# INDUSTRIAL AND ENGINEERING CHEMISTRY

## ANALYTICAL EDITION

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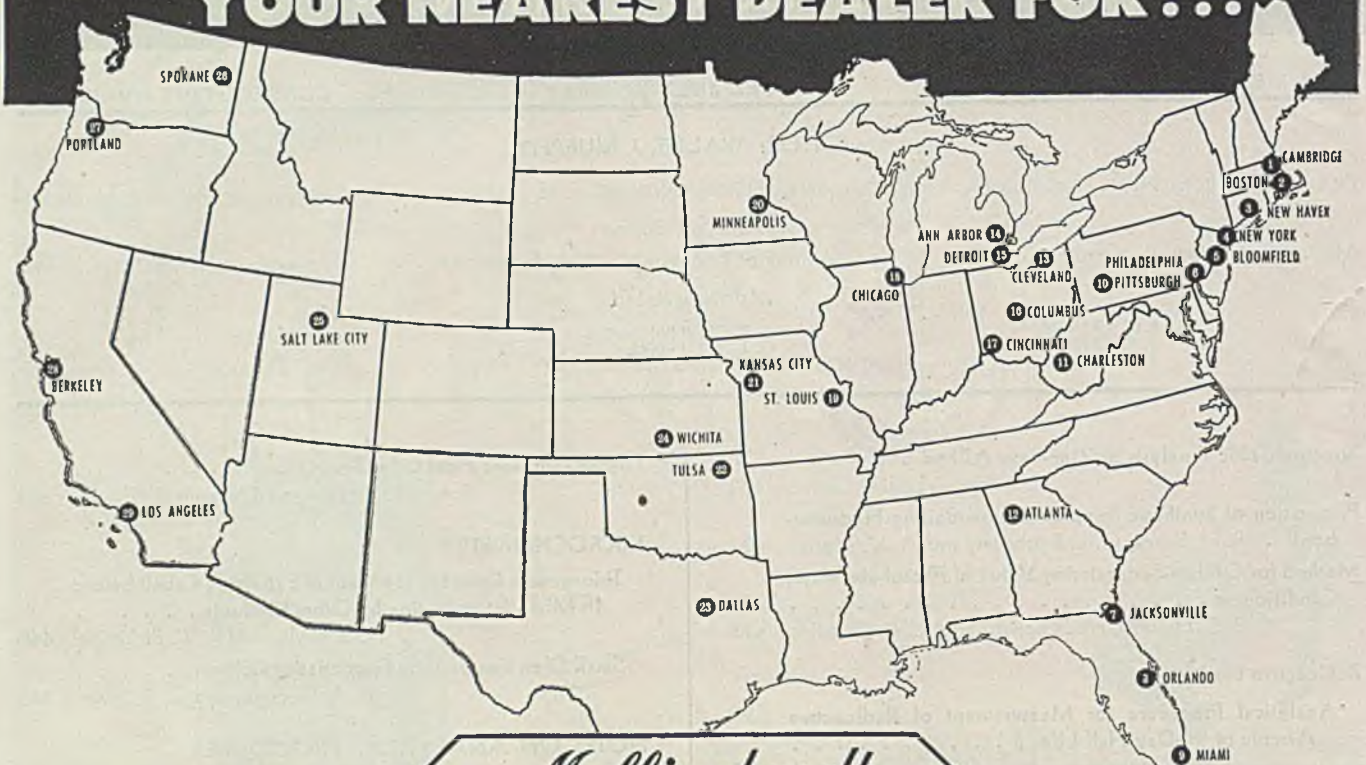

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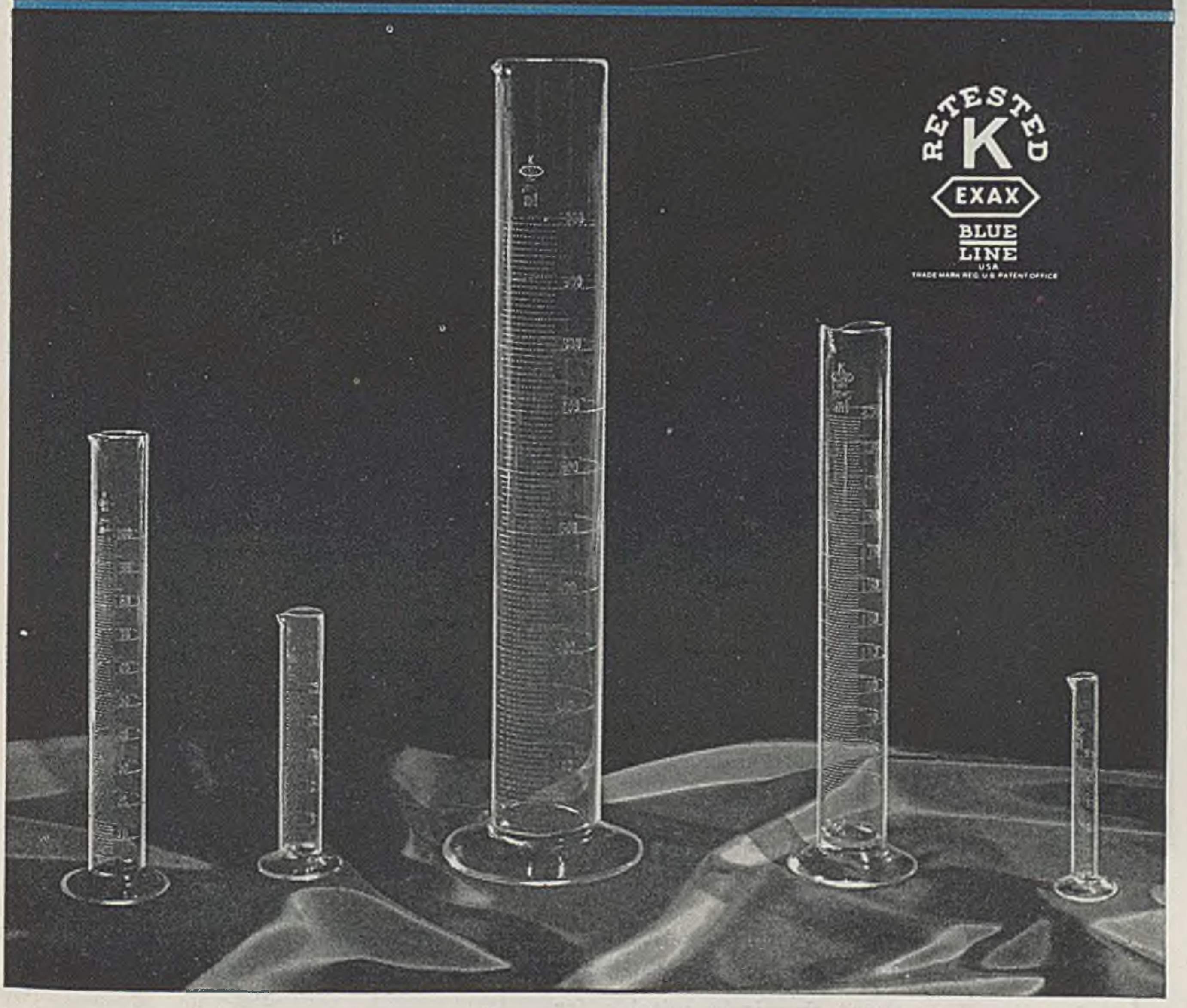
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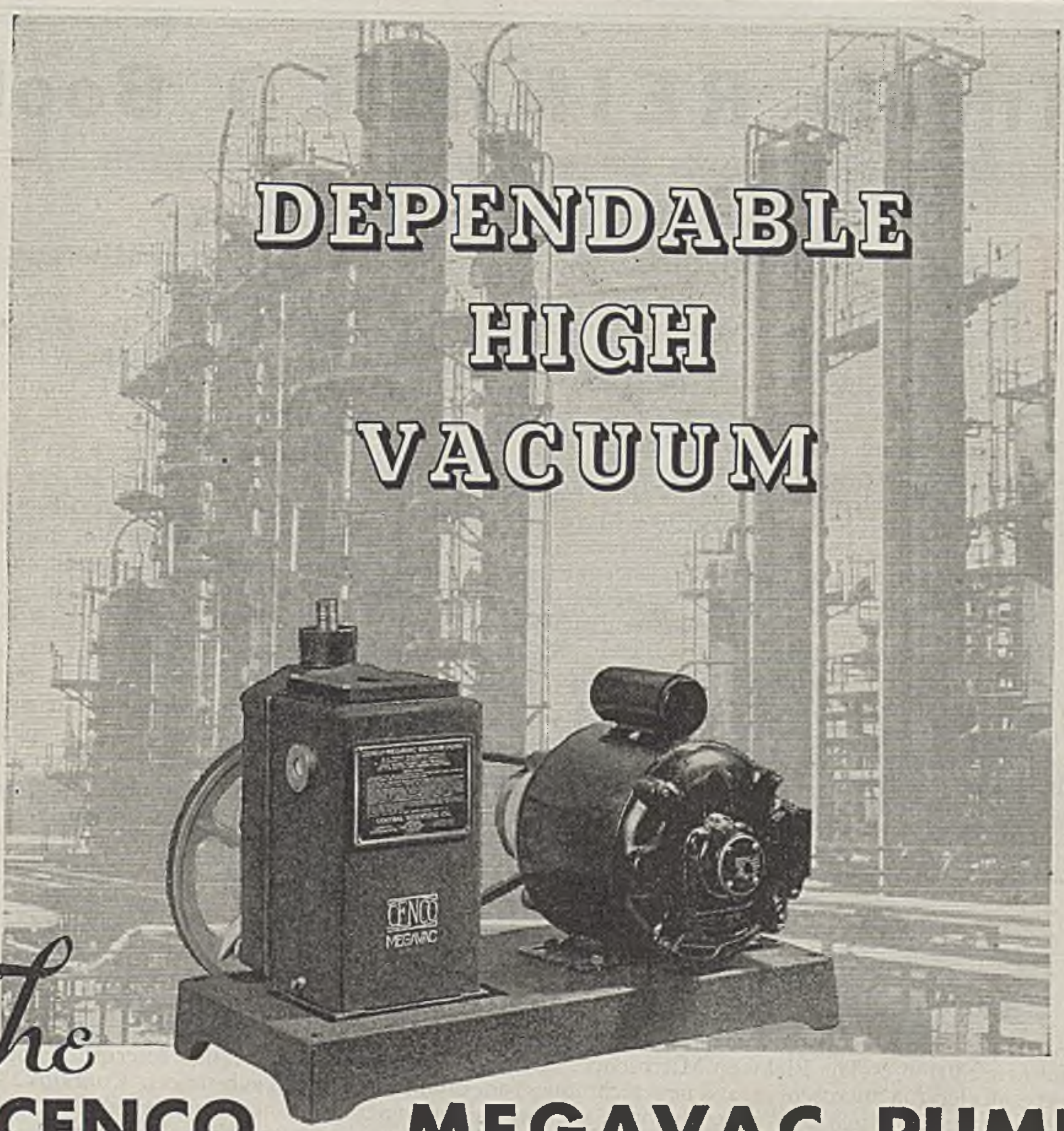

