

Figure 7. Effect of Concentration at 6 Mc.

Titration of 0.988 N hydrochloric acid with 1.007 N sodium hydroxide and 0.0098 N hydrochloric acid with 0.10 N sodium hydroxide

difference in capacity between the initial balance and the end point increases, and the break in the curve at the end point is sharp. The break in the curve at 1 Mc. is sharp; it does not show to advantage on the scale of these figures. Above 10 Mc. there is a decrease in the difference between the initial balance and the end point, the break in the curve at the end point becomes blunt, and at still higher frequencies it becomes rounded.

At 1 Mc. for the 0.1 N solutions the differences in conductance between the initial balance and the successive balances are all positive and the break at the end point is very sharp. As the frequency is increased, the curve rises but becomes rounded, and at 3.8 Mc. it is almost flat for several milliliters in the vicinity of the end point. From this frequency to 10 Mc. the curve shows, with increasing depth and sharpness, a dip at the end point. Above 10 Mc. the conductance changes up to the end point are all negative and rapidly increase in magnitude with frequency. The numerical increments for 18 and 30 Mc. have been divided by 10 for plotting.

EFFECT OF CONCENTRATION. Experiments were conducted with 0.01 N and 1.0 N hydrochloric acid (diluted as before) and the corresponding concentrations of sodium hydroxide. The results at 6 Mc. are shown in Figure 7. As a first approximation the effect of dilution resembles the effect of increasing frequency and the effect of increasing the concentration resembles the effect for decreasing the frequency.

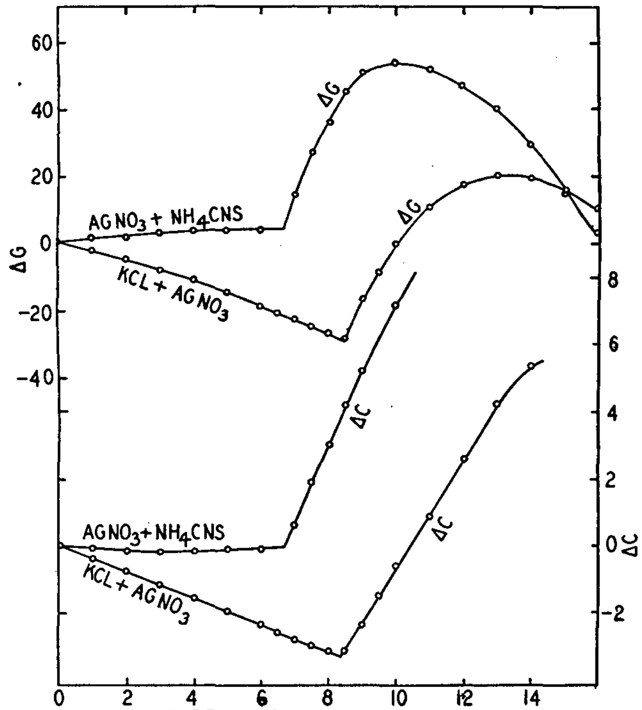

Figure 8. Titration at 6 Mc. of 0.1 M Silver Nitrate with 0.12 M Ammonium Thiocyanate and 0.1 M Potassium Chloride with 0.1 M Silver Nitrate

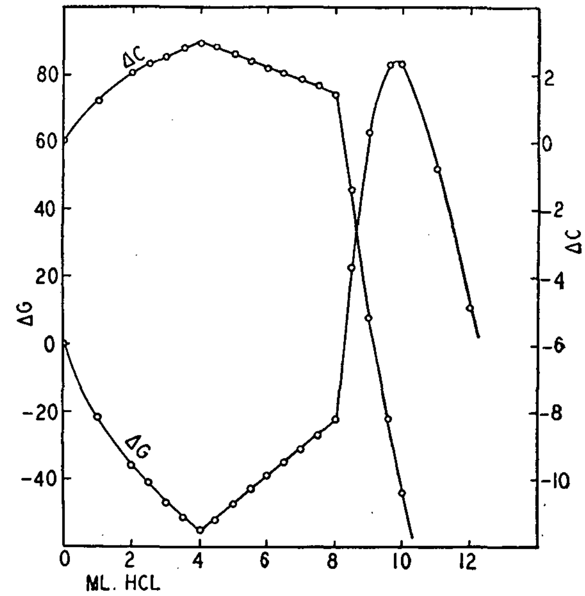

Figure 9. Titration of 0.05 M Sodium Carbonate with 0.1 M Hydrochloric Acid

Precipitation Reactions. Silver nitrate was titrated with ammonium thiocyanate and potassium chloride was titrated with silver nitrate. The results for 6 Mc. are shown in Figure 8. Both capacitance and conductance end points are easily read and of satisfactory precision.

Carbonate-Bicarbonate Titrations. Approximately 0.05 M sodium carbonate was titrated with 0.1 N hydrochloric acid at 6 Mc. The results are shown in Figure 9. The carbonate and bicarbonate end points are well defined on both the conductance and capacitance curves.

DISCUSSION

Although the end point for a given pair of reactants is independent of the frequency, the curve form changes in a way that is as yet unexplained. In Figure 6, for example, the ΔG curves reverse direction between the highest and lowest frequencies used and they show a peculiar shape in the range in which the reversal takes place. In Figure 7, somewhat similar reversals are noted with concentration changes at a fixed frequency. In Figures 8 and 9 there is a reversal of the direction of the conductance change with excess reagent after the end point is passed. Further investigations in progress should lead to an explanation of these facts. The data of Anderson, Bettis, and Revinson (*1*) show some similar dependence of curve form on frequency.

ACKNOWLEDGMENT

The authors express their thanks to Joseph Collett, who constructed the cell and aided with some preliminary experimental work on this equipment. They also appreciate the permission of the General Radio Co. to use Figure 1.

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Polychromatic X-Ray Beams

Nonlinear Relationship between Composition and Absorbance

H. A. LIEBHAFSKY AND P. D. ZEMANY
Research Laboratory, General Electric Co., Schenectady, N. Y.

For monochromatic x-ray beams, the mass absorption coefficient of a mixture (or solution) stands in additive relationship to the coefficients of the elements, free or combined, contained therein. The existence of this relationship facilitates the use of x-ray absorption methods in analytical chemistry. Ordinarily the additivity exists also for polychromatic beams, but marked deviations therefrom occur in the zirconium-hafnium system. The present investigation proves that such deviations are traceable to absorption edges. For selected pairs of elements, the occurrence of an absorption edge can cause an inversion in the relationship of their absorption coefficients for monochromatic beams—that is, the element having the greater coefficient at wave lengths below that of the edge may have the smaller coefficient at wave lengths above it. If the inversion occurs within the wave-length range of a polychromatic beam, the deviations in question may result. In the two systems studied, these deviations take the form of absorbance maxima as composition is varied, but other forms are possible. While the occurrence of these deviations restricts the usefulness of polychromatic beams in chemical analysis, it will often be possible to carry out the analysis by x-ray methods under other experimental conditions.

THE improved means now available for measuring x-ray intensities have operated to increase the usefulness of x-ray absorption methods in analytical chemistry (*3*). Although it is desirable in principle to use monochromatic x-rays in applying these methods, there are cases for which the concomitant reduction in beam intensity cannot (or need not) be tolerated, and polychromatic beams are consequently employed.

It is well known that x-ray absorption is an atomic property, and that the mass absorption coefficient (*2*) of a compound or of a mixture can be computed from those of the elements, provided the beam is monochromatic.

For example, consider a sample containing only one or both of the binary compounds *AB* and *CD*, *m* and *n* being the proportions by weight of *A* and *C* in these compounds. The mass absorption coefficient of a sample, *S*, containing the proportion by weight *x* of compound *AB* is then given by

$$(mx)\,\mu_m^A + (x - mx)\mu_m^B + (n - nx)\mu_m^C + (1 - n)(1 - x)\mu_m^D = \mu_m^S \quad (1)$$

Superscripts identify mass absorption coefficients.

Equation 1 contains only two variables, x and μ_m^S, and the mass absorption coefficient of the mixture is an additive function of the coefficients for the four constituent elements. As a consequence, the relationship between x-ray absorbance and composition will also be linear for samples equal in mass.

This paper is concerned with the deviations from linearity that can occur with samples of equal mass when the incident beam is polychromatic.

ZIRCONIA-HAFNIA MIXTURES

Such deviations were first encountered (*6*) when the x-ray absorptions of five known zirconia-hafnia mixtures, kindly lent by H. H. Willard, University of Michigan, were investigated on a laboratory photometer (*4*), in which x-ray intensity was measured by means of a detector consisting essentially of a phosphor and a multiplier phototube. The work on these mixtures was done by the direct method (*4*), in which the intensity of the x-ray beam is adjusted to some standard initial value by adjusting the x-ray tube voltage and current until the desired output current is obtained with a standard thickness of aluminum in the beam, the voltage across the detector and the amplifier setting being fixed. The weighed sample contained in the cell was then carefully placed in the beam to ensure proper alignment, and an average value of output current was obtained, usually from ten readings of the ammeter taken 10 seconds apart. Owing to the difficulties of working with powdered samples of this size (about 40 mg.), very painstaking manipulation was required.

Under the simplest conditions, the expected relationships among x-ray absorbance, output currents, and composition (as characterized by mass absorption coefficients) in the foregoing experiments may be written

$$\log\,[I_1/I_2] = \log\,[i_1/i_2] = m\left(\mu\,{}^{S_2}_{m} - \mu^{S_1}_{m}\right)\Big/2.303\,a \qquad (2)$$

where the I's represent x-ray intensities, and the i's output currents for samples 1 and 2, which differ in composition, but are identical in mass m and cross-sectional area a, and have the mass absorption coefficients shown. (The superscripts S_1 and S_2 mean sample 1 and sample 2.) If these coefficients obey Equation 1, a straight line should evidently result when the output currents are plotted on a logarithmic scale against composition. The curve in Figure 1 shows the experimental results corrected to a sample weight of precisely 40 mg. A molybdenum target was used in these experiments.

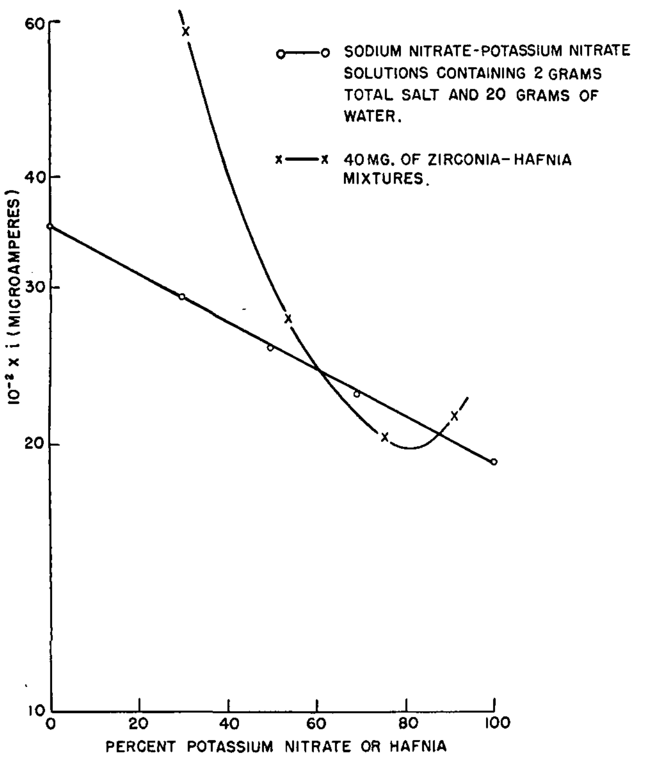

Figure 1. Data for Two Systems

One shows deviation from linearity (see text) caused by inversion in relationship of two mass absorption coefficients

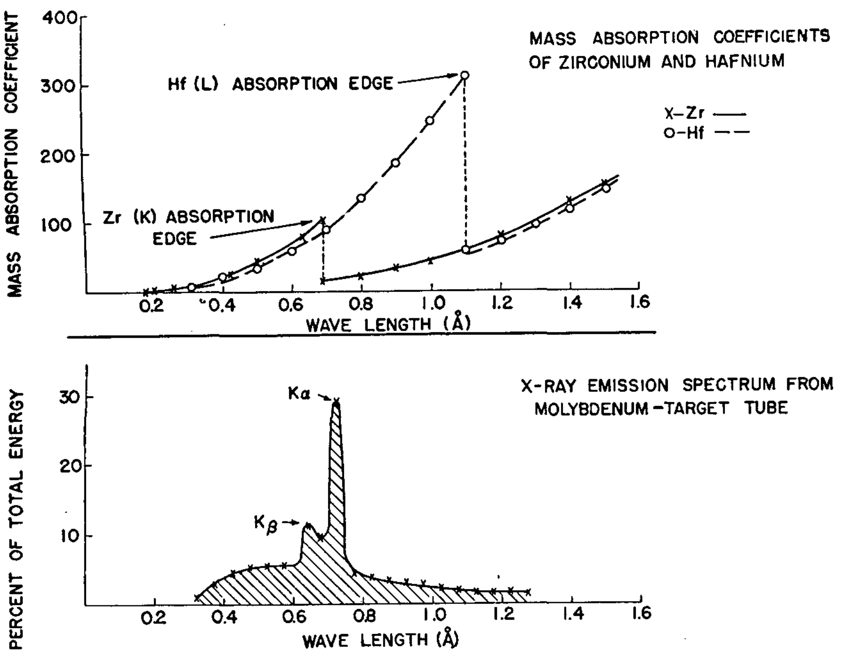

Figure 2. Auxiliary Data Relating to Deviation from Linearity

These data have qualitative significance only. The L absorption edges of hafnium are not shown in detail. Mass absorption coefficients were calculated by use of the λ^3 law from data given for neighboring elements in (*3*). The intensity distribution for the molybdenum target was calculated from the results of Treloar (*5*).

To show that this curvature was not usually obtained, similar measurements were made under comparable experimental conditions on aqueous solutions of sodium and potassium nitrates. Within the experimental error these results lie on a straight line, and this proves the applicability of Equation 2. (It is proof also that the detection and amplification systems are linear—i.e., that I and i are proportional over the range of experimental conditions.) The sodium-potassium nitrate case is typical of most systems so far investigated.

THE DEVIATION EXPLAINED

The probable cause of the curvature in Figure 1 is clear from data in Figure 2, which lead to these qualitative conclusions.

Any effect involving the L absorption edge of hafnium is negligible, owing to the low intensity of the x-ray beam transmitted through the sample in this wave-length region.

At wave lengths below its K absorption edge, the mass absorption coefficient of zirconium exceeds that of hafnium.

At wave lengths immediately above this edge, the reverse is true.

This inversion of the mass absorption coefficient relationship could produce a minimum in a plot like Figure 2—i.e., a deviation from linearity in the relationship between absorbance and composition.

Because the $K\alpha$ line of molybdenum lies on the long wave-length side of the absorption edge involved, the minimum was probably enhanced.

Attempts to account quantitatively for the curvature in Figure 1 were only moderately successful. The following calculation was carried through for each composition investigated. The percentage of total radiant energy, I_{λ_0} in the emission spectrum was estimated for each interval of 0.05 A. From the corresponding calculated absorption coefficient of the sample, the transmitted intensity, I_λ, for that interval was calculated and plotted against λ. Graphical integration then gave a quantity taken as proportional to the intensity of the transmitted x-ray beam. When these quantities were plotted against composition in the manner of Figure 1, a curve roughly resembling that in the figure was obtained. Further confirmation was provided by the results of similar calculations on a simplified system consisting of two hypothetical elements, A and C (cf. Equation 1), with absorption coefficients related to each other somewhat as are those of zirconium and hafnium.

COPPER-SILVER NITRATE SOLUTIONS

Finally, measurements were made to show the absorption of x-rays from a copper target by aqueous solutions of copper and silver nitrates. This combination was selected because the pertinent data (*2*) for it resemble those of Figure 2, one difference being the greater spread between the low-wave-length absorption edge (the K edge of silver at 0.48 A.) and the characteristic lines (for copper, near 1.5 A.) in the incident beam. Each of the nitrate solutions was made up to contain 10 grams of dissolved metal per liter. The measurements were done by the comparative method (*6*) with aluminum as the standard. Typical results are given in Figure 3, in which a maximum corresponds to a minimum in Figure 1 owing to the difference in ordinates. It is clear immediately that deviations from linearity do occur, for a maximum was obtained under some conditions with a sample of each of the volumes listed. The magnitude of the deviations is, of course, reduced by the appreciable absorption of x-rays by the nonmetallic elements in the samples.

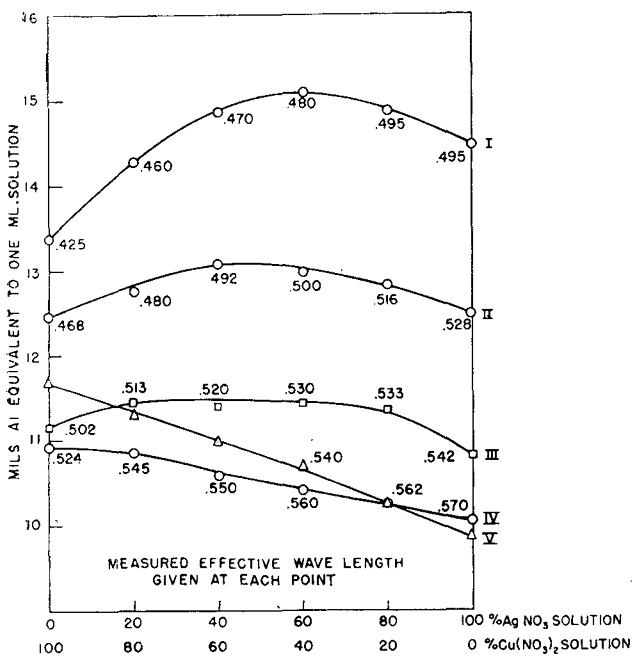

Figure 3. Deviation from Linearity for Solutions of Copper and Silver Nitrate

Curve	Volume of Solution, Ml.	Peak Voltage, Kv.
I	50	34.5
II	25	34.5
IV	10	34.5
III	10	42.0
V	25	28.5

Under the simplest conditions, the ordinates (mils of aluminum equivalent to 1 ml. of solution) should be identical for all solutions of copper nitrate alone. That they are not is probably due to another type of deviation commonly encountered with polychromatic beams—namely, the well-known variation of μ_m with wave length for monochromatic beams. As a consequence of this variation, the mass absorption coefficient of a sample for a polychromatic beam decreases with the thickness of the sample because the effective wave length decreases continuously as the beam progresses through the sample. This deviation is more pronounced for aluminum (owing to its lower mass absorption coefficient) than for copper, and the equivalent thickness of aluminum per milliliter of copper nitrate consequently increases with the thickness of the copper nitrate sample. The same argument applies to solutions of silver nitrate (in this connection, see *1*, Table XIII, and *4*, Figure 3).

When polychromatic x-ray beams are used in absorptiometry, it is ordinarily useful to consider their "effective wave lengths," these being the wave lengths of the corresponding monochromatic beams toward which the sample exhibits the same absorption coefficient. The true effective wave lengths of the beams operating on the solutions of Figure 3 are unknown. In default of these, effective wave lengths of the beams emerging from the solutions were measured by determining the absorbances of thin aluminum foil therein (*4*). The resulting values are given in Figure 3 alongside most experimental points.

Effective wave lengths obtained as just described often serve for the estimation of absorbance (Equation 2) when polychromatic beams are used and Equation 1 is valid—e.g., in the case of the nitrate solutions of Figure 1. When the deviations under discussion occur, however, Figure 3 shows that absorbances may pass through maxima while effective wave lengths vary in one direction. Circumstances such as this tend to reduce the usefulness of the concept of effective wave length.

For a given volume of sample Figure 3 shows that the tendency to produce a maximum is greater as the voltage on the x-ray tube is increased. This effect is no doubt due to the concomitant change in the energy distribution in the beam incident on the sample, but the authors have not attempted to prove this quantitatively, partly because all the requisite data are not available. In the case of curves III and V, however, such proof is scarcely required.

For curve III, the short wave-length limit (0.43 A. at 28.5 kv.) is almost coincident with the absorption edge (that of silver near 0.48 A.) responsible for the maximum. Accordingly, the beam will contain very little energy in the neighborhood of the absorption edge, and no appreciable deviation from linearity traceable to this absorption edge is to be expected (contrast with Figure 1). There is no such close coincidence for curve V.

CONCLUSION

It appears to be established that the presence of absorption edges can lead to deviations from the linear mass absorption coefficient relationship when a polychromatic x-ray beam is incident upon a sample containing more than one element. It is certain that this article does not describe all the systems in which such deviations are possible, and it is probable that these may take forms different from those shown in Figures 1 and 3. Although the occurrence of these deviations restricts the usefulness of polychromatic beams for purposes of chemical analysis, this restriction should not prove generally serious, provided the investigator is forewarned. When such deviations occur, it will often be possible to carry out the analysis by x-ray methods under other experimental conditions.

ACKNOWLEDGMENT

The authors wish to thank Kurt Berman for doing the calculations on hypothetical elements *A* and *C*, and Grace Poellmitz for carrying out the measurements on the copper-silver nitrate solutions.

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Correction. In the article on "Design and Operational Characteristics of Cartesian Manostats" [Anal. Chem., **23**, 157 (1951)] the model referred to as the Ritzer manostat should have been the Holzschuh-Long manostat.

Roger Gilmont

Acidimetric Titrations in the Fluosilicic Acid System

S. MILTON THOMSEN, *Radio Corp. of America, R.C.A. Laboratories Division, Princeton, N. J.*

The observation that commercial fluosilicic acids dissolved silicic acid, up to about 30 grams per liter, led initially to the presumption that some hydrofluoric acid was present in them. Analysis by published acidimetric methods indicated the absence of hydrofluoric acid and failed to distinguish between the silica-enriched acid and the original acid. Equilibrium studies indicated the modifications required in the acidimetric method to permit its use in characterizing the silica-enriched (high-silica) fluosilicic acids. The modified method functions equally well for the low-silica fluosilicic acids (mixtures of hydrofluoric and fluosilicic acids). Any homogeneous liquid reaction product in the system water-silica-hydrogen fluoride may, therefore, be characterized by this method. Accuracy is within 1% in moderately high concentrations. Other acidimetrically active substances must be absent. In its restricted application, the method is much quicker than the more generally applicable gravimetric methods involving separations.

IN EXPLANATION of the Katz (*2*) effect (the loss of titratable acidity upon mixing hydrofluoric acid with fluosilicic acid) Tannanaev (*9*) reported finding in fluosilicic acid solutions more silica than is indicated by the formula H_2SiF_6. Solutions prepared by dissolving hydrated silica in fluosilicic acid have been used to produce low reflection films, both by a vapor process (*4, 5*) and by a liquid bath process (*6, 11, 12*). Easily demonstrated qualitative evidence of the presence of "extra" silica in high-silica fluosilicic acids has been reported (*10*).

HIGH-SILICA FLUOSILICIC ACIDS

Quantitative characterization of high-silica fluosilicic acids, by the gravimetric determination of precipitated silica, is laborious. The volumetric method reported here is rapid and accurate within 1%.

This method is similar to published two-titration methods (*7*) for characterizing mixtures of hydrofluoric acid and fluosilicic acid. The second titration is well known for fluosilicates. The essential novelty is the addition of sodium fluoride, without which the extra silica would precipitate as the acid is neutralized, and the method would therefore fail. The choice of the first end point at a pH of 8 is justified below.

Procedure. To a 5.00-ml. sample in a plastic dish are added 3 grams of powdered C.P. sodium fluoride, 0.5 ml. of 0.1% bromothymol blue, and 1.0 ml. of 0.1% phenolphthalein. After being stirred, the mixture is titrated with 3 *M* sodium hydroxide to a greenish blue color (pH 8). The mixture is then transferred to a borosilicate glass beaker, diluted with water to 200 ml., heated nearly to boiling, and titrated at that temperature to the phenolphthalein end point (pH 10).

Comment on Procedure. The mixture of sodium fluoride and fluosilicic acid contains a gritty residue, which is broken up with a Bakelite rod as the first end point is approached. Titration is continued until the deep greenish blue color no longer changes to lighter yellow-green upon stirring for a few seconds. At the phenolphthalein end point, the color changes from blue to purple. Titration is continued near the boiling point until the purple color no longer changes to blue upon stirring for a few seconds. Both end points are permanent when these precautions are taken.

Potassium and sodium hydroxides performed equally well. The alkali was titrated against standard sulfuric acid, using both bromothymol blue and phenolphthalein as indicators. Failure of the two end points to coincide indicates presence of impurity, such as silicate or carbonate, and the difference constitutes a "blank" on the reagent. Freshly prepared solutions gave negligible blanks.

Only samples having concentrations 1 *M* and higher have been used. The high concentration of standard alkali was used to minimize dilution of the sample; dilution diminishes the sharpness of the first end point.

Sodium fluoride is used rather than potassium fluoride, because its limited solubility permits saturating the titrated mixture, thereby keeping the fluoride concentration nearly constant. The quantity used does not enter into computation of the result.

It is convenient to have a color reference for the titration using bromothymol blue. For this, a slurry is made of about 3 grams each of powdered sodium fluoride, powdered sodium fluosilicate, and hydrated silica, with a 0.5 ml. of 0.1% of bromothymol blue and 5 ml. of water.

Method of Expressing Results. The two quantities, *a*, milliequivalents of sodium hydroxide in the first tritration, and *b*, total milliequivalents for both titrations, characterize the sample. From them are derived results in more useful forms, as one chooses.

Because the extra silica may be considered to be present as fluodisilicic acid, $H_2SiF_6.SiF_4$, one might specify the concentrations of this and of fluosilicic acid, H_2SiF_6. A similar course is usually followed for mixtures of hydrofluoric acid and fluosilicic acid. Perhaps the two simplest components to specify are hydrogen fluoride and silica. In this case, the sample contains *b* millimoles of HF and $(b-a)/4$ millimoles of silica.

It is desirable to avoid the speculative fluodisilicic acid, and also to conform to the usage by which these products have been prepared, labeled, and known as "fluosilicic acid," while their extra silica content remained unrecognized.

Accordingly, the two quantities, *C*, concentration of the hydrogen fluoride component expressed as moles of H_2SiF_6 per liter, and *S*, silica number, have been chosen for characterizing a high-silica fluosilicic acid. The value of *C* is calculated as in the past by ignoring the silica, and is given by $C = b/6v$ moles per liter, using a sample of *v* ml. The value of *S* is the number of moles of silica present for each 6 moles of HF, so that H_2SiF_6 itself has an *S* value of unity. The silica number is given by $S = 3(b - a)/2b$, without involving the size of the sample.

Another advantage of using the quantities *C* and *S* chosen in this way is that one of them, *S*, is independent of dilution, and, therefore, by itself characterizes the solute. The other quantity, *C*, is independent of the amount of silica present.

This titration method functions equally well with mixtures of hydrofluoric and fluosilicic acids. Such mixtures can also be characterized in terms of *C* and *S*. They then have *S* values less than unity, and may be called low-silica fluosilicic acids. It is convenient to be able to use a single experimental method and a single system of designation for both the high-silica and low-silica fluosilicic acids, particularly when both are being used, and the sample may be either.

Practical Evaluation. Many fluosilicic acid solutions, of both high-silica and low-silica types, have been prepared by mixing computed amounts of known ingredients. Composition found by titration agreed with that expected.

Table I. Titration Results

Fluosilicic acid (C = 2.50, S = 1.100) taken, ml.	432	424	416	408
15.0 N HF taken, ml.	8	16	24	32
C found	2.51	2.50	2.50	2.48
S found	1.082	1.056	1.043	1.019
S expected (±0.005)	1.080	1.060	1.040	1.020

From a drum of commercial fluosilicic acid having $C = 2.63$ and $S = 1.100$, four samples having a range of S values between 1.10 and 1.00 were prepared. The fluosilicic acid was diluted to 2.50 M, and 400-ml. portions were mixed with computed amounts of 15.0 M hydrofluoric acid reagent. This reagent can be viewed as fluosilicic acid having $C = 2.50$, $S = 0$. The values of C and S found agree within 1% of those expected, as shown in Table I.

A sample of high-silica fluosilicic acid was prepared by dissolving hydrated silica in hydrofluoric acid. A 1.000-gram portion of hydrated silica, 83.7% silica by gravimetric assay, was dissolved in 6.00 ml. of 13.3 M hydrofluoric acid, having present as an impurity 0.02 mole per liter of silica or fluosilicic acid. This product, a clear solution, was expected to have $S = 1.07$. Titration gave $S = 1.076 \pm 0.005$.

Commercial fluosilicic acids vary in composition. Six lots had silica numbers of 1.03, 1.06, 1.18, 1.04, 1.10, and 1.01. The last three were drums of acid bought some months apart from the same manufacturer.

Titration Curves. Figure 1, showing quinhydrone titration curves for silica-saturated fluosilicic acid alone and with sodium fluoride added, demonstrates several facts.

Equivalence, given by the vertical slope on the curves, occurs sooner with the fluoride present and because of the extra silica. True fluosilicic acid, H_2SiF_6, would not be expected to show this behavior, and does not.

Without fluoride present, the titration is that of a strong acid, and equivalence occurs at pH 3 to 4. Titration of any high-silica fluosilicic acid to the methyl orange end point takes one third as much alkali as the titration to the 95° C. phenolphthalein end point, and both end points are sharp and stable.

With sodium fluoride added, the titration curve is that of the weak hydrofluoric acid. Although methyl orange is now useless as an indicator, because equivalence occurs at a pH of about 8, bromothymol blue is useful.

The hydrolysis of the fluosilicate ion, which sets in at pH 4 to 5 without fluoride present, is delayed beyond pH 8 or 9 in the presence of fluoride.

MIXTURES OF FLUOSILICIC AND HYDROFLUORIC ACIDS

The method described for characterizing the high-silica fluosilicic acids performs equally well for the low-silica acids, which are mixtures of fluosilicic and hydrofluoric acids. Similar published methods employ phenolphthalein in the first titration, and to minimize the hydrolysis of fluosilicate, either add potassium salts and alcohol (*2*), or add potassium salts and titrate at 0° C. (*7*). While these devices greatly diminish the rate of fluosilicate hydrolysis, they do not stop it. Consequently, the phenolphthalein end point fades. The fading is less severe, but not absent, if the mixture is rich in hydrofluoric acid, so that a high fluoride concentration is present at the end of the titration. Difficulty with these published methods has been experienced by others (*3*), as well as by the author.

The composition of the mixture in terms of C and S is computed from the titration values of a and b as for the high-silica acids, giving in this case S values less than unity. In terms of the component acids, the sample is $(3a - b)/2v$ or $(1 - S)(6C)$ molar in hydrofluoric acid and is $(b - a)/4v$ or $(S)(C)$ molar in fluosilicic acid.

The following data show that the method performs equally well with low-silica and high-silica fluosilicic acids. Three samples were prepared by taking 94, 100, and 106 ml. of silica-saturated 2.50 M fluosilicic acid ($S = 1.18$), and adding enough 15.0 N hydrofluoric acid ($S = 0$, $C = 2.50$) to make the volume 118 ml. By titration, S values of 0.95, 0.99, and 1.05 resulted, as compared with the 0.94, 1.00, and 1.06 expected.

SILICA READILY SOLUBLE IN HYDROFLUORIC ACID

In some cases, silica can obviously be determined after reaction with hydrofluoric acid, by titrating the reaction product. That no such method appears to have gained wide usage reflects the inadequacy of published methods for titrating the reaction product, a low-silica or high-silica fluosilicic acid. Siegel (*8*) suggests such a method, but gives no numerical data, and because of evidence presented earlier, his end point with methyl red does not seem suitable.

Materials such as hydrated silica, colloidal silica suspensions, and alkali silicate solutions have been assayed for silica in this manner. A modified procedure, using sodium fluoride and standardized sulfuric acid in place of the hydrofluoric acid, has been found to have some advantages. Two examples are given.

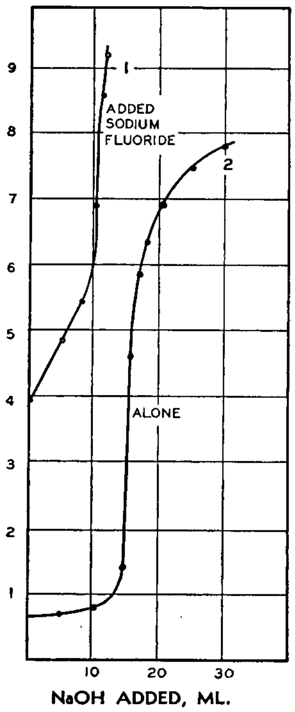

Figure 1. Titration of High-Silica Fluosilicic Acid

Example 1. Hydrated Silica, Using Hydrofluoric Acid. A weighed 0.5-gram sample of hydrated silica in a plastic dish was moistened with water, a 3-ml. portion of 48% hydrofluoric acid was added, and the mixture was stirred until the sample had dissolved. A 5-gram portion of powdered sodium fluoride and 0.5 ml. of 0.1% bromothymol blue solution were added, and the mixture was titrated with potassium hydroxide (about 4 M) to a bluish green color. With hot water the sample was transferred to a borosilicate glass beaker, the volume was brought up to about 200 ml., and 1.0 ml. of 0.1% phenolphthalein solution was added. With the mixture kept near the boiling point, the titration was continued to a permanent purple (pink plus blue) color. Similarly, a blank was run.

In equivalents, the silica equals the alkali used between the two end points, and four equivalents equal 1 mole of silica. This gave 83.6 ± 0.8% of silica; gravimetric assay gave 83.7 ± 0.2% on the same material (Mallinckrodt bulky silica).

Example 2. Liquid Samples, Potassium Silicate Solution, and Colloidal Silica Suspension, Using Modified Procedure. A 1.00-ml. sample, diluted with 5 ml. of water, was titrated to the color change of methyl orange, using 7 N sulfuric acid. From this result, the alkali content was computed.

An additional 3.00-ml. portion of sulfuric acid was delivered to the sample (in a plastic dish), a 3-gram portion of powdered sodium fluoride was added, and the mixture was stirred. After about 2 minutes, the mixture was titrated to the bromothymol blue end point as in the first example.

In equivalents, the silica equals the acid added after the methyl orange end point, minus the alkali used in back-titration. Results are shown in Table II.

Table II. Silica Assay of Liquid Samples by Modified Procedure

	Kasil[a]	Ludox[b]
% SiO_2, acidimetric	20.7 ± 0.2	17.6 ± 0.2
% SiO_2, gravimetric	20.4 ± 0.0	17.6 ± 0.0

[a] Potassium silicate solution, Philadelphia Quartz Co.
[b] Colloidal silica suspension, Du Pont.

An acid-retaining gritty residue was again encountered, and it appeared to be more troublesome with hydrochloric acid used in place of the sulfuric acid. The amounts of sodium fluoride and hydrofluoric acid do not enter into computations; rough measurement suffices. The modified procedure affords two advantages: no hydrofluoric acid reagent is handled, and a single titration per sample suffices, aside from the alkali determination.

ALKALI FLUORIDE

Acidimetric titration of fluoride in an alkali fluoride, containing only acidimetrically inert impurities (such as sodium chloride), differs from the three determinations already described by involving a different equilibrium, and, therefore, a different end point.

Mineral acid and silica, hydrated or colloidal, are added to the sample, and fluosilicic acid forms. At the end of the reaction, however, no fluoride ion is present, and the reaction product cannot be titrated beyond a pH of about 4, if fluosilicate hydrolysis is to be negligible. Siegel (*8*) reports the use of methyl red for this titration, but the author prefers methyl orange. The acidimetric method of Geffecken and Hamann (*1*) requires four titrations per sample, and appears to offer no advantages.

Several variations were tried on samples of C.P. sodium fluoride. A satisfactory procedure follows:

To a 5-gram weighed sample in a plastic dish were added 10 ml. of water, 0.1 ml. of 0.1% methyl orange, and 5 grams of silica (Mallinckrodt bulky). This mixture was titrated with 7 *N* sulfuric acid to a pink color, with thorough stirring as the end point approached.

In equivalents, the amount of fluoride present equals 1.5 times the amount of acid used. The sodium fluoride reagent assayed 99.4 ± 0.5% NaF by this acidimetric method. A sample of it was examined gravimetrically, by converting it to sulfate and igniting. The weighed sulfate was 99.1 ± 0.2% of that expected. Thus, the fluoride found acidimetrically agrees, within experimental error, with the sodium found gravimetrically.

More than 1.5 equivalents of acid may actually be used as the sample reacts with acid and silica, because extra silica dissolves to form high-silica fluosilicic acid. However, the neutralization to a pH of 4 reprecipitates the extra silica, and the small amount of extra acid is regenerated.

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Determination of Citrus Pectic Substances by Optical Rotation

R. M. McCREADY, A. D. SHEPHERD, H. A. SWENSON, ROBERTA F. ERLANDSEN, AND W. D. MACLAY
Western Regional Research Laboratory, Albany, Calif.

Research on production of pectic materials from citrus fruits required a rapid method of analysis adaptable to chemical control. Classical methods are time-consuming and not applicable to this purpose. A simple and rapid procedure was developed for determining the concentration of citrus pectic substances in solution. The optical rotation of a solution was measured, followed by quantitative and selective removal of the pectic compound with cupric ion. The net rotation was used with the previously determined specific rotation of the pectic compound to obtain its concentration. Data on the effects of pH, concentration, viscosity, alkali, and other factors that influence the rotation of pectic substances suggest that the general procedure for citrus pectic compounds can be applied to the analysis of pectic compounds from other sources, where their specific rotations and completeness of precipitation with cupric ion can be determined.

IN WORK on the preparation and isolation of pectinates from fruit waste it was necessary to use a rapid method for determining the concentration of pectinate in solution. Purified pectinate solutions have been analyzed by measurement of optical rotation (*2*) and it appeared that a simple rotation method could be devised for more complicated systems. A satisfactory procedure has been developed.

The rotation of a solution of pectinate, pectate, or both is measured at pH 4.5 to 7.0; cupric ion is then added, which precipitates these substances from solution. The precipitate is filtered and the rotation of the filtrate is measured and subtracted from that of the rotation of the original solution. The net rotation is used to calculate the concentration of pectic substances in the original solution. The accuracy of the method is ±1% on solutions of purified pectic substances. The error is due to inaccuracies in determining rotations of colloidal solutions. When solutions of pectic substances contain optically active impurities, errors of ±3% may be incurred. Pectic substances in solution can be determined in about 15 minutes.

Table I. Effect of Concentration on Rotation of Citrus Pectinate and Pectate Solutions

Substance in Solution	Concentration[a]	Tube Length, Dm.	Rotation, Degrees: Average	Rotation, Degrees: Standard deviation	Rotation, Degrees: Calcd. to 0.1% in 4-dm. tube
Sodium pectinate (pH 6.0)	1.00	2	+12.93	0.056	+2.59
	0.50	4	+13.06	0.045	+2.61
	0.25	4	+ 6.61	0.046	+2.65
	0.10	4	+ 2.63	0.037	+2.63
Sodium pectate (pH 7.5)	1.00	4	+29.16	0.046	+2.92
	0.50	4	+14.65	0.030	+2.93
	0.25	4	+ 7.36	0.056	+2.95
	0.10	4	+ 2.94	0.028	+2.94

[a] Expressed in terms of weight of free pectinic or pectic acid, uncorrected for moisture and ash.

REAGENTS

Cupric Sulfate Buffer Solution. Dissolve 27.2 grams of sodium acetate trihydrate crystals, 12.0 ml. of glacial acetic acid, and 9.4 grams of cupric sulfate pentahydrate in water and dilute to 1000 ml.

PROCEDURE

Average six or more readings of rotations of the solution of pectic substances at pH 4.5 to 7.0. (Rotations were determined with a saccharimeter. The measurements are reported in degrees Bates-Jackson, and specific rotations are calculated from the saccharimeter readings at 25° C., where C is concentration in grams per 100 grams of solution and L is the tube length in decimeters.) Add 25 ml. of cupric sulfate buffer to an equal volume of solution. Stir thoroughly and filter the precipitate. Read the rotation of the clear filtrate in a tube twice the length of the original. The difference in the rotations is due to pectinate, pectate, or both, and is directly proportional to the concentration.

Pectinate Extract from Orange Peel. The average specific rotation of orange pectinate extracted from several source materials and isolated by copper precipitation (anhydrouronic acid content, 83.3%) was +230°. The rotation of an orange pectinate solution in a 1-dm. tube in a saccharimeter was +4.2°. After copper precipitation and filtration, the rotation of the filtrate in a 2-dm. tube was −0.2°. From the net rotation of +4.4°, the concentration was calculated from the equation:

$$C = \frac{\text{rotation} \times 0.346 \times 100}{\text{specific rotation} \times L}$$

The pectinate concentration was, therefore, 0.66%.

COMPLETENESS OF PRECIPITATION OF PECTINATE WITH COPPER SULFATE

A Valencia orange extract containing 0.7% pectinate (anhydrouronic acid content 80.6%, specific rotation +230°) was treated with cupric sulfate according to the recommended procedure and the precipitated copper pectinate was removed by centrifugation. The pH of the solution was adjusted to 2 and then 2 volumes of ethyl alcohol were added. The alcohol precipitate was collected, washed, and dried. From 3500 ml. of cupric sulfate–treated solution, 4.6 grams of dried alcohol-insoluble material were obtained, which analyzed 6% anhydrouronic acid. The concentration of pectin precipitated with alcohol after copper precipitation was less than 0.01%. More than 98% of the pectinate was, therefore, removed from solution by copper precipitation.

Materials. Citrus pectinic acid used to study the variables and limitations was prepared from unstandardized commercial citrus pectin by solution and copper precipitation. The copper was removed by washing repeatedly with dilute hydrochloric acid–ethyl alcohol and the mineral acid was removed by washing in 65% ethyl alcohol.

Pectic acid was prepared from the above pectinic acid by alkaline saponification, and isolated by precipitation in dilute hydrochloric acid. Hydrochloric acid was then removed as described. The hydrochloric acid–free materials were further dehydrated with 95% ethyl alcohol and dried in vacuo at 60° C.

Pectinic acid isolated from citrus extracts by alcohol precipitation is rarely, if ever, as pure as the copper-isolated material. Repeated solution and precipitation in dilute acidified ethyl alcohol may serve to purify such materials to the same anhydrouronic acid content as the copper-isolated substance. Pectinic acid isolated by copper precipitation, followed by removal of the copper, cannot be further purified by physical means (as judged by the anhydrouronic acid content). Such materials are, therefore, representative of the pectins obtained from citrus fruits by the usual hot dilute acid extraction.

Clarification. Solutions of pectic substances were usually clarified by centrifugation or filtration with analytical-grade filter aid. Sometimes it is necessary to make a preliminary alcohol precipitation for the removal of pigments. The precipitate can then be dissolved and the analytical procedure applied as described.

Effect of Concentration. Pectinic acid was dissolved in water and the pH adjusted to 6.0 with sodium hydroxide. Pectic acid was dissolved in water with the aid of dilute sodium hydroxide and the pH adjusted to 7.5. The rotations of these solutions were measured, varying the concentration of pectic material. The results, summarized in Table I, indicate that within the experimental error the rotation of the pectic substance is constant over a range of concentrations at least from 0.1 to 1.0%.

Effect of pH. The rotations of approximately 1% solutions of pectic substances were measured at various pH values (Table II). No alkaline pH values were used in the pectinate solutions because of possible de-esterification or degradation.

There is a slight decrease in rotations of pectinate solutions as the pH values vary from 1.2 to 6.5, but its magnitude is very small. In the case of pectate solutions, no differences in rotations are apparent above pH 4.3, but below this value there is an in-

Table II. Effect of pH on Rotation of Citrus Pectinate and Pectate Solutions

Substance in 1.00% Concentration[a]	pH	Tube Length, Dm.	Rotation, Degrees: Average	Rotation, Degrees: Standard deviation
Pectinic acid or sodium pectinate	1.2	2	+12.95	0.025
	2.6	2	+12.90	0.047
	5.3	2	+12.84	0.029
	6.0	2	+12.93	0.056
	6.5	2	+12.83	0.031
Pectic acid or sodium pectate	3.1[b]	4	+30.40	0.023
	3.7	4	+30.01	0.026
	4.3	4	+28.91	0.021
	4.6	4	+28.95	0.044
	6.1	4	+28.87	0.041
	7.0	4	+28.91	0.014
	7.5	4	+29.16	0.046
	8.5	4	+28.95	0.043
	11.3	4	+29.00	0.031

[a] Expressed in terms of weight of free pectinic or pectic acid, uncorrected for moisture and ash.

[b] Gelation occurred below pH 3.1 under conditions of experiment.

Table III. Effect of Saponification on Specific Rotations

Source	Anhydrouronic Acid, %	Specific Rotation, Degrees: Pectinic acid	Specific Rotation, Degrees: Pectic acid[a]	Specific Rotation, Degrees: Anhydrouronic acid[b]
Commercial citrus[c]				
A. Pectinic acid	81.9	234	245	286
B. A saponified 1 hour at 25° C. in solution	81.9	243	254	297
C. Pectic acid isolated from B	93.1	...	274	295
Valencia orange[d]				
D. Pectinic acid	81.1	229	240	282
E. D saponified 1 hour at 25° C. in solution	81.1	240	251	296
F. Pectic acid isolated	89.7	...	265	295

[a] Calculated from specific rotation of pectinic acid corrected for methylene content.

[b] Calculated from specific rotation of pectinic acid corrected to 100% anhydrouronic acid.

[c] Commercial citrus pectin, Pectinum NFVII, analyzed 9.8% methoxyl (4.4% CH_2 or methylene).

[d] Valencia orange pectin, precipitated with cupric sulfate and purified by washing with acid–ethyl alcohol, analyzed 9.7% methoxyl (4.4% CH_2 or methylene).

Table IV. Recovery of Citrus Pectinate in Presence of Optically Active Impurities

Solution Analyzed	Initial Rotation, Degrees		Tube Length, Dm.	Rotation after Precipitation, Degrees		Tube Length, Dm.	Net Rotation[a], Degrees	Recovery of Pectinate[b], %
	Average	Standard deviation		Average	Standard deviation			
0.50% pectinate	+12.90	0	4	0	0	4	+12.90	100
+0.1% fructose	+12.00	0	4	−0.47	0.047	4	+12.94	100.3
+0.1% glucose	+13.78	0.043	4	+0.30	0	4	+13.18	102.2
+0.1% sucrose	+13.88	0.050	4	+0.35	0.050	4	+13.18	102.2
+0.5% fructose	+ 7.70	0.061	4	−1.40	0	2	+13.30	103.1
+0.5% glucose	+ 7.95	0.078	2	+1.54	0	4	+12.82	98.6
+0.5% sucrose	+16.75	0.050	4	+1.0	0	2	+12.75	98.8
0.50% pectinate	+ 6.50	0.097	2	0	0	2	+ 6.50	100
+0.1% guaran[c]	+ 6.69	0.050	2	−0.03	0	4	+ 6.72	103.4
+0.1% gum acacia	+ 6.24	0	2	−0.21	0.035	4	+ 6.45	99.2
+0.1% starch	+ 8.14	0	2	+0.58	0	4	+ 7.56	116.4

[a] Obtained by subtracting rotation after precipitation from initial rotation, where tube length of rotation after precipitation is twice that of initial. Otherwise convert rotation after precipitation to basis where direct subtraction from initial can be made.

[b] Calculated from net rotations compared with control without added impurities.

[c] Soluble mannogalactan polysaccharide of guar seeds.

crease. The rotation is about 5% higher at pH 3.1 than at pH above 4.3. One per cent solutions of pectic acid gelled below pH 3.1; rotations below this value were not determined.

Effect of Viscosity. A 1% solution of a commercial citrus pectin at pH 3.7 was heated at 100° C. under reflux. The intrinsic viscosity of the pectin determined according to Owens *et al.* (*1*, *4*) decreased from 3.6 to 0.9 dl. per gram in 5 hours, while the specific rotation remained unchanged at +230°. The jelly grade of the original pectin was 180 and that after degradation less than 50. A 1% solution of the degraded pectin of intrinsic viscosity 0.9 dl. per gram was treated with cupric sulfate and filtered as recommended in the procedure. The proof that degraded pectinate precipitated quantitatively was shown by a zero rotation of the filtrate.

Effect of Saponification. Samples of purified pectins were dissolved in water, the pH was adjusted to 6.0, and the rotations were measured. Alkali was added to give pH 12 for 1 hour at 25° C. The pH was adjusted to 6.0 for measurement of rotations. Pectic acid was isolated from the solutions by precipitation in dilute hydrochloric acid, washed free of mineral acid with 50 and 65% ethyl alcohol, and then dried. The pectic acids were dissolved in water at pH 6.0 for rotation measurements.

Table III shows that the specific rotation of sodium pectate is higher than the pectinate from which it was prepared, compared on the same basis. Removal of ester groups accounts for most of the change. However, the difference in rotation between the pectate in the reaction medium and after isolation indicates that some other factor is involved. Some increase in purity in terms of anhydrouronic acid content has been effected, even allowing for loss of 4.4% methylene. The fact that the specific rotations of the pectates on the anhydrouronic acid bases are substantially the same indicates that the substances removed by saponification and/or isolation have no net rotation.

Reliability of Optical Rotation Method for Pectic Substances in Presence of Optically Active Impurities. Solutions of various sugars and polysaccharides were added to pectinic acid solutions and the proposed method of analysis was applied (Table IV). Copper sulfate removed the pectinate selectively and quantitatively. Recoveries of pectinate were made within ±3% in all cases with the exception of starch-pectinate solutions. Solutions known to contain starch should therefore be treated with salivary or other amylase before the proposed peocedure is applied.

DISCUSSION

When dry samples containing sugars are dissolved in water, care should be taken to allow mutarotation to occur prior to observing the initial rotation.

High acidities should be avoided where hydrolysis of sucrose or other glycosides might occur to change the optical properties of the solution.

Plant proteins in the concentrations that normally occur in citrus pectinate or pectate extracts do not interfere. On other extracts it may sometimes be necessary to deproteinize solutions before analysis. Modification of the procedure along these lines should cause little difficulty. The soluble alginates are precipitated with copper in the same manner as the pectic substances, but they do not naturally occur together.

Morell and Link (*3*) determined the rotations on some galacturonic acid derivatives. Specific rotations reported for methyl galacturonide methyl ester monohydrate, methyl galacturonide dihydrate, and methyl galacturonide barium salt were +124°, +129.6°, and +99.1°, respectively. When these values are calculated to an anhydrous methyl galacturonide basis, the specific rotations are +143°, +150°, and +131°, respectively. The glycoside ester, the glycoside acid, and its salt all have a different rotatory power even when expressed on the same basis.

In a like manner, the specific rotation of pectinate increases upon conversion to pectic acid and the specific rotation of pectic acid, from pH 3.1 to 4.3 and above, decreases. Because alkali produces other effects besides de-esterification, no data are presented here on the effect of methoxyl alone. This effect and the relation of the anhydrouronic acid contents of various pectic substances to their specific rotations are under investigation and will be reported later.

Lemon, orange, and grapefruit pectins that analyze from 8 to 14% methoxyl and 80 to 85% anhydrouronic acid, have specific rotations from +227° to 234°. If greater accuracy is desired, it may be advisable to determine the specific rotation of pectin from the variety of material in question.

In using the proposed method for other than citrus substances, it is necessary to isolate and purify a sample of pectin from the variety of material to be analyzed and determine its specific rotation. This value can then be used under the conditions recommended in the procedure.

SUMMARY

In a rapid method of analysis applicable to solutions of citrus pectic substances containing optically active impurities, the rotation of a solution of pectic substance plus impurities is measured, followed by quantitative precipitation of the pectic substance with cupric ion. The net rotation is used with a previously determined specific rotation of the pectic substance to calculate its concentration.

Citrus pectinate (orange, lemon, and grapefruit pectin) has an average specific rotation of +230°.

The rotation of pectic substances is constant over a concentration range of at least 0.1 to 1%. For practical purposes the rotation of citrus pectinate (methoxyl content about 10%) is constant from pH 1 to 6. The rotation of pectate is constant above pH 4.3 and increases 5% as the pH is lowered to 3.1. Treatment of pectinate with dilute alkali results in the formation of pectate, accompanied by an increase in rotation.

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Recovery of Inorganic Ash from Petroleum Oils

Radiochemical Evaluation

L. O. MORGAN AND S. E. TURNER
The University of Texas, Austin, Tex.

Ashing techniques in common use for the determination of inorganic ash components in petroleum oils may lead to volatilization and combustion losses, thereby contributing to analytical error. This study was carried out in an attempt to evaluate the significance of the possible errors. Radiochemical techniques were used to trace the metallic constituents of contaminants added to several typical oils through the standard combustion and ignition processes. Essentially complete recovery of the iron, calcium, and sodium tracers was obtained when they were added to the oils as naphthenates, salicylates, and inorganic salts, if combustion was carefully controlled and ignition was carried out at less than 550° C. Traces of water and other sources of surface turbulence during combustion led to losses. It was concluded that properly controlled combustions and ignitions yield ash samples representing quantitative recovery of metallic contaminants from petroleum oils, if the additives used are considered to be typical of those normally occurring as contaminants.

IN THE operation of fluid catalytic cracking processes it is desirable to have reasonably accurate information concerning the amounts of inorganic or metallo-organic contaminants in the feed stocks. Contamination may be present in the crude oils, or may be accumulated in the processing or storage of the oils or oil fractions.

The accuracy of the determination of the metallic elements depends upon the efficiency with which the elements may be recovered from the oil. The most convenient and widely used method of recovery is the standard ashing procedure of the American Society for Testing Materials (*1*). The procedure is subject to three possible major sources of error: loss of ash-forming constituents by volatilization during combustion, loss of ash by mechanical entrainment of ash particles during combustion, and loss by volatilization during ignition. It has been found (*2*) that ignition of the ash with a blast burner (ca. 900° C.) results in significant loss of some volatile ash components, such as sodium chloride. The loss may be reduced to practical insignificance by ignition in an electric furnace at 550° C., if the ignition period is less than 24 hours. In the same work a number of synthetic blends were analyzed and found to yield results which suggested that losses attributable to volatilization and entrainment during combustion were not highly significant. The majority of blends investigated contained large amounts of contamination to increase the precision of the chemical analysis and may not have revealed possible losses at low concentrations. Very little is known of the compound form of the metallic ash-forming constituents in petroleum oils and it is possible that the additives did not adequately represent the true situation with respect to the native or accumulated contamination.

It was decided to repeat and extend the last experiments, using radioactive tracer techniques, in the hope that the greater sensitivity and discrimination of the method would contribute to a better understanding of the problem. The use of radioactive tracers should permit the analysis and determination of smaller amounts of ash and reduce errors caused by accidental experimental contamination. Iron, sodium, and calcium were chosen to represent the elements commonly occurring as contaminants. The elements were added in the form of inorganic compounds, naphthenates, and salicylates to provide a range of compound types.

MATERIALS AND METHODS

Petroleum oils and residua used as bases for the synthetic blends in this investigation were supplied by the Humble Oil and Refining Co.

Sample A. Deasphalted residuum produced experimentally by deasphalting a bottoms fraction from distillation of coastal crude oil. Total ash content, 0.0012 weight % (standard method) principally nickel.

Sample B. Residuum comprising the bottoms fraction obtained by distillation of mid-continent crude oil and containing a considerable amount of asphalt. Total ash content, 0.0490 weight %, mostly sodium chloride and calcium salts.

Sample C. Process gas oil, which had been in storage in a metal container for several months. Ash content increased gradually during this period. Incremental ash was mostly iron oxide. Total ash content, 0.0028 weight %.

The radioactive tracers used were obtained from the Isotopes Division, United States Atomic Energy Commission. Sodium 24 (half-life 14.8 hours) was received as sodium carbonate; calcium 45 (half-life 180 days), as calcium carbonate; iron 55, 59 (half-life ca. 4 years, 46.3 days), as metal. Stock solutions of the tracers were prepared by dissolving the samples in water (sodium carbonate) or hydrochloric acid (iron and calcium carbonate). Individual compounds were prepared by evaporation of aliquots of the stock solutions and solution in the appropriate acids. Naphthenates and salicylates were retained in xylene solution; inorganic salts were dried and used as finely ground solids. Samples were blended by addition of aliquots of the xylene solutions, or by trituration of the solid materials in the basis oil. All chemicals used were of reagent grade, except the naphthenic acid mixture, which was commercial grade.

Oil samples were burned in porcelain crucibles having total volumes of approximately 20 ml. Samples smaller than 15 ml. were blended in the crucibles; larger samples were blended in flasks and added to the crucibles as needed. In the latter cases, the flasks were washed with xylene, which was then burned with the main samples. Combustion was carried out by heating the oils to the fire point and then allowing them to burn until solid carbonaceous residues were obtained. The residues were then ignited to constant weight in an electric furnace at 550° C. Experiments in which entrained ash was to be recovered were carried out in a closed glass chamber. Effluent gases, smoke, and possible entrained ash were passed through a compact, low-ash filter to remove solid particles. Incoming air was filtered to remove the majority of dust particles. Upon completion of combustion, collected carbon and entrained ash were removed and ignited in porcelain crucibles.

The activity of ashed samples was determined by counting the crucibles after ignition. In each sequence, the residual activity was compared to control samples prepared from the stock solutions in such a way as to duplicate the condition of the test samples. The crucibles were counted at 0.5% geometry to minimize differences in distribution of active material in the crucibles. Any ash remaining on the upper walls of the crucibles was scraped to the bottom before counting. A Radiation Counter Laboratories pressure-seal, mica window (2.5 mg. per sq. cm.) counter tube was used in the activity measurements.

In all experiments, the total mass of ash was limited, so that loss of counting efficiency attributable to self-absorption in the

Table I. Comparison of Counting Methods

Sample	Crucible Method Counts/min.	%	Aliquot Method Counts/min.	%
Standard A	795		1.28×10^4	
Test A1	677	85	1.10×10^4	86
Test A2	730	92	1.21×10^4	94
Test A3	717	89	1.17×10^4	91
Test A4	740	93	1.19×10^4	93
Standard B[a]	1576		3.45×10^4	
Test B1	1610	102	3.50×10^4	101
Test B2	1655	105	3.54×10^4	103

[a] In series B, crucibles were counted at a geometry slightly lower than 0.5%.

Table II. Compounds of Sodium

	Weight % (as Na_2CO_3) Added	Weight % (as Na_2CO_3) Found (mean)
Sodium naphthenate		
Sample A	0.0017	0.0015
	0.0063	0.0058
	0.0315	0.0313
	0.0945	0.0966
Sample B	0.0062	0.0062
	0.0294	0.0288
Sample C	0.0038	0.0038
	0.0058	0.0058
Sodium chloride		
Sample B	0.0059	0.0059
Sample C	0.0038	0.0038
Sodium carbonate		
Sample C	0.0038	0.0038
	0.0058	0.0055
Sodium sulfate		
Sample C	0.0038	0.0038

samples was minimized. A standard deviation of 1.7% was calculated from the range of error in replicate samples. A series of iron samples which had been measured by counting the samples in the crucibles was checked by sampling the dissolved ash and counting the dried aliquots at 10% geometry. The sample aliquots were mounted on glass microscope slide cover glasses and dried under an infrared lamp. The two methods yielded comparable results in terms of percentage of the standard samples (Table I).

RESULTS

Data obtained in the experiments are given in Tables II to IV. Listed values for weight per cent found usually represent duplicate results; a few were obtained in quadruplicate. In general, recovery of the added tracer activities was satisfactory, although deviations of possible significance were observed with low concentrations of sodium and iron naphthenates in oils A and C, respectively. Comparable deviations were not observed in corresponding experiments carried out in the closed system (Table V).

It is probable that losses observed in the open combustions represent experimental error arising from improper combustion of the oil samples. Exploratory experiments indicated that high rates of combustion and the presence of traces of water in the oils caused a considerable amount of surface turbulence during combustion and in these cases high and variable losses were observed. Oils containing constituents of widely divergent boiling points may show marked surface turbulence unless combustion is rigorously controlled.

Table III. Compounds of Iron

	Weight % (as Fe_2O_3) Added	Weight % (as Fe_2O_3) Found (mean)
Iron naphthenate		
Sample A	0.0077	0.0076
Sample C	0.0023	0.0020
	0.0073	0.0072
	0.0077	0.0071
	0.0154	0.0145
	0.0237	0.0232
	0.0362	0.0357
Iron salicylate		
Sample C	0.0062	0.0061
Iron oxide		
Sample C	0.0023	0.0023

In the combustion of some samples, particularly those with high fire points, crawling of the oil over the edge of the crucible was observed. When the displaced oil was checked with a Geiger counter, no activity could be detected. Crawling of the oil across the flame boundary would thus appear to have been a process of distillation in which compounds of the metallic elements played no significant part. Losses observed in turbulent combustion may then be attributed to the entrainment of ash formed in the combustion of drops or filaments above the surface of the burning oil. The controlled air supply in closed system combustions contributed to smoother burning and, therefore, to decreased loss.

The thermal stability of the compounds studied was probably not so great as that expected for some of the more highly organized chelate compounds. Thus, some portion of native contaminants may be lost by volatilization during the combustion step. In principle, it should be possible to irradiate characteristic petroleum oils with thermal neutrons in order to synthesize the radioactive species in their native compound form. In the absence of appreciable activated decomposition, the results would be representative of the true state of affairs. It is probable that decomposition would be extensive for such compounds and that exchange of the active products with inactive, undissociated species would be small. It is planned to investigate this mode of approach in later experiments.

It is concluded that, if the additives used in this study adequately represent the condition of normally occurring metallic contaminants, losses attributable to volatilization and entrainment of ash components are not of great significance in properly conducted analyses.

Table IV. Compounds of Calcium

	Weight % (as $CaCO_3$) Added	Weight % (as $CaCO_3$) Found (mean)
Calcium naphthenate		
Sample A	0.0015	0.0015
Sample C	0.0023	0.0022
	0.0077	0.0077

Table V. Closed System Combustions

Compound	Sample	Weight % (as Na_2CO_3 or Fe_2O_3) Added	Weight % (as Na_2CO_3 or Fe_2O_3) Entrained
Sodium naphthenate	A	0.0058	1.5×10^{-5}
Iron naphthenate	A	0.0019	Not detectable[a]
	C	0.0362	Not detectable[a]
	C	0.0990	Not detectable[a]

[a] Limit of detection was approximately 10^{-5} weight %.

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Iodopermanganate Determination of Nitrites in the Presence of Nitric Acid

ROBERT C. BRASTED
School of Chemistry, University of Minnesota, Minneapolis, Minn.

The iodopermanganate method was critically surveyed to determine the effect of acidifying the permanganate solution with concentrated nitric instead of sulfuric acid. Solid sodium nitrite was found to lose less than 0.1% of its original weight on heating for 28 hours at 115° C. Solutions of sodium nitrite are stable over 90 days' standing. In the presence of concentrated nitric acid, added to standard permanganate prior to the addition of sodium nitrite solution, accurate results are obtained only if the nitric acid has been pretreated with crystals of sulfamic acid or freshly boiled. As little as 0.1 gram of sodium nitrite can be determined in a permanganate solution which is 8 *M* in nitric acid. Because large amounts of nitric acid (free of nitrous acid) do not interfere, the iodopermanganate method is suitable for the determination of nitrites in the presence of nitrates. Iodine may be titrated by thiosulfate in solutions containing a large amount of 8 *M* nitric acid. Nitrous acid is removed from concentrated nitric acid quickly and conveniently by the use of sulfamic acid crystals.

A NUMBER of quantitative titrimetric determinations of nitrite ion have been suggested. A few (*9, 22, 26, 29*) methods mention the effect of nitrates on the determination of nitrites, but none concern themselves with the effect of nitric acid on the iodopermanganate method. Polarographic methods (*10, 23, 27*) are available in which nitrite and nitrate ions may be independently determined. A variety of colorimetric (*2, 3, 5, 6, 16, 22, 28, 30*) and redox titrimetric methods employing a variety of indicators are reported in the literature. A turbidimetric determination described by Lang (*18*) provides for the estimation of small quantities of nitrites and nitrous acid in the presence of very large quantities of nitric acid.

One of the simplest titrimetric nitrite determinations is that described by Kolthoff and coworkers (*14, 15*), referred to by the present author as the iodopermanganate method. The procedure might be described as a combination of the direct permanganate method of Lunge (*20*) and its several variations (*11, 12, 25*) with a normal iodometric titration. Other investigators (*1, 4, 19, 21, 24, 31*) have described the determination of nitrite by an iodometric titration, but no survey of a titration in the presence of nitric acid has been reported.

According to the procedure currently under consideration (the iodopermanganate method), an aliquot portion of the nitrite solution to be analyzed is added to a known volume of standard 0.1 *N* permanganate solution acidified with 5 *N* sulfuric acid. (When the analyses involve the study of nitric acid interference, and when the amount of nitric acid added provides sufficient acidity for the redox reaction, no sulfuric acid is added.) After completion of the relatively slow reaction between the nitrite and permanganate ions, the excess permanganate is reduced with iodide and the liberated iodine is titrated with standard 0.1 *N* thiosulfate. Within any series of aliquot determinations the precision is about one part per thousand. The purpose of this investigation was to study the effect on nitrite determination when the permanganate solution was acidified with varying amounts of nitric acid instead of sulfuric acid; to study the effect of impurities likely to be found in commercial concentrated nitric acid; to investigate means of removing interfering substances from concentrated nitric acid; and to study the effect of titrating thiosulfate solution in highly acidified nitric acid solutions. Such an investigation should foretell also the effect of a large quantity of nitrate ion on the determination of nitrite ion by the iodopermanganate titration.

In conjunction with the nitric acid–nitrite study, it was necessary to obtain quantitative information on the stability of sodium nitrite. Cool and Yoe (*4*) stated that solutions of sodium nitrite are stable for 4 to 5 weeks, but gave no experimental data. In the present studies the 110° C. stability of solid sodium nitrite and of solutions over 3-months' standing at room temperature was determined.

The catalytic effect of nitrous acid as well as oxides of nitrogen in the oxidizing action of nitric acid is well known (*7, 8, 13, 17*). Although nitric acid itself might not have a rapid or noticeable effect on the potassium iodide added to the excess permanganate in the iodometric portion of the titration, the effect of presence of high concentrations of nitric acid and traces of lower oxides of nitrogen or nitrous acid might be appreciable.

REAGENTS

Sodium Nitrite. Merck, reagent, granular, minimum assay 97%.

Nitric Acid. Du Pont, C.P. reagent, 70% by weight, specific gravity 1.42.

Sulfamic Acid. Du Pont, commercial, recrystallized from water, sulfate-free.

EXPERIMENTAL

Stability of Sodium Nitrite. Analysis of a solution containing 4 grams of sodium nitrite per 500 ml. gave 100.2% by the iodopermanganate method when first prepared, and 100.1% at the end of 40 days. Intermediate analyses at 7-day intervals agreed with the initial analysis within 0.1%. A second solution containing 20 grams per liter changed from 99.55 to 99.25% over a 90-day period. Such a change is hardly more than the limit of accuracy of the iodopermanganate determination.

A sample of sodium nitrite weighing 10.3619 grams decreased 0.0102 gram in weight on heating at 110° C. for 28 hours—less than 0.1%. A drop from 100.2 to 99.81% over this heating period as shown by chemical analysis is not enough to indicate other changes than dehydration.

Ten individually weighed samples varying from 0.06 to 0.3 gram of sodium nitrite from a C.P. reagent bottle were analyzed. The variation from 101.0 to 99.72% is an indication of the uniformity of the sodium nitrite and not of the precision of the analysis. Other investigators have reported values over 100% in terms of purity of sodium nitrite (*4*). The average of the ten samples indicated a purity of 100.4% with an average deviation of ±0.4%. That such a purity is probably correct is indicated by the analysis of a solution prepared by dissolving 20 grams in a liter of solution—100.3% with an average deviation of ±0.1%.

Action of Nitric Acid on Potassium Iodide–Qualitative Observations. Although both untreated and freshly boiled concentrated nitric acid react instantly with potassium iodide to form iodine, the rate of reaction between the iodide ion and freshly

Table I. Iodopermanganometric Titration in Presence of Nitric Acid

(Blank determinations)

Pretreatment of Nitric Acid	HNO_3 Added, Grams	$NaNO_2$ Found, Gram
None	1.38	+0.0002
None	1.97	+0.0003
Sulfamic acid	1.97	+0.0001
None	2.76	+0.0002
None	6.89	+0.0003
None	9.94	+0.0013
Sulfamic acid	9.94	+0.0000
None	24.8	+0.0015
Sulfamic acid	24.8	+0.0000
None	34.2	+0.0028
Freshly boiled	34.2	+0.0001
Sulfamic acid	34.2	−0.0001
None	48.4	+0.0092
Freshly boiled	48.4	+0.0000

boiled nitric acid decreases markedly with even slight dilution. Untreated acid diluted from 15 to 3 *M* requires about 30 seconds for enough iodine to form to cause an error in an iodometric titration. It was observed that nitric acid treated with sulfamic acid crystals is rendered oxide-free and behaves essentially as if it had been freshly boiled and cooled.

Effect of Nitric Acid on Iodopermanganate Titration. A series of blank analyses was run using varying concentrations of nitric acid. In each case standard 0.1 *N* permanganate solution was pipetted into a titration flask and diluted to about 40 ml., and concentrated nitric acid was added. After standing for 15 minutes, approximately 2 grams of potassium iodide crystals were added and the liberated iodine was titrated with 0.1 *N* thiosulfate solution. Table I is a summary of the data obtained on these blank samples. The positive sign affixed to the values signifies that some permanganate is being reduced, although no sodium nitrite has been added. Less thiosulfate is therefore needed in the iodometric titration than if the permanganate had been unaffected.

The effect which nitric acid, freed of its nitrous acid and lower oxide impurities, has on the actual nitrite determination was next determined (Table II). In each case the aliquot of sodium nitrite was added to the permanganate solution, followed by the addition of the nitric acid. The volume of the solution was approximately 60 ml. before the final titration with thiosulfate.

The difference between the grams of sodium nitrite added and found when the nitric acid is not pretreated is clearly shown in Table III. Instead of a small error, usually negative (see Table II), the errors become substantial and positive with the addition of large amounts of nitric acid.

Table II. Effect of Pretreated Nitric Acid on Nitrite Determination

$NaNO_2$ Added, Gram	HNO_2 Added, Grams	$NaNO_2$ Found, Gram	Error, Gram
0.0751	9.94[a]	0.0748	−0.0003
0.0751	4.97[a]	0.0750	−0.0001
0.0000	9.94[a]	0.0000	0.0000
0.0751	0.00	0.0750	−0.0001
0.0000	1.99[a]	0.0001	+0.0001
0.0751	19.88[a]	0.0752	−0.0001
0.0759	24.8 [b]	0.0758	−0.0001
0.0759	34.2 [b]	0.0770	+0.0011
0.0759	48.4 [b]	0.0762	+0.0003

[a] Concentrated nitric acid pretreated with sulfamic acid crystals.
[b] Concentrated nitric acid freshly boiled.

Table III. Effect of Untreated Nitric Acid on Nitrite Determination

$NaNO_2$ Added, Gram	HNO_3 Added, Grams	$NaNO_2$ Found, Gram	Error, Gram
0.0789	0.138[a]	0.0790	+0.0001
0.0789	1.38	0.0792	+0.0003
0.0751	1.99	0.0758	+0.0007
0.0751	4.97	0.0759	+0.0008
0.0751	6.89	0.0761	+0.0010
0.0751	9.94	0.0760	+0.0009
0.0751	19.88	0.0766	+0.0015
0.0759	24.8	0.0774	+0.0015
0.0759	34.2	0.0776	+0.0017
0.0759	48.4[a]	0.0785	+0.0026
0.0000	9.94	0.0013	+0.0013

[a] Solutions vary from 0.036 to 7.88 *M* in HNO_3.

Oxidative Effect of Nitric Acid on Potassium Iodide. Delayed Titrations. In a series of delayed titrations the length of time between the addition of potassium iodide to a dilute nitric acid solution and the introduction of thiosulfate was continuously increased (Table IV). The nitric acid was added in the form of untreated concentrated acid to the permanganate-nitrite solutions.

Table IV. Delayed Titrations

Sample No.	$NaNO_2$, Gram		Error, Gram	Time, Min.	HNO_3 Added, Grams
	Added	Found			
1	0.0759	0.0761	+0.0002	0[a]	0.0
2	0.0759	0.0764	+0.0005	0[a]	4.94[b]
3	0.0759	0.0760	+0.0001	3	4.94
4	0.0759	0.0764	+0.0005	6	4.94
5	0.0759	0.0765	+0.0006	11	4.94
6	0.0759	0.0762	+0.0003	18	4.94
7	0.0759	0.0764	+0.0005	37	4.94
8	0.0759	0.0744	−0.0015	15 hours	4.94

[a] In practice some 35 seconds elapse between addition of potassium iodide and completion of thiosulfate titration.
[b] Solutions approximately 1.25 *M* with respect to HNO_3.

A relatively small effect is indicated in Table IV, whether the sample is titrated immediately or within a half-hour period. However, if the solutions are allowed to stand a long time (sample 8), the error changes from a small positive value to a much larger negative value. More standard thiosulfate is being consumed than can be accounted for by the given amount of sodium nitrite. Sample 8 was checked against samples 2 to 7 by stoppering the samples after completion of the thiosulfate titration and allowing them to stand for 15 hours. The amount of thiosulfate needed to reduce the iodine formed in the interim was equivalent to 0.0011 ± 0.0001 gram of sodium nitrite.

Table V. Air *vs.* Nitric Acid Oxidation of Iodide

Sample No.	$NaNO_2$, Gram		Treatment after Initial Titn.	Time Elapsed after Titn. Hours	$NaNO_2$, Gram
	Added	Found			
1[a]	0.2000	0.2003	Open to atmos.	42	−0.0007
2[b]	0.2000	0.2001	Open to atmos.	42	−0.0007
3[a]	0.2000	0.1988	Flushed with He and stoppered	42	−0.0003
4[b]	0.2000	0.2003	Flushed with He and stoppered	42	−0.0006
5[a]	0.2000	0.1998	Flushed with He and stoppered	42	−0.0003
				Days	
6[b]	0.2000	0.1992	Open to atmos.	8	−0.0041
7[b]	0.2000	0.1992	Open to atmos.	8	−0.0042
8[b]	0.0789	0.0792	Stoppered	4	−0.0048
9[b]	0.0789	0.0795	Open to atmos.	4	−0.0053

[a] Samples acidified with 5 ml. of 2 *M* nitric acid.
[b] Samples acidified with 5 ml. of 5 *M* sulfuric acid.

Iodine Formation by Air *vs.* Nitric Acid Oxidation of Potassium Iodide. The low results in the determination of nitrite in experiment 8 of Table IV might be due to oxidation of iodide by air or by nitric acid. In the case of the latter oxidant a trace of nitrous acid might catalyze the reaction.