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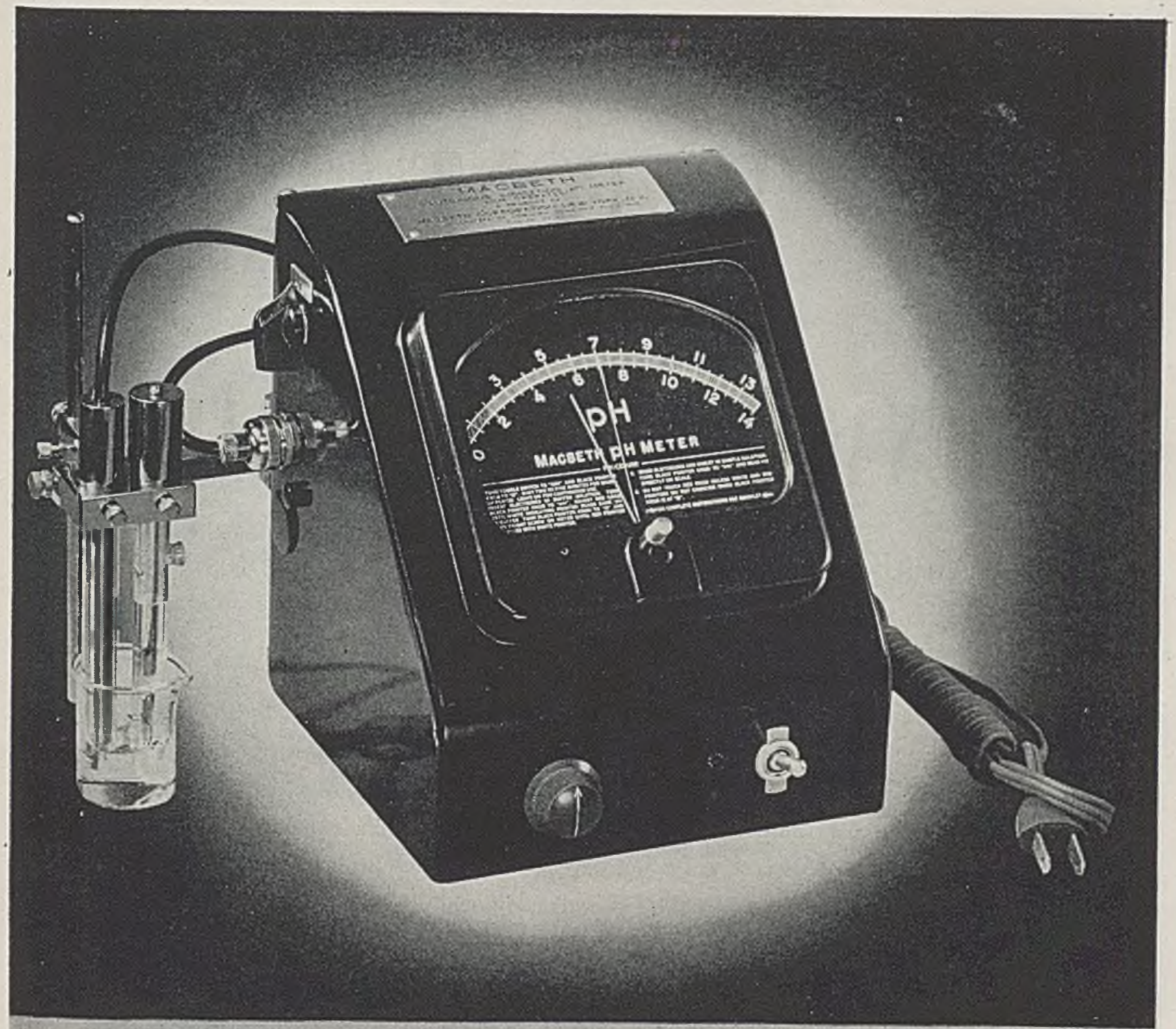
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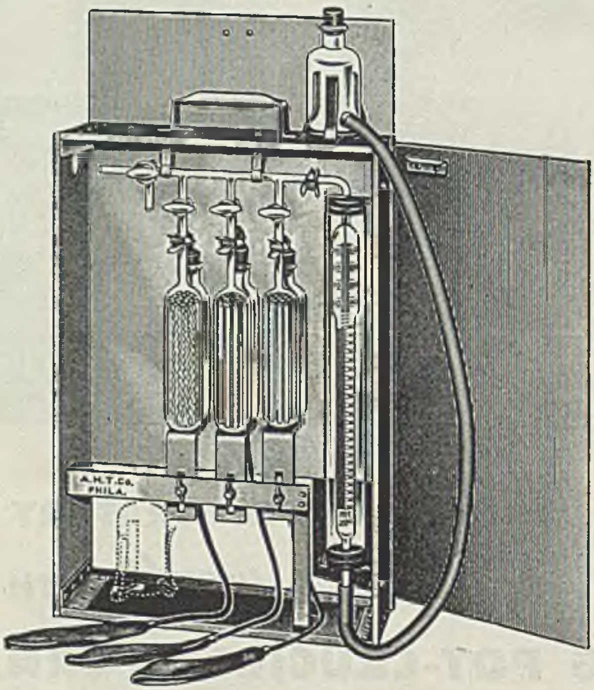

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# Spectrographic Analysis of Zinc-Base Alloys

LESLIE LARRIEU, Morris P. Kirk & Son, Inc., Los Angeles 23, Calif.

**A rapid and accurate spark spectrochemical system incorporating the use of the ammonium chloride–packed electrode and the flat disk self-electrode has been developed. A commercial high-voltage spark source unit with extra inductance is used for excitation of flat disk samples on a Petrey spark stand. A grating spectrograph is employed. Comparator-densitometers are used for transmission measurements and conversion to intensity ratios is made on calculating boards. The system provides for simultaneous evaluation of all zinc alloy constituents and impurities quantitatively on one spectrogram. The method accurately measures lead in the range of 0.002 to 0.015, tin 0.002 to 0.015, cadmium 0.002 to 0.010, magnesium 0.01 to 0.10, iron 0.01 to 0.10, copper 0.75 to 3.25, and aluminum 3.50 to 4.50%.**

THE accurate and complete analysis of zinc-base alloys for all alloy constituents and impurities by chemical methods is tedious, time-consuming, and often subject to serious discrepancies. Using the accepted chemical methods of analyses for this type of alloy, rapid routine determinations are difficult, since the chemist often has to approach his analytical problems as if they were of umpire quality. For some analyses he has to use large samples, make multiple precipitations, exercise the utmost care, and hope that his result truly represents his sample.

Zinc-base alloys are manufactured under one of the closest specification allowances of any alloy blended today; the specification prohibits the presence of more than 0.005% cadmium and similarly low amounts of tin and lead in the alloy. The spectrograph therefore offers emancipation from the drudgery of difficult and sometimes questionable chemical analyses.

Two and a half years ago the laboratories of Morris P. Kirk & Son, Inc., subsidiary of the National Lead Company, acquired spectrographic equipment for the express purpose of controlling the production of nonferrous metals and alloys. These alloys consist of tin-base, lead-base, zinc-base, and a wide range of aluminum alloys. Today over 75% of all these analyses are made spectrographically, thanks largely to the development of a special, but simple, electrode.

This special electrode (Figure 1) introduces ammonium chloride into the spark discharge from its tip, where the salt has been placed in a hole drilled in the electrode tip. These ammonium chloride–packed electrodes are processed from National Carbon Company "spectroscopic carbons" by means of a special cutting tool, which simultaneously fashions a hemispherical tip and drills a hole 0.156 cm. ($^1/_{16}$ inch) in diameter and 0.234 cm. ($^3/_{32}$ inch) in depth. This cutting tool is chucked in a high-speed electrode machine, which contributes ease and speed to quantity production of electrodes. The electrode may be prepared without the services of the special tool by cutting a hemispherical tip with a standard tool, then slightly blunting the tip with a fine file and by means of a $^1/_{16}$-inch drill, mounted in a sleeve, drilling the hole to the desired depth. It is essential that care be observed in electrode fabrication concerning the position of the periphery of the tip. The electrode tip, as outlined by the periphery of the drilled hole, must be at right angles to the side of the electrode; if this condition is not attained the spark becomes deflected and produces an irregular pattern on the sample disk. This deflection invariably causes discordant results. However, a cutting tool with the drill mounted in the center of the cutting blades produces a perfectly formed electrode, requiring no further corrections.

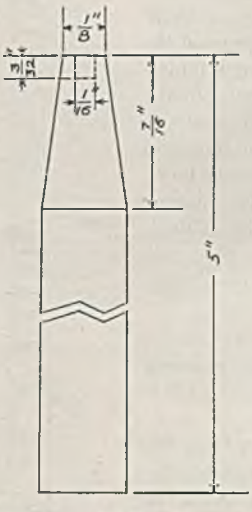

Figure 1. Hollow-Tipped Special Electrode

The spectrochemical system of analysis employed for the production control of the zinc-base alloys has been chosen for presentation here, rather than other problems handled by this method, because of the unusual requirements in analysis of high and low levels of alloy content and the very low level of impurities allowed. All constituents, alloying elements, and impurity elements are evaluated as a simultaneous quantitative estimation on one spectrogram.

The alloy under discussion, often referred to as No. 2 Zamak, contains aluminum 3.50 to 4.60%, copper 2.50 to 3.50%, magnesium 0.02 to 0.10%, iron 0.10% maximum, cadmium 0.005% maximum, tin 0.005% maximum, and lead 0.007% maximum. The literature offers few spectrochemical methods for the analysis of this type of alloy. Indeed, for the zinc-base alloys no method, including that of the A.S.T.M., provides for the quantitative determination of alloy constituents and the very low concentrations of allowable impurity elements in a single spectrographic operation, involving the spark technique. This is accomplished with the flat disk technique utilizing the Petrey spark stand, ammonium chloride–packed counterelectrode, and high-voltage spark source with extra inductance.

The method employed in the spectrochemical analysis of zinc-base alloys involves sample procurement and preparation, electrode preparation, excitation of sample and registration of spectral lines, film preparation, densitometry, and calculations.

## SAMPLES AND PREPARATION

Samples for analysis may be specimens of any convenient size that have sufficient dimensions to rest on the Petrey stand. However, chill-cast disks measuring 2.5 inches in diameter and 0.5 inch in thickness have been found convenient to process in the laboratory. Figure 2 is a photograph of chill-cast disk and packed electrode. Die castings, parts of gates, sprues, and sawed slices from metal ingots have been utilized as samples for this type of alloy. Nondestructive analyses are often made on smooth casting surfaces with surprising accuracy. However, standard practice in this laboratory is to impart a smooth surface to each sample by means of the lathe cutting tool.

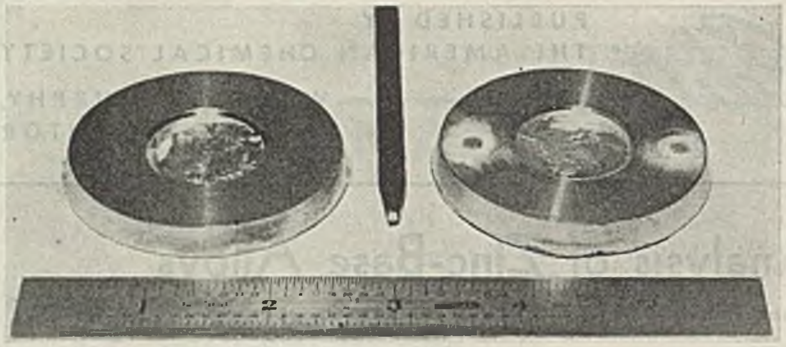

Figure 2. Chill-Cast Disk and Packed Electrode

#### SPARK EXCITATION CONDITIONS AND FILM DEVELOPMENT

The special, hollow-tipped electrode is packed with the ammonium chloride salt by tamping it into a dish of the ground salt and smoothing flush with the periphery tip by means of a spatula or fine file. The fully prepared electrode is then placed in the lower clip-holder of the Petrey stand and adjusted for a 3-mm. gap by the swing-away gage. The smoothly machined disk, ingot slice, or casting segment is placed on the stand as the upper electrode.

The A.R.L.-Dietert, high-voltage spark unit is set at full power (2 kva.), and use is made of an additional inductance so that 1.46 millihenrys are available for the system. Excitation is made on an A.R.L.-Dietert grating spectrograph possessing a dispersion of 7 Å. per mm. Two 30-second sparking operations are performed on different parts of the sample surface. A new electrode is used for each excitation and the two 30-second exposures, without prespark, are superimposed on one spectrogram.

Registration is made on Eastman Spectrum No. 2 film which is processed 3 minutes in D19 developer at 16° C. The film is taken through all stages of processing under constant-temperature conditions and in rocker-type developer trays. A new electrode is employed for each 30-second excitation to give identical conditions of superimposition, because it was found desirable to maintain maximum gassing conditions over the full 60 seconds of sparking. Prespark is eliminated, because of the initial volatility of such elements as cadmium and lead.

The film calibration curve is obtained by sparking a standard iron sample for 1 minute, using the step-sector method. A single screen of 200-mesh wire cloth is placed before the lens to lessen the intensity and the high inductance unit is maintained in the circuit with output power dropped to 4/3 kva. Transmission values are selected from the 2800 to 3000 Å. region, and a plot of these data on log-log paper, using transmissions as ordinates and intensities as abscissas, derives the film calibration curve.

#### DENSITOMETRY AND CALCULATIONS

An exposure of one minute for zinc alloys produces a background which has to be accounted for in the calculations and the accurate measurement of the difference between line with underlying background, and background is utilized to measure the extremely small percentages of tin, cadmium, and lead encountered. Densitometry, therefore, includes measurement of transmission values for line plus background and adjacent background. The internal standard method of quantitative analysis is employed and all transmissions are referred to the 2670 Å. zinc internal standard line. All films are measured on two A.R.L.-Dietert comparator densitometers which are used interchangeably.

Calculations are made on calculating boards, and each element's spectral line, with underlying background and average adjacent background, is compared with the internal zinc line plus background.

A simple subtraction of background intensity ratio, from line plus background intensity ratio, gives the line intensity ratio corrected for background. No effort is made to measure the intensity of the 2670 Å. zinc line without background, since this line's background intensity becomes a constant in the calculation, and can be included with line intensity for all ratio derivations. A schematic presentation for the 2833 Å. lead line is:

$$\text{Intensity ratio } \frac{\text{Pb 2833 Å. + background}}{\text{Zn 2760 Å. + background}} -$$

$$\text{intensity ratio } \frac{\text{background at 2833 Å.}}{\text{Zn 2670 Å. + background}} =$$

$$\text{intensity ratio } \frac{\text{Pb 2833 Å.}}{\text{Zn 2670 Å + background}}$$

Background readings, after some experience and practice, are made rapidly and the calculation of dual intensity ratios with a simple subtraction does not materially burden this phase of the analysis.

For the analysis of the copper-bearing, zinc-base alloys the following spectrum element lines have been found satisfactory:

| | Å. |
|---|---|
| Zinc (internal standard) | 2670 |
| Cadmium | 2288 |
| Lead | 2833 |
| Magnesium | 2928.7 |
| Iron | 2967 |
| Aluminum | 3060 |
| Tin | 3175 |
| Copper | 3194 |

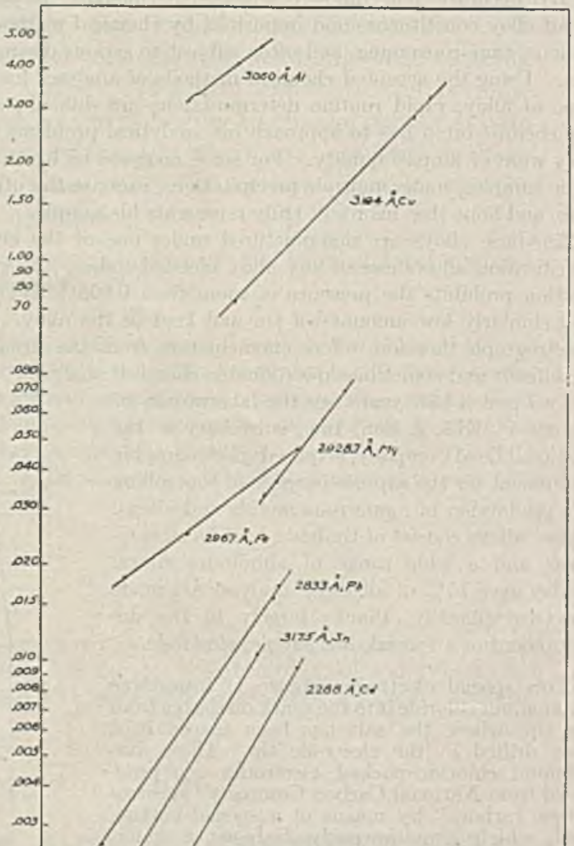

Figure 3. Working Curves Derived from Spectrochemical Data of Table II

Curves are valid for quantitative determination of aluminum and copper in Nos. 2 and 5 Zamak and for quantitative determination of magnesium, iron, lead, tin, and cadmium in Nos. 2, 5, and 3 Zamak

### Table I. Typical Transmission Data, Lot 2142

| | Zinc, 2670 Å. | Cadmium, 2288 Å. | Lead, 2833 Å. | Magnesium, 2028.7 Å. | Iron, 2967 Å. | Aluminum, 3060 Å. | Tin, 3175 Å. | Copper, 2194 Å. |
|---|---|---|---|---|---|---|---|---|
| Transmission of line plus background | 11.4 | 43.5 | 35.7 | 22.8 | 45.5 | 43.5 | 64.3 | 39.9 |
| Transmission of background | .. | 56.0 | 43.0 | 71.0 | 64.0 | 68.0 | 70.5 | 71.0 |
| Intensity ratio-line plus background | .. | 0.280 | 0.350 | 0.545 | 0.287 | 0.278 | 0.159 | 0.31 |
| Intensity ratio of background | .. | 0.200 | 0.280 | 0.130 | 0.160 | 0.142 | 0.133 | 0.13 |
| Intensity ratio of line | .. | 0.080 | 0.070 | 0.415 | 0.127 | 0.136 | 0.026 | 0.180 |

### Table II. Data for Plotting Working Curve

| Lot No. | | Cadmium | Lead | Magnesium | Iron | Aluminum | Tin | Copper |
|---|---|---|---|---|---|---|---|---|
| 2142 | Duplicate intensity ratios | 0.080 | 0.070 | 0.415 | 0.127 | 0.136 | 0.026 | 0.180 |
| | | 0.078 | 0.068 | 0.393 | 0.129 | 0.136 | 0.026 | 0.180 |
| | Av. | 0.079 | 0.069 | 0.404 | 0.128 | 0.136 | 0.026 | 0.180 |
| | Chemical analysis, % | 0.00097 | 0.0026 | 0.071 | 0.025 | 3.30 | Trace | 0.74 |
| 2200 | Duplicate intensity ratios | 0.290 | 0.237 | 0.220 | 0.291 | 0.181 | 0.218 | 0.750 |
| | | 0.280 | 0.237 | 0.233 | 0.276 | 0.188 | 0.210 | 0.730 |
| | Av. | 0.285 | 0.237 | 0.226 | 0.283 | 0.185 | 0.214 | 0.74 |
| | Chemical analysis, % | 0.0094 | 0.0157 | 0.033 | 0.046 | 4.13 | 0.0103 | 3.25 |
| 2201 | Duplicate intensity ratios | 0.118 | 0.250 | 0.248 | 0.079 | 0.215 | 0.085 | 0.640 |
| | | 0.109 | 0.245 | 0.243 | 0.085 | 0.222 | 0.080 | 0.670 |
| | Av. | 0.114 | 0.248 | 0.246 | 0.082 | 0.219 | 0.083 | 0.66 |
| | Chemical analysis, % | 0.0019 | 0.0172 | 0.037 | 0.018 | 4.70 | 0.0022 | 2.83 |

### Table III. Comparison of Spectrographic and Chemical Analytical Results, Lot 2198

| | Cadmium | Lead | Magnesium | Iron | Aluminum | Tin | Copper |
|---|---|---|---|---|---|---|---|
| Duplicate intensity ratio | 0.145 | 0.138 | 0.235 | 0.285 | 0.180 | 0.105 | 0.724 |
| | 0.150 | 0.140 | 0.233 | 0.300 | 0.181 | 0.100 | 0.735 |
| Av. | 0.148 | 0.139 | 0.234 | 0.292 | 0.181 | 0.103 | 0.730 |
| Spectrographic, % | 0.00295 | 0.00722 | 0.034 | 0.047 | 4.08 | 0.00312 | 3.18 |
| Chemical, % | 0.00280 | 0.00730 | 0.032 | 0.045 | 4.13 | 0.00297 | 3.25 |

## COMPARATIVE ANALYSIS OF A ZINC-BASE ALLOY BY SPECTROCHEMICAL AND CHEMICAL METHODS

Three standard samples covering the compositional range of Zamak No. 2 and with sufficient impurity variations were selected to establish working curves for the spectrochemical analysis of a fourth sample designated "unknown". The analyses of each of the three standard samples, lots 2142, 2200, and 2201, are listed in Table II, with the duplicate intensity ratios derived for the respective element spectral lines by spark excitation of the three standards and one unknown, all in duplicate. The eight spectrograms comprising this film were made as in daily routine procedure and no undue precautions were exercised in the execution of the steps of the analysis.