To study further the effect of atmospheric oxygen on the iodide–nitric acid solution remaining after the normal iodopermanganate titration, a series of analyses was made (Table V). The additional quantity of thiosulfate needed to discharge the iodine-starch complex is reported as a negative quantity of sodium nitrite.

After 18 hours of standing, samples 1 and 2 showed signs of iodine formation by appearance of starch-iodine blue complex. In this period no coloration was shown by the helium-flushed and stoppered samples 3, 4, and 5. The first color (most rapid oxidation) was shown by No. 4, which contained no nitric acid. Sample 5 showed iodine formation after 36 hours.

It may be concluded that the initial titration by thiosulfate may be carried out in the presence of either dilute nitric acid or sulfuric acid (Tables I to IV). Both air and nitric acid contribute to iodide oxidation over a long period of time; however, no error would be introduced in the normal iodopermanganate titration. The rate of air oxidation of iodide is slower than one might expect over such a long period of time.

DISCUSSION

The results tabulated in Table I suggest that concentrated nitric acid which contains lower oxides of nitrogen would interfere with the iodopermanganate nitrite determination. In low concentrations the interference should be small or negligible. If the lower oxides are removed either by boiling or, more conveniently, by treatment with crystals of sulfamic acid the interference should be decreased or eliminated.

The reactions which lead to the quantitative estimation of the nitrite ion in the iodopermanganate method are represented by:

$$2H^+ + 3NO_2^- + 2MnO_4^- \longrightarrow 3NO_3^- + 2MnO_2 + H_2O \quad (1)$$

$$4H^+ + MnO_2 + 2I^- \longrightarrow I_2 + Mn^{++} + 2H_2O \quad (2)$$

$$16H^+ + 2MnO_4^- + 10I^- \longrightarrow 5I_2 + 2Mn^{++} + 8H_2O \quad (3)$$

$$I_2 + 2S_2O_3^{--} \longrightarrow S_4O_6^{--} + 2I^- \quad (4)$$

The reaction represented by Equation 1 is relatively slow; actually no single stoichiometric relationship can be written. There will be some manganese(II) formed in the solution as well as some unreacted permanganate. The rapidity with which the brownish manganese dioxide color is developed has been shown to depend upon whether the sodium nitrite aliquot solution is added to the acidified permanganate or the acid is added to the nitrite-permanganate mixture. There is no significant difference in the amount of sodium nitrite found in either case. The latter condition favors a more rapid reaction. When a large amount of nitric acid—e.g., ~50 grams—is added, the reaction appears to be five times as fast. If the nitrite were to decompose to nitrogen trioxide through intermediate nitrous acid formation before the reaction represented by Equation 1 could take place, a negative error would result. With the loss of nitrogen trioxide less permanganate would be reduced, more iodine later formed, and finally more thiosulfate used in the titration. The infrequency of negative errors and their small magnitude when they do occur (Tables II and III) would indicate that the loss of nitrogen trioxide is not an interference under the conditions of the analysis.

A variety of factors might lead to the formation of iodine, other than the desired reactions represented by Equations 2 and 3.

$$6H^+ + 6I^- + 2HNO_3 \longrightarrow 2NO + 3I_2 + 4H_2O \quad (5)$$

$$2H^+ + 2I^- + 2HNO_3 \longrightarrow 2NO_2 + I_2 + 2H_2O \quad (6)$$

$$2H^+ + [O]\ (\text{air}) + 2I^- \longrightarrow H_2O + I_2 \quad (7)$$

Equations 5 and 6 represent reactions greatly catalyzed by the presence of small quantities of nitrous acid or oxides of nitrogen —e.g., N_2O_3. All of the reactions (represented by Equations 5 through 7) would lead to a negative error in the sodium nitrite calculation due to the utilization of more thiosulfate than that attributable to nitrite ion. The increase in acidity as more nitric acid is added to the system might be expected to favor the forward reactions from a mass effect. Such is the case when the iodide ion is allowed to stand for a long time in contact with either nitric acid or the air (Table IV); however, within the normal time limit usually required for titration, when the iodide ion is susceptible to oxidation by nitric acid or air, the effect is so slight as to be negligible (see Table II and III).

When standard thiosulfate solution is added to a nitric acid solution, it is reasonable to consider several reactions other than that resulting in the reduction of iodine and the formation of tetrathionate.

$$S_2O_3^{--} + H^+ \longrightarrow HSO_3^- + S \quad (8)$$

$$HSO_3^- + I_2 + H_2O \longrightarrow HSO_4^- + 2I^- + 2H^+ \quad (9)$$

$$8HNO_3 + 3S_2O_3^{--} \longrightarrow 6SO_4^{--} + 8NO + H_2O + 6H^+ \quad (10)$$

If the reactions represented by Equations 8 and 10 occurred to any marked extent, the negative error (more thiosulfate than that traceable to sodium nitrite added) would be more pronounced than is actually the case. If the hydrogen sulfite ion, formed in the acid decomposition of thiosulfate, were to react with iodine, as per Equation 9, there would be a cancellation of errors. In practice, the rate of the thiosulfate-iodine reaction would seem to be so rapid that even in highly concentrated (up to 8 *M*) nitric acid no error is found atrributable to decomposition of the thiosulfate.

The addition of untreated nitric acid to the permanganate nitrite system causes a positive error which increases in magnitude with the amount of nitric acid added—from no more than 0.1 mg. with no nitric acid to 2.6 mg. per 0.0759 gram of sodium nitrite with the addition of 50 ml. of concentrated nitric acid. The most important contributing factor to this positive error is the presence of nitrous acid and lower oxides of nitrogen in the concentrated acid. These impurities act essentially as sodium nitrite would act in the reduction of permanganate. With a decrease in the permanganate there will be a decrease in the amount of iodine liberated and a corresponding decrease in the volume of thiosulfate needed. The net result is noted as a positive error. A comparison of the error columns in Tables II and III shows clearly that the impurities in nitric acid contribute to the error. As long as excess permanganate (or manganese dioxide) is present no nitrous acid is formed from the nitric acid; however, after the excess permanganate is destroyed by potassium iodide, more iodine may be formed by the action of nitric acid catalyzed by nitrous acid. That three oxidants (air, and nitric and nitrous acids) actually contribute to the formation of excess iodine has been proved if the system is allowed to stand for a long time (Tables IV and V).

The pretreatment of nitric acid either by boiling or by sulfamic acid crystals prior to its addition to the nitrite-permanganate mixture reduces the error in the nitrite determination to a negligible value. There seems to be little choice in the effectiveness of the pretreatments; it is simpler to add crystals of sulfamic acid and decant the nitric acid to be used. The results of the analyses indicate from a quantitative standpoint that very little sulfamic acid dissolves in nitric acid of 70% concentration. Any sulfamic acid that did dissolve would preferentially react with nitrite (in Equation 11) before the latter could be oxidized to nitrate by the permanganate.

$$NaNO_2 + NH_2SO_3H \longrightarrow NaHSO_4 + N_2 + H_2O \quad (11)$$

A large negative error in the final calculation would result. A simple method of removing oxides of nitrogen from concentrated nitric acid is thus suggested. It is not now known at what concentration the solubility of sulfamic acid in nitric acid becomes appreciable. These measurements are being made in this laboratory.

CONCLUSIONS

The stability of sodium nitrite in solution has been ascertained over a 90-day period. Any change in composition over this period is equal to or less than the limit of accuracy of the iodopermanganate method of analysis. C.P. reagent grade sodium nitrite is stable at 110° C. for at least 28 hours, and so little loss in weight is noted in this period of time that no purpose is served by a drying procedure.

The iodopermanganate method for titrating nitrite solutions may be carried out in permanganate solutions highly acidified with nitric acid if the acid has been pretreated with sulfamic acid crystals or by preboiling. The ease of the former operation suggests a simple procedure for freeing concentrated nitric acid of lower oxides of nitrogen. Successful titrations have been carried out with less than 0.1 gram of sodium nitrite in 48 grams of concentrated nitric acid. The final concentration of the solution with regard to nitric acid under these conditions is almost 8 *M*. The oxidation of iodide to iodine is insignificant within the time required for a thiosulfate titration. Thiosulfate does not undergo decomposition in the highly acidified medium before it reacts with iodine.

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Chemical Differentiation between Nicotinic Acid and Nicotinamide

JAMES P. SWEENEY AND WALLACE L. HALL
Division of Nutrition, Food and Drug Administration, Federal Security Agency, Washington 25, D. C.

It may be of importance to the clinician and to the control chemist to be able to differentiate between nicotinic acid and nicotinamide. In the chemical estimation of these compounds their pyridine rings are split with cyanogen bromide by the Koenig reaction and the reaction products are coupled with sulfanilic acid. At 430 mμ, where the color complexes are measured, the absorbancy of the nicotinic acid color is approximately twice that of the color produced with nicotinamide. As nicotinamide is converted quantitatively to nicotinic acid by hydrolysis, the percentage composition of a mixture may be determined by absorbancy measurements before and after hydrolysis. Tobias acid (2-naphthylamine-1-sulfonic acid) may be used in place of sulfanilic acid for the development of the color complexes; colors produced with nicotinic acid and nicotinamide are differentiated visually. This permits its use in a qualitative test. Data and graphs demonstrate the applicability of these methods.

IN THE examination of vitamin products available commercially it is at times important to differentiate between nicotinic acid and nicotinamide. Because of an unpleasant flushing reaction in some patients to whom nicotinic acid is administered, there is a clinical preference for the amide, which is without such effect (*6*). The microbiological procedure for the determination of nicotinic acid included in the U. S. Pharmacopeia XIV does not distinguish between the two forms, for the organism used can utilize the acid and amide equally.

Chemical methods described by Lamb (*4*) and Melnick and Oser (*5*), in which differences in color intensity are obtained when the acid and amide react with cyanogen bromide and aniline, have been criticized by Ciusa (*2*) from the standpoint of lack of precision. Ciusa demonstrated that the amide, but not the acid, will react with benzyl chloride to form a complex that is not converted to a colored compound in the presence of cyanogen bromide and an aromatic amine, and proposed this as a method for differentiation. Such a method is too cumbersome for routine control purposes. Chaudhuri and Kodicek (*1*) describe a procedure in which a measure is made of the fluorescence produced when the amide reacts with cyanogen bromide and the solution is subsequently made alkaline. A number of compounds, among them thiamine and pyridoxine, are known to give a similar fluorescence. Therefore, it is necessary to pretreat the vitamin solution prior to the cyanogen bromide reaction in order to remove the interfering fluorescence. This method also is too elaborate for routine use.

A method for the determination of nicotinic acid, developed in this laboratory, is based on the color reaction of König (*3*) but makes use of sulfanilic acid as the aromatic amine. The advantages of the use of sulfanilic acid have been covered (*7–9*). This method has been applied to a variety of natural materials and commercial products containing the vitamin and, following collaborative study, has been adopted for control purposes by the Association of Official Agricultural Chemists. Provision is made in this method for conversion of the amide to the acid form by hydrolysis and measurement by means of a spectrophotometer of the color formed at wave length 450 mμ, the point of maximum absorption.

A comparison of the absorption spectra of the nicotinic acid and nicotinamide colors as developed with cyanogen bromide and sulfanilic acid revealed that between wave lengths 400 and 430 mμ the nicotinic acid color has approximately double the absorbancy of the nicotinamide color. Figure 1 shows the absorption spectra of nicotinic acid and nicotinamide colors. The concentration of nicotinic acid and nicotinamide in each case was 10 micrograms in a volume of 10 ml. Because the molecular weights of nicotinic acid and nicotinamide are 123 and 122, respectively, the weights used can be considered molecular equivalents.

It is possible to measure accurately the difference in absorbancy between nicotinic acid and nicotinamide at any wave length between 400 and 475 mμ. However, the difference in absorbancy is greatest at 430 mμ, and all results reported in this paper have been determined on the basis of the absorbancy at 430 mμ. As the amide is readily converted to the acid by hydrolysis, the percentage composition of nicotinic acid and nicotinamide can be determined by measuring the absorbancy at 430 mμ of the color produced with cyanogen bromide and sulfanilic acid before and after hydrolysis.

Presented here are a procedure for the quantitative differentiation of nicotinic acid and nicotinamide, and the details of a simplified method for qualitative differentiation of these compounds employing the aromatic amine 2-naphthylamine-1-sulfonic acid (Tobias acid), in place of sulfanilic acid. The method described is applicable to pharmaceutical preparations containing amounts of nicotinic acid or nicotinamide usually dispensed.

QUANTITATIVE DIFFERENTIATION OF NICOTINIC ACID AND NICOTINAMIDE

Reagents. Ammonium hydroxide, 5 ml. of concentrated ammonium hydroxide diluted to 250 ml.

Hydrochloric acid, 1 volume of concentrated hydrochloric acid added to 4 volumes of water.

Cyanogen bromide, 10% aqueous solution. This should be prepared under a hood.

Sulfanilic acid, 10% solution. Place 20 grams of sulfanilic acid in 170 ml. of water, and add concentrated ammonium hydroxide, 1 ml. at a time, until solution is obtained. Adjust pH to 4.5, using bromocresol green indicator. Use a spot plate for testing pH. Make up to 200 ml. with water.

Nicotinic acid stock solution, 50 mg. of U.S.P. nicotinic acid reference standard made up to 500 ml. with 95% ethyl alcohol. (Keep in refrigerator.)

Nicotinic acid standard solution, 5 ml. of stock solution diluted to 50 ml. with water; 1 ml. of this solution contains 10 micrograms of nicotinic acid.

Nicotinamide standard solutions are prepared in the same manner as the nicotinic acid standard solutions.

Instrument. A spectrophotometer or filter photometer should be used for absorbancy measurements. If a simple nonamplifying filter photometer is used, it must be equipped with a filter or filters which have a high percentage transmittance at a narrow band range. Interference filters are useful for this purpose.

Procedure. Preparation of Sample. For many samples it is convenient to prepare a dilution or extract that contains approximately 100 micrograms of total nicotinic acid or nicotinamide per milliliter. For tablets, the sample is finely ground in a mortar and extracted with hot water for 15 minutes. Then the extract and residue are transferred to a volumetric flask and made to the proper volume. For capsules, the sample is dispersed in hot water and made to a similar volume. A 10-ml. aliquot is added to 10 ml. of concentrated hydrochloric acid, the resulting solution is evaporated on a hot plate to a volume of about 2 ml., and 50 to 75 ml. of water are added. The solution is made alkaline to bromothymol blue indicator by addition of sodium hydroxide (use of pellets is convenient). A spot plate is used for the pH adjustment. The solution is then made to a volume that contains approximately 10 micrograms of total nicotinic acid per ml. A 10-ml. aliquot of the unhydrolyzed solution is also made to a volume that contains approximately 10 micrograms of total nicotinic acid or nicotinamide per ml.

Color Development. The color development of these solutions is carried out in selected 18-mm. test tubes according to Table I.

The sample solution or standard solution, water, and ammonium hydroxide are added to the tubes as indicated. Sulfanilic acid and one drop of concentrated hydrochloric acid are added to the blank tube. The tube is placed in the instrument, which is adjusted to read 100% transmittance at 430 mμ. The cyanogen bromide is added to a sample or standard tube from a pipet with swirling to ensure mixing, and immediately after this addition the sulfanilic acid is measured into the tube in a similar manner. The tube is placed in the instrument and the transmittance reading is taken at the time of maximum absorption (1.5 to 2 minutes).

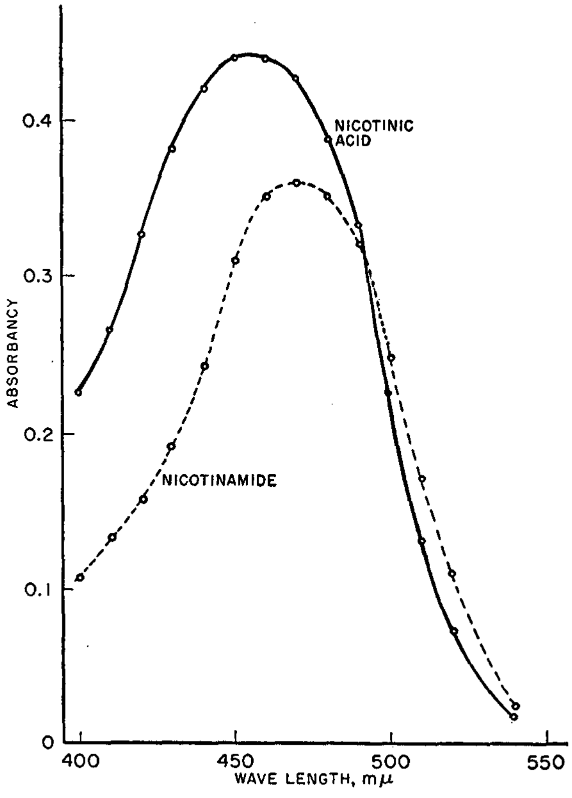

Figure 1. Absorption Spectra of Nicotinic Acid and Nicotinamide Colors Developed with Cyanogen Bromide and Sulfanilic Acid

Calculation. The color is first developed on an aliquot of the test solution which contains both nicotinic acid and nicotinamide. The nicotinamide on another aliquot is then converted to nico-

Table I. Development of Color

	Blank	Nicotinic Acid	Nicotinamide	Unhydrolyzed Sample Blank	Unhydrolyzed Sample	Hydrolyzed Sample Blank	Hydrolyzed Sample
Nicotinic acid standard, ml.	1	1	...	...	...	...	...
Nicotinamide standard, ml.	...	...	1	...	...	...	...
Unhydrolyzed sample, ml.	...	...	...	1	1	...	...
Hydrolyzed sample, ml.	...	...	...	...	...	1	1
Water, ml.	6.5	1.5	1.5	6.5	1.5	6.5	1.5
NH_4OH, ml.	0.5	0.5	0.5	0.5	0.5	0.5	0.5
CNBr, ml.	...	5.0	5.0	...	5.0	...	5.0
Sulfanilic acid, ml.	2.0	2.0	2.0	2.0	2.0	2.0	2.0
Concd. HCl, drop	1	...	...	1	...	1	...
Water, drop	...	1	1	...	1	...	1

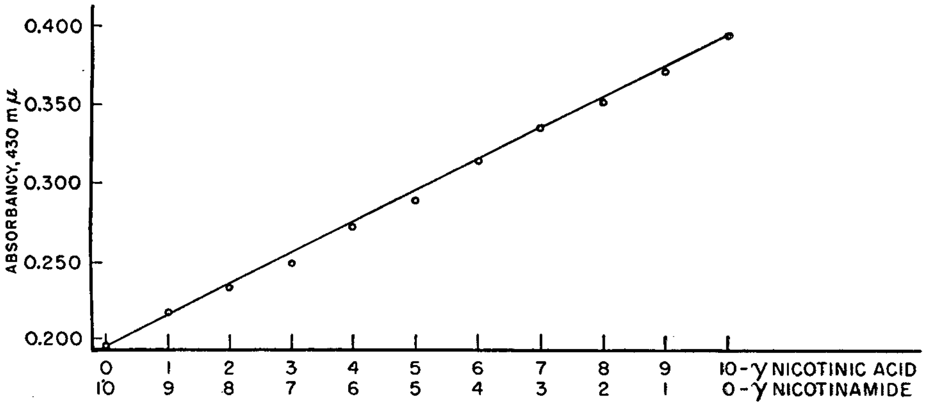

Figure 2. Absorbancy Values at 430 mμ

Colors produced by reaction of cyanogen bromide and sulfanilic acid with mixtures of nicotinic acid and nicotinamide. Solutions contained a total of 10 micrograms of two compounds in indicated ratios

tinic acid by hydrolysis. Any increase in color developed in this aliquot as compared to that produced in the previous aliquot is the result of the conversion of nicotinamide to nicotinic acid, and the amount of increase is proportional to the amount of nicotinamide originally present. A sample calculation follows:

1.	Absorbancy of 10 micrograms of nicotinic acid standard =	0.400
2.	Absorbancy of 10 micrograms of nicotinamide standard =	0.200
3.	Absorbancy of 1 ml. of unhydrolyzed sample =	0.320
4.	Absorbancy of 1 ml. of hydrolyzed sample =	0.400
5.	Increase in absorbancy due to hydrolysis	0.080

$$\frac{0.400 - 0.200}{10} = \text{difference in absorbancy between 1 microgram of nicotinic acid and 1 microgram of nicotinamide} = 0.020$$

$$\frac{0.400 - 0.320}{0.020} = \frac{0.080}{0.02} = 4 \text{ micrograms of nicotinamide in unhydrolyzed sample}$$

$$\frac{0.320 - 0.080}{0.040} = \frac{0.240}{0.040} = 6 \text{ micrograms of nicotinic acid in unhydrolyzed sample}$$

The use of a standard reference curve has proved to be a more practical means of determining the percentage composition of a mixture of nicotinic acid and nicotinamide. For this purpose a standard curve similar to that illustrated in Figure 2 may be used, in which the absorbancy values of colors produced by the reaction of cyanogen bromide and sulfanilic acid with standard nicotinic acid and nicotinamide are plotted. The total nicotinic acid content of an aliquot of the hydrolyzed test solution is first determined. An aliquot of the unhydrolyzed test solution is then diluted so that it contains the same total nicotinic acid plus nicotinamide concentration as do the standards used in construction of the reference curve. The absorbancy of the color produced by the unhydrolyzed test solution, when developed with cyanogen bromide and sulfanilic acid, is then read at 430 mμ and the percentage composition is determined by interpolation from the standard curve.

Results. Standard solutions containing known amounts of nicotinic acid and nicotinamide were tested. Figure 2 shows the effect of increased ratios of nicotinic acid to nicotinamide on the absorbancy of the color produced by the reaction with cyanogen bromide and sulfanilic acid. The total amount of nicotinic acid plus nicotinamide in each case was 10 micrograms in a volume of 10 ml. The readings were taken at 430 mμ with a Beckman Model B spectrophotometer, using selected 18-mm. test tubes.

To demonstrate the applicability of the quantitative method to pharmaceutical products, a series of determinations was made on various types of vitamin preparations. Results are presented in Table II, in which amounts of nicotinic acid and nicotinamide, obtained by differentiation, are compared with the total amount found by the method of the Association of Official Agricultural Chemists.

Samples 1 to 3 and 11 to 15, inclusive, contained mixtures of nicotinic acid and nicotinamide. The percentage composition, as determined by the authors, was in close agreement with that stated by the label claim. Samples 4 to 10, inclusive, were labeled nicotinamide and were proved to be nicotinamide by analysis. None of the samples tested gave any evidence of a breakdown of nicotinamide to nicotinic acid.

Precision. The results obtained in the determination of total nicotinic acid by the sulfanilic acid method (*7*, *9*) are reproducible to within ±2%. However, such precision is not possible in the differentiation method proposed here. Because of the number of measurements required, and the possibility that errors may be additive, individual determinations may differ from each other by as much as ±5%.

Table II. Determination of Nicotinic Acid and Nicotinamide

Commercial Samples	Amounts Found by Differentiation Analyses: Nicotinic acid	Amounts Found by Differentiation Analyses: Nicotinamide	Equivalent Nicotinic Acid, Columns 2 + 3	Total Nicotinic Acid by AOAC Method
1	25.2	27.0	52.2	51.0
2	9.6	70.4	80.0	82.0
3	18.0	77.0	95.0	95.0
4	None	52.0	52.0	52.0
5	None	100.0	100.0	100.0
6	None	102.0	102.0	102.0
7	None	13.0	13.0	13.0
8	None	2750.0	2750.0	2750.0
9	None	103.0	103.0	103.0
10	None	103.0	103.0	103.0
11	11.8	8.8	20.6	20.0
12	9.5	9.8	19.3	19.7
13	25.0	25.0	50.0	50.0
14	13.5	15.9	29.4	30.0
15	12.4	9.8	22.2	21.0

After submission of this paper an opportunity was afforded to review the paper of Wollish and associates (*10*), in which previous methods for differentiating between nicotinic acid and nicotinamide were criticized and a means of accomplishing this differentiation by a paper chromatographic procedure was described. The authors are pleased to note that another means of differentiation has been devised, but point to the advantage of their simpler procedure for routine control purposes.

QUALITATIVE DIFFERENTIATION OF NICOTINIC ACID AND NICOTINAMIDE

Although the use of sulfanilic acid as the aromatic amine is satisfactory for the quantitative measurement described above, the colors formed with nicotinic acid and nicotinamide are not of sufficiently different shade to permit its use in a rapid visual qualitative test. For this purpose Tobias acid is valuable. Tobias acid (2-naphthylamine-1-sulfonic acid) gives an orange with nicotinic acid, and a pink with nicotinamide, colors which can be easily distinguished. The test can be carried out using either nicotinic acid or nicotinamide solutions ranging in concentration from one to several hundred micrograms per milliliter. The difference in color is most readily distinguished in the range of 5 to 100 micrograms per ml. The color obtained when developed with cyanogen bromide and Tobias acid should be compared with that given by standard solutions of nicotinic acid or nicotinamide of similar concentration.

If the sample contains a mixture of the two compounds, this will be indicated by a blend of pink and orange colors. An approximate estimate of the proportions present may be made by comparing the color obtained with that produced with various known mixtures of nicotinic acid and nicotinamide.

Reagents. TOBIAS ACID. Add 20 grams Tobias acid to 170 ml. of warm water (not over 75° C.), and add concentrated sodium hydroxide solution, drop by drop, until solution is obtained. Adjust pH to 4.5 with 1 to 1 hydrochloric acid, using bromocresol green indicator and a spot plate. Add 5 grams of Norite, warm 5 minutes, and filter. Make the filtrate to 200 ml. with water and store in a brown bottle.

PHOSPHATE BUFFER. Dissolve 17.6 grams of potassium dihydrogen phosphate and 10.24 grams of sodium monohydrogen phosphate dodecahydrate in water and make to a volume of 250 ml. Other reagents are similar to those used in the quantitative procedure.

Procedure. A sample solution containing 5 to 100 micrograms of nicotinic acid or nicotinamide per ml. is used. For tablets, or capsules, the sample is extracted as in the quantitative procedure. Two milliliters of phosphate buffer are added to 1 ml. of the sample solution in an 18-mm. test tube. Five milliliters of cyanogen bromide are then added from a pipet with swirling, followed by 4 ml. of Tobias acid, added in a similar manner. The color observed between 4 and 15 minutes after addition of the Tobias acid indicates the form of the vitamin present. The following series of color changes will be observed at room temperature:

Time Interval after Addition of Tobias Acid, Min.	Nicotinic Acid	Nicotinamide
0	Intense yellow orange	Orange
2–3	Intense orange	Intense orange
3–4	Orange	Pink
15–20	Orange with tinge of red	Pink starts to fade slowly to orange
1 hour	Red orange	Red orange
2 hours	Orange pink	Orange
3 hours	Salmon pink	Orange
7 hours	Pink	Orange

The speed of the initial stages of the reaction at 0° C. is approximately the same as at room temperature. Nicotinamide forms a pink color in 3 to 4 minutes, while the nicotinic acid color is orange. At the lower temperature these colors are stable for several hours. The test cannot be carried out satisfactorily at elevated temperatures because of rapid fading of the colors.

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Reductometric Titration of Antimony, Copper, and Tin with Chromous Ion

JAMES J. LINGANE AND CLEMENS AUERBACH
Harvard University, Cambridge 38, Mass.

THAT chromous ion in hydrochloric acid medium is a powerful enough reductant to reduce antimony(V) to antimony(III) and to the metal, cupric copper to the cuprous state and to the metal, and tin(IV) to the stannous state, is known from the pioneer studies of Zintl and coworkers (*6–8*) and Brintzinger and Rodis (*1*). However, the reports of these authors neither define the optimum conditions for the titrations, nor furnish adequate information on the precision and accuracy that can be obtained. The present investigation was undertaken to obtain this information.

Because of the extensive hydrolysis of antimony(V) and tin(IV), a complexing titration medium is necessary. A medium containing both hydrogen ion and chloride ion, in which the three elements exist principally as chloro complexes, is the most advantageous. A systematic study of the influence of hydrogen and chloride ion concentrations on the potentiometric titration curves of the elements individually has established optimum conditions for the analysis of mixtures, and provided data on the accuracy of individual titrations and analysis of mixtures.

EXPERIMENTAL TECHNIQUE

Solutions of 0.1 *M* chromous sulfate in ca. 0.5 *M* sulfuric acid were prepared (*5*) and standardized by titration of known amounts of copper(II) in hydrochloric acid medium. This standardization has been shown to be accurate to at least ±0.1%. The titrant solution was delivered from a calibrated 50-ml. or a 5-ml. microburet, depending on the volume required.

Titrations were performed potentiometrically. The titration vessel consisted of a 300-ml. lipless beaker closed by a rubber stopper, provided with appropriate holes for insertion of the buret tip, salt bridge, indicator electrode, gas inlet tube, and thermometer. A magnetic stirrer was employed. Titrations were performed in an atmosphere of carbon dioxide, which was freed from oxygen by scrubbing through chromous sulfate solution. Carbon dioxide was passed through the test solution for 15 minutes before and during each titration.

Stock solutions of the various metals were prepared by accepted methods and their concentrations were known to ±0.2% or better.

A saturated calomel reference electrode was connected to the test solution by a salt bridge filled with 0.5 *M* sulfuric acid. The bright platinum indicator electrode was fabricated from platinum

This study was initiated to determine the optimum conditions for the potentiometric titration with chromous ion of antimony(V), copper(II), and tin(IV), singly and in mixtures. The accuracy of the titrations has been established in media of various hydrogen and chloride ion concentrations; in general, optimum conditions are 5 *M* or greater hydrochloric acid and a temperature of 85° C. A mercury indicator electrode is superior to platinum in the titration of tin(IV), when antimony and/or bismuth are absent. Antimony-copper mixtures with ratios from about 100 to 0.01 can be analyzed accurately. Small amounts of antimony and/or copper are determinable in the presence of large amounts of tin—e.g., in tin-base alloys. The tin determination is satisfactory in the presence of an equal or smaller amount of antimony and/or copper, but not with larger amounts of these metals.

wire, and the mercury electrode used for some titrations was of the type previously described (*3*).

BEHAVIOR OF INDIVIDUAL ELEMENTS

Copper. In sulfuric acid medium copper(II) is reduced directly to the metal by chromous ion, but in hydrochloric acid medium the titration curve shows two breaks corresponding to stepwise reduction to the cuprous state and to the metal (*5*). The second equivalence point is clearly defined only when the solution is at room temperature or below, and it disappears when the titration is performed at 85° C.

The typical titration curves, 1 to 3 at room temperature shown in Figure 1, demonstrate the influence of the chloride ion concentration between 0.1 and 5 *M* at a constant hydrogen ion concentration of 5 *M*. With decreasing chloride ion concentration the magnitude of the potential change at the first equivalence point diminishes and that at the second equivalence point increases, owing to a decrease in the cupric-cuprous potential and an increase in the cuprous-copper potential. When the chloride ion concentration is as small as 0.1 *M*, the cuprous copper formed in the first stage of the titration precipitates as cuprous chloride, but with larger chloride ion concentrations it remains in solution as a chloro-cuprous complex anion. Over a range of chloride ion concentration from 0.1 to 5 *M* the accuracy of the titration to the first equivalence point is limited only by the accuracy of the buret reading, and equilibrium is very quickly attained. Equally good results are obtained when the titration is performed at 85° C.

Titration to the second equivalence point is not satisfactorily accurate at any chloride ion concentration from 0.1 to 5 *M* at a constant hydrogen ion concentration of 5 *M*. The volume of 0.1 *M* chromous sulfate required to titrate 10-ml. portions of 0.1 cupric ion in a total volume of 75 ml. averaged 0.3 ml. greater than that required up to the first equivalence point. This overconsumption of chromous ion appears to be caused by the reaction

$$2Cr^{++} + 2H^{+} = 2Cr^{+++} + H_2$$

which probably is catalyzed by the finely divided metallic copper produced during the second stage of the titration. Furthermore, equilibrium is only slowly established during the second stage of the titration.

When the chloride ion concentration is decreased from 5 to 1 *M* at a constant hydrogen ion concentration of 5 *M*, the potential at the sharp bend which marks the beginning of the second stage increases from −0.37 volt *vs.* S.C.E. to −0.27 volt. The theoretical shift for the half-reaction

$$CuCl_2^{-} + e = Cu + 2Cl^{-}$$

is 0.08 volt at room temperature, and for the reaction

$$CuCl_3^{--} + e = Cu + 3Cl^{-}$$

it is 0.12 volt. The observed shift of 0.10 volt indicates that the complexes $CuCl_2^{-}$ and $CuCl_3^{--}$ are both present over this range of chloride ion concentrations.

The potential at the mid-point of the first stage of the titration, where one half the cupric copper is reduced to the cuprous state, decreases from +0.27 volt *vs.* S.C.E. to +0.12 volt when the chloride ion concentration is decreased from 5 to 0.1 *M*. The theoretical shift of this formal potential for the consumption of one chloride ion is 0.10 volt, and for two chloride ions consumed it is 0.20 volt. The observed shift of 0.15 volt, combined with the foregoing evidence that both cuprous species, $CuCl_2^{-}$ and $CuCl_3^{--}$, are present, admits the existence over this range of chloride ion concentrations of any two or all of the copper(II) species Cu^{++}, $CuCl^{+}$, and $CuCl_2$, but it does not permit a conclusion as to which predominates.

Using mixtures of hydrochloric acid and sodium chloride, the influence of varying hydrogen ion concentration from 5 *M* to 0.1 *M* at a constant chloride

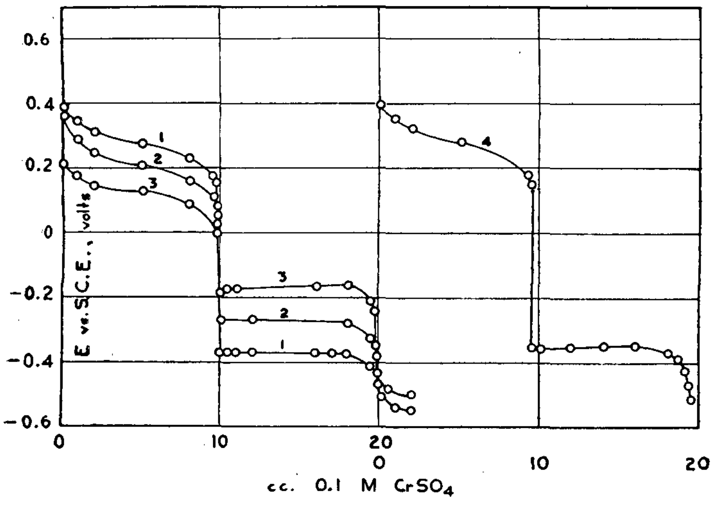

Figure 1. Titration of Copper in Chloride Media

Room temperature. Platinum electrode. V_0 = 75 ml.

1. 5 *M* hydrochloric acid
2. 1 *M* hydrochloric acid, 4 *M* sulfuric acid
3. 0.1 *M* hydrochloric acid, 4.9 *M* sulfuric acid
4. 2 *M* hydrochloric acid, 3 *M* sodium chloride

ion concentration of 5 *M* was investigated. There was no change in the excellent precision and accuracy of the first stage of the titration as the acidity was decreased. The accuracy of the second stage remained poor (several per cent excess consumption of chromous ion) regardless of the acidity.

The potential at the sharp bend at the beginning of the second stage of the titration increased from −0.37 volt *vs.* S.C.E. to −0.31 volt when the hydrogen ion concentration was decreased from 5 to 1 *M* at a constant chloride ion concentration of 5 *M*. Under the same conditions the formal potential of the cupric-cuprous couple (mid-point of the first stage of the titration) increased from +0.27 volt *vs.* S.C.E. to +0.29 volt. That these shifts are caused chiefly by change of the liquid-junction potential with varying hydrogen ion concentration was established by measuring the e.m.f. of the cell

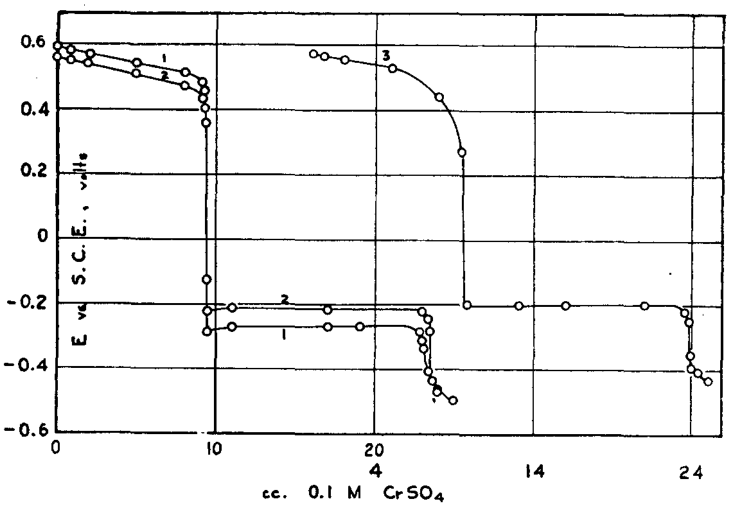

Figure 2. Titration of Antimony in Chloride Media

85° C. Platinum electrode. V_0 = 75 ml.
1. 5 *M* hydrochloric acid
2. 1 *M* hydrochloric acid, 4 *M* sulfuric acid
3. 1 *M* hydrochloric acid, 4 *M* sodium chloride

$$Ag/AgCl(s),\ HCl\ (5\ M)/H_2SO_4\ (0.5\ M)/HCl\ (1\ M),\ NaCl\ (4\ M)\ AgCl(s)/Ag$$

The observed e.m.f. was 0.055 volt, and because the chloride ion activity must be at least approximately the same in both solutions, this is a good approximation of the net liquid-junction potential. The observed shift of 0.06 volt in the potential at the sharp bend is fully accounted for by this change in the liquid-junction potential. However, the observed shift of only 0.02 volt in the formal potential of the cupric-cuprous couple is considerably too small to be due to the change in liquid-junction potential alone, and it points to the existence of a complex species of copper(II) containing both oxygen and chloride ion at low acidities. This is also indicated by a pronounced diminution of the greenish-yellow color of the solutions as the acidity is decreased.

The behavior of copper in bromide media containing from 0.1 to 5 *M* sodium bromide, and at hydrogen ion concentrations between 0.1 and 5 *M*, was also investigated. The complexation of cuprous ion with bromide ion is much stronger than with chloride ion. Consequently the cuprous-copper potential is displaced to such a negative (reducing) value that a potential break is not observed at the completion of the second stage of the titration when the bromide ion concentration exceeds about 1 *M*. Even with smaller concentrations of bromide ion, the second break is too small to be of practical value.

The cupric-cuprous couple assumes a more positive (oxidizing) value in bromide than in chloride medium, showing that the degree of complexation of the cuprous state relative to the cupric state is greater with bromide than with chloride. The formal potential is +0.39 volt *vs.* S.C.E. in 5 *M* hydrobromic acid compared to +0.27 volt in 5 *M* hydrochloric acid. As a consequence, the potential break at the first equivalence point is even larger in bromide than in chloride medium, and the precision and accuracy are as good as in chloride media. However, a bromide medium has no significant practical advantage over a chloride medium.

Antimony. The titration of antimony(V) with chromous ion was studied very briefly by Brintzinger and Rodis (*1*), but only in the presence of stannic tin and copper and in only one electrolyte (2 *M* hydrochloric acid and 1.5 *M* calcium chloride at 90°).

The typical titration curves in Figure 2 demonstrate the stepwise reduction of antimony(V) to antimony(III) and to the metal. Titrations were performed at 85° because the reactions were prohibitively slow at room temperature.

With mixtures of hydrochloric and sulfuric acids at a constant hydrogen ion concentration of 5 *M*, the potential break at the first equivalence point decreases slightly, and that at the second increases, when the chloride ion concentration is decreased from 5 to 1 *M*. With 5 *M* chloride ion the potential at the mid-point of the first stage of the titration is +0.54 volt *vs.* S.C.E., and the potential at the sharp bend marking the beginning of the second stage is −0.29 volt. With 1 *M* chloride ion the corresponding values are, respectively, +0.51 and −0.23 volt. The potentials at the mid-point of the first stage agree well with the formal potentials at 25° of the antimonic-antimonous couple recently reported by Brown and Swift (*2*) at corresponding chloride ion concentrations.

Several minutes are required to attain potential ebuilibrium after each addition of the chromous solution, but a titration can be completed fairly rapidly by titrating directly to the equivalence point potentials at 85°. For practical purposes the first equivalence point potential may be taken as +0.20 volt (with a tolerance of ±0.1 volt) in a solution 5 *M* in hydrochloric acid. Under these conditions the accuracy of titrations to the first equivalence point of 6- to 150-mg. quantities of antimony in a volume of 75 to 100 ml. is limited only by the accuracy of the buret readings.

Titration to the second equivalence point is not as accurate as to the first. When the titration is performed slowly there is a pronounced tendency toward 1 to 2% overconsumption of chromous ion, apparently because the oxidation of chromous ion by hydrogen ion is catalyzed by the finely divided metallic antimony. By titrating rapidly to the equivalence point potential, this oxidation is minimized and results accurate to 0.5% or better are obtainable. In 5 *M* hydrogen ion and 1 to 5 *M* chloride ion at 85° the second equivalence point potential is −0.33 ± 0.02 volt *vs.* S.C.E.

Using mixtures of hydrochloric acid and sodium chloride at a constant chloride ion concentration of 5 *M*, the potential at the mid-point of the first stage of the titration was found to remain virtually constant at +0.54 volt when the hydrogen ion concentration was decreased from 5 to 1 *M*, while the potential at the sharp bend at the beginning of the second stage increased from −0.29 to −0.21 volt. Correspondingly, the potential break at the first equivalence point decreases somewhat, and that at the second increases, with decreasing acidity. From the studies of Lingane and Nishida (*4*) and Brown and Swift (*2*) there is good evidence that the antimony(V) in these solutions must exist as an oxygenated chloro complex, such as $SbO_2Cl_2^-$. As hydrogen ion is consumed in the reduction of such a species to the chloro complex of antimony(III) (probably $SbCl_4^-$) the potential of the antimonic-antimonous couple actually must decrease (become less oxidizing) with decreasing hydrogen ion concentration. The apparent formal potential of the couple remains constant because this effect is nearly exactly compensated by the increase in the liquid-junction potential. When the acidity is decreased below about 4 *M* at a constant chloride ion concentration of 5 *M*, the accuracy of the titration to both equivalence points deteriorates, and with 1 *M* hydrogen ion as much as 3% too little chromous ion is required to reach the first equivalence point.

It follows that the optimum conditions for the titration of antimony are a temperature of about 85° C., chloride ion concentration of 1 to 5 *M*, and hydrogen ion concentration of at least 4 *M*. The use of only 2 *M* hydrochloric acid with addition of calcium or potassium chloride as recommended by Brintzinger and Rodis (*1*) does not correspond to these optimum conditions and is unsatisfactory.

Tin (with Platinum Indicator Electrode). In hydrochloric acid medium tin(IV) is reduced by chromous ion only to tin(II). The reaction is prohibitively slow at room temperature and in the present study all titrations were performed at 85° C. Even at 85° the titration of pure solutions of tin(IV) is unsatisfactory when a platinum indicator electrode is used. Near the equivalence point an excessively long time is required to attain even approximately constant potentials after each increment of chromous ion is added, and a 1 to 2% overconsumption of chromous ion invariably was observed. Apparently the slowness of the reaction permits appreciable oxidation of chromous ion by hydrogen ion before it is oxidized by the stannic tin.

In agreement with Brintzinger and Rodis (*1*) a small amount of bismuth(III) was found to catalyze the stannic-chromous reaction, and with bismuth present satisfactorily accurate results are obtainable. This catalytic action rests on the fact that bismuth(III) is very rapidly reduced to the metallic state by chromous ion, and the finely divided metallic bismuth reduces tin(IV) much more quickly than does chromous ion.

Typical titration curves of tin(IV) in the presence of a small amount of bismuth at different acidities and chloride ion concentrations with a platinum indicator electrode are shown by curves 1 to 3 in Figure 3. The first break corresponds to the reduction of the tin(IV) to the stannous state and the second to the reduction of the bismuth(III) to the metal. The optimum amount of bismuth is 5 to 10% of the amount of tin present.

Although the break at the tin equivalence point is rather small, a precision and accuracy of 0.3% were obtained in the titration of 60 to 150 mg. of tin in 5 *M* hydrochloric acid in a volume of 100 ml. With smaller amounts (25 mg.) results were unsatisfactory and 5 to 10% too much chromous ion was consumed.

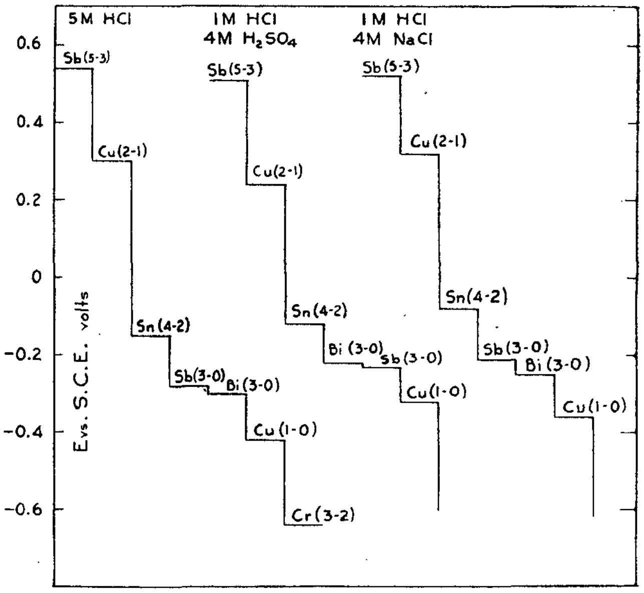

Figure 4. Formal Potentials of Antimony, Copper, Tin, and Bismuth Couples in Chloride Media at 85° C.

Tripositive antimony also serves to catalyze the stannic-chromous reaction, and the characteristics of the titration in 5 *M* hydrochloric acid with antimony present are very similar to titrations in the presence of bismuth.

The characteristics of the tin titration in the presence of bismuth were studied with various concentrations of hydrogen ion and chloride ion. At a constant hydrogen ion concentration (sulfuric acid) of 5 *M*, variation of the chloride ion concentration from 1 to 5 *M* has no significant effect on the accuracy. When the chloride ion concentration is less than 1 *M* the reaction becomes inconveniently slow near the equivalence point, and the potential break becomes too small for accurate measurement. The formal potential of the stannic-stannous couple increases from −0.15 volt *vs.* S.C.E. in 5 *M* chloride to −0.10 volt in 0.5 *M* chloride at a constant hydrogen ion concentration of 5 *M*.

At a constant chloride ion concentration of 5 *M*, the speed of the reaction diminishes when the hydrogen ion concentration is smaller than 5 *M*. When the hydrogen ion concentration is less than about 3 *M*, significant underconsumption of chromous ion results.

Tin (with Mercury Indicator Electrode). Previous experience in the titration of titanium(IV) with chromous ion (*3*) has demonstrated the unsuitability of a platinum

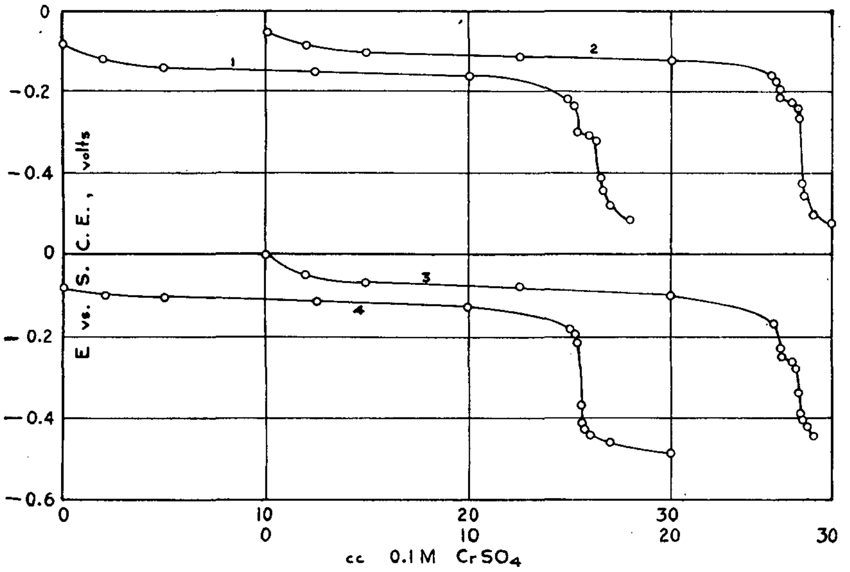

Figure 3. Titration of Stannic Tin in Chloride Media

1. 85° C. Platinum electrode; 7 mg. bismuth (III) present. V_0 = 75 ml. 5 *M* hydrochloric acid
2. Same as (1). 1 *M* hydrochloric acid, 4 *M* sulfuric acid
3. Same as (1). 1 *M* hydrochloric acid, 4 *M* sodium chloride
4. 85° C. Mercury electrode: bismuth absent. V_0 = 120 ml. 5 *M* hydrochloric acid

indicator electrode in titrations where the potential becomes more negative (more reducing) than the potential of the hydrogen-hydrogen ion half-reaction (ca. −0.20 volt *vs.* S.C.E. in 5 *M* hydrogen ion). Under this circumstance the platinum electrode functions partially as a hydrogen electrode, because the reaction $2Cr^{++} + 2H^{+} = 2Cr^{+++} + H_2$ is catalyzed at the platinum surface. This is chiefly responsible for the slow attainment of potential equilibrium when tin(IV) is titrated in the absence of a catalyst, using a platinum indicator electrode.

When instead of platinum a mercury indicator electrode of the type previously described (*3*) is used, potential equilibrium is very quickly established in the titration of tin(IV) with chromous ion in 5 *M* hydrochloric acid at 85° C. No bismuth or other catalyst is required and consequently the potential break at the equivalence point, not being limited by the subsequent reduction of a catalyst, is very much larger than when a platinum indicator electrode is used. A typical titration curve is shown as No. 4 in Figure 3.

With the mercury indicator electrode it is feasible to titrate directly to the equivalence point potential, and consequently the titration can be completed quickly. In 5 *M* hydrochloric acid at 85° C. the equivalence point potential is −0.33 volt *vs.* S.C.E.

In the titration of 150-mg. quantities of tin in a volume of 100 ml. a precision and accuracy of ±0.2% are easily attained, and quantities as small as 6 mg. can be titrated with an accuracy of ±1%. The fact that small as well as large quantities of tin can be titrated accurately is a further advantage of the mercury electrode over the platinum electrode.

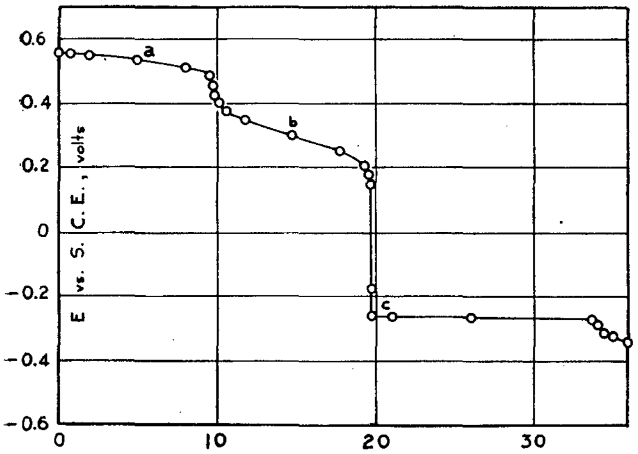

Figure 5. Titration of Mixture of Antimony(V) and Copper(II)

5 *M* hydrochloric acid. 85° C. Platinum electrode. V_0 = 120 ml.
a. Sb(5-3)
b. Cu(2-1)
c. Sb(3-0)

The mercury electrode cannot be used when bismuth or antimony is present. The amalgam formation when these metal ions are reduced makes their reduction potentials more positive (more oxidizing) than those of the solid metals. Consequently no distinct potential break is observed after the completion of the reduction of the tin(IV) when bismuth(III) or antimony is present.

ANALYSIS OF MIXTURES

The formal potentials of the antimony, copper, tin, and bismuth couples in three media with a ratio of hydrogen ion to chloride ion concentrations between 5 to 1 and 1 to 5 at 85° C. are summarized in Figure 4. This graph indicates that the analysis of binary or ternary mixtures of antimony, copper, and tin in their highest oxidation states should be possible. The results of a systematic study of the titration of mixtures of these three metals are summarized in the following paragraphs. In all cases the titrations were performed at 85° C.

Table I. Analysis of Bureau of Standards Tin-Base Bearing Metal 54b

(Certificate values: Sb 7.39, Cu 3.19, Sn 87.45, Pb 1.81, Bi 0.027, Ag 0.030 As 0.051, and Fe 0.029)

	Sb, %	Cu, %	Sn, %
	7.36	3.17	87.16
	7.34	3.25	87.36
	7.36	3.21	87.34
	7.35	3.15	87.18
Av.	7.35 ± 0.01	3.22 ± 0.04	87.26 ± 0.09

To obtain satisfactory precision in titrations involving disproportionate quantities of two metal ions two burets were used: an ordinary 50-ml. buret graduated in 0.1 ml., and a 5-ml. microburet graduated in 0.01 ml. Both burets were connected to the same titrant storage flask, and their tips were connected by a Y-tube to a common delivery tip. When the first metal titrated was present in the larger amount, most of the titrant was delivered from the macroburet, the titration to the first equivalence point was completed with the microburet, and the titration of the minor metal was then performed with the microburet. Conversely, when the minor metal was reduced first, its titration was performed with the microburet, and the macroburet was used in the subsequent titration of the major metal.

Antimony-Copper. The optimum medium for the titration of mixtures of antimony(V) and copper is 5 to 7 *M* hydrochloric acid. The higher acid concentration is preferable because it yields the largest break at the antimony equivalence point. A typical titration curve is reproduced in Figure 5.

Although the potential change is small at the antimony equivalence point, equilibrium is quickly established at 85° and the titration is accurate. With 60 to 150 mg. each of antimony and copper in a volume of 120 ml. the determination of each metal is accurate to ±0.5%. The determination of antimony becomes increasingly difficult as the amount of copper is increased, and the antimony end point is obscured entirely when the ratio of copper to antimony is greater than about 100. Copper can be titrated accurately in the presence of an equal amount of antimony, but positive errors of about 1% are observed when the antimony to copper ratio is about 100.

Ferric iron is reduced to the ferrous state along with copper, but amounts of iron up to 60 mg. in a volume of 100 ml. do not interfere with the titration of antimony in 7 *M* hydrochloric acid.

The precision and accuracy of titration of mixtures of antimony, copper, and tin are demonstrated by the data in Table I obtained in the analysis of Bureau of Standards tin-base bearing metal 54b.

One-gram samples were decomposed by boiling with 10 ml. of concentrated sulfuric acid. The resulting suspension was diluted with 25 ml. of water, dissolved by means of 50 ml. of 12 *M* hydrochloric acid, transferred to a 250-ml. volumetric flask, and diluted to the mark. A 50-ml. aliquot of this sample solution was placed in the titration cell, and 0.02 *M* potassium permanganate was added dropwise until a slight excess was present (brown coloration) to oxidize antimony to the (V) state. Forty milliliters of 12 *M* hydrochloric acid were then added, and the solution was heated to 90°, and swept with carbon dioxide for 15 minutes to remove the chlorine formed by the reduction of the excess permanganate by chloride ion. The solution was then titrated at 85° C. with 0.1 *M* chromous sulfate.

Antimony-Tin. A typical titration curve of a mixture of antimony(V) and tin(IV) in 5 *M* hydrochloric acid at 85° is shown in Figure 6. The first large break corresponds to the reduction of antimony(V) to antimony(III), the second to the reduction of stannic tin to the stannous state, and the third to the reduction of antimony(III) to the metal.

The determination of antimony by titration to the III state in the presence of tin presents no difficulties. Sixty- to 150-mg. quantities of antimony can be titrated with an accuracy of ±0.5% or better in the presence of as much as 6 grams of tin in a volume of 100 ml. As little as 1 mg. of antimony can be titrated with an accuracy of ±1% in the presence of 150 mg. of tin.

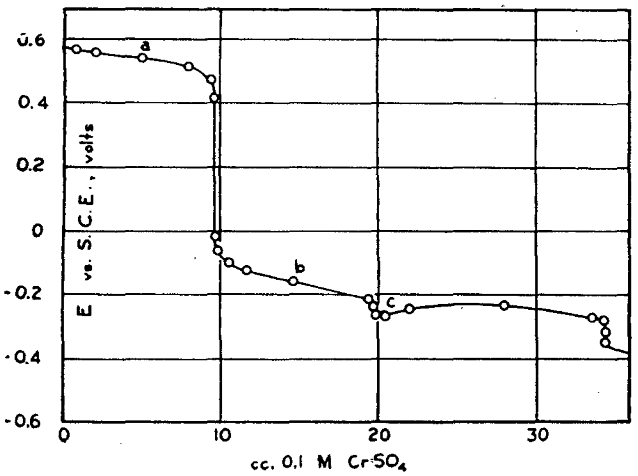

Figure 6. Titration of Mixture of Antimony(V) and Tin(IV)

5 *M* hydrochloric acid. 85° C. Platinum electrode. V_0 = 100 ml.
a. Sb(5-3)
b. Sn(4-2)
c. Sb(3-0)

The use of the second antimony equivalence point in the presence of tin is less satisfactory: overconsumption of chromous ion to the extent of several per cent is observed.

The titration of 60- to 150-mg. quantities of tin in the presence of 6 mg. of antimony in a volume of 100 ml. is accurate to about 0.2%, with a slight tendency toward low results. With larger concentrations of antimony the potential break at the tin equivalence point is worsened somewhat; in the presence of 150 mg. of antimony the accuracy deteriorates to about 0.5% when 150 mg. of tin are titrated and is still poorer with smaller quantities of tin. These observations all pertain to the platinum indicator electrode, which necessarily must be used with antimony-tin mixtures. It is possible to titrate as little as 6 mg. of tin in the presence of not more than 6 mg. of antimony, but accuracy and precision are only about ±2% at best, and steady potentials are established very slowly near the equivalence point.

Copper-Tin. This combination is of special interest because of its prevalence in many types of copper-base alloys. A typical titration curve of a mixture of copper(II) and tin(IV) with 7 mg. of bismuth(III) present as a catalyst for the tin titration. is shown in Figure 7 (platinum indicator electrode, 120 ml, volume, 5 *M* hydrochloric acid, 85° C.). The first inflection marks the reduction of copper(II) to copper(I), the second the reduction of stannic to stannous tin, and the third small one the reduction of the bismuth(III) to the metal.

Sixty- to 150-mg. quantities of copper can be titrated with an accuracy of ±0.2% or better in the presence of as much as 6 grams of tin under the conditions of Figure 7. As little as 6 mg. of copper can be titrated with an accuracy of ±1% in the presence of 150 mg. (and probably more) of tin.

With mixtures of 150 mg. of copper and 60 to 150 mg. of tin in a volume of 100 ml. the tin determination is accurate to 0.5%, or somewhat better, with a tendency toward negative rather than positive errors. When the amount of tin exceeds the amount of copper, the determination of the tin is accurate to about 0.2%. It is necessary to wait 2 to 3 minutes for the establishment of steady potentials in the vicinity of the tin equivalence point. In the presence of 150 mg. of copper, the accuracy of the tin determination deteriorates seriously when the amount of tin is relatively small; with 15 mg. of tin positive errors as large as 4% were observed. Under these conditions transient precipitation of metallic copper occurs during the tin titration, and the overconsumption of chromous ion probably is associated with the slow reoxidation of the copper by the stannic tin. All attempts to improve the accuracy of the titration of small amounts of tin in the presence of large amounts of copper were abortive. The use of chromous titration to determine tin in copper-base alloys is feasible only when the tin content is greater than about 30%.

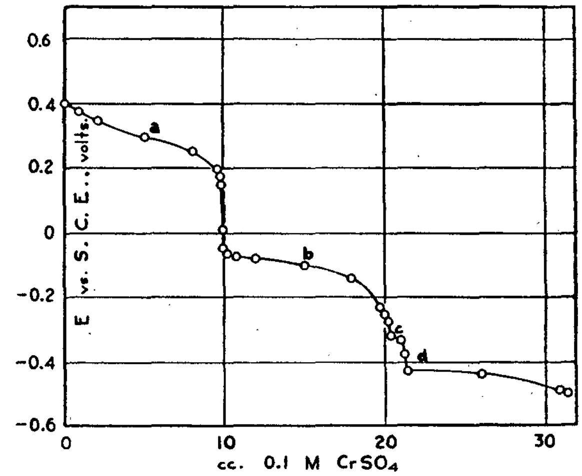

Figure 7. Titration of Mixture of Copper(II) and Tin(IV)

5 *M* hydrochloric acid. 85° C. Platinum electrode. 7 mg. bismuth(III) present. V_0 = 120 ml.
a. Cu(2-1)
b. Sn(4-2)
c. Bi(3-0)
d. Cu(1-0)

Small amounts of tin can be determined in copper-base alloys by preliminary removal of the copper (and antimony and bismuth if present) by controlled potential electrolytic deposition from a hydrochloric acid solution. The tin in the residual solution may then be titrated accurately, using the mercury indicator electrode.

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Determination of Boron in Metal Borides

HERMAN BLUMENTHAL
American Electro Metal Corp., Yonkers, N. Y.

In the search for a method that could be used for the determination of boron in metal borides, it was found that the standard procedure of separating boron in the form of methyl borate from the metals by distillation was too time-consuming and not always accurate. The method described carries this separation out by precipitating the metals with barium carbonate after using a sodium carbonate fusion to bring the sample into solution. It has been successfully applied to the borides of iron, chromium, tungsten, titanium, zirconium, thorium, vanadium, niobium, tantalum, calcium, cerium and aluminum, boron carbide, boron nitride, and amorphous and electrolytic boron. The borides of transition metals have become recently of great interest because of their physical properties at high temperatures. This method should therefore be useful for fast and accurate routine determinations.

THE borides of some transition metals have recently become of great technical interest. They are metallic refractories and good conductors of heat and electricity, have high melting points, and some of them are corrosion-resistant at high temperatures. In the course of metallurgical investigations, sponsored by the Office of Naval Research, the lack of a fast and accurate method for the determination of boron in these borides became obvious.

PREVIOUS WORK

Boron has generally been determined in chemical compounds, alloys, and mixtures by transforming the element into boric acid, separating this acid from the rest of the constituents, and titrating it with sodium hydroxide. All elements that would interfere in the titration by reacting with sodium hydroxide have been eliminated by three inherently different methods (*2*). The oldest and still most common, originated by Chapin (*1*), consists of distillation of boron in the form of methyl borate. The second (*7*) separates the metals from the boron by plating them on a mercury cathode, and the third, recommended by the authors only for the separation of boron from a very limited number of metals, precipitates the metals with calcium carbonate (*5*), barium hydroxide (*6*), or a mixture of sodium hydroxide and sodium carbonate (*4*).

The first method, involving two distillations, is long and tedious. The second, which was not tested by the author, requires special apparatus and is believed not to function satisfactorily (*3*). Special attention was given to the precipitation method, which was felt to require the least time, apparatus, and attention. The method developed in the course of this investigation is based on this principle and has been tested on many hundreds of samples of various borides, including so-called amorphous and electrolytic boron.

EXPERIMENTAL

Whereas available methods recommend solution of the sample by boiling with acids under a reflux condenser to avoid loss of boron, the method discussed suggests fusion of the sample with sodium or potassium carbonate in a platinum crucible, the basic nature of these salts effectively preventing loss of boron.

The melt is decomposed either with hydrochloric acid or, in some cases, with water. Experiments were carried out in which the metals were then precipitated with barium hydroxide, sodium hydroxide, calcium carbonate, or barium carbonate. Results were low when the first three reagents were used.

Barium carbonate is the only reagent which can be used successfully unless special precautions are taken. Barium hydroxide and sodium hydroxide make the solution too basic; this can be avoided by careful adjustment of the pH, but it is unnecessary when barium carbonate is used. In addition, sodium hydroxide might cause the formation of a sodium borate of low solubility where the concentration of the boric acid is high. Calcium carbonate will behave in a similar manner, also forming a salt of low solubility under these conditions, and there is a greater danger with high pH of retaining the boron by the metal precipitate. When barium carbonate is used as precipitant, the solution never gets above pH 6.5, so that there is no danger of picking up excess carbon dioxide from the air, and barium borate is very soluble in water. Sodium hydroxide is used, but only partly to neutralize the hydrochloric acid.

The precipitated metals are filtered off, and the filtrate is slightly acidified with hydrochloric acid and heated to boiling to expel carbon dioxide, which, if present, would titrate as boric acid. This boiling must be done gently and in a well covered beaker. Boiling for 1 to 3 minutes is sufficient, but experiments showed that boiling for 10 minutes under the above conditions caused no loss of boron. The use of a reflux condenser is unnecessary.

Table I. Reproducibility of Boron Determinations

Sample	Boron Found, % I	Boron Found, % II
Iron boride, FeB	16.59	16.66
Chromium boride	9.20	9.20
Chromium boride, CrB	14.52	14.70
Chromium boride, CrB_2	28.45	28.30
Tungsten boride, WB	5.59	5.76
Titanium boride (TiB?)	16.03	16.18
Titanium boride, TiB_2	25.84	25.91
Zirconium boride, ZrB_2	18.80	18.94
Thorium boride, ThB_2	8.98	8.92
Vanadium boride, VB_2	21.85	21.69
Niobium boride, NbB_2	17.20	17.37
Tantalum boride, TaB_2	9.85	9.96
Calcium boride, CaB_6	42.56	42.45
Cerium boride, CeB_6	30.29	30.09
Aluminum boride, AlB_{12}	65.40	65.48
Boron carbide, B_4C	75.76	75.66
Boron nitride, BN	43.23	43.29
Amorphous boron	82.10	81.90
Electrolytic boron	100.00	100.20

The filtrate may be titrated with sodium hydroxide in the presence of mannitol visually or potentiometrically. If done visually, a mixed indicator solution of methyl red, bromocresol green, phenolphthalein, and thymolphthalein is used, which gives more distinct end points than the common *p*-nitrophenol and phenolphthalein, especially at a temperature of about 50° C. This indicator mixture gives a distinct color change from pink to green when the hydrochloric acid is neutralized, the starting point of the boric acid titration, and changes to purple at the end point of the boric acid titration. Titration at elevated temperature shortens the time for cooling the boiling solution and there is, therefore, less danger of picking up carbon dioxide from the air. Potentiometric titrations were done at about 40° C., as this was the highest temperature at which the available pH meter could be operated.

Figure 1 gives an actual boric acid titration curve for a chromium boride sample. Neutralization of hydrochloric acid occurs at pH 6.3 and of the boric acid complex at pH 9.1, while the indicator end points, indicated by arrows, are at pH 5.3 and 8.9, respectively. Any pH between 5 and 7 may be chosen as a starting point and between 8.6 and 9.4 as an end point for the potentiometric titration, as the parts of the titration curve between these points are practically parallel. The sodium hydroxide solution used for the titrations must, of course, be standardized against a known amount of boric acid at the same pH at which the titration is to be performed.

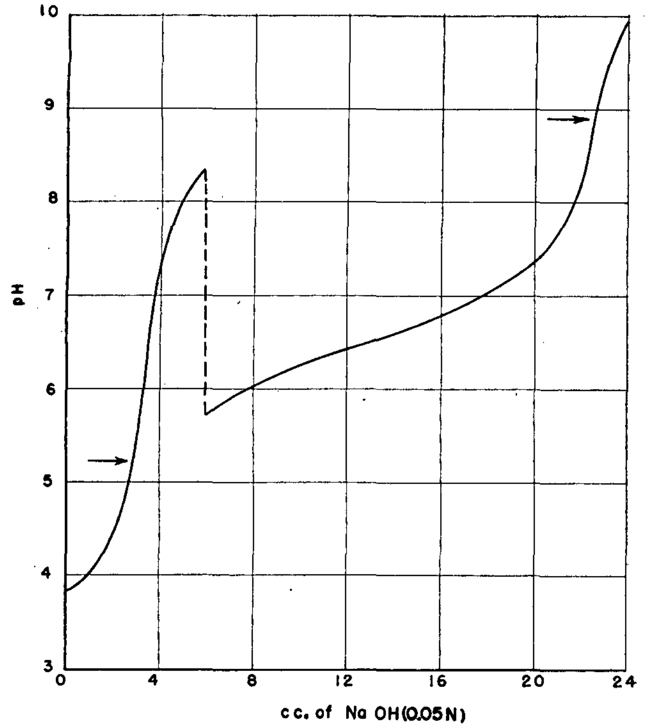

Figure 1. Determination of Boron in Chromium Boride

The outcome of duplicate determinations given in Table I shows the reproducibility of results obtained with the described method.

Some of these borides were produced in the course of the metallurgical investigation; others are commercial grades. For this reason analysis results sometimes are far from the theoretical values.

As no standard boride samples were available, two series of experiments were conducted to prove the reliability of the method.

Addition of Known Amount of Boron to Previously Analyzed Samples. After the fused sample of the respective boride was decomposed with hydrochloric acid, a known amount of boron was added in the form of 25 ml. of a boric acid solution containing about 1 gram of H_3BO_3 per liter. Table II shows the amounts of boron added to the various borides and the amounts recovered.

Addition of Known Amount of Boron to Solutions of Metals. A known amount of boron in the form of boric acid was added to solutions of the metals under study. The ratio of metal to boron in these mixtures was the same as in the respective borides. For these mixtures either a metal salt solution, chloride or nitrate, was used, or a metal oxide was fused according to the procedure described in this paper. The mixtures, metal salt plus boric acid, were then treated like a metal boride solution—namely, the metal was precipitated and the boric acid determined by titration. Table III shows the results of these experiments.

These data prove the reliability and accuracy of the described method for the determination of boron in the metal borides mentioned as well as in elemental boron. Only for tantalum boride is the accuracy somewhat below the usual analytical standard. For a number of other borides—e.g., those of nickel and manganese—the method is not applicable in its present form, as they are not completely precipitated with barium carbonate. These will be dealt with in a later publication.

REAGENTS REQUIRED

The mixed indicator solution is made by dissolving 0.05 gram of methyl red, 0.1 gram of bromocresol green, 0.30 gram of phenolphthalein, and 0.30 gram of thymolphthalein in 100 ml. of methyl alcohol.

Mannitol, reagent grade.

Sodium hydroxide stock solution is prepared by dissolving 50 grams of C.P. sodium hydroxide pellets in 50 ml. of distilled water and transferring to a large test tube. Enough barium hydroxide is added to precipitate carbonate present (see analysis on label), and the solution is shaken well, stoppered tightly, and let stand in vertical position until the supernatant liquid is clear.

Sodium hydroxide, 0.05 *N*, is made by withdrawing 2.5 ml. of the clear stock solution with a pipet and running it into 1 liter of freshly boiled and cooled water. It is mixed well and stored away from contact with air, protected at all times by Caroxite tubes (indicating carbon dioxide absorbent). The solution is standardized against potassium acid phthalate or twice recrystallized C.P. boric acid.

PROCEDURE

Solution of Sample. The well pulverized sample of about 100 mg. (all through a 100-mesh screen) is fused with ten times its weight of sodium carbonate in a platinum crucible. After about 5 minutes, when a good fusion has been accomplished, the burner is removed and the melt in the crucible is well shaken and spread around the walls with the help of crucible tongs. When the melt has solidified and somewhat cooled, about 100 to to 200 mg. of sodium nitrate are introduced and the fusion is continued carefully, the temperature being raised gradually.

After the fusion is complete, which takes about 20 minutes, the crucible is cooled and the melt is digested with 50 ml. of 1 to 1 hydrochloric acid. Boiling must be avoided.

Table II. Recovery of Boron after Boric Acid Additions to Borides

Sample	Boron Added *Mg.*	Boron Recovered *Mg.*	Deviation *Mg.*
Iron boride	4.39	4.40	+0.01
Chromium boride	4.39	4.40	+0.01
Tungsten boride	4.37	4.43	+0.06
Titanium boride	4.37	4.52	+0.15
Zirconium boride	4.37	4.25	−0.12
Thorium boride	4.37	4.41	+0.04
Vanadium boride	4.37	4.26	−0.11
Niobium boride	4.37	4.25	−0.12
Tantalum boride	4.33	4.14	−0.19
Calcium boride	4.39	4.51	+0.12
Cerium boride	4.37	4.42	+0.05
Aluminum boride	4.39	4.40	+0.01
Boron carbide	4.37	4.29	−0.08
Boron nitride	4.88	4.82	−0.06

Table III. Recovery of Boron after Boric Acid Additions to Metal Salt Solutions

Metal in Solution	Boron Added *Mg.*	Boron Recovered *Mg.*	Deviation *Mg.*
Iron	25.5	25.4	−0.1
Chromium	17.7	17.8	+0.1
Tungsten	18.2	18.2	0
Titanium	17.8	17.8	0
Zirconium	18.1	18.2	+0.1
Thorium	18.0	18.2	+0.2
Vanadium	18.2	18.3	+0.1
Niobium	17.5	17.4	−0.1
Tantalum	17.5	17.0	−0.5
Calcium	18.2	18.0	−0.2
Aluminum	18.8	19.0	+0.2

In the case of elemental boron and other high boron-containing materials which are aliquoted before precipitation of the metals, it is advisable to double the amount of sodium carbonate.

Aluminum boride and chromium boride have to be fused with a sodium carbonate–sodium nitrate mixture. Chromium boride does not dissolve in carbonate only, and aluminum boride forms metallic aluminum which alloys with platinum.

The borides of tantalum and niobium are fused with potassium carbonate and potassium nitrate to avoid the formation of sodium salts of low solubility. Their melts as well as that of tungsten boride are later completely decomposed with cold water, then 50 ml. of 1 to 1 hydrochloric acid are added, and the analysis is completed as usual.

To ensure complete precipitation of vanadium, ferric chloride is added to the vanadium boride solution before precipitation. (A ferric chloride solution for this purpose was made by dissolving 50 mg. of Bureau of Standards open hearth iron, sample 55a, in a little hydrochloric acid and oxidizing it with hydrogen peroxide.)

Precipitation of Metals. The hydrochloric acid solution is diluted to 200 ml., and 20 ml. of 1 to 2 sodium hydroxide solution are added. Ten grams of finely powdered barium carbonate are added under stirring, and the solution is then slowly heated to boiling, and kept boiling for about 5 minutes. Care should be taken that a small excess of barium carbonate is present at the bottom of the beaker. The precipitate is allowed to settle on the hot plate for 0.5 hour, filtered off using suction, and washed with hot water.

Barium carbonate will not precipitate chromate ions completely. In the case of chromium boride, it is therefore necessary to add 10 ml. of a 10% barium chloride solution and bring again to a short boil.

Titration of Boric Acid. The filtrate, the volume of which at this point should be 400 ml., is made slightly acidic to litmus with 3 drops of 1 to 3 hydrochloric acid and boiled for 3 minutes to expel all carbon dioxide. After rapid cooling to 50° to 60° C., 6 drops of mixed indicator solution are added and the solution is titrated with 0.05 *N* sodium hydroxide solution until the first green tinge is observed, which indicates neutralization of the hydrochloric acid. Eight grams of mannitol are introduced and the boric acid is titrated to a purple end point.

In the potentiometric titration 0.05 *N* sodium hydroxide is added dropwise until pH 6.2 is reached, mannitol is added, and boric acid is titrated to pH 9.0. A blank titration with the same amounts of all reagents is subtracted from all determinations.

ACKNOWLEDGMENT

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Ionophoretic Analyses in Agar Gels

QUINTIN P. PENISTON, HILDA D. AGAR, AND JOSEPH L. McCARTHY
University of Washington, Seattle, Wash.

An ionophoretic procedure has been developed to provide a method for analyzing mixtures of low molecular weight ionic substances of similar chemical behavior, and for characterization of these solutes. Of particular interest were mixtures of sulfonated aromatic substances comprising dialyzable lignin sulfonic acids, and of phenolic substances obtained by alkaline oxidative degradation of lignin. Ionic components of a sample mixture are made to migrate from an initial short sample section through an agar gel in a long straight tube under constant electrical potential gradient, so that distances migrated are proportional to net mobilities. Under favorable conditions approximately complete separation of components is achieved, so that individual solutes can be not only quantitatively determined, but also characterized by measurement of such properties as absorption spectra and diffusion constants. The use of agar gel to eliminate convection, and of direct photometric scanning of the ionophoresis tube for positional analysis, permits the ionophoretic procedure to be carried out relatively simply with apparatus of moderate cost and with limited expenditure of research time. In some cases, as little as 10 micrograms of a component suffices for analysis. The method should be useful in research on many types of substances such as antibiotics, alkaloids, hormones, and radioactive compounds.

IN WORKING toward separation and identification of lignins and lignin degradation products of low molecular weight (*5, 12, 13*), an analytical procedure was needed which would permit determination of the concentration in which such ionically dispersed substances were present as constituents of complex mixtures in aqueous solution. Because the technique of electrophoresis or ionophoresis seemed well suited to this purpose, a relatively simple and inexpensive apparatus and procedure were devised which differ from the well-known Tiselius method (*15*) of electrophoresis in that migration proceeds in an agar gel without substantial convection, and also over a considerable distance from the initial short sample region, so that more or less complete separation of the ionic species occurs, depending on mobility differences and extent of dispersive effects. In this paper the apparatus and procedure are described, factors influencing separation are discussed, and examples of application to known mixtures are given.

APPARATUS AND PROCEDURES

Migration Apparatus. The following parts make up the migration apparatus (see Figure 1).

The migration tube, *A*, is a straight glass tube approximately 8 mm. in inside diameter and of variable length, depending on the migration conditions. The authors have used Vycor tubing because it has good transparency down to about 2500 A. and permits analysis after migration by direct scanning of the tube for absorption of ultraviolet radiation by use of a spectrophotometer.

The electrode vessels, *B*, are cylindrical borosilicate glass chambers with bend and constriction to join the migration tube, using rubber sleeve couplings and fitted with inlet and overflow tubes for perfusion of buffer solution during the migration.

The electrodes are graphite bars approximately 2 × 2.5 × 20 cm.

Constant head reservoirs and a flow control device are used for buffer perfusion.

A water bath is used for circulation of cooling water at constant temperature.

Milliammeter.

A regulated direct current power supply, 500 to 2000 volts. A power supply found to function satisfactorily for the present purpose has been designed by A. B. Jacobsen, University of Washington Engineering Experiment Station, and built by F. C. Stults, R. Davis, and Eric Reaville of these laboratories. The circuit is somewhat similar to ones earlier described by Jacobsen (*8*), but combines regulated and unregulated voltage sources with over-all compensation.

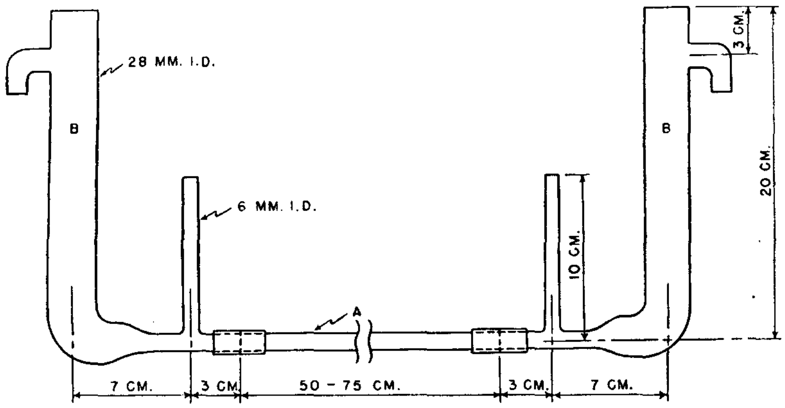


Figure 1. Migration Apparatus

Migration. As the Difco powdered agar used in present experiments has been found to contain soluble substances (presumably agar molecules of low molecular weight) (*6*) which migrate in the electric field and absorb ultraviolet radiation, the material is purified by suspending powdered agar in a large volume of distilled water, stirring for 0.5 to 1 hour, and filtering through a cloth bag. This extraction is repeated four or five times. The extracted product is dried by immersion in ethyl alcohol followed by ether and then placed in a desiccator, and the solvent is removed with a vacuum pump to yield a fluffy white powder which is readily dispersible in hot water to give clear homogeneous sols with low conductance.

Large volumes of buffer solution are required for electrode perfusion during the migration to prevent contamination of the tube with electrolysis products and to maintain uniform potential gradients. In general, ten equivalents of buffer salts at each electrode per faraday passed through the tube have been found satisfactory—e.g., for a current of 50 ma. the flow of 0.06 *M* sodium acetate–0.06 *M* acetic acid buffer should be about 300 ml. per hour at each electrode. In the present work only two buffer systems have been used: sodium acetate–acetic acid, either 0.06 or 0.12 *M* in each component, ca. pH 4.6, and monosodium phosphate–disodium phosphate, 0.06 *M*, ca. pH 7.0.

Before filling, the migration tube is washed with dichromate cleaning solution, rinsed and dried, and then clamped in a vertical position with the bottom end stoppered. A 1% agar sol is prepared by heating 1 gram of purified agar in 100 ml. of the perfusion buffer, using an autoclave or water bath at 100° C. for 15 minutes. The migration tube is filled to the sample region with the hot agar sol and is then cooled rapidly with running water, preferably upward from the tube bottom to provide a flatter meniscus. The sample section is then poured, using a similarly prepared 1% agar sol containing both buffer and sample with a ratio of buffer ions to sample ions of about 10 to 1 and having nearly the same specific conductance as the buffer sol; the amount of sample added may be measured by use of a weight buret, by weighing the migration tube before and after sample addition, or by other means. The tube is again cooled and any spillage of sample is carefully wiped from the walls of the tube with cotton swabs. The tube is finally completely filled with the buffer sol, cooled, and then attached to the electrode vessels. These are packed with glass wool to reduce erosion of gel near the ends of the migration tube and are filled with the perfusion buffer before the migration tube is attached. Care is taken to expel all air bubbles from the glass wool packing and the coupling between tube and electrode vessel.

The migration is then conducted for the desired time period, and a record is kept of applied voltage, current, bath temperature, and perfusion buffer flow. At the end of the period the current is discontinued and the tube is removed from the assembly for analysis.

Analysis. For mixtures of substances absorbing ultraviolet radiation a direct scanning technique using the Beckman quartz spectrophotometer has proved simple and rapid for analysis of the gel after migration. The apparatus shown in Figure 2 was designed and constructed for this purpose.

It consists of a brass tube and a square brass rod notched at 2.5-mm. intervals. These are assembled on a cover plate constructed to fit the sample chamber of the Beckman spectrophotometer. Protruding from the cover plate into the sample chamber is situated a guide tube with a slit (2 × 5 mm.) on each side, oriented with the light path of the instrument. A hole is drilled through the cell carriage plate and floor plate of the sample chamber of the Beckman spectrophotometer, so that the migration tube can be passed down through the instrument into a bag of black, light-excluding cloth. By this means in a few minutes the entire migration tube can be scanned at 2.5- to 10-mm. intervals for optical density at a selected wave length.

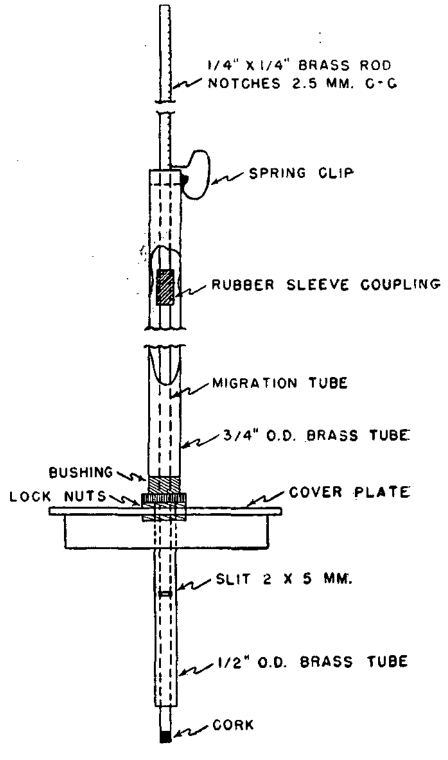


Figure 2. Tube Scanning Device

The operation can be repeated at several wave lengths to differentiate substances with different absorption spectra.

By locating the migration tube at a position corresponding to a peak in the optical density–distance curve, and then determining absorption at various wave lengths for this position, absorption spectra curves can be obtained for the substance or substances giving rise to the peak in the optical density–distance curve.

Diffusion constants can be estimated by following the rate of dispersion of the peaks manifested by the separated components.

Integration of the optical density–distance curves can be used for quantitative estimation of separated substances when extinction coefficients are known. Presumably, the procedure could be adapted for use of radioactive substances with scanning by a Geiger counter.

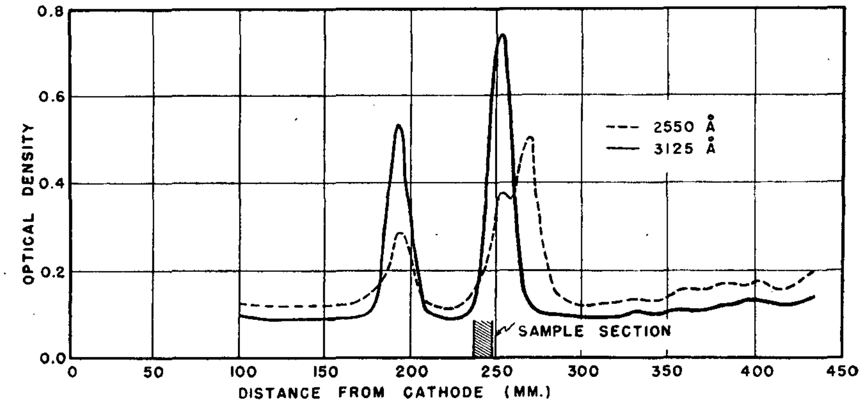


Figure 3. Migration of Vanillin and Vanillic and Ferulic Acids

Example of Experimental Conditions. A known mixture of vanillin, vanillic acid, and ferulic acid was migrated under the following conditions. Samples, 15 mg. per liter of each component. Buffer, 0.12 *M* acetic acid and 0.12 *M* sodium acetate. Tube, No. V-6; length, 761.0 mm.; average inside diameter, 0.78 cm.; average cross section, 0.48 sq. cm. Agar, water leached, 1% gel. Sample section length, 1.2 cm. Sample section location, 236 to 248 mm. from cathode end of tube. Time of migration, 3.5 hours. Bath temperature, 10.0° C. Average applied voltage, 390 volts. Average current, 37.5 ma. (2 tubes in parallel). Specific conductance, 0.0058 Ω^{-1} cm.$^{-1}$ Average voltage gradient, 6.73 volts per cm.

The migration pattern obtained by scanning the tube at 2550 and 3125 A. is shown in Figure 3. At the lower wave length partial separation of ferulic and vanillic acids is indicated, but at 3125 A. negligible absorption occurs for vanillic acid and the ferulic acid peak is augmented.

DISCUSSION

Electrolyte Concentration and Potential Gradient. Factors governing the migration of ions in an electric field have been thoroughly developed for the Tiselius procedure of electrophoresis (*2*) and for moving boundary studies (*9*). For the present case significant relationships may be summarized as follows:

The migration of ions occurs under the influence of an electric field which can be described in terms of voltage gradient, X, and can be related by Ohm's law to the total current, i, and the specific conductance, k:

$$X = \left(\frac{\partial E}{\partial x}\right) = -\frac{i}{k} \tag{1}$$

The total current flowing is related to the current carried by any particular jth ionic species, i_j, by the transference number for that species, T_j, and the current carried by the jth species will be total current multiplied by the mobility-concentration product for the jth species, u_jc_j, divided by the sum of the mobility concentration products for all species present:

$$i_j = (T_j)(i) = \left[\frac{u_jc_j}{\sum\limits_1^n (u_jc_j)}\right] \cdot i \tag{2}$$

where the sum of the transference numbers for all species present is unity.

$$\sum_1^n (T_j) = 1 \tag{3}$$

The specific conductance is equal to the summation of the mobility-concentration products for the several ionic species in which both mobility and concentration are signed quantities, positive for anions, negative for cations:

$$k = \sum_1^n (u_jc_j) \tag{4}$$

Assuming that all migration of ions occurs by electrical conduction, a one-dimensional continuity equation can be set up for migration of the jth species in the electrophoresis tube,

$$\frac{\partial E}{\partial x} \times u_j \left[\frac{\partial c_j}{\partial x} - \frac{c_j}{k} \times \frac{\partial k}{\partial x}\right] = \frac{\partial c_j}{\partial t} \tag{5}$$

and if the specific conductance is maintained approximately constant throughout the tube by establishing a high ratio of supporting electrolyte ion to sample ion concentration,

$$\frac{\partial k}{\partial x} \approx 0 \tag{6}$$

then the mobility of the jth species of sample ion can be calculated from its observed migration velocity, v_j, and from the voltage gradient, X:

$$u_j = \frac{1}{\frac{\partial E}{\partial x}} \times \frac{\partial c_j}{\partial t} \bigg/ \frac{\partial c_j}{\partial x} = \frac{1}{X}\frac{\partial c_j}{\partial t} \times \frac{\partial x}{\partial c_j} = \frac{v_j}{X} \tag{7}$$

Endosmosis. In calculations of mobility, there must be taken into account the endosmosis which occurs in the present procedure as a result of use of an agar gel to eliminate convection. Under the conditions of this work, the flow is toward the cathode. Because this varies about linearly with voltage gradient, it may be treated as a mobility correction to be added for anions and subtracted for cations. The value of this correction may be determined by observing the migration of an uncharged substance such as acetone or benzophenone (*13*). Endosmosis will, of course, vary with factors influencing the electrokinetic potential and viscosity of the solution—i.e., pH, buffer composition, ionic strength, and pretreatment of agar (*1*).

Calculation of Ion Mobility. For the example migration experiment described above, ion mobilities for vanillin, ferulic acid, and vanillic acid have been calculated from observations of the positions of the concentration peaks as evident in Figure 3, and from experimental values for the average voltage gradient and time, to yield the "apparent mobilities" shown in Table I.

Migration of acetone was also observed under the same experimental conditions to determine endosmotic velocity and this value was used to calculate ion mobilities corrected for endosmosis. Table I shows that in the buffer system used at about pH 4.6, vanillin is almost completely undissociated, whereas ferulic and vanillic acids show substantial mobility and thus are at least in part dissociated. However, when migration of vanillin is conducted in a buffer system at about pH 7, the substance is found (*5*) to manifest substantial mobility (Figure 4) resulting from dissociation of the phenolic hydroxyl group.

It would be very useful to be able to predict absolute ion mobilities from characteristics of the molecular structure and the environment, but this problem is probably more complex than for the case of large colloidal particles. This seems to follow from the lack of "easy" shape—i.e., particles with electric fields which can be represented by simple surfaces without irregularities or re-entrant curves—uneven charge distribution and, for small ions, the similarity in size of supporting electrolyte ions and solvent molecules. However, application of Gorin's equation (*2*) has been found in some experiments to yield results in rough agreement with observed mobilities and may be useful to predict the order of mobilities for changes in molecular weight or charge.

It is of interest to consider in this regard the mobility relationships for an ionic polymer series. Moilliet and associates (*10*) have shown that for the similar case of aggregates of dye ions, the particle charge increases with the first power of the number of

Table I. Example Migration of Vanillin, Ferulic Acid, and Vanillic Acid

	Vanillin	Ferulic Acid	Vanillic Acid
Peak positions, mm. from cathode	192.5	252.5	270.0
Apparent mobilities, sq. cm./(volt) (sec.) × 10^5	−5.84	1.24	3.3
Mobilities corrected for endosmosis, sq. cm./(volt)(sec.)	+0.16	7.24	9.3

monomer units while the frictional resistance, assuming closely packed spheres, increases with the particle radius or the one third power of the degree of aggregation. The mobility therefore would increase with the two thirds power of the degree of polymerization for a polyelectrolyte having homogeneous structural units. This, of course, would be modified by correction for varying shape factor and effect of supporting electrolyte ions (*2*). Very considerable differences remain, however, for the first few members of a polyelectrolyte series, so that separation can be achieved by the migration procedure, which thus becomes useful for study of the initial stages of such reactions. For higher members of the series mobilities converge to preclude observation of separated individual components.

Mobility hindrance by agar gels is apparently small or negligible for acidic or neutral substances (*6*). Since completion of the present work, some studies on electrophoresis of proteins in agar gels (*7*) have come to the authors' attention, in which separations were obtained for protein molecules such as egg albumin, hemoglobin, and hemocyanin with molecular weights up to 8,500,000.

Temperature Effects. The passage of electric current through contents of the cylindrical migration tube results in conversion of electrical to heat energy. At steady state heat flows radially from the interior of the migration tube to and through the wall into the ambient fluid of the constant temperature bath. This heat transfer gives rise to a parabolic temperature distribution, with the temperature difference between the core and wall being determined by the total current flowing and the voltage gradient by the equation:

$$T_c - T_r = \frac{aIE}{4\pi lk}\frac{r^2}{r_0^2} \tag{8}$$

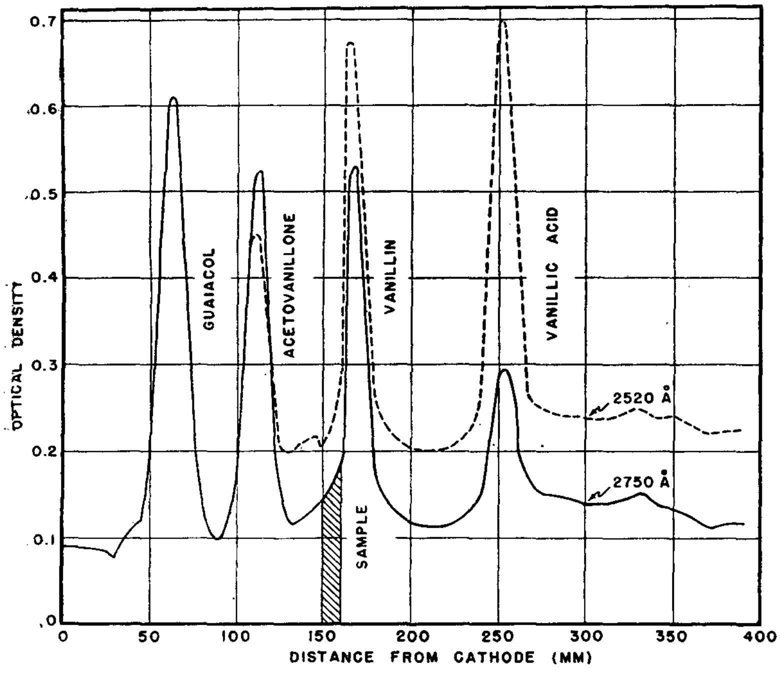


Figure 4. Separation of Phenolic Substances

where T_c and T_r = ° C. temperature at center and at r cm. from tube center; a = 0.239 = calories per watt second; k = thermal conductivity = $(1.45)(10^{-3})$ calories per second per ° C. per centimeter for water at 25° C.; I = current, amperes; E = total applied voltage; l and r_0 = length and radius of tube, centimeters.

By applying Equation 8 to the example migration described above, the difference between the center line and the wall temperature is calculated to amount to about 2.5° C. As ionic mobilities increase with absolute temperature, a parabolic distribution of components develops and this elongates with increasing time of migration. Free diffusion also increases with temperature and may proceed in the three-dimensional concentration gradients resulting from effect of temperature on mobility. These factors limit the allowable energy dissipation per unit length of tube for a desired degree of component separation. While the situation could be improved by use of tubes of thin rectangular cross section as in the Tiselius procedure (*15*) where convective mixing must also be considered, this would substantially increase the cost and complicate the analytical procedure for the present apparatus and thus has not been attempted in present studies.

Dispersion by Free Diffusion. The placing of the sample initially at constant concentration, c_0, in a band of width $2b$ creates a condition in which widening of the band and decrease in concentration occur by free diffusion as time passes and migration proceeds. For linear diffusion with these boundary conditions, integration of Fick's law leads (*3*) to the expression,

$$\frac{c}{c_0} = \frac{1}{\sqrt{\pi}}\int_{\frac{-b+x}{2\sqrt{D.t}}}^{\frac{b-x}{2\sqrt{D.t}}} l^{-\beta^2}.d\beta \tag{9}$$

which can be expressed as the difference between two integrals

$$\frac{c}{c_0} = \frac{1}{2}\left[\frac{2}{\sqrt{\pi}}\int_0^{\frac{b-x}{2\sqrt{D.t}}} l^{-\beta^2}d\beta - \frac{2}{\sqrt{\pi}}\int_0^{\frac{-b+x}{2\sqrt{D.t}}} l^{-\beta^2}d\beta\right] \tag{10}$$

so that the solution can readily be constructed from the usual form of probability integral tables. For example, Figure 5 shows the rate of dispersion from an initial 1-cm. sample strip in terms of the reciprocal parameters D (sq. mm. per day) and t (days). The rate of dispersion is roughly inversely proportional to the square of the initial width of the sample section, and this function imposes limits on the extent to which the width of the sample section may be reduced in order to achieve equivalent separation of components with shorter migration distances—i.e., by shorter migration times or lower voltage gradients. In general, experimental results with the present apparatus show considerably greater dispersion of concentration distribution during migration than is to be expected from diffusion constants and the above relations. This results from temperature effects and also from initial boundary imperfections.

However, isolated migration peaks can generally be closely fitted by probability integral distributions and this makes possible the estimation of diffusion coefficients by rescanning the migration tube after it has remained standing for a definite time period. For this purpose it is necessary to use an external standard—e.g., potassium phthalate solution—as a reference for the optical density obtained on scanning the tube before and after the diffusion period, since the agar gel will generally increase in optical density with time. A satisfactory procedure for estimating diffusion coefficients is as follows:

A large scale graph of optical density versus tube position before and after the diffusion period is prepared and shapes of individual peaks are estimated.

Areas under the peaks and above the agar base lines are measured with a planimeter and converted to units of "optical density–centimeters" of tube length; assuming the validity of Beer's law, these areas should be equal for the two distributions.

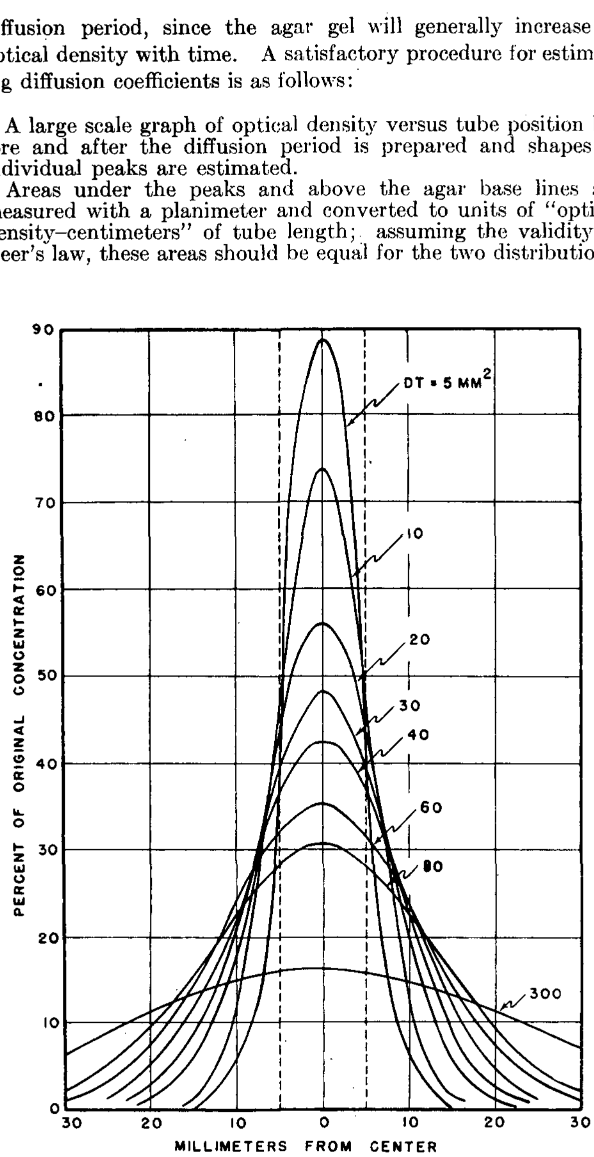


Figure 5. Free Diffusion from 1-Cm. Sample Section

Peak heights in optical density units above the agar base lines are observed.

The average calculated area under the peak is divided by the measured length of the initial sample section, thus giving an initial peak height at zero time, assuming perfect boundaries for the sample section.

The observed peak heights before and after the diffusion period are now calculated as fractions of the above initial peak height, giving:

$$\left(\frac{c}{c_0}\right)_{x\,=\,0,\;t\,=\,t_1} = A,\quad \left(\frac{c}{c_0}\right)_{x\,=\,0,\;t\,=\,t_2} = B \qquad (11)$$

The values of the products of the diffusion coefficient and the times before and after the diffusion period may now be calculated by using probability tables along with Equation 11, which for $x = 0$ reduces to:

$$\left(\frac{c}{c_0}\right)_{x\,=\,0,\;t} = \frac{2}{\sqrt{\pi}}\int_0^{\frac{b}{2\sqrt{Dt}}} l^{-\beta^2}d\beta \qquad (12)$$

The diffusion coefficient is calculated from the relation:

$$D = \frac{Dt_2 - Dt_1}{\Delta t_{2-1}} \qquad (13)$$

The foregoing calculation assumes that the rate of decay of the peak height is in agreement with that for normal diffusion and that the combined effects of imperfect boundaries, peak distortion during migration, and free diffusion during migration can be expressed as an artificial time factor, t_1. This then may be used as a criterion of electrophoretic performance.

Separability. The degree to which ionic components of a mixture may be separated in a migration experiment is dependent primarily on the difference in their mobilities. Thus, if u_A and u_B are mobilities of components A and B, and if X and t are the voltage gradient and the migration time, respectively, the separation of peaks in terms of distance migrated can be represented by:

$$d_A - d_B = (u_A - u_B)Xt \qquad (14)$$

For weak electrolytes net mobilities of the ion constituents will depend on the degree of dissociation. The selection of conditions to obtain maximum difference in net mobility for such systems has been treated by Consden, Gordon, and Martin (*4*).

Aside from mobility differences, however, dispersion of components during the migration must be considered. This can be dealt with practically by assumption of pseudo diffusion coefficients which combine effects of boundary imperfections, temperature gradients, and free diffusion. The relation of such pseudo diffusion coefficients to true diffusion coefficients will vary with experimental techniques and procedures and should be estimated by experiments with known materials. Curve sets such as Figure 5 for different original sample widths may then be used as templates with Equation 14 to estimate the extent of cross contamination by graphical means.

A more rigorous analytical treatment of cross contamination is possible by use of Pearson's tables for bivariate surfaces (*11*) to give areas under the distribution curves for different positions along the tube. This treatment is, however, probably not warranted without exacting refinement of experimental procedures.

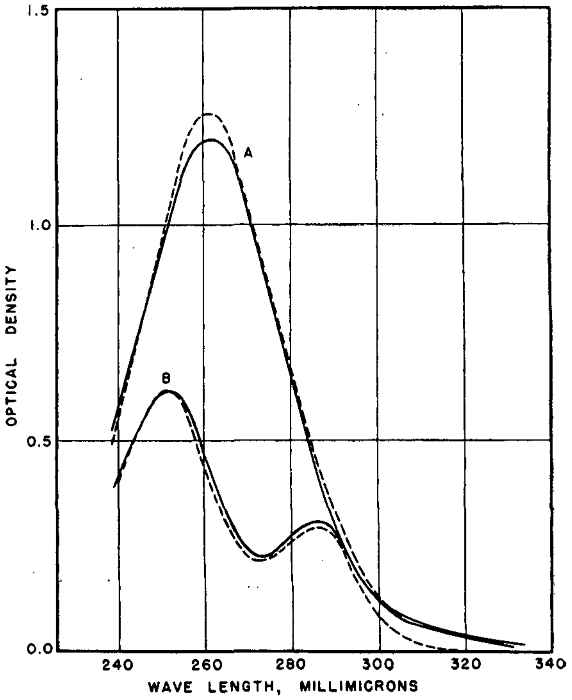


Figure 6. Ultraviolet Absorption Spectra

Solid lines. Experimental spectra of peaks 4A (*A*) and 4B (*B*), migration *X*, experiment ACXI-B

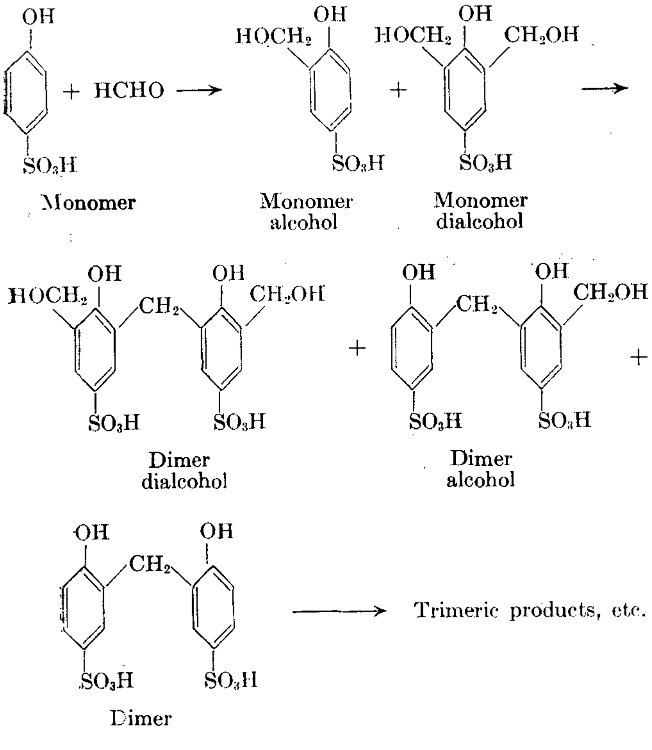
Dotted lines. Calculated spectra in pH 7 phosphate buffer for
***A*. 70 mg. per liter syringic acid**
***B*. 29.0 mg. per liter vanillic acid**

Some Applications. Ionophoreses of known mixtures of the four phenols—guaiacol, acetovanillone, vanillin, and vanillic acid—have been carried out in a pH 7 phosphate buffer system by Davis *et al.* (*5*) in this laboratory. A resulting migration pattern (Figure 4) shows good separation of the components. For the first three substances, the mobility differences arise predominantly from differences in phenolic hydroxyl dissociation.

Quantitative determination of these phenols to within about 5% accuracy has been found possible by integration of optical density patterns together with knowledge of appropriate extinction coefficients and of the calibration of migration tubes. The ionophoretic technique is being used in this laboratory in a quantitative study of phenols of this type obtained by alkaline cleavage of lignin sulfonic acids.

Work by Ryan (*13*) with the authors has shown that spectra may be determined by examining a substance in an ionophoresis tube after bringing about its separation by migration. Thus in connection with study of alkaline cleavage of hardwood lignin sulfonic acids, the spectra of syringic and vanillic acids in migration tubes of an actual electrophoresis experiment were observed as indicated by the full lines shown in Figure 6. The dotted lines in Figure 6 show the spectra calculated for syringic acid at 70 mg. per liter, and for vanillic acid at 29.0 mg. per liter, in a cell with a light path equivalent to that of the migration tube. The agreement found between the full and dotted lines indicates the at least rough validity of spectra determined on substances separated by migration. Thus spectra curves as well as mobility data may be used to identify substances giving rise to peaks on migration patterns, or to characterize unknown substances.

The utility of the procedure in studies of complex reaction kinetics has been shown by Stults (*14*), who with one of the authors has investigated the initial stages of the polycondensation of formaldehyde with *p*-phenol sulfonic acid. As illustrated in Figure 7, migration patterns have been obtained showing distinct peaks for each of the following six pertinent substances:



Because the dissociation of sulfonate groupings was nearly complete while that of phenolic hydroxyl groupings was apparently negligible under the conditions used, the differences found in mobility of the several substances were attributed to frictional factors and on this basis additional evidence was secured to confirm the identity of the several substances giving rise to peaks in the electrophoresis patterns. Graphical integrations of optical density distributions were used to determine the amounts of products present after reaction under various conditions and from these data there were calculated reaction velocity constants involved in this polycondensation. A factor of importance in possible applications of the procedure is the very small amount of material required. Thus in the example experiment discussed above, only 9 micrograms of each of the three phenols were used.

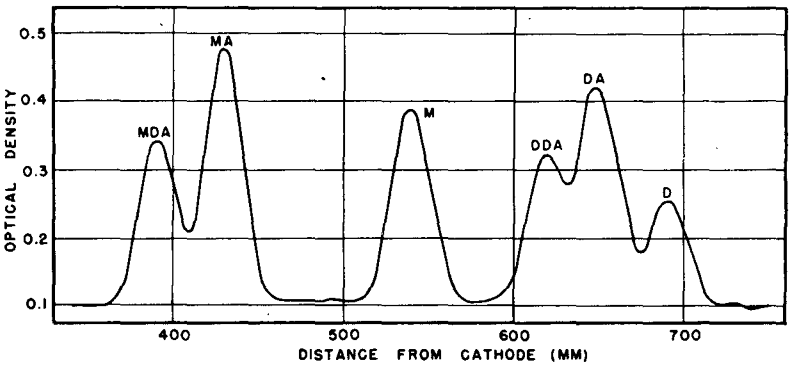


Figure 7. Separation of *p*-Phenol Sulfonic Acid–Formaldehyde Condensation Products

The migration procedure is also being used in these laboratories for study of the low molecular weight members of the polymeric lignin sulfonic acids occurring in sulfite waste liquor.

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Isotopic Determination of Nitrogen and Carbon

By Means of a Microwave Spectrograph

A. L. SOUTHERN, H. W. MORGAN, G. W. KEILHOLTZ, AND WILLIAM V. SMITH
Oak Ridge National Laboratory, Y-12 Area, Oak Ridge, Tenn.

Research on the use of a microwave spectrograph for isotopic analyses was undertaken as part of a program of the Oak Ridge National Laboratory to develop new methods of isotope assay. Analytical procedures have been developed for nitrogen 15 in ammonia and for carbon 13 in cyanogen chloride, as being typical of the stable tracer isotopes. Nitrogen 15, in the range 0.38 to 4.5%, can be determined to within approximately 3% of its concentration. For carbon 13, in the range 1.1 to 10%, the average error is less than 2% of the concentration. For each element, samples of known enrichment must be examined to determine a standard curve. A complete analysis requires 0.00015 mole of gas, the major portion of which may be recovered. The microwave spectrograph can be used for analysis of isotopes of many of the lighter elements with an accuracy comparable to that for nitrogen and carbon. Accuracy, sample requirements, and characteristics indicate application to both routine and special analyses.

THE techniques of microwave spectroscopy have been employed almost exclusively for the determination of molecular structure parameters and nuclear constants. Some of the earliest papers, however, indicated the possibility of performing isotope analyses by comparing the relative intensities of absorption lines arising from different isotopes. Perhaps the first abundance ratio to be checked in this manner, though qualitatively, was the Cl^{37} to Cl^{35} ratio measured as 0.3 to 1 by comparing the intensity of the $Cl^{37}CN$ absorption line at 23,389 Mc. with that of the $Cl^{35}CN$ line at 23,885 Mc. (*16*).

Spectra in the microwave region arise principally from transitions between different rotational states of a molecule (*8*). The resulting frequencies are inversely proportional to the moments of inertia of the molecules, which in turn are functions of the nuclear masses. For the great majority of molecules there are no problems in resolving the isotope structure, as the absorption lines can be made narrower than 1 Mc. if necessary. This high resolving power practically eliminates the possibility of confusion with any lines arising from impurities. The principal difficulties in the analysis arise from the relatively large separations of the lines due to different isotopes. Because the microwave components used—oscillator, tuning stubs, wave guide, etc.—are frequency-sensitive, a very careful calibration of apparatus is necessary for accurate results. A high percentage of impurities in a sample does not affect a microwave isotopic analysis, save for a small decrease in sensitivity. With microwave spectrographic technique, isotopic analyses are in general simpler to perform than chemical element or compound analyses.

To observe rotational spectra at microwave frequencies, the compound must be in the gas phase and must have a permanent dipole moment. For use in analysis it is necessary that the absorption be strong, that the gas be nonreactive in contact with the cell, and that the lines lie in a convenient region of the microwave spectrum. Fulfilling these conditions, there are many molecules available for the analysis of the more common stable isotopes: oxygen, hydrogen, nitrogen, carbon, etc. Actual choice of the compound to be used is dependent on the availability or ease of preparation and the accuracy required in the analysis.

MICROWAVE SPECTROGRAPH

A schematic diagram of the spectrograph is shown in Figure 1.

The source of microwave radiation is a 2K-33 klystron, operated by a well regulated high voltage power supply of conventional design (*13, 14*). The tube, manufactured commercially, was chosen to oscillate in the region 22,000 to 25,000 Mc., to include both the ammonia and cyanogen chloride absorption lines. The microwave energy from the klystron, after passing through a calibrated attenuator and a directional coupler wave meter, traverses the Stark cell. This cell is a 10-foot section of a 1 × 2 inch silver-plated brass wave guide. The Stark cell is joined to the smaller K-band guide by tapers with mica windows to define the vacuum system. The Stark electrode is placed in the center of the cell parallel to the wide dimension and supported on Teflon strips.

A 1N26 crystal detector receives and rectifies the microwave energy which passes through the cell. This energy is diminished at the absorption frequencies of the molecules; also, the absorption frequencies are displaced every half cycle by the 4-kc. square wave (one side grounded to the cell) which is applied to the center electrode. Thus the crystal output contains a 4-kc. note which is amplified by a lock-in amplifier of conventional design with a band pass of a few cycles (*12*). A Helmholtz coil phase shifter is used to provide a reference signal of suitable phase to the lock-in amplifier. The output of the amplifier is then displayed on a Brown Electronik strip chart recorder. Owing to the phase-sensitive nature of the lock-in amplifier, the undisplaced line and the Stark components give deflections in opposite senses.

For convenience in test and tune-up procedures, a 60-cycle sawtooth sweep applied to the reflector electrode of the klystron varies the frequency and provides a display of the klystron mode when the output of the crystal detector is connected to the vertical plates of an oscilloscope. The 60-cycle sweep is not used in the actual operation of the spectrograph; instead, the klystron is tuned mechanically by a motor and gear assembly which turns the cavity spacing adjustment screw $^1/_{20}$ revolution per minute. This corresponds to a frequency scanning speed of approximately 35 Mc. per minute.

The Stark cell is provided with heating coils for degassing between samples, which proved to be an important aspect of the ammonia analysis. The large dimensions of the cell used decrease the ratio of surface to volume and hence minimize degassing problems. However, it is believed that satisfactory results can be obtained with guide of smaller cross section.

THE AMMONIA SPECTRUM

The papers of Cleeton and Williams (*4*), Bleaney and Penrose (*2*), and a host of other investigators have clearly established the unique position held by the ammonia molecule in microwave spectroscopy. It was the first molecule found to exhibit a microwave nuclear quadrupole interaction (*1, 7*) and the first to find an engineering application in stabilizing the frequency of an electronic oscillator (*6, 15*). The reason for ammonia's unique position lies in the intensity of its absorption, almost 10% in a meter cell for the strongest line. This high intensity is due to the inversion, or "turning inside out" of the molecule, whose pure rotational spectrum lies in the far infrared. The rotational levels split the inversion spectrum into many lines, clustered in the region 20,000 to 25,000 Mc. Only certain few of these lines possess strong absorption.

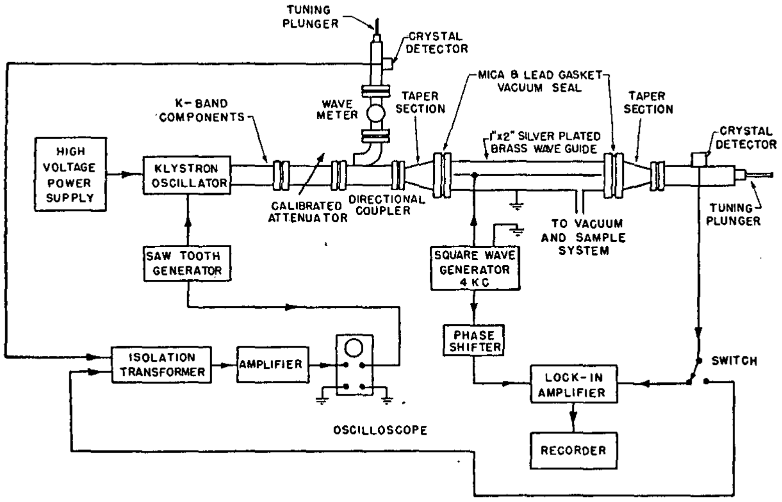

Figure 1. Schematic Diagram of Stark System

A convenient tabulation of both $N^{14}H_3$ and $N^{15}H_3$ lines is given by Townes (*11*). Two groups of these lines are given in Table I, columns 1 through 5. The intensities tabulated are the theoretical peak values at the resonance frequencies and are independent of pressure over a wide range of pressures. In the computation the assumption was made that all lines have equal widths at a given pressure, the width being caused by collisions among the molecules and the number of collisions being in turn proportional to the pressure. Thus the ratios of peak intensities are the same as the ratios of integrated intensities. Experimentally, Bleaney and Penrose (*2*) have found that the line widths are proportional to $\sqrt{K^2/J(J+1)}$. This variation in line width implies an inversely proportional variation in peak intensity which is tabulated in the last column of Table I.

Table I. Selected Isotopic Combinations of Ammonia

Nitrogen Isotope	Line Classification, (*J*, *K*)	Frequency	Integrated Relative Intensity in $N^{14}H_3$	Relative Peak in $N^{14}H_3$
N^{15}	2,2	22,649.85	320	332
N^{14}	5,4	22,653.00	170	190
N^{14}	6,5	22,732.43	150	162
N^{15}	3,3	22,789.41	720	720
N^{14}	3,2	22,834.17	130	170

The close frequency spacing of the $N^{15}H_3$ 2,2 and the $N^{14}H_3$ 5,4 lines was at first considered to be ideal, as it practically eliminated monitoring problems. In the course of the investigation, however, it proved necessary to use pressures near 100 microns in order to avoid excessive pressure drifts arising from adsorption of the ammonia on the wave guide walls. At this pressure these lines overlapped, so that all data reported here were taken using the $N^{15}H_3$ 3,3 and $N^{14}H_3$ 6,5 lines. This choice has the advantage of comparing the strongest $N^{15}H_3$ line with a relatively weak $N^{14}H_3$ line. Because the integrated (and therefore peak) absorptions are proportional to the isotopic concentrations, a comparison of the $N^{14}H_3$ and $N^{15}H_3$ absorption lines, together with the theoretical ratios of these lines in normal ammonia, should give an absolute measurement of isotopic concentration. Use of the Stark effect, however, allows the height to be measured from the peak of the main line to the peak of the Stark component. This has the advantage of eliminating the base line, but requires that a calibration curve be employed for the analysis.

A feature of the recording spectrograph is its use of an audio-frequency square wave electric field to modulate the spectrum line frequencies, a technique introduced into microwave spectroscopy by Hughes and Wilson (*9*). Ammonia possesses a second-order Stark effect given approximately by (*5*):

$$\Delta \text{ megacycles} = 4.5\ [MK/J(J+1)]^2E^2$$

where E is given in electrostatic units, and is directed parallel to the high-frequency electric field, so that only transitions corresponding to $\Delta M = 0$ are observed. M is the magnetic quantum number ranging from $M = 0$ to $M = J$ in integral steps, giving rise to $(J + 1)$ levels corresponding to different values of M. A typical field of 600 volts per cm. (2 electrostatic units) thus splits the 3,3 line into four components displaced from the unperturbed line by 0, 1, 4.5, and 10 Mc. At pressures around 100 microns, this splitting is only partially resolved.

CALIBRATION AND MEASUREMENTS FOR NITROGEN 15 ANALYSIS

The Stark cell described requires 3 to 5 cc. of ammonia at 1-atmosphere pressure for an analysis. This volume allows the cell to be flushed and measurements to be made on several samples in the wave guide. Each new sample requires several minutes to reach an equilibrium with the walls, during which time the pressure may vary slowly. For an accurate analysis it is essential that the cell be at equilibrium and the pressure constant.

An analysis can be performed in 20 to 30 minutes, including 10 to 15 measurements of the intensity ratios on the recorder. The present equipment will give results of the accuracy tabulated below with five measurements.

A thorough degassing of the Stark cell between samples is necessary, because of the strong surface adsorption of the ammonia molecule. This can be accomplished by heating the cell at 200° C. for 1 hour with continuous pumping below 1 micron. The cycle between samples requires approximately 2 hours; thus the total time required for each analysis is about 2.5 hours.

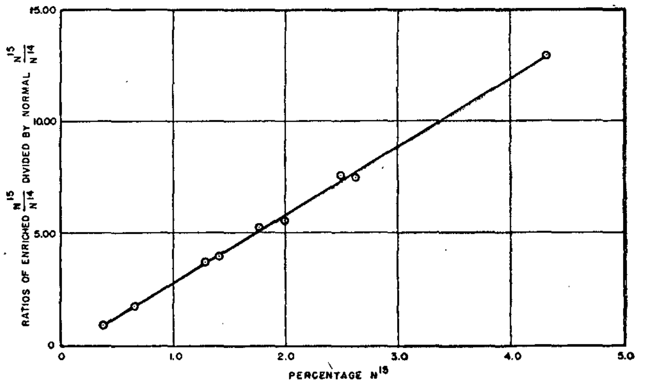

Figure 2. Standardization Curve for Nitrogen 15 Analysis

In making an analysis, the ratio of the heights of the 3,3 $N^{15}H_3$ and the 6,5 $N^{14}H_3$ lines is measured for each sample. A plot is made of enriched $\frac{N^{15}H_3}{N^{14}H_3}\Big/$ normal $\frac{N^{15}H_3}{N^{14}H_3}$ line heights versus per cent N^{15}, as shown in Figure 2, by using samples of known enrichment. This standard curve can then be used directly in the analyses of unknown samples.

Table II shows the ratios, enriched $\frac{N^{15}H_3}{N^{14}H_3}\Big/$normal $\frac{N^{15}H_3}{N^{14}H_3}$, which are obtained with standard percentages of N^{15}. The normal gas was examined alternately with the standards in the

Table II. Ratios

Standards, % N^{15}	Enriched $\frac{N^{15}}{N^{14}}$/Normal $\frac{N^{15}}{N^{14}}$	% N^{14} Deviations
0.38	1.00	0.00
0.66	1.86	0.00
1.29	3.81	+0.02
1.41	4.04	−0.03
1.76	5.31	+0.04
2.00	5.64	−0.09
2.49	7.64	+0.08
2.61	7.59	−0.06
4.30	13.00	+0.04

Table III. Average Deviation

% N^{15}	Average Deviation
0.38 to 0.50	+0.01
0.50 to 1.50	+0.04
1.50 to 2.50	+0.07
2.50 to 4.00	+0.10

measurements for the standard curve. The third column shows the deviations of individual samples from the standard curve itself.

To prepare the standards used in obtaining the above curve, shown in Figure 2, ammonium nitrate enriched in N^{15}, produced by the Eastman Kodak Co., was mixed with normal material in the proper ratios. Analyses of the enriched ammonium nitrate and of the ammonia prepared from it have been made in the Mass Spectrometer Laboratory at Y-12. A further check is given by the fact that normal ammonia with $N^{15}H_3$ as 0.38% falls on the straight line of the standard curve.

The results from 25 samples of known concentration, consisting of 10 enriched samples and 15 samples of normal material, may be examined for average deviation in Table III.

Over a period of time the peak ratios may vary, owing to adjustment of the crystal or of one or more of the other wave guide components. These changes may be made without affecting the accuracy of the analysis, because results are based on the ratio of the line heights for normal material, and any such changes cause the enriched and normal ratios to vary proportionally.

The actual absorptions of the 6,5 N^{14} and the 3,3 N^{14} lines in normal ammonia are in the ratio of 80 to 1. In recording, the height of the 6,5 N^{14} line is reduced by a factor of 10 in the amplifier to allow direct comparison of the peak heights. Figure 3 illustrates typical peaks obtained with normal and enriched samples.

SAMPLE PREPARATION

Each of the standard samples was prepared in a vacuum by the dry reaction of calcium hydroxide and ammonium nitrate under low heat. The gas was dried by contact with calcium oxide and then quantitatively transferred to the wave guide.

Samples of nitrogen compounds must be transformed into ammonia for analysis by the microwave methods described above. In the case of ammonium salts, the sample may be obtained by reaction with calcium hydroxide or any convenient hydroxide. For other compounds, nitrogen fixation procedures such as the formation of ammonia by the Kjeldahl method may be used. The sample required for an analysis represents approximately 0.002 gram of nitrogen or 0.00015 mole of ammonia.

THE SPECTRUM OF CYANOGEN CHLORIDE

The spectrum of cyanogen chloride is that of a linear molecule with moderately strong rotational lines spaced equidistant throughout the microwave spectrum. A tabulation of the first three transitions is given in Table IV.

The $J = 1 \rightarrow 2$ transition falls in the same general region as the ammonia lines discussed above and thus was chosen for the carbon isotope analysis. The carbon isotope lines are each split by interactions of the quadrupole moments of the Cl^{35} and N^{14} nuclei into some twenty-two components covering a region of approximately 40 Mc. (*17*). To simplify measurements it was necessary to obtain one main line of maximum height for each isotope. This was done by using a pressure of 100 microns and a Stark voltage of 750 volts per centimeter, causing the many components to coalesce into one very intense line and two satellite lines of low intensity. These satellite lines are obscured by the Stark components of the main line. Figure 4 shows tracings of the cyanogen lines obtained with different concentrations of C^{13}. As in the previous analysis, the height of the stronger line has been reduced by a factor of 10 to allow direct comparison of the heights.

The separation of the isotopic cyanogen chloride lines is 124 Mc., which is ideal for purposes of comparison by the recorder technique. Because both lines correspond to the same transition and thus have identical widths, the peak heights may be assumed proportional to the integrated areas and thus to the relative concentrations. Measurements are made for this analysis, as for ammonia, from the peak of the main line to the peak of the high frequency Stark component, and again a calibration curve must be prepared.

CALIBRATION AND MEASUREMENTS FOR CARBON 13 ANALYSIS

The Stark cell requires 2 to 3 cc. of cyanogen chloride at 1 atmosphere for an analysis, allowing measurements to be made on several samples. In practice, the first sample put in the system has given results of the accuracy tabulated in Table V.

Table IV. First Three Transitions

	$Cl^{35}C^{12}N^{14}$, Mc.	$Cl^{35}C^{13}N^{14}$, Mc.
$J = 0 \rightarrow 1$	11879	11941
$1 \rightarrow 2$	23759	23883
$2 \rightarrow 3$	35638	35824

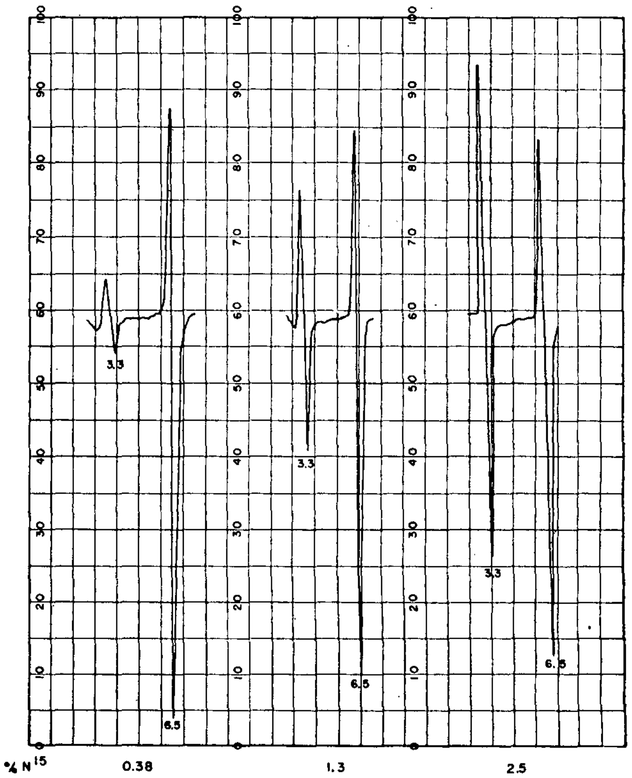

Figure 3. Recorder Traces for Ammonia

125-micron pressure

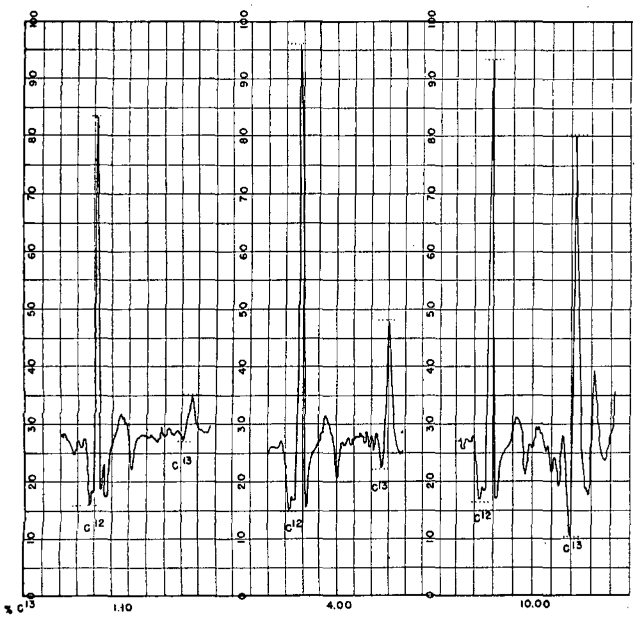

Figure 4. Recorder Traces for Cyanogen Chloride

100-micron pressure

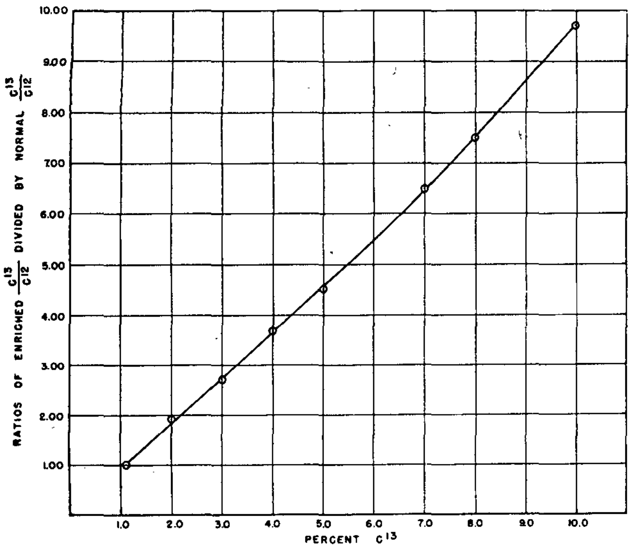

Figure 5. Standardization Curve for Carbon 13 Analysis

The actual analysis may be performed in 50 minutes or less, comprising ten measurements of the line ratios on the recorder. For degassing the system between samples, it has been found sufficient to pump on the cell for 45 minutes at a pressure below 1 micron. Thus the full cycle for an analysis runs slightly over 1.5 hours.

It has been found sufficient to determine the ratio of the line heights for normal cyanogen chloride once each day for comparison against samples of unknown concentration. Although the ratios for normal cyanogen chloride and for the standard enriched samples vary slightly from day to day, the ratio of these values, plotted in Figure 5, remains constant. The plot of enriched $\frac{ClC^{13}N}{ClC^{12}N}\Big/$normal $\frac{ClC^{13}N}{ClC^{12}N}$ line heights versus per cent carbon 13 is essentially a straight line in the 1 to 5% C^{13} range. Above 5% there is a gradual curve, due to slight nonlinearities in the characteristics of the system. Results are reliable when ten or more readings are taken to average out the small random variations introduced by the electronic system. The values shown in Figure 5 are independent of variations in crystals and wave guide adjustments. Table V shows the data taken to establish the standard curve and indicates the accuracy obtainable from ten comparisons of the line ratios.

In general, the per cent error is less than 2% of the C^{13} concentration, as indicated in Table V.

The C^{13} in the form $KC^{13}N$ used for standardization was purchased from the Eastman Kodak Co., Rochester, N. Y., and the sample was standardized by the Y-12 Mass Spectrometer Laboratory.

SAMPLE PREPARATION

Proper isotopic ratios of C^{13} and C^{12} were prepared from standard $KC^{13}N$ solutions and the carbon was completely precipitated in the form of silver cyanide. The sample was then filtered and transferred to a glass system where chlorine gas reacted with silver cyanide to form cyanogen chloride. Excess chlorine was removed with amalgamated copper turnings. All carbon samples were sealed in glass break-seals containing sodium pyrophosphate, which prevents polymerization in the presence of moisture (*10*), and stored until use. Immediate use in analysis would eliminate the need for this drying agent. The samples were then attached to a glass vacuum system and admitted to the wave guide cell as required.

In tracer work the carbon is often present as carbon dioxide and must be transformed into cyanogen chloride for analysis. Carbon dioxide can be reduced to potassium cyanide with potassium and ammonia with yields of 90 to 96% (*3*).

DISCUSSION

The results shown for the above analyses are those to be expected under the usual laboratory conditions. They represent intermittent operation, changing of crystals and small variations in wave guide geometry, and operation in the same area as other electronic equipment which proved to be the source of intermittent noise.

The molecule cyanogen chloride may be employed for the analysis of the chlorine and nitrogen isotopes, in addition to carbon, using the same procedure and obtaining about the same accuracy as for C^{13}. By proper choice of molecule the same sample may, in fact, be used for the analysis of two or more elements. Carbonyl sulfide and sulfur dioxide may both be examined for the analyses of the sulfur and the oxygen isotopes, while a comparison of the HDO line at 22,307 Mc. with the water line at 22,235 Mc. allows a determination of hydrogen-deuterium mixtures. These are a few suggested molecules, and do not begin to exhaust the compounds which might be used for isotope analysis. A list of microwave molecules and their absorption frequencies has been published by Kisliuk and Townes (*11*).

Table V. Standardization Curve Data

Standards, % C^{13}	Enriched $\frac{C^{13}}{C^{12}}\Big/$Normal $\frac{C^{13}}{C^{12}}$	Deviations, % C^{13}
1.11	1.00	0.00
2.00	1.92	+0.10
3.00	2.71	−0.04
4.00	3.69	+0.04
5.00	4.50	−0.07
7.00	6.55	+0.06
8.00	7.45	−0.06
10.00	9.63	0.00

ACKNOWLEDGMENT

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Detection of Trace Quantities of Radioactive Materials in Waste Streams

PAUL R. FIELDS AND GRAY L. PYLE
Argonne National Laboratory, Chicago, Ill.

Some general considerations in determining microquantities of radioactive isotopes are presented. In order to concentrate on the radiochemical problems, the general analytical chemistry has been limited to uranium, as an example of an alpha emitter, and to I^{131}, as an example of a beta emitter. A fluorophotometric method and a radiochemical method of determining uranium are discussed. Some of the problems encountered in analyzing and identifying beta-emitting isotopes are illustrated by a procedure for isolating I^{131} from a waste solution. Certain corrections must be applied to the recorded beta count to obtain the absolute disintegration rate.

THIS paper is intended to serve as a brief introduction to radiochemistry for waste disposal scientists who have had little or no experience in the field of radioactivity. In order to simplify the coverage of such a broad and complicated subject, the general analytical chemistry is limited here to only two elements. Uranium is taken as an example of an alpha emitter and I^{131} as an example of a beta emitter.

PERMISSIBLE LEVELS OF RADIOACTIVITY

At a recent Waste Disposal Symposium (*11*) 10^{-7} microcurie per milliliter of alpha and beta activity was proposed as the probable maximum permissible concentration of general radioactive contaminants in a water supply outside a controlled area. This, with other considerations discussed below, must be kept in mind when deciding on the volumes of waste solutions to be taken for analysis.

The following procedure would probably be satisfactory for detecting the presence of this level of activity. For an alpha assay, about 25 ml. could be evaporated to dryness in a flat metal dish about 10 sq. cm. in area. Assuming 10^{-7} microcurie per milliliter, the sample would contain 2.5 counts per minute, a level of alpha activity that can easily be determined in an ordinary alpha counter. Unless there was more than the usual amount of nonvolatile material in the water, this aliquot would give a dry residue of a little less than 1 mg. per sq. cm. Although this is a little thick for alpha counting, the amount of alpha activity could be determined with fair accuracy, provided the material was spread uniformly. The percentage of alpha activity lost in samples of various surface densities can be seen in Table I (*6*).

In beta counting a larger aliquot must be taken than in alpha counting, because the natural background of a beta counter is about 25 counts per minute whereas that of the alpha counters is practically zero. Therefore, 1 liter of the solution may be evaporated to dryness under alkaline conditions. The solid residue, when spread over an area of approximately 6 sq. cm., would be about 50 mg. per sq. cm. This sample could be counted with an end-window Geiger counter, the windows of which are generally about 8 sq. cm. in area. Only the very soft betas would be missed by this method; these would require special techniques. Examples of isotopes emitting soft betas—i.e., beta rays with very low energies—are C^{14} and S^{35}.

Table I. Self-Absorption Losses for Various Surface Densities of Carrier Calculated for Polonium Alpha Particles

(Range 3.8 cm. air and carrier with mass stopping power one half that of air)

Carrier surface density, mg./sq. cm.	0.05	0.1	0.2	0.3	0.5	1.0	5.0	10.0	20.0	50.0
% of count lost	0.27	0.53	1.1	1.6	2.7	5.32	7.0	53.0	78.0	91.0

ABSORPTION OF RADIATION

Absorption is an important factor in radioassays. The term "absorption" applies to that process wherein the emitted particle or ray gives up some or all of its energy in passing through material. In discussing absorption in the field of radiochemistry the unit "mg. per sq. cm." is used to express thickness, because it is approximately proportional to the number of electrons through which the charged particles will have to travel. Because the main process by which charged particles lose their energy in passing through matter is the interaction with the electrons of the atoms of the absorber, a measure of the number of electrons in the path of the traversing particle would be a rough measure of the energy lost by this particle while passing through the absorber. Thus, if a certain percentage of I^{131} betas was found to penetrate an aluminum absorber of 20 mg. per sq. cm. then approximately the same percentage would penetrate 20 mg. per sq. cm. of mica.

Because alpha particles have a greater charge and mass than beta particles, they lose their energy in matter more rapidly and hence can penetrate only thin layers of matter. For example, the range of the U^{238} alpha particle with an energy of 4.18 m.e.v. (*10*) is about 3.3 mg. per sq. cm. (*8*), whereas the I^{131} beta particle with an energy of 0.6 m.e.v. (*10*) has a range of 220 mg. per sq. cm. and will penetrate about 60 times the thickness of matter that an alpha particle will. This is another reason why the volume of the solution originally evaporated for alpha-particle detection was about one fortieth that used for the beta-ray detection.

It is assumed in this discussion that some alpha counts were detected in the evaporated 25-ml. sample and some beta counts in the 1-liter sample, that part of the beta activity is due to I^{131} and part of the alpha activity is due to uranium, and that the amount of uranium present will have to be determined.

DETERMINATION OF URANIUM

Here the problem is simplified because there is a convenient chemical analysis for uranium, the fluorophotometric (*9*) method, which depends on the fluorescence of uranium when it is fused with sodium fluoride and the mixture is exposed to ultraviolet light. The accuracy of the determination is about 10%, but its sensitivity is as great as 10^{-7} mg. This low limit makes the method much more sensitive than counting the alpha particles. A milligram of uranium will have in the neighborhood of 700 counts per minute, and 10^{-7} mg. could not be detected by alpha counting. One disadvantage of the fluorophotometric method is the quenching of the uranium fluorescence caused by the presence of impurities such as iron, chromium, calcium, copper, some other metals, and a few anions. Fortunately, the fluorescence produced by uranium is a linear function of the amount of the uranium, both in the absence of a quencher and in the presence of a constant amount of quencher. This fact makes it possible to correct for the quenching by adding a known amount of uranium to an aliquot of the test solution and noting the change in fluorescence. Because of the high sensitivity of the method, very small samples may be used, and this in many cases reduces the quenchers to negligible quantities. Uranium appears to be the only element in the heavy end of the periodic table ($Z > 82$) with a high degree of fluorescence under these conditions. However, a radiochemical procedure is more representative of the procedures used when determining other alpha emitters.

If radioactivity is to be used as a means of measuring the uranium content of the unknown solution, a larger sample should be taken and the uranium separated chemically from inert materials and other alpha emitters. There are two courses open for the treatment of a large bulk of solution. The obvious method is to evaporate the solution to a small volume in order to concentrate the uranium and to make it more convenient for the next step in the procedure. Or, some ferric ion may be added to the large volume and iron hydroxide precipitated by making the solution alkaline. The ferric hydroxide will carry down the insoluble alkaline diuranate and will serve to separate the uranium from some of the inert material which would have concentrated during the evaporation. In order to count the uranium, it will have to be purified from the iron and any other inert material because of the problem of absorption.

One of the simplest methods of purification is solvent extraction. Its success depends on the fact that from a 1 to 3 *M* nitric acid solution which contains a high concentration of some salt, the uranium will have a distribution coefficient in favor of an organic solvent and will pass into the organic layer.

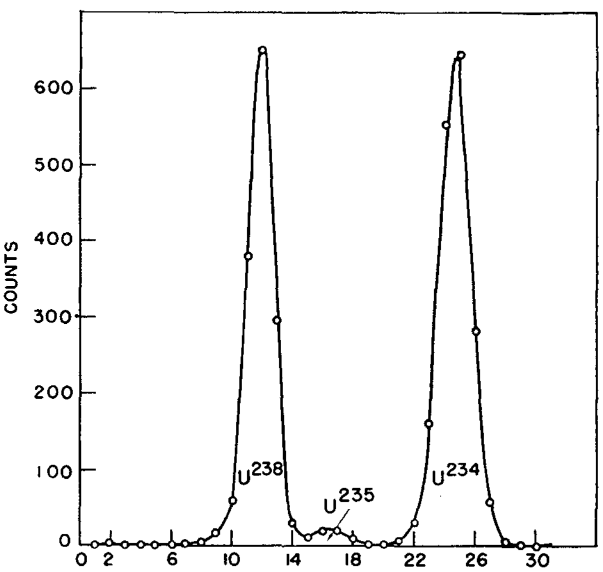

Figure 1. Pulse Analysis Curve of Pure Uranium

Some of the salts which may be used are ammonium nitrate, calcium nitrate, and aluminum nitrate, and two of the more common solvents are methyl isobutyl ketone and diethyl ether. If a large quantity of iron has been used as a carrier for the uranium, the resulting ferric nitrate can be used as the salting agent; otherwise, ammonium nitrate can be added to bring the salt concentration up to the desired strength.

Once the hydroxide precipitate has been dissolved in acid and the salt concentration adjusted, the salt layer is vigorously mixed with about an equal volume of the organic solvent. Approximately 50% or more of the uranium will pass into the organic phase. The uranium is re-extracted from the organic phase by washing with water. Three or four successive contacts of the original solution with organic solvent are usually sufficient to remove the uranium. The impurities of lower atomic number, such as the iron carrier, are largely left behind in the salt layer. The water layer which was used to wash the solvent is evaporated, and the uranium plus other heavy elements which were also solvent-extracted are transferred to a platinum disk for counting.

In order to determine how many alpha particles are being emitted by uranium, the sample can be submitted to the differential alpha pulse analyzer (*2*). This is a fairly recent development, which has simplified the detection and identification of alpha-emitting substances.

The instrument consists essentially of a chamber in which the alpha particle expends all its energy and in turn generates a voltage pulse which is approximately proportional to the particle energy. The voltage pulses are amplified and fed into an electronic device which determines the relative number of pulses of various sizes. Because the pulse size is proportional to the alpha energy, one has a measure of the number of alphas of a given energy.

The alpha-particle energy of an alpha-emitting isotope is almost specific to that isotope, as can be seen from Table II. Hence an analysis of the purified uranium fraction by this machine would essentially be determining what number of the alpha particles being emitted are due to uranium and possibly what other alpha emitters followed the uranium through the solvent extraction process. Figure 1 shows a typical pulse analysis of a pure uranium sample. Determining the amount of uranium in the uranium fraction would be a much more complicated task without the pulse analyzer, but it could still be done by further radiochemical separations which would eliminate all the other possible alpha emitters.

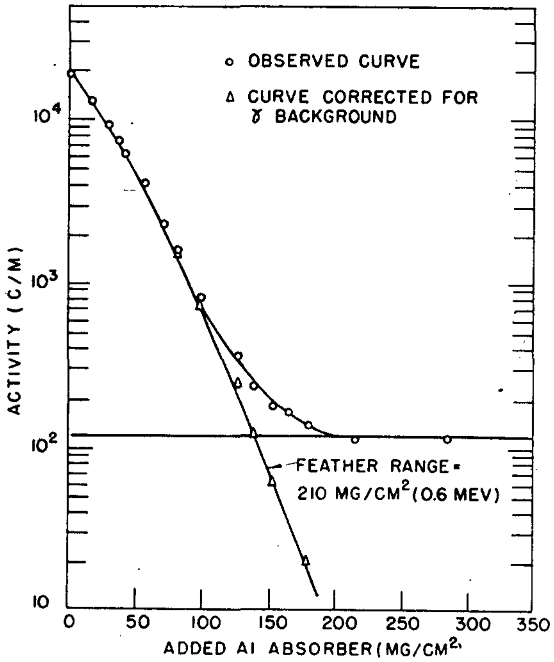

Figure 2. Aluminum Absorption Curve of 8-Day I^{131}

Taken on third shelf, absorbers on second shelf

Table II. Energies of Some Typical Alpha Particle Emitters

Isotope	Energy, M.e.v.
U^{238}	4.18
U^{234}	4.76
U^{233}	4.82
Th^{232}	3.98
Ra^{226}	4.79 4.61
Po^{210}	5.30
Po^{209}	4.95
Np^{237}	4.77
Pu^{239}	5.14
Pu^{240}	5.15
Pu^{238}	5.49
Am^{241}	5.48
Cm^{242}	6.08
Rn	5.49

DETERMINATION OF I^{131}

The problems of beta counting are probably even more numerous than those of alpha counting. However, the greater penetrating power of beta particles alleviates to some extent the problem of absorption within the sample itself.

The usual procedure for determining the concentration of a given beta emitter is to add as a carrier milligram quantities of a nonradioactive isotope of the same element and then precipitate some insoluble compound. By a carrier is meant an agent which the radioactive material will follow in a chemical reaction. It need not be the same element. Often the situation is not as simple and straightforward as this. Some of the problems involved in analyzing for beta emitters are illustrated by I^{131} (*5*).

Once the presence of beta activity has been confirmed, an aliquot of several liters may be taken for the determination of the fraction of this activity due to I^{131}. A known amount of natural iodine is added as the iodide ion, and the solution is made alkaline and evaporated to a convenient volume, say 50 to 100 ml. The iodide is then oxidized to periodate with sodium hypochlorite. The oxidation is carried out to ensure exchange between the stable and the radioactive isotopes.

It is probable that the iodine carrier which is added could be in a different valence state or as a different ionic species from that of the radioactive iodine. In this case, any subsequent chemistry might not be followed identically by both materials, and a recovery of the stable iodine would not necessarily mean a recovery of the radioactive isotope. In passing through all the valence states of iodine, the carrier has an opportunity to exchange with the I^{131}, regardless of the latter's valence state.

The periodate is then reduced to free iodine with hydroxylamine and extracted into carbon tetrachloride. The iodine is re-extracted into an aqueous phase containing some sulfur dioxide. At this state, if bromine is suspected to be present, another oxidation can be made, this time with sodium nitrite in an acid solution. Another carbon tetrachloride extraction followed by a washing with a sulfite solution should completely purify the iodine.

This procedure actually separates iodine from bromine in two places. In reducing the periodate to free iodine with hydroxylamine, the bromate ion is reduced to bromide, which is left behind in the carbon tetrachloride extraction. The second point of separation is the reoxidation of iodide to iodine by using sodium nitrite. The bromide ion is not oxidized by sodium nitrite. The iodine in the final sulfite solution is precipitated as silver iodide or cadmium iodide. The precipitate is then transferred to an assay disk for the next step in the analysis—counting the beta activity carried down by the precipitate. The precipitate can be weighed at this point to determine the chemical yield. For counting, a thin-window Geiger tube is probably used.

Many corrections must be applied to the counts recorded before the actual number of disintegrations occurring on the plate can be ascertained; some of these are discussed below. From the known recovery of the stable iodine and the calculated disintegration rate of the I^{131}, the amount of active iodine in the original sample can be determined.