The three standard samples and the unknown sample were very carefully analyzed in duplicate by two or more chemists, each of whom practiced precise and approved methods of chemical analysis, such as those sponsored by the New Jersey Zinc Company research laboratories. Large samples were employed for the analysis of low percentage impurity elements lead, tin, and cadmium, and for these elements more than one method of analysis was used.

Table I presents typical spectrochemical data derived from the spark excitation of No. 2142, one of the standard samples. Table II lists the individual average element intensity ratios and the corresponding chemical compositions for each standard sample used in this analysis. The working curves shown in Figure 3 were derived from plotting the values in Table II. An interesting and gratifying feature of the working curves is the accuracy with which all points fall on straight lines. Table III presents the results of the analysis on the unknown lot 2198 by spectrochemical and chemical methods.

A consideration of the average arithmetical per cent error in determinations of the various elements reveals that the major constituents, copper and aluminum, were measured well within an error of 3% of the amount present. The error expressed as per cent deviation from the chemical value of each element is: magnesium 6.2%, cadmium 5.3%, tin 5.0%, iron 4.4%, copper 2.1%, aluminum 1.2%, and lead 1.0%. The 6.2% deviation for magnesium might at first glance appear high enough to invalidate the worth of this determination. However, when the figure 6.2% is arithmetically applied to the accepted value of 0.032% we obtain a difference of 0.00198%, which, if equaled in routine chemical analyses, would be considered satisfactory. The accuracy of the cadmium evaluation could, of course, be helped materially by the use of a calibration curve constructed from transmission results taken in that region of the spectrum. The yardstick phrase "measuring an element within an error of 3 to 5% of the amount present" loses some of its comparative signification when applied to an element such as tin, which, in the case under consideration, is present in the amount of only 0.00297%. We can, therefore, accept higher values than 5% when we seek to evaluate elements present in a concentration on the order of 0.003%, since in the case of the tin evaluation in this analysis 5% of 0.00297% is 0.000148%, a negligible quantity in routine control analysis. A decrease in the accuracy of analysis at low concentrations is to be expected, particularly at levels where the difference between line with underlying background intensity and background intensity is small compared to background.

## ANALYSIS TIME REQUIREMENTS

Sample procurement and sample preparation are in many spectrochemical methods great consumers of time. The flat disk technique simplifies sample procurement and, since no chemical treatment is necessary in sample preparation (only simple lathe machining), very rapid treatment is possible.

An analysis time of 5 to 7 minutes per element is easily achieved for a single sample; under normal routine conditions an analysis time of 2 minutes per element is achieved for a full film of seven unknown samples and one standard sample. Seven elements, of course, are evaluated for both the full film containing seven spectrograms and the film with only one spectrogram.

If one were to double these routine spectrochemical production time intervals of analysis per element, a comparison with time requirements for the chemical analysis of certain elements would still be meaningless; one cannot compare 30 minutes to 12 hours, which are the time requirements for determining cadmium. The 30-minute figure can be used for the spectrochemical evaluation of cadmium only if all film processing time is charged against one determination; 12 hours is a charitable time interval for a precise chemical cadmium determination by approved methods for the No. 2 Zamak alloy.

Iron, copper, and lead can be rapidly analyzed by chemical and electrolytic methods. Aluminum, magnesium, cadmium, and tin are the difficult time-consuming chemical determinations.

When the analytical problem is placed on a volume basis where many samples are handled each day for complete analyses, the spectrochemical method, as set forth in this paper, gains in attractiveness from the time-requirement standpoint.

## ACCUMULATED DATA FROM LABORATORY CONTROL WORK

It is standard practice in this laboratory to assemble day to day analytical data on prospective standards before placing them in service in the capacity of control standards. Opportunity is therefore offered to present data on the lead content of lot 2198, a standard sample which has been used on numerous films, with standard lot 2200, used in the analysis described above. Some 21 separate spectrochemical values for lead are presented which are, in all instances, based on the working curve shift from day to day as dictated by the 2200 standard. Lot 2199 was accurately determined by chemical methods to contain 0.0107% lead. The assembled data are given in Table IV.

In a similar manner data are available to show the day by day results for aluminum, the constituent present in the alloy in highest percentage (Table V). Lot 2144 was placed on many films along with standard lot 2200, not for the purpose of reliability checks, but rather for the more accurate evaluation of aluminum in the lower copper-bearing zinc alloys. At certain times it is expedient to place both high and low copper-bearing zinc alloys on the same film. The accurate and accepted chemical value for No. 2144 is 4.00% aluminum.

It is significant that lot 2200, which was used as the standard, contains 3.25% copper and that lot 2144 contains 1.00% copper. Experimental and production work has shown that in the analysis of zinc alloys for aluminum, standard sample and unknown sample should contain copper in similar amount. Consequently, the author never attempts to evaluate aluminum in No. 3 Zamak (copper-free) on the basis of a copper-bearing standard.

Table IV. Determination of Lead

| Date of Analysis | Spectrochemical<br>% | Difference from Chemical Value of 0.0107%<br>% |
|---|---|---|
| January, 1945 | 0.0115 | 0.0008 |
| | 0.0115 | 0.0008 |
| | 0.0110 | 0.0003 |
| | 0.0112 | 0.0005 |
| March, 1945 | 0.0117 | 0.0010 |
| | 0.0110 | 0.0007 |
| | 0.0112 | 0.0005 |
| | 0.0108 | 0.0001 |
| | 0.0107 | .... |
| April, 1945 | 0.0096 | 0.0011 |
| | 0.0107 | .... |
| May, 1945 | 0.0102 | 0.0005 |
| | 0.0100 | 0.0007 |
| | 0.0105 | 0.0002 |
| | 0.0105 | 0.0002 |
| June, 1945 | 0.0101 | 0.0006 |
| | 0.0105 | 0.0002 |
| | 0.0098 | 0.0009 |
| | 0.0114 | 0.0007 |
| | 0.0112 | 0.0005 |
| | 0.0098 | 0.0009 |
| Average lead content, % | | 0.01066 |
| Average per cent difference, % | | 0.00053 |
| Deviation (% of quantity measured) | | 5.0 |
| Standard deviation, % | | 0.000639 |

Table V. Determination of Aluminum

| Date of Analysis | Spectrochemical<br>% | Difference from Chemical Value of 4.00%<br>% |
|---|---|---|
| August, 1944 | 4.13 | 0.13 |
| | 4.05 | 0.05 |
| | 4.22 | 0.22 |
| November, 1944 | 4.03 | 0.03 |
| | 3.88 | 0.12 |
| | 4.11 | 0.11 |
| January, 1945 | 4.13 | 0.13 |
| | 4.10 | 0.10 |
| | 4.12 | 0.12 |
| February, 1945 | 4.22 | 0.22 |
| | 3.92 | 0.08 |
| | 4.11 | 0.11 |
| | 4.13 | 0.13 |
| March, 1945 | 4.13 | 0.13 |
| | 4.03 | 0.03 |
| Average aluminum content, % | | 4.09 |
| Average per cent difference, % | | 0.114 |
| Deviation (% of amount measured) | | 2.85 |
| Standard deviation, % | | 0.13 |

## DEVELOPMENT OF AMMONIUM CHLORIDE-PACKED ELECTRODE

The development of the ammonium chloride electrode resulted from research on the use and effect of chemical salts in the spectrochemical analytical system involving the spark technique. Incentive for this type of research emanated from a desire to gain increased sensitivity and yet retain the speed and accuracy of the spark method.

Initial efforts to analyze flat disk zinc alloy samples using plain hemispherical tipped electrodes indicated that long exposure would be necessary to bring the transmission of the 2833 Å. lead spectral line to a measurable level. When total exposure was increased to include three and four 30-second intervals of spark excitation superimposed on one spectrogram, difficulties arose which, under the prevailing conditions, were insurmountable. Undesirable effects related to the high volatility of zinc resulted in erratic reproducibility of spectral-line intensity ratios for all elements. Backgrounds became very dense and in the cases of the low percentage elements, insufficient difference resulted between line and background intensities to give quantitative accuracy.

Ammonium chloride-packed electrodes, used in the first experimental runs as they are used in routine work today, lessened background, increased contrast between line and background, and produced a high degree of reproducibility.

The use of chemical salts in spectrochemical analysis is not new. However, in so far as the author has been able to discover, its use in the spark method is a radical departure. Hasler and Harvey (*1*) describe a method incorporating ammonium chloride in an arc analysis of zinc alloy. A metal peg of the zinc alloy is encased in ammonium chloride and contained in a graphite sleeve holder. This assembly becomes the lower electrode and graphite is utilized as the upper electrode. Four seconds' arcing time is employed and, according to the authors, a large amount of sample is energized in the discharge. A good degree of accuracy and reproducibility is indicated by the published results.

## SUMMARY

A rapid and accurate spark spectrochemical system incorporating the use of the ammonium chloride-packed electrode and the flat disk self-electrode has been developed. A commercial high-voltage spark source unit with extra inductance is used for excitation of flat disk samples on a Petrey spark stand. A grating spectrograph is employed and spectral line registration is made on Eastman No. 2 film. Comparator-densitometers are used for all transmission measurements and conversion to intensity ratios is made on calculating boards.

The system provides for the simultaneous evaluation of all zinc alloy constituents and impurities in a quantitative manner on one spectrogram. The method is applicable to the Zamak series of zinc alloys over the full compositional range as well as to other types of alloys.