To learn whether any activity other than that of iodine has been carried along through the separation procedure, the energy of the beta particle and the half-life of the isotope are usually determined. An absorption curve is taken to obtain the energy and purity of the beta particles being emitted from the sample of silver iodide. The curve is constructed by counting the active

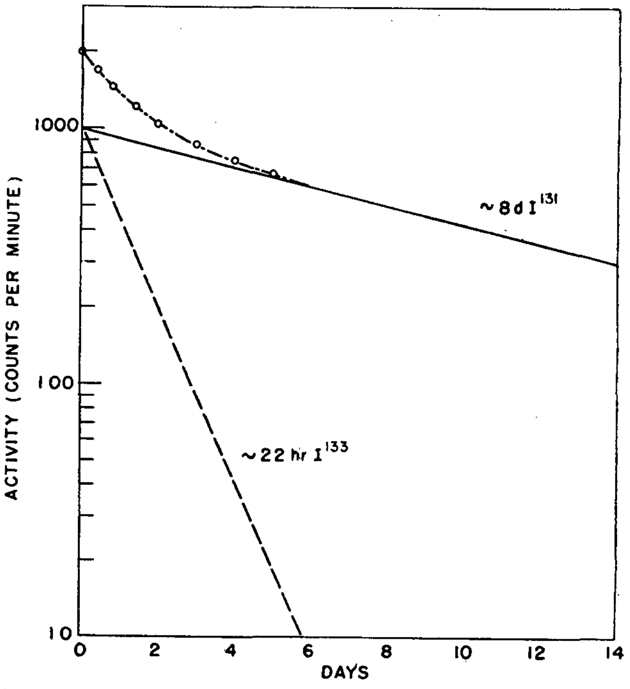

Figure 3. Decay Curve of I^{131} and I^{133} with Equal Activity of Each

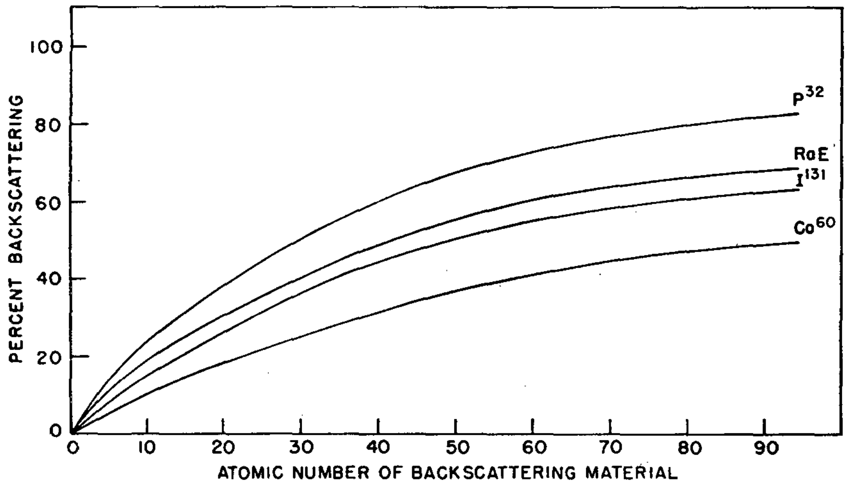

Figure 4. Saturation Back-Scattered Radiation

As % of forward radiation

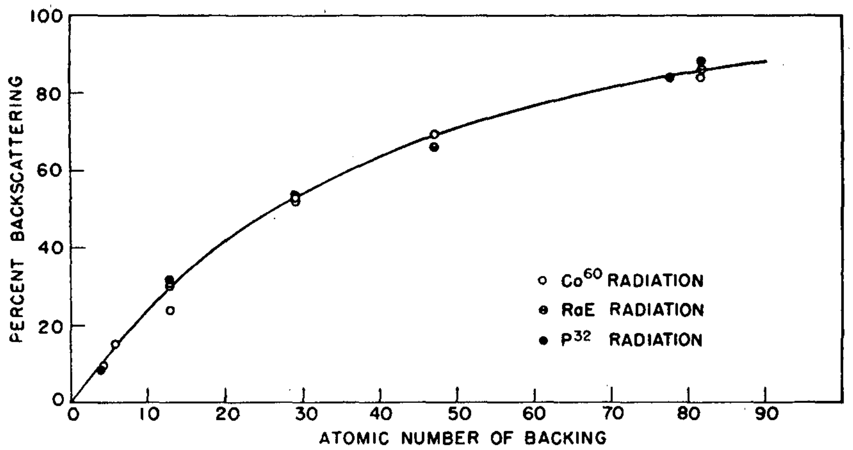

Figure 5. Saturation Back-Scattering Determined by Extrapolation Method

sample through different thicknesses of aluminum absorber and plotting the logarithm of the recorded activity against the thickness of absorber as expressed in milligrams of aluminum per square centimeter (*3*). If iodine is the only beta-emitting substance in this precipitate an absorption curve with a slope and a range characteristic of I^{131} will be obtained. Figure 2 shows a typical absorption curve (*7*). As I^{131} has a half-life of 8 days, the decay of the sample can be followed and a decay curve drawn by plotting the logarithm of the activity at different times over a period of several days or weeks against the time. If this plot gives a straight line with a slope characteristic of an 8-day half-life, one can feel fairly certain that the major activity is I^{131}. Beta emitters of different half-lives will show up in the plot as deviations from a straight line. Figure 3 illustrates the effect of an equal quantity of I^{133} activity in the initial sample on a decay curve of I^{131}.

Various factors must be taken into account when calculating the number of disintegrations in the sample from the number of counts recorded by the beta counter. One factor is the effective geometry of the counter—i.e., the percentage of the total betas being emitted which actually enter and are counted by the Geiger tube. This percentage is usually determined by counting a sample whose disintegration rate is known. Such standards or standard solutions may be obtained from the National Bureau of Standards. Once the effective geometry of the counter is known for the standard, it can then be applied to other samples, if they are mounted on the same material and counted under the same geometrical arrangement, and if these future samples do not have beta energies too far different from that of the standard. The reason for these two stipulations is the phenomenon of back-scattering.

When a sample of a beta emitter is placed on a plate for counting, statistical considerations would suggest that half of the particles being emitted go in the upward direction and half in the downward direction. However, of the half emitted in the downward direction, a large fraction may be scattered back into the upward direction by successive collisions with the atoms in the backing plate. The net result is that more than 50% of the particles will appear to have been emitted from the plate in the upward direction. The exact number of particles which are scattered back in the upward direction depends on the thickness of the backing plate, its atomic number, and the energy of the beta particle. If the sample and standard are mounted on different types of plates, a correction must be made for the difference in back-scattering (*12*, *13*). The energy dependence of back-scattering is only an apparent effect and disappears when a correction is made for the absorption of the back-scattered betas in the window of the tube and in the air between the tube and sample (see Figures 4 and 5).

The back-scattering problem can be eliminated in either of two ways. In some cases, the simplest method is to mount the sample and the standard on an organic film thin enough to give essentially no back-scattering of the beta particles. The second method is to mount the sample and standard on identical plates, thus cancelling the back-scattering correction.

Still other corrections are necessary in determining the amount of I^{131} present in the original solution. One of these is the fraction of betas absorbed in the counting tube window. The correction for the thickness of the tube window is made by assuming that the mica, of which the window is made, is equivalent to an aluminum absorber of the same thickness (*1*, *3*, *13*). Another factor is the fraction of betas absorbed and scattered in the sample itself (*4*). The latter factor is usually determined experimentally. The correction can be determined as follows.

Several equal aliquots containing a known amount of I^{131} as iodide are mixed with different weights of the stable isotope I^{127} as iodide, and silver iodide is precipitated from each solution. The silver iodide precipitates are spread over an equal area and then counted. From the increase or decrease in the counts recorded as the weight of the silver iodide increases, the absorption and scattering of I^{131} betas in silver iodide can be calculated or plotted as a function of the weight of the silver iodide.

Two effects are being measured, the scattering and the absorption in the sample. Because of scattering, activity generally increases as the amount of carrier is increased, but beyond a certain thickness the self-absorption effect overrides the scattering and the counting rate decreases. The self-scattering effect generally reaches a maximum at a source thickness equal to 5 to 10% of the range of the beta radiation.

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Determination of Sulfur after Combustion in a Small Oxygen Bomb

Rapid Titrimetric Method

R. K. SIEGFRIEDT, J. S. WIBERLEY, AND R. W. MOORE
Socony-Vacuum Laboratories, Brooklyn, N. Y.

A need for a small scale oxygen bomb and a more rapid method for the determination of sulfur led to the construction and testing of a 40-ml. bomb for analytical use. A convenient microprocedure for sulfur was devised which, by increasing the sample size, may also provide a rapid routine method for determining sulfur in petroleum products. Such a small bomb has been found suitable for the combustion of organic samples weighing from 2 to 200 mg. The bomb washings are titrated for sulfate with 0.02 *N* barium chloride, using tetrahydroxyquinone as indicator. It is not necessary to add at least 3 ml. of barium chloride, as some authors have supposed. A magnetic stirrer is advantageous in obtaining rapid end points and no difficulty has been experienced in seeing the color change. Sulfur in the range of 0.01 to 100% may be determined without interference from most common elements. A single determination requires less than 1 hour of elapsed time with 20 to 30 minutes of operator time.

CHEMICAL procedures for the determination of sulfur in organic compounds generally consist of two separate phases. The first is the quantitative conversion of all sulfur into a single chemical form—i.e., a sulfate or sulfide—and the second is the estimation of the amount of this sulfur product. Many combinations are possible. An analyst may alternately use any one of several methods in one phase of the determination, while retaining a single technique for the other.

Organic matter can be completely oxidized in a number of ways for the conversion of sulfur to inorganic sulfate. Wet oxidation with nitric acid according to Carius (*11, 14, 28, 32*), oxidation with perchloric acid (*15*), combustion in a tube in a stream of oxygen (*12, 19, 28, 32, 40*), combustion in a lamp with air (*4, 6, 43*), fusion in a crucible with sodium carbonate or Eschka's mixture (*3, 7, 9*), fusion in a bomb with sodium peroxide (*3, 13, 28, 30*), and combustion in a bomb with oxygen under pressure (*5, 35*) are extensively used. Reduction methods, such as catalytic hydrogenation (*16, 17, 41, 42*), have been less widely used. A few investigators have combined oxidation and reduction (*22, 25, 37*).

The second phase of the sulfur determination also offers many possibilities. The gravimetric method based on the weighing of sulfur as barium sulfate is still the most commonly used in spite of the considerable expenditure of time, if the precipitate is allowed to stand before filtration (*3–5, 7*). Recently, a rapid gravimetric method was reported in which the sulfur trioxide is collected by silver gauze and weighed as silver sulfate (*39*). Volumetric as well as gravimetric methods employing benzidine for the precipitant have long been known (*10*). Simple acidimetric methods are sometimes applicable, but difficulties arise in the presence of other acid-forming elements, such as chlorine (*6, 8, 28, 32*). Barium chromate methods have been described (*18, 27*), and the literature of the past 15 years contains many references to the titrimetric procedure which uses tetrahydroxyquinone as indicator (*2, 9, 20, 23, 24, 26, 29, 31, 33–36, 38, 40, 43*). The last method has been the subject of a great deal of discussion, particularly concerning the ease of detecting end points, reliability in the hands of inexperienced operators, and the stoichiometry of the titration.

When the product formed is sulfide, it may be determined iodometrically (*21*), oxidimetrically with hypochlorite (*22*), colorimetrically with methylene blue (*17*), or by precipitation of a heavy metal (*16*).

A method for general industrial analytical work should be applicable to the determination of high and low concentrations of sulfur in the presence of common metallic and nonmetallic elements. It should be rapid with respect to both operator time and total elapsed time and, if possible, should be suitable for microanalytical work. It seemed interesting to investigate the application of a small oxygen bomb, which at that time was neither commercially available nor described in the literature. The method set forth in this article combines the oxidation in such a bomb with an improved titrimetric tetrahydroxyquinone procedure.

APPARATUS

Oxygen Bomb. The bomb (Figure 1) has a capacity of approximately 40 ml., and is so constructed that it will prevent losses due to leakage of gases and permit quantitative collection of the combustion product with a minimum of wash liquid. The inner surface of the bomb may be made of stainless steel or any other material that will not be affected by the combustion process or the products of combustion. Materials used in the bomb assembly, such as the head gasket and lead-wire insulation, should be resistant to heat and chemical action, and should not undergo any reaction which will affect the sulfur content of the liquid in the bomb. A Parr oxygen microbomb has been found satisfactory for this application.

The platinum sample cup, 12 mm. in outside diameter, has a rim with an outside diameter of 20 mm. Over-all height is 5 mm. and weight is about 2 grams.

Platinum, firing wire, approximately No. 38 B.&S. gage, is used.

The magnetic stirrer and stirring bars may be obtained from Arthur H. Thomas Co., Philadelphia, Pa.

The titration stand should be capable of holding two burets, and have a white background illuminated with light such as that from a white fluorescent bulb.

A glass color filter, Corning, with transmittance of approximately 37% at 550 mμ, may be obtained from Arthur H. Thomas Co., Philadelphia, Pa. (Catalog No. 9324-H).

REAGENTS

White mineral oil, sulfur-free.

Oxygen, free of combustible material, available at a pressure of 600 pounds per square inch.

Phenolphthalein, 1% in 95% ethyl alcohol.

Sodium hydroxide, C.P., approximately 1 *N*.

Hydrochloric acid, C.P., approximately 0.05 *N*.

Tetrahydroxyquinone, prepared indicator with measuring scoop, supplied by W. H. and L. D. Betz, Philadelphia, Pa.

Ethyl alcohol, 95%, sulfur-free. Formula 30 or 3-A is acceptable.

Barium Chloride Standard Solution, 0.02 *N*. Dissolve 2.435 grams C.P. barium chloride dihydrate in water and dilute to 1 liter in a volumetric flask. Verify the normality of the solution by titrating 5-ml. portions of a standard sulfate solution prepared by dissolving 1.400 grams (weighed to the nearest milligram) of anhydrous sodium sulfate in water to give 1 liter of solution.

PROCEDURE

If the bomb is still wet from a previous rinsing, shake the head to remove large droplets of water which might subsequently drop into the sample cup and prevent complete combustion.

In the center of a piece of firing wire about 8 cm. in length, form a small coil of about seven loops 1 mm. in diameter. Connect the wire to the bomb terminals, arranging it in such a fashion that the coil touches the sample when the sample cup is properly placed in the bomb. Place several drops of water (approximately 0.5 ml.) in the bomb and rotate the bomb in such a manner that the entire bottom surface is moistened.

Introduce into the cup a quantity of sample estimated to contain between 0.3 and 2.5 mg. of sulfur. If the sample is a solid or weighs less than 50 mg., add 1 drop of sulfur-free white oil to the sample in the cup. The total of sample plus white oil should not exceed 200 mg.

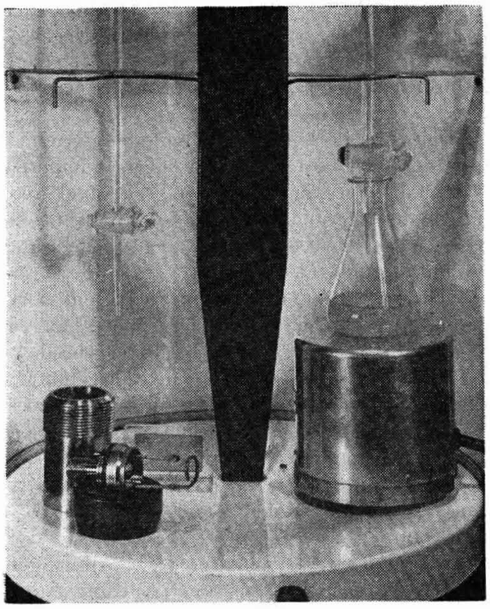

Figure 1. Titration Stand, Magnetic Stirrer, Color Filter, and Oxygen Bomb

Place the sample cup in position, assemble the bomb, and tighten the cover securely. Admit oxygen slowly (to avoid blowing the sample from the cup) until a pressure of 500 to 550 pounds per square inch is reached.

It is essential that the bomb does not leak under pressure. Leaks can be detected by filling the bomb with oxygen at 500 pounds per square inch pressure and immersing it in water. If no bubbles appear, the bomb is correctly sealed.

Connect the terminals to the electrical circuit and ignite the sample. Cool the bomb in running water and rinse with distilled water. Wait 10 minutes and release the pressure slowly at a uniform rate. Open the bomb and examine the inside for traces of unburned sample or soot. If either is found, repeat the determination.

Wash the interior of the bomb thoroughly with a fine jet of distilled water and collect the rinsings in a 150-ml. beaker. Fifty milliliters of wash water are usually sufficient.

Add approximately 3 ml. of saturated bromine water to the washings, place a cover glass on the beaker, and boil off the excess bromine. When the bromine has boiled off (several minutes' boiling), add 2 drops of phenolphthalein and then 1 *N* sodium hydroxide dropwise until the solution is alkaline. Permit the solution to cool briefly and filter through qualitative filter paper into a 125-ml. Erlenmeyer flask. Rinse the beaker three times with 2 to 3 ml. of water, pouring the rinsings through the filter paper. Wash the filter paper twice with 3 to 5 ml. of water. Evaporate the filtrate in the Erlenmeyer flask to 20 ± 5 ml., cool to room temperature, then carefully neutralize with 0.05 *N* hydrochloric acid until the red phenolphthalein color is just discharged.

Add a measuring cup full of tetrahydroxyquinone indicator (approximately 100 mg.) and 20 ml. of 95% ethyl alcohol.

Place the Erlenmeyer flask containing a stirring bar on the magnetic stirrer and arrange the orange filter near the flask, so that light from the titration stand can easily be seen passing through both.

Titrate the contents of the flask with standard 0.02 *N* barium chloride while stirring vigorously. When 1 drop of barium chloride causes the color of the solution to become darker than the color of the filter and the darker color persists for 1 minute of vigorous stirring, the end point has been reached.

When the tetrahydroxyquinone and the alcohol have been added, the solution has a yellow color. As barium chloride is added, the solution may momentarily become red-orange, but stirring rapidly changes the color back to yellow. At the end point, the solution is a dark orange, and the dark orange color will not fade even after several minutes' stirring. If the end point has been passed, the solution will have a pronounced red hue.

Make a blank test using the specified quantities of reagents and following the above procedure except for the combustion. If white oil is used, a combustion of the white oil should be made.

Calculation. Calculate the sulfur content of the sample as follows:

$$\%\ \text{sulfur} = \frac{1603\ N\ (A - B)}{W}$$

where

A = ml. of barium chloride used in titrating sample
B = ml. of barium chloride used in titrating blank
N = normality of barium chloride
W = weight of sample, mg.

DISCUSSION

Oxygen Bomb. When this project was initiated, an oxygen bomb acceptable for microanalytical work was not available. A suitable bomb was designed and constructed by the engineering and machine shop staff. The design of the customary Parr oxygen bomb 1102 was scaled down to one tenth, which gave the small bomb a capacity of 40 ml. Thus, when filled with oxygen to a pressure of 500 pounds per square inch, it is suitable for samples of from 1 to 200 mg. in weight. Tests on the bomb showed it to be capable of oxidizing a variety of products. Pure organic compounds, petroleum products, deposits, etc., were burned without the formation of a carbon residue. Because the sample size can be varied over a wide range, this apparatus suffices for samples containing a few tenths of 1% of sulfur as well as for materials in which sulfur is a major constituent. The bomb is sufficiently small for microanalytical work, but is large enough to present no difficulty to the easy introduction of the sample and connection of the electrical firing wire.

Shortly after completion of these studies, it was learned that the Parr Instrument Co. was independently perfecting a 50-ml. oxygen microbomb for essentially the same purpose. This bomb has since been used by Agazzi, Parks, and Brooks in determination of sulfur and chlorine. In their procedure sulfur is determined gravimetrically (*1*). One of these bombs was obtained on loan and evaluated with the same samples that had been previously analyzed. The results were found to agree within the limits of the method, so that the Parr bomb could be used interchangeably with the one the authors had constructed. As a satisfactory oxygen microbomb is now available, plans of the bomb built at the Socony-Vacuum Laboratories are not being published at this time.

Titration. The successful use of tetrahydroxyquinone in barium chloride titrations of sulfate depends upon the ease with which an operator can detect the end point. Pseudo end points cause the greatest concern. They arise from the slow precipitation of barium sulfate and the localized formation of the red barium salt of the indicator, which tend to appear toward the end of the titration.

Initially, after the indicator and the alcohol have been added, the solution is pale yellow. The addition of barium chloride produces tiny patches of the red salt of the indicator, but these quickly disappear as the solution is agitated. As the end point is approached, the yellow color gradually gives way to an orange hue. At this stage, when most of the sulfate has been precipitated, further addition of barium chloride requires a longer time to react with the remaining sulfate. Because barium ions in solution will combine with the indicator to form a bright red salt, insufficient shaking will lead to the selection of a premature end point. The true end point is reached when the solution has a persistent dark orange color. Further additions of barium chloride will produce intense red shades.

One may conclude, therefore, that rapid stirring is essential to the successful completion of a titration. Consequently, a magnetic stirrer is a great improvement over shaking or stirring by hand, and reproducible end points are quickly obtained without imposing any strain on the operator.

An orange color filter provides a convenient means of repeatedly arriving at the proper shade of color and thereby selecting identical end points. Numerous titrations have shown that it is possible for different operators to reproduce end points with a precision of 0.02 ml. of 0.02 *N* barium chloride.

Of considerable importance is the question of the stoichiometry of the titration. Ogg *et al.* (*29*) have reported that the use of at least 3 ml. of 0.02 *N* barium chloride is necessary for a satisfactory titration. They state that, if less than 3 ml. of barium chloride is used in the standardization, the apparent normality will show rapid changes with corresponding small changes in the total volume of standard barium chloride solution used. Their curve has been reproduced as curve *A* in Figure 2.

Actually, the normality does not change as curve *A* would lead one to believe. The shape of the curve is easily explained by taking into consideration an indicator blank. The authors' work with zero concentrations of sulfate showed that 0.12 ml. of standard barium chloride solution was consistently consumed in each such titration. This amount was interpreted as the indicator error—i.e., the quantity of barium chloride needed to produce a perceptible change in the color of the titrated solution. Several observers have pointed this out (*20, 33–35, 40*). Because 0.12 ml. is a significant volume of standard solution, it should be subtracted from the total volume of standard solution consumed in any titration. The effect of this indicator error on the apparent normality can be seen by referring to Figure 2. Curve *B* shows the change of the apparent normality of the barium chloride solution when standardized against 1-, 2-, 3-, 4-, 5-, 6-, and 10-ml. portions of 0.0200 *N* sodium sulfate solution without consideration of the indicator blank. If only 1 ml. of barium solution is used in the titration, the indicator error accounts for about 10% of the total volume of standard solution required. The resulting normality, therefore, must appear low by 10%. With larger total volumes of barium chloride solution, the percentage error will diminish and the apparent normality will seem to approach a constant value, as shown by curves *A* and *B*. This behavior disappears, as illustrated by curve *C*, if the buret readings are corrected for the indicator error. The normality then appears constant within 1% over the whole range from 1 to 10 ml., and the requirement may be dropped that more than 3 ml. of standard solution must be used in titrations.

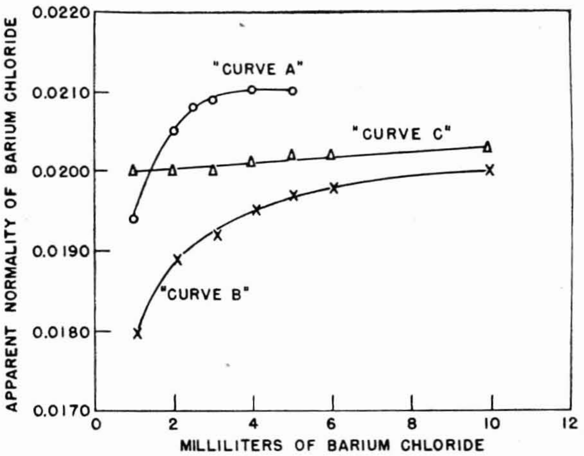

Figure 2. Apparent Normality of Barium Chloride

There is a close resemblance between curve *A* obtained by Ogg *et al.* and curve *B* calculated from the authors' data. Thus, it appears that failure to use a correction for the indicator blank leads to exactly the same deviations as observed by Ogg *et al.*, who seem to have missed this important point. They claim that standardizing the barium chloride with a standard sulfate solution "eliminates a correction factor." They fail to observe, however, that it is the neglect of the indicator blank which produces the peculiar behavior of their apparent normality. Furthermore, their normality does not become constant when more than 3 ml. of barium chloride solution are used for titration; their apparent normality increases 1% from 3 to 5 ml. and again 1% from 5 to 10 ml. of barium chloride used in titration. The authors' assumption that the indicator error is constant, which may not be strictly true (*20*), never leads to results that are in error by more than 1% throughout the range of 0 to 10 ml. of barium chloride solution.

Because Ogg *et al.* do not provide for the determination of a blank, there is no safeguard against the effects of impurities in the reagents. Sulfate contaminations have been found, and it is believed that a blank determination should always be made.

For the reasons given above, the frequently cited procedure of Ogg *et al.* is not recommended.

Interferences have been treated by Sheen and Kahler (*34*). Barium contained in the sample precipitates an equivalent amount of sulfate, so that less barium chloride is needed in the titration. If the barium content is known, a correction may be applied by increasing the percentage of sulfur by 0.23 times the percentage of barium. Phosphorus interferes at the pH specified for the titration, but moderate amounts of phosphorus, up to 60 p.p.m. in the final solution, can be tolerated in the titration, if the pH is reduced to 4.0. Lead compounds should not be burned in the platinum cup.

Results on samples of both high and low sulfur contents are shown in Table I. Emphasis has been placed on samples low in sulfur, because the primary objective was the development of a more rapid procedure than that of the ASTM (*5*). It may be seen that the tetrahydroxyquinone titration provides adequate

Table I. Comparison of Sulfur Results Obtained by Titrimetric–Oxygen Bomb Method with Theory or ASTM Values

Sample	Comparison Method and Value		Titrimetric–Oxygen Bomb Result
Motor oil	D 894–48T	0.18	0.20
		0.21	0.20
		0.19	0.20
		0.19	0.20
Cutting oil	D 129–44	0.51	0.49
		0.51	0.51
		0.47	0.49
		0.50	0.50
Motor oil	D 894–48T	0.60	0.62
		0.60	0.66
		0.60	0.65
		0.60	0.64
Heavy lube oil	D 894–48T	0.86	0.87
		0.89	0.89
		0.88	0.85
		0.88	0.87
Diesel oil	D 129–44	1.16	1.11
		1.16	1.12
		1.14	1.10
		1.15	1.11
Cutting oil	D 129–44	1.52	1.47
		1.48	1.50
		1.49	1.50
		1.50	1.49
Fuel oil	D 129–44	1.80	1.79
		1.78	1.78
		1.84	1.80
		1.81	1.79
Fuel oil	D 129–44	2.42	2.40
		2.44	2.42
		2.41	2.39
		2.42	2.40
Cystine (Bureau of Standards)	Theory	26.7	26.6
Sulfur (U.S.P.)	Theory	Over 99.5	100.0
			99.2
			99.6

accuracy. A single determination requires less than 1 hour of total elapsed time, 20 to 30 minutes of which are operator time. In routine use about sixteen determinations per operator per day might be expected.

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Determination of Sulfur and Chlorine in Organic Materials

Reduced Scale Oxygen Bomb

ELIGIO J. AGAZZI, THOMAS D. PARKS[1], AND FRANCIS R. BROOKS, *Shell Development Co., Emeryville, Calif.*

THE sulfur or chlorine content of organic materials is generally determined in microanalysis by combustion methods such as the Sundberg and Royer (*6*) modification of the method of Grote and Krekeler (*3*). These methods are widely applicable and generally satisfactory. However, in order to increase their sensitivity for materials that have a low sulfur or chlorine content, the sample size must be increased proportionally. Proper quartz-tube combustion of large (25 to 50 mg.) samples is in many cases time-consuming and requires considerable care.

It was believed that utilization of an oxygen bomb for the combustion of such samples might be advantageous, inasmuch as the combustion, which is carried out in a great excess of oxygen under pressure, requires very little operator time and attention. Sulfur and chlorine are determined using an oxygen bomb by standard methods of the American Society for Testing Materials (*1*, *2*). However, the standard Parr bomb employed has a capacity of at least 300 ml., and washing the products of combustion from the bomb requires 300 to 400 ml. of water, which makes evaporation to a volume suitable for the determination of small amounts of

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[1] Present address, Stanford Research Institute, Stanford, Calif.

In the determination of sulfur and chlorine in organic substances, the oxygen bomb methods (ASTM D 129 and D 808) have proved very useful, particularly for materials containing metallic constituents. A miniature oxygen bomb has been developed, in cooperation with the Parr Instrument Co., to provide a means for the rapid combustion of small samples. The bomb has been applied, with good success, to the analysis of 5- to 150-mg. samples of a number of materials, using existing procedures for the determination of sulfate and chloride. A significant saving in combustion time is achieved, compared to other combustion methods, when samples larger than 25 mg. are employed.

sulfate or chloride a rather lengthy step. It appeared that this objection could be removed by the use of a smaller bomb and, as smaller bombs were not commercially available, arrangements were made with the Parr Instrument Co., Moline, Ill., for the design and construction of a bomb of approximately 50-ml. capacity.

Although it was realized that the reduced scale bomb would be most useful for analysis of materials of low sulfur or chlorine content, a number of organic compounds containing larger proportions of these elements were also analyzed in order to test the applicability of the method to such materials. The bomb combustion techniques employed were modifications of existing ASTM procedures. The sulfate ion content of the bomb washings was determined gravimetrically as barium sulfate and the chloride ion content was determined by amperometric titration with silver ion (*4*). A promising rapid procedure for volumetric determination of the sulfate is described by Siegfriedt, Wiberley, and Moore (*5*).

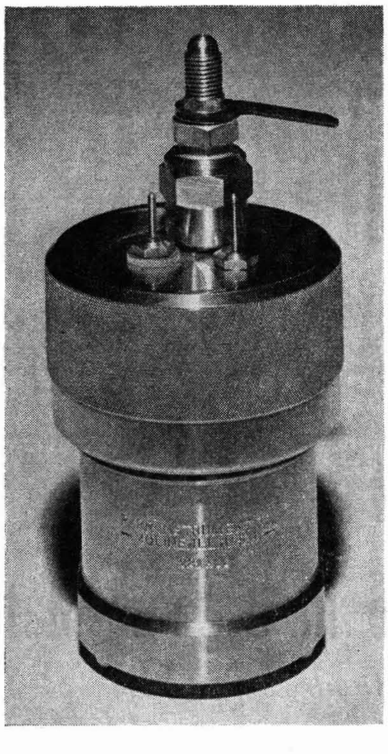

Figure 1. Parr Reduced Scale Oxygen Bomb

APPARATUS

The assembled oxygen bomb is shown in Figure 1 and the component parts are shown in Figure 2.

The bomb is constructed of stainless steel, weighs approximately 1700 grams, and is about 6 cm. in diameter and 7 cm. tall. Hand tightening of the screw cap produces a gas-tight seal between the head and body by compression of a rubber ring. To ignite the sample the ASTM technique (*1*) is employed. The firing mechanism includes a coil of platinum wire 1.6 inches (4 cm.) long and 0.008 inch in diameter (Figure 2). This is located above and to one side of the 1-ml. platinum sample cup in order to avoid fusion of the coil during ignition of the sample. For igniting the sample, sufficient current is passed through the wire to cause the platinum to glow without melting. The bomb is provided with an adapter line, complete with a pressure gage and the proper fittings, for connecting the bomb to an oxygen cylinder.

PROCEDURE

Sulfur. Insert between loops of the platinum coil a piece of cotton or nylon thread of such length that one end will extend into the sample cup. Place about 2 ml. of 1% sodium carbonate in the bomb, wetting the walls and head as thoroughly as possible. Introduce sufficient sample into the cup to give 5 to 10 mg. of barium sulfate, if possible, but do not use more than 150 mg. of sample. Add a sulfur-free nonvolatile diluent, if necessary, until the weight of sample plus diluent is 100 to 150 mg. Homogenize the mixture by stirring with a piece of platinum wire; allow the wire to remain in the cup. If the sample is a solid, dissolve it in a suitable solvent before adding diluent; if the sample does not dissolve readily, mix it intimately with the diluent.

Place the sample cup in position, dip the end of the thread into the sample, and assemble the bomb. Admit oxygen slowly until a pressure of 40 atmospheres is reached. Immerse the bomb in

Table I. Sulfur Content of Organic Materials

(By reduced scale oxygen bomb method)

Sample	Approx. Wt. of Sample, Mg.	Sulfur, % Present	Sulfur, % Found
White oil	100	0.00	0.01 0.01
White oil plus *n*-amyl disulfide	100	1.47	1.44 1.45 1.50 1.47
Diesel fuel	40	1.02[a]	1.04 1.08
Lubricating oil	40	2.48[a]	2.56
Oil sample A (6.9% $CaSO_4$)	40	3.09[b]	3.02
Oil sample B (8.7% Ba)	40	3.43[b]	3.27
Oil sample C (4.6% Ba; 0.5% P)	40	4.14[b]	4.09
Oil sample D (8.7% Ba; 1% P)	40	5.44[b]	5.38
High-sulfur oil	14	10.3[a]	10.4 10.4 9.9 10.1
3-Sulfolene (butadiene sulfone)	7	27.1	26.9 26.3
p-Toluene sulfonylamide	10	18.7	18.3 18.4

[a] Analyzed according to ASTM method (*1*, Appendix VII, November 1948).

[b] Analyzed by ASTM Method D 129-49.

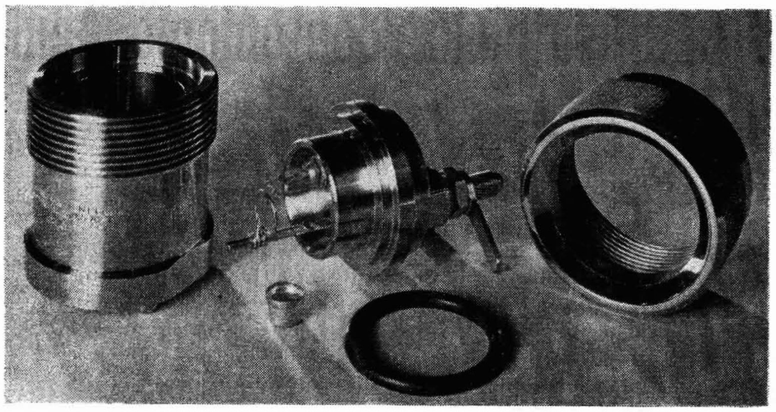

Figure 2. Component Parts of Oxygen Bomb

cold distilled water and ignite the sample. After immersion for at least 10 minutes, release the pressure (slowly, to avoid loss of liquid from the bomb by splashing; this operation should require at least 1 minute). Open the bomb, and if unburned sample or sooty deposits are found, discard the determination. Rinse the interior, including the sample cup, with a fine jet of distilled water, collecting the washings (about 100 ml.) in a 150-ml. beaker. To remove any precipitate from the sample cup, place it in a 20-ml. beaker, and add 0.5 ml. of concentrated hydrochloric acid and sufficient water to cover the cup. Heat just below boiling for 3 to 4 minutes. Transfer the contents of the beaker and sample cup to the 150-ml. beaker, add 1 ml. of saturated bromine water to oxidize all sulfur to sulfate, and evaporate to about 5 ml. (this requires approximately 40 minutes). Determine the sulfate ion content of the solution by a microgravimetric procedure. After each analysis rinse the bomb thoroughly with water.

Chlorine. To prevent corrosion of the bomb, coat the interior with a viscous 4% gelatin solution containing 2.5% sodium carbonate. Ignite the sample as described above, using sufficient sample to give 0.5 to 2.0 mg. of chlorine, if possible. Rinse the bomb and sample cup with water and add a crystal of sodium sulfite to ensure complete reduction of chlorine to chloride. Evaporate the alkaline solution to approximately 20 ml. and determine the chloride ion content by amperometric titration with 0.01 N silver nitrate solution.

RESULTS AND DISCUSSION

A number of organic materials of known sulfur content were analyzed, with the results shown in Table I. A comparison of the values obtained by this method with those obtained by calculation or by established macromethods shows good agreement; results obtained with the bomb tended to be slightly low. When a sample containing little or no sulfur was analyzed immediately after the analysis of a sample high in sulfur, high results were invariably obtained. The last traces of sulfate could be removed by rinsing the bomb thoroughly in a large volume of distilled water after the analysis of high-sulfur samples.

Results obtained for various chlorine-containing materials are shown in Table II. As in the case of the sulfur analyses, good agreement was obtained between the determined and known values. The tendency for the bomb results to be slightly low was again observed. Occasionally there was evidence of corrosion in the bomb, generally at the base of the terminals, which could be the cause of the low results in these cases. The use of an alkaline gelatin solution to coat the interior of the bomb was generally more effective in preventing corrosion than the ASTM expedient of maintaining the chlorine content of the mixture in the sample cup at a low level by suitable choice of weight of sample and diluent. An aqueous alkaline solution is less satisfactory for this purpose, because it does not coat the bomb walls completely. In the combustion of *p*-chloroacetanilide and 2-chlorobenzoic acid samples, a small but significant amount of chlorine was found in the gas released from the bomb after combustion. In order to eliminate this source of error, the bomb gas was passed through dilute sodium carbonate solution, which in turn was analyzed for chloride, and the amount found was added to the results for these samples. Because these results would otherwise have been low, this precautionary step is recommended for combustion of materials high (greater than 5%) in chlorine.

To aid in the combustion of samples, particularly when only a small amount of sample was used, a high boiling diluent was added. The total weight of diluent plus sample recommended was arbitrarily obtained by reducing the amount specified in the ASTM methods (0.6 to 0.8 gram) in the ratio of the small to large bomb volumes. The diluent employed must be readily combustible and must also have a sufficiently high boiling point to prevent errors in weighing due to losses by vaporization. Because it is believed that best combustion is achieved with homogeneous mixtures, solids were dissolved in a small amount of suitable solvent prior to the addition of diluent. Although best results are obtained by solution of solid samples, solids which are insoluble can generally be burned by mixing thoroughly with a diluent.

Table II. Chlorine Content of Organic Materials

(By reduced scale oxygen bomb method)

Sample	Approx. Wt. of Sample, Mg.	Chlorine, %	
		Present	Found
White oil	50	0.00	0.02 0.00 0.01
Simulated high additive oil	45	1.67[a]	1.73 1.74
Chlorinated wax in white oil			
A	60	0.49	0.47 0.48
B	50	0.81	0.78
C	35	3.39	3.25
2-Chlorobenzoic acid (NBS 144)	5	22.6	22.4 21.9[b] 22.4
p-Chloroacetanilide	6	20.9	20.6 20.6
Chlorinated wax	9	17.3	17.1
S-Benzylisothiourea hydrochloride	6	17.5	17.1 17.3

[a] Analyzed by ASTM Method D 808-49T.
[b] Appreciable corrosion in bomb.

For the analysis of 5- to 10-mg. samples the method offers little or no saving of operator time over a conventional combustion method such as that of Grote and Krekeler (*3*, *6*). However, it appears to be useful for testing samples when the amount available is too small to permit use of a macromethod, and when the sulfur or chlorine content is so low as to require a sample of 25 to 50 mg.

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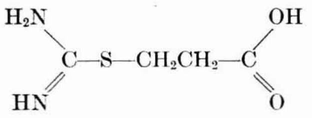
Reaction of Nickel(II) and Beta-Isothioureidopropionic Acid

LYDIA JANE UHLIG AND HENRY FREISER, *University of Pittsburgh, Pittsburgh, Pa.*

This study was initiated to investigate the reactions of β-isothioureidopropionic acid, since its structure is such that coordination or chelation with metals seemed likely. As preliminary tests revealed that in ammoniacal solution a reaction of this acid with nickel(II) ions resulted in the formation of a highly colored complex, the analytical application of this reaction was studied. A colorimetric method for the determination of trace amounts of nickel based on this reaction has been developed. On samples containing from 0.3 to 1.0 mg. of nickel(II) per 50 ml. results were obtained which are reliable to better than 0.005 mg. An approach has been made to the elucidation of the mechanism of the color-forming reaction. It is postulated that β-mercaptopropionic acid, formed by hydrolysis, chelates with the nickel to give the colored body. This method offers a simple, rapid, sensitive determination of nickel, in the presence of aluminum, zinc, and a moderate amount of copper. Iron and cobalt interfere.

THIS study was initiated to investigate the reactions of β-isothioureidopropionic acid, a recently synthesized compound (*1*), with various cations and to evaluate its possible use as an analytical reagent. The structure of this acid is such that co-



ordination or chelation with metals seemed likely. Preliminary tests revealed that in ammoniacal solution a reaction with nickel(II) ions resulted in the formation of a highly colored complex. A quantitative study of the reaction served as a basis for a procedure which permits the determination of nickel in concentrations of 0.1 to 1.0 mg. in 50 ml. with an average error of about 0.005 mg.

The nature of the reaction is not yet completely understood. It seems clear that the β-isothioureidopropionic acid undergoes a preliminary reaction, probably hydrolysis, whose product then combines with nickel in the color-forming reaction. The intermediate may be β-mercaptopropionic acid.

EXPERIMENTAL

No reaction between β-isothioureidopropionic acid and nickel(II) was observed until ammonia water was added. When the ammoniacal solution was heated, a brown precipitate was formed. An increase of either acid or ammonia resulted in the formation of a reddish-brown color, which disappeared upon the addition of excess ammonia. Once lost, the color could not be restored by reducing the ammonia concentration through either boiling or neutralization. A light-sensitive color of constant intensity was obtained when a ratio of 8 parts of ammonia to 1 part of β-isothioureidopropionic acid was employed. This color could be developed on standing without heating; it required about 1.5 to 2 hours to reach a maximum, after which it began to fade slowly.

Attempts were made to reduce the time required for color development. Raising the temperature of the mixture 10° was found to cut the developing time by half, but the stability of the color decreased. When the β-isothioureidopropionic acid and ammonia solutions were mixed and allowed to stand, a color developed almost immediately upon the addition of the standard nickel(II) solution. The intensity of the color developed in this manner was greater than that obtained previously. The mixture of ammonia solution and β-isothioureidopropionic acid solution mixed and aged as described could be used for 3 to 4 weeks before any change in the color intensity could be observed. An attempt was made to simplify the "aging" process for the reagent by heating the mixture. Boiling the mixture for several minutes resulted in a reagent which reacted quickly with nickel(II) to give complete color development. This solution (improved reagent) was used in all subsequent work.

Instruments. Transmittance spectra were measured with a Model DU Beckman quartz spectrophotometer. The colorimetric readings were obtained with a Fisher AC electrophotometer using a Fisher color filter-B which transmits light in the region of 425 mμ. All pH readings were taken with a Beckman line-operated pH meter, Model H.

Reagents. The β-isothioureidopropionic acid first used in this study was prepared from thiourea and β-propiolactone according to the method of Gresham and coworkers (*1*). Since that time β-isothioureidopropionic acid has become available through the B. F. Goodrich Co. The authors are indebted to the B. F. Goodrich Co. for samples of both β-propiolactone and β-isothioureidopropionic acid.

Improved reagent solution was prepared by dissolving 11.62 grams (0.0784 mole) of β-isothioureidopropionic acid in about 200 ml. of distilled water, adding 15 ml. of concentrated ammonia and boiling the mixture for 15 minutes. This was diluted to about 500 ml., its pH was adjusted to 9.2 ± 0.5 units by the dropwise addition of concentrated ammonia and, finally, it was diluted to 1 liter with distilled water. This solution could be used for about 4 weeks before any change could be detected.

A standard nickel(II) solution was prepared by dissolving 24.77 grams of nickel nitrate hexahydrate in distilled water and diluting to 1 liter. One milliliter of this solution contained 5.00 mg. of nickel(II). This was checked by the gravimetric dimethylglyoxime procedure. Suitable dilutions were made with distilled water as needed.

Solutions of other cations such as cobalt(II), copper(II), and iron(III) containing 5 mg. of metal per ml. were prepared by direct weighing of the corresponding nitrates. Chemically pure salts were used throughout.

Effect of pH on Color Development. To a measured excess of improved reagent whose pH had been adjusted to a previously determined value by means of concentrated ammonia, 4 ml. of standard nickel(II) solution, containing 0.1 mg. of nickel(II) per ml., were added, the mixture was diluted to volume in a 50-ml. volumetric flask, and its transmittancy was measured. The results of a series of such measurements, summarized in Table I, indicate that the reagent is most effective when the pH value is maintained within the limits of 8.7 and 9.7.

Table I. Effect of pH on Transmittance

pH	% Transmittance
7.0	100
8.0	96
8.5	89
8.6	86
8.7	49.0
8.9	49.0
9.2	49.0
9.4	49.0
9.8	49.0
10.0	49.5
10.1	50.0
10.3	51.5
10.5	53.2
10.7	98
11.0	100

Transmittance Spectra. An excess of improved reagent was added to each of four 50-ml. volumetric flasks containing 2, 4, 6, and 8 ml. of standard nickel(II) solution [0.1 mg. of nickel(II) per ml.], respectively. These were diluted to volume with distilled water, and transferred to the Beckman spectrophotometer cells (1 cm.). The transmittance curves are shown in Figure 1.

Optimal Mole Ratio of β-Isothioureidopropionic Acid to Nickel(II). Varying amounts of improved reagent were added to 4 ml. of standard nickel(II) solution [0.1 mg. of nickel(II) per ml.] in 50-ml. volumetric flasks, diluted to volume, and placed in the Fisher electrophotometer. Scale A readings were plotted against the mole ratio of β-isothioureidopropionic acid to nickel(II) as shown in Figure 2. At the equivalence point, determined by the intersection of the dotted lines, the mole ratio of acid to nickel is about 22 to 1. As may be seen from Figure 2, the transmittance is constant at higher mole ratios of acid to nickel.

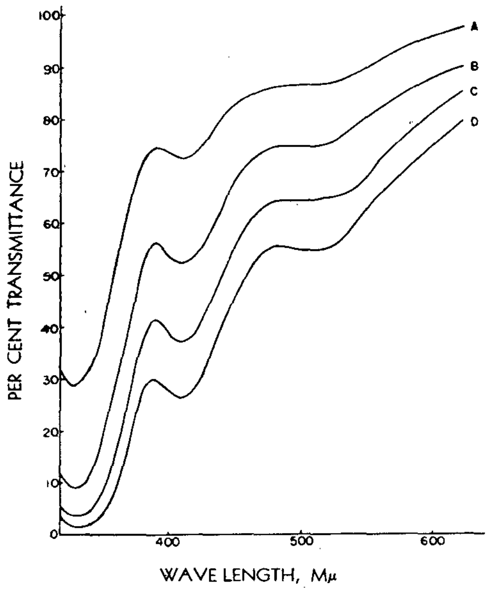


Figure 1. Transmittance Spectra of Colored Complex

Nickel(II), *M*	Mg. Ni(II)/Ml.
A. 6.7×10^{-5}	0.004
B. 1.4×10^{-4}	0.008
C. 2.0×10^{-4}	0.012
D. 2.7×10^{-4}	0.016

Color Stability. After mixing the improved reagent with nickel(II) solution, the color developed completely within 3 minutes, after which readings were taken. The color was perfectly stable for more than 6 hours, after which it faded very slowly, requiring about 5 days to disappear completely.

PROCEDURE

Based on the conditions outlined above, the following procedure was adopted.

Approximately 10 ml. of a solution having a nickel(II) content between 0.1 and 1.0 mg. of nickel(II) are mixed with 10 ml. of improved reagent in a 50-ml. volumetric flask and brought to volume with distilled water. After 3 minutes a portion of this solution is placed in the absorption vessel of the Fisher electrophotometer and the scale A reading is taken.

Calibration Curve. Using standard solutions of known nickel content, the above procedure was carried out. The results shown in Table II indicate that the colored complex conforms to Beer's law. An equation relating scale reading and nickel concentration was obtained by the application of the method of least squares to the calibration data. This equation,

$$C = 0.01290R - 0.0065$$

where C = nickel(II) concentration in mg. per 50 ml. and R = colorimeter (scale A) reading was used to evaluate the reliability of the method. Concentration values of nickel calculated from this equation were compared to the known values as noted in Table II. The agreement between the calculated and known values averaged about 0.005 mg. of nickel(II).

INTERFERENCES

The extent of interferences by various cations was studied. Of the metals commonly associated with nickel, aluminum and zinc did not interfere at all, while copper(II) in fivefold excess of nickel or less had no effect on the transmittance. The limit of tolerance to copper(II) was increased to about 15 to 1 when a solution of copper(II) of about equal concentration to that in the sample was mixed with reagent and used as blank in place of distilled water.

Cobalt(II) and iron(III) interfered if present in amounts larger than 1 or 5 per 100 of nickel, respectively, owing to the formation of yellow-brown and red colors, respectively, with these two ions.

None of the common anions such as chloride, bromide, nitrate, or sulfate had any effect on the nickel color.

Table II. Determination of Known Amounts of Nickel

Colorimeter Readings (Scale A)	Nickel Present, Mg.	Nickel Calculated, Mg.	Difference, Mg.
7.3	0.100	0.088	−0.012
15.5	0.200	0.194	−0.006
23.9	0.300	0.301	+0.001
31.5	0.400	0.400	0.000
39.5	0.500	0.502	+0.002
47.6	0.600	0.608	+0.008
55.4	0.700	0.707	+0.007
63.0	0.800	0.804	+0.004
70.0	0.900	0.896	+0.004
78.0	1.000	0.999	−0.001

DISCUSSION

Although the method outlined above cannot be applied to samples containing cobalt, as can that employing dimethylglyoxime, it offers an advantage of speed and simplicity over the photometric dimethylglyoxime procedure in that chloroform extractions are not needed.

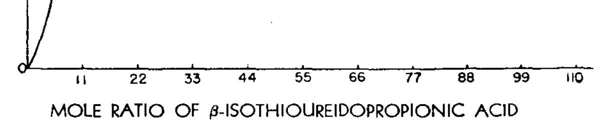
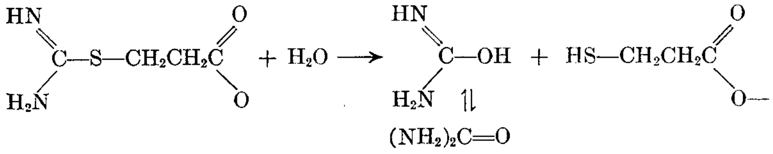


Figure 2. Stoichiometry of Reaction

Mole ratio of β-isothioureidopropionic acid to nickel(II) $1.4 \times 10^{-}$ *M* nickel(II), 0.008 mg. per ml.

The reaction between the β-isothioureidopropionic acid and nickel(II) is somewhat complex—for example, the stoichiometry as determined colorimetrically (Figure 2) indicates a complex in which there are 22 acid molecules to 1 nickel ion. No coordination compound of this composition could be imagined. The fact that the acid does not at once give a color reaction with nickel indicates that the acid undergoes a preliminary reaction, one of whose products is actually the color-forming reagent. This preliminary reaction is thought of as a hydrolysis reaction. Because β-isothioureidopropionic acid might hydrolyze to give thiourea and hydracrylic acid, these two substances were tested but gave no color reaction with nickel. The acid probably hydrolyzes as follows:



$$\mathrm{(HN)(H_2N)C{-}S{-}CH_2CH_2C(=O)O} + H_2O \longrightarrow \mathrm{(HN)(H_2N)C{-}OH} + \mathrm{HS{-}CH_2CH_2C(=O)O^-}$$

$$\mathrm{(HN)(H_2N)C{-}OH} \rightleftharpoons \mathrm{(NH_2)_2C{=}O}$$

giving β-mercaptopropionic acid, which would be the active ingredient of the reagent. The abnormally high mole ratio of β-isothioureidopropionic acid to nickel(II) can be explained as due to the incomplete hydrolysis of the acid. The fact that the improved reagent is capable of reducing cold, dilute potassium permanganate, while a fresh solution of β-isothioureidopropionic acid cannot, lends strength to the supposed presence of a compound containing a sulfhydryl group. If β-mercaptopropionic acid is indeed the actual reagent, use of β-isothioureidopropionic acid still offers the advantages of greater stability and lack of disagreeable odor.

ACKNOWLEDGMENT

The authors are indebted to the B. F. Goodrich Co. for a sample of β-mercaptopropionic acid which enabled them to prove the validity of their assumption. With the assistance of George C. Harrison, spectrophotometric measurements were carried out which showed the color to be due to a 2 to 1 β-mercaptopropionic acid–nickel complex.

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Received June 22, 1950. From a master's thesis submitted by Lydia Jane Uhlig to the Graduate School, University of Pittsburgh, 1950. Contribution 779, Department of Chemistry, University of Pittsburgh.

Gasometric Determination of Nitrite and Sulfamate

W. N. CARSON, Jr., *Hanford Works, General Electric Co., Richland, Wash.*

A micromethod, suitable for the determination of small amounts of nitrite in the presence of a large amount of nitrate, and with a minimum number of manipulations of the actual sample because of radiation hazard, was required. A gasometric determination has been developed that can determine 0.01 mg. of nitrite with a precision of ±3.0% and 0.8 mg. with a precision of ±0.3%. The method is highly specific and few interferences are encountered. The entire procedure requires 20 minutes. A simple modification of the procedure allows the determination of sulfamate with a precision of ±5% for samples containing 2 mg. Interferences with the method are limited to compounds that contain the amino (—NH_2) group. The method described permits a rapid determination of nitrite and sulfamate with minimum sample manipulation. It is possible that the method could be adapted to the determination of the amino group in compounds other than sulfamate.

This investigation was made to develop a rapid and precise method for the determination of small quantities of nitrite in the presence of large amounts of foreign ions and diluents. A simple modification of the procedure enables a similar determination of sulfamate to be made.

The determination is based on the rapid quantitative reaction of nitrite with sulfamate in acid solution,

$$NaNO_2 + HSO_3NH_2 = NaHSO_4 + N_2 + H_2O$$

and the subsequent measurement of the volume of nitrogen evolved. This reaction is the basis for a titration method for sulfamic acid which was first suggested by Baumgarten and Margraff (*2*).

Some substances which interfere with the method can exist in alkaline solution with nitrite; nitrite will oxidize or reduce these substances when the sample is acidified. Other interfering substances react with sulfamic solution in acid solution to give gases which are unabsorbable in alkali. Halogens and chlorates react with sulfamic acid to give nitrogen; permanganate, ferric iron, and chromic acid do not react (*1*). Concentrated (81%) nitric acid reacts with sulfamic acid to give nitrous oxide; dilute acid (less than 75%) does not react. Substances containing the primary amino group (—NH_2) react with nitrite to give nitrogen.

A survey of the apparatus that is useful for measuring small volumes of nitrogen showed that a modified micro-Dumas apparatus was most feasible. In this apparatus, the nitrogen is evolved in a reaction flask and is swept into an azotometer with a stream of pure carbon dioxide which is removed by absorption in sodium hydroxide.

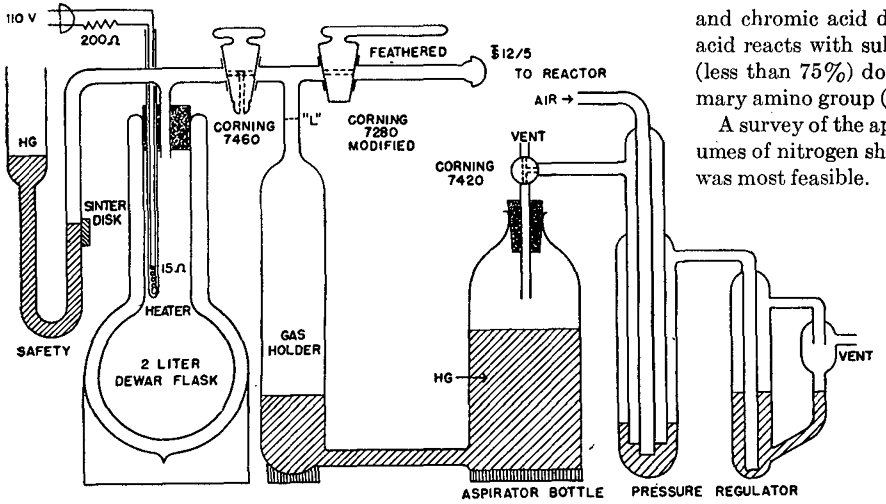

Figure 1. Carbon Dioxide Generator and Gas Holder

NITRITE DETERMINATION

Apparatus. The apparatus is shown in Figures 1 to 3. The carbon dioxide generator is essentially that described by Niederl and Niederl (*4*), but the safety vent is modified in that a sintered-glass disk is used in place of the filter paper assembly. In use, solid carbon dioxide is placed in the Dewar flask and the sublimed gas is kept at a sufficiently high pressure so that gas is continually vented through this disk. The pressure is adjusted by adding or removing mercury in the safety reservoir. A pressure of 30 to 40 mm. of mercury above atmospheric pressure is used. The heater is often necessary to augment the "heat leak" of the flask in order to provide gas in the quantities needed. After the flask is flushed for 24 hours, the blank is 0.002 to 0.003 ml. per 100 ml. of gas used. One filling of dry ice is ordinarily sufficient for several weeks; however, the flask was recharged every week during this investigation. The gas holder is similar to the one described by Niederl and Niederl (*4*), but the mercury is manipulated with a pressure lift which may be omitted. The pressure of the incoming air is regulated by the pressure regulator to a value just sufficient to raise the mercury to level *L* (Figure 1), and thus mercury cannot be accidentally forced into the train. The pressure regulator is the one described by Carson (*3*). The adjusted capacity of the gas holder is 100 ml. The capacity is altered by varying the amount of mercury in the aspirator bottle.

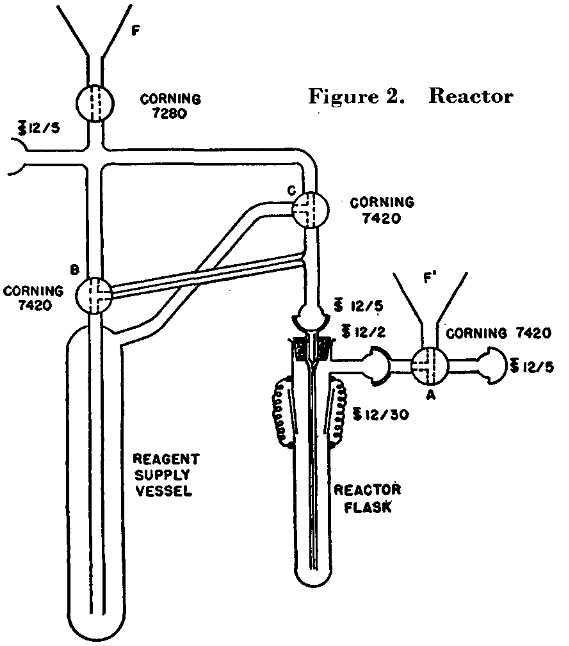

Figure 2. Reactor

The reactor design (Figure 2) permits complete outgassing of the reaction flask and reagent. Stopcock *A* permits back-flushing of the reaction flask head, which prevents premature reaction of the sample with any sulfamic acid splashed there during the previous determination. It also serves to shorten the train during outgassing, as the air in the reaction flask can be vented through it rather than through the entire train on the outgassing sweep. Funnel *F* provides a means of flushing out the reactor between samples to prevent premature reaction of the sample. The capacity of the reagent supply vessel is 60 ml. which is sufficient for a hundred or more determinations; the vessel is outgassed (once per filling) by suitable adjustment of stopcocks *B* and *C*. Reagent is added to the outgassed sample by manipulation of stopcock *C* so that carbon dioxide can enter the reagent supply vessel, but not the reaction flask, and stopcock *B* so that liquid can rise in the tube and pass into the capillary. The volume of the capillary is about 0.5 ml.; this amount of 0.1 *N* reagent is sufficient to decompose any sample that can be measured in the azotometer. When the capillary is full, stopcock *B* is turned so that carbon dioxide from the generator forces the reagent into the reactor flask.

Figure 3 gives the diagram of the microazotometer used. The measuring portion consists of a 1-mm. capillary with a scale in millimeters attached. In use, the nitrogen collects in a large bubble at the base of the capillary. At the end of a run, this bubble is forced into the capillary by lifting the leveling bulb and opening the stopcock. The volume of the gas bubble is measured by the determination of the length of the capillary occupied. The capacity was 187.3 microliters for a 200-mm. length and the capillary was assumed to be of uniform bore. The semimicroazotometer used was the standard model available from supply houses, with a capacity of 1.5 ml. In use, the azotometers are filled with 50% potassium hydroxide and mercury in the usual manner.

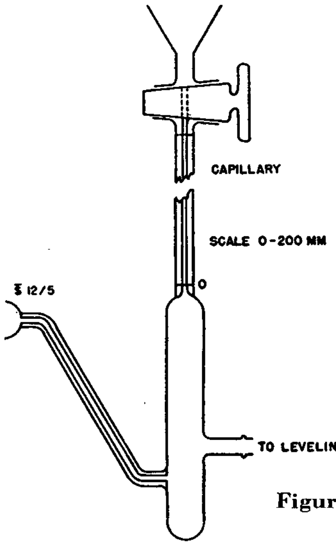

Figure 3. Microazotometer

Procedure. Use a sample of sufficient size to give a conveniently measured amount of nitrogen (0.5 to 1.2 ml. for the semimicroazotometer, 80 to 100 microliters for the microazotometer). For samples of low nitrite content, increase the size of the reaction flask to the size necessary to hold the sample. Neutralize acid solutions to alkalinity, but avoid a large excess of base. Attach the reactor flask to the apparatus, and outgas the sample with 200 ml. of carbon dioxide. If the train has been swept previously on that day, vent the gas through stopcock *A* and funnel *F'* (Figure 2). If the train has not been used that day pass the gas through the entire train, using such additional gas as necessary to remove all air. All air is removed when only microbubbles appear in the azotometer. Shut off the gas flow at the gas holder, and test the system for leaks by lowering the leveling bulb of the azotometer. A leak will appear as a continuous stream of bubbles. A few bubbles will appear when the bulb is first lowered but will not continue if the apparatus is gas tight.

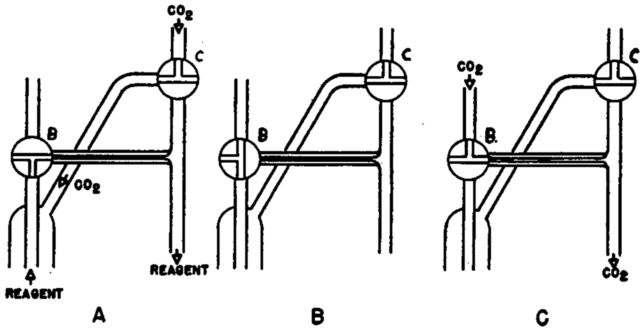

Figure 4. Position of Stopcocks during Manipulations

Introduce the sulfamic reagent (0.1 *N* sulfuric acid + 0.1 *N* sulfamic acid) as follows: (Figure 4 gives the position of the stopcocks of the reactor during this step in the determination. Part *A* shows the position while the capillary is being filled; part *B* shows the position after it is filled.) Fill the gas holder, and bring the gas in it to the pressure of the pressure regulator by manipulation of the air-lift stopcock. Heat the solution in the reaction flask by raising a large test tube filled with water at the

Table I. Determination of Nitrite

	Nitrite Added, Grams/Liter	
	4.399[a]	0.593[b]
	Nitrite found, grams/liter	
	4.407	0.600
	4.389	0.621
	4.389	0.610
	4.382	0.610
	4.371	0.621
	4.389	0.597
	4.362	0.574
	4.388	0.617
	4.405	...
	4.397	. ...
	4.396	...
	4.407	...
	4.403	...
Average	4.391	0.603
Standard deviation		
Grams/liter	±0.013	±0.018
Per cent	±0.31	±3.0

[a] Approximate volume nitrogen collected, 0.50 ml.
[b] Approximate volume nitrogen collected, 0.070 ml.

boiling point (but not actually boiling) around the reaction flask. Cautiously open stopcock *B* (Figure 4) to the position in part *C*, and allow the reagent to enter the reaction flask. Turn stopcock *B* back to the position in *B* (Figure 4) and heat the reactor flask again. Now allow just sufficient carbon dioxide to pass into the reaction vessel so that the cooling of the reactor contents does not cause a partial vacuum. Allow to cool for 1 minute, and adjust the gas flow from the gas holder to a rate such that 1 bubble of gas per second enters the azotometer. It is imperative that this rate be low, or undesirably large bubbles of nitrogen will be formed in the azotometer. When most of the nitrogen has passed into the azotometer as shown by the decreased bubble size, increase the sweeping rate to approximately 0.2 ml. per second, until the gas holder is three fourths empty, at which time increase the rate to 0.5 ml. per second. Use only one gas holder full of carbon dioxide to sweep. Raise the azotometer bulb, open stopcock *A* (Figure 2) to vent, and remove the sample flask. Flush out the reactor by setting the stopcocks of the reactor so that water cannot enter the reagent supply vessel, and adding water to both funnels (*F* and *F'*, Figure 2); allow to rinse thoroughly. Place the next sample flask on the reactor, and outgas as outlined above. During the sweep adjust the leveling bulb of the azotometer, obtain the reading of the volume of gas, and note the temperature and pressure. Remove the nitrogen by opening the stopcock and raising the leveling bulb. At the end of each day, remove the azotometer from the train, and remove the leveling bulb and tubing. Allow the bulb and tubing to drain but do not rinse. If the tubing is rinsed, the dilute alkali formed attacks the rubber and causes the appearance of a marked discoloration in the next day's alkali. Thoroughly rinse the azotometer and remove the stopcock. Do not replace the stopcock until just before use to prevent sticking. It must be heavily greased, preferably with white vaseline.

Calculations. To compute the grams per liter of nitrite, the following formula is used:

$$\text{Nitrite (grams/liter)} = (V - b) \times \frac{T_0 \times (P - c)}{T \times P_0} \times m \times \frac{NO_2}{N_2} \times \frac{10^6}{S} \quad (1)$$

where V = observed volume of nitrogen in ml.
P = observed pressure of nitrogen in mm. of mercury
T = observed temperature of nitrogen in ° K.
b = correction to volume of nitrogen contributed by calibration of azotometer, adhesion of alkali on wall, and blank of nitrogen in carbon dioxide
c = correction to barometric pressure contributed by aqueous tension above the alkali, and barometer corrections (brass scale, etc.)
m = mass of 1 ml. of nitrogen at 0° C. and 760 mm. of mercury = 1.2505 mg. per ml.
$\frac{NO_2}{N_2}$ = factor for nitrite in nitrogen = 1.6422
S = sample size in microliters
T_0 = 273.1° K.
P_0 = 760 mm. of mercury

After substitution for the constants, the formula reduces to,

$$\text{Nitrite (grams/liter)} = 737.9 \frac{(V - b)(P - c)}{S\,(273.1 + t)} \quad (2)$$

where t = observed temperature in ° C.

Values for some of the corrections can be found in Niederl and Niederl (*5*) (aqueous tension and adsorption of alkali on the wall). Barometer corrections are obtainable from standard handbooks. The other corrections are experimentally determined. The blank should be determined by performing an actual run without a sample. It is advisable not to "zero" the azotometer for this determination because the volume of the blank is so small, but to lower the level of the alkali in the azotometer to a convenient mark, read the azotometer, run the blank, and determine the blank value by difference. It is important that gas from the generator be vented at all times through the safety valve, as otherwise the quantity in the gas holder will vary.

Results. Two standard solutions of sodium nitrite standardized by titration with permanganate were analyzed by the method described herein. The sample size taken was 202.0 microliters. The results obtained are given in Table I.

SULFAMATE DETERMINATION

Preliminary Investigation. The reaction of sulfamate and nitrite to give nitrogen can be used to determine sulfamate as well as nitrite. A difficulty arises because the final reaction mixture is an acid solution of nitrite, which on prolonged sweeping with inert gas evolves variable quantities of nitric oxide which is nonabsorbable in alkali. Consequently, an absorption section for nitric oxide removal must be added to the apparatus.

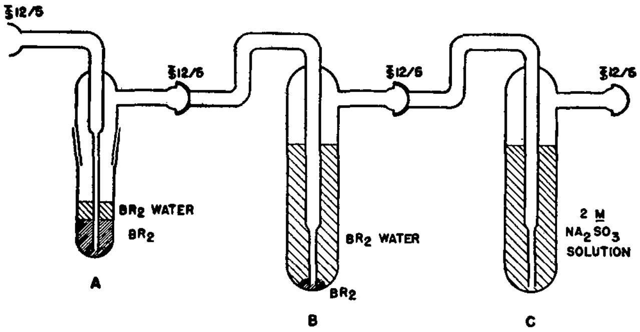

Figure 5. Nitric Oxide Scrubbing System

The common reagents in gas analysis for removal of nitric oxide are ferrous sulfate in dilute sulfuric acid and acid permanganate. Tests with numerous types of scrubbers showed neither of the reagents to be effective under the conditions of the determination. Other oxidizing agents were tried; hypochlorite and hypobromite were unsatisfactory because both gave oxygen when treated with carbon dioxide, and ammonium hexanitratocerate was unsatisfactory when the sweeping rate was above 50 ml. per hour.

The scrubbing system adopted is based on the reaction of bromine with nitric oxide in the presence of water:

$$2NO + 3Br_2 + 4H_2O \longrightarrow 2HNO_3 + 6HBr$$

The scrubber system saturates the gas stream with bromine and water vapor. This combination gives efficient scrubbing. Bromine vapor reacts with the mercury in the azotometer; thus it must be removed from the gas stream. The best reagent for this purpose was 2 *M* sodium sulfite. Acid sulfites would give more capacity, but they evolve sulfur dioxide which, although readily absorbed by the 50% potassium hydroxide in the azotometer, forms the relatively insoluble potassium sulfite, which clogs the azotometer.

Apparatus. Figure 5 gives the design and details of the scrubbers. Scrubber *A* contains liquid bromine below a water layer and saturates the gas stream with bromine and water vapor. Scrubber *B* is used to prolong the scrubbing and contains bromine water. Scrubber *C* holds the sodium sulfite solution used to remove bromine vapor.

The remainder of the apparatus used is identical with that used in the determination of nitrite, except that the reagent vessel is now filled with 5% sodium nitrite. The scrubbers are inserted in the train between stopcock *A* (Figure 2) and the azotometer.

Procedure. The sample is added to the reactor flask and acidified strongly with sulfuric acid. The procedure from this point on is identical with that for nitrite.

Calculations. The value of the sulfate is given by a formula analogous to that used to compute nitrite except for the factor $\frac{NH_2SO_3}{N_2}$ (factor for sulfamate in nitrogen).

$$\text{Sulfamate (grams/liter)} = 1541.2 \times \frac{(V - b)(P - c)}{(S)\,(273.1 + t)} \qquad (3)$$

Results. Table II gives the results of the determination of standard sulfamate solution. These solutions were made from primary standard sulfamic acid and triple distilled water and were checked by titration against base. The sample size used was 190.9 microliters.

Table II. Determination of Sulfamate

	Sulfamate Added, Grams/Liter	
	7.14	10.66
	Sulfamate found, grams/liter	
	7.20	10.80
	7.21	10.84
	7.14	10.63
	...	10.27
	...	10.88
	...	10.75
	...	10.75
Average	7.17	10.70
Standard deviation		
Grams/liter	...	±0.20
Per cent	...	±1.87

DISCUSSION

Although no work has been done on the adaptation of the method for sulfamate to the determination of other substances containing an amino (—NH_2) group, it is probable that this could be done. Conversely, substances containing these groups are the only known interference with the sulfamate method.

The apparatus described has proved serviceable. Breakage in use has been confined to the capillary extending into the sample reactor flask which has been made easily replaceable. Determination of the correct blank for use with the microazotometer is difficult to obtain directly. However, if a number of standard samples, say 5, is run, the average blank can be determined with fair precision. This indirect method is much more precise than the direct method and is more easily performed. Nitrite samples are neutralized to minimize decomposition in the outgassing sweep. This neutralization is not critical, but should be carefully done so that a large excess of alkali is avoided. The reaction mixture must be acid for the reaction between nitrite and sulfamate to proceed, and if a large excess of base is used on the preliminary neutralization, the acid normally added may not be sufficient. Additional reagent can be added, however, if necessary.

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Coulometric Determination of Acid

W. N. CARSON, Jr., and ROY KO
Hanford Works, General Electric Co., Richland, Wash.

A microdetermination of organic acid in the presence of large amounts of mineral acid was required. Previous techniques had interferences of high blanks and required difficultly prepared reagents. A convenient coulometric microtitration of organic acids by electrolytic generation of base in an isopropyl alcohol medium that eliminated these difficulties was developed. The work was extended to acid titration in aqueous mediums and found highly practical. Two successful methods for the electrolytic generation of base were studied in detail, and are described. Precision and accuracy are good and the titration is adaptable to a wide variety of acids. The work utilizes methods of coulometric analysis in the general field of volumetric analysis. Extension of this method of analysis is thereby facilitated.

A COULOMETRIC titration, by analogy to conventional titrations, can be said to be the titration of a substance using an electric current for the standard solution, and using a coulometer as the buret. This is accomplished by means of a suitable electrolysis; the application of Faraday's laws of electrochemical equivalence permits the calculation of the quantity of substance titrated from the number of coulombs of electricity used. An excellent review of previous work in this field is given by Cooke and Furman (*3*) in the discussion of their coulometric titration of oxidizing agents.

A coulometric method of analysis requires the following: (*a*) a source of current; (*b*) a coulometer system; (*c*) a suitable electrolysis scheme to perform the titration; and (*d*) a suitable indicating system for the end point. The first two requirements are usually combined and met by the use of the constant current–time method. At constant current, the number of coulombs used in a titration is directly proportional to the time of the titration. Hence, a highly practical coulometer is an electric stopwatch or timer wired to a constant current supply so that the timer is turned on whenever current passes through the electrolysis cell. The third replacement is the most difficult to meet and is the limiting factor in coulometric methods of analysis. However, there have been reported electrolysis schemes which give acidic, basic, oxidizing, or reducing effects; thus, a wide variety of titrations is possible. The paper by Cooke and Furman (*3*) discusses the available redox schemes. Acid for titration of bases can be generated by the method of Szébellédy and Somogyi (*7*). Epstein, Sober, and Silver (*4*) used a coulometric method for the microtitration of acid in aqueous mediums. The last requirement is general for all types of titrations; indicators for coulometric titrations do not differ in principle or kind from those used in conventional titrations although some are more useful in coulometric titrations owing to the nature of the electrolysis.

Table I. Titration of Acetic Acid in 70% Isopropyl Alcohol with Electrolytic Generation of Base

CH_3COOH Added, Gram/Liter	CH_3COOH Found, Gram/Liter	Av.	Precision, %
0.326 (with a 10-fold excess of HNO_3)	0.317	0.318	±1.8
	0.326		
	0.311		
	0.325		
	0.309		
0.130 (with a 25-fold excess of HNO_3)	0.128	0.130	±3.1
	0.133		
	0.105		
	0.128		
	0.129		
	0.136		
	0.132		

BASE GENERATION

Electrolytic generation of base consists of the deposition of hydrogen at the cathode. Hydrogen ion is removed either by direct deposition

$$2H^+ + 2e^- \longrightarrow H_2$$

or by reaction with the hydroxyl ion generated by the reaction (*5*)

$$2H_2O + 2e \longrightarrow H_2 + 2OH^-$$

when the hydrogen ion concentration is low. In either case, the net effect is the same as the addition of base. This deposition of hydrogen ion can be accomplished in two distinct ways for the purposes of titration of acid. The first, which was used by Epstein *et al.*, is by use of a cell divided into anode and cathode compartments, connected by a salt bridge. The sample plus supporting electrolyte (a neutral salt) is added to the cathode compartment. Hydrogen is evolved at the cathode as above. If an inert anode is in the same compartment, the result of the electrolysis is generally mere decomposition of water, because the anode reaction regenerates hydrogen ion

$$2H_2O - 4e^- \longrightarrow 4H^+ + O_2$$

and no change in acid concentration results. By separation of the electrodes the anode reaction cannot interfere with the removal of hydrogen ion at the cathode, and the titration can proceed.