The method presented accurately measures the quantity of lead in the 0.002 to 0.015 range, tin in the 0.002 to 0.015 range, cadmium in the 0.002 to 0.010 range, magnesium in the 0.01 to 0.10 range, iron in the 0.01 to 0.10 range, copper in the 0.75 to 3.25 range, and aluminum in the 3.50 to 4.50% range.

Data presented in all instances represent results obtained in the routine execution of the method. Certain selective refinements of method manipulation could have been practiced in the production of the data cited, but the true validity of the system is shown by results obtained under daily routine conditions.

The application of the ammonium chloride-packed electrode in the analysis of other types of alloys has necessarily had to suffer in this paper. However, better than 70% of all the author's spectrographic results are obtained by the use of this electrode, which has controlled the production of many thousands of tons of specification alloys for over two years.

The speed of sample preparation (nondestructive, if necessary), simplicity, and directness of manipulation combined with a high degree of analytical accuracy are advantages of the method.

ACKNOWLEDGMENT

The author wishes to express his thanks and appreciation to M. F. Hasler for his most helpful cooperation on the many problems which arose in the standardization of the method, and to B. M. Luckenbill of the Spectrographic Laboratory and E. Knapp of the Chemical Laboratory for their indispensable analytical work.

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# Preparation of Synthetic Samples of Low-Boiling Hydrocarbons

R. H. BUSEY[1], G. L. BARTHAUER, AND A. V. METLER
Field Research Department, Magnolia Petroleum Company, Dallas, Texas

**The design and operation of an apparatus for the blending of low-boiling hydrocarbons are described. The apparatus is so designed that standard samples containing any number of components may be prepared rapidly, in any size, and with a degree of accuracy far superior to present methods of analysis. The apparatus has been thoroughly tested. Data are presented for samples in the butane and pentane range.**

With the constantly increasing emphasis placed upon newer physical methods of hydrocarbon analysis (*2*)—i.e., infrared spectroscopy, mass spectroscopy, etc.—a growing need has been felt for synthetic mixtures of low-boiling hydrocarbons. Not only are such mixtures necessary as a final test upon calibration data but periodically a check sample must be run to ensure continued satisfactory performance of the instrument.

Several years ago the need for such a method became apparent in these laboratories. A literature search revealed very little in the way of blending units versatile enough to satisfy the varied requirements of the work. Not only were small "spot" samples required for infrared and mass spectrographic work, but large samples occasionally were necessary to develop adequately a variety of methods, ranging from Matuszak procedures and bromine numbers to low-temperature distillation analyses.

The usual practice for obtaining such samples has taken either of two forms. The sample may be prepared upon a pressure basis, putting each component successively into a constant-volume device and measuring the pressure increments added. Large volumes are necessary if the sample is to be of appreciable size and the introduction of inert material, either from a small leak in the system or from the hydrocarbons themselves, may introduce serious error. Deviations from the gas law equation may also be appreciable if mixtures containing components having a different number of carbon atoms are blended or if relatively high pressures are used.

In the second method the composition of a mixture is obtained by another method of analysis. The instrument or method tested may then be evaluated on the basis of a study of this so-called "secondary standard". The objections to such an evaluation are obvious, in that the evaluation of the tested method is limited to the accuracy of the method used in obtaining the sample composition. With the ready availability of the greater number of pure low-boiling hydrocarbons on the market today, direct preparation of the sample from pure materials is the only satisfactory method.

The blending apparatus described by McMillan (*1*) for the testing of low-temperature distillation procedures approaches most closely the apparatus developed in this laboratory. The sample was prepared upon a pressure basis, inert material being removed prior to preparation in the manner described below. Although satisfactory for the purpose at hand, the blending unit lacked the extreme versatility required in the present-day analytical laboratory.

## DESCRIPTION OF APPARATUS

A schematic drawing of the apparatus is shown in Figures 1 and 2.

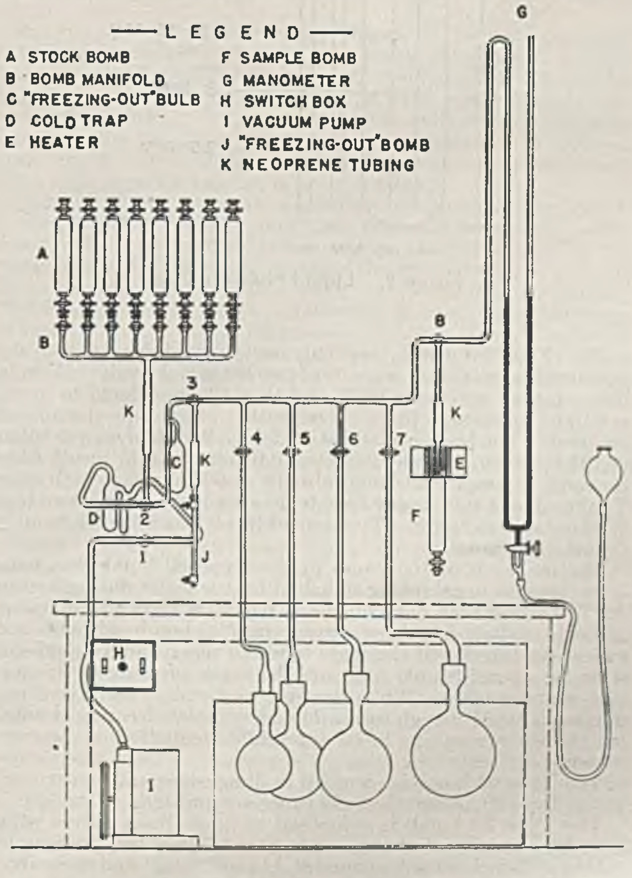

Figure 1. Schematic Drawing of Apparatus

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[1] Present address, The University of California, Berkeley, Calif.

Essentially the apparatus consists of the following:

A stainless steel bomb manifold, *B*, equipped with eight brass Hoke valves. To each valve is attached a brass compression fitting (for $^1/_4$-inch pipe thread) similar to that shown in Figure 3.

A constant-volume manometer, *G*, complete with leveling bulb.

A 500-watt Calrod heater with shield, *E*, so arranged as to prevent freezing of hydrocarbon in the narrow neck of the enclosed Hoke valve.

A water bath surrounding four boiling flasks of the indicated sizes. Each flask is equipped with a mercury seal standard-taper joint to preclude leakage during sample make-up.

Three bomb types (Types 59, 65, 80), described in detail below.

A glass manifold equipped with the indicated stopcocks, "freezing-out" bulb, *C*, and liquid nitrogen traps, *D*.

A vacuum pump, *I*.

The apparatus is mounted as an integral unit on an angle-iron table having a 2.5-cm. (1-inch) Transite top. The manifold system and the expansion flasks are rigidly held in place by clamps leading from the various supports which, in turn, are securely bolted to the table top. A grill consisting of iron rod (0.5 inch) welded in 4-inch squares has been found most satisfactory for supporting equipment above the table top.

The apparatus measures 42 inches across the front and is 18 inches deep and 65 inches high.

### SAMPLE BOMBS

A highly satisfactory type of small bomb has been evolved in this laboratory. Double-exit bombs have been found to be much superior to single-exit types on two important counts: They are more readily cleaned by flushing with the proper solvents and dried by passage of air current, and pressuring of samples is more readily accomplished.

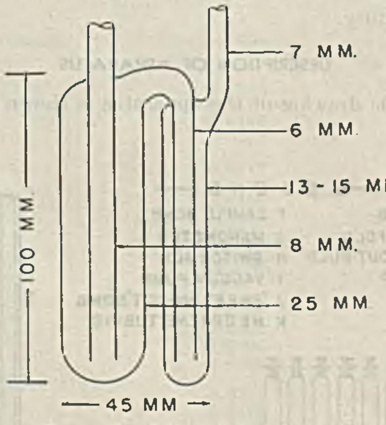

Figure 2. Liquid Nitrogen Trap

The Type 80 bomb, specially constructed for synthesis of hydrocarbon mixtures, consists of two brass Hoke valves threaded into a copper and brass body and then silver-soldered to form a gas-tight junction. Hoke valves with $^1/_4$-inch pipe thread ends are used. The body is made of a 5.5-inch length of copper tubing (1.125 inches in outside diameter, 0.065-inch wall), inside which six vanes or fins are set longitudinally at 60° angles to each other. To the ends of this copper tube body are silver-soldered two brass swedge-type reducers. The assembly of this type of bomb is shown in Figure 3.

The inclusion of the vanes in the Type 80 bomb was found advantageous in achieving sufficient heat transfer during freezing out of hydrocarbon components. When an appreciable amount of hydrocarbon has been frozen into a bomb without such vanes, the interior of the mass tends to remain in a liquid-solid state for a considerable time and the vapor pressure of this mixture is appreciable. When the fin-type bomb is used, heat conduction is rapid enough to accomplish complete freezing throughout the mass, resulting in an appreciable reduction of the vapor pressure.

The Type 65 bomb is identical in dimensions and construction to the Type 80, except that the vanes are omitted.

The Type 59 bomb is composed of brass Hoke valves which have been machined at one end to fit a 4.5-inch length of copper tubing (0.5-inch outside diameter, $^1/_{32}$-inch wall) and then silver-soldered in position (see Figure 3). Considerable material can be machined off the body of the valves to reduce materially the net weight of the bomb.

Each bomb is provided with two brass caps equipped with 16-gage sheet-lead liners which insure against loss of sample during storage.

A special brass compression fitting is used for connection to the $^1/_4$-inch pipe thread of the valve-ends. Details of the cap and fitting are shown in Figure 3.

Chrome plating of these bombs is advantageous in that wear on the threaded surfaces and hence change in weight of the bomb are less. There is also less tendency to pick up stray mercury on the surface of the bomb.

### CALIBRATION

Prior to preparation of synthetic samples, certain instrument constants must be obtained—the relative volumes of all flask and manifold combinations which may conceivably be used in sample make-up.

It has been found convenient to assign a value of unity to that volume occupied by the 500-ml. flask and the apparatus manifold. The manifold volume, in this case, includes all space from the reference mark of the manometer (explained below) to the Hoke valves of the steel bomb manifold, excluding the volume occupied by the sample bomb, the freezing-out bomb, and the liquid nitrogen traps. The relative volumes of all other flask combinations are thus stated in multiples of this so-called "unit volume".

All ratios are determined in a similar manner. Illustrative of the procedure is the determination of the ratio of the volume of the 1000-ml. flask to the unit volume.

Procedure. After testing the apparatus thoroughly for leaks, adjust the mercury columns in the manometer by means of the leveling bulb until the total of the readings in both arms is not more than 950 mm. and not less than 925 mm. (This is most important. Failure to observe this precaution whenever the system is evacuated may result in forcing mercury into the glass manifold.)

With stopcocks 1, 4, and 5 open, stopcocks 3 and 8 by-passing the respective bombs, and stopcock 2 connecting all arms, evacuate the system. After the system is evacuated, close stopcock 1 and adjust the mercury column in the left arm of the manometer to the 900-mm. reference mark. Record the height of the mercury column in the right arm as the zero reading.

Now close stopcock 5 and, by means of stopcock 2, connect the bomb manifold to the system leading to the manometer, by-passing that volume between stopcocks 1 and 2. Open one of the Hoke valves on the bomb manifold and allow atmospheric pressure to enter the system. Close the Hoke valve and again adjust the mercury column to the reference mark. Record the reading in the right arm as sample reading.

After lowering the mercury in the manometer as previously instructed, open stopcock 5 leading to the evacuated 1000-ml. flask and allow the system to come to equilibrium. Measure the pressure in the usual manner and record as equalized pressure reading.

From these data determine $r_{1000}$, the ratio of the 1000-ml. flask to the unit volume, as follows:

$$r_{1000} = \frac{\text{sample reading} - \text{equalized pressure reading}}{\text{equalized pressure reading} - \text{zero reading}} \tag{1}$$

In a similar manner determine $r_{2000}$ and $r_{3000}$.

In addition to these three ratios a fourth, $k_{500}$, must be determined. This is defined as:

$$k_{500} = \frac{\text{volume of 500-ml. flask}}{\text{volume of apparatus manifold}} \tag{2}$$

Determine $k_{500}$ directly in the above-described manner, in this special case using the manifold alone in place of the unit volume and measuring the pressure drop when the 500-ml. flask is turned into the system. The use of $k_{500}$ will be apparent later.

Calculation of *R* Values. Since it is obviously impossible to use any flask or combination of flasks without employing the use of the manifold volume, the measured ratios ($r_{1000}$, $r_{2000}$, $r_{3000}$, and $k_{500}$) cannot be used per se but serve as data for calculating the ratio of any flask combination plus manifold to the unit volume.

These latter ratios are referred to as *R* values. The *R* values, once determined for any given instrument, serve as a basis for computation with any subsequent sample prepared using the apparatus.

It is obvious from Equation 2 that for a single flask, *a*,

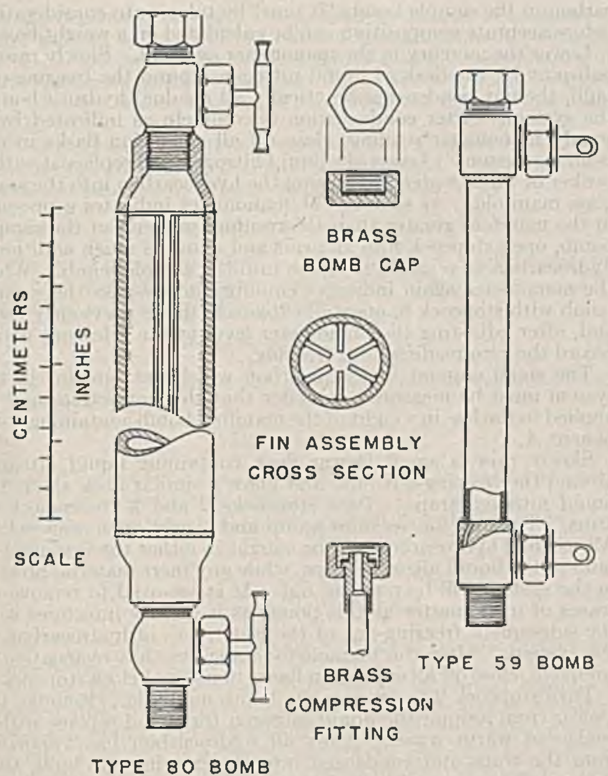

Figure 3. Bomb Detail

$$R_a = \frac{V_a + V_m}{\text{unit volume}} = r_a + \frac{V_m}{V_m + V_m k_{500}} = r_a + \frac{1}{k_{500} + 1} \quad (3)$$

Likewise for any combination of flasks

$$R_{(a + b + \ldots x)} = r_a + r_b + \ldots r_x + \frac{1}{k_{500} + 1} \quad (4)$$

For those flask combinations involving the use of the 500-ml. flask, the following simplified relationship may be derived

$$R_{(a + 500)} = \frac{V_a + V_{500} + V_m}{\text{unit volume}} = r_a + 1 \quad (5)$$

Occasionally it has proved necessary to prepare a sample containing only a trace of one component. On these occasions it is desirable to use the volume of the manifold alone. Consequently, $R_m$ must be calculated.

$$R_m = \frac{V_m}{V_{500} + V_m} = \frac{1}{k_{500} + 1} \quad (6)$$

Using Equations 3 to 6, calculate the ratios for all flask combinations and for the manifold alone, tabulating the various ratios in suitable form.

Volume of the Apparatus. The number of entries of a given component into the apparatus is determined by the volume of the flask combination used, the sample size, and the percentage of that component desired in the finished sample. At this stage, we are primarily interested in the first of these considerations, the volume of any given flask combination. Since the $R$ values calculated above relate all combinations to the unit volume, it is necessary to determine only the latter.

The volume is obtained by entering any pure hydrocarbon from a small weighed copper bomb into the unit volume of the apparatus. The pressure of the gas is measured and using the loss in weight of the small bomb, the approximate volume calculated. By reference to the $R$ values, the volume of any flask composition may readily be obtained.

## SAMPLE PREPARATION

Preliminary Calculations. Assuming that the total weight and composition of the desired sample have been established, it is now necessary to determine the flask combination and the approximate pressures to be used for each individual component. As an actual example, the calculations involved in the preparation of a butane-pentane sample are presented.

Letting $a$ represent the mole fraction of component $A$ in the finished sample and $V_s$ the total sample volume desired (liquid ml.), it can be calculated that the approximate gaseous volume (760 mm. and 27° C.) to be added if $A$ is $C_4$ material is

$$\text{Volume } (C_4 \text{ material}) = 254\ V_s a \quad (7)$$

Similarly, if $A$ is $C_5$ material

$$\text{Volume } (C_5 \text{ material}) = 205\ V_s a \quad (8)$$

The volume calculated by Equation 7 or 8 is now divided by the capacity of the unit volume, obtained in the preceding calibration. The number so obtained represents the number of unit volumes which must be introduced into the apparatus at 760-mm. pressure to obtain the desired amount of component $A$.

At this point, however, deviation from the ideal gas law must be considered. It can be calculated that, should $C_4$ and $C_5$ materials be entered at 760-mm. pressure, the deviation of the former from ideality would amount to approximately 3.1% while the deviation of $C_5$ material would be 4.6%. This is obviously too high a differential for accurate preparation. Consequently, it has been the practice in this laboratory to enter the $C_4$ materials at 300-mm. and the $C_5$ materials at 150-mm. pressure. Under these conditions the successive entries of a component may be kept to a reasonable number and the deviations from ideality safely disregarded.

Multiplication by the appropriate pressure factor yields values which may now be compared directly with the $R$ values obtained in the calibration procedure. The flask combination having an $R$ number or multiple thereof approach most closely the calculated value is chosen as that to be used for the component under consideration. (These directions assume that each entry will be made at 300-mm. for $C_4$ materials and 150-mm. pressure for $C_5$ materials. If preparation to an exact predetermined percentage is desired, the pressure of each entry must be modified accordingly. The conversion factor is simply the ratio of the desired and actual $R$ values.) It is obviously desirable to keep the number of entries to a minimum and the pressure of a single entry to a maximum (not over 300 mm. for $C_4$ materials, nor 150 mm. for $C_5$ materials).

The above calculations are repeated for each component in the sample.

Filling and Weighing Copper Bombs. If only 5 to 6 grams of hydrocarbons are required for a single component, a small copper bomb (Type 59) may be used; otherwise it will be necessary to use the larger type (Type 65). (The smaller bomb may be weighed with an ordinary analytical balance but the large bombs require the use of a balance of high capacity. A series of small bombs may be used, however, if large volumes are necessary and a high-capacity balance is not available.)

Connect the copper bomb to a large stock bomb of pure hydrocarbon, attach a vacuum pump, and evacuate the system to the closed valve of the stock bomb. Close the valve next to the pump, disconnect the pump, and cool the copper bomb by pouring liquid nitrogen over its surface from one Dewar flask to another. Now hold the stock bomb in an inverted position such that when its valve is opened the liquid phase of the contained hydrocarbon will flow into the cooled bomb. Open the valve on the stock bomb and, after a suitable interval, close the valve on the small bomb. Tilt the system in such a way that excess liquid hydrocarbon may drain from the connecting link into the stock bomb. Close the valve on the stock bomb and disconnect. Hold the small bomb in a vertical position and vent approximately 0.5 gram of the hydrocarbon from the bottom valve. (When a liquid-full bomb is warmed it becomes slightly distorted in shape.) Allow the bomb to warm to room temperature. No hazard is involved, since liquid-full copper bombs stretch without rupturing on warming to room temperature.

For hydrocarbons normally liquid under atmospheric conditions, the following technique is used.

Connect the evacuated copper bomb to a funnel by means of a clean piece of neoprene tubing. Support funnel and bomb in a vertical position and pour into the funnel the desired amount of liquid hydrocarbon. Open the upper valve of the bomb slightly and cool the bomb with liquid nitrogen until all hydrocarbon passes into the bomb. Close the valve, disconnect the funnel, vent approximately 0.5 gram of material, and allow the bomb to warm to room temperature. After washing with acetone and drying, accurately weigh each filled bomb on an analytical balance.