The use of a salt bridge in electrolysis is a distinct drawback, especially for microtitrations. By making the anode of an attackable material and using a suitable anion in the electrolyte, it is possible to avoid acid generation at the anode, and hence the anode can be placed in the same electrolyte as the cathode. The best material for this electrode is silver if the electrolyte contains chloride or bromide. The reaction is as follows:

$$Ag + Br^- - e^- \longrightarrow AgBr$$

The silver-platinum electrode pair has been used by Lingane and Small (*6*) as the basis for an electrolytic coulometer in which the hydroxide generated is titrated with standard acid.

Other electrodes were investigated in the authors' laboratory for this use. Selection was based on the inertness to free dilute acid, and the nature of the products of electrolysis. Amalgamated cadmium, amalgamated zinc, copper, mercury, lead, and aluminum electrodes were tried. In noncomplexing supporting electrolyte, none are usable because the ions formed in solution hydrolyze at the end point. Complexing agents were tried such as chloride and bromide for cadmium and lead, cyanide for copper, cadmium, and zinc, and fluoride for aluminum. Cyanide and fluoride gave rise to buffer solutions which are unsuited for acid-base titrations. Chloride and bromide are not strong enough complexing agents to prevent the hydrolysis of cadmium and lead ions. Mercury in chloride or bromide mediums can be used if the end point is below about pH 6; above this pH the mercurous salt formed is a basic salt, and the electrolysis is not stoichiometric with respect to acid titration. The useful property of silver is that silver halides are not easily metathesized in basic solutions, and the electrolysis can be continued to a basic end point.

INSTRUMENTATION

The coulometer system used was the constant current–time system. The constant current source used in this investigation was an electronically controlled source which has been described previously (*2*). The source output is continuously variable from approximately 0.5 to 20 ma. This source was modified to facilitate the precise adjustment of the current to a desired value by changing the fixed 1000-ohm wire-wound resistor of the two-voltage reference circuit resistors to a 1000-ohm wire-wound potentiometer. This was used as a fine adjustment. The standardization and operation of the source have been described (*2*).

Computer. A computer can be put into the electrical system because a constant current is used for the titration. The number of equivalents of base generated is proportional to the number of coulombs used, which is, under conditions of constant current, proportional to the time of generation. Hence, the amount of acid titrated is proportional to the time. All that is required for a direct reading of the acid value is to set the current to a value such that the time units are equal to the units in which the acid value is desired, or to some simple ratio of the units—for example, if the acid value is desired in grams per liter of nitric acid, and the time unit is 1 minute, the value of the current necessary to make 1 minute of titration time equivalent to 1 gram per liter of nitric acid in the sample is calculated as follows:

$$\text{Grams per liter (nitric acid)} = \text{equivalents of base generated} \times \frac{\text{equivalent weight of } HNO_3}{\text{volume of sample in liters}} \quad (1)$$

$$\text{Grams/liter (nitric acid)} = \frac{i \times t}{F} \times \frac{HNO_3}{S} \times 10^6 \quad (2)$$

where

i = current in amperes
t = time in seconds
F = Faraday = 96,500 coulombs
HNO_3 = equivalent weight of HNO_3 = 63.02 grams
grams/liter = $t/60$ (by conditions of operation)
S = sample size in microliters
solving for i,
$i = 0.00002552 \times S$ amperes
$i = 0.02552 \times S$ milliamperes

A similar calculation can be performed for any coulometric titration performed at constant current. The electronically controlled constant current source is suitable for this use if modified as described herein. Almost all of the aqueous runs reported were computed by the computer; the ratio of grams per liter to time was varied to keep the titration time to about 10 minutes, or to keep the current below 10 ma. The use of this computer system greatly facilitates routine analysis and prevents errors which may result from calculation.

TITRATION OF ORGANIC ACIDS IN ISOPROPYL ALCOHOL MEDIUM

The microdetermination of weak acids in the presence of an excess quantity of strong acid can be performed by titration with standard alkali in an isopropyl alcohol medium. The advantages of titration in this medium are not pertinent to this paper, except that the titration is much more precise than a similar titration in water. In the preliminary investigation of the determination of small amounts of organic acid in dilute nitric acid solutions, this titration offered a possible means for a direct method for the determination. Preliminary experiments revealed the serious and insoluble problem of high blanks in the alkali.

The method consists of titration in a 90% isopropyl alcohol medium with a standard solution of potassium hydroxide in methanol. Preparation and storage of carbonate-free and silicate-free standard base were not successful. In spite of many precautions, the blank resulting from the alkali, although low when fresh, often exceeded 3 grams per liter (acetic acid equivalent) upon standing for 1 to 2 days. This high blank was due to the fact that from 10 to 100 times the quantity of base necessary to titrate the organic acid was needed to preneutralize the strong acid also present in the sample; thus a small absolute concentration of carbonate in the base had a relatively large effect. The magnitude of this blank often exceeded the organic acid content of the samples. Inasmuch as a coulometric-type titration does not require the use of a standard solution, the use of electrolytically generated base in this titration was investigated.

Experimental. The base generation scheme used in the isopropyl alcohol medium was the divided cell method. The sample was introduced into the cathode compartment which was provided with a platinum wire cathode, a stirrer, a silver-silver chloride reference electrode, and a micro glass electrode (Beckman No. 290), and was covered by a loose fitting cap. The anode compartment was connected to the cathode compartment by a saturated potassium chloride salt bridge with an agar-agar binder. The anode was a smooth platinum wire immersed in a dilute potassium chloride solution.

A model G Beckman pH meter was used. Two glass electrodes were used for extended series of titrations in order to alternate the electrodes between titrations. When not used in the titration, the electrode was soaked in distilled water. A single electrode could be used if it were allowed to soak in water for 5 minutes after each titration.

A 400-microliter sample was placed in the cathode compartment, diluted to approximately 5 ml. with freshly distilled isopropyl alcohol and carbon dioxide-free water to make the solution 70% alcohol. One drop of 0.1 *M* lithium chloride was added, and the initial pH of the solution was taken. Titration of the strong acid was then carried out by electrolyzing the solution at 10 to 15 ma., until a pH change of 1.5 units occurred. The current was now decreased to 3 ma., and the titration was continued as follows: For samples which contained 0.3 gram per liter or greater of acetic acid equivalent, the electrolysis was performed at 10-second increments—that is, the solution was electrolyzed for 10 seconds, and then the current was turned off until a stable pH reading was obtained. For solutions of less than 0.3 gram of acetic acid per liter, the interval was 5 seconds. The titration was continued until two breaks in the pH-time curve were obtained. These correspond to the end point of the mineral acid and organic acid neutralizations, respectively.

To obtain the time of the two end points, the following interpolation formula was used (*1*):

$$E.P. = E + \frac{A - B}{2A - (B + C)} \times D \tag{3}$$

where

A = maximum pH change within one time increment
B = pH change in the increment immediately preceding A
C = pH change in the increment immediately following A
D = time increment in seconds (5 to 10)
E = total time in seconds corresponding to start of A increment
$E.P.$ = total time in seconds of end point (from start of titration at 3 ma.)

The difference between the time of the two end points represented the time required to titrate the organic acid. This time multiplied by the titration current in milliamperes and divided by 96,500 gives the milliequivalents of organic acid, from which the concentration of acid can be computed.

The results of the titration of two solutions of acetic acid are shown in Table I. For the determination, 400 microliters of sample were taken and added directly to the titration vessel. The current used was approximately 3 ma. The precision is given in terms of the best estimate of standard deviation computed by

$$\sigma = \pm \sqrt{\frac{\Sigma (x - \bar{x})^2}{n - 1}} \tag{4}$$

where $\Sigma(x - \bar{x})^2$ is the sum of squares of deviations from the mean, and n is the number of samples.

Titration of organic acid present in larger quantities than 0.3 gram per liter offers no difficulties and is straightforward. Figure 1 shows a typical titration curve for this determination.

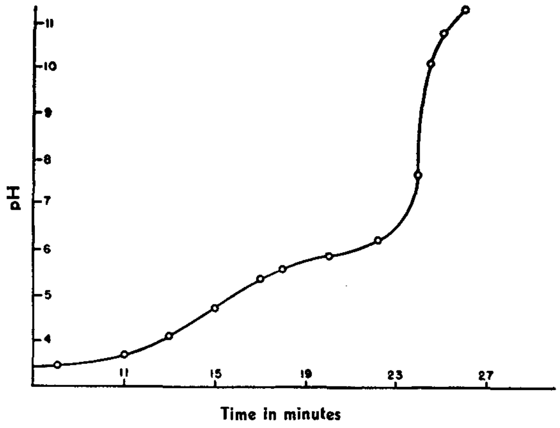

Figure 1. Typical Titration Curve

Acetic acid in presence of excess nitric acid

Discussion. Other lower aliphatic organic acids titrate similarly to acetic acid. Propionic, butyric, and valeric acids were tried. Oxalic and adipic acids show two inflections in the titration curve (pH against time) as expected. Weak mineral acids, such as carbonic and silicic, titrate similarly to acetic acid, but with more poorly defined inflections. These acids are a serious interference in this titration.

The original procedure called for a medium of 90% alcohol. This was found to be impractical for coulometric analysis because the strong mineral acid (nitric) present in the samples was reduced at the cathode. Titration in 50% isopropyl alcohol was unsuccessful and 70% was arbitrarily chosen. No investigation was made on the optimum alcohol concentration; the titration in 70% isopropyl alcohol was satisfactory.

Lithium chloride was used because of its solubility in the solvent. If more than 1 drop of 0.1 *M* solution was added, the indicating system was inoperative. This behavior was unexpected, and has not been explained. The original calomel reference electrode gave poor and erratic results, primarily owing to the necessary salt bridge. Although not completely suitable, the silver-silver chloride electrode was used because of its simplicity and stability in the medium. In a divided compartment cell the reference electrode cannot be placed in the

Table II. Titration of Nitric Acid with Electrolytic Generation of Base

Sample	Sample Added, Grams/Liter	Sample Found, Grams/Liter (Av.)	Sample Size, Microliters	No. of Detns.	Precision, %	Type of Base Generation	Electrolyte	Indicator
Dilute HNO_3	6.30	6.28	200	5	±1.0	Divided cell	0.01 *N* KCl	Methyl red
	19.5	19.4	200	5	±0.35	Divided cell	0.02 *N* KCl	Phenolphthalein
	6.20	6.17	200	29	±0.38	Pt-Ag	0.05 *N* KBr	Methyl red
81% HNO_3	810.0	811.0	5	5	±0.02	Divided cell	0.05 *N* KCl	Glass electrode
		816.0	1	12	±1.8	Divided cell	0.05 *N* KCl	Glass electrode
3*M* HNO_3 + 0.15 *M* $Pb(NO_3)_2$	196.0	193.0	10	5	±2.7	Divided cell	0.02 *N* Na_2SO_4	Glass electrode
		185.0	10	5	±0.45	Divided cell	0.04 *M* KIO_3	Glass electrode
		187.0	10	7	±2.7	Pt-Ag	0.1% Versene[a] + 1% NaCl	Thymol blue
		197.0	10	9	±2.5	Pt-Ag	1% NaCl	Cresol red + thymol blue
		195.0	10	5	±0.45	Pt-Ag	0.1% Versene + 1% NaCl	Methyl red
		195.0	10	4	±1.1	Pt-Ag	0.1% Versene + 1% NaCl	Cresol red
		195.0	10	12	±0.95	Pt-Ag	1% NaCl	Cresol red

[a] Versene is the trade name of sodium ethylenediaminetetraacetate.

anode compartment because the flow of electrolysis current through the salt-bridge causes a large *IR* (current times resistance) drop which upsets the pH meter to such a degree that unstable readings are obtained for several minutes after the current is discontinued.

The glass electrode responded slowly to change in acid concentration and up to 2 minutes of waiting were required after each increment of electrolysis for the pH reading to become stable. This slowness was also noticed using standard base; it is probably due to the isopropyl alcohol medium. The interpolation formula (Equation 3) used to determine the end point strictly applies only to symmetrical titration curves, but the errors involved in its use for titrations of the type described herein are small.

TITRATION OF ACIDS IN AQUEOUS MEDIUM

The investigation of the titration of acids in aqueous medium by electrolytic generation of base was a continuation of the work on organic acids. The titrations in water were conducted by two base generation schemes—the divided cell and the single cell with attackable electrode. The chemistry of these two schemes has been discussed under base generation.

Experimental. The divided cells used in these experiments were in most details similar to the one used in the organic acid work, except for electrolyte. Platinum electrodes were used.

The single cells used were beakers fitted with the reference electrodes (usually calomel and glass) if a potentiometric end point was used; otherwise they were fitted with an attackable electrode (anode), a smooth platinum cathode, and a stirrer. For the results reported in this paper, the attackable electrode was a tight helix of about 10 inches of No. 22 silver wire. The electrolyte varied with the nature of the experiment, but always contained bromide or chloride.

The procedure employed varied somewhat, but in general, it consisted of diluting the sample to 5 to 10 ml. with electrolyte, and adding a complexing agent for the interfering metal ions, if needed. If a colorimetric end point was used, indicator was added. For potentiometric end points the glass electrode must be shielded carefully from the generator electrode system. This can be done by using a coil of wire (or gauze) for the cathode with the anode inside, which localizes the electric field of the generator system. For a potentiometric end point, intervals of 5 to 10 seconds as described above were used in the vicinity of the end point, and the end point was determined by Equation 3.

Results. The results of a number of determinations of nitric acid are given in Table II. Lead was chosen as a typical metal interference. Various complexing agents were tried for this ion; the table shows the more successful. The type of base generation used is indicated by divided cell or "Pt-Ag" for the single compartment cell. The indicator system used is indicated by glass electrode for the potentiometric end points, and by the name of the indicator for the colorimetric end points. The various indicators used were selected to aid in observing the end point which was poorly defined owing to the buffering action of the Versene (sodium ethylenediaminetetraacetate) used to complex the lead.

Discussion. Other strong mineral acids have been titrated in a similar manner with no difficulties. For relatively pure solutions any acid titratable in aqueous mediums with standard base could be titrated coulometrically. Thus, small amounts of pure organic acids, carbonic acid, and acid salts were successfully titrated. This phase of the investigation was conducted only sketchily, but inasmuch as no reason for the failure of the base generation systems exists, except in the presence of ions more easily reduced than hydrogen, a coulometric titration of acid in aqueous mediums can, in general, be made wherever conventional titrations can be used.

The silver anode must be cleaned after each titration or the resistivity of the silver halide layer becomes too great. The voltage drop at the electrode then rises until oxygen evolution is observed, which defeats the purpose of the silver anode. The halide deposit can be most easily cleaned with 1 *M* potassium cyanide, and less easily by concentrated ammonia solution. It is not necessary that all halide be removed each time if a relatively large surface of silver is left exposed.

CONCLUSIONS

The use of electrolytically generated base is feasible for acid titrations by coulometric methods of analysis both in aqueous and isopropyl alcohol mediums. In general, those solutions which can be titrated with standard solutions can also be titrated coulometrically. Precision and accuracy for microsamples are as good or better than the precision and accuracy obtained by use of burets and standard solutions.

Both potentiometric and colorimetric indicator systems can be used, depending on the nature of the sample. In addition, the result may be computed directly by a simple manipulation of the apparatus (setting the constant current source to the calculated value).

ACKNOWLEDGMENT

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Determination of Germanium

Colorimetric Determination of Microgram Amounts with Oxidized Hematoxylin

HANNA NEWCOMBE, W. A. E. MCBRYDE, JOHN BARTLETT, AND F. E. BEAMISH
University of Toronto, Toronto, Canada

For the determination and separation of very small amounts of germanium, a method was desired which would avoid some of the disadvantages of present methods and be applicable to zinc refinery by-products and other industrial sources. A new colorimetric procedure for determining 0.08 to 1.6 p.p.m. of germanium is based upon the formation of a purple color when germanium solutions are treated with oxidized hematoxylin solution. Germanium can be separated from numerous other elements by distillation from hydrochloric acid, and extraction from the distillate into carbon tetrachloride. In view of the increasing industrial importance of germanium—for example, in the manufacture of some types of electronic equipment—and the realization of potential supplies of the metal in industrial by-products, this method may fill a definite need, because of its sensitivity and specificity.

THE most generally used colorimetric method for the determination of germanium is that based on the production of "molybdenum blue" (*6, 9–11, 16–18*); another uses the yellow color of germanomolybdic acid (*3, 14*). These methods suffer from a serious interference by phosphate, arsenate, and especially silica. A systematic search of organic reagents led to the discovery of the color reaction of oxidized hematoxylin with germanium. This reaction forms a purple compound, of the formula Ge(Ht)$_2$, as determined by the method of continuous variations. The product is highly insoluble, and therefore the measurement is carried out on a suspension stabilized with gelatin. The reaction is carried out at a pH of 3.2.

APPARATUS AND REAGENTS

Apparatus. The absorbancy measurements were obtained with a Klett-Summerson photoelectric colorimeter, using the test tube and Photovolt "narrow band" filters. Absorbancy measurements for the determination of the stoichiometry of the color reaction were made in a Beckman Model D spectrophotometer adjusted to band widths of about 1 mμ. A Coleman pH meter was used for pH measurements. The distillations were carried out in the apparatus illustrated in Figure 1.

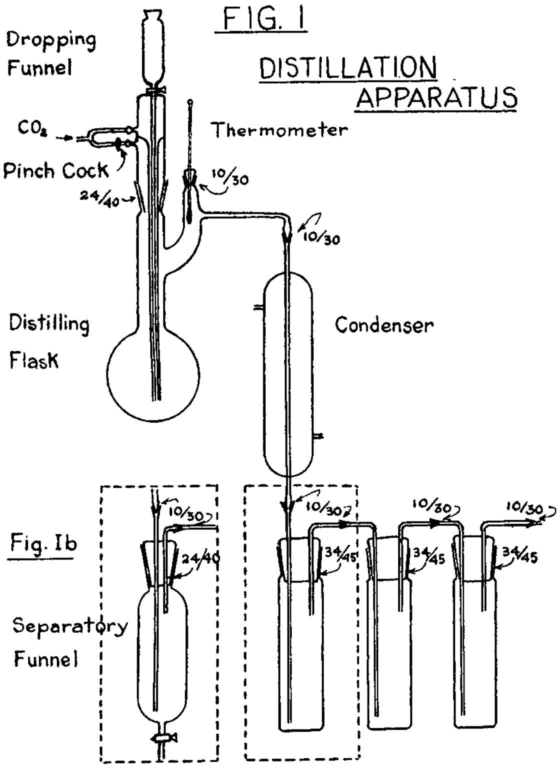

FIG. I
DISTILLATION APPARATUS

Germanium Dioxide Solution. Spectrographically pure germanium dioxide (1.456 grams) obtained from the Eagle-Picher Co., Cincinnati, Ohio, was dissolved in water and made up to 1 liter. This solution should contain 2.019 mg. of germanium per ml. A later standardization, by evaporation of an aliquot in a platinum crucible, ignition at 900° C., and weighing as the dioxide, gave 2.031 ± 0.003 mg. of germanium per ml. as the average of four determinations. From this, standard solutions were made containing 203, 20.3, 10.2, and 2.0 micrograms of germanium per ml.

Oxidized Hematoxylin Reagent. Hematoxylin (3.0 grams) obtained from the British Drug Houses Co. was dissolved in a solution of 500 ml. of water and 200 ml. of 95% ethyl alcohol, 20 ml. of 5% hydrogen peroxide were added, and the solution was heated in a boiling water bath for 15 minutes. After cooling, the solution was made up to 1 liter with water. This solution was stable enough to be used indefinitely. The action of hydrogen peroxide on hematoxylin may produce hematein; hematein gave a similar color with germanium solutions.

Buffer, pH 3.2. The buffer was prepared by mixing 250 ml. of 0.1 *N* potassium hydrogen phthalate and 73.5 ml. of 0.1 *N* hydrochloric acid and making the solution up to 500 ml. with water. The pH was checked with a pH meter.

Gelatin. One gram of gelatin was dissolved in 100 ml. of water, and a crystal of thymol was added as a preservative.

Carbon Tetrachloride. The C.P. product was redistilled.

Concentrated Hydrochloric Acid. Five hundred milliliters of the C.P. product were extracted with 100 ml. of redistilled carbon tetrachloride. It is not known what impurity was removed, but the treated acid gave more consistent results.

Sodium Silicate Solution. A solution containing 2 mg. of silicon per ml. was prepared by dissolving 0.87 gram of sodium silicate in water and making up to 100 ml.

Reagents for Molybdenum Blue Determination were prepared according to the instructions of Hybbinette and Sandell (*11*).

Customs Zinc Concentrate was obtained from the Consolidated Mining and Smelting Co., Trail, B. C. It consisted mainly of zinc sulfide, with small amounts of lead and iron sulfides. According to the company's analysis, it contained 60.0% zinc, 30.0% sulfur, 1.0% iron, 0.6% lead, 0.4% silica, 0.1% copper, 0.15% cadmium, and less than 0.1% antimony and chlorine. The germanium content, disclosed only after the authors' experiments were completed, was 0.005%, obtained by the company by a method involving hydrochloric acid distillation and tannin precipitation of a 20- to 50-gram sample.

Zinc Oxide Fume was obtained from the same company. It consisted mainly of zinc oxide, with some basic lead sulfate and normal lead sulfate. The company's analysis showed 60.0% zinc, 14.0% lead, 1.7% sulfur, 1.5% sulfate-sulfur, 1.3% silica, 0.6% iron, 0.02% cadmium, 0.02% chlorine, and traces of silver, copper, bismuth, tin, calcium, magnesium, aluminum, fluorine, manganese, arsenic, and antimony. The germanium content, disclosed only after the authors' experiments were completed, was 0.004%, obtained by the company by a method similar to that used for customs zinc concentrate.

COLOR REACTION

Effect of Kind of Filter. A spectral distribution curve was (Figure 2) obtained for both an oxidized hematoxylin blank and a germanium-hematoxylin solution. The filter at 550 mμ was chosen for future use, because the greatest difference between sample and blank occurred at this wave length.

Effect of pH. Hematoxylin acts as an indicator (*19*); only in the pH range from 2 to 4.5 is its own color light enough not to interfere with the colorimetric determination of germanium. By using a series of Clark and Lubs buffers (*15*) in this range, the greatest sensitivity was found at a pH of 3.2.

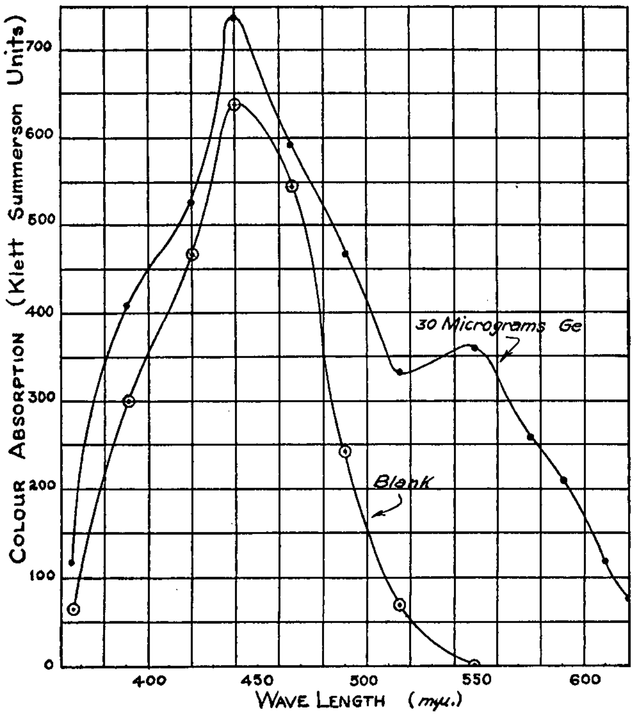

Figure 2. Absorption Curves of Reagent and Colored Complex

Effect of Hydrogen Peroxide. In the preliminary development of the method, the ratio of hydrogen peroxide to hematoxylin in the oxidized hematoxylin reagent was varied. The sensitivity was greatly decreased when no hydrogen peroxide, or too much, was used. The optimum ratio was found to be 1 mg. of hydrogen peroxide to 6 mg. of hematoxylin.

Effect of Time of Standing before and after Dilution. The colors are slow to develop, but an interval of 45 minutes between mixing and final dilution was sufficient to attain a constant color intensity. The solutions did not fade appreciably after dilution; nevertheless, readings were always taken immediately after dilution.

Effect of Initial Volume. Small variations from the initial volume of the germanium sample were found to have no effect on the final color intensity, but immediate dilution to 25 ml. greatly hindered color development. In view of this fact, the initial volume was always kept at 5 ± 1 ml.

Effect of Sodium or Ammonium Chloride. Because germanium is always isolated from other elements by distillation from hydrochloric acid solution, the neutralization of the distillate to a pH of 3.2 would necessarily produce a salt. The effect of various amounts of sodium chloride on the color development and stability, using various germanium concentrations, and the effect of centrifuging for 2 minutes at 2000 to 3450 r.p.m. after the final dilution, were therefore studied. The results obtained, illustrated in Figure 3, showed a complex behavior. The solutions containing high concentrations of salt and of germanium were noticeably turbid. All these results can be explained by two assumptions: The colored complex is not in true solution; it consists of particles too small to settle under gravity, but large enough to settle partially in an ordinary centrifuge. Salt causes an agglomeration of these particles, which increases the color absorption in some cases, owing to the turbidity produced, and decreases it in other cases, because of the material settled out.

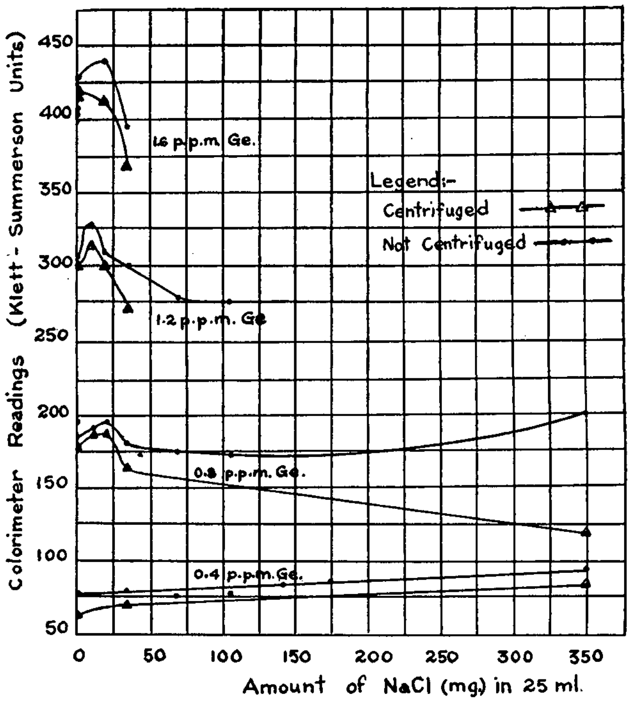

Figure 3. Effect of Sodium Chloride on Color Absorption of Germanium-Hematoxylin Solutions

1 Klett-Summerson (K.S.) unit is equal to absorbance multiplied by 500

Because hematoxylin itself is much more soluble in ethyl alcohol than in water, it was thought that the same might be true of the colored complex. However, the addition of ethyl alcohol was found to decrease the sensitivity without decreasing the turbidity. The use of gelatin as a "protective colloid" gave excellent results, of undiminished sensitivity, decreased turbidity, and improved precision.

Calibration curves were then determined, using gelatin-stabilized solutions, without salt and in the presence of 1 gram of ammonium chloride. Both were straight lines diverging from a common origin, with slopes corresponding to an absorbancy of 0.55 and 0.65 per p.p.m. of germanium, respectively. This showed that Beer's law was followed in both cases.

Range of Greatest Sensitivity. Ayres (*5*) stated that in cases where Beer's law applies the concentration of solutions could be obtained photometrically with the greatest accuracy when the transmittancy is 36.3%, but that over the range 20 to 60% transmittancy the error is not much greater. In the present case, the points of maximum accuracy occur at 0.788 and 0.668 p.p.m. of germanium, respectively, and the ranges of satisfactory accuracy are 0.4 to 1.24 and 0.36 to 1.08 p.p.m. of germanium, respectively. Whenever possible, the size of a sample should always be adjusted to make the final concentration lie within these limits.

Stoichiometry of Colored Complex. The stoichiometry of the reaction between germanium and the oxidized hematoxylin reagent was investigated by the technique of "continuous variations" (*12*, *21*). Solutions of germanium and oxidized hematoxylin of equal molarity were prepared and mixed in various proportions such that the total volume was 10 ml. This solution was treated with gelatin and after 45 minutes diluted with buffer to the prescribed volume. The oxidized hematoxylin solution was found to lose its effectiveness for this reaction rather soon after preparation at the low concentrations used in these experiments. It was assumed that the molarity of the reagent solution could be computed from the molecular weight of hematoxylin. Values of the *Y* function for four wave lengths (450, 500, 550, and 600 mμ) showed maxima corresponding to a germanium to reagent molar ratio of 1 to 2. These observations are interpreted to indicate that one compound is formed in the reaction and that it is of the form $Ge(Ht)_2$.

Comparison with Molybdenum Blue Method. INTERFERENCE OF SILICA. Molybdenum blue colors were developed according to the method of Hybbinette and Sandell (*11*), and read using the 730 mμ filter. By means of the sodium silicate solution, the interference of silica in both the molybdenum blue and the hematoxylin method was studied. The results illustrated in Figure 4 show that the hematoxylin method is more sensitive, and that 0.4 p.p.m. of silicon interfered seriously in the molybdenum blue method. It was found that 80 p.p.m. of silicon was the lower limit of interference in the hematoxylin method.

Final Procedure for Colorimetric Determination of Germanium with Oxidized Hematoxylin. To 5 ml. of the germanium solution at a pH of 2 to 4 in a 25-ml. volumetric flask were added 1 ml. of the 1% gelatin solution and 1 ml. of the oxidized hematoxylin reagent. After 45 ± 1 minutes, the solution was diluted to 25 ml. with the buffer, pH 3.2, and the absorbancy was determined, against a blank containing buffer instead of germanium solution, with the 550 mμ filter.

SEPARATION OF GERMANIUM FROM OTHER ELEMENTS

Distillation from Hydrochloric Acid. Carbon dioxide from a cylinder, purified by passing through glass wool, concentrated sulfuric acid, and potassium permanganate solution, was bubbled through the distillation train (see Figure 1); a part was diverted to sweep out the vapors in the dead space in the upper part of the flask. The receivers were cooled with ice. After the germanium sample had been placed in the distilling flask, the train was assembled, the gas stream was started, and then 20 ml. of concentrated hydrochloric acid were dropped through the dropping funnel. The distillation was conducted for about 45 minutes at the boiling point of the system, which eventually reached 112° C., until the level of the liquid fell below the lower end of the gas bubbling tube.

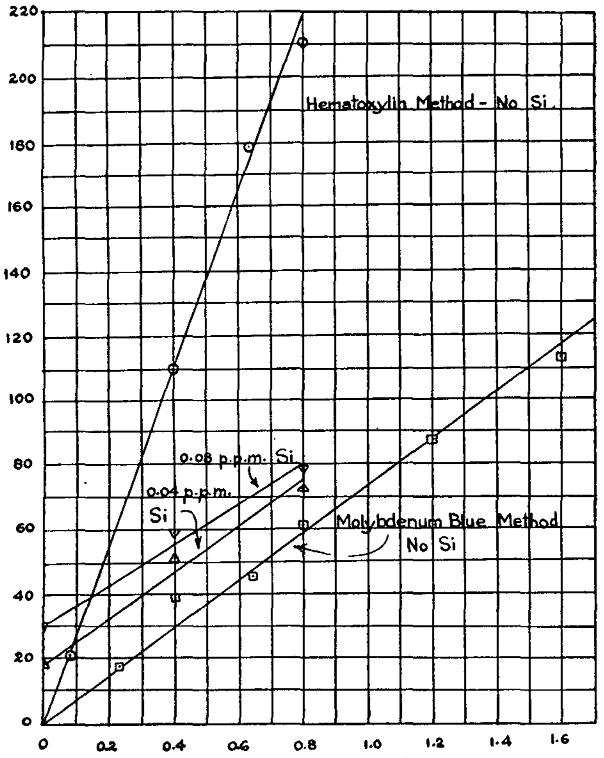

Figure 4. Calibration Curves for Colorimetric Determination of Germanium

For samples containing several milligrams of germanium, 50 ml. of water were used in each of the first two receivers to collect the distillate; an excess of concentrated ammonium hydroxide was added while cooling in ice; the solution was evaporated and made up to volume in a volumetric flask; and aliquots were taken for colorimetric determination. In three determinations using 5.06 mg. of germanium, the average result obtained was 5.07 mg. of germanium, with an average deviation of 0.09 mg. of germanium. In these and all subsequent distillations, a blank, obtained by repeating the whole procedure without using germanium, was subtracted; and the completeness of the distillation, and of the collection of germanium in the distillate, was ascertained by testing the residue in the distilling flask and the contents of the third receiver.

This method could not be applied to microgram samples, where the whole sample rather than an aliquot would have to be used for the colorimetric determination, because neutralization would produce more ammonium chloride than would dissolve in 5 ml. of water. A method was obviously needed for either using less hydrochloric acid during the distillation, or removing some of it from the distillate.

Early attempts at the latter approach failed. Precipitation of germanium disulfide and redissolution in ammoniacal hydrogen peroxide (*2*, *4*, *7*, *9*, *13*, *14*), while satisfactory for amounts of germanium exceeding 50 mg., gave low results with smaller samples. Precipitation of the hydrochloric acid with silver carbonate, or its removal with an anion exchanger (Amberlite IR-4), was unsuccessful, because a considerable part of the germanium was adsorbed on the silver chloride or on the resin. Hydrochloric acid solutions of germanium could not be evaporated on the steam bath, even in the presence of oxalic acid as a complexing agent, without almost complete loss of germanium by volatilization.

Extraction with Carbon Tetrachloride. While no measurable extraction into carbon tetrachloride occurred from 4.8 *N* hydrochloric acid, the distribution coefficient was about 0.1 in 5 *N* acid, about 1.2 at 8 *N*, and about 4.9 at 10 *N*. A simple calculation showed that four extractions of 40 ml. of 10 *N* hydrochloric acid with 20-ml. portions of carbon tetrachloride would recover 99% of the germanium; in practice, this series of extractions led to quantitative recoveries, as far as the colorimetric method could detect.

The extraction from carbon tetrachloride was slow, perhaps because the hydrolysis of germanium tetrachloride to the dioxide is a necessary first step. It was found, however, that if 80 to 90 ml. of the carbon tetrachloride extract were stirred or shaken mechanically with 100 ml. of water, the recovery of germanium was 86% in 2.5 hours, and quantitative in 4 hours. The addition of ammonium hydroxide failed to speed up the extraction.

Distillation from Hydrochloric Acid with Carbon Tetrachloride Extraction. In the distillation as described above, 20 ml. of carbon tetrachloride and 5 ml. of concentrated hydrochloric acid were used in the first receiver, and 20 ml. of carbon tetrachloride in the second; the third was filled with water to serve as a trap for hydrogen chloride. The separatory funnel illustrated in Figure 1b was used as the first receiver. After the distillation, the contents of the second receiver and the carbon tetrachloride layer from the first receiver were transferred to a glass-stoppered flask containing 100 ml. of water. The condenser and the second receiver were rinsed with carbon tetrachloride. Then 20 ml. of concentrated hydrochloric acid were added to the first receiver in order to bring the normality to 10 *N*, and three more extractions with 20-ml. portions of carbon tetrachloride were carried out. All rinsings and extracts were transferred to the flask mentioned above; this was then shaken mechanically for 4 hours at a speed such that the phases were just kept thoroughly mixed at all times. The aqueous phase was then transferred to a beaker, made alkaline with concentrated ammonium hydroxide, and evaporated to 5 ml. Colorimetric determination followed. The results are summarized in Table I.

Distillation from Sulfuric Acid. Instead of the 20-ml. of concentrated hydrochloric acid, 15 ml. of 1 to 1 sulfuric acid and 3 ml. of 1 to 1 hydrochloric acid were used in the distilling flask; 50 ml. of water were used in each of the first two receivers. The distillation was conducted for 15 to 20 minutes at about 105° C., until fumes became visible. The distillate was made alkaline and evaporated as before, and colorimetric determination was carried out. The results are summarized in Table I.

Table I. Distillation from Hydrochloric or Sulfuric Acid

	Hydrochloric Acid Method			Sulfuric Acid Method		
Ge Added γ	Ge recovered γ	No. of detns.	Av. deviation γ	Ge recovered γ	No. of detns.	Av. deviation γ
2.0	1.9	3	0.0	2.1	6	0.3
4.0	4.9	2	0.6	...	...	...
6.1	6.3	2	0.5	6.0	4	0.2
8.1	8.5	3	0.5	...	...	...
10.2	9.7	8	0.9	9.6	3	0.4
12.2	12.1	4	0.7	...	...	...
14.2	14.9	2	1.0	...	...	...
16.2	17.2	4	2.8	15.9	4	0.5
18.3	18.1	3	1.6	...	...	...
20.3	20.3	4	0.4	20.4	3	0.7
22.3	22.3	2	0.2	...	...	...
24.4	24.1	1	...	...	...	...
26.4	26.1	2	0.9	...	...	...
30.5	30.0	2	0.7	...	...	...

Interferences of Other Elements. A series of elements was tested for interference in both the hydrochloric and the sulfuric acid distillation methods: arsenic, selenium, antimony, tin, aluminum, iron, chromium, copper, zinc, mercury, manganese, silicon, lead, bismuth, cadmium, titanium, tellurium, and molybdenum. The equivalent of 2 mg. of each element, in the form of a solution of a suitable compound, was used, and tested both alone and in conjunction with 10.2 micrograms of germanium.

Arsenic did not interfere in either method, although it can be presumed to distill quantitatively, and was also shown to accompany germanium quantitatively in the extraction with carbon tetrachloride; it does not, however, give a colored product with hematoxylin. This is another advantage of the hematoxylin method, for, although it is possible to separate germanium and arsenic by distillation (*1*, *8*), this step is unnecessary here. Antimony did not interfere in the distillation from hydrochloric acid, but gave high results in the sulfuric acid method, probably owing to codistillation; it forms a colored complex with hematoxylin (*20*). The presence of tin or lead caused low results in the distillation from sulfuric acid, but not in the distillation from hydrochloric acid. In the case of lead, this may be due to adsorption of germanium on the lead sulfate produced. No other elements interfered.

Arsenic, antimony, and tin were also tested as to their behavior in an extraction from hydrochloric acid into carbon tetrachloride. Enough difference in extractability was found to warrant hope that these three elements may be separated from each other and from germanium without distillation, but the subject was not pursued further.

DETERMINATION OF GERMANIUM IN CUSTOMS ZINC CONCENTRATE AND ZINC OXIDE FUME

A 0.3- to 0.5-gram sample was weighed in a small platinum crucible. The customs zinc concentrate was then roasted at 900° C. for 15 minutes to convert sulfides to oxides; the zinc oxide fume was fused with 0.1 gram of sodium carbonate and 0.1 gram of potassium carbonate at 900° C. for 15 minutes. After cooling, the crucible was dropped in the distilling flask, and a distillation either from hydrochloric or from sulfuric acid was carried out, as described above. A second distillation was sometimes necessary; the results from both were added to give the final result. "Salted" samples were analyzed by adding germanium in the form of a standard solution, and evaporating to dryness at 100° C. before roasting or fusing with carbonate. There was no significant loss of germanium in roasting or carbonate fusion, as shown by testing the fumes from each process from a 10-gram sample.

Table II shows that the sulfuric acid method gave low results with both materials, especially with zinc oxide fume, and that the differences in results obtained with salted and unsalted samples in these cases were considerable. This can probably be explained as due to the presence of lead which interferes. Spectrographic examination of the distillation residues disclosed the presence of more than 5 micrograms of germanium in the sulfuric acid distillation of zinc oxide fume, but not in the other cases.

SUMMARY

Hematoxylin warmed with hydrogen peroxide furnishes a stable reagent suitable for the colorimetric determination of germanium. The color reaction produces an insoluble product of the form $Ge(Ht)_2$, but the addition of gelatin yields a stable suspension satisfactory for color measurement. The pH must be maintained at 3.2 by a phthalate buffer. The optimum concentration range for which this colorimetric procedure may be applied is 0.4 to 1.2 p.p.m. Germanium may be isolated from most other metallic elements by distillation from hydrochloric acid or sulfuric acid. In the former case the large amount of acid carried over yields a distillate too concentrated in electrolyte for the successful application of this colorimetric procedure to the whole. In this case germanium may be quantitatively extracted from 10 *N* hydrochloric acid into carbon tetrachloride, and may subsequently be extracted back into water. The colorimetric procedure may be applied to this evaporated aqueous extract. Distillation from sulfuric acid proved satisfactory for many cases because only a small amount of hydrochloric acid is carried over with the germanium. In this case some interference was observed when tin, lead, or antimony was present with germanium. Many other elements gave no interference in either procedure for the isolation and subsequent determination of this element.

Table II. Determination of Germanium in Customs Zinc Concentrate and Zinc Oxide Fume

Sample	Additional Ge γ	Distillation Method	Av. Ge Found %	No. of Detns.	Av. Deviation %
Customs zinc conc.	None	H_2SO_4	0.00402	6	0.00019
	10.2	H_2SO_4	0.00356	4	0.00017
	None	HCl	0.00494	10	0.00017
	2.0	HCl	0.00479	2	0.00033
	10.2	HCl	0.00501	4	0.00029
Zinc oxide fume	None	H_2SO_4	0.00267	8	0.00039
	10.2	H_2SO_4	0.00127	4	0.00050
	None	HCl	0.00414	6	0.00026
	2.0	HCl	0.00427	4	0.00036
	10.2	HCl	0.00410	4	0.00037

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Dumas Microdetermination of Nitrogen in Refractory Organic Compounds

Modification of Zimmermann's Method

PAUL D. STERNGLANZ, RUTH C. THOMPSON, and WALTER L. SAVELL
Chemical Research Division, Remington Rand, Inc., South Norwalk, Conn.

A REVIEW of procedures for the Dumas microdetermination of nitrogen in refractory substances has shown the need for a simple method applicable to both tractable and refractory compounds. Some of the existing methods which claim excellent results (*9, 18*) are not of general applicability—for instance, the potassium chlorate method of Spies and Harris (*18*) and the copper acetate method of Hayman and Adler (*9*) were applied to pteridines without success (*1*). Brancone and Fulmor (*1*) were able to analyze pteridines merely by raising the temperature of the movable burner to 900° C.; oxidation aids were omitted. The results, however, show a somewhat greater spread than might be desired.

Other Dumas modifications for refractory compounds have been published. One (*11*) involves the use of nickel oxide as combustion tube filling, a temperature of 1000° C., and a rather complicated setup. In another (*22*), oxygen generated by the decomposition of 30% hydrogen peroxide is introduced. All these methods have in common an inherent drawback of the conventional Dumas method: A carefully controlled combustion with painstaking observation of bubble speed is required, if accuracy and reproducibility are to be achieved (*14*). If the Dumas method is adapted to the analysis of refractory compounds by adding oxidation aids (*7, 9, 18*), the changes involved may cause inconsistent results, as some investigators have reported (*1, 8, 10, 17*). Without certain modifications, however, refractory compounds, such as certain pyrimidines, purines, and pteridines, give extremely erratic results (*1, 8–10, 12, 13, 17, 18*).

A review of procedures for Dumas microdetermination of nitrogen in refractory substances has shown the need for a simple method applicable to both tractable and refractory compounds. Some existing methods are not of general applicability, and all require a carefully controlled combustion with painstaking observation of bubble speed. Zimmermann's method, designed to facilitate the analysis of tractable compounds, eliminates concern about bubble speed. An attempt was made to simplify this method and to extend it to the analysis of such refractory substances as certain pyrimidines, purines, and pteridines. The procedure, simplified by adapting the tube filling to a boat combustion, was successfully applied to tractable compounds. Refractory compounds required the addition of an oxidation catalyst. Cobaltic oxide was found to be suitable. The movable burner was kept at a temperature of 800° to 830° C. The mixing chamber was redesigned. The automatic setup was replaced by inexpensive standard American equipment. The proposed method is quick and simple, and requires no special care on the part of the operator.

Concern about bubble speed was eliminated in a method published by Zimmermann in 1943 (*23*). His Dumas modification was designed to facilitate the analysis of compounds of normal combustion behavior. In his setup, the precautions which would be required during the combustion period in the conventional Dumas method became superfluous.

> During the combustion period the gases are blocked at the three way stopcock of the nitrometer, and are conducted into a special mixing chamber located at the opposite end of the tube. Here the gases are mixed and diluted with carbon dioxide. Gases to be reduced, such as oxides of nitrogen, and gases to be oxidized, such as carbon monoxide, are now present in a lower concentration. The dilution in the chamber allows the mixed gases to be driven through the combustion tube much faster (*23*) than is feasible in the conventional Dumas method. Equally important is the fact that a uniform rate of gas flow through the combustion tube is readily maintained by this procedure (*3*).

Although Zimmermann's method is a considerable improvement over other Dumas modifications, adherence to Pregl's way of mixing the sample with copper oxide and transferring it from a mixing tube to the combustion tube is objectionable, as several investigators have stated (*13, 18*). Also, Zimmermann's change of the temporary filling from the 40- to 100-mesh copper oxide (as specified by Niederl, *14*) to a fine powder seemed undesirable. Such fine powder in a 15-cm. layer retards the passage of the combustion gases (*16*). It seemed preferable, therefore, to distribute the sample in a combustion boat and to use coarser copper oxide. With these changes, the method was successfully applied in this laboratory to tractable compounds.

An attempt was then made to extend the Zimmermann method to the analysis of refractory compounds. The results which were obtained with 4-amino-6-hydroxy-2-thiol pyrimidine monohydrate were found to be low. It was, therefore, necessary to develop a modification of the method. Introduction of an oxidation aid was considered. Because the gaseous combustion products enter the mixing chamber rather than the nitrometer during the combustion, the increased rate of evolution of gases could not affect the rate of gas flow into the nitrometer. Potassium chlorate or chromates were inconvenient to use because they are likely to fuse the combustion boat to the combustion tube. Cobaltic oxide, however, was found to be suitable. Its catalytic oxidizing efficiency has been reported by Campbell and Gray (*4*).

A temperature of 800° to 830° C. for the movable burner was found adequate for even difficultly combustible compounds. A manual adaptation of Zimmermann's setup was devised, so that available, inexpensive, American standard equipment (*14, 20*) could be used. The mixing chamber was redesigned, as discussed under Apparatus.

The modification described gives accurate and precise results for tractable and refractory compounds.

REAGENTS

Coarse and fine copper oxide, as described by Niederl (*14*); cobaltic oxide, black, C.P., Eimer & Amend.

APPARATUS

The apparatus is arranged as shown in Figure 1. Carbon dioxide is supplied by a double Kipp generator, according to Niederl (*14, 20*). The gasometer used is of standard make (*14, 20*).

A modification of Zimmermann's mixing chamber is inserted between the Niederl gasometer and the combustion tube (Figure 2). One of the capillary tubes joins the mixing chamber with the Niederl gasometer by means of pressure tubing. The other capillary tube, drawn out to a tip and fitted with a micro rubber stopper, joins the chamber with the combustion tube. The mixing chamber was redesigned to guard against dead space; the mercury can be raised almost to the stopcocks, displacing the greater part of the combustion gases. The chance of forcing mercury into the combustion tube is minimized by having the original horizontal capillary exit changed to an almost vertical one. Stopcock *E* (Figure 1), not present in the Zimmermann chamber, was added because of its usefulness during the sweeping-out process.

A stationary electric furnace (Eimer & Amend, Item 20-286), a 520-mm. standard length microcombustion tube of Vycor No. 790, and a movable burner of the Meker type with a 42-mm. grid (Eimer & Amend, Item 3-902) are utilized.

The nitrometer used is of the Stehr type (*19*), as supplied by Arthur H. Thomas Co., Philadelphia. Instead of an iron wire to loosen nitrogen bubbles from the mercury surface (*15*), an iron bar encased in borosilicate glass (about 15 mm. long and 5 mm. in diameter) is used, as well as several steel chips. The chips and bar are held by a horseshoe magnet at the mercury–potassium hydroxide interface just above the place where the gases enter the nitrometer. Forced by this device to rise directly, the bubbles cannot combine at the mercury–potassium hydroxide interface to form oversize bubbles which stick in the neck of the nitrometer.

METHOD

Tube Filling. The proposed modification requires changes in Zimmermann's tube filling as well as in his procedure. The permanent filling consists of a 27-cm. layer of coarse copper oxide interrupted twice by reduced copper gauze rolls (each about 2.5 cm. long) and the appropriate asbestos plugs. The first copper roll is located 7 cm. from the tapered end of the tube; the second, 16 cm. (Figure 1). At the 27-cm. mark the temporary filling begins. This consists, first, of a 3-cm. layer of fine copper oxide to which about 20 mg. of copper acetate may be added.

The sample, weighed in a charging tube, is transferred to a 5-cm. porcelain boat (size 00). Then 50 mg. of cobaltic oxide are mixed intimately with the sample by means of a bit of platinum wire. The wire is allowed to remain in the boat after the mixing is completed. Filled to the brim with fine copper oxide, the boat is pushed into the tube against the 3-cm. layer. Then a 2-cm. layer of fine copper oxide is added, followed by enough coarse copper oxide to fill the rest of the tube.

The system of clamping the tube tip down in an almost horizontal position before installing the boat and the temporary filling was found to be highly satisfactory. The copper oxide can be charged into the tube with little trouble by means of a chute (any conveniently bent metal sheet) and a wire poker. The tube should be tapped lightly during the charging to prevent the formation of air gaps. The temporary filling may be re-used until the copper oxide shows signs of being reduced.

Procedure. The tube is attached to the train; care is taken that a 4- to 5-cm. layer of copper oxide extends outside the stationary furnace to serve as cold zone. The air in the system is displaced by carbon dioxide while the furnace heats up to 700° C. At about 550° C., the usual test for microbubbles should be made. If the result is satisfactory, stopcock *D* is closed, *E* is opened, and *F* is opened to the air. The carbon dioxide in the mixing chamber is displaced by mercury up to the capillary tubes by raising leveling container *C*-2. Then the two mercury surfaces should be on the same level. The three-way stopcock, *F*, is then moved so that it is partially open to the nitrometer. To prevent the gases from entering the nitrometer, *C*-3 is raised as high as the top socket joint (*3*).

When the stationary furnace is heated to 700° to 750° C., the combustion is started. The Meker burner is set under the tube at a point about 13 cm. from the sample and is slowly moved toward the furnace. The first combustion lasts 7 minutes; the second, 5 minutes. A 10-cm. square of Nichrome gauze, conveniently bent, is used to reflect the heat toward the top of the tube; a Nichrome gauze roll 7 cm. long surrounds the tube. Care must be taken, especially during the first combustion, to have 4 cm. of the tube red hot before the Meker burner is moved ahead (*23*).

During the first combustion, *C*-2 is lowered as needed to avoid having excess pressure in the system (*3*). At the end of the second combustion, *C*-2 is lowered so that its mercury level is about 5 mm. below the mercury level of the mixing chamber. Then *C*-3 is set on a level with the bottom of the nitrometer. Stopcocks *C* and *D* are opened in this order to allow 50 ml. of carbon dioxide to pass within 7 minutes from the Niederl gasometer into the mixing chamber under a pressure head of 50 mm. of mercury. Stopcock *F* was left partially open to the nitrometer at the beginning of the combustion. If the gases enter the nitrometer too rapidly now, a fine adjustment of this stopcock should be made (*3*). After the 50 ml. of carbon dioxide are displaced by gradually raising *C*-1, *D* is closed and the gases in the mixing chamber are displaced (in about 4 minutes) by gradually raising *C*-2.

Sweeping is now begun. *E* is closed and *C*-2 is lowered until its mercury level is about 60 mm. lower than that of the mixing chamber. It is important to drive the carbon dioxide into the chamber with a considerable pressure head (about 100 mm. of mercury), so that the entering carbon dioxide stirs and mixes the remaining traces of nitrogen. When 30 ml. of carbon dioxide are driven in, *D* is closed and *E* is opened. Again the gases in the chamber are displaced by mercury. This sweeping procedure should be carried out two or three times, depending on the diminution of the gas bubbles to microbubbles. The

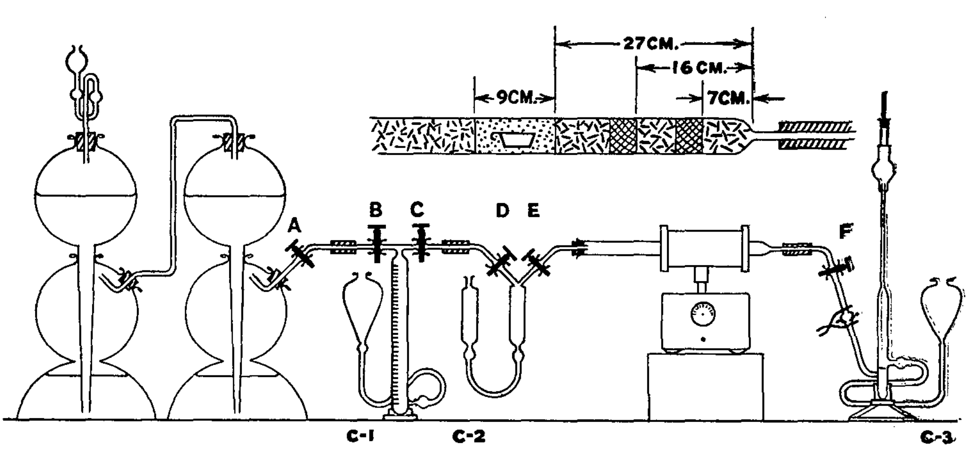

Figure 1. Over-All View of Apparatus and Enlargement of Filled Combustion Tube

Capital letters designate stopcocks
C-1, *C*-2, *C*-3 designate leveling bulbs

volume is read after 30 minutes, and a 1.1% volume correction applied. The temperature of the air near the nitrometer is taken as the temperature of the collected nitrogen.

DISCUSSION AND RESULTS

A temperature of 800° to 830° C. for the part of the tube heated by the movable burner has been found adequate for the combustion of all the compounds analyzed. The temperature was measured inside the combustion tube using a platinum–platinum + 10% rhodium thermocouple. Zimmermann had simply stated that a high temperature is needed for the movable burner (*23*). It seemed inadvisable to use a temperature lower than 800° C. During the pyrolysis of the sample, methane might be formed. Because methane is not completely oxidized when passing over copper oxide heated lower than 800° C. (*21*), high results would be obtained. Temperatures much higher than 830° C. are undesirable because they shorten the life of the combustion tube.

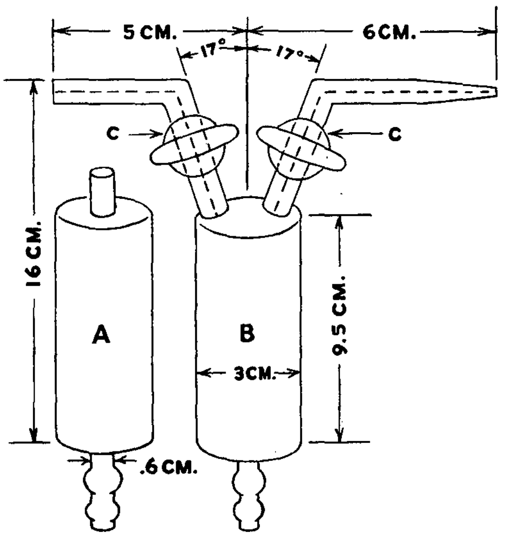

Figure 2. Mixing Chamber

A. **Leveling container**
B. **Mixing chamber, 50-ml. capacity, made of wide borosilicate glass tubing**
C. **Precision stopcocks with 2-mm. bore capillary tubing (Eck and Krebs item 5004)**
50-cm. length of rubber tubing joins *A* and *B*

Cobaltic oxide was chosen because of its catalytic oxidizing efficiency (*4*). Other attributes favorable to its use are nonvolatility before and after reduction, and lack of affinity for nitrogen at the temperature applied (*5*). Cobaltic oxide is converted to cobalto-cobaltic oxide at 372° C. (*2*). Its dissociation pressure according to the reaction $Co_3O_4 \rightarrow 3CoO + {}^1/_2O_2$ is about 20 mm. of mercury at 825° C. (*6*). Therefore, it functions to some extent as a generator of oxygen, which is especially needed for the combustion of refractory compounds. In this respect it is superior to copper oxide, which has a much lower dissociation pressure at this temperature (about 2 mm. of mercury).

Copper acetate may be added to the temporary filling of the combustion tube to minimize concern about bubbles sticking in the constricted part of the nitrometer. The carbon dioxide produced when the movable burner heats the copper salt helps to drive the combustion gases out of the tube, into the mixing chamber. In this way, there is an effective mixing and dilution of the gases with carbon dioxide. Later, when the diluted gases enter the nitrometer, the bubbles which rise are smaller than they would be, were the copper salt omitted.

Table I. Nitrogen Results Obtained by Modified Zimmermann Method

Compound	Nitrogen, % Calcd.	Proposed modification	Proposed modification without cobaltic oxide
Tractable Compounds			
Glycine	18.66	18.67, 18.76 18.76	18.80, 18.72 18.62
Benzyl isothiourea hydrochloride	13.82	13.84, 14.01 13.76, 13.76	13.73, 13.96
Refractory Compounds			
4-Amino-6-hydroxy-2-thiol pyrimidine monohydrate[a]	26.07	26.22, 25.95 25.80, 25.94 25.88, 26.09	25.59, 25.91 25.48, 25.58 25.62
Vitamin B_1 (thiamine hydrochloride)	16.61	16.72, 16.70 16.54, 16.72 16.65	16.73 16.89
2-Amino-4-hydroxyl-6-methylpteridine[b]	39.53	39.56, 39.74 39.31, 39.47 39.62, 39.55	...
2,4-Diamino-6,7-diphenylpteridine[c]	26.74	26.77, 26.91 26.74, 26.79	26.87 26.74
6-Amino-2-hydroxy purine D-riboside[d]	24.73	24.76, 24.65 24.62, 24.70 24.48	24.38 24.40

[a] Supplied through the courtesy of L. W. Hartzel, Remington Rand, Inc., South Norwalk, Conn.

[b] Supplied through the courtesy of L. M. Brancone, Lederle Laboratories Division, American Cyanamid Co., Pearl River, N. Y.

[c] Supplied through the courtesy of C. K. Cain, McNeil Laboratories, Inc., Philadelphia, Pa.

[d] Supplied through the courtesy of J. R. Spies, Allergen Research Division, U. S. Department of Agriculture, Washington, D. C.

It was established that amounts of cobaltic oxide up to 100 mg. do not increase the blank. To make sure that cobaltic oxide has no other adverse effects, the proposed modification was tested on two compounds of normal combustion behavior. The results are shown in Table I.

After these preliminary tests, the method was tried on refractory compounds; satisfactory results were obtained (Table I). Experiments were then repeated, omitting cobaltic oxide. The results obtained with 4-amino-6-hydroxy-2-thiol pyrimidine were low and erratic (Table I). Although the other refractory compounds could be analyzed without cobaltic oxide, it is considered safer to use it in all cases.

The compounds chosen in Table I have been reported in the literature as refractory (*1*, *9*, *12*, *18*) and, therefore, were considered suitable for testing the proposed modification. All substances were checked for purity by carbon, hydrogen, and moisture analyses, and for chlorine and sulfur, when those elements were present. In particular, 2,4-diamino-6,7-diphenylpteridine was chosen because it was reported that nitrogen analyses could be obtained only by the Kjeldahl method (*12*).

To compare the precision of the proposed modification with that obtained by Brancone and Fulmor (*1*), 2-amino-4-hydroxyl-6-methylpteridine was analyzed. The average deviation of the arithmetical mean of 39.54% is ±0.041% for the proposed modification, compared to their ±0.082%. The accuracy of the arithmetical mean of 39.54% is satisfactory in both cases, the theoretical value being 39.53%.

ACKNOWLEDGMENT

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NOTES ON ANALYTICAL PROCEDURES . . .

Constant-Current Supply for Coulometric Analysis

CHARLES N. REILLEY, W. DONALD COOKE, AND N. HOWELL FURMAN
Princeton University, Princeton, N. J.

THERE has been much recent interest in coulometric methods in which the time required for a constant current to complete a chemical change is measured. The constant current has been obtained by the use of a high-voltage source, such as a rack of storage batteries (*2*), or a regulated power supply (*1, 4*), in conjunction with a resistor in series to regulate the current. These systems work well for coulometric micro "titrations," where currents of 20 ma. or less are employed. If only small constant currents are available the determination of macro quantities of substances extends the time requirement unduly. With these systems for constant current, macro work requires either an averaging of the current (*10*) or a continuous varying of a series resistor (*2*) to compensate for changes in the resistance of the electrolytic cell.

There are certain circuits known that maintain a constant current automatically.

Trishin (*11*) utilized a balanced circuit in which a galvanometer-phototube combination regulated the operation of a motor-driven potentiometer to adjust the voltage applied to the cell. Such circuits have the inherent slow response of mechanical feedback loops. Lingane (*7*) described another constant-current circuit that has a rather wide dead-zone regulation and a slow response caused by mechanical feedback. Elmore and Sands (*3*) have published details of a constant-current circuit for a mass spectrometer magnet that has a rapid response and excellent stability. This circuit is of a heavy-duty, high-current type that is more bulky and complicated than the circuit described here. Gittings (*5*) reported a general five-tube circuit of quick response, and regulation within 0.015%, according to theory. Details of circuit values and actual test runs were not reported.

The simple three-tube constant-current source described in this paper has been in use in this laboratory for 6 months. The current that it supplies to the electrolytic cell is almost independent of changes in cell resistance. In fact, a change of only 0.01% in the current through a standard resistor occurred when the cell was shorted at 150 ma. A constant voltage source of 200,000 volts would be required for a similar result with a conventional power supply. Regulation is so rapid that no transient deflection is seen on the galvanometer of the potentiometer that is used in testing the constancy of the current. By holding the current within very narrow limits, this supply allows the operator's attention to be directed to the course of the titration, particularly near the end point. Several cells may be used with the same power supply; the number depends on the currents drawn, the resistive values of the cells, and the regulation desired. Thus, with several cells, the operator can be preparing for additional titrations while one or more are in process. A trigger circuit similar to that of Lingane and Müller (*8*) has been used in this laboratory to open the time and current circuits at the end points of titrations.

DESCRIPTION OF CIRCUIT

The circuit in Figure 1 has two outputs, a regulated voltage output intended for use in microtitrations and a regulated current output for use in macrotitrations. Switch S_4 is open when constant current is employed and closed when constant voltage is

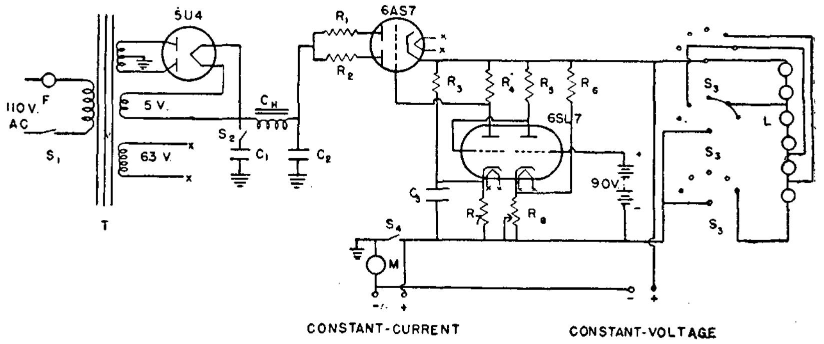

Figure 1. Schematic Diagram of Constant-Current and Constant-Voltage Supply

C_1.	2-mfd., 1000-volt capacitor
C_2.	8-mfd., 1000-volt capacitor
C_3.	0.1-mfd., 600-volt capacitor
C_H.	10-henry, 200-ma. filter reactor
F.	2-ampere fuse
L.	3- or 6-watt, 110-volt tungsten lamps
M.	0–200-ma. meter
R_1, R_2.	100-ohm, 10-watt resistors
R_3, R_6.	12,000-ohm, 25-watt resistors
R_4, R_5.	470,000-ohm, 2-watt resistors
R_7.	15,000-ohm, 25-watt resistor
R_8.	10,000-ohm, 25-watt variable resistor
S_1, S_2, S_4.	S.P.S.T. toggle switches
S_3.	3-circuit, 5-position switch
T.	425-0-425-volt, 165-ma. power transformer

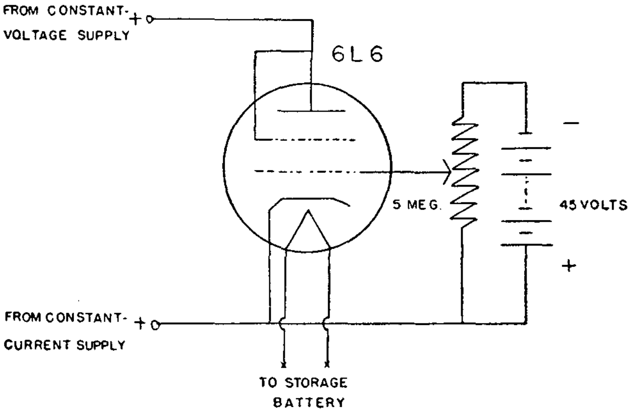

Figure 2. Variable-Current Circuit

used. The regulated current circuit is essentially a modified constant-voltage supply. When a constant voltage is placed across a constant resistance, constant current must result, according to Ohm's law.

Figure 1 shows the regulated voltage being applied to a resistance of lamps (L), resistors (R_3, R_4, R_5, R_6, R_7, R_8), and tube (6SL7). Because these resistances change little during operation, a constant current may be expected to flow through the cell. The constant-voltage circuit, centering around the 6SL7 and 6AS7, operates in the following manner: The grid potential of the input half of the 6SL7 is held constant by the 90-volt battery. Any variation in the voltage across the lamps causes a change in the cathode voltage of the 6SL7. This grid-cathode potential change is amplified by the right and then the left half of the 6SL7, and the resulting amplified change is applied to the control grids of the 6AS7 in correct phase to compensate for this variation. Regulation is dependent upon the gain of the 6SL7 circuit and 6AS7 tube. Drift is dependent upon the constancy of the resistors (especially R_6 and R_8), the resistance of the bulbs, and the filament voltage of the 6SL7.

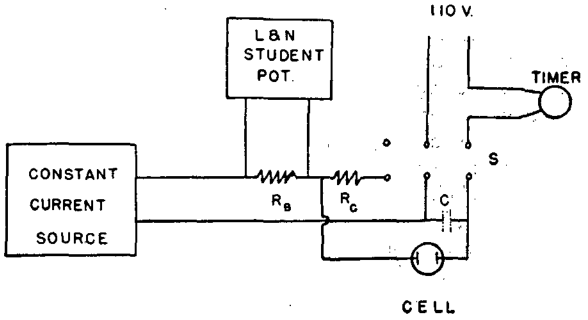

Figure 3. External Circuit for Macrotitrations

S.	**D.P.D.T. shorting-type switch**
R_A.	**Variable series resistor**
R_B.	**Standard resistor**
R_C.	**Dummy resistor (recommended when more than one cell is used) (same resistance as cell)**
C.	**5-mfd. paper capacitor (do not use if R_C is also used)**

The fluctuation caused by line voltage irregularities is due to a large extent to the variation of this heater potential (*3, 6*). Nonfrosted candelabra-base lamp bulbs (3- or 6-watt, 110-volt) are used in preference to wire-wound resistors, because the former reach energy equilibrium with their surroundings quickly and have a nonlinear resistance that favors a constant current (*6, 9*). They are also less bulky and less expensive than oil-immersed manganin-wire resistors (*3*). However, bulbs have a disadvantage in that the current can be varied only in fixed steps. If continuously variable current settings are necessary, the circuit in Figure 2 may be used in place of the light bulbs.

A storage battery was found to be essential in operating the filament of the 6L6 minimizing drift. However, the lamps have proved entirely satisfactory for use in the coulometric work. When no lamps are in the circuit, a minimum regulated current of approximately 28 ma. is passed by way of the 6SL7 and resistors R_3, R_4, R_5, R_6, R_7, and R_8. Best regulation is obtained when a voltage of 325 to 400 volts exists between the input to the resistors, R_1 and R_2, and the negative side of the bulbs. This means that the voltage from the power supply filter minus the voltage drop across the cell should be 325 to 400 volts. When the current is high enough (ca. 150 ma.) through a cell to bring the voltage below 325 volts, condenser C_1 is placed in the circuit by switch S_2 to increase the total voltage so that the difference will fall within the recommended range. The battery is used in preference to a voltage regulator tube for better stability. Battery life should be nearly equivalent to shelf life, since very little current is drawn. Care should be taken to place the battery away from the warmer parts of the instrument, as its voltage is sensitive to temperature (*6*). Resistors are of the high-wattage type to decrease thermal drift. Connections should be made electrically and mechanically sound.

OPERATION

With switch S_4 (Figure 1) in constant-voltage position, rheostat R_8 is adjusted until the regulated output voltage measures approximately 250 volts. This adjustment need be repeated only occasionally according to the aging of the tubes or reference battery. The supply is now ready for use as a regulated-current or regulated-voltage source, depending upon position of switch S_4 (see Figures 3 and 4). A warm-up period of about 5 to 10 minutes is needed for 0.1% regulation (mostly drift) with increasing regulation for longer periods.

In actual operation it is undesirable to short the titration cell when not actually titrating, inasmuch as a back current will flow through the cell and lead to high results. This back current is caused by having two half-cells of different potential connected together. One half-cell may be the hydrogen or oxygen in contact with platinum, while the other may be the platinum in contact with the titrating solution. Therefore the switching arrangement in Figures 3 and 4 is employed. Thus the input from the supply is shorted (or dummy load substituted), the leads to the cell are opened, and the clock is stopped in one movement. This mode of operation is chosen because opening the load causes no current to flow through the circuit, with a consequent warm-up drift of the resistors and bulbs when replaced in operation. For this reason also a shorting-type switch is employed, so that the load is never opened. If a relay is used as a switch, a condenser, C (Figure 3), may be used to pass current during the brief moment the switch is moving or whenever the shorting mechanism does not work properly.

Care should be taken not to jar the lamps while in operation, as this will alter their resistance, thus changing the current in the course of a titration. By varying the wattage and arrangements of bulbs, one may obtain several convenient current values. The circuit in Figure 1 uses switch S_3 to make various series and/or parallel connections with the lamps. The supply is usually left on overnight, saving the initial warm-up time and taking advantage of the superior stability obtained after long periods of warm-up.

RESULTS

The constant-current circuit was tested by measuring the current indirectly with a calibrated standard resistor (Knott Mfg.

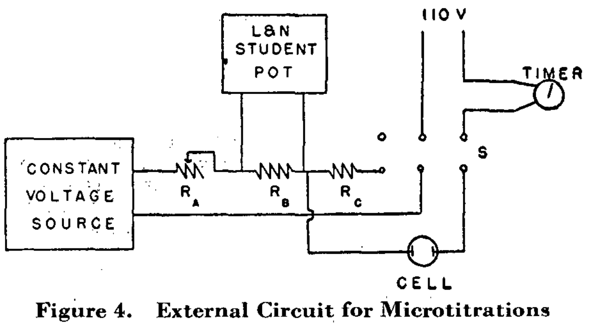

Figure 4. External Circuit for Microtitrations

S.	**D.P.D.T. shorting-type switch**
R_A.	**Variable series resistor**
R_B.	**Standard resistor**
R_C.	**Dummy resistor**

Table I. Performance of Constant-Current Circuit

(Stability over 1-hour period)

Mean Current, Ma.	Maximum Spread, %	Maximum Deviation, %	Mean Deviation, %
28.388	0.03	0.01	0.01
57.731	0.03	0.02	0.01
78.859	0.05	0.03	0.02
84.674	0.02	0.01	0.01
112.250	0.02	0.01	0.01
152.734	0.02	0.01	0.01

Table II. Performance of Constant-Voltage Circuit

(Variation of output with time)

Time, Hours	Voltage
0	256.10
14	256.44
17	256.50
22	256.52
39	256.50

Co., 10.001-ohm) in series with the dummy resistor (Figure 3); the voltage drop was measured with a Leeds & Northrup Type K potentiometer. After an initial warm-up period of 30 minutes, readings were taken for a period of 1 hour at 5-minute intervals (Table I). Short-range shifts about a mean position when the potentiometer is read continuously for a period of 1 minute were approximately 0.005% when the supply was connected directly to the power line and approximately 0.001% when connected to a constant-voltage transformer. A 5% change in line voltage caused an output change of 0.06%. Where line-voltage variations are severe, a constant-voltage transformer may be used.

The constant-voltage performance was determined with the circuit of Figure 4, using a 120,000-ohm manganin-wire resistor for R_A. The voltage drop across a 30-ohm standard resistor measured with a Leeds & Northrup student potentiometer was used in calculating the voltage of the output. The results are given in Table II. Adding a load of 90 ma. to the constant-voltage terminals of the supply (Figure 1) caused a change of 0.02% in the output voltage. A 5% fluctuation in line voltage is followed by a 0.10 to 0.15% change in output voltage.

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Identification and Separation of Amines Employing Beta-Resorcylic Acid

K. W. WILSON, FLOYD E. ANDERSON[1], AND ROBERT W. DONOHOE
West Virginia University, Morgantown, W. Va.

IT WAS observed that β-resorcylic acid forms crystalline salts with certain amines. This reaction has been studied to discover which amines form salts and to determine whether these salts would be suitable derivatives for identification of amines.

EXPERIMENTAL

Koppers β-resorcylic acid was purified as described in "Organic Syntheses" (*5*). This product was suspended in benzene and any residual moisture was removed by azeotropic distillation with benzene. The original Koppers product and the purified compound gave salts of equal purity.

Most of the amines were Eastman products, which were dried over solid potassium hydroxide and used directly without further purification.

The salts were prepared by dissolving 1.00 gram of β-resorcylic acid in 10 ml. of dry ether and adding the calculated amount of amine dropwise with shaking. Solid amines were dissolved in ether before adding. In most cases a crystalline salt formed immediately, but when an oil was produced it could be caused to crystallize by vigorous scratching with a metal spatula. When no visible reaction occurred, the mixture was allowed to stand overnight to ensure ample time for salt formation and crystallization. The salt was then removed by filtration, washed with dry ether, and dried in air. The product was crystallized from ethyl acetate until a constant melting point was obtained. When the amine is pure, the salt separates in a high state of purity and requires no recrystallization. The salts are almost insoluble in ether and are obtained in about 80% yield.