Testing the Apparatus. Mount the weighed bombs filled with hydrocarbon on the bomb manifold, making sure that the neoprene gaskets in the manifold connections are in good condi-

Table I. Typical Samples

| Sample No. | Component | Pressure Basis *Mole %* | Weight Basis *Mole %* |
|---|---|---|---|
| 1 | 2-Methylpropane | 19.89 | 19.85 |
| | 2-Methylpropene | 9.80 | 9.80 |
| | 1-Butene | 10.53 | 10.52 |
| | 2-Butene | 20.21 | 20.25 |
| | *n*-Butane | 39.57 | 39.58 |
| 2 | 2-Methylpropane | 69.86 | 69.88 |
| | 2-Methylpropene | 5.03 | 5.05 |
| | 1-Butene | 5.00 | 4.98 |
| | 2-Butene | 5.08 | 5.08 |
| | *n*-Butane | 15.03 | 15.01 |
| 3 | 2-Methylpropene | 2.22 | 2.24 |
| | 2-Butene | 11.33 | 11.34 |
| | 2-Methylbutane | 59.20 | 59.21 |
| | 1-Pentene | 19.52 | 19.49 |
| | *n*-Pentane | 7.73 | 7.72 |
| 4 | 2-Methylpropene | 2.41 | 2.44 |
| | 2-Butene | 11.98 | 12.09 |
| | 2-Methylbutane | 57.12 | 57.03 |
| | 1-Pentene | 20.23 | 20.23 |
| | *n*-Pentane | 8.27 | 8.22 |
| 5 | 2-Methylpropane | 3.26 | 3.21 |
| | 1-Butene | 1.71 | 1.68 |
| | 2-Butene | 2.40 | 2.38 |
| | *n*-Butane | 8.55 | 8.48 |
| | 3-Methyl-1-butene | 4.16 | 4.12 |
| | 2-Methylbutane | 57.43 | 57.80 |
| | 1-Pentene | 16.26 | 16.12 |
| | *n*-Pentane | 4.86 | 4.84 |
| | 2-Pentene | 0.69 | 0.69 |
| | 2-Methyl-2-butene | 0.68 | 0.69 |

tion. Connect the weighed sample bomb (with a lead-lined cap on the lower end) and the freezing-out bomb to the appropriate connection. Fill the water bath and regrease all stopcocks which turn with difficulty or appear streaked. Adjust the mercury columns in the manometer as previously described and evacuate the entire system including the sample bomb, freezing-out bomb, expansion flasks, and manifold. Open the Hoke valves on the manifold below the bombs, permitting evacuation to the bombs containing the hydrocarbons.

With the system evacuated, close off the expansion flasks by means of stopcocks 4, 5, 6, and 7. Place the system "on test" by closing stopcock 1, and observe the manometer. Eliminate any leaks by isolating critical parts of the system.

When the mercury remains steady, turn stopcock 8 to connect the sample bomb directly to the manometer. Turn the heater switch to "on" and cool the sample bomb in liquid nitrogen.

If no leak is apparent after the bomb has completely cooled, the sample bomb with its connection is satisfactory for use. If a leak is observed, remove the bomb and reconnect it to the apparatus by means of the other valve. If a leak is still apparent, replace with another weighed sample bomb.

Introduction of Hydrocarbons. Enter first that hydrocarbon which will be present in the smallest amount in the finished sample. The next largest component is then entered, etc.; enter last that hydrocarbon present in the greatest amount in the finished sample. (This order of entry is followed in the preparation of samples containing $C_4$ and $C_5$ materials. It may prove desirable with lighter hydrocarbons to enter the components in the reverse order of their molecular weight, thus keeping the residual pressure after condensation to a minimum.)

Open to the system the expansion flask (or combination thereof) to be used for component *A*. Close all Hoke valves on the bomb manifold except the one beneath the bomb containing component *A*. Evacuate the system and record the zero reading in the usual manner. Turn stopcocks 3 and 8 to by-pass the bombs. Close stopcock 1 and turn stopcock 2 to connect the bomb manifold to the system leading to the manometer. Carefully open the valve on the bomb containing component A, allowing hydrocarbon to vaporize into the system until the appropriate pressure is obtained. Close the valve on the bomb. Adjust the mercury column in the left arm of the manometer to the 900-mm. reference mark and record the sample reading.

Withdraw the mercury from the manometer until the total length (sum of readings in both arms) does not exceed 950 mm. Turn stopcock 8 to connect all arms. Add liquid nitrogen to the Dewar flask surrounding the sample bomb if necessary. After the manometer indicates no further condensation, turn stopcock 8 to by-pass the sample bomb.

The procedure to be followed at this point depends upon the number of entries of this component which are to be made.

*Case I. A Single Entry.* Usually a small amount of hydrocarbon will not freeze into the sample bomb. The residual pressure is due to phase equilibria at the surface of the cold hydrocarbon in the sample bomb; it must be taken into consideration before accurate composition can be calculated on a weight basis.

Lower the mercury in the manometer as usual. Slowly raise a half-pint Dewar flask of liquid nitrogen around the freezing-out bulb, thereby condensing practically all residual hydrocarbon in the system. After condensation is complete as indicated by a steady manometer reading, close off all expansion flasks in use from the system. Lower the liquid nitrogen and replace it with a beaker of warm water, vaporizing the hydrocarbon into the small glass manifold. As soon as the manometer indicates a pressure in the manifold greater than the residual pressure of the sample bomb, open stopcock 8 to all arms and allow as much additional hydrocarbon as possible to freeze into the sample bomb. When the manometer again indicates equilibrium, by-pass the sample bomb with stopcock 8, open all expansion flasks previously used, and, after adjusting the manometer level to the reference mark, record the zero reading after freezing.

The small amount of hydrocarbon which yet remains in the system must be measured, in order that this correction may be applied to the loss in weight of the manifold bomb containing component *A*.

Slowly raise a small Dewar flask containing liquid nitrogen around the freezing-out bulb and place a similar flask about the liquid nitrogen traps. Turn stopcocks 2 and 3 to connect all arms. Turn on the vacuum pump and slowly open stopcock 1. All residual hydrocarbon will be caught in either the freezing-out bulb or the liquid nitrogen traps, while any inert material present in the system will be pumped out. It is essential to remove all traces of inert matter at this point, as it greatly interferes with the subsequent freezing-out of the last traces of hydrocarbon in the system. After the manometer indicates that evacuation is complete, close off all expansion flasks in use and close stopcock 1.

Turn stopcock 2 to by-pass the bomb manifold. Remove the Dewar from around the liquid nitrogen traps and replace with a beaker of warm water. After all hydrocarbon has vaporized from the traps and condensed into the freezing-out bulb, turn stopcock 2 to connect the bomb manifold and the liquid nitrogen traps, thereby isolating all hydrocarbon in the small glass manifold leading to the manometer. (Because of vacuum inside the traps, heat is transferred slowly to the inner tubes containing the hydrocarbon. Be certain all material has vaporized from these tubes before turning stopcock 2.)

Remove the liquid nitrogen from around the freezing-out bulb and place it around the freezing-out bomb, covering only about an inch of the bomb above the lower valve. Place a beaker of warm water around the freezing-out bulb to vaporize hydrocarbon from the bulb to the bomb. When the transfer is complete, close the upper bomb valve and, after by-passing the bomb with stopcock 3, disconnect it. Warm the bomb to room temperature under tap water, wash both its surface and ends with acetone, and remove any residual acetone in the ends with a vacuum pump. Wipe with a clean cloth and weigh. Evacuate the contents with a vacuum pump and reweigh.

*Case II. More Than One Entry.* Immediately after by-passing stopcock 8, adjust the mercury level to the reference mark, and record the zero reading after freezing.

Treat all subsequent entries except the last one exactly like the first entry, recording only the sample reading and zero reading after freezing for each entry. The residual pressure after condensation is not pumped out between successive entries of a single component. Make all corrections upon the last entry. Treat the last entry exactly as described in Case I.

Repeat the above procedure for each component comprising the sample, evacuating the system between the entries with the

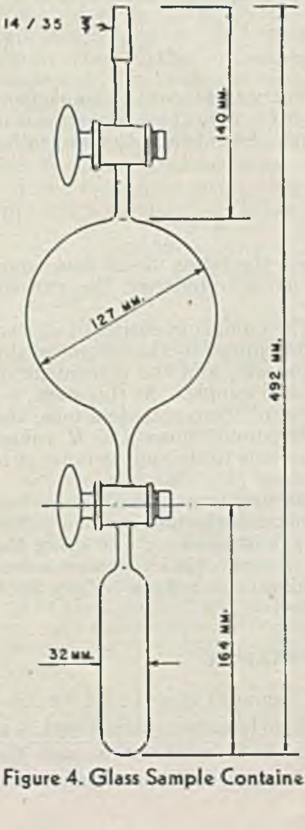

Figure 4. Glass Sample Container

sample bomb cut off from the system by means of stopcock 8. After the last component has entered the sample bomb, close the valve on the latter, remove the liquid nitrogen surrounding it, and disconnect it from the apparatus. Warm to room temperature with tap water, wash with acetone in the usual manner, and weigh.

Calculation of Sample Composition. *Pressure Basis.* The pressure, $p_1$, of a single entry of component *A* with respect to a given combination of expansion flasks is obtained by

$$p_1 = \text{sample reading} - \text{zero reading after freezing} \tag{9}$$

The total partial pressure, $p_a$, of component *A* with respect to that flask combination is simply the sum of the pressures of the individual entries of that component.

$$p_a = p_1 + p_2 + \ldots + p_n \tag{10}$$

The total partial pressure, $P_a$, with respect to the unit volume is calculated as

$$P_a = p_a R_a \tag{11}$$

where $R_a$ is that ratio listed in the table of ratios for the combination of flasks used for this component.

The mole percentage, $C_a$, of component *A* in the finished sample is then:

$$C_a = \frac{100\ P_a}{P_a + P_b + P_c \ldots + P_n} \tag{12}$$

where $P_b$, $P_c$, etc., are similarly calculated partial pressures of components *B*, *C*, etc.

*Weight Basis.* The total weight of an individual component released into the system is equal to the loss in weight of the copper bomb containing that component before and after sample preparation. The weight actually present in the sample, however, is the above value minus that found in the freezing-out bomb after removal of the residual hydrocarbon in the system.

Using the combined weight data, the mole percentage composition is calculated in the usual manner.

## TYPICAL SAMPLES

Table I illustrates the accuracy with which samples (50 liquid ml.) in the butane and pentane range may be prepared. All butanes and butenes, as well as the *n*-pentane, isopentane, and 1-pentene, were research grade material purchased from Phillips Petroleum Company.

## COMMENTS

On the basis of the experience of this laboratory, it is estimated that a 50-liquid ml. sample containing six components can be prepared, obtaining both weight and pressure data, in 8 man-hours. Although this appears to be a considerable period, it must be remembered that a 50-ml. volume permits analysis of more than fifty infrared or mass spectrograph samples. Assuming that one check a day is made on these instruments, a single preparation would last approximately two months.

The time of preparation of large samples is greatly reduced if only pressure data are obtained. Approximately 4 man-hours are required to prepare a sample of any composition since, under these circumstances, weighings are unnecessary and the time necessary to freeze out the residual hydrocarbon of each component is saved.

The usual practice in this laboratory, when introducing an operator to these techniques, is to require him to prepare about four samples obtaining data which permit calculation of the composition on both a weight and pressure basis. At the end of this period enough experience has been acquired to obtain accurate results on a pressure basis alone.