All reported decomposition points are corrected; they were taken in capillaries. The values represent, to the nearest degree, the temperatures at which the last crystals disappeared. Slightly lower decomposition points were obtained using the Fisher melting point apparatus.

The nitrogen analyses were done by the Kjeldahl method of Marcali and Rieman (*4*).

RESULTS AND DISCUSSION

The experimental results are summarized in Table I. The authors believe that these salts are not superior to the usual derivatives employed in the identification of primary and secondary amines; however, they should prove useful in the identification of tertiary amines. Accordingly, the table contains a relatively complete listing of common tertiary amines, but no attempt has been made to include all common primary and secondary amines.

The decomposition points are dependent to a slight extent on the rate of heating; however, if the temperature rise is not greater than 5° per minute the compounds decompose within a 1° range. The melting points of the different salts lie fairly close together; however, nearly any amine can be satisfactorily identified if its boiling point is also known. The salts are almost nonhydroscopic, but they will absorb a little moisture if allowed to stand uncovered for several weeks. The melting point of a mixture of two salts shows in most cases a definite lowering from the melting points of the pure salts (Table I). The compounds are very easily prepared; a pure dry derivative can be made in less than 10 minutes.

Aniline, ethylaniline, dimethylaniline, diethylaniline, *o*-toluidine, *p*-toluidine, *o*-anisidine, 1-naphthylamine, and isoquinoline formed no salts under the conditions of the experiment. There is no sharp dividing line which separates these amines from those listed in the table. Apparently as the base strength of the amine decreases the salts become gradually more soluble in ether and decompose less sharply. Salts can be obtained from the above amines by mixing β-resorcylic acid and the amine, using no ether or only a small amount of ether; however, they do not decompose sharply and cannot be recrystallized. Using the base strengths of various amines as obtained by Felsing and Biggs (*2*), Barron (*1*), and Hall and Sprinkle (*3*), it appears that amines more strongly basic than pyridine will form salts under these experimental conditions. (It is realized that base strengths measured in aqueous solution may not give an accurate comparison of base strengths in ether.) This generalization does not hold for two of the amines which were investigated; the weak base, quinoline, forms a salt, while diethylaniline, which is reported to be a considerably stronger base than pyridine (*3*), gives no salt. It would be difficult to predict with absolute

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[1] Present address, Pyridine Corp., Yonkers, N. Y

Table I. Experimental Results

Amine	M.P. (Corr.) of β-Resorcylate	Formula of Salt	% N Theory	% N Found
Mono-*n*-propyl	123	$C_{10}H_{15}O_4N$	6.57	6.50
Mono-*n*-butyl	133	$C_{11}H_{17}O_4N$	6.17	6.10
Monoisoamyl	138	$C_{12}H_{19}O_4N$	5.82	5.83
Diethyl	128	$C_{11}H_{17}O_4N$	6.17	6.28
Di-*n*-propyl	97	$C_{13}H_{21}O_4N$	5.49	5.39
Diisobutyl	144	$C_{15}H_{25}O_4N$	4.95	4.93
Di-*sec*-butyl	146	$C_{15}H_{25}O_4N$	4.95	4.93
Di-*n*-butyl	123	$C_{15}H_{25}O_4N$	4.95	4.91
Diisoamyl	146	$C_{17}H_{29}O_4N$	4.49	4.30
Triethyl	120	$C_{13}H_{21}O_4N$	5.49	5.46
Tri-*n*-butyl	121	$C_{19}H_{33}O_4N$	4.12	4.24
Tribenzyl	141	$C_{28}H_{27}O_4N$	3.17	3.19
Pyridine	145	$C_{12}H_{11}O_4N$	6.01	5.78
α-Picoline	141	$C_{13}H_{13}O_4N$	5.67	5.78
γ-Picoline	125	$C_{13}H_{13}O_4N$	5.67	5.54
2,4-Lutidine	143	$C_{14}H_{15}O_4N$	5.36	5.41
2-Vinylpyridine	113	$C_{14}H_{13}O_4N$	5.40	5.49
Quinoline	128	$C_{16}H_{13}O_4N$	4.95	5.11
Quinaldine	145	$C_{17}H_{15}O_4N$	4.72	4.88
8-Quinolinol	150	$C_{16}H_{13}O_5N$	4.68	4.53
β-Diethylaminoethanol	91	$C_{13}H_{20}O_5N$	5.16	5.18
p-Anisidine	143	$C_{14}H_{15}O_5N$	4.88	4.91
p-Phenetidine	137	$C_{15}H_{17}O_5N$	4.65	4.56
Triethanolamine	Oil	.....	..	..
Di-*o*-tolylguanidine	107–115[a]	.....	..	..
Mixture of diisobutyl and di-*sec*-butyl	138–142	.....	..	..
Mixture of triethyl and tri-*n*-butyl	103–108	.....	..	..
Mixture of pyridine and α-picoline	130–132	.....	..	..
Mixture of mono-*n*-butyl and monoisoamyl	132–133	.....	..	..

[a] After 4 recrystallizations.

certainty whether or not a given amine would form a salt, but the correlation between base strength and salt formation seems to be applicable in most cases.

SEPARATION OF MIXTURES OF AMINES

The fact that β-resorcylic acid does not form salts with most aromatic amines suggested that it might be used in the separation of mixtures of various amines.

The separation of quinoline and aniline encountered in the Skraup synthesis can be accomplished by this method.

A mixture of 0.84 gram of quinoline and 0.66 gram of aniline was added to 2.00 grams of β-resorcylic acid in 15 ml. of ether. After standing overnight the quinoline β-resorcylate was removed by filtration, washed with a small amount of ether (the salt is slightly soluble in ether), and dried in air; 1.4 grams of quinoline β-resorcylate were isolated, representing 78% recovery of quinoline. Aniline was recovered by evaporation of the ether from the filtrate after removal of the excess β-resorcylic acid. The acid was removed by washing with successive portions of sodium carbonate solution and drying over solid sodium hydroxide; 0.35 gram of aniline was recovered, representing 53% of the original amount.

A mixture of 1.00 gram of pyridine and 1.00 gram of dimethylaniline was separated by treatment with 3.0 grams of β-resorcylic acid in 25 ml. of ether in a manner similar to that described above; 2.51 grams of pyridine β-resorcylate were isolated, representing 85% recovery of pyridine. Recovery of dimethylaniline was practically quantitative.

A mixture of 1.20 grams of tri-*n*-butylamine and 0.93 gram of 2-naphthylamine was separated by treatment with 2.0 grams of β-resorcylic acid in 15 ml. of ether as above; 1.5 grams of tri-*n*-butylamine β-resorcylate were isolated, representing 68% recovery of the amine, and 0.85 gram (92%) of the 2-naphthylamine was recovered.

The free amines can be regenerated from the β-resorcylates simply by shaking the salt with sodium carbonate solution or sodium hydroxide solution. It seems probable that these salts might find use in isolation of amines from reaction mixtures as well as in separation of mixtures of amines.

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Paper Chromatography of Volatile Acids

E. P. KENNEDY[1] AND H. A. BARKER

Division of Plant Biochemistry, University of California, Berkeley, Calif.

DURING an investigation of the fatty acid metabolism of the bacterium *Clostridium kluyveri*, it became necessary to identify and separate small amounts (1 to 2 micromoles) of volatile fatty acids ranging in chain length from 2 to 6 carbon atoms. The valuable method of Elsden (*2*), based on chromatography of the fatty acid mixture on silica, could not be used because it requires considerably larger amounts of material. Therefore a paper chromatographic method was developed that would permit the separation and identification of fatty acids in micromole quantities.

The separation of nonvolatile organic acids by chromatography on paper has been described by Lugg and Overell (*5*), but in this method the substances to be separated are applied to the paper as the free acids, a technique that obviously cannot be used with volatile acids. The conversion of volatile acids to their nonvolatile hydroxamic acid derivatives by the method of Fink and Fink (*3*) is objectionable because it involves several additional steps. In the method described in this report, the volatile acids are applied to the paper as ammonium salts, and the chromatograms are developed in solvents containing free ammonia, so that the acids are present at all times as the completely ionized ammonium salts. The location of the spots after development is accomplished by spraying the dried paper with bromophenol blue indicator, made acid with a little citric acid.

Since this method was worked out, two papers by Brown and Hall (*1*) and Hiscox and Berridge (*4*) have appeared, which describe the paper chromatography of volatile acids in ammonia-butanol mixtures. The method described below, while similar in principle, differs in important details and in the authors' hands appears to offer some advantages. In particular, the recommended indicator gives a more even background and sharply defined spots, the use of ammonium salts eliminates the intense and frequently confusing alkaline spots due to other cations, and the pretreatment of the paper with oxalic acid eliminates "ghost" spots.

EXPERIMENTAL

Whatman No. 1 filter paper was used throughout the study. It was found necessary to wash the paper before use in order to avoid troublesome streaking and ghost spots. Good results were obtained when the paper was thoroughly washed before use with 1% oxalic acid, then with copious amounts of distilled water, and finally dried at room temperature.

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[1] Present address, Biochemical Research Laboratory, Massachusetts General Hospital, Boston, Mass.

Unidimensional chromatograms, made by the "ascending method," were used in most of these experiments. The chromatograms were developed at room temperature (20–23° C.) for 6 to 8 hours. Thoroughly washed, dried papers 45 cm. in length and 25 cm. in width were used, and the ammonium salts of the acids were applied to a starting line 2.5 cm. from the bottom of the paper, usually in 0.01 ml. of aqueous solution, containing 0.5 to 1.5 micromoles of each acid. If the fatty acids were added to the paper as the sodium salts, as in the method of Brown and Hall (*1*), the rates of migration of the acids with ethyl alcohol–ammonia as the developing solvent were considerably slower, and regions of excess alkalinity usually marked the tracks of the acids. If a solution of the sodium salts was first mixed with an equimolar amount of ammonium sulfate and made alkaline with a little free ammonia, and this mixture was applied to the paper, the rates of migration were then approximately the same as those of the pure ammonium salts alone. After application of the salts of the acids, the paper was rolled into a cylinder and pinned together, and the chromatogram was developed.

A number of developing solvents were used successfully. These included aqueous ethyl alcohol–ammonia solutions, aqueous acetone–ammonia, and aqueous butanol–ammonia. With the first two solvents, which are miscible with water, the R_f values could be altered considerably by varying the percentage of water. In general, the addition of a larger portion of water to the mixture caused the organic acids to travel more rapidly on the chromatogram. This flexibility of such water-miscible solvents may prove useful in separating the ammonium salts of dibasic acids which do not move appreciably in the aqueous ammonia–butanol mixture described by Brown and Hall.

A simple solvent mixture that proved useful in this work was composed of 100 ml. of 95% ethyl alcohol, to which was added 1 ml. of concentrated ammonium hydroxide. R_f values of a number of acids in this system are shown in Table I.

After development of the chromatogram, the papers were dried in an oven at 100° C. for 5 minutes. The spots were then located by spraying with a solution of 50 mg. of bromophenol blue in 100 ml. of water, made acid with 200 mg. of citric acid. Because of the buffer capacity of the acid anions, the location of the spots is shown by the intense blue (alkaline) color of the indicator in these regions, while the background is orange-yellow. This method of locating the spots was found to be more satisfactory than the use of bromocresol green made alkaline with a little sodium hydroxide (*1*, *4*).

Table I. R_f Values of Acids in Ammoniacal Ethyl Alcohol Solution

Acid	R_f
Formic	0.31
Acetic	0.33
Propionic	0.44
n-Butyric	0.54
n-Valeric	0.60
n-Caproic	0.68
n-Heptanoic	0.72
n-Octanoic	0.76
Vinylacetic	0.46
n-β-Ketohexanoic	0.53

In experiments in which radioactive fatty acids were to be separated, and it was desired to make radioautographs of the chromatograms, the papers were not sprayed with indicator, but instead were sprayed before drying with a 0.5 *M* solution of potassium monohydrogen phosphate, which fixes the acids on the paper as the potassium salts. Radioautographs of the papers may then be made by conventional techniques.

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Modified Photometric Determination of Copper in Ferrous Alloys

KENDALL W. NANCE
Kaiser Steel Corp., Fontana, Calif.

THE photometric determination of copper in ferrous alloys, according to the method of Dunleavy, Wiberley, and Harley (*1*), may be modified to obviate the use of a pH meter. Such a modification simplifies the method as an implement for the control analyst.

The following procedure will produce a solution from which optimum extraction of the copper complex with α-benzoinoxime is obtained.

REAGENTS

Boric Acid. Prepare 1 liter of saturated solution. Let the solution stand overnight at a temperature of 23° C. and then filter through a rapid paper at 23° C. The boric acid may be standardized with 0.2 *N* sodium hydroxide solution. Measure out 10 ml., add mannitol, and titrate with 0.2 *N* sodium hydroxide to a phenolphthalein end point. A titration of 42.65 ml. should be obtained.

Potassium-Sodium Hydroxide Mixture. Five liters of solution contain 280.0 grams of potassium hydroxide and 395.0 grams of sodium hydroxide. Pipet 10 ml. into a 250-ml. volumetric flask, make up to the mark with distilled water, and mix well. Pipet 25 ml. into a titrating flask. Add 20 ml. (buret) of 0.2 *N* sulfuric acid and boil to remove traces of carbon dioxide. Cool, add phenolphthalein, and titrate with 0.2 *N* sodium hydroxide. Adjust the strength of the initial caustic solution until the 25-ml. aliquot is equivalent to 13.86 ml. of 0.2 *N* sulfuric acid.

Sulfuric-Tartaric Acid Mixture. Dissolve 800 grams of tartaric acid in 1500 ml. of water, add 935 ml. of 2 *N* sulfuric acid, and dilute to 2500 ml. Pipet 10 ml. into a 250-ml. volumetric flask. Make up to the mark. Mix well and pipet a 25-ml. aliquot into a titrating flask. Heat to boiling, add phenolphthalein, and titrate with 0,2 *N* sodium hydroxide. The 25-ml. aliquot (1 ml. of acid mixture) is equivalent to 24.55 of 0.2 *N* sodium hydroxide.

Table I. Determination of Steel and Cast Iron

B.S. Steel	pH 1	pH 2	pH 3	Klett-Summerson, % 1	Klett-Summerson, % 2	Klett-Summerson, % 3	True Value, %
16c	12.1	11.4	12.0	0.061	0.061	0.062	0.060
20d	12.3	12.4	12.1	0.164	0.161	0.164	0.164
21c	12.1	12.3	12.3	0.056	0.054	0.054	0.050
55b	12.3	12.3	12.3	0.039	0.039	0.040	0.040
Cast iron 4g	12.0	12.0	11.4	0.236	0.252	0.239	0.240

The above reagents appear to be relatively stable. No appreciable alteration has been noted in solutions used over a 6-month period.

PROCEDURE FOR DETERMINATION OF COPPER

In Steel. Weigh a 0.500-gram sample of steel into a 400-ml. beaker and add 15 ml. (buret) of boric acid solution and 7 ml. of concentrated nitric acid. Cover with a borosilicate glass cover glass and evaporate to dryness. Remove the cover glass and invert it upon the hot plate (270° C.). Bake the sample and cover for 3 minutes. Samples baked for 7 minutes yield equally well to subsequent manipulations. Cool somewhat and add 25 ml. (buret) of the sulfuric-tartaric acid mixture. Cover, heat to boiling, and boil for a minute or two until the sample is in solution. Cool slightly, wash down the cover glass with a small amount of water, and add 50 ml. (buret or pipet) of the caustic mixture. Add 2 ml. of 0.5% α-benzoinoxime solution and transfer to a separatory funnel. Extract with chloroform and measure the quantity of copper, according to the procedure of Dunleavy, Wiberley, and Harley (*1*).

In Cast Irons. It is advisable to allow more time for the solution of the cast iron sample than for steel. Cast irons may be dissolved in a mixture of 20 ml. of 1 to 1 nitric acid solution and 15 ml. (buret) of boric acid solution. Complete the analysis according to the procedure for steel.

ANALYTICAL RESULTS

Four of the National Bureau of Standard Steels used by Dunleavy *et al.* (*1*) were available to determine how this modification compares with the original method. The results obtained with these samples and with Bureau of Standards cast iron 4g are given in Table I.

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Detection of Nitrogen in Organic Compounds

LAWRENCE E. BROWN and CARROLL L. HOFFPAUIR

Southern Regional Research Laboratory, New Orleans, La.

A NEW and sensitive test for ammonia, which makes use of the fluorescence exhibited by the chelate complex of zinc with 8-quinolinol, has recently been described by Velluz and Pesez (*7*). At low pH the complex dissociates and shows no fluorescence, but a solution or sensitized paper made from the complex, after exposure to ammonia, emits an intense greenish-yellow fluoresence under ultraviolet light. In adapting this test to the detection of nitrogen in organic compounds Velluz and Pesez (*8*) recommend a sample size of 1 mg., and use a lengthy digestion and distillation procedure. A more sensitive and reliable technique for converting nitrogen in organic compounds to ammonia is the pyrolysis of the sample in the presence of calcium oxide (*1–4, 6*). A number of reagents have been suggested for the detection of the ammonia released in the pyrolysis, including litmus, silver-manganese sulfate, mercurous nitrate, and Nessler's reagent. None of these combines both the convenience and sensitivity of the 8-quinolinol–zinc complex. By adapting the fluorescence method of detecting ammonia to the calcium oxide test, a rapid and simple test for nitrogen on a microgram scale has been developed.

APPARATUS

A source of ultraviolet light, such as a General Electric Purple-X bulb or a No. 360BL fluorescent tube, is required. The use of a view box (*5*) is convenient but is not essential.

The combustion apparatus consists of a hard-glass test tube (10 × 75 mm.) equipped with a No. 0000 one-hole stopper in which is mounted a 5.5-cm. length of 5-mm. tubing. The test tube is mounted through a hole in an asbestos board, so that the lower part can be heated with a microburner.

REAGENTS

Calcium Oxide. Satisfactory calcium oxide can be prepared by igniting analytical reagent grade calcium oxalate for 1 hour at 950° C. in a platinum dish.

Test Paper. A neutral, fairly thick, absorbent filter paper, such as S. & S. 598 or 589 Green Ribbon, cut into 3 × 70 mm. strips.

Test Solution. About 0.5 gram of crystalline zinc sulfate heptahydrate and 0.50 gram of 8-quinolinol are dissolved in 4 ml. of 1 *N* sulfuric acid. While stirring, 60 ml. of 0.005 *N* sodium hydroxide are slowly added, followed by 35 ml. of water. The solution should have a pH of 3.0 ± 0.05 and is relatively stable. The pH of the solution may drop to 2.8 or 2.9 after several weeks, but this results only in a slightly lower sensitivity.

PROCEDURE

Place a few micrograms of the sample material in the bottom of the test tube. Solutions should be evaporated to dryness. Add about 0.1 gram of calcium oxide by means of a funnel to prevent the lime from adhering to the walls of the tube. Tap the tube to compact the lime and place it in the combustion apparatus so that it extends 2 to 3 cm. below the asbestos board. Dip a strip of test paper about 1 cm. down into the test solution and insert it into the tubing in the stopper until it extends within 2 to 3 mm. of the lower end. Bend over the upper end of the strip to hold it in position. Examine the paper under ultraviolet light to establish the absence of fluorescence. Place the stopper in the test tube so that the end of the test strip is about 1.5 cm. above the asbestos board. Heat the calcium oxide with a microburner from the top down until all the calcium oxide has been heated to redness. Remove the stopper and again examine the test paper under ultraviolet light. A greenish-yellow fluorescence extending upward from the end is evidence of nitrogen in the sample.

DISCUSSION

Using satisfactory reagent and freshly cleaned apparatus, a blank test on a sample containing no nitrogen will be completely negative. The sensitivity of the test varies with the nitrogen compound present—from less than 1 microgram for sulfanilic acid to about 3 micrograms for methyl orange, corresponding to about 0.05 to 0.30 microgram of nitrogen. If the type of nitrogen compound present is known, an indication of whether it is present in large or small amounts can be obtained by observing the area of the fluorescent spot on the test paper, or, alternatively, by using an 8-quinolinol–zinc reagent, the sensitivity of which has been reduced by the addition of excess acid. If preferred, the test may be applied to samples weighing 0.5 to 1.0 mg. by substituting water for the sodium hydroxide in making the test solution, so that the pH is about 2.5, and pyrolyzing the sample in a 12 × 75 mm. test tube, using 0.5 gram of calcium oxide.

Positive tests have been obtained with one or more nitrogen compounds of the following types: amino, amide, nitro, nitroso, nitrile, oxime, azo, ring, semicarbazone, and organic nitrate. Because the fluorescence is dependent on pH, positive tests are obtained with volatile bases other than ammonia. Hence, the test does not fail with compounds, such as trimethylamine oxide, which yield a volatile base other than ammonia on incomplete pyrolysis. No nitrogen-containing compounds have been encountered which gave a negative test.

Nonnitrogenous compounds including those containing phosphorus, arsenic, antimony, and bismuth all gave negative tests.

Compounds that are naturally fluorescent, such as anthracene, should be burned carefully to avoid volatilizing unchanged material onto the test strip. A poor combustion of such a sample is, however, readily detected by the different color of the fluorescence and the fact that the fluorescence is diffused over the inner tube instead of being only on the test strip.

The use of manganese dioxide with the calcium oxide as recommended by Feigl (*4*) is unnecessary; pyro compounds, if formed, do not give false positive tests in this procedure. Furthermore, its use was found to reduce the sensitivity of the test, probably through oxidation of part of the ammonia. The use of zinc powder mixed with the lime as suggested by Bennett *et al.* (*1*) gave a false positive test with triphenyl phosphate. Copper powder in the calcium oxide as suggested by Emich and Schneider (*3*, *6*) offers no advantage, since compounds containing nitrogen linked to oxygen give positive tests with lime alone.

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Colorimetric Assay of Diacyl Amides

J. B. POLYA and P. L. TARDEW
Chemistry Department, University of Tasmania, Hobart, Australia

LIPMANN and Tuttle (*5*) have developed a procedure for assaying acyl phosphates by converting the organic acyl radicals to hydroxamic acids, which give intense coloration with ferric chloride. Because purely organic anhydrides or acyl chlorides are not likely to occur under biological conditions, and esters or amides do not react under the experimental conditions, the method is claimed to be specific for acyl phosphates in biological materials. It is possible, however, that diacylamides of the general formula $RCO.NR'.COR''$ may occur in biological systems. The Lipmann-Tuttle assay was applied to a number of representative compounds of this class. Dibenzamide (*1*), formyl benzamide (*4*), diacetamide (*10*), and other diacyl amides with $R' = H$ (*8*) were prepared by previously described methods. Other diacyl amides were prepared by the acylation of the appropriate amines or amides with anhydrides in the presence of acyl halides or thionyl chloride in catalytic amounts (*3*). Other reagents were commercial products of analytical quality.

The reagent solutions were those recommended by Lipmann and Tuttle. They were prepared fresh and used in the quantities and order as suggested by the originators of the method. The colors were compared with a Hilger Spekker absorptiometer using 1-cm. cells, Ilford 608 gelatin filters, and a mixture of the reagents only as reference. This gave convenient readings for the assay of succinic anhydride or acetyl phosphate in concentrations ranging from 0.025 to 0.100 M with an error of ±4%.

This procedure was not suitable for diacyl amides, because some of them were not sufficiently soluble and even diacetamide gave low density readings with an error of ±18%. Table I refers to average values from four measurements each, with probable errors indicated above.

Table I. Optical Density

Molar Concentration	Optical Density	
	Succinic anhydride	Diacetamide
0.100	1.18	0.13
0.075	0.89	0.11
0.050	0.59	0.09
0.025	0.30	0.05

Better results were obtained by increasing the alkalinity of the reaction mixture and limiting the reaction time to 2 minutes.

In this modified procedure 1 ml. each of 4 M hydroxylamine hydrochloride solution and 3.5 M sodium hydroxide are mixed and 1.8 ml. of the recommended acetate buffer are added. The solution to be analyzed (2 ml.) followed by another 0.2 ml. of the 3.5 M sodium hydroxide is added in this order and the mixture is allowed to stand for 2 minutes at room temperature (18° to 20°). The subsequent operations are those recommended by Lipmann and Tuttle. Ilford 604 gelatin filters were used in the modified procedure as they were found to give better results than Ilford 608.

Dibenzamide is not sufficiently soluble in water and was used dissolved in 1% sodium hydroxide. Other relatively insoluble diacyl amides like acetyl and propionyl benzamide hydrolyze too rapidly in alkaline solutions. In such cases the assays had to be restricted to lower concentrations in water only. Although N-methyldiacetamide is very soluble in water, such solutions hydrolyze rapidly and the assay must be carried out without delay. Even then the assay has an error of ±7% against ±4% in other cases, with the exception of acetyl chloroacetamide, which is assayed with an error of ±22%. The method is not suitable for the assay of N-formyl amides, as the color fades within a few seconds. The reaction therefore proceeds as $PhCONHCHO + NH_2OH \rightarrow PhCONH_2 + HC(:O)NHOH$, in agreement with previous theories (*8*). Hydantoin, N-methyl-N'-acetylurea, succinimide, and acetamidine gave little or no color. Acetamide in a 5% (0.847M) solution gave an intensity of 0.27 ± 0.02, corresponding to that given by approximately 0.0025 M solutions of diacyl amides. The N-bromo and N-bromomagnesium derivatives of diacetamide (*6*) gave the color test which, however, was not suitable for quantitative purposes, owing to the instability of these compounds under the experimental conditions. The same applies to a lesser extent to acetyl chloroacetamide, but the colorimetric assay of some halogenated diacyl amides could be supplemented by fluorometric or spectrographic methods (*7*, *9*). Esters interfere in the presence of excess alkali (*11*), although this is not the case in the original method of Lipmann and Tuttle. However, the removal of esters from solutions containing acyl phosphates is difficult or impossible, whereas the separation of esters from most diacyl amides is comparatively simple.

Average results of six assays (four assays only for acetyl chloroacetamide) are shown in Table II. The errors indicated above refer to concentrations from 0.0025 to 0.0100 M. At 0.0010 M concentration the errors are estimated at ±9 to ±10%. The curves of density versus concentration may be regarded as linear within the stated range of errors and may be used for the rapid determination of small amounts of diacyl amides. The assays may be duplicated with an error of ±2% only if succinic anhydride is used in the reference cell as in the original Lipmann-Tuttle procedure. Diacetamide is unsatisfactory as a reference in the original but useful in the modified method.

Analytically pure disilver acetyl phosphamide has been prepared by dehydrating and acylating monoammonium phosphate with acetic anhydride in excess in the presence of thionyl or acetyl chloride and precipitating from an aqueous solution with silver nitrate (*2*). Like benzoyl phosphamide (*12*), acetyl phosphamide appears to be relatively stable in aqueous solution. Removal of the silver by thioacetamide resulted in solutions from which the original silver compound salt could be regenerated with a loss of 71 to 86%. Such silver-free solutions could not be used for the assay because of a slowly fading green color due to residual thioacetamide in the solution. Fresh extracts of disilver acetyl

Table II. Optical Density

Compound	Optical Density				
	0.0100 *M*	0.0075 *M*	0.0050 *M*	0.0025 *M*	0.0010 *M*
Succinic anhydride	1.18	0.89	0.59	0.30	0.14
Diacetamide	1.33	0.99	0.65	0.33	0.15
N-Methyldiacetamide	1.07	0.73	0.50	0.26	0.12
Diacetanilide	1.33	0.97	0.65	0.30	01.4
Acetyl propionamide	1.29	0.95	0.64	0.32	0.15
Dipropionamide	1.39	1.02	0.69	0.34	0.14
Acetyl benzamide	Insol.	Insol.	0.69	0.36	0.16
Propionyl benzamide	Insol.	Insol.	0.72	0.35	0.16
Dibenzamide	1.75	1.25	0.82	0.41	0.19
Acetyl chloroacetamide	1.10	0.65	0.52	0.27	...

phosphamide with a slight excess of 10% sodium chloride solution did not give the test by either the original or the modified Lipmann-Tuttle procedure. A faint color appeared occasionally after standing for a few hours. This suggests that the cleavage of acetyl phosphamide by hydroxylamine yields acetamide and phosphohydroxylamine, probably followed by the rapid hydrolysis of the latter.

The original and modified test has been applied to cancer, diabetes, pregnancy, and normal human serum and to albumin, globulin, euglobulin, and pseudoglobulin fractions of such sera. As a rule the test was negative, but a few fresh, defibrinated sera from diabetic patients gave a faint purple color which was retained in the centrifuged precipitated proteins.

ACKNOWLEDGMENT

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Determination of Total Chlorine in Inorganic Salts

WILLIAM A. JAMES AND RICHARD E. BELSER[1]
Midwest Research Institute, Kansas City, Mo.

IN MANY of the methods (*5*) available for the analysis of mixtures containing chloride, chlorate, perchlorate, thiocyanate, and cyanide ions, the total chlorine is determined with some difficulty. In mixtures containing chloride, thiocyanate, and cyanide ions it is necessary first to liberate the cyanide ions and destroy the thiocyanate ions or determine the amount of each present before the "chloride chlorine" is obtained. To overcome these difficulties, a method for the direct determination of the total chlorine has been developed. Should the mixture contain chlorate or perchlorate ions, the "chlorate chlorine" and "perchlorate chlorine" would also be determined with no additional handling or treatment of the sample.

PRINCIPLES OF METHOD

The technique employed is similar to that used by LaForce *et al.* (*2*) in determining the carbon dioxide content of inorganic carbonates. Their method involves fusion of the sample with potassium bisulfate in a micro combustion boat placed in the standard organic carbon-hydrogen train. In the chlorine determination the reaction takes place in a spiral or Friedrich tube used for the determination of chlorine in organic compounds (*3*).

In addition, manganese dioxide is added to the fusion mixture to ensure complete liberation of the chlorine. Preising *et al.* (*4*) have shown that heating chlorates and perchlorates with manganese dioxide releases the chlorate chlorine and the perchlorate chlorine. The reaction with potassium perchlorate is

$$2KClO_4 + 2H_2SO_4 + MnO_2 \longrightarrow Cl_2 + MnSO_4 + K_2SO_4 + 2H_2O + 4O_2$$

The chlorine gas formed then reacts with a mixture of sodium carbonate and hydrogen peroxide in the spiral of the tube to form the chloride, which is titrated with standard silver nitrate.

PROCEDURE

The spiral tube is prepared in the following manner: One milliliter of a saturated solution of sodium carbonate and 4 ml. of 3% hydrogen peroxide are mixed in a 125-ml. Erlenmeyer flask and drawn into the tube until the spiral is covered. The mixture is drained back into the flask, and after the tube is positioned in the furnace, the flask is hung over the exit end. Any material spraying from the tube is retained by the flask. The platinum catalysts are positioned and heated to between 600° and 700° C. The train is then ready to receive the boat containing the fusion mixture.

The sample, weighing 10 to 20 mg., depending upon the amount of chlorine present, is weighed in a semimicro porcelain combustion boat. Sixty mg. of potassium bisulfate and 9 mg. of manganese dioxide are added without mixing with the sample.

The boat is placed in the train and the oxygen is connected. The flow is regulated to a rate of 5 to 6 ml. per minute.

The boat is first heated cautiously to prevent excessive foaming. After the foaming ceases, gradual heating is continued until the full heat of the burner can be applied. After completion of the fusion, which requires approximately 20 minutes, the tube is removed from the furnace and allowed to cool, the oxygen continuing to pass through the tube. When the tube has reached room temperature, the boat is removed and the contents of the tube are rinsed into the flask with distilled water.

The carbonate solution in the flask is acidified with dilute nitric acid (1 to 1) and concentrated to 5 or 10 ml. After cooling, an equal volume of acetone and two drops of 0.1% dichlorofluorescein indicator (0.1 gram in 100 ml. of 70% alcohol) are added (*1*). The pH is then adjusted by adding small increments of solid sodium bicarbonate until the indicator is greenish and fluorescent. Acetone is added because it gives greater dispersion of the silver chloride precipitate and therefore yields a sharper end point.

The titration with 0.01 *N* silver nitrate is conducted in a partially darkened room using a black background. The titration flask is illuminated with a daylight lamp located to the side and slightly to the rear of the observer.

A blank is carried through all steps of the combustion. Because the chloride solution must be at least 0.005 *N* in sodium chloride to obtain an end point, it is necessary to add, accurately,

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[1] Present address, Remington Arms, Inc., Independence, Mo.

Table I. Recovery of Chlorine from Chlorides and Chlorine-Containing Anions

Compounds Present	Chlorine Present, Mg.	Chlorine Found, Mg.
Sodium chloride	10.65	10.58
Sodium chloride	4.61	4.59
Sodium chloride + KSCN and KCN	3.01	3.01
Sodium chloride + KSCN and KCN	4.75	4.76
Potassium perchlorate	2.70	2.71
Potassium perchlorate	2.83	2.84
Potassium chlorate	2.21	2.28
Potassium chlorate	3.68	3.70
Sample MR-1	7.35%	7.31%

5 ml. of a 0.01 *N* sodium chloride solution before titrating. An equivalent amount of silver nitrate is then deducted to obtain the blank.

Results obtained by this method were in very good agreement with the theory as shown in Table I.

DISCUSSION OF RESULTS

The method was first used with the chemically pure salts listed in Table I. In addition, many samples of a smoke residue were analyzed by this method and all results were typical of those shown for sample MR-1. All samples contained cyanide, thiocyanate, chloride, and approximately ten different metal ions.

Six determinations were made on all samples similar to MR-1, using approximately 15 mg. for the fusion in each analysis. In all cases it was necessary to add more sodium chloride before the titration. The average deviation of the mean was ±0.05. The total chlorine present in sample MR-1 was also determined by the gravimetric method after a sodium peroxide fusion, and the result, 7.35%, represents an average of six determinations.

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Improved Toximetric Agar-Dish Test for Evaluation of Wood Preservatives

ROBERT W. FINHOLT[1]
Union College, Schenectady, N. Y.

IN THE past 30 years methods have been proposed for toximetric laboratory evaluation of wood preservatives. Two test methods have achieved prominence. The first, in point of view of age and use, is the agar-dish method of Humphrey and Fleming (*5*), Bateman and Henningson (*2*), Schmitz (*8*, *9*), and Baechler (*1*). The newest is the soil-block test, which is an improved form of the standard agar-block European test. This soil-block test was developed by Flerov and Popov (*4*) and Leutritz (*6*), and has been studied by Richards and Addoms (*7*) and Duncan and Richards (*3*). These tests have been developed to fill the need for an accurate and rapid method for the evaluation of possible wood preservatives. The agar-dish method gives results in 2 to 3 weeks; the soil-block method, in 2 to 4 months. Both methods give much more rapid results than the quickest outdoor test which, using wooden stakes, usually requires 1 to 3 years. The chief criticism of the laboratory methods has come over their lack of similarity to actual conditions.

The agar-dish test is rather far removed from natural conditions, but in spite of criticism it has held on because of its rapidity and low cost. The wood-soil test simulates natural conditions in giving the fungus its natural food and in providing a very favorable environment, but is both more expensive and time-consuming than the agar-dish test. Actually, the two tests may seem to give the same approximate results in a qualitative sense, but they part company in most quantitative comparisons. In spite of its limitations, the agar-dish method is a very useful tool in fundamental research on toxic materials, if results are used only after careful interpretation. In this laboratory it has been found necessary to institute two changes in the prescribed method in order to get reliable results.

The first modification was in the method of mixing the agar solution with the chemical being tested. Mixing had been done by swirling the toxic material with the agar solution (*8*) or by continued stirring with a motor-driven stirrer (*1*) when rather insoluble materials were used; neither method gave adequate and reproducible dispersions. A better method was found, which used a Waring Blendor for mixing the oil and agar solution. The Blendor, a high speed mechanical homogenizer, mixed creosote and agar so intimately that no droplets could be seen even under 300 magnifications. Use of this mixer under standard conditions made it possible to get good results even with oils and removed one of the sources of error that previous workers had recognized (*1*, *8*).

The second change was in the definition of a toxic point at which the concentration of poison is high enough to halt the growth of a test fungus. Schmitz and others defined a "total inhibition point" and a "killing point." The total inhibition point was taken as the minimum concentration that would allow "no signs of growth either on the nutrient agar or on the inoculum" (*9*). The killing point was taken as the minimum concentration of poison that would inactivate the fungus inoculum, so that when the plug of inoculum was removed and placed on an unpoisoned slant there would be no growth. These definitions had a fundamental error in considering the state of growth of the fungus on the inoculum plug as the criterion. It is only the growth or lack of growth on the surface of the poisoned gel itself that has any validity for many poisons. Because the plug contains no poison when placed in use, the only poison in it is that which diffuses into it from the main body of gel. If the test poison happens to be water-insoluble, as is the case with most wood preservatives, the rate of diffusion is very slow and furthermore is dependent on contact between the plug and the main body of agar.

Thus the previously defined "killing point" is a function of both the toxicity of the test poison and its rate of diffusion. As a consequence, it was found that these values varied as much as 200% in testing oil-type poisons; sometimes a killing point was not found at all, although the growth of the fungus was inhibited. The definition of total inhibition point did not make it clear whether growth meant an increase in the amount of fungus over the original planting or simply the presence of a visible mycelium, no matter how small. In either case, the judgment of the in-

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[1] Present address, Research Laboratory, General Electric Co., Schenectady, N. Y.

dividual experimenter was of key importance. In actual laboratory tests, different experimenters varied by as much as 25% in their estimates on the same series of test flasks.

Because of these difficulties a new definition was formulated that seemed to avoid both the error and judgment factors of the previous definitions. The inhibition point was defined as the minimum concentration by weight percentage of poison necessary to prevent any radial growth on the surface of the poisoned agar after a standard period of incubation. This point was called the apparent inhibition point (AIP) to differentiate it from the old total inhibition point (TIP). The incubation time was varied, depending on the fungus being used. Madison 517 (incorrectly called *Fomes annosus*) gave good results in the 2-week period that Schmitz had recommended, but *Lentinus lepideus* needed 3 weeks to give conclusive results. There would undoubtedly be different times for other species. In this laboratory use of the improved mixing method and the new apparent inhibition point gave results of high accuracy. The precision was at least within ±5% with any type of poison. Besides this improvement in experimental results, considerable work was saved in end point determinations, as there was no need for further transplanting to tell whether a fungus inoculum was dead or not.

EXPERIMENTAL

The procedure was based on previous test methods (*1–4*) but was improved and simplified in several respects. The overall time for making the test has been reduced with no loss in accuracy or precision.

The culture medium was prepared by adding 15 grams of Difco bacto-agar to 1 liter of distilled water that had been heated to 95° C. The mixture was mechanically stirred for about 0.5 hour and the clear solution was filtered through cloth. To the filtered solution were added 25 grams of Trommers malt extract (plain) and the hot solution was weighed into 500-ml. Erlenmeyer flasks, 100 grams per flask. A double-pan balance was used and the solution was added by means of a large buret. This gave an accuracy of about ±0.1 gram. The flasks were stoppered with aluminum foil and sterilized at 15 p.s.i. gage pressure (121° C.) for 15 minutes, and the pressure was allowed to come back to normal in another 15 minutes. The average loss in weight on sterilization was 1 gram. Most of the poisons used in this laboratory were not sterilized, but the test chemicals that were to be sterilized were sealed in pressure tubes and sterilized at the same time as the agar-malt solution.

Table I. Sample Data for Determination of Apparent Inhibition Point of a Creosote Fraction

Vol. of Stock Solution *Ml.*	Poison %	Poison Rounded Off %	Total Diameter of Growth *Cm*
0.10	0.0047	0.005	6.5
0.20	0.0094	0.009	4.0
0.30	0.0140	0.014	1.6
0.37	0.0182	0.018	1.2
0.40	0.0188	0.019	1.0, AIP
0.43	0.0200	0.020	1.0
0.53	0.0247	0.025	0.5, TIP
0.90	0.0420	0.042	None, killing Point

Test Fungus—Madison 517

To a single sterile flask, 5 grams of test chemical were added and this mixture was used as a stock solution from which dilutions were made up. The mixture was then poured into a sterile 250-ml. Monel metal Waring Blendor cup and mixed for 2 minutes with the cover on. The flask was then twice rinsed with the mix and blended for an additional 30 seconds. The Blendor cup could be effectively sterilized by flaming or by ordinary sterilization.

Calculated volumes of the hot (60° C.) solution were withdrawn from the mixer using a graduated 1-ml. pipet (previously kept warm in boiling water) and various amounts were added to the other flasks. Care had to be taken to draw the liquid from the bottom of the mixer, so as not to get froth in the pipet. After addition of the poison emulsion, the flasks were reclosed with the original aluminum foil and given a slight swirling motion to disperse the emulsion. It was found convenient to keep the flasks hot before addition of the poison by using a large kettle canner. Eight flasks could be handled with ease this way, as the canner had a wire rack and lid. The mixed dispersions were allowed to stand overnight in a 26.7° C. cabinet before inoculation.

The inoculum was a circular path of fungus taken from the outer portion of a culture grown on a plate by pouring 25 ml. of agar solution into a 90-mm. Petri dish. The culture was 14 days old when *Lentinus lepideus* (Madison 534) was used and 10 days old when Madison 517 was used. The circular patch was cut using a sterile 1-cm. cork borer and the transplanting was done using a long thin spatula sharply bent at the ends. These procedures require a lengthy exposure to air with consequent possible contamination, but in actual practice little trouble was encountered when suitable care was taken.

After plating, the flasks were returned to the constant temperature cabinet and incubated in the dark for 14 days with Madison 517 and 3 weeks with Madison 534. At the end of this time the flasks were lined up in order and examined for signs of growth. The apparent inhibition point was taken as the lowest concentration that prevented any radial growth on the poisoned agar. In most cases the apparent inhibition point was obvious if the concentrations differed by 5% or more.

A typical set of test results is shown in Table I. The apparent inhibition point is the first point where there is 1 cm. of growth, as that was the diameter of the inoculum plug. The diameter of the growth is the average of two flasks of similar composition, since all tests were run in duplicate and with unpoisoned control flasks.

The stock solution contained 5 grams of creosote fraction 3. The total volume of stock solution was 107 ml. and weighed 104 grams, which made 0.1 ml. of stock solution containing 0.0047 gram of creosote. The weight of the final solutions was assumed to be 100 grams in each case, although it varied from 99.1 to 99.9 grams. This difference was negligible in this test. The apparent inhibition point was taken to be 0.019 ± 5% of this value.

SUMMARY

Fungitoxic materials can be evaluated as wood preservatives by mixing the toxic substance with a malt extract–agar solution and then testing the mix against standard fungi. The mixing can be done effectively using a Waring Blendor, and the effectiveness of the preservatives is judged by finding the least concentration needed to prevent growth on the gel surface. This method is effective with oil-soluble preservatives which are ordinarily difficult to test in agar solutions, and check results can usually be obtained to ±5%.

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Vibrating Dropping Mercury Electrode

For Polarographic Analysis of Agitated Solutions

DAVID A. BERMAN, PAUL R. SAUNDERS, AND RICHARD J. WINZLER
School of Medicine, University of Southern California, Los Angeles, Calif.

THE dropping mercury electrode has been limited chiefly to solutions that are free from agitation, for any stirring results in irregular dropping of mercury from the capillary and consequent fluctuations in current. The shielded dropping mercury electrode (*8*, *11*) has been successfully applied to agitated solutions, but has the disadvantage of introducing a time lag in the current readings (*7*).

A vibrating dropping mercury electrode was developed by this laboratory to fill the need of applying the polarographic method to biological systems requiring continuous agitation. Enforced drop electrodes, which have been developed chiefly for increasing the accuracy of the current readings or for synchronizing the drop rates of multiple capillaries, have been described by several investigators. Kanner and Coleman (*4*) incorporated a solenoid in the design of their apparatus as a means of initiating a new mercury drop after the current measurement. Heyrovský (*3*) used the device developed by Cermak and Hanus (*2*) for obtaining derivative curves. The drop rates of the electrodes in this device were synchronized by a solenoid. Skobets and Kavetskiĭ (*9*) positioned a glass hoe under the dropping mercury electrode for the purpose of controlling the drop rate, and demonstrated that it was possible with this arrangement to increase the accuracy of the current readings. None of the authors describing such enforced drop electrodes indicated, however, that their devices could be applied to stirred solutions.

The vibrating dropping mercury electrode described in this paper was developed specifically for systems requiring continuous agitation. Although the device was designed primarily for measuring the oxygen uptake of contracting isolated cardiac muscle preparations, it is also suited for other analytical procedures where agitation of the solution is required.

APPARATUS AND PROCEDURES

Figure 1 presents the details of construction of the vibrating dropping mercury electrode.

The device is driven by a 0.05-hp., 1800 r.p.m. synchronous motor, *A*, geared up through a 1 to 2.7 spur gear train, *B* and *C*, to 4860 r.p.m. Spur gear *C* is mounted on one end of a shaft, *D*, which passes through a brass sleeve bearing, *F*, and terminates with a 0.25-inch extension with an eccentricity of 0.012 inch. A phosphor bronze shaft, 0.025 inch thick, *G*, attached to the mounting of ball bearing *E*, links the eccentric portion of *D* with a flexible phosphor bronze plate, *H*, 0.025 inch thick. The rigid steel shaft, *I*, 0.125 inch in diameter, connects *H* to a capillary holder, *J*. The capillary, mercury reservoir, and tubing (not shown) are the types used in the conventional dropping mercury electrode (*5*). The height of the mercury column was approximately 80 cm., and the drop time in the absence of vibration was 4 seconds.

Sargent-Heyrovský polarograph Models XI and XII were used in this study. A saturated calomel electrode served as the anode. The temperature in all experiments was 25° ± 0.1° C. All chemicals were reagent grade, and all solutions were prepared with double-distilled water.

EXPERIMENTAL RESULTS

With the rapidly vibrating electrode, the drop size and time were greatly reduced and moderate agitation of the solution under these circumstances did not affect the reproducibility of the current significantly. The vibrating assembly was mounted on rubber to eliminate any appreciable vibration other than that of the electrode. Only slight irregularities in current were observed (Figure 2) when the apparatus was free of secondary vibration.

A comparison between polarograms of 0.001 *M* lead nitrate, taken with the conventional dropping mercury and the vibrating dropping mercury electrode in the absence of oxygen, is shown in Figure 2. In the lower curve, *B*, taken with the vibrating dropping mercury electrode, nitrogen was continually passed through the solution. Some reduction in sensitivity is apparent with the vibrating electrode.

A linear relationship between oxygen tension and current was demonstrated. Tenth molar potassium chloride containing 0.03% gelatin as a maximum suppressor was equilibrated with four gas mixtures of oxygen and nitrogen containing 99.7 ± 0.2% oxygen, 49.9 ± 0.2% oxygen, 20.9% oxygen (air), and 0% oxygen (nitrogen). The gas mixture was bubbled continuously into the solution during the recording of the current at a constant voltage (−0.6 volt *vs.* S.C.E.).

The dropping mercury electrode has been successfully applied to the study of the rate of oxygen consumption of yeast by Baumberger (*1*) and Winzler (*10*); the Q_{O_2} values agreed with values obtained with conventional manometric methods. Figure 3 shows that the rate of oxygen consumption of yeast, measured with the vibrating electrode, agrees with that determined for the same yeast suspension with the conventional electrode. The readings obtained when the solution was saturated with air are indicated by *A* for the dropping mercury electrode and by *B* for the vibrating mercury electrode. The rate of oxygen utilization as determined with the vibrating and conventional elec-

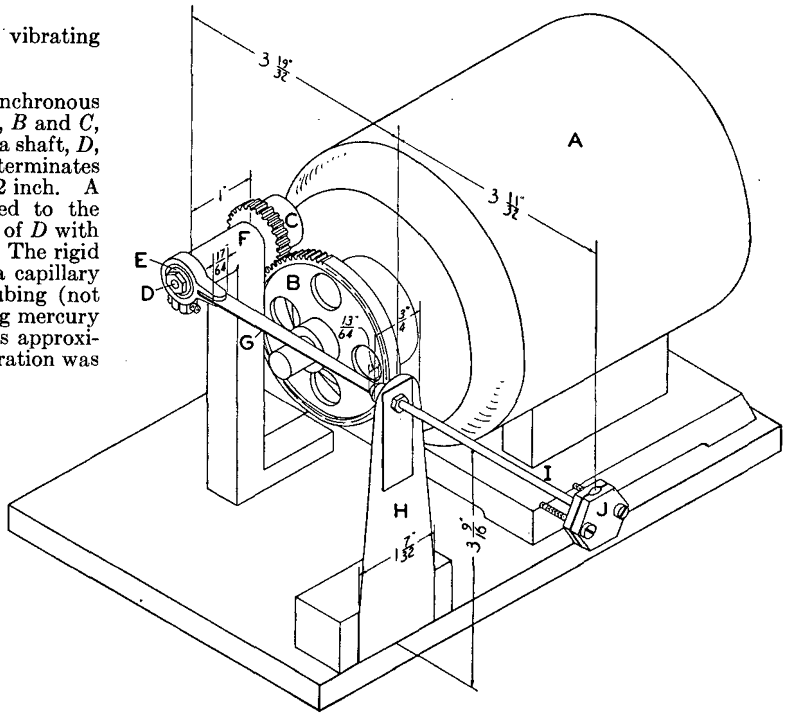

Figure 1. Diagram of Vibrating Dropping Mercury Electrode

Table I. Relation between Current and Concentration of Lead Ion

Electrode	$Pb(NO_3)_2$ Concn., Millimoles/Liter	Current (Corrected for Residual Current), μa.	μa./Millimole/Liter
Vibrating	1.0	3.90	3.90
Vibrating	0.5	1.97	3.94
Conventional	1.0	6.83	6.83
Conventional	0.5	3.41	6.82

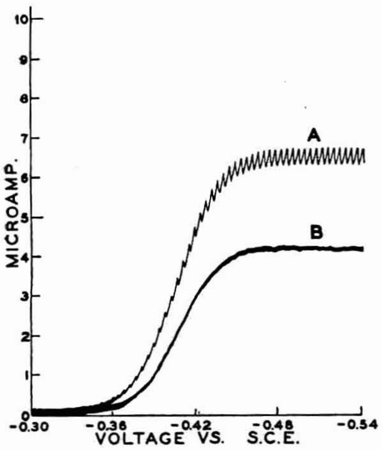

Figure 2. Polarograms of Oxygen-Free 0.001 *M* Lead Nitrate in 0.1 *M* Potassium Chloride and 0.03% Gelatin

A. Dropping mercury electrode
B. Vibrating dropping mercury electrode

trodes was 13.5 and 13.2 cu. mm. per minute, respectively. No time lag was observed with the vibrating electrode.

Table I shows that with both the vibrating and conventional electrodes a linear relationship between current and lead concentration is obtained. Two concentrations of lead nitrate in 0.1 *M* potassium chloride plus 0.03% gelatin were used. The current was measured at a potential of −0.8 volt with respect to the saturated calomel electrode. Nitrogen gas was passed continuously through the solution during the recording of the current with the vibrating dropping mercury electrode.

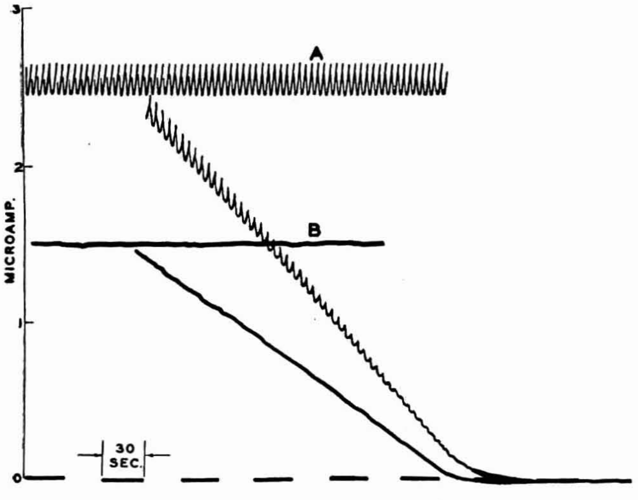

Figure 3. Rates of Oxygen Utilization of Yeast Determined with Vibrating and Dropping Mercury Electrodes

50 mg. of yeast (Fleischmann's) in 10 ml. of 0.1 *M* phosphate buffer, pH 6.8, containing 1% glucose. Voltage *vs.* S.C.E., −0.6

The use of the dropping mercury electrode for the amperometric titration of lead has been described by Kolthoff and Pan (*6*).

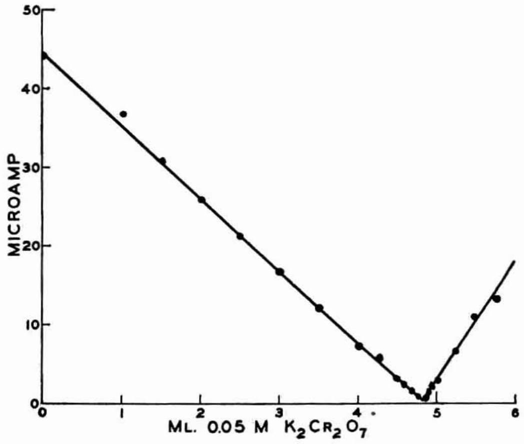

Figure 4. Amperometric Titration with Vibrating Dropping Mercury Electrode

Titration of 50 ml. of 0.0096 *M* $Pb(NO_3)_2$ in 0.1 *M* KNO_3 with 0.05 *M* $K_2Cr_2O_7$ at voltage *vs.* S.C.E. = −1.0. Nitrogen passed continuously through solution during titration. Theoretical end point = 4.80 ml. of 0.05 *M* $K_2Cr_2O_7$

This titration was selected as an example of the applicability of the vibrating dropping mercury electrode to amperometric titrations performed at voltages at which oxygen is reduced (Figure 4). A disadvantage of the dropping mercury electrode in amperometric titrations where oxygen is an interfering substance is that, unless air-free reagents are used, an inert gas must be passed into the system after each addition of reagent, and then the solution must be allowed to come to rest before the current can be measured. With the vibrating dropping mercury electrode, amperometric titrations can be performed more rapidly because an inert gas can be passed into the system continuously without interfering with the current measurement.

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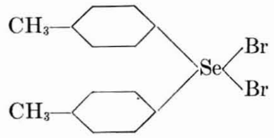
CRYSTALLOGRAPHIC DATA

46. Di-*p*-Tolylselenium Dibromide

Contributed by GEORGE J. NEUERBERG, University of California, Los Angeles, Calif., and WALTER C. MCCRONE, Armour Research Foundation of Illinois Institute of Technology, Chicago 16, Ill.



Structural Formula for Di-*p*-tolylselenium Dibromide

THE sample of di-*p*-tolylselenium dibromide was kindly furnished by J. D. McCullough of the University of California. The sample was synthesized by Campbell (*1*), using a modification of the method described by Leicester and Bergstrom (*2*). The sample was identified by the method described by McCullough, Campbell, and Krilanovitch (*3*).

Excellent crystals may be obtained for x-ray and optical crystallography by recrystallization from methanol-benzene (2 to 1), carbon tetrachloride, and carbon disulfide. Benzyl alcohol is more suitable as a solvent for recrystallizations on a microscope slide (Figure 1, *A*) because of its lower volatility and higher surface tension.

CRYSTAL MORPHOLOGY

Crystal System. Orthorhombic.

Form and Habit. The crystals are usually stubby orthorhombic prisms with the prism {110} and brachydome {011} always present. The brachy pinacoid {010} is also often present. The additional forms: basal pinacoid {001}, prisms {1·16·0} and {2·15·0}, orthodome {101}, and bipyramids {567}, {111}, and {12·4·1} are often observed on slow recrystallization.

Axial Ratio. $a:b:c = 0.5949:1:0.3979$ (goniometry). 0.594:1:0.399 (x-ray). 0.594:1:0.399 (x-ray). [These authors (*4*) have chosen a crystal orientation with *a* and *b* reversed with respect to this description.]

Interfacial Angles (Polar). $110 \wedge 1\bar{1}0 = 61° 26'$ (x-ray); $011 \wedge 0\bar{1}1 = 43° 30'$ (x-ray).

X-RAY DIFFRACTION DATA

Space Group. $P2_12_12_1 - D_2^3$.

Cell Dimensions. $a = 8.65$ A.; $b = 14.56$ A.; $c = 5.81$ A. $a = 14.60$ A.; $b = 8.64$ A.; $c = 5.82$ A. (*4*).

Formula Weights per Cell. 2.

Formula Weight. 420.9.

Density. 1.909 (flotation, pycnometer); 1.924 (x-ray).

Principal Lines

d	I/I_1	*d*	I/I_1
7.34	0.80	2.70	0.09
5.82	0.51	2.61	0.08
5.41	0.11	2.54	0.37
4.83	0.11	2.48	0.22
4.55	1.00	2.43	0.17
4.32	0.08	2.38	0.05
4.14	Very faint	2.28	0.22
4.01	0.08	2.24	0.14
3.88	Very faint	2.20	0.03
3.73	0.37	2.16	0.06
3.64	0.26	2.11	0.03
3.47	0.05	2.06	0.12
3.38	0.20	2.02	0.11
3.22	0.03	1.997	0.06
3.09	0.42	1.963	0.09
2.99	Very faint	1.929	0.17
2.91	0.14	1.885	0.06
2.84	0.31	1.860	0.08

OPTICAL PROPERTIES

Refractive Indexes (5893 A.; 25° C.). $\alpha = 1.715 \pm 0.004$. $\beta = 1.83 \pm 0.01$. $\gamma = 2.05 \pm 0.04$.

Optic Axial Angles. (5893 A.; 25° C.). $2V = 80° \pm 5°$. $2H = 102°$.

Dispersion. Very strong $r > v$.

Optic Axial Plane. 101.

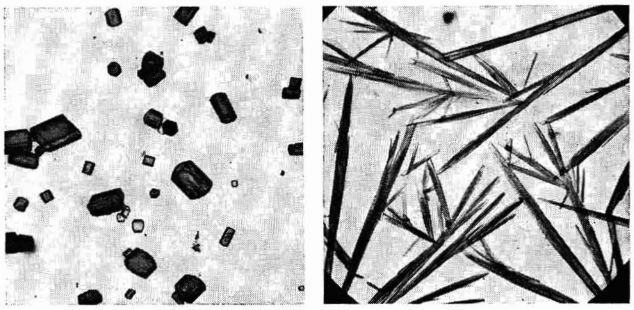

A *B*

Figure 1. Di-*p*-tolylselenium Dibromide

A. Crystals from benzyl alcohol on microscope slide
B. Crystals from melt on microscope slide

Sign of Double Refraction. Positive.

Acute Bisectrix. γ.

Molecular Refraction (R) (5893 A.; 25° C.). $\sqrt[3]{\alpha\beta\gamma} = 1.86$. R(calcd.) = 99.24 [assuming R(Se) = 21.86]. R(obsd.) = 99.24.

Pleochroism. Light yellow (X); deep yellow (Y); and orange-red (Z).

FUSION DATA. Di-*p*-tolylselenium dibromide decomposes badly, but supercools to a mobile melt which on seeding gives rods and needles of the undecomposed material (Figure 1, *B*). These are elongated parallel to c (α). The refractive index of the melt at room temperature is usually less than 1.715 (α), although this depends on the extent of decomposition. Some sublimation on heating gives needles and rods similar to those from the melt.

Occasionally needle crystals of a colorless decomposition product appear in the melt on cooling. They are similar in appearance to the undecomposed material but are not colored, have a positive sign of elongation in some views at least, and dissolve or melt on only slight rewarming. If extreme decomposition occurs, the melt becomes colorless and seeding produces no crystals of di-*p*-tolylselenium dibromide. On the other hand, if any color remains in the melt, seeding will give rods and needles of the undecomposed dibromide.

ACKNOWLEDGMENT

The original goniometric study on which this work was based was carried out under the direction of Joseph Murdock of the University of California. The x-ray powder diffraction data were determined by Irene Corvin and Anne Humphreys.

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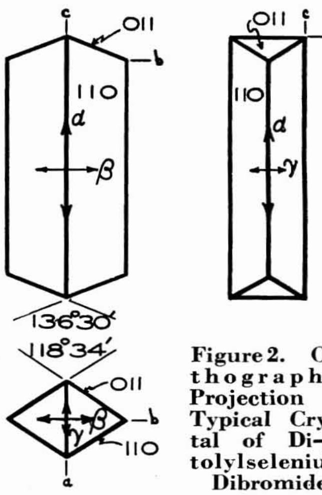

Figure 2. Orthographic Projection of Typical Crystal of Di-*p*-tolylselenium Dibromide

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.

Book Review

Amino Acid Composition of Proteins and Foods. Analytical Methods and Results. *Richard J. Block* and *Diana Bolling*, 2nd ed., revised and enlarged. xx + 601 pages. Charles C Thomas, Springfield, Ill., 1951. Price, $10.50.

The authors state in the preface that their object is to present to the average reader the widely scattered literature on the methods and results of protein analysis in the most easily usable form. They have succeeded in including most of the important contributions up to about 1948. A list of 86 papers, appended to the bibliography of 1160 titles as too late to be included in the text, contains 74 1949 publications. This lag is unfortunate in a field which has been rapidly developing. The novice could not depend solely upon the many detailed directions of methods outlined without further reading. From this point of view perhaps so much detail on many outmoded methods is superfluous. In general, the treatment of methods is uneven. More space is given to a detailed description of the Craig countercurrent apparatus than to microbiological methods. The basal media shown for the latter were those proposed in 1946. Paper chromatographic methods are described in some detail.

The 230 tables of amino acid analyses will probably be of greatest usefulness, although here also the reader will have to use critical judgment in many cases to distinguish the more likely values. The final chapter contains ten tables showing the amounts of amino acids supplied by the components of the diets of several different income groups in the United States.

This book will be a necessary addition to the libraries of those interested in food and protein composition. Paper and printing are excellent. HAROLD S. OLCOTT

Proceedings of First International Polarographic Congress

The first two volumes of the Proceedings of the First International Polarographic Congress, held in Prague in February 1951, are now ready for distribution.

Volume I contains (in English, German, French, or Italian) 44 communications in some 550 pages, sent as contributions to be published in honor of Heyrovský's 60th birthday. It also contains 200 pages of abbreviated papers in Russian, German, English, or French. Volume II presents in 250 pages a full bibliography of polarographic literature from 1922 to 1950, revised by Heyrovský and collaborators.

Both volumes may be obtained through Orbis-Export-Import, Národní 37, Prague I, Czechoslovakia.

Molecular Structure and Spectroscopy

A SYMPOSIUM on Molecular Structure and Spectroscopy was held at Ohio State University, Columbus, Ohio, June 11 to 15, 1951, under the joint sponsorship of Ohio State University and the American Physical Society. Abstracts of the papers of greatest interest to analytical chemists are presented here.

Determination of Low-Temperature Ultraviolet Absorption Spectra with the Cary Spectrophotometer. R. N. JONES AND D. S. KEIR, Division of Chemistry, National Research Council, Ottawa, Ont., Canada

A low-temperature quartz cell has been developed which fits conveniently into the upper cell compartment of the Cary spectrophotometer. The cell has a path length of 4 cm.; a vacuum jacket provides thermal insulation and temperature can be regulated within a range of ±5° C. by a controlled gravity flow of liquid nitrogen. The cell is being applied to the determination of the ultraviolet absorption spectra of polynuclear aromatic hydrocarbons in solution in binary mixtures of isopentane and methyl cyclohexane at temperatures down to −170° C.

Emission Spectra of Some Free Polyatomic Radicals. P. J. DYNE, Division of Physics, National Research Council, Ottawa, Ont., Canada

Two methods of exciting the spectra of free radicals were described. The first is, essentially, a photochemical method. A vapor is irradiated with short-wave length (Schumann region) radiation. In this frequency range one quantum is sufficiently energetic to dissociate the molecule into two radicals or atoms, one of which is electronically excited. The spectrum of the radical or atom is then observed as a fluorescence. The second method consists of a high-frequency (electrodeless) discharge in which the conditions of power input, pressure, and rate of flow have been adjusted to give mild excitation such that the spectra of secondary (diatomic) decomposition products are not predominant.

The ethylene flame bands, attributed by their discoverer to the radical HCO, have been observed in fluorescence in formaldehyde, and a few of the stronger members of the system have been excited in a discharge in formaldehyde. These observations support the original assignment which has recently been criticized.

A band system lying in the blue and near-ultraviolet can be observed in fluorescence in formic acid. This was originally attributed to the HCO radical, but the present work has shown that it is more probably due to the HCO_2 radical. The band system can also be excited in the discharge in formic acid with much higher intensity. A new band system excited in the discharge in fast flowing acetylene was briefly described. The emitter is not known; but it is, fairly certainly, polyatomic.

Theory of Spectra of Molecular Complexes. R. S. MULLIKEN, Physics Department, University of Chicago, Chicago, Ill.

Generalization of previous ideas [especially of Weiss and Brackmann; also Pauling, Dewar, and Woodward. See Mulliken, *J. Am. Chem. Soc.*, 72, 600 (1950); *J. Chem. Phys.*, 19, 514 (1951)] gives a simple quantum-mechanical theory of molecular complexes. Let A be an electron acceptor (Lewis acid) and B a base (electron donor). Typically, A may be a neutral molecule or a positive atom-ion, B a neutral molecule or negative atom-ion. For example, A may be I_2 or Ag^+; B may be benzene or I^-.

Most often, A and B have even-electron diamagnetic structures. Then A and B, and therefore the complex $A.B$ in its ground state, have totally symmetrical singlet (${}^1A_1$) wave functions. These can be written as

$$\psi_N = a\psi_0 + b\psi_1 + \dots \qquad (1)$$

[Equation 1 can be improved by additional terms. If A and B (or A^- and B^+) are identical, or are nearly alike in acid and base properties, these terms are indispensable.]

Here ψ_0 is usually a no-bond function $\psi\,(A,B)$, and ψ_1 a dative function $\psi(A^- - B^+)$ with covalent bond between A^- and B^+ (weak in loose complexes, strong in molecules such as $R_3N.BX_3$).

Complementary to ψ of Equation 1, the complex (in addition to states with A or B alone excited) has a characteristic excited electronic state

$$\psi_E = a'\psi_1 - b'\psi_0 + \dots \qquad (2)$$

An intense absorption band $\psi_N \rightarrow \psi_E$ is predicted, even for a loose complex. Essentially, this probably often accounts for the colors observed when molecular complexes are formed. These $N \rightarrow E$ spectra may be called (in general, intermolecular) charge-transfer spectra. They constitute a generalization of the familiar intense interatomic charge-transfer ($N \rightarrow V$) spectra of molecules.

The $N \rightarrow E$ oscillator strength, f, is easily computed. For the Bz.I complex (Bz = benzene), assuming the I_2 axis to lie parallel to the Bz plane with its center on the z-axis (Bz symmetry axis),

$$f = (4.704 \times 10^{-7})\gamma\mu_{EN}{}^2 \text{ (γ in cm.}^{-1}\text{, μ_{EN} in Debye units)}$$
$$\text{with } \mu_{EN} = a'be(z_{\mathrm{Bz}} - z_{\mathrm{I_2}}) + (aa' - bb')eS(z_{\mathrm{Bz}} - \bar{z})$$

where S is an overlap integral of estimated value 0.1. Hildebrand and Benesi's strong λ3000 transition may be identified as $N \rightarrow E$ of $Bz.I_2$. Using Fairbrother's dielectric constant measurements on I_2 in Bz solution, $0.7D$ is then obtained for the permanent dipole moment of $Bz.I^2$. This yields 0.17 for b in Equation 1 ($b^2 = 0.028$). From b and S, a, a', and b', and then estimating $z_{\mathrm{Bz}} - z_{\mathrm{I_2}}$ as 3.4 A., μ_{EN}

and f can be computed. The computed and observed b-values are 0.19 and 0.30, respectively, a satisfactory agreement.

The theory outlined appears capable of explaining the structure and spectra of Ar.Hl complexes in general (Ar = aromatic hydrocarbon, Hl = halogen molecule) and of numerous other types of complexes.

The "charge-transfer" forces corresponding to resonance of ψ_1 with ψ_0 in Equation 1 to some extent resemble London's dispersion forces. However, they should have strong orientational properties, of possible importance in determining how molecules pack in crystals or liquids. This is because resonance requires that ψ_1 and ψ_0 have the same group-theoretical symmetry. Thus in $Ag^+.Bz$, $\psi_1(Ag - Bz^+)$ violates this requirement if the silver atom is either on the benzene sixfold axis or in the ring plane. (This is because the Bz^+ wave function has nodal planes through both locations, while the Ag function has none.) An intermediate location is thus indicated. This prediction is supported by experimental evidence. In $Bz.I_2$, similar symmetry considerations point to the model assumed above.

Spectra, Stability Constants, and Structures of Aniline-Polynitrobenzene Complexes. J. Landauer and H. McConnell, Physics Department, University of Chicago, Chicago, Ill.

The stability constants and absorption spectra of the 1:1 complexes between aniline and m-dinitrobenzene (mN) and between p-dinitrobenzene (pN) and s-trinitrobenzene (sN) have been determined by a spectrophotometric study of chloroform solutions containing the polynitrobenzenes (N) and aniline. The formation of these complexes may be represented in the equilibria,

$$N + A \rightleftharpoons NA, \qquad K = (NA)/(N)[A]$$

Quantities in parentheses denote molar concentrations and [A] is the mole fraction of aniline. Our calculated values for the stability constants, K, are:

$$K(\text{mNA}) = 0.72; \quad K(\text{pNA}) = 0.70; \quad K(\text{sNA}) = 5.1$$

The spectra were determined in the 340 to 600μ range. The spectrum of the sNA complex has a maximum at 400μ with $\log \epsilon = 3.4$. The extinction coefficients of the mNA and pNA complexes increase continuously with decreasing wave length in the above wave-length range, but exhibit pronounced inflections at ca. 380μ with $\log \epsilon$ again about 3.4.

Evidence for the existence of 1:2 complexes, NA_2, has been obtained. Equations have been formulated which show how variations in the K's and ϵ's with solvent composition can affect the interpretation of the spectrophotometric data.

The stabilities and spectra of the NA complexes can be semiquantitatively understood in terms of the quantum-mechanical theory of acid-base (in the Lewis sense) interactions formulated by Mulliken [*J. Chem. Phys.*, **19**, 514 (1951)]. The theory indicates the improbability of certain symmetrical geometrical structures for the NA complexes. Probable structures were suggested.

Absorption Spectra of the Complexes of Aromatic Hydrocarbons with Metal Ions. G. Jura and L. Grotz, Department of Chemistry, University of California, Berkeley, Calif.

Mesitylene forms complexes with all the metal ions except the alkali metals, strontium, and barium. The work also indicates that radium and thallous ions will not form complexes. The reaction is not restricted to mesitylene, but is found to be general with the aromatic hydrocarbons. Presumably, this is a Lewis acid-base reaction in which two of the π electrons of the aromatic hydrocarbon are involved.

The absorption spectra of a number of these complexes have been determined in solution and on the surface of silica gel. The solution spectra were obtained by dissolving the laurate of the metal in the hydrocarbon. The spectra were determined only above 2800 A. Below this wave length, the solutions become essentially opaque owing to the absorption of the hydrocarbon. The spectra of the complexes of silver, magnesium, zinc, manganous, aluminum, erbium, neodymium, and thorium laurates with mesitylene were determined. All the complexes had a strong band with a maximum between 2900 and 2950 A. The molar extinction coefficients of the magnesium and aluminum complexes were found to be 160, thorium 600, manganese 4000, and the remainder near 1000.

On the surface of the gel, all the complexes except those of thorium and cerium had a band with a maximum at 5600. The spectra of the complexes on the surface were determined to 3200 A. It was not possible to work at shorter wave lengths because of the scattering from the surface of the gel. At wave lengths below 5600 A. there are a number of weaker bands. These bands are dependent upon the metal ion which is complexed. The intensity of the band at 5600 A. varied as the ion potential.

Measurements of the fluorescence of the complexes indicate that the 5600 band on the surface of the gel is probably due to a breakdown of selection rules in the asymmetric field of the solid.

Modifications of Absorption Spectra of Anions Induced by Complex Formation. L. I. Katzin, Chemistry Division, Argonne National Laboratory, Chicago, Ill.

As the majority of inorganic anions are colorless and the ions of metallic elements which most readily form chemical complexes with anions are generally colored, the altered absorption spectrum produced in the visible region of the spectrum by the complex formation is usually referred to as the absorption spectrum of the complex. However, the absorption spectrum of the nitrate ion, with a characteristic peak at about 300 mμ, is altered by complexing with metal ions; and in a given case one can identify shifts of both the anion and cation absorption spectra. The type of nitrate absorption shift found is related to the electronic configuration of the metal atom. Thiocyanate ion also has an absorption in part in reach of the Beckman spectrophotometer (>220 mμ), and in *tert*-butyl alcohol medium can be shown to give a markedly shifted absorption in the presence of cobaltous or nickelous perchlorate, while the spectra in the visible region show characteristic changes in the absorption of the metal ion.

Solid lithium chloride (and hence, presumably, chloride ion) absorbs far in the vacuum ultraviolet. Solutions of lithium chloride in *tert*-butyl alcohol do not absorb appreciably above background in the region above 220 mμ, and neither does cobaltous perchlorate. In mixture, strong absorption in the region 220 to 260 mμ is apparent, in addition to the characteristic cobalt chloride blue color in the visible region. Nickelous perchlorate, in similar fashion, evokes a characteristic absorption spectrum in the same region of the ultraviolet. Bromide and iodide ions, which absorb in the ultraviolet above 220 mμ, also show spectral modifications on forming complexes and allow one to follow the changes in greater detail.

Some features of the quantitative relations of the absorptions were pointed out.

Spectra and Electronic Spectra of Chromate and Permanganate Ions and Related Molecules. M. Wolfsberg and L. Helmholz, Chemistry Department, Washington University, St. Louis, Mo.

An approximate molecular orbital treatment has been carried through for tetrahedral ions of the type CrO_4^{--}, MnO_4^-, ClO_4^- in an effort to arrive at a satisfactory description of the electronic structure of these ions. The visible and near ultraviolet spectra of the transition group ions (VO_4^{---}, CrO_4^{--}, MnO_4^-, etc.) show regularities which should be accounted for qualitatively by a satisfactory theory. Such a theory should also predict that perchlorate and sulfate ions show no near-ultraviolet absorption.

The approximations employed in the solution of the secular equations for the orbitals of different symmetries are radical and probably seriously in error; but it is hoped that the similarity of the molecules for which the calculations were made would allow qualitative conclusions to be drawn from the results. The theory predicts that the first transition will be due to the excitation of a t_1 nonbonding electron to a t_2 essentially antibonding orbital; the second transition, the excitation of a t_2 bonding electron to a t_2 antibonding orbital. The variation in the energy of these transitions with changing central atom is in accord with experiment, as are the relative f-values for the first transition.

The spectra of permanganate ions in different crystalline fields (in solid solution in different nonabsorbing perchlorates) [Teltow, J., *Z. phys. Chem.*, **43**, 198 (1939) (Abt. B)] show the existence of a number of excited states to which transition would be forbidden in the absence of perturbing fields or vibrations. The symmetries and positions (roughly) of these are in agreement with the prediction of the simplified theory.

Intensities of Infrared Bands. D. Z. Robinson, Baird Associates, Inc., Cambridge, Mass.

The method of measurement and the interpretation of the intensities of infrared absorption bands of simple molecules were described. Ordinary methods of making measurements give poor results because the absorption coefficient varies rapidly over the slit width. The true intensity can be obtained by eliminating the violent fluctuations of intensity by broadening the rotational lines with a nonabsorbing foreign gas and eliminating the error due to variations of envelope intensity by extrapolating the integrated absorption coefficient to zero partial pressure [Wilson, E. B., Jr., and Wells, A. J., *J. Chem. Phys.*, **14**, 578 (1946)].

The main emphasis of the paper was on the interpretation of the intensities in terms of bond constants. Bond moments, μ, and changes of bond moment with distance $\partial\mu/\partial r$ can be obtained from the intensities if the normal modes of motion are known. As an example of the method, some of these parameters in CO_2, CS_2, and OCS are obtained. Whenever a rotational mode has the same symmetry as the vibrational mode, the true vibrational mode must be carefully determined.

The future use of absolute intensities to give information for band assignments and to aid in quantitative analysis was discussed.

Vibrational Intensities. Carbon Dioxide and Nitrous Oxide. D. F. Eggers, Jr., and B. L. Crawford, Jr., University of Minnesota, Minneapolis, Minn.

Experimental intensity measurements can be combined with known harmonic and anharmonic potential constants of molecules to determine the variation of dipole moment with displacement. The authors have used a finite Taylor's series for both potential energy and dipole moment. The effect on intensity of frequency variation over the band is included explicitly for both parallel and perpendicular bands, as is Fermi resonance between several bands. Intensities of two fundamental and four combination bands in carbon dioxide were measured. A complete second-order perturbation treatment of intensities was carried out for several bands in carbon dioxide, and the possible relation of the results to resonance structures was mentioned. The relative importance of electrical and mechanical anharmonicity was indicated. An anomalous envelope was found for the 2076 cm.$^{-1}$ band.

Two cubic potential constants were determined for nitrous oxide from measured intensities, rotational convergences, normal coordinates, and bond distances. Using these constants, a first-order intensity treatment was carried out for several combination bands. The intensities of three fundamental and three combination bands were measured. Discrepancies in measured rotational convergences were mentioned, and possible lines were suggested for further work.

Intensities of Some Characteristic Infrared Bands of Hydrocarbons and Oxygenated Hydrocarbons. S. A. Francis, Beacon Laboratories, Texas Co., Beacon, N. Y.

Integrated intensity data were presented for the characteristic CH absorption bands near 2900, 1460, and 1360 cm.$^{-1}$ for a number of hydrocarbons and oxygenated hydrocarbons and for the carbonyl stretching band near 1720 cm.$^{-1}$ for a number of oxygenated hydrocarbons. From these data, structural-group integrated intensities are calculated for $—CH_3$, $>CH_2$, $\rightarrow CH$, and $>C=O$ structural groups. The structural-group intensities are insensitive to the arrangement of the groups within the molecule for the paraffin hydrocarbons. However, the 2900 cm.$^{-1}$ structural-group intensities for $—CH_3$, $>CH_2$, and $\rightarrow CH$ groups adjacent to carbonyl and ester groups are reduced in comparison with similar groups in paraffin hydrocarbons, while the 1460 and 1360 cm.$^{-1}$ intensities are increased. The $C=O$ structural-group intensity remains constant for any one type of oxygenated compound, but different values are obtained for different types such as ketones, esters, and acids. It is concluded that the structural-group intensities remain constant from molecule to molecule as long as the environment of the structural group does not change, but that large changes in intensity can occur when the environment changes. The observed effects of structural-group environment upon structural-group intensities are interpreted qualitatively in terms of bond charge distributions and the nature of the vibrational modes.

Intensities and Shapes of Infrared Absorption Bands in Liquids and Solutions. D. A. Ramsay and R. N. Jones, National Research Council, Ottawa, Ont., Canada

Three methods were described for the experimental determination of the absolute intensities of infrared absorption bands of liquids and solutions. These methods are dependent on a knowledge of the true shape of the absorption band, which may be approximated satisfactorily by a Lorentz equation.

The first method involves direct integration of this equation, a correction factor being applied for the effect of finite slit width. The other methods involve extensions of the extrapolation procedures used by Wilson and Wells and by Bourgin. Assuming a Lorentz band shape and a triangular slit function, the natures of these extrapolations may be calculated for various experimental conditions. Applications of these methods to the measurement of carbonyl intensities in steroids were discussed.

Infrared Measurements on Liquid Methanol and on Solid Methanol above and below the Lambda Point. P. L. Browne, E. E. Bell, and J. G. Daunt, Department of Physics and Astronomy, The Ohio State University, Columbus, Ohio

A satisfactory transmission cell and cryostat system which is capable of being used at very low temperatures was described. Changes observed in the infrared spectrum of methanol as the liquid was cooled, upon solidification, and upon passing through the lambda transition region were reported. Although the results are subject to several interpretations, they appear to favor the assignments of the 1100 cm.$^{-1}$ band in the liquid to the CH_3 rocking motion and the 1420 cm.$^{-1}$ absorption in the liquid to the OH bending motion.

Position and Intensity Trends in Fundamental Frequencies of Symmetrical End-Group Ethane Derivatives. D. C. Smith, Naval Research Laboratory, Washington, D. C., and J. R. Nielsen, University of Oklahoma, Norman, Okla.

New infrared (2 to 38μ) and Raman spectra have been obtained for most ethane derivatives containing fluorine and/or chlorine, and having at least one symmetrical end group ($CH_3—$, $CF_3—$, or $CCl_3—$). Assigned fundamentals in series of related molecules ($CH_3—CH_3 \rightarrow CH_3—CF_3$, $CH_3—CF_3 \rightarrow CH_3—CCl_3$, and $CF_3—CF_3 \rightarrow CF_3—CCl_3$) were reviewed briefly, and certain interesting regularities in the position or intensity of bands were pointed out.

Infrared Bands of the CbO Molecule. V. Ramakrishna Rao, Illinois Institute of Technology, Chicago, Ill.

A new band system, attributable on experimental grounds to the diatomic molecule CbO, was obtained at 6000 to 8800 A. The bands were excited in the d.c. arc between pure columbium electrodes and were photographed on a Hilger E_1 spectrograph with glass optics. The system consists of about 240 bands degraded to the red and apparently divided into 5 sequences. The strongest sequence (between 6496 and 6828 A.) possibly corresponds to $\Delta v = 0$, and a preliminary analysis indicates lower-state differences of 981, 970 cm.$^{-1}$, etc. This suggests the possibility of the system's having a common lower state with the earlier studied [Rao, V. R., *Indian J. Phys.*, **24**, 35 (1950)] system, A, in the visible region. The present system (designated C) should correspond to a transition between quartet or doublet terms involving multiplet structure. This together with the considerable overlap of system C on system B might explain the difficulty experienced in following up any sequence, as can be expected if the multiplet separation is near the vibrational separation. Detailed analysis of the bands is in progress. Facilities for this work were afforded by the University of Chicago.

Present Status of Microwave Spectroscopy. C. H. Townes, Department of Physics, Columbia University, New York, N. Y.

The status of microwave spectroscopy, developments during the past year, present problems, and some possible future developments were briefly reviewed. Much of the recent work has been in extending known techniques and theories. About 2000 lines are now reported, and the range of gas absorption techniques has been extended over the wave-length range 0.125 to 20 cm. In most cases the spectra have been analyzed, giving a wide variety of molecular and nuclear information. This mass of new and accurate data calls for improved theories in many areas. Several new effects and techniques have been reported during the past year. Probably the most important single development is the observation of direct quadrupole transitions in liquids and solids. This is not microwave spectroscopy of the usual type, but at least is closely related to it. A number of other recent individual experiments were mentioned.

Microwave Spectrum of Methyl Alcohol between 20,000 and 40,000 Mc. R. H. Hughes, W. E. Good, and D. K. Coles, Westinghouse Research Laboratories, East Pittsburgh, Pa.

Further progress on the methyl alcohol spectrum was reported. A series of absorption lines of $C^{12}H_3O^{16}H$ has been followed from $J = 2$ up to $J = 30$. The corresponding series for $C^{13}H_3O^{16}H$ and $C^{12}H_3O^{18}H$ have been found and measured up to $J = 31$ and $J = 26$, respectively. The lines of these three series have first-order Stark effects. About twenty lines have been found which have a second-order Stark effect. Some of these are grouped in a way which suggests that they are due to transitions between K-type doublets. Altogether for the three isotopic molecules about 140 lines have been measured and classified according to the order of their Stark effects. J-values have been determined and quantitative Stark effect measurements have been made in many cases.

Microwave Spectrum of Hydrazine. D. J. Millen, Department of Chemistry, Howard University, Cambridge, Mass.

The microwave spectrum of hydrazine in the 18,000 to 35,000 Mc. region has been examined and frequency measurements have been made on about 60 lines. Of these lines, 30 are strong and appear in 8 groups. The remaining lines are weak and are scattered throughout the spectrum. From a consideration of the interaction of the paired electrons of the nitrogen atoms, Sutherland and Penney [Sutherland and Penney, *J. Chem. Phys.*, 2, 242 (1934)] have concluded that the configuration of minimum potential energy is that in which the planes bisecting the NH_2 groups are at right angles. On this basis the hydrazine molecule is a slightly asymmetric rotor, and it is difficult to account for the appearance of such a large number of lines as pure rotational transitions. However, the interchange of the hydrogen atoms on each nitrogen atom and relative rotation of the NH_2 groups leads to eight identical potential minima. Tunneling between these potential minima will produce a splitting of the eightfold degeneracy. The magnitude of this splitting will vary with the rotational energy level and a large number of lines are possible.

Pure Quadrupole Spectra of Solid Chlorine Compounds. R. Livingston, Chemistry Division, Oak Ridge National Laboratory, Oak Ridge, Tenn.

The pure quadrupole spectra of over twenty covalently bonded chlorine compounds have been observed as solids at liquid-nitrogen temperature. These include chlorides of Sn, As, P, Si, Ge, B, and Sb in addition to the substances described below. Small splittings were frequently seen and were interpreted as crystalline field effects. Approximate quadrupole couplings for chlorine may be computed. The approximate Cl^{35} coupling in solid CF_3Cl is −76.18 Mc. as compared with the value of −78.05 Mc. for the gas [Coles, D. K., and Hughes, R. H., *Phys. Rev.*, **76**, 858 (1949)] obtained by microwaves. The Cl^{35} coupling in solid chlorine is −108.5 Mc., which indicates that the chemical bond uses a *p*-orbital with little or no *s*-hybridization. The magnitude of the couplings increases in the sequence CH_2Cl_2, $CHFCl_2$, and CF_2Cl_2 as well as in the sequence $CHCl_3$ and $CFCl_3$. This can be explained by a polarization or inductive effect that makes the C to Cl bond less ionic when highly electronegative F replaces H. The magnitude also increases in the sequence CH_2Cl_2, $CHCl_3$, and CCl_4, but to a more marked degree than that produced by more highly electronegative F, implying that an explanation in addition to the polarization effect is needed. Work at this laboratory on chlorine compounds is continuing.

Measurement of the Microwave Inversion Spectrum of ND_3, ND_2H, and NDH_2. R. G. Nuckolls, L. J. Rueger, and H. Lyons, National Bureau of Standards, Washington, D. C.

Measurement of the inversion spectrum of ND_3, previously reported [Lyons, H., Rueger, L. J., Nuckolls, R. G., and Kessler, M., *Phys. Rev.*, **81**, 630 (1951)] between 2094 and 2533 Mc., has been extended to below 1600 Mc. The main $K = J$ series of absorption lines has been identified and has its low-frequency limit at approximately 1600 Mc. This frequency is to be compared with the figure 2000 estimated by Weiss and Strandberg [Weiss, M. T., and Strandberg, M. W. P., *Phys. Rev.*, **81**, 286 (1951)], and 1600 estimated by Townes (private communication). The apparent intensity distribution is shifted to higher J,K-values than for NH_3, as expected.

A newly designed Stark-modulation, 10-foot, coaxial-absorption cell ($^3/_4 \times {}^5/_{16}$ inch radii) was used with special wave guide transformer sections. Frequencies were read to 0.01 Mc., using a frequency-multiplier system based upon the NBS 100-kc. primary-frequency standard, and are believed accurate to better than 0.1 Mc. A brief discussion was given of measurements on ND_2H and NDH_2, covering the techniques used to identify lines by isotopic species.

Structure and Microwave Spectrum of Methylene Chloride. W. D. Gwinn and R. J. Myers, Department of Chemistry, University of California, Berkeley, Calif.

The microwave spectra of $CH_2Cl_2^{35}$, $CH_2Cl^{35}Cl^{37}$, $CHDCl_2^{35}$, $CHDCl^{35}Cl^{37}$, $CD_2Cl_2^{35}$, and $CD_2Cl^{35}Cl^{37}$ have been determined and assigned. The microwave spectra of $CH_2Cl_2^{37}$, $CHDCl_2^{37}$, and $CD_2Cl_2^{37}$ have been partially determined. This large volume of data is interesting in showing the amount of self-consistency in the effective interatomic distances when the interaction of rotation and vibration is neglected.

Methylene chloride is a nearly symmetric top with the dipole moment perpendicular to the figure axis. As a result, the spectrum has an unusually high density of lines (about 20 multiplets per 1000 Mc.). Most of the lines are due to transitions involving high J-levels. The initial assignment was based mainly on the quadrupole structure of the lines. The appearance of a line of high J-value is very different from a line of low J-value. This assignment was verified by the temperature dependence of some of the lines, by the Stark effect of the $0_{00} - 1_{11}$ lines of 6 different isotopic species and by the self-consistency of the data. The quadrupole multiplets are too weak to be observed in the direct-absorption spectrograph, and the Stark-modulation spectrograph only partially resolved the quadrupole multiplets. However, there is good agreement between the pattern of the partially resolved multiplets and the pattern predicted on the basis of the first-order quadrupole theory.

	$CH_2Cl_2^{35}$, Mc.	$CD_2Cl_2^{35}$, Mc.
a	32,001.7	23,677
b	3,320.5	3,284
c	3,065.3	2,994

C—H distance, A.	1.07
C—Cl distance, A.	1.773
HCH angle, °	112
ClCCl angle	111° 44′
Dipole moment, e.s.u.	1.62×10^{-18}

Determination of the Intensities of Raman Lines. E. J. Rosenbaum, C. C. Cerato, and J. L. Lauer, The Sun Oil Co., Norwood, Pa.

Attention was called to the desirability of obtaining intensity data for Raman lines which would permit quantitative comparisons between laboratories using different apparatus. A simple method for obtaining such data is possible by using the 459 cm.$^{-1}$ line of carbon tetrachloride as a reference and by eliminating the spectrometer and detector properties by calibrating with the radiation from an incandescent lamp, standardized as Illuminant A by the National Bureau of Standards.

Method of Calibrating an Infrared Prism Spectrometer. W. L. Ross and D. E. Little, Washington State Institute of Technology, Pullman, Wash.

This calibration method, developed for a Perkin-Elmer Model-12 spectrometer, covers the regions 5 to 15 μ (NaCl) and 2 to 5 μ (LiF). Standardized techniques lowered the standard deviation of the spectrometer itself to 0.10 cm.$^{-1}$ at 1000 cm.$^{-1}$ The McKinney and Friedel formula, $T_i = T_0 + \frac{a}{\nu_i^2 - \nu_0^2}$, is shown to be analogous in form and method of solution to the Hartmann dispersion formula, $\lambda_i = \lambda_0 + \frac{c}{d_0 + d_i}$. Thus Hartmann-formula techniques have been applied to the McKinney and Friedel equation. Solutions are readily handled on a calculating machine; graphical interpolations are obviated. The results have a standard deviation of 0.28 cm.$^{-1}$ at 1000 cm.$^{-1}$

Design of Effective Raman Sources. W. R. Busing, Metcalf Research Laboratory, Brown University, Providence, R. I.

New techniques in Raman spectroscopy have made increasingly evident the desirability of irradiating the sample with exciting light of as high an intensity as practical. The efficiency of a source is defined as the fraction of the total light which falls on the sample and the effective power is given by the product of the efficiency and the power supplied to the lamps. Approximate calculations have been made comparing the effective power of various types of sources. Some of these calculations have been experimentally verified.

Sources using an enclosed magnesium oxide diffuse reflector are potentially the most effective known. Their high efficiency depends, however, on keeping to a minimum the escape or absorption of light; in practice other sources may be superior in performance and convenience. The use of elliptical mirrors results in a highly efficient source. The use of more than two lamps in this type of source provides little or no improvement in the effective power. A source using a spiral low-pressure arc has a low efficiency which may make it less effective than either of the above sources in spite of its high power.

Photoelectric Recording Raman Spectrograph. W. R. Busing and D. F. Hornig, Metcalf Research Laboratory, Brown University, Providence, R. I.

A photoelectric recording Raman spectrograph has been constructed and is now in use in this laboratory. The main component of the instrument is an autocollimating monochromator using a single 5-inch off-axis parabolic mirror. The dispersing elements consist of two large glass prisms, 60° and 30°, respectively, in a Littrow arrangement so that they are equivalent to three 60° prisms. The spectrum is scanned by rotating the prisms as a unit. A variety of conventional Raman sources has been used.

Before entering the monochromator, the scattered light is chopped by a shutter at a frequency of 30 cycles. The photomultiplier at the exit slit produces an alternating-current signal which is amplified and then rectified by synchronous switches operating from the same shaft as the chopping disk. The resulting direct-current signal is supplied to a Leeds & Northrup recording potentiometer.

A second photomultiplier may be used to monitor the mercury arcs and regulate the slide-wire current of the recorder, thus making the recorded spectrum substantially independent of fluctuations in the exciting lamps.

Split-Beam Recording Photometer with a Single Detector and Automatic Slit Control. R. G. Stokes and J. J. Oberly, Crystal Branch, Metallurgy Division, Naval Research Laboratory, Washington, D. C.

A photometer unit has been developed for use with a variety of monochromators to convert them to spectrophotometers. The utilization of a split beam and a single phase-sensitive detector, with the two radiation beams chopped 90° out of phase, is similar to the Savitsky system [Savitsky, A., and Halford, R. S., *Rev. Sci. Instruments*, **21**, 203 (1950)]. An automatic slit control has been added to maintain a constant reference-signal level from the detector over a wide spectral region for any combination of source and detector. The two beams have also been separated widely and extended over a long path containing only mirrors in order to admit specimen holders for a variety of conditions—temperature, pressure, etc. Fast response is achieved with a wide-band amplifier and a minimum of filtering, the latter being facilitated by square-wave chopping of the radiation beams. The two d.c. voltages from the phase detector are applied to a high-impedance ratio taker whose output can then be applied to any unmodified recorder.

The photometer has been first applied to a Beckman quartz monochromator. The full range 0.2 to 2.0 microns is covered with photomultipliers, a thalofide cell, and a lead sulfide cell as detectors. The unit may also be used with the Golay cell in the far infrared without modification. The spectral transmittance curve of a didymium-glass filter was run from 0.4 to 1.2 microns with a thalofide detector in 2 minutes without appreciable distortion of the small features of the spectrum, and in 40 seconds with a maximum error of 5%.

A Review of Recent Near-Infrared Grating Spectroscopy. A. H. NIELSEN, Department of Physics, The University of Tennessee, Knoxville, Tenn.

Recent papers on infrared grating spectroscopy as well as work which has come to the author's attention privately were reviewed.

Humphreys, Plyler, and Benedict at the National Bureau of Standards are pursuing important work on standard lines in the infrared. They have remeasured the overtone of CO to correct the earlier frequencies by Lagemann, Nielsen, and Dickey, and to compare the lines with those computed by Rao. Other accurately measured spectra from this laboratory were reviewed.

Investigation of the earth's atmosphere and study of atomic lines in the sun are being carried on by Goldberg, Mohler, McMath, and others at Michigan, by Migeotte and colleagues at Liege, and by Shaw, Chapman, and others at Ohio State University. Beautiful atmospheric spectra and new data concerning a number of gases, CO_2, N_2O, CH_4, have been reported by these investigators. In a recent search for NO in the atmosphere (at Ohio State) no evidence of it was found. At the University of Tennessee ν_2 and ν_3 of $C^{14}O_2$ have been resolved. It is suggested that intensities of these lines, if observable in atmospheric spectra, might give information on the formation of $C^{14}O_2$ from cosmic ray bombardment of N^{14}.

Evidence of CO and OH in flame spectra and a discussion of the temperature of flames were given jointly by Silverman, Benedict, Plyler, and Humphreys, Applied Physics Laboratory and National Bureau of Standards. A vacuum-grating spectrometer of great resolving power has recently been constructed for some of this work.

Thompson and coworkers at Oxford have reported spectra and constants for a number of molecules such as $CFHCH_2$. Evidence of a Coriolis interaction in allene similar to that found in CH_2O was reported.

At the National Research Council of Ottawa, Herzberg and colleagues have published some beautiful measurements of combination and overtone bands observed with a 21-foot grating and a multiple reflection cell of great length. Notable among their recent papers are those on HNCO and N_2O. New values of x_{ij} and ω_i are given from about 34 analyzed bands of N_2O.

The work of the Ohio State group particularly highlights the importance of vacuum instrumentation. The most important paper is that on C_2H_2 by Bell and Nielsen. About thirty bands have been analyzed, and new constants are given. New measurements on the disputed 3.7μ band of H_2S verify earlier work. A beautifully resolved record of the 10μ NH_3 band was published by Wood, Bell, and Nielsen showing the line splitting in great detail.

The University of Tennessee, cooperating with K-25 Laboratories at Oak Ridge, has carried along a number of problems: The diatomic molecules HI, DI, and CIF have been investigated. New values of the constants have been determined. Talley has completed investigation of C_2D_2 from 1 to 20μ. With a multiple reflection cell he examined the lead sulfide region and for C_2H_2 filled the gap between Herzberg's photographic and Bell's near-infrared measurements. About 55 new bands have been added to the normal and deuterated acetylene data with which a consistent vibrational analysis may be attempted. With the same cell Kaylor has resolved many new bands in CH_4 and CD_4. Resolution of several bands in F_2CO and FNO have aided Smith and Magnuson in interpreting many of the microwave lines observed for these molecules. ClO_2 has been reexamined and an unexplained band has been found at 290 cm.$^{-1}$ A comparison of the molecular shape predicted from electron diffraction and infrared data was given. Other molecules being investigated with the grating are CF_4 and GeF_4.

Infrared Spectrum and Molecular Structure of Cyclopropane. H. W. NEILL AND G. B. B. M. SUTHERLAND, Randall Laboratory of Physics, University of Michigan, Ann Arbor, Mich.

The infrared spectrum of cyclopropane has been re-examined between 6000 and 700 cm.$^{-1}$ About 40 absorption bands have been detected in this region; several have been studied in more detail with grating instruments under a resolving power of about 5000.

The bands at 4601 and 3103 cm.$^{-1}$ are parallel-type bands with simple P—Q—R structure. The former gives a rotation spacing of $B'' = 0.69$ cm.$^{-1}$, while the latter gives $B'' = 0.66$ cm.$^{-1}$ The latter value will probably be more reliable for calculation of the common moment of inertia, since it is associated with a fundamental frequency, whereas the former is associated with a combination frequency.

The bands at 1028 and 870 cm.$^{-1}$, which show very similar contours under moderate resolving power (consisting of P, Q, and R branches with a subsidiary peak on the high frequency side of the Q branch), are entirely different under high resolving power. The 1028 cm.$^{-1}$ band appears to be a pure perpendicular band and exhibits a remarkable series of lines stretching from 1020 to 1054 cm.$^{-1}$ with a nearly constant spacing of 0.44 cm^{-1}. The general weak-weak-strong trend of these lines proves that the three carbon atoms lie at the vertices of an equilateral triangle, although the intensity distribution of the central lines deviates considerably from that given by theory. The absorption centered at 870 cm.$^{-1}$ appears to arise from two frequencies, one parallel and one perpendicular, with strong Coriolis interaction.

Emission and Absorption Spectrum of CO in the Region of 2.3μ. S. SILVERMAN, Applied Physics Laboratory, The Johns Hopkins University, Silver Spring, Md., AND E. K. PLYLER AND W. S. BENEDICT, National Bureau of Standards, Washington, D. C.

New measurements have been made in the CO spectrum in the region of the overtone band, both in emission and in absorption, using the 15,000-line grating spectrograph at the National Bureau of Standards and the 7200-line vacuum-grating spectrograph at the Applied Physics Laboratory. In absorption, the 2-0 band of $C^{12}O^{16}$ has been measured between R-30 and P-29, and 27 lines of $C^{13}O^{16}$ and 8 lines of $C^{12}O^{18}$ have also been measured. In emission from oxyacetylene and CO-oxygen flames, the 2-0, 3-1, 4-2, and 5-3 bands, which form heads in the R branch near $J = 50$, have been identified. The 2-0 band shows resolved lines out to $J = 46$ in both the R and P branches.

The wave lengths were determined by superposing emission lines in higher orders of Kr, A, Xe, and Hg discharges. In this way a number of lines, which fall close to one or another of the standard lines, could be measured with high accuracy. The remaining lines could be measured by interpolation between these secondary standards. The measurements are believed accurate to better than ± 0.02 cm^{-1}.

The measurements show small but definite discrepancies from the values calculated according to the constants of Herzberg and Rao [*J. Chem. Phys.*, **17**, 1099 (1949)] and Rao [*J. Chem. Phys.*, **18**, 213 (1950)]. The lines of $J \leqslant 25$, in the 2-0 branch, are consistently 0.08 cm.$^{-1}$ lower than the predicted values; at higher J the R-branch lines fall above and the P-branch lines fall below their values. A comparison of provisional constants derived from the authors' measurements with their values is:

Constant	ω_e	$X_e\omega_e$	$Y_e\omega_e$	B_e	α_e	D_e	β_e
Value, cm.$^{-1}$ according to SPB	2169.82	13.295	0.0112	1.93129	0.017515	5.82×10^{-6}	0.02×10^{-6}
Value, cm.$^{-1}$ according to H and R	2170.21	13.461	0.0308	1.93139	0.017485	6.43×10^{-6}	0.04×10^{-6}

The observed isotope shift of the 2-0 band region, for C^{12}-C^{13}, is 93.253 ± 0.01 cm^{-1}. Using the authors' molecular constants, and the atomic masses $C^{12} = 12.00382$ and $C^{13} = 13.00751$, the calculated shift is 93.241 cm^{-1}. For O^{16}-O^{18} the observed shift is 101.01 ± 0.05 cm.$^{-1}$, and the calculated shift, with $O^{18} = 18.0049$, 101.025 cm^{-1}.

The emission spectra permit the determination of vibrational and rotational "temperatures" with an accuracy of $\pm 5\%$. Agreement between the two modes is observed in the outer cone of the CO-oxygen flame, but in the region just above the reaction zone the rotational temperatures are several hundred degrees higher.

Emission of H_2O in the Region 1.7 to 2.2μ. A. M. BASS, W. S. BENEDICT, AND E. K. PLYLER, National Bureau of Standards, Washington, D. C.

The emission of oxyhydrogen and oxyacetylene flames has been studied under high resolution with a 15,000-line grating spectrometer and lead sulfide cell. Slits as narrow as 0.2 cm.$^{-1}$ could be employed. The water-vapor band, which in room-temperature absorption extends from about 1.80 to 1.96μ, is broadened in emission from 1.7 to 2.2μ (5000 to 4550 cm.$^{-1}$). Over 600 strong lines have been measured in this region, and a number of weaker, partially resolved lines appear reproducibly. The analysis of the rotational structures is progressing. Many lines of the (011–000) band agree with those found in laboratory and atmospheric absorption [Nelson, R. C., and Benedict, W. S., *Phys. Rev.*, **74**, 703 (1948)], when allowance is made for the greatly increased effective temperature, and many additional lines from higher energy levels may be identified. The principal series $JJ \longleftrightarrow (J+1)\,(J+1)$ may be followed out to $J' = 22$ in both the P and R branches. Corresponding lines in the upper-state bands (021–010) and (031–020) have also been identified with somewhat lower intensity, and a few lines may be assigned to the (041–030), (111–100), and (012–001) bands.

Quantitative Infrared-Intensity and Line-Width Measurements on HCl, HBr, and NO. S. S. Penner and D. Weber, Jet Propulsion Laboratory, California Institute of Technology, Pasadena, Calif.

Quantitative infrared intensity measurements on HCl, HBr, and NO have been carried out by two independent experimental methods. In one group of tests an infrared-inactive gas was used to produce sufficient pressure-broadening of the rotational lines to permit quantitative measurements with a standard infrared spectrometer. In another series of investigations, the desired experimental conditions were obtained by the judicious use of self-broadening. The concordance between values for the integrated absorption obtained by the two methods was found to be within the limits of experimental error. The results for HCl are in good agreement with the numerical values reported by other investigators [Bourgin, D. E., *Phys. Rev.*, **29,** 794 (1927); Rollefson, R., and Rollefson, A. H., *Phys. Rev.*, **48,** 779 (1935)].

For pressures not exceeding 10 atmospheres, the experimentally determined absorption measurements are correlated quantitatively by the use of theoretical relations derivable from the dispersion formula for rotational line width. By carrying out numerical calculations, with the rotational half-width treated as a variable parameter, a direct comparison between calculated and observed infrared absorption has been used to determine rotational half-widths. Lower limits for the rotational half-widths have been determined by using Elsasser's treatment (Elsasser, W. M., Harvard Meteorological Studies No. 6, Milton, Mass., 1942) for equally spaced and equally intense rotational lines.

Representative results of intensity and line-width measurements are summarized in Table I.

Table I. Integrated Absorption and Rotational Half-Width for Several Diatomic Molecules

Molecule	α_F[a], Cm.$^{-2}$ Atm.$^{-1}$*	α_O[b], Cm.$^{-2}$ Atm.$^{-1}$	δ_F[c], Cm.$^{-1}$ Atm.$^{-1}$	δ_O[d], Cm.$^{-1}$ Atm.$^{-1}$
HCl	150	3.69	1.5	1.2
HBr	56.4	0.6	0.8	...
NO	61.4	1.94	0.9	1.1

* Pressure corresponds to equivalent pressure of ideal gas.

[a] α_F = integrated absorption for fundamental vibration-rotation band.
[b] α_O = integrated absorption for first overtone.
[c] δ_F = rotational half-width of fundamental for self-broadening.
[d] δ_O = rotational half-width of first overtone for self-broadening.

Raman Spectroscopy. F. F. Cleveland, Spectroscopy Laboratory, Department of Physics, Illinois Institute of Technology, Chicago, Ill.

The Raman effect was discovered in 1928 and since that time an average of 125 papers per year on this subject have appeared. Our Raman spectrograms are obtained by use of two cylindrical, horizontal, low-pressure, Pyrex Hg arcs. Raman-displacement spectrograms are obtained with a 2-prism spectrograph having a dispersion of 33 A. per mm. and depolarization-factor spectrograms with a Hilger E518 spectrograph having a dispersion of 63 A. per mm., both at 4500 A. Relative intensities are obtained with a microdensitometer and a microphotometer. A reliable single-exposure method [*J. Chem. Phys.*, **13,** 101 (1945)] is used for the depolarization factors because short-cut methods can lead to erroneous conclusions about molecular structure.

As some vibrations are not observable in Raman spectra, an infrared spectrometer is a necessary supplement. Infrared data are especially needed from 100 to 400 cm.$^{-1}$ and with greater resolution above 2000 cm.$^{-1}$

Group theory selection rules predict the spectra that should result for various assumed structures of the molecule [*Am. J. Phys.*, **11,** 239 (1943)]. Comparison with experimental data may thus enable one to determine the structure. Dangerous assumptions—frequently made—are that all the observed Raman lines are fundamentals, and that fundamentals correspond only to strong bands. Hence, a reliable assignment of the fundamentals is necessary. Meister suggests that an anharmonicity treatment, even if incomplete, may provide useful additional checks upon the assignments. Another important check is a normal coordinate treatment, using the most general potential-energy expression possible [*Am. J. Phys.*, **14,** 13 (1946)]. Even this, however, does not always lead to an unambiguous assignment for all lines, especially when two fundamentals fall close together. The final decision on the assignment of the fundamentals must be a matter of considered judgment in which all the possible tests are taken into account.

When the fundamentals have been reliably assigned, and their degeneracies determined, one can then calculate thermodynamic properties for the ideal gaseous state, provided the product of the three principal moments of inertia, or the bond distances and interbond angles, are known [*Chem. Rev.*, **27,** 17 (1940)].

Infrared and Raman Spectra of Diacetylene. A. Vallance Jones, Division of Physics, National Research Council, Ottawa, Ont., Canada

The infrared absorption spectrum of gaseous diacetylene has been measured from 500 to 4000 cm.$^{-1}$ and the contours of the bands have been resolved. Several new bands have been found including a very strong perpendicular-type band at 629 cm^{-1}. In the photographic infrared region three parallel-type infrared bands have been resolved with a 21-foot grating. The lines of these bands show an intensity alternation similar to that found for acetylene. The Raman spectrum of liquid diacetylene at −20° to −30° C. has been photographed and the polarization of the lines measured. Several new Raman lines were obtained.

These results lead to a new assignment of the vibrational spectrum. The symmetrical C—C stretching mode, ν_3 (in Herzberg's notation), is assigned to a polarized Raman line at 878 cm.$^{-1}$, while the depolarized line at 642 cm.$^{-1}$ is ascribed to the π_g hydrogen bending mode. The other π_g vibrational mode, ν_7, has been identified with the Raman line at 483 cm.$^{-1}$, while the π_u mode, ν_8, has been correlated with the strong infrared band at 629 cm.$^{-1}$

This assignment leads to a force constant for the central C—C bond which is higher than that in ethane, in agreement with the anomalously small C—C single bond distance. The difficulty experienced by previous authors with regard to this point is thus removed. A provisional analysis of the photographic infrared bands indicates that the moment of inertia of the molecule is consistent with the internuclear distances obtained from electron diffraction experiments by Pauling, Springall, and Palmer.

Force Constants and Fundamental Frequencies of Dimethyldiacetylene and Diacetylene. S. M. Ferigle, F. F. Cleveland, and A. G. Meister, Illinois Institute of Technology, Chicago, Ill.

Redetermination of the depolarization factors of dimethyldiacetylene indicates that the 475 cm.$^{-1}$ line is depolarized. Using force constants taken from previous work on methylacetylene, methylhaloacetylenes, and dimethylacetylene, it is found that the 475 cm.$^{-1}$ line should be a bending frequency instead of the central C—C stretching frequency. This stretching frequency falls in the region 450–550 cm.$^{-1}$ when the central C—C stretching force constant varies from 4 to 6.5 millidynes per A. The end C—C stretching frequency lies in the region 950 to 1150 cm.$^{-1}$, its value being greatly affected by the value chosen for the central C—C stretching force constant. Additional Raman spectra of liquid dimethyldiacetylene are being taken in order to determine more accurately the location of these two frequencies; for the spectra obtained from solutions of dimethyldiacetylene only one very weak line was found in each region.

Assuming the 644 cm.$^{-1}$ band of diacetylene is a bending frequency, a reasonable set of force constants for the doubly degenerate vibrations results. The determination of the force constants for the nondegenerate vibrations and the calculated value of the C—C stretching frequency is in progress for this molecule.

Vibrational Spectra of the Acetone Molecule. D. H. Rank, R. E. Kagarise, and E. R. Shull, Pennsylvania State College, State College, Pa.

The authors have prepared acetone-d_6 in high purity and have obtained Raman and infrared spectra and polarizations. They have also obtained the infrared spectrum of the gas and liquid in the rock-salt region. They have taken some low-temperature Raman spectra of the acetone which gives rise to some interesting results. They have performed a vibrational analysis which is complete for certain classes of vibrations, since in these cases they can unequivocally apply the Teller-Redlich product rule.

Vibrational Spectra of Symmetrical Tetrachloro- and Tetrabromoethane. R. E. Kagarise and D. H. Rank, Pennsylvania State College, State College, Pa.

The Raman and infrared spectra of liquid 1,1,2,2-tetrachloro- and 1,1,2,2-tetrabromoethane have been investigated. Using a grating spectrograph of 3.8 A. per mm. dispersion, the authors have observed the chlorine isotope effect for the $\Delta\nu$ = 353 and 366 cm.$^{-1}$ line pair, and have verified the previous results of Rank, Sheppard, and Szasz concerning the "anomalous" intensity contour exhibited by the 353 cm.$^{-1}$ vibration. From temperature intensity measurements in the Raman effect and Raman-infrared correspondences, they conclude that the two forms possess C_{2h} and C_2 symmetry, with the C_2 form being the more stable one. On the basis of this conclusion they are able to explain the intensity contours observed in the chlorine isotope effect. The value of ΔH for the reaction $C_2 \rightarrow C_{2h}$ in *s*-tetrabromoethane was found to be 910 calories per mole.

Raman Spectral Studies of Equilibria in Electrolytic Solutions. T. F. Young, Department of Chemistry, University of Chicago, Chicago, Ill.

Raman spectra have long been used to determine the structures (symmetries) of ions in solution. Intensities of strong lines have been used to trace variations in degrees of dissociation, but accuracy has, hitherto, been unsatisfactory because of limitations of photographic methods.

With photoelectric cells (multiplier type) integrated intensities can be determined, under suitable conditions, with probable errors considerably better than 1%. Lamps of special design, a power supply monitored with a potentiometer, and a calibrated d.c. amplifier (all well shielded) are essential features of the instrumentation. Concentrations as small as 0.01 molar can be measured.

Determinations of NO_3^- and HNO_3 concentrations (in nitric acid solutions) supplement and confirm each other. Similarly, concentrations of SO_4^{--}, HSO_4^-, and H_2SO_4 have been determined as functions of concentration, temperature, etc. Various properties of sulfuric acid solutions can be explained in terms of the Raman data. The method is able to detect complex ions not hitherto known, and then produce information concerning equilibria involving them. The shapes of Raman lines remain remarkably constant throughout wide variations of conditions. Under certain conditions, however, variations in "half-widths" have been detected and measured precisely.

Rotational Structure of the ν_3 Raman Band of Methane. H. L. Welsh, B. P. Stoicheff, C. Cumming, and G. E. St. John. Department of Physics, University of Toronto, Toronto, Canada

A multiple reflection Raman tube was used with a quartz spectrograph, giving a dispersion of 25.7 cm.$^{-1}$ per mm. at λ2537, to study the fine structure of the ν_3 band of methane at a pressure of 4 atmospheres. Seventy-five lines in the band were resolved, and evidence for most of the fifteen theoretically predicted subbranches was found. Various combination relations were used to calculate the molecular constants from the frequencies of selected, unblended, Raman lines and the infrared frequencies of Nielsen and Nielsen [Nielsen, A. H., and Nielsen, H. H., *Phys. Rev.*, 48, 864 (1935)]. The analysis gave three different rotational constants B_1^+, B_1^0, and B_1^- for the upper vibrational state and, surprisingly, three different values for the ground state. The average rotational constants are $B_1 = 5.207$, $D_1 = 1.6 \times 10^{-4}$ and $B_0 = 5.244$ and $D_0 = 1.3 \times 10^{-4}$. The values of ν_0 and ζ_3 were found to be 3018.1 cm.$^{-1}$ and 0.055.

Infrared Spectra and Structure of Proteins. H. Kessler, A. V. Stuart, G. B. B. M. Sutherland, and K. N. Tanner, Randall Laboratory of Physics, University of Michigan, Ann Arbor, Mich.

The infrared spectra of 23 proteins of various types have been investigated in the range 2 to 15μ using a Perkin-Elmer double-beam spectrophotometer with a rock-salt prism. Although there is a considerable general resemblance between the spectra of all the proteins, there are also marked differences—e.g., in the relative intensities of common bands and in their fine structure. Moreover, certain proteins exhibit bands not found in others. The extent to which differences in the spectra can be related to differences in amino acid composition was considered.

In order to throw some light on the interpretation of these spectra, observations have been made on amides and on nylon. In the former, the effects of hydrogen bonding have been found to be much more complex than was previously suspected in the region between 6 and 15μ; in nylon it has been found that raising the temperature causes shifts in the bands at 6 and 6.5μ very similar to those attributed by others to the change in a protein from the α to the β configuration. Since nylon is considered to remain in the β configuration to high temperatures, this throws doubt on the correlation of these shifts with the transition from an α to a β configuration. Experiments have been made on partially deuterating certain proteins by repeated immersion in heavy water. It is found that the bands at 3.08, 3.28, 6.5, 8.1, and 14.2μ decrease in intensity, while increased intensity of absorption is observed at 4.15 and 6.96μ. Observations have also been made using polarized radiation with oriented materials. The significance of all these results on the interpretation of protein spectra was discussed.

Infrared Spectroscopy and Polymorphic Forms of Crystals. D. N. Kendall, American Cyanamid Co., Calco Chemical Division, Bound Brook, N. J.

The application of infrared spectroscopy to the study of tautomerism, stereoisomerism, and molecular structure through the use of isotopes is well known. It has now been found that infrared techniques can be applied to the identification of polymorphic forms of both organic and inorganic crystals. Infrared spectroscopy has been conveniently and successfully used to distinguish between different crystalline forms of substances of the same chemical composition. The method complements and supplements the x-ray, microscopical, and electron diffraction techniques. The advantages and disadvantages of these various techniques for study of polymorphism were discussed. The value of the infrared method was illustrated by the results obtained on such pigments as the titanium dioxides, copper phthalocyanine blues, and para reds.

Future Instrumentation in Infrared. B. H. Billings, Research Laboratory, Baird Associates, Inc., Cambridge, Mass.

During the past decade research has been in progress on various techniques and devices which in the next decade will probably become elements of new infrared instrumentation. Some of these techniques and devices were discussed. They include such things as narrow-band filters, new varieties of sources, and interference spectroscopy. An attempt was made to show some examples of new infrared instrumentation which might arise from some of these tools. Infrared spectroscopy as it is used today in structure analysis and in chemical analysis is frequently limited by the resolution which can be obtained. The resolution limit in existing instruments in the near infrared appears to be set by the optics rather than by the detector. With the narrow-band filters now being developed and with interference spectroscopy, it should be possible to extend the resolution limit beyond present instrumentation to the point where it is again limited by receiver sensitivity. Some experiments were shown which indicated the magnitude of the resolution increase.

Diffraction-Grating Design. D. Richardson and N. A. Finkelstein, Bausch and Lomb Optical Co., Rochester, N. Y.

In planning the most effective diffraction-grating instrument for a given application, it is desirable to consider the performance requirements in their relation to the wide range of properties available from modern methods for the production of gratings and echelles.

The primary operational specifications of wave-length region, resolution, dispersion, available energy, and space can be related to the secondary considerations of type of mounting, optical aperture of the instrument, cross dispersion, and free spectral range by appropriate relationships. Proper evaluation of all these factors reduces to a grating design for which the ruled area, the number of grooves, the groove face angle, and the quality are determined.

The precise control of groove angle and spacing, coupled with freedom in the choice of the grating constant and area of ruling, point the way to new spectrograph designs with outstanding performance. A series of equations relating the important parameters was given together with graphical solutions which facilitate the design of grating instruments.

High Resolution in the 10-Micron Region. C. W. Peters, Randall Laboratory of Physics, University of Michigan, Ann Arbor, Mich.

Resolution of about 0.1 cm.$^{-1}$ has been obtained in the 8 to 14 micron range with the grating spectrometer built by Hardy in 1932. This is within a factor of two of the Rayleigh limit for the diffraction grating used, and compares to previous values between 0.25 and 0.33 cm.$^{-1}$ Part of the improvement results from the elimination of spurious noises in the amplifying system, particularly in the Firestone photoelectric preamplifier; and part from a new 2400-line-per-inch diffraction grating that is considerably superior to previous ones ruled here. Results on the 10-micron absorption band of ammonia were shown.

Optical Crystals in Infrared Instrumentation. S. S. Ballard, Department of Physics, Tufts College, Medford, Mass.

The use of optical crystals is becoming much more widespread, owing principally to the ready availability of artificially grown crystals, and the increase of practical interest in the infrared region of the spectrum, where optical glass does not transmit. There is also a growing industrial interest in the ultraviolet spectral region, due to the increasing use of ultraviolet spectrophotometry and to recent developments in ultraviolet microscopy. The various synthetic crystals which are now employed in optical instrumentation were discussed in terms of their current availability and their physical properties. Charts were presented which facilitate the evaluation of several materials for infrared and ultraviolet transmission limits, dispersive power, elastic constants, cold flow, thermal expansion, thermal conductivity, melting point, solubility, and hardness.

Precision Micrometer Adjustments to a Perkin-Elmer Infrared Spectrometer. R. M. Hainer, Arthur D. Little, Inc., Cambridge, Mass.

Modifications to the standard optical supports of the Perkin-Elmer infrared spectrometer have been made to facilitate alignment, obtain the best resolution, and simplify change of prisms. Seventeen micrometer adjustments control the displacements of three figured mirrors, two plane mirrors, and the thermocouple, and allow the setting of mirrors to the required tolerance, the mapping of response over the full range of displacement, the reproducibility of any configuration without loss of alternative settings, and the compensations for the variations in homogeneity of different prisms.

The precision of the micrometers is greater than the equivalent precision of the optical components. The tolerance of the settings, as found empirically, can be related to the limiting optical properties of the system—e.g., diffraction of the prism, circle of confusion, and flatness of the field of the collimator. The tolerance of adjustment of the collimator is approximately 0.001 inch in terms of displacements of the mirror for several independent adjustments. From this it is apparent how great is the number of configurations which approximate alignment but do not adequately attain it, and how difficult it is to achieve adjustment which is not reproducible to this precision.

An improved procedure for alignment of the optics has been achieved by utilizing a fine-mesh screen, by mapping distortion over a range in units of the fundamental tolerances, and by judging a given image without recourse to comparison of image quality from memory. The alignment achieved by these means was demonstrated in terms of a new and exact theory of limiting resolution now in the course of development.

Optical Modification of a Double-Beam Infrared Spectrophotometer for Establishing Linearity at Low Sample Transmissions. L. W. Herscher and C. W. Young, The Dow Chemical Co., Midland, Mich.

An optical system was described for introducing an auxiliary beam of light into the sample beam path of a Baird Associates double-beam infrared spectrophotometer. The auxiliary-beam intensity is a constant fraction of the reference-beam intensity. This arrangement avoids working in the nonlinear range of the reference-beam attenuator near complete closure. In addition, a dynamically balanced zero is obtained at complete sample absorption, a condition not satisfied by the instrument before the modification was introduced.

Flame Spectrophotometer with Interval Burner-Atomizer. P. Gilbert, Beckman Scientific Instruments, Bethesda, Md.

A simplified flame accessory for Beckman spectrophotometers embodies a miniature one-piece burner-atomizer combination which sprays small samples directly into an oxygen-acetylene or oxygen-hydrogen flame. Glass construction, with palladium capillary, permits several structural simplifications. The instrument provides exceptionally rapid reading without difficulty from drift, contamination, warm-up requirement, or clogging. Precision is better than 0.5% and calibration is held from day to day. Any liquid of viscosity up to several centipoises can be analyzed, and there is no limit on solute concentration. The hotter flame gives improved detection limits for many metals. An outstanding example is the determination of lead in gasoline. A revised and enlarged tabulation of flame spectra was given. Analytical procedures and interferences were discussed.

Chemical Analysis by Infrared Spectroscopy. J. Y. Beach, California Research Corp., Richmond, Calif.

The use of infrared spectroscopic measurements for chemical analysis continues to increase. New instrumentation has made earlier procedures easier to apply and has facilitated the development of new procedures. Recent papers have described detailed analysis of complicated liquid petroleum hydrocarbon mixtures, which would be virtually impossible by other analytical methods. Some new applications to the analysis of mixtures of hydrocarbon and other gases have been presented, including methods for circumventing difficulties from pressure broadening. Other recent examples of infrared analysis of multicomponent mixtures were described. Infrared measurements have been used for determining the deuterium content of substances and this has been used in isotope-dilution chemical analysis for organic compounds. Additional use has been made of the fact that characteristic infrared absorption bonds can be attributed to certain chemical groups in a variety of molecules. Spectra of derivatives of long-chain compounds can be described in terms of trans-olefin, ester, alcohol, peroxide, and hydroperoxide groups.

In the writer's laboratory a mechanical slit cam has been installed on a Beckman IR-2 spectrometer for giving absorption spectra in approximate per cent transmission. Construction and operation of the apparatus were described. Examples were shown of the applicability of the double-beam feature of the Perkin-Elmer Model 21 spectrometer to the identification and analysis of gases in multicomponent gas mixtures.

Punched-Card Identification of Mixtures by Combined Use of Infrared-Band Positions and No-Band Regions. N. Wright and C. W. Young, Dow Chemical Co., Midland, Mich., and Ascher Opler, The Dow Chemical Co., Great Western Division, Pittsburg, Calif.

The problem of identifying the several components of a mixture is considerably more complicated than that of identifying a single, isolated compound. The latter can easily be handled by an index system, by hand-manipulated punched cards, or by simple sorting machines.

A method was described which uses, in addition to band positions information as to regions in which the unknown spectrum does not have bands. By accepting from the standard file compounds having a band in at least one of the several positions at which the unknown has bands, and by rejecting all compounds having strong bands in the no-band regions of the unknown, there results a narrowing of the field of search to 10% or less of the starting file. Of primary importance is the fact that in this process of concentration none of the components of the mixture is lost. Coupling with this procedure the customary narrowing according to presence or absence of easily recognized groupings, such as C═O, OH, etc., reduces the field to 1 to 2% of the entire standard file.

As it is laborious to apply this method using hand-manipulated (Keysort) cards or the IBM sorting machine, a technique for using the IBM-077 collator was presented. With this machine it is possible to search a punched-card file of spectra to drop out cards (compounds) meeting all the following requirements in one pass through the machine: Strong bands are absent in designated spectral positions. At least one of a selected group of bands is present. Specified structural groupings are absent.

Details of the punching code and of the plug-board wiring were presented. Examples of application of the method were described.

Preparation of Samples in the Solid State for Spectroscopic Study in the Infrared and Ultraviolet Regions. Sister Miriam Michael Stimson, Sienna Heights College, Adrian, Mich.

The desirability of correlating both the ultraviolet and infrared absorption for characterization and for theoretical consideration is recognized. However, the limitation imposed by the solubility of many organic solids makes uniform conditions for solution work over this range of the spectrum impossible. The further problem of solvent-sample interaction and of solvent absorption, where this is selective, cannot be overlooked. A method for readily preparing organic materials for spectrophotometric study in both the ultraviolet and infrared regions has been developed.

The method involves the thorough mixing of the finely ground organic with solid potassium bromide and subsequent pressing into disks. The method described has been employed for study of the free base of guanine and also for the hydrochloride, and also has been used for anhydrous cytosine and the crystalline hydrate. Other types of compounds also were shown. The range of concentrations and disk thicknesses which will permit quantitative determination of intensity as expressed by molecular extinction coefficients was discussed.

An Automatic Prism-Changing Infrared Spectrophotometer. J. J. Shipman and R. F. Miller, B. F. Goodrich Co., Research Center, Brecksville, Ohio

An infrared spectrophotometer has been built incorporating a photometer system which uses light from the same area on the source in both the sample and reference beams. The spectrometer is equipped with four prisms, KBr, NaCl, CaF_2, and LiF, and switches automatically from KBr to NaCl, from NaCl to CaF_2, and from CaF_2 to LiF in scanning the region from 25 to 2 microns.

The reference beam is attenuated to match the sample beam by means of a comb mechanically coupled to the recorder pen. Balance is achieved through the agency of 5-cps. chopped radiation, an a.c. amplifier having a voltage gain of 10^8, full-wave synchronous rectification, and a d.c. amplifier having a voltage gain of 140 controlling the armature current of a d.c. motor driving the comb. The a.c. amplifier band width is 5 cps. The residual a.c. signal at balance is used through a separate channel to control the slit width. Manual control of wave length and slit width is also provided.

Modification of a Beckman Model DU Spectrophotometer for Automatic Operation at 220 to 2050μ. Wilbur Kaye, Cham Canon, and R. G. Devaney, Tennessee Eastman Co., Kingsport, Tenn.

A Beckman Model DU quartz spectrophotometer has been modified to record automatically absorption spectra from 220 to 2050μ. This improvement has been achieved through replacement of the red-sensitive phototube with a lead sulfide cell, provision of a rotating slotted drum to interrupt the light beam, and use of an electronic recorder. The null meter circuit of the spectrophotometer may be used if desired. All the standard Beckman accessories may be used without modification.

In view of the demonstrated resolving power in the near-infrared region, the ruggedness, and the relative low cost of this modified instrument, it is believed a new field for analysis has been opened.

Recent Investigations in the Infrared Spectrum. J. LECOMTE, Laboratoire des Recherches Physiques à la Sorbonne, l'Université de Paris, Paris, France

The spectra of metallic metaborates, the general formula of which is BO_2Me (Me = monovalent metal), taken by the powder method reveal the presence of other groups, probably B_4O_7 and BO_3 (Duval and Lecomte). It has been possible by the same method to follow the modifications of structure as the sample is heated (Dupuy). The spectra of minerals (chiefly carbonates) currently are being studied with polarized radiation together with the spectra of crystalline powders and powders prepared synthetically having the same chemical composition, in an effort to identify the observed bands (Louisfert). Vincent is, at present, carrying out theoretical and experimental studies on the intensities of the absorption bands of gases (HCl and CO) and plans to measure the variation of the intensities for successive harmonics at different temperatures. The fine structure, between 1.5 and 1.9 μ approximately, of the vibration-rotation spectra of the halogen derivatives of methane and hydrogen sulfide was obtained by Mathis. She has already published a satisfactory interpretation for the band in water vapor at 2.6 and 1.87μ which she has resolved very well, and is currently attempting to explain the very numerous lines obtained for the other compounds. Gauthier again has set about to study the harmonic bands and combination bands in the near-infrared with different aliphatic hydrocarbon and liquid benzene by means of a grating spectrograph. His interpretations are now applied to the study of chemical reactions in the liquid state. Finally, Larnaudie has calculated the position of the 32 fundamental vibrations of cyclohexane, and the agreement with experiment proves very satisfactory (determination of force and interaction constants). This study is now being extended to other derivatives of cyclohexane.

Symposia on Analysis and Metallography of Titanium and on Surfaces

W. C. MCCRONE, *Armour Research Foundation, Illinois Institute of Technology, Chicago 16, Ill.*, AND
A. F. KIRKPATRICK, *American Cyanamid Co., Stamford, Conn.*

THESE consecutive Symposia on Analysis and Metallography of Titanium and on Surfaces formed the fourth of an annual series of symposia sponsored by the Armour Research Foundation of Illinois Institute of Technology. The Symposium on Analysis and Metallography of Titanium was held on June 11, 12, and 13; the Symposium on Surfaces was held June 14, 15, and 16. All sessions met in the Sheraton Hotel, Chicago, Ill. Nearly 400 people representing many branches of chemistry, physics, metallurgy, and engineering registered.

After introductory remarks and a welcome from H. A. Leedy, Director, Armour Research Foundation, the Symposium on Analysis and Metallography of Titanium was conducted in five sessions designated as: Analytical Methods for Commercial Titanium, Analytical Methods in Titanium Alloy Development, Determination of Oxygen in Titanium, Instrumental Methods for Titanium and Its Alloys, and Metallography of Titanium and Its Alloys. The moderators for these sessions were, respectively: Steven Urban, National Lead Co.; E. J. Center, Battelle Memorial Institute; E. J. Chapin, Naval Research Laboratory, Washington, D. C.; B. F. Scriber, National Bureau of Standards; J. R. Long, National Research Council; and W. L. Finlay, Ren-Cru Titanium, Inc. These moderators were aided by panels made up of active workers in the various fields. The panel members presented semiformal summaries of the various subjects under discussion. As has been the practice in these symposia, the audience informally and spontaneously participated in the discussions. The questions and contributions greatly enhanced the value of the symposium to those attending.

The cochairmen of the Titanium Symposium, Julian Glasser and Max Hansen, are to be commended for organizing the first full-scale symposium on analytical methods for titanium and its alloys and on the metallography of these materials. The importance of titanium and its alloys, principally because of their high strength-to-weight ratio, has brought this metal in less than 5 years to a developmental stage that took 50 years for aluminum. Unfortunately, the analytical methods for titanium and its alloying elements have not kept pace with the engineering developments. Because so many laboratories are proceeding so rapidly in the development of analytical methods, there is no hope for publication as a means of exchanging information at this stage and a symposium with ample discussion time was shown during this week to be the answer to this need.

The first session on analytical methods for commercial titanium and commercial alloys opened with some orienting remarks and a discussion of sampling methods by Steven Urban of the National Lead Co. Further discussion covered the analysis of titanium sponge and the determination of carbon, tungsten, manganese, chromium, iron, and aluminum in titanium ingot and commercial alloys. Of these the determination for iron by ammonium thiocyanate is excellent in low concentrations and in the absence of chromium; the determination for chromium by the ammonium persulfate method is satisfactory if titanium is kept in solution; the combustion for carbon is routine if high temperatures, particularly with the new dielectric heating furnaces, are used; with care the manganese determination by oxidation to permanganate and titration with sodium arsenite are satisfactory; the cinchonine method for tungsten gives low results; and aluminum may be determined chemically, using cupferron, or spectrographically. Chromium can also be determined simultaneously by the latter technique.

In the Monday afternoon session covering analytical methods in titanium alloy development, chemical methods for nickel, cobalt, copper, niobium, tantalum, molybdenum, vanadium, and beryllium were discussed. Nickel can be determined either gravimetrically or photometrically, copper by electrodeposition, and cobalt colorimetrically using Nitroso-R salt at 520 millimicrons. Additional work is needed on the other elements covered.

The use of neutron activation techniques has been applied to tungsten and chlorine in titanium where the sensitivities are 0.03 and 0.003 microgram, respectively. These methods may be useful for the analysis of spectrographic standards or for special homogeneity experiments; however, the application to routine analysis depends, of course, on the availability of high intensity neutron sources.

Titanium, as the metal, has the unusual ability to dissolve oxygen and other gases to an amazing degree with attendant effects on the physical properties. The importance of being able to determine the oxygen content in titanium resulted in a full morning session devoted to this subject. The moderator, Edwin J. Chapin, was able to present a well-coordinated discussion from his discussion leaders and the audience. It was decided that the results obtained by the much, and probably justly, maligned vacuum fusion method depend on the skill, ingenuity, and patience of the operator. It is hoped that a simpler and more trustworthy method may be developed in the future. Spectrographic approaches, a neutron activation technique, a mass spectrometric method, two fluorinations, and a hydrogen chloride procedure were all presented as hopeful possibilities. Much work remains to be done, however, on the determination of oxygen in titanium.

The Tuesday afternoon session on instrumental methods of analysis for titanium and its alloys dealt more with possibilities than eventualities but was complete with an evaluation of each of several physical analytical methods by authorities in their use. The potentialities of x-ray fluorescence, polarography, the emission spectrograph, electron microscopy, and electron diffraction were all ably covered.

On Wednesday the discussion turned to metallography which was to serve as a bridge between the analytical discussions of the previous two days and the Symposium on Surfaces of the succeeding three days. Metallography is an analytical tool since the various solid phases can be recognized and often measured quantitatively by a real analysis. At the same time the metallographer is interested in polishing and etching techniques in addition to light and electron microscopy, all of which were more completely discussed on Thursday and Friday.

The metallography of titanium was included in order to bring together people from both research and industry, to discuss informally and freely the many problems confronting this relatively new metallurgical field. Formal presentations by experts on subjects such as metallographic techniques, interpretation of microstructures of titanium and its alloys, kinetics of structural changes occurring during heat treatment, etc., were followed by stimulating and informative discussions. These discussions, possibly even more than the more formal parts of the meeting, resulted in the free exchange of information and a better understanding of the many problems related to the metallography of titanium, in particular, and the industrial development of titanium, in general. The large attendance at the meeting, and the active discussion, reflected the fact that although there is a great interest in this new, promising material, there are also many attendant problems to be solved before it can find wide commercial application.

During the session on metallography, it was emphasized that titanium is a very difficult material for study. Its allotropic transformation, tendency to smear and flow, susceptibility to cold working, weak diffraction, and strong fluorescence with x-rays, and the unknown effects of impurities contribute to the difficulties of the preparation and examination of specimens. The various methods for cutting, grinding, polishing, and etching metallographic specimens were compared. The general opinion was that electrolytic polishing and etching offered the most promise. With these techniques, the production of surface artifacts is minimized. There was considerable discussion of various chemical etchants that can be used. The present status of the metallographic structure of pure and commercial titanium was summarized. A great deal of information remains to be determined on the nature and identity of impurities. A session was spent in consideration of the various aspects of the transformation kinetics of titanium and its alloys. Time-temperature curves like those for austenitic transformations in steels have been and are being determined for titanium alloys and are being applied to metallurgical treatments.

The cochairmen, W. C. McCrone and C. F. Tufts, organized the program so that the session on metallography successfully connected this symposium with the Symposium on Surfaces.

After a welcome and introductory remarks by K. W. Miller, Assistant Director of Research, Armour Research Foundation, the Symposium on Surfaces was conducted in four sessions designated as: Formation of Surfaces, Geometry of Surfaces, Structure of Surfaces, and Problems and Applications. The moderators for these sessions were, respectively: C. S. Smith, Institute for the Study of Metals, University of Chicago; E. J. Abbott, Physicists Research Co.; Georg Hass, Fort Belvoir; and J. J. Bikerman, Merck & Co. A discussion group consisting of five or six commentators aided the moderators. This symposium differed from the former in that no extended summaries of the subject matters were presented; instead, an outline of the topics to be considered was presented at the start of each session and the commentators initiated the discussion. Progress was governed largely by comments and questions from the audience.

The first session on the formation of surfaces was characterized by the attention to metals as would be expected from the influence of the preceding symposium. Considerable time was spent in discussion of the mechanism of polishing and abrading, and the influence of these procedures on the observed structures of surface layers. The relatively new technique of ion bombardment at low pressures for the preparation of metallic surfaces was reviewed. A surface may be cleaned, etched, and brightened by controlling the accelerating voltage and the gas pressure. Although optical contrast is usually not good, it can be enhanced by the process of "heat tinting," which is the introduction of air into the vacuum chamber and the subsequent formation of oxide films. As it has been found that the sample surface may reach a temperature of 700° C., it is necessary that the temperature effect must not be overlooked when this procedure is being considered for sample preparation. Tilting of the sample with respect to the ion beam results in a great increase in the rate of action. Ion bombardment yields surfaces that are excellent for examination by electron diffraction.

Fractographic techniques were shown to be of value in the examination of crystals, metals, and resins. Fractographic examination of silicon carbide crystals produced evidence that was in complete agreement with the stepwise spiral growth that had been observed with the high temperature microscope. Electron micrographs of replicas of fracture surfaces of resins generally show detail that allow a determination of the number of resinous phases present, the distribution of fillers, and an estimation of the macromolecular weight.

The session on the geometry of surfaces covered a large number of ways to examine surfaces. These ranged from a simple adaptation of the Foucault "knife-edge" test for low power microscopical examination, through phase and interference microscopy, multiple reflection interferometry, stereoscopic examination with both the optical and electron microscopes, to the tracer point methods of the machine shop. Tracer point and profilometer methods are now being applied to surfaces other than metals, such as linoleum and paper.

C. P. Saylor summarized the highlights of the colloquium on Microscopical Phase and Interference Contrast recently held in Paris. He briefly described some of the newer microscopes using the principles of phase change and interference for improving contrast. A new lens system for increasing the working distance of a normal objective was described by Francesco Scandone of Officine Galileo.

Progress is being made in the development of the two-step microscope of Gabor and of the point emission microscope of Mueller. Both instruments offer the promise of the availability of high resolving power; however, serious technical difficulties must be overcome before they can become of general use.

The session on the structure of surfaces included a discussion of the application of electron and x-ray diffraction, spectroscopy, microscopy, and other techniques. It was re-emphasized that each instrument or method is not universal in its application but must take its place in conjunction with all possible methods of approach to a problem. Investigations are in progress of the use of higher voltages, greater than 30 to 60 kv., for electron diffraction. The diffraction patterns obtained are essentially the same as those obtained with the normal voltages. Five hundred kilovolts have been used with good results for specimens up to 6 to 7 A. in thickness. Sometimes these higher voltages produce changes in the specimens.

The session on problems and applications covered the range of the following subjects: friction, wear, gloss, luster, wettability, adsorption, adhesion, lubrication, and catalysis. There was considerable discussion of friction. The present status of the fundamental thinking on this subject was summarized. Apparently, the basic concepts are controversial, for there was an active, but good natured, discussion.

These two symposia were thoroughly successful in carrying out the tradition of the annual series of symposia sponsored by the Armour Research Foundation. It is certainly hoped that the series will be continued through the years.

ASTM Symposia

The 54th annual meeting of the American Society for Testing Materials, held at Atlantic City, N. J., from June 18 to 22, 1951, featured two symposia of special interest to analytical chemists.

SYMPOSIUM ON FLAME PHOTOMETRY

The principle of flame photometry has been known for a good many years. However, the practical use of this principle has increased during the past few years as a result of the production of commercially available flame photometers. The analytical chemist has always been faced with a long, tedious method of chemical analysis for sodium, potassium, lithium, calcium, and magnesium. During the recent war years, the need for quick, accurate analyses of small amounts of sodium and potassium in blood probably accelerated the work of developing a flame photometer which could meet these specification requirements.

Realizing that the flame photometer had certain inherent limitations, members of Committee C-1 investigated the possible application of this instrument to the determination of sodium and potassium in portland cement. A method of analysis was developed, using a commercial flame photometer, which gave accuracies within the limits set up by the Methods of Chemical Analysis of Portland Cement C 114-47. A tentative method of flame photometric test for Na_2O and K_2O in portland cement was adopted by the society at the annual meeting in June 1949, and designated ASTM C 228-49 T. This tentative method has facilitated and accelerated many research programs on the effect of sodium oxide and potassium oxide on cement and concrete. However, new and improved test methods have to be devised to keep abreast of new developments.

The members of Committee C-1 on Cement and Committee D-2 on Petroleum Products and Lubricants are all aware of the importance to industry of testing methods. Accordingly, they have arranged this symposium devoted entirely to methods of analysis by flame photometry so that information on new testing methods will be available. Because the use of the flame photometer in testing methods is rather new, it was felt that all members of these committees would be interested in hearing papers devoted to the fundamentals and limitations of the flame photometer and to its specific applications in these committees' respective fields.

Flame Photometry. Review and Prospect. V. M. Meloche, University of Wisconsin.

In introducing the subject of flame photometry, this paper attempted to create a background for the papers which follow. A general review of representative contributions in this field was given. Advantages and limitations of the method were highlighted. Although the procedure is used for a wide variety of samples, the widest application of the method at present involves the determination of sodium, potassium, and calcium. Among the difficulties described, those due to unfavorable ratios between background and element radiation still seem important. Of the instrumental types described special mention was made of the latest Beckman and Weichselbaum instruments.

Design Construction, and Operation of a Stable Internal Standard Flame Photometer for Sodium, Potassium, and Lithium Analysis in Biological Fluids. C. L. Fox, Jr., Columbia University.

Flame photometry offers an exceptionally rapid method for the determination of sodium, potassium, and lithium in blood, urine, body fluids, and tissues if the requisite accuracy can be obtained under routine laboratory conditions with such complex samples. With the instrument described, analyses are very rapidly performed with an accuracy of $\pm 1\%$. This photometer is relatively independent of fluctuations in various experimental conditions which affect the accuracy of other instruments.

Use of the Beckman and Perkin-Elmer Flame Photometers for the Determination of Alkalies in Portland Cement. J. J. Diamond and B. L. Bean, National Bureau of Standards.

A procedure was described for the determination of Na_2O and K_2O in portland cement using the original model 11300 Beckman flame photometer. The results obtained on several representative cements indicate a precision and accuracy about the same as those obtainable by gravimetric methods and by the ASTM Tentative Method C 228–49 T using the Perkin-Elmer flame photometer. It is suggested that the ASTM and federal specifications permit the use, for these determinations, of other suitable instruments in addition to the Perkin-Elmer, and that the Beckman model 11300 be among those permitted.

Applications of Flame Photometry to Materials Investigations. J. L. Gilliland, Bureau of Reclamation.

Flame photometry, one of the newer techniques of instrumental analytical chemistry, is finding increasing use in a variety of materials investigations. In this paper, applications to analytical work on irrigation water, lubricating oil, ores, metals, and silicate materials, including portland cement, were discussed. Studies on the water-soluble alkalies in hydrating cements, base exchange in pozzuolanas, optimum gypsum content of cements, base exchange capacity of soils, and false setting behavior of cements are described, with special reference to the use of the flame photometer in this work. The paper includes an extensive list of references.

Determination of Lithium Oxide in Portland Cement. W. J. McCoy and G. G. Christiansen, Lehigh Portland Cement Co.

The paper suggested a rapid and reasonably accurate method for the determination of Li_2O in portland cement by the flame photometer. The need for such a method is suggested by several factors; (1) the present ASTM Referee Method C 114-47 (gravimetric) for the determination of K_2O and Na_2O includes any Li_2O that might be present with the Na_2O while the ASTM Tentative Method C 228–49 T (Flame Photometer) does not, (2) the classical methods for determination of lithium are tedious, time-consuming, and sometimes inaccurate; (3) that in some instances lithium has been found to have an effect opposite to that of sodium on the expansion associated with the alkali-aggregate reaction in concrete.

Control of Interferences Caused by Acids and Salts in the Flame Photometric Determination of Sodium and Potassium. Frank T. Eggertsen, Garrard Wyld, and Louis Lykken, Shell Development Co.

In the flame photometric determination of sodium and potassium, substantial negative errors are produced by moderate concentrations of common acids and salts, when the instrument operates on a mist produced in a spray chamber and an internal standard is not used. These errors appear to be due principally to differences in the amount of evaporation from the mist droplets which occurs in the spray chamber. Interference from this source can be virtually eliminated by adding a high concentration of a salt or acid, as a buffer, to both the test solution and comparison standards.

The Effect of Organic Solvents on the Flame Photometric Emission of Certain Elements. G. W. Curtis, H. E. Knauer, and L. E. Hunter, Socony-Vacuum Oil Co.

Experience with a limited number of hydrocarbons used as solvents in flame photometric procedures with metallo-organic compounds suggested the possibility that other nonaqueous materials may exert an influence upon the emission characteristics of metals. In order to explore this possibility, a variety of compounds including hydrocarbons, oxygen-, nitrogen-, and halogen-containing materials were tested using both alkali and alkaline-earth metals in the form of metalloorganic compounds. The data obtained from the various combinations are presented and discussed.

Determination of Tetraethyllead in Gasoline by Flame Photometry. P. T. Gilbert, Jr., Beckman Instruments, Inc.

A very rapid method of determining lead in gasoline is provided by the new flame photometry attachment for the Beckman quartz spectrophotometer. At 405.8 $m\mu$ in the oxyhydrogen or oxyacetylene flame, comparisons accurate to 0.01 ml. of tetraethyllead per gallon can be made between gasolines of the same base stock. Routine determinations can be carried out at the rate of 30 or more samples per hour. It is shown that it should be possible with suitable burners to compare gasolines of different base stocks, by employing the ratio of lead emission to spectral background or to fluidity.

Determination of Calcium in Lubricating Oil by Flame Spectrophotometer. M. L. Moberg, V. B. Waithman, W. H. Ellis, and H. D. DeBois, California Research Corp.

A rapid method for determining the calcium content of oil has been devised using the flame spectrophotometer. A Beckman instrument was used for this work. The sample is dissolved in benzene and the resulting solution atomized into the flame, the intensity at 6260 A. wave length measured, and the intensity compared with that given by a pair of standards. At concentrations of 2 per cent or less sample in benzene, variations of viscosity of the sample have negligible effect on the accuracy. The presence of phosphorus not combined with the calcium will give no interference. Phosphorus chemically combined with the calcium will cause low results. The presence of sodium, sulfur, zinc, and lead has no effect.

A Modified Recording Flame Photometer. W. H. King and W. M. Priestley, Esso Laboratories.

A Beckman flame photometer has been modified for use as a recording instrument and has been in service for over a year in this laboratory. The use of a recording technique has proved to be advantageous in flame photometer work since zero drift, sensitivity drift, and aspirator change difficulties are compensated by a recording technique. The flame spectrum of a sample may be scanned in a few minutes, thereby presenting a rapid qualitative analysis. Unexpected elements have shown up in recorded flame spectra which otherwise may have been overlooked.

The instrument described here uses a photomultiplier detector which permits operation at extremely low light intensity levels. Through this sensitive detector system the minimum detectable amounts of many elements have been lowered.

The Flame Photometer in the Analysis of Water and Water-Formed Deposits. R. K. Scott, V. M. Marcy, and J. J. Hronas, Hall Laboratories, Inc.

The use of the flame photometer in the determination of sodium and potassium in industrial water and water-formed deposits is discussed. The flame photometer is shown to give results of sufficient precision and accuracy for routine determinations without the numerous separations required in classical chemical analysis.

Raw waters, treated waters, and boiler waters are run without preliminary treatment. Deposits require only solution of the sample, the procedure for which is presented.

Since a single flame photometer determination is a matter of 10 to 15 sec. it becomes entirely practical to determine approximately the sodium or potassium content of the sample, run standard samples to bracket the estimated concentration, and interpolate linearly, for the final value. A complete determination, including calculations, can thus be done in a matter of a few minutes.

SYMPOSIUM ON CHEMICAL ANALYSES OF INORGANIC SOLIDS BY MEANS OF MASS SPECTROMETER

Mass Spectrometric Analysis of Solids with the High Frequency Spark. J. A. Hipple, National Bureau of Standards, Washington, D. C.

A method of using a direct electrical detection with a source employing a high frequency spark was described. The erratic fluctuations of the source are monitored with an auxiliary electrode and the ratios of the various types of ions to this monitor current are recorded as the magnetic field is varied to scan the mass spectrum across the exit slit of the spectrometer. The successful application of this technique to the analysis of some solid samples of known chemical composition was discussed.

Mass Spectrometric Analysis of Copper for Cuprous Oxide Rectifiers. W. M. Hickam, Westinghouse Research Laboratories, East Pittsburgh, Pa.

A number of analyses of Chilean coppers used for cuprous oxide rectifiers have been made by mass spectrometric analysis of a molecular beam obtained by vaporization of the copper samples, and mass spectrometric analysis of gas obtained using vacuum fusion techniques. The results from a number of analyses were presented and correlation with rectifier performance was indicated.

Isotopic Tracers as an Aid to Chemical Analyses with the Mass Spectrometer. Mark G. Inghram, Argonne National Laboratory, Chicago, Ill.

There are two fundamentally different methods of doing chemical analyses with the mass spectrometer. The first is the Dempster hot spark method, and the second is the isotopic dilution method. The former has the advantage that it can analyze for "every" element present in a solid sample without chemical manipulation. The second, while it requires chemical manipulation, has sensitivities of 10^3 to 10^4 times that of the hot spark method—of the order of 1 part in 10^{10}. The second of these methods was described in the present paper.

The isotopic dilution method involves dissolving the sample to be analyzed, adding a known amount of isotope tracer, and measuring the isotopic composition of the resulting mixture with a mass spectrometer. The isotopic composition gives the weight of the element or elements in question in terms of the weight of sample dissolved and the weight of the tracer added. The method is independent of chemical yields in any processing of the sample—i. e., it does not involve an undetermined systematic error. Examples of the technique were shown in which the sensitivities were better than 1 part per billion.

Discussion included remarks by A. E. Cameron, Union Carbide and Carbon Corp., Oak Ridge, Tenn.

Philadelphia Analytical Group Officers

The following officers of the Analytical and Microchemical Group of the Philadelphia Section, American Chemical Society, have been elected for 1951–52.

Chairman, Albert B. Sample, Bryn Mawr Hospital
Vice Chairman, Walter Clavan, Pennsylvania Salt Manufacturing Co.
Secretary, Ruth Savacool McCard, Smith, Kline & French Laboratories
Executive Committee, William G. Batt, Biochemical Research Foundation; Herbert K. Alber, Arthur H. Thomas Co.; O. Davis Shreve, E. I. du Pont de Nemours & Co.

The Analyst's Calendar

Gordon Research Conferences

Since publication of the program of analytical papers of the Gordon Research Conferences [Anal. Chem., **23**, 812 (1951)] changes have been made in the program on "Current Trends in Analytical Chemistry," to be presented at New Hampton, N. H.

August 6

Philosophy of Trace Analysis. S. E. Q. Ashley, General Electric Co.
Logarithmic Diagrams in Trade Analysis. J. Gillis, University of Ghent
Colorimetric Trace Analysis. J. H. Yoe, University of Virginia

August 7

Trace Analysis of Petroleum Products. H. Levin, The Texas Co.
Fluorescence Analysis. C. E. White, University of Maryland
Spot Test Methods. P. W. West, Louisiana State University

August 8

Coulometric Analysis. E. H. Swift, California Institute of Technology
Coulometric Analysis. W. D. Cooke, Princeton University
Electrolytic Trace Analysis Involving Radioactive Indicators. L. B. Rogers, Massachusetts Institute of Technology
Trace Analysis Based on Electrochemical Reactions at a Rotated Mercury Electrode. T. S. Lee, University of Chicago

August 9

Radioactive Tracer Methods. J. F. Flagg, General Electric Co.
Isotopic Dilution Analysis. N. Trenner, Merck & Co., Inc.

August 10

Trace Gas Analysis. L. K. Nash, Massachusetts Institute of Technology

American Association for the Advancement of Science. Gordon Research Conference, Colby Junior College, New London, N. H., and New Hampton School, New Hampton, N. H., July 23 to August 10
International Congress on Analytical Chemistry. United Kingdom, August 8 to 13

AIDS FOR THE ANALYST.....

Index for Identifying Spectrograms Viewed on a Comparator.

A. J. Mitteldorf (present address, Armour Research Foundation of Illinois Institute of Technology, Chicago 16, Ill.), and J. P. Cestaro, National Lead Co. Research Laboratories, Brooklyn 1, N. Y.

In spectrochemical analysis work from 10 to 30 spectrograms are generally photographed on a single plate or strip of 35-mm. film. In order to determine which of these spectrograms are being viewed on the screen of a projection-type comparator, it is necessary to turn to the first (or last) spectrogram and then count until the proper spectrograms appear on the screen. The device photographed in Figure 1 makes this unnecessary. When mounted on an A.R.L. comparator-densitometer, a number corresponding to each spectrogram is projected alongside the proper spectrogram.

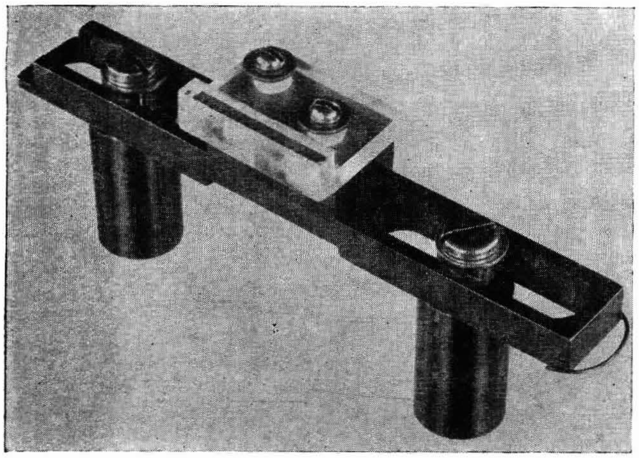

Figure 1. Comparator Index, Showing Numbers Engraved on Lucite Block and Sliding Brass Support

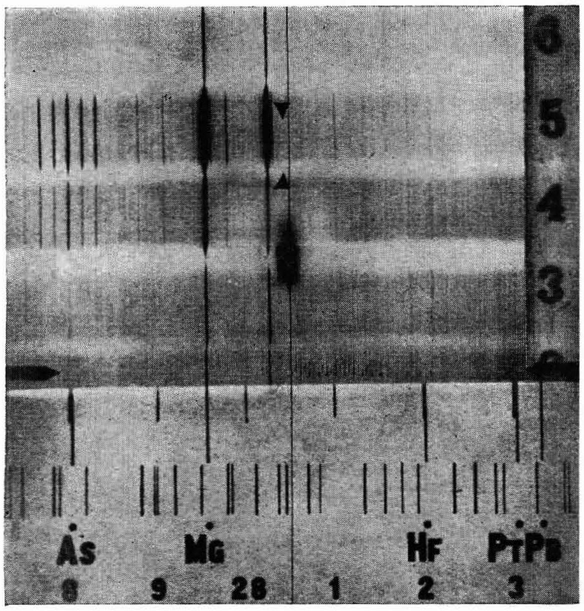

Figure 2. Viewing Screen of ARL Comparator with Numbers Identifying Spectrograms

The constructional details of the index may be seen from Figure 1. Consecutive numbers, whose spacing is equal to the spacing between consecutive spectrograms, are engraved on a Lucite block and painted black. The block is mounted on a brass support which slides in a direction perpendicular to the length of the spectrograms on the shoulders of two brass cylinders. These, in turn, are screwed to the base of the comparator. The ends of the sliding member fit into the plate holder, a spring at one end of the former taking up any play. The dimensions and positioning are such that the numbers on the Lucite block are directly beneath the film or plate and at the edge of the optical path. As a result, when the spectrograms are racked from one to the next, the index is moved at the same rate and the appropriate numbers always appear next to their corresponding spectrogram.

Figure 2 is a photograph of the viewing screen as it appears with numbers projected alongside each spectrogram.

Transfer Syringe for Manual Countercurrent Distribution.

Morton Beroza, Entomology and Plant Quarantine, United States Department of Agriculture, Beltsville, Md.

In a recent countercurrent distribution study a simple apparatus gave results satisfactory for homogeneity studies. The apparatus consists of glass-stoppered bottles and the illustrated syringe which is used to transfer the solutions. Countercurrent distribution procedure is the same as that described by Craig *et al.* [*J. Biol. Chem.*, **161**, 321 (1945)] for use with separatory funnels.

The syringe may be easily made from a glass hypodermic syringe with an offset Luer tip, *E*, of a capacity equal to or slightly greater than the volume of liquid to be transferred. A metal plate, *B*, is securely attached to the plunger, *F*, by means of three rubber faucet washers, *C*, trimmed to size, and three machine screws, *D*. A long machine screw, *A*, passes through a threaded hole in the plate and, when properly aligned, meets the base, *J*, of a wooden platform, *I*, secured to the barrel, *G*, of the syringe with Scotch tape, *H*. Tygon tubing, *K*, is used to hold a glass tube, *L*, of sufficient length to reach the bottom of the bottle.

To remove the lower layer from a bottle, the tip of *L* is held at the bottom of the bottle, as illustrated, and the plunger is pulled out. When almost all of the lower layer is drawn up into the syringe, the plunger is swung clockwise and *A* is adjusted so that it meets the wood platform, *J*. When *A* is rotated clockwise, the plunger draws up the last of the lower layer into the syringe and holds it there. The syringe is then withdrawn from the bottle, and contents are emptied into the next bottle by turning the plunger counterclockwise one-quarter turn and pushing the plunger into the barrel. The small amount of liquid remaining in the glass tube may be ejected by alternately withdrawing and pushing in the plunger about 0.25 inch several times.

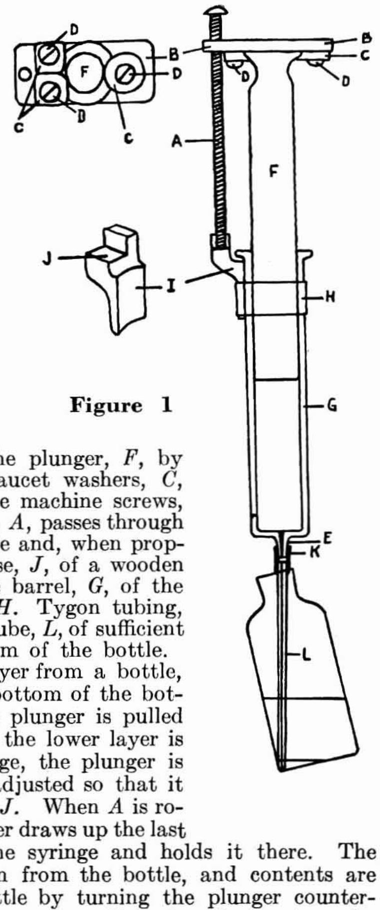

Figure 1

One-ounce glass-stoppered bottles have been found convenient in distributions employing 10-ml. phases.

Considerable time and effort may be saved by employing a shaking machine, such as a Fisher-Kahn shaker, to mix the solutions. While a transfer is being made (about 1 minute), the bottle into which the previous transfer was made can be equilibrated by mechanical shaking. By this means an eight-plate distribution can be carried out in about 1 hour and a twenty-plate distribution in 6 hours, exclusive of the time necessary for analysis of the substance in the bottles.

Craig *et al.* point out that a manual eight-plate distribution can be achieved without much trouble and recommend such a distribution for preliminary investigations. The present apparatus has an advantage over separatory funnels in that satisfactory results may be obtained with smaller volumes of liquid and contamination with stopcock grease is avoided; the distribution is more accurate and it can be carried out more rapidly than with separatory funnels if a shaking machine is employed.

Where emulsions are encountered, the distribution may be carried out in stoppered centrifuge tubes and tubes centrifuged to separate the layers. Acids, such as hydrochloric, which attack stainless steel, may be employed in this setup. The bottles should be kept closed when liquid is not being added or withdrawn, as loss of solvents by evaporation may introduce an error.

Use of Sintered-Glass Disk in Preparation of Radioactive Precipitates.

John J. Pinajian[1] and John M. Cross,[2] Brookhaven National Laboratory, Upton, L. I., N. Y.

A VARIETY of devices and procedures for the mounting of radioactive samples for activity measurements have been described (*1–14*). The authors have devised a convenient apparatus (Figures 1 and 2) for collecting fairly large samples of radioactive precipitates in a reproducible manner. The precipitate is filtered, washed, dried, and subsequently counted on a modified sintered-glass filtering disk.

Several 22-mm. stock sintered-glass (F) crucibles were ground down so that a portion of the sintered glass was removed, leaving approximately 1.5 mm. as the thickness of the disk. The bottoms were ground so that the total height was exactly 6.7 mm. Glass rings 15.5 mm. in inside diameter and 1.1 mm. thick were ground out from the central portion of a glass tube. The ring was cemented on the top surface of the crucible with Sauereisen Insa-Lute adhesive cement No. 1. The unit was clamped together and treated in an oven. The ring, thus situated, covered that portion of the sintered glass which was fused with the side wall of the crucible.

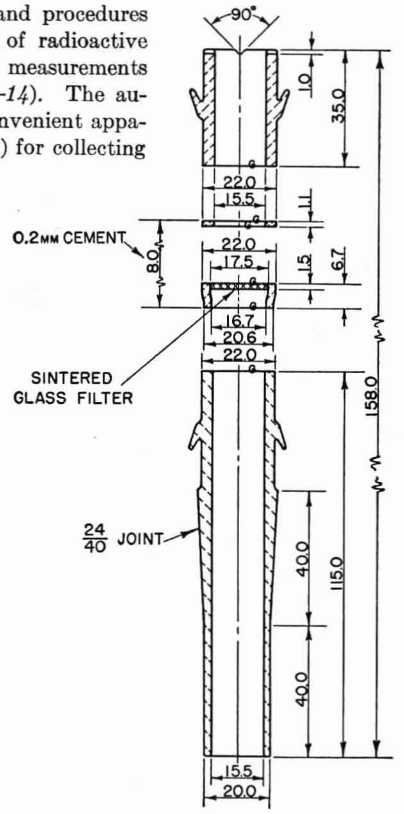

Figure 1. Sintered-Glass Counting Disk with Base and Chimney

A chimney was made of the same piece of glass tubing, with the lower edge ground so that a water seal might be made. Two glass hooks were drawn out on the chimney.

The two units rested on the ground surface of a glass tube fitted with a ₮ 24/40 joint, allowing the entire assembly to rest in a suction flask. Glass hooks were placed on the base so that rubber bands could be used to lock the assembly together.

The filtering unit was used to determine the minimum "infinite" thickness of mercuric oxide labeled with Hg^{203}—that is, such a thickness that a further increase in thickness would not result in a change in electron counting rate.

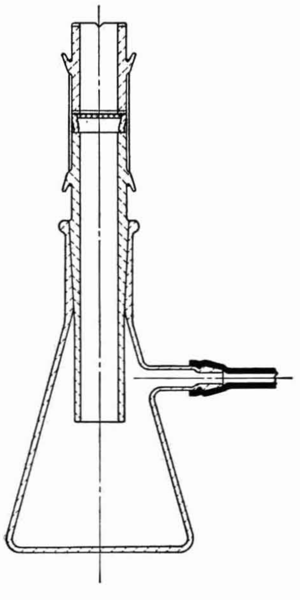

Figure 2. Complete Assembly

Hg*O was precipitated and a quantity well in excess of that required for a sample of infinite thickness was collected in a filtering unit. The precipitate was washed with water, alcohol, and ether and then air-dried for several minutes. The disk with the precipitate was placed in a desiccator and dried to constant weight. A count was made and the unit reassembled. Ether was added and the precipitate stirred to form a slurry. A portion was siphoned off and the suction applied to remove the ether. The precipitate was air dried, placed in a desiccator, dried to constant weight, and then counted. The results of several such manipulations were plotted and the minimum infinite thickness was found to be 79.5 mg. of mercuric oxide per sq. cm. These results were reproducible.

The disks were easily cleaned by rinsing with dilute acetic acid and were checked for background readings.

An aluminum card type holder with a groove to hold the disk was used to support the sample on a shelf below the mica-window Geiger-Müller tube.

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[1] Present address, Graduate School of Pharmacy, Purdue University, West Lafayette, Ind.

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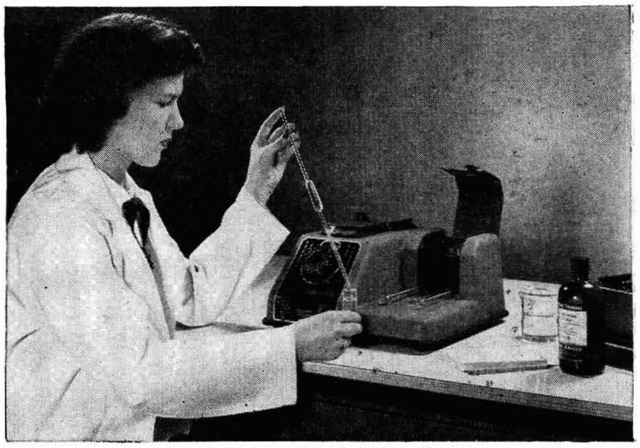

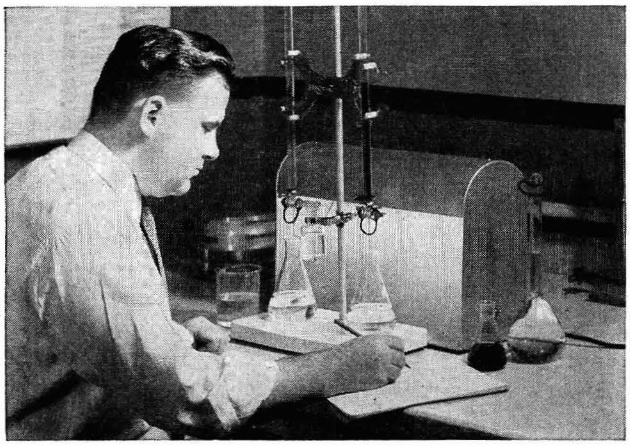

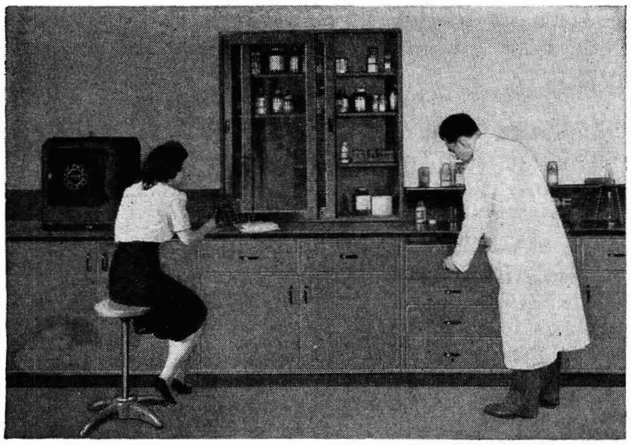

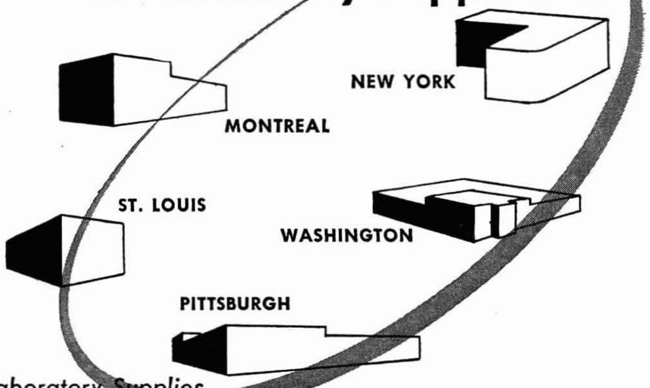
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INSTRUMENTATION

A hot-cathode helium-filled diode that can control large currents continuously at low voltages may achieve smooth control as an inherent tube property

by R. H. Müller

GRID-controlled gas discharge tubes, such as the Thyratron, have long enjoyed widespread use in numerous measuring and control devices. The chemist has encountered these tubes chiefly in thermostatic control systems or as components in servo-systems.

The thyratron, to use the term in a generic sense, has had certain characteristics which were at once both advantages and disadvantages. Aside from certain definite changes in electrode parameters, a thyratron is essentially a triode or tetrode, in which the envelope is filled with an inert gas at an optimum pressure, either mercury vapor or one of the noble gases. Under normal operating conditions, conduction between cathode and anode is prevented by a suitable negative bias on the control grid. When a sufficiently positive potential, with respect to the cathode, is applied to the control grid, conduction ensues and the resultant anode current sets in, and is limited only by the applied anode potential and the load resistance.

Like any arc device, the thyratron has a negative resistance characteristic, and the maximum current is entirely dependent upon circuit-limiting conditions. Contrary to "hard tube" behavior, the grid of a thyratron cannot regain control of the anode current by making it more negative, at least for reasonable values of grid-cathode potential. This apparent disadvantage is put to good use in certain "lock-in" characteristics. For example, in many instances, it is highly desirable to utilize this characteristic in detecting a condition, or state of affairs, where a continuous or persistent indication of a transient event will prevail until an observer takes cognizance of it, applies a corrective measure, and once more resets the thyratron. All this can be done automatically, if the anode voltage is applied periodically—i.e., if a.c. is applied to the anode. Under these conditions, the thyratron will regain control once every half-cycle, because whenever its anode is negative, the arc discharge must cease, regardless of control-grid potential.

A distinctive property of the thyratron has been its relatively high current-carrying capacity, low potential drop across it, and the ease with which it can be switched from the nonconducting to the conducting state. It was essentially an "all or nothing" device from which the term "thyratron" was derived. It was not until Langmuir, in this country, and Toulon in France, developed the phase-shift technique, that it was possible to achieve a more or less smooth variation of anode current from zero to maximum. These techniques used reactive circuit elements to achieve a displacement in time between the grid and anode voltages and thus fix the fraction of the positive cycle during which the tube could conduct. This has been a widely employed means of getting smooth output control of these power devices and of overcoming an inherent limitation of the device. Fundamentally, the large current-carrying capacity of a thyratron depends upon the neutralization of space-charge around the electron-emitting cathodes, by the positive ions of the gas discharge.

Plasmatron

Recently, the R.C.A. laboratories at Princeton have produced a developmental tube called the Plasmatron which gives good promise of achieving smooth control as an inherent tube property, rather than circuitwise. As described by E. O. Johnson of R.C.A. [*Electronics,* **24,** 107 (1951)], the Plasmatron is a hot-cathode helium-filled diode capable of controlling large currents continuously at low voltages. A small control current sets on an auxiliary discharge that provides the ionization to neutralize space charge.

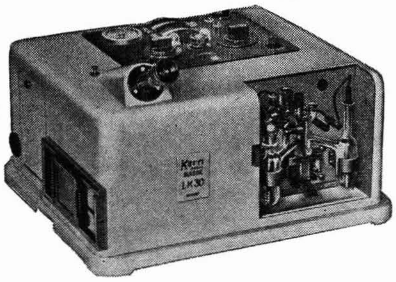
The main cathode of the Plasmatron is oval and is surrounded by a U-shaped anode. Facing the open end of the U is the auxiliary cathode, which is completely surrounded by a cylinder that acts as a constricting grid. A narrow aperture in the latter permits the auxiliary discharge to pass into the main part of the tube, where it controls the plasma density and hence the main anode current. The increase in the plasma density arises from the fact that the constriction in the discharge path raises the voltage drop across the auxiliary discharge. This imparts more energy to the discharge electrons and increases their ability to ionize the gas.

Some of the positive ions and electrons recombine in the interelectrode spaces of the tube, but at the 1-mm. pressure of helium used, these losses are negligible. The steady-state density of charged particles in the plasma depends upon equilibrium between generation and loss rates and is very nearly proportional to the magnitude of the auxiliary or controlling current.

The presence of the plasma, of controllable density, between the main electrodes permits the passage of large currents between the main cathode and anode, even at anode potentials of a few volts. As a matter of fact, anode potentials higher than the ionization potential of the gas cannot be used because continuous ionization and conduction would be maintained independent of the auxiliary current and the control feature would be lost.

In practice, an ordinary vacuum tube such as 6J5 is placed in series with the auxiliary current circuit. A variation of the grid-cathode potential of the vacuum tube will then vary the auxiliary current and thus control the output current.

A typical tube characteristic for the Plasmatron shows the anode current as a function of the auxiliary or controlling current. This is almost linear and is slightly concave to the control current axis. In a typical case a control current of 12 ma. yields an anode



INSTRUMENTATION

current of 950 ma., at an applied anode potential of only 6 volts. The average slope of this curve corresponds to a current amplification of about 90 to 1. If an attempt is made to exceed a certain output, the retarding field at the cathode disappears and the output saturates at a limit set by temperature-limited emission of the cathode.

The dynamic response of the Plasmatron is encouragingly high. The gain as a function of frequency is constant and equal to the steady or d.c. value of gain up to 2 or 3 kilocycles. At 10 kc. it is still 83% of maximum and appears to drop off rapidly above that value, to attain about 50% at 20 kc. This behavior is characteristic of all gas tubes and is determined by the rate of diffusion of the changed particles to the electrode surfaces. The time constant of plasma decay varies directly as the gas pressure, directly as the square root of the mass of the gas atoms, and as the square of the geometric dimensions of the plasma region.

Experimental forms of the tube have been used for direct speaker drive in audio amplifiers, in motor control circuits, in pulsing circuits, and in other electronic applications. It promises much in applications requiring low frequency, low impedance performance whose continuous variation of relatively large currents is required. The analyst may expect to see the Plasmatron employed in many devices for control or measurement.

No extensive data are as yet available concerning life or reproducibility, but from the experience gained on older types, usually operating under much higher voltages, the prospects seem very favorable for dependable service.

Patents on Electron Tubes

Some years ago we had the opportunity to examine a comprehensive collection of patents dealing with electron tubes. It was astonishing to note the advanced thinking and skilled experimentation which these depositions revealed. Very little of this information has ever appeared in the more formal scientific literature, and perhaps no more than 5% of these devices have ever reached commercial production. In the scientific sense, this is unfortunate, though understandable. At the time, we gained the impression that

(Continued on page 26 A)

Announcing the COLEMAN Model 19

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INSTRUMENTATION

almost every conceivable means of electron-flow control had been tried and evaluated. The more we think about it, the more profitable it seems to exhume some of these devices and re-examine them in the light of present-day problems. The lack of wide scale industrial application accounted for much of the situation, but it is altogether likely that many measurement and control problems are being studied today at great expenditure of time and effort, for which some of these forgotten devices would supply an immediate answer. To the best of our knowledge, the movable anode vacuum tube is about 20 years old. Only recently it has been revived and put to use in measuring surface finish, as a sensitive micrometer and as the pickup element in record players. At least as many years ago, English investigators modified a cathode ray tube in order to deflect the beam into two or more cups, collectors, or "Faraday cages" and used the device for high speed switching purposes. In their hands, it was developed into an anticollision device for aircraft.

The economic excuse for this state of affairs is good enough, but the information, for the benefit of students and investigators, is largely hidden and in inaccessible form. Our own ingrained and chronic prejudices incline us to the view that this is a natural consequence of the general attitude toward instrumentation. In the past, it has seemed perfectly logical to assume that the problem comes first. After it is defined, one then seeks a means for its solution. With the growing interest in instrumentation for its own sake, one seeks every conceivable mode of measurement, examines every obscure phenomenon, and extracts from it those possibilities which will permit a new mode of measurement or control. Recent experience has shown that for every discovery or development of this sort, a dozen or more applications are at once suggested. Recent developments in crystal physics have led to the varistor, thermistor, transistor, and the phototransistor, and the practical development of these devices has tapped the best resources of chemistry and metallurgy as well as physics. There is more than a remote possibility that, in some applications, these devices will render the vacuum tube obsolete.

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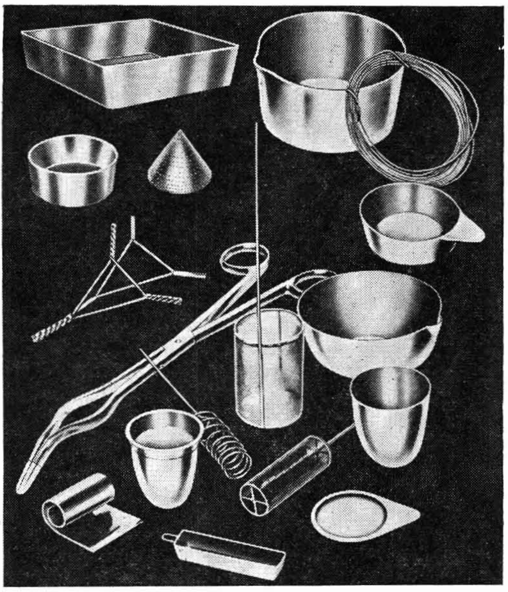

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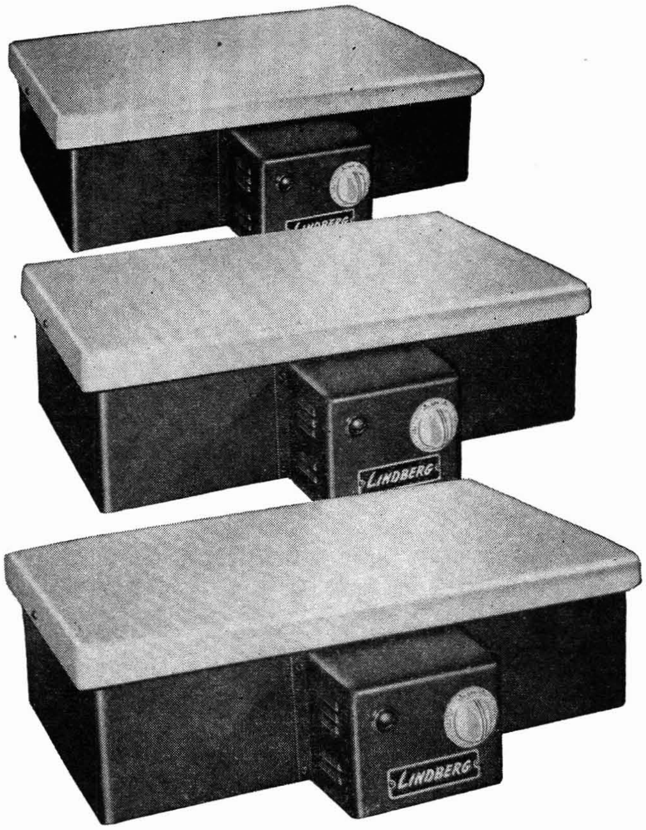

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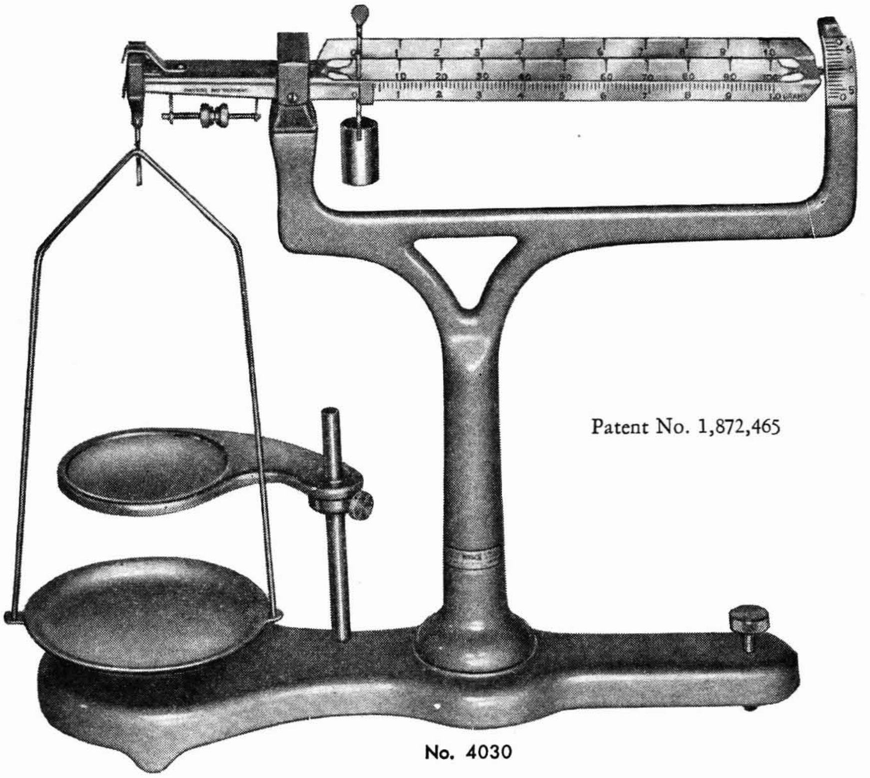
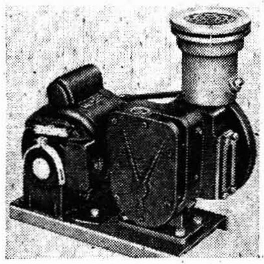


NEW PRODUCTS FOR ANALYSTS

Equipment, Apparatus, Instruments, Reagents, Materials

Vacuum Pump

Model CVM 3153 is now being offered by the Kinney Manufacturing Co. for applications requiring a small vacuum pump capable of producing low pressures rapidly and dependably. This new compound pump has a free air displacement of 2 cubic feet per minute. Designed for portability, the complete unit, including 0.25-hp. motor, base, and pump, weighs only 70 pounds. The unit produces McLeod gage absolute pressures of 0.1 micron or better and is capable of retaining a high percentage of its volumetric efficiency at low pressures. The pump is reported to be of value both in research and production—for lamp and tube manufacture, laboratory uses, backing diffusion pumps, servicing refrigerating equipment, and other applications. **1**



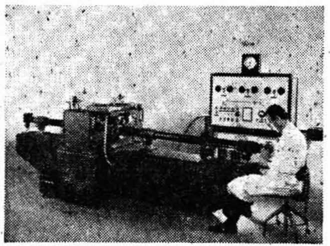
Nitrogen Source

The Nitroneal generator made by Baker & Co. is designed to produce gaseous nitrogen inexpensively and with a controllable hydrogen content. The apparatus is capable of generating a gaseous output completely free of oxygen and consisting only of nitrogen, hydrogen, and water vapor. The hydrogen content is variable from 0.25 to 35%. The generator is fully automatic and provides an output having a uniform gas analysis. Gas composition remains constant within 1% of the set point, and the unit can be operated anywhere in the range of 25 to 100% of the rated capacity without affecting the outlet gas composition. Units are available with maximum generating capacities of 100, 500, 1500, 3000, 6000, and 10,000 cubic feet per hour.

The generator employs the Englehard process for the simultaneous catalytic oxidation of ammonia and the controlled reduction of the hydrogen content. Liquid ammonia from supply cylinders is vaporized, mixed with compressed air, and fed to the catalytic converter. In the first stage of the converter, an exothermic reaction takes place in which the mixture of ammonia and air is catalytically burned, thereby producing a mixture of nitrogen and water vapor, with an excess of hydrogen. This mixture is passed on through to the second stage of the converter, where a precisely controlled volume of air is admitted to permit the further catalytic burning of the mixture and thereby reduce the hydrogen content to an exact amount. The volume of air admitted and therefore the amount of hydrogen consumed are regulated by a diaphragm-operated control valve. **2**

Electrophoresis Apparatus

The Type LKB 3021 Tiselius-Svensson electrophoresis apparatus offered by LKB-Produkter is a high-precision instrument designed for research work on the electrophoretic migration of colloids and for analytical work based on refractive index measurements. The optical method used in this instrument is a combination of the schlieren method and a new interferometric method, which gives two curve systems simultaneously and on the same photographic film. The first system represents the gradient of the refractive index along the cell axis and is proportional to the concentration gradient. The second system consists of a number of interference fringes, each of which represents the refractive index itself, which is proportional to the concentration of the colloid—that is, the integral of the first curve. The two-curve systems have the cell coordinate axis in common, so that maxima and minima of the gradient curve are situated exactly below inflections in the integral curves. Thus, quantitative determination of the components of the sample is greatly facilitated.



In earlier methods, the composition of the sample was calculated from measurements of the areas below the peaks of the gradient curve. With the new optical system, area measurement is replaced by a counting of the number of interference fringes between successive minima along a straight line parallel with the base line. As the fringes are equidistant along an axis perpendicular to the cell axis, the number of fringes is proportional to the "step" height of any one fringe. The fringes are easily counted on the film by

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means of a low-power microscope with cross-hair eyepiece and movable stage, or on an enlarged print of the film. The ultimate resolving power which is obtainable with good cells and careful work corresponds to a concentration of 2.5 p.p.m. In less careful routine work, a concentration increment of an electrophoretic component can readily be measured with a precision of ±25 p.p.m., if the component in question is well resolved from its neighbors.

The optical system of the instrument consists of one illumination unit and one recording unit, with the water bath between. These two units are contained in dustproof tubes and are completely adjusted before delivery. Practically monochromatic light of different wave lengths is obtained by means of interchangeable mercury and tungsten lamps in combination with a set of light filters. The water bath is kept at the desired temperature, usually 0.5° C., by means of a Freon-type refrigerator. The bath can accommodate up to three cell units which are supported, each in its holder, on a carriage electrically driven on two rails on top of the water bath. Push buttons control the motor which drives the cell carriage in a direction at right angles to the optic axis.

The recording unit contains an astigmatic optical system in combination with an inclined slit or edge. The camera is a standard amateur camera for 24 × 36 mm. film, with mirror-type view finder. **3**

Automatic Degasser

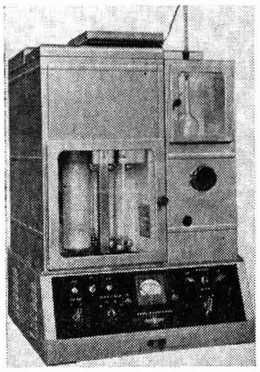
A new model automatic degasser has been announced by Hagan Corp. It is distinguished by a new case of mild steel, finished in black and specially treated to minimize corrosion. The new design increases the accessibility of the interior mechanism and simplifies the job of disassembling the instrument. The structural members of the case have been strengthened. Designed primarily for use in the determination of steam purity, the degasser produces continuously and automatically an approximately 50-50 split of a flowing steam sample. One fraction contains any dissolved solids that may be present and the other any dissolved gases. **4**

Low-Cost Geiger Counter

The Snooper is a low-priced Geiger counter for use as a civilian defense instrument as well as for prospecting and school use. It is so small that it will fit in the palm of the hand or in the hip pocket and yet is said to be more sensitive than many larger, more expensive instruments. The device uses an ordinary flashlight battery for power and comes in a plastic case. It is supplied with earphone, a radioactive sample, and complete instructions. A miniature amplifier emits a loud signal whenever the Snooper approaches a source of radioactivity. Manufactured by Precision Radiation Instruments, Inc., the device is 1.5 × 3 × 5 inches. It weighs 1.25 pounds and sells for $24.95. **5**

Automatic Distillations

Precision Scientific Co., in cooperation with the Shell Development Co., has announced the availability of an automatic distillation apparatus. The instrument releases the operator from time-consuming chores and minimizes errors. Temperature and volume are plotted continuously. The time is recorded every 2 minutes. The distillation rate, controlled electronically, may be varied from 4.5 to 9.0 ml. per minute.



The instrument is simple to operate. After the sample flask is set in place, one adjustment is made to obtain proper initial heat and distillation rate, then the line switch is turned on. There are no other operational steps besides the removal of the distillation chart. The apparatus is enclosed within stainless steel walls. Controls are mounted on one panel directly in front of the operator.

The instrument will perform the following ASTM tests: D 86, distillation of gasoline, naphtha, kerosene, and similar petroleum products; D 268, sampling and testing of lacquer solvents and diluents; D 1078, distillation range of lacquer solvents and diluents; and D 447, distillation of plant spray oils. With a slight modification, the instrument may also be used for D 216, distillation of natural gasolines. **6**

Uranium Test Kit

A pocket-size uranium test kit designed for the quick, on-the-spot identification of radioactive ores is being offered by Menlo Research Laboratory. Used in conjunction with any type of ultraviolet instrument, the kit will eliminate the necessity of shipping every radioactive sample to a testing laboratory for the determination of uranium. Field experience has proved that nearly 50 materials—of which uranium is just one—are radioactive and will be recorded by electronic detector instruments such as a Geiger counter. Hence there is a need for positive supplementary tests.

The complete kit, which retails at $4.95, contains packages of testing chemicals, a 2000° F. blow torch, solid fire tablets,

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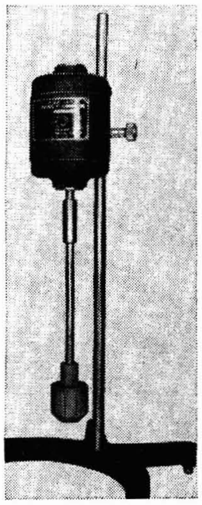
special wires for forming beads, and tongs for holding the beads while they are being formed and examined. All elements are standard and individually replaceable. From 25 to 30 bead tests can be made from a single kit. When a likely ore is tested at the prospect scene, a chemical bead is formed on a wire, fused with crushed ore particles, then examined under ultraviolet light. Uranium fluoresces a distinctive lemon-yellow color. The entire test is said to require less than 5 minutes.

Kits may be ordered through dealers or directly from the Menlo Research Laboratory, which also manufactures the Fluoretor, a portable ultraviolet instrument with a built-in dark chamber that enables it to be used in broad daylight. **7**

High-Speed Mixer



A new mixing device called the Simplex Dispersator is now being manufactured by the Premium Mill Corp. Designed for operations where propellers are generally ineffective, the Dispersator can be used for speedy emulsification, dispersion, and intimate mixing. The manufacturer states that the device achieves satisfactory results in a fraction of the time required for other types of agitators or mixers. The Dispersator consists of a cylinder rotating at high speed. The centrifugal force resulting from this fast rotation forces the product through narrow slots in the wall of the cylinder under considerable pressure. The effect is twofold: The product is sheared at high speed as it passes through the slots; and the columns of liquid emerging from the slots are further sheared by coming into contact with the slower moving mass of liquid in the mixing vessel. **8**

Anthrone

Jasonols Chemical Corp. reports the availability of anthrone (9,10-dihydro-9-ketoanthracene), a pale yellow powder used for determining carbohydrates both qualitatively and quantitatively. Anthrone is also useful for determining mono- and polysaccharides and their esters, as well as mannosidostreptomycin and dihydromannosidostreptomycin. It may be used to indicate the presence of gums, glucosides, starches, and complex sugars with organic groups, such as glycolipides and nucleic acids. For the quantitative analysis of carbohydrates, the color produced with anthrone is measured with an instrument capable of determining color intensity. Only a very few substances have been found to interfere with this reagent. **9**

Detergents

The Pennsylvania Salt Manufacturing Co. has developed a class of cleaning compositions called solubilizing cleaners. The action of these compositions is based on oversize micelles or groups of molecules, formed from the various ingredients, which have the property of dissolving not only water-soluble soils taken up by normal soap solutions but also water-insoluble soils which can normally be removed only by organic solvents. The solubilizing cleaners have little saponifying action and do not remove fatty soils by this mechanism. The range of solvent power of these cleaners makes them effective in removing such complex soils as buffing compounds, greases, and pigmented drawing compounds.

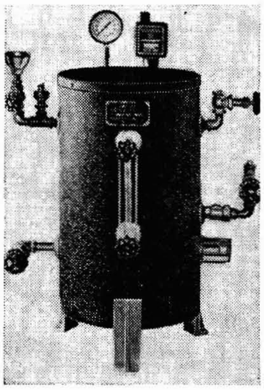
Pennsalt researchers have found that one of the cleaners, SC-3, is an effective hand cleaner, with or without water rinse, and may be used to remove embedded grime, paint, tar, or printing ink. Another cleaner efficiently removes embedded buffing compounds from the intricate designs in flat silver.

These cleaners are clear liquids—yellow, dark brown, or cherry red in color. They have practically neutral pH, good solubility and dispersibility in water, moderately high flash point, and exhibit high adsorption at interfaces. **10**

Count Rate Meters

Two count rate meters developed by the Atomic Instrument Co. have accuracies of 2 and 5%. Model 410, having an accuracy of 2%, is employed in laboratory radioactivity work. The instrument is suitable for use with an alpha scintillation probe, in addition to the standard Geiger probe. Incorporation of a Schmitt discriminator permits sine wave, square wave, and pulse counting without change in calibration. Model 409 is accurate to 5% and is suited for applications which are somewhat less exacting, such as in general safety work, monitoring, and searching. The instrument measures 3.75 × 4.75 × 6.75 inches. **11**

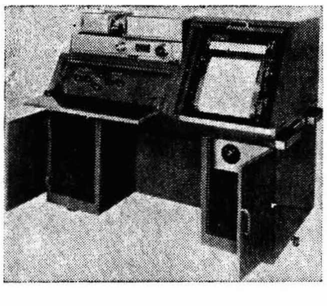
Steam Generators



Palo Laboratory Supplies, Inc., has introduced a new miniature automatic steam generator designed to be used with any laboratory apparatus for which steam is required. The generator is available in four sizes. The small size, having a water capacity of 2 gallons, contains a 7.5 × 16 inch boiler. The unit weighs 140 pounds and is priced at $192.50.

The automatic regulator delivers up to 30 pounds per square inch pressure. Working pressure is 100 pounds per square inch. A low water feed, which makes low pressure models completely automatic, may be obtained at a slight additional cost. The power is electrical, and all models reach maximum operating pressure within 20 minutes. An automatic cutoff protects the heating elements, which are submerged to provide optimum heat transfer. The boiler, insulated with rockwool, is made of ASME code heavy welded steel. **12**

Infrared Spectrometer



A new mobile infrared spectrometer, Model 12-C, is in production at the Perkin-Elmer Corp. The caster-mounted cabinet and spectrometer literally "take the lab to the problem." The entire unit, measuring 54 × 46 × 30 inches, passes through ordinary industrial doors and is ready for immediate operation wherever water and electricity are available. The protective door mounted over the controls folds down to form a work shelf for sample preparation and notebooks, while a similar door over the recorder slides away to expose the chart for marking the spectrum as it is run. Ample storage space is provided below for cells, solvents, and other accessories. Back panels are easily removed to simplify servicing.

Reduced recording time of a complete spectrum is obtained by automatic speed change programming on the wavelength drive. A densitometer attachment, reading directly in absorbance or transmittance, permits accurate quantitative analyses. The 2-second Leeds & Northrup Speedomax G recorder will be included as standard equipment on all future Model 12-C instruments to accommodate the increased chopper speed of the new Model 81 amplifier. Brown Electronik recorders may also be obtained. **13**

MANUFACTURERS' LITERATURE

Spectrochemistry. Illustrated pamphlet presents brief description of spectrochemical principles. Coleman Instruments, Inc. **14**

Cyanoacetamide. Bulletin contains information on the properties, specifications, and suggested applications of cyanoacetamide. The compound, an important intermediate particularly in the pharmaceutical field, is used in the synthesis of B-complex vitamins and barbiturates. Kay-Fries Chemicals, Inc. **15**

Automatic Titrations. Method of conducting automatic titrations is outlined in new folder. A pH meter that operates directly on line current, without the use of batteries, is covered, as well as electrolytic apparatus and several other improved instruments. Wilkens-Anderson Co. **16**

Brush and Weed Control. Data on methods and results in chemical brush and weed control, as practiced by a wide range of industrial and agricultural organizations, are presented in new company manual. Booklet describes such products as 2,4-D, 2,4,5-T, and TCA. E. I. du Pont de Nemours & Co., Inc. **17**

Aluminum. A 48-page booklet contains details on company's manufacturing facilities, products, and fields served. The production of aluminum from bauxite and characteristics of aluminum are covered. The publication, containing over 250 illustrations, includes full-color reproductions on foil of nationally known consumer goods packaged in aluminum. Reynolds Metals Co. **18**

Laboratory Gases. Pamphlet gives an up-to-date descriptive listing of laboratory gas prices, as well as a tabulation of the basic properties of gases and a summary of principal impurities. Ohio Chemical and Surgical Equipment Co. **19**

Paint Formulations. Sixteen suggested formulations designed to meet U. S. Government paint specifications are presented in 32-page booklet. The formulations cover such products as interior gloss enamel, synthetic primer for ferrous metal and wood surfaces, alkyd resin solutions, black heat-resisting glyceryl phthalate enamel, and zinc chromate primer for aircraft use. Rohm & Haas Co. **20**

Cellulose Gum. Technical booklet supplies information on Hercules CMC-CT, an unpurified cellulose gum that improves the whiteness-retention properties of synthetic detergents and built tallow soaps. Booklet contains a table listing typical properties of product and typical formulas of CMC-CT with detergents and soaps. Hercules Powder Co. **21**

Synthetic Crystals. A 4-page leaflet gives melting point, hardness, specific gravity, specific heat, chemical resistance, thermal expansion coefficient, refractive index, and other properties of such synthetic crystals as sapphire, spinel, titania, calcium tungstate, and cadmium tungstate. Pamphlet discusses uses, forms, and colors of synthetic crystals. Linde Air Products Co. **22**

Ceramic Standards. Leaflet describes company's reflectance, color, and gloss standards and announces new porcelain-enamel color standards for use with color-difference meter or reflectometer. All standard panels are 4.25 × 4.25 × 0.31 inches, with the exception of the 3 × 9 inch 85° sheen standards. Henry A. Gardner Laboratory, Inc. **23**

Organic Chemicals. Such organic chemicals as sodium, potassium, copper, zinc, vinyl, and aluminum acetate, acetaldehyde, paraldehyde, crotonaldehyde, and acetonitrile are discussed in 54-page booklet. Information is given on physical and chemical properties, applications, and operating procedures. Niacet Chemicals Division. **24**

Lighting Fixtures. A 16-page booklet discusses fluorescent, mercury-vapor, and incandescent lighting. Booklet stresses the importance of proper lighting as a means of reducing costs, increasing efficiency by ensuring accuracy, and minimizing accidents by clearly exposing dangerous operations. Westinghouse Electric Corp. **25**

Handling Volumetric Apparatus. A 22-page booklet describes the proper handling, care, and calibration of volumetric glassware. Containing 16 illustrations and 6 tables, the brochure discusses systems of weights and measure, the cleaning of apparatus, the reading of a meniscus, gravimetric and volumetric calibration, and the drainage time of burets and pipets. Kimble Glass. **26**

Laboratory Apparatus. Stereoscopic microscopes, magnifier lights, fluorescent illuminators, microlights, magnifiers, and other apparatus are described in 8-page pamphlet. Arthur S. LaPine and Co. **27**

DDT Formulations. A 20-page instruction booklet for the use of DDT dusts and sprays discusses several types of DDT formulations, including wettable powders, dusts, emulsions, solutions, and aerosols. Details are given on type of formulation, timing, dosage, and necessary equipment for controlling insects. Monsanto Chemical Co. **28**

Foot Switch. Bulletin gives information on miniature foot switch, which may be used to control sound and transmission equipment, relays, solenoids, magnetic switches, and other devices requiring the instantaneous and accurate control of relatively low amperage loads. Foot switch comes in two models, each with a heavy rubber tread on the actuating treadle and a base of slip-proof cork and rubber. Simonds Machine Co. **29**

Carbon Dioxide Recorder. Bulletin on automatic carbon dioxide recorder covers uses of instrument and gives description of Orsat principle of operation, complete with schematic drawing. Such features as temperature compensation and self-leveling are explained. Hays Corp. **30**

***N*-Bromosuccinimide.** A 42-page booklet discusses the reactions and uses of *N*-bromosuccinimide. Substitution reactions, dehydrogenations, oxidations, addition reactions, rearrangements, introduction of double bonds, and proof of structure are described. Bibliography includes 282 references. Arapahoe Chemicals, Inc. **31**

Dry Blender. Informative 4-page publication describes 4- and 8-quart twin-shell laboratory dry blenders, which exhibit the same performance characteristics as larger production models ranging up to 250 cubic foot working capacity. Patterson-Kelley Co., Inc. **32**

Voltage Regulators. Bulletin S351 gives details on the workings of automatic voltage regulators which maintain a constant output voltage regardless of fluctuations in a.c. line voltages and changes in output load. The Type IE regulator is completely electronic, contains no moving parts, and features low wave form distortion. A rating chart on the back cover of the bulletin provides engineering information for ease in selecting a unit suitable for a specific application. Superior Electric Co. **33**

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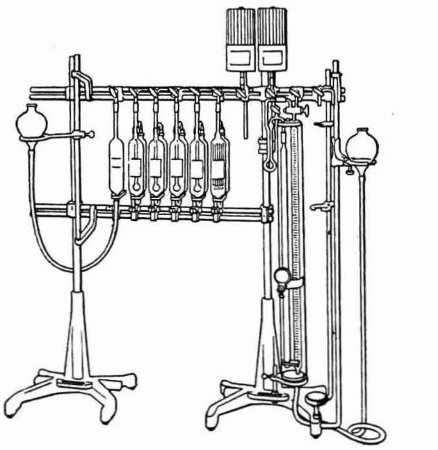
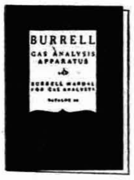


THE BURRELL DE LUXE MODEL J, pictured, is one of the most frequently specified types of gas analysis apparatus. Designed for adaptability and efficiency in the laboratory, any simple or complex mixture may be handled with speed and accuracy. Because all of the necessary equipment for all the commonly used methods is incorporated, the analyst needs only to select the method best suited to the gas sample. This versatile Burrell gas analyzer is delivered with all needed equipment and accessories for prompt operation. For more detailed information about this and other models, write for Burrell Catalog 80, which contains a helpful Manual for Gas Analysts.



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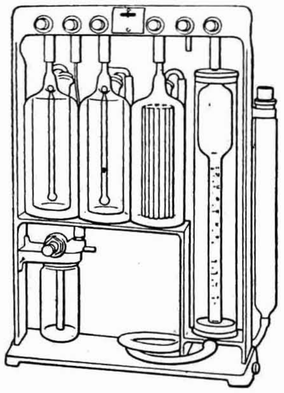

THE BURRELL INDUSTRO GAS ANALYZERS are compact, portable and easily operated units for the industrial gas analyst. Designed for on-the-job use, these "Industros" are rugged and trouble-free. The frame is all metal and there are no glass stopcocks to handle with care. Model B (shown), is used for mixtures such as flue gases where determination of carbon dioxide, oxygen, and carbon monoxide is desired. Model C offers added facilities for more complicated mixtures. For detailed information about these efficient Burrell Industro Gas Analyzers, ask for Bulletin No. 313.

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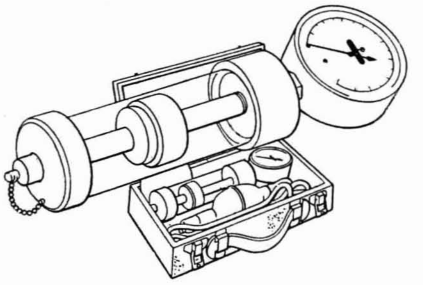

THE BURRELL CO_2 INDICATOR is a necessity for all combustion engineers. By measuring the CO_2 content and the temperature of the chimney gas, amount of heat loss can readily be determined. The Burrell CO_2 Indicator is light and sturdy with an easy-to-read scale. No installation or time consuming preparations are needed—a small hole in the stack makes immediate testing possible. A complete kit includes all accessories and instructions for use. Ask for Burrell Bulletin No. 206.

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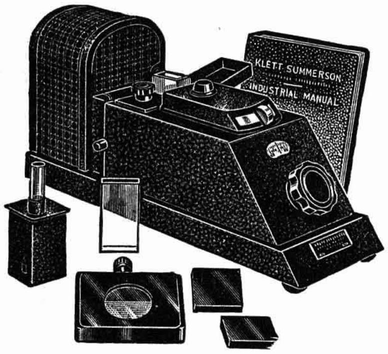

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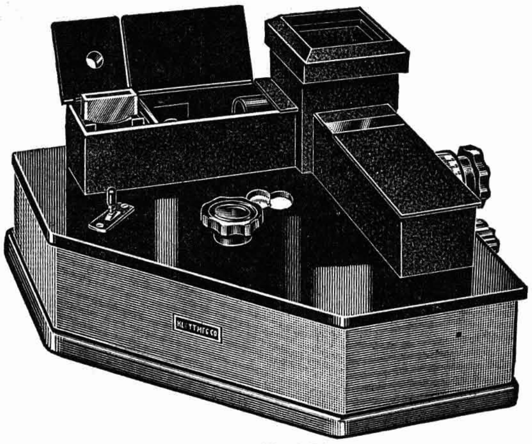

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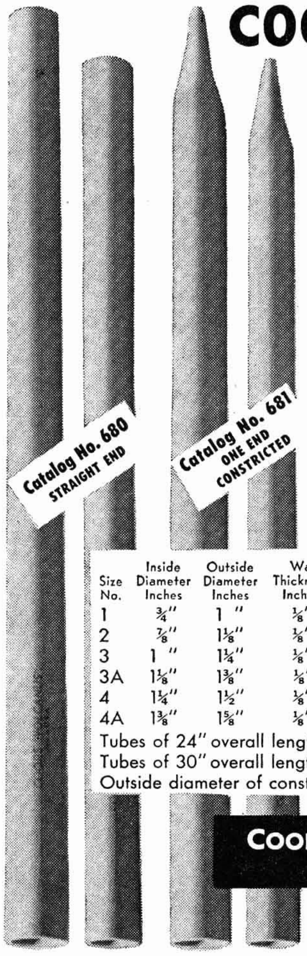

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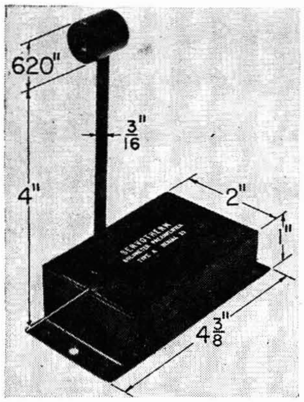

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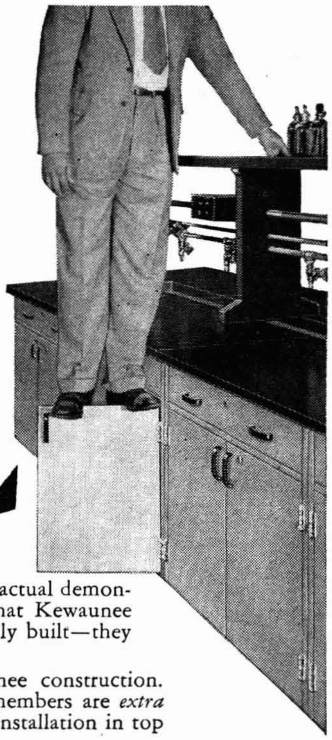

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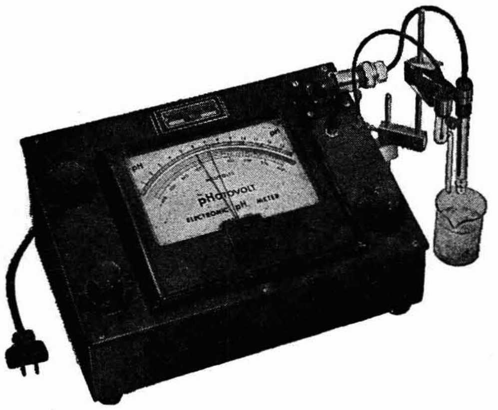

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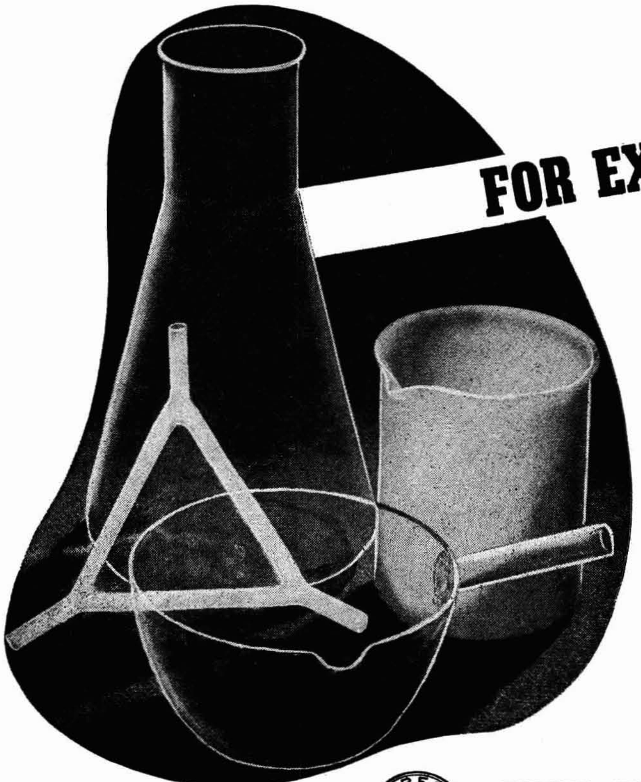

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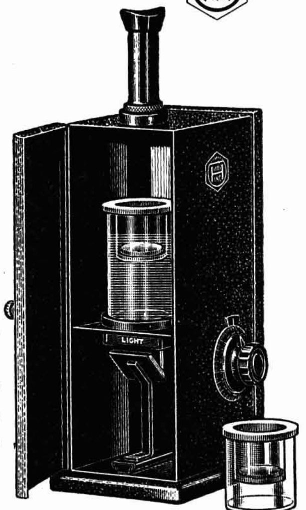

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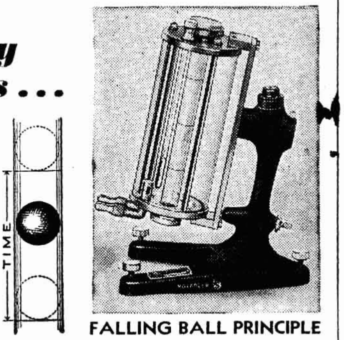

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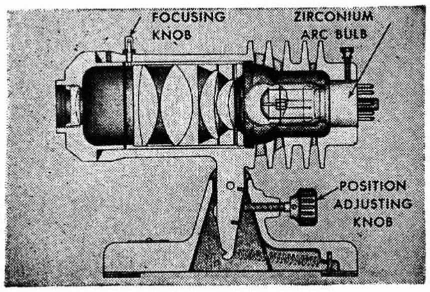

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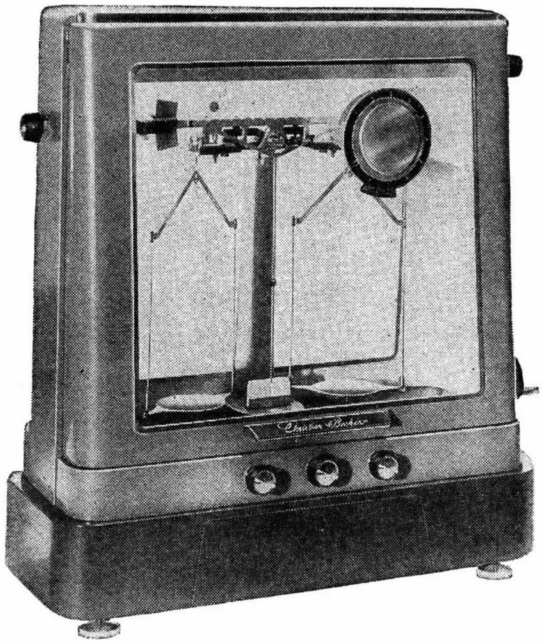

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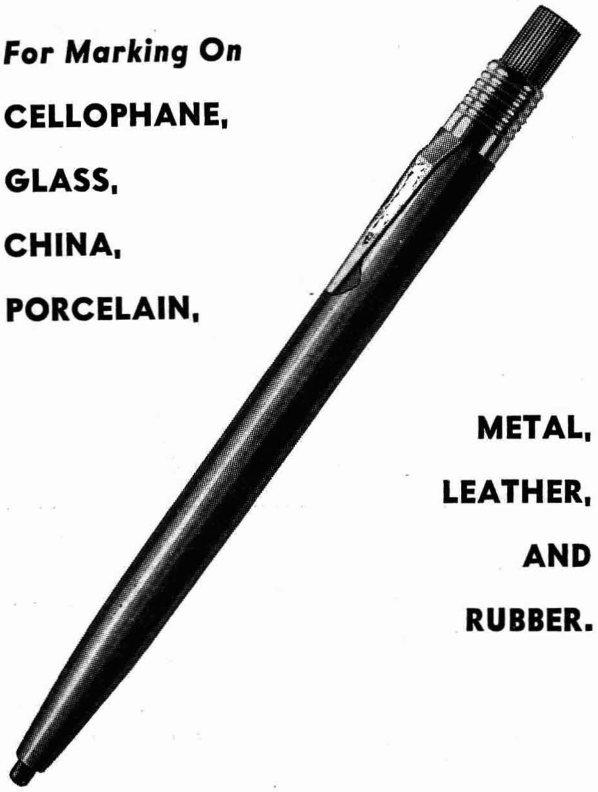

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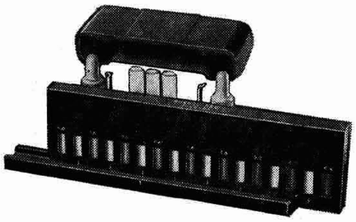


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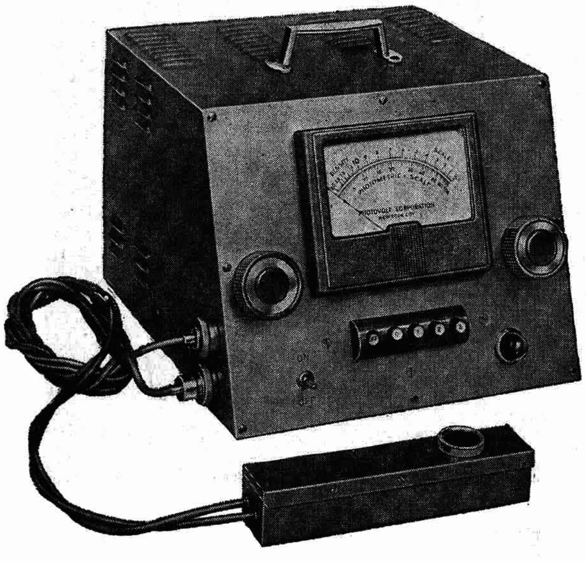

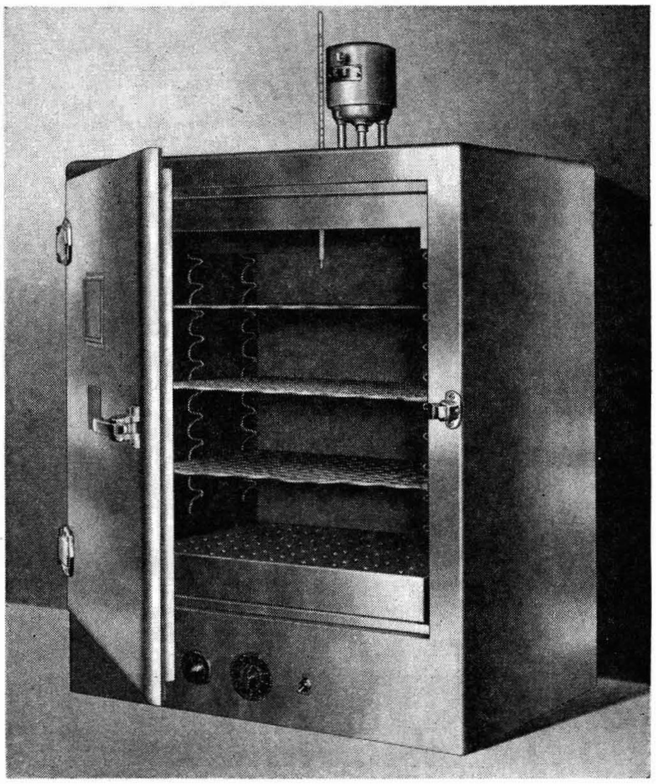

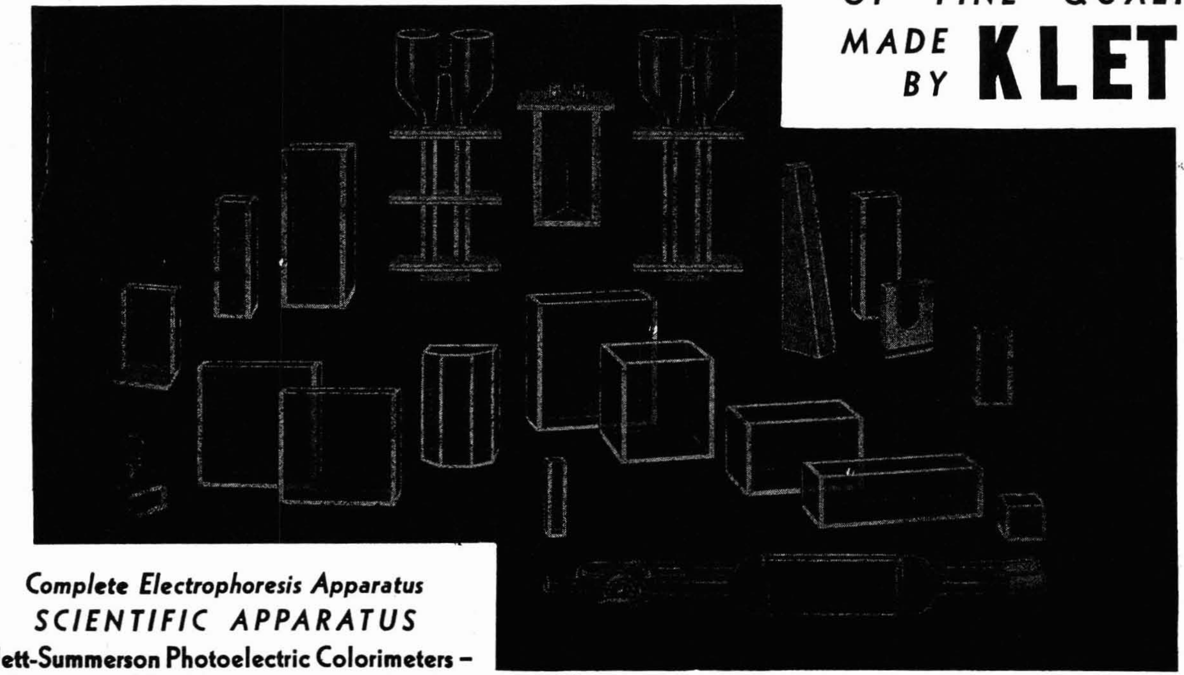

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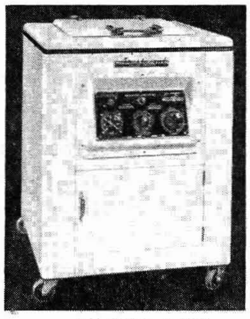

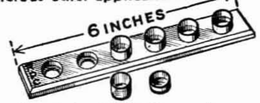

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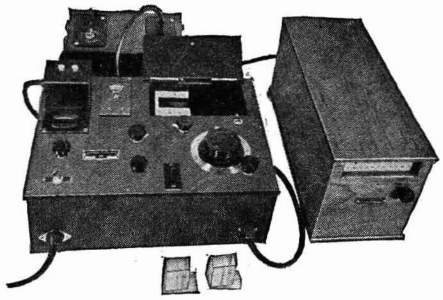

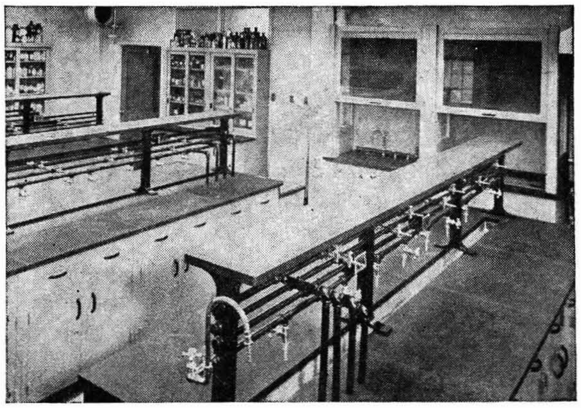

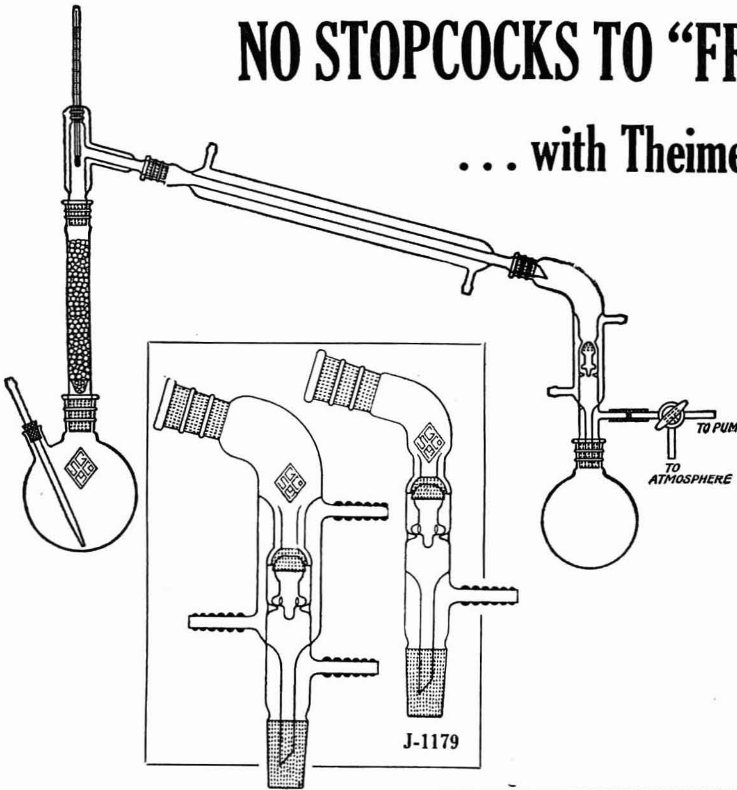
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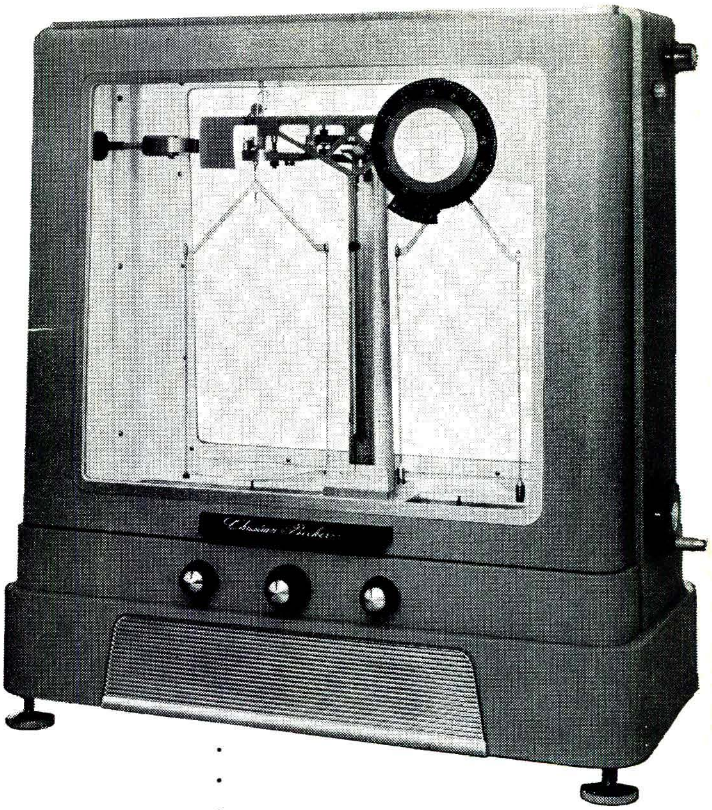

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