Occasionally a "spot" sample of definite composition is required in conjunction with the infrared work. A small six-component mixture may be blended rapidly (less than 30 minutes), substituting the glass sample container shown in Figure 4 for the sample bomb. These samples are prepared on a pressure basis, using the glass manifold and the glass sample container (minus the cold finger) as the gas volume. Each component is frozen successively into the cold finger and any inert material removed with the pump exactly as described above.

Although the apparatus has been used only in conjunction with hydrocarbons, it is obviously applicable to the preparation of any sample whose components are liquefiable with liquid nitrogen.

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# Method for Calcium-Sequestering Value of Phosphate Water Conditioners

B. C HAFFORD, FRED LEONARD[1], AND R. W. CUMMINS, Westvaco Chlorine Products Corporation, Carteret, N. J.

COMPARATIVELY recently molecularly dehydrated sodium phosphates have received considerable attention in the fields of water conditioning and detergency because of their ability to sequester calcium, magnesium, and other metal ions in soluble form such that these ions are not precipitated by fatty acid and other radicals. Since the use of these phosphate water conditioners depends primarily upon this ability, it is becoming increasingly important to have available a precise analytical method for its determination.

A number of investigators have studied the calcium-sequestering properties of polyphosphates, but few data are available which may be used to ascertain the true worth of the analytical methods employed.

Huber (*3*) and Watzel (*6*) used a "residual hardness method" in which the polyphosphate is added to water of known calcium content and the excess calcium determined by titration with standard soap solution. Andress and Wüst (*1*) preferred to titrate directly with standard calcium chloride solution, the end point being marked by the appearance of a white turbidity. They titrated 0.4-gram samples at pH 10.0 to 10.5 to a definite turbidity as measured with a Zeiss-Pulfrich photometer and pointed out that the calcium values so obtained decrease with increasing concentration and temperature, but increase with increasing pH. Chwala and Martina (*2*) also titrated directly with calcium chloride, confirming the effect of pH in a general way, and pointing out that sharper end points are obtained at higher temperatures.

Rudy, Schloesser, and Watzel (*5*) noted that in the direct titration method the pH of the polyphosphate solution is progressively lowered by calcium chloride addition and attempted to eliminate this factor by keeping the pH fairly constant by adding sodium hydroxide from time to time during the titration. They also measured the calcium sequestering power of polyphosphates in the presence of precipitating anions such as oxalate and fatty acid radicals.

The present paper offers a tested procedure for determining "calcium value" and presents data showing the effects of some of the more important variables. In the past, this property has been expressed in terms of grams of calcium sequestered by 1 gram of sample. It is now proposed that calcium value be expressed as grams of calcium per 100 grams of sample—that is,

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[1] Present address, Polytechnic Institute of Brooklyn, Brooklyn, N. Y.

**A photometric titration method for precisely determining the ability of a molecularly dehydrated sodium phosphate to sequester calcium is described, and it is proposed that results be expressed as grams of calcium sequestered per 100 grams of sample. The effect of pH on results is marked and varies with the type of sample analyzed. Ability to sequester calcium increases with decreasing concentration, but this is not marked enough to affect results using the recommended sample size. The influence of variables suggests that the procedure be rigidly standardized and that departures from the standard conditions be indicated in presenting results. The method has a limit of uncertainty of ±0.4 for sodium tripolyphosphate having an average "calcium value" of 10.4. Duplication of results is usually excellent.**

the per cent calcium sequestered by the material on the basis of the original sample. Thus, a calcium value formerly written as 0.127 becomes 12.7 (grams of calcium per 100 grams of sample), providing a simpler and more readable number and affording a better basis for comparing different values.

### REAGENTS AND APPARATUS

The only reagents required are approximately 0.1 *N* sodium hydroxide and standard calcium chloride solutions. The sodium hydroxide solution is prepared carbonate-free without the addition of barium hydroxide; this is conveniently done by diluting a clarified 50% solution of analytical grade sodium hydroxide with boiled distilled water. The standard calcium chloride solution is prepared by dissolving 7.00 grams of pure calcium chloride (Baker's c.p. anhydrous, lump, for reagent use) in 1 liter of distilled water to give a neutral solution containing about 0.25 gram of calcium per 100 ml. The calcium chloride solution is conveniently standardized by the well-known precipitation of calcium oxalate and subsequent titration with potassium permanganate. However, use of the specified grade of calcium chloride permits standardization by simply titrating the chloride present: Duplicate 25-ml. aliquots are titrated in the presence of 1 ml. of 5% aqueous potassium chromate to a salmon end point with standard 0.1 *N* silver nitrate. Two solutions analyzing 0.252 and 0.236 gram of calcium per 100 ml. by the oxalate-permanganate method gave values of 0.251 and 0.236, respectively, by the silver nitrate titration method.

A filter photometer employing a 40 × 40 × 60 mm. optical cell is used to locate the end point of the calcium chloride titration. An Eimer and Amend photoelectric colorimeter, consisting of a pair of electrically opposed barrier layer type photocells whose balance is ascertained by means of a Wheatstone bridge, was used in the present work. This particular instrument is no longer on the market, but any fairly stable spectro- or filter photometer measuring light transmittance through a cell of approximately the indicated dimensions should be equally satisfactory, provided there is enough space available to position a stirrer and titrating buret over the cell. Also necessary is a glass electrode pH meter to adjust the pH of the sample solution before titration. The Beckman pH meter, Laboratory Model G, was used throughout the present work. The assembly of apparatus is completed by a motor-driven stirrer consisting simply of a 15-cm. length of 6-mm. Pyrex glass rod slightly flattened at the lower end, a 50-ml. buret with offset delivery tube, and a square yard of light weight black cloth.

### PROCEDURE

Dissolve a 4.000-gram sample and dilute to exactly 250 ml. with distilled water. After thorough mixing, if the solution is turbid, allow the insoluble matter to settle out or filter through a dry No. 42 Whatman paper into a dry vessel. Pipet 25 ml. of the clear solution into the 40 × 40 × 60 mm. optical cell, dilute to about 45 ml., and adjust the pH to 10.0 by dropwise addition of 0.1 *N* sodium hydroxide, using the pH meter and ordinary glass electrode and omitting the correction for sodium-ion concentration. After rinsing the electrode assembly into the optical cell, dilute the solution to about 55 ml., conveniently determined by previously calibrating the cell. Place the optical cell in the photoelectric colorimeter and insert the glass stirrer in the right-hand corner of the cell nearest the light source. Place the titrating buret in position and completely hood the optical cell and adjacent sections of the apparatus with the black cloth. Adjust the colorimeter to read 100% transmittance with the stirrer on, using Wratten filter H No. 45 in the Eimer and Amend instrument, or any available deep blue filter in a similar instrument.

Titrate with the standard calcium chloride solution until a sharp decrease in transmittance is obtained, taking at least three readings at 0.5-ml. intervals after the end point. For samples having calcium values of 9.0 or higher, it is advantageous to add about 14 ml. of titrant before making a reading. Readings at 1-ml. intervals should then be taken until the end point is reached, when the intervals should be cut to 0.5 ml.

The calcium value of the sample, expressed as grams of calcium sequestered by 100 grams of sample, is obtained by plotting the observed transmittance readings against the corresponding milliliters of titrant added and drawing the best straight lines through the points before and after the break. The intersection of these lines gives the milliliters of calcium chloride required by the following calculation:

$$\text{Calcium value} = (\text{ml. of } CaCl_2)(\text{grams of Ca}/100\text{ ml.})(2.5)$$

Often during a titration small changes in transmittance will occur due to fluctuations in line voltage, etc. If such a change is followed by essentially constant readings, it should be attributed to a change in the 100% transmittance setting and the prior readings disregarded in drawing the straight line through the plotted data.

### EXPERIMENTAL WORK

Development of Method. The direct titration with standard calcium chloride was chosen as representing the simplest and most rapid method for determining calcium value. Before the procedure described above had been developed, and following the general technique of previous investigators, 0.4-gram polyphosphate samples dissolved in 25 ml. of distilled water and adjusted to pH 10.1 to 10.3 were titrated with 0.06 *M* calcium chloride to the first appearance of a turbidity. The end point was observed visually, a flashlight beam being directed through the titration cell to increase sensitivity. Rather extensive testing of the precision of this procedure, using different analysts, indicated that while fair duplication of results was usually obtained at any given time, visual location of the end point is unreliable because of inability of the analyst to duplicate his previous day's values. The situation is also complicated by the occasional appearance of a slight turbidity before the true end point and by the varying behavior of different types of samples. Accordingly, it was considered advisable to locate the end point photometrically if a precise method were to be developed.

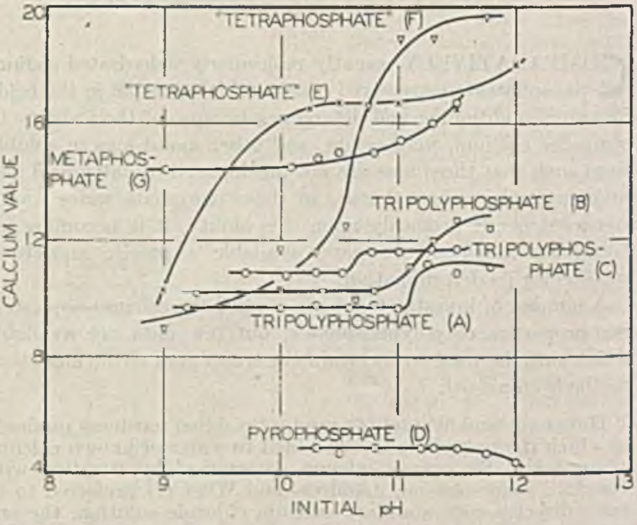

Figure 1. Effect of Initial pH on Calcium Values of Various Polyphosphates

Photometric titrations on different samples were carried out by dissolving 0.4 gram of sample in 50 ml. of distilled water and adjusting the pH to 10.0. This solution was placed in the 40 × 40 × 60 mm. optical cell in the path of the light beam in the Eimer and Amend colorimeter. A motor-driven stirrer, consisting of a straight glass rod flattened at the lower end, was inserted in the solution, and the light transmittance adjusted to read 100%. Standard calcium chloride solution was then added, the transmittance being determined at intervals during titration.

The results obtained made it clear that in the majority of cases the transmittance remains at or near 100% until the end point is reached and then decreases linearly with added titrant. This enables the analyst to draw straight lines through the plotted points after the break as well as through those before the break, and to take their intersection as the end point. This procedure would appear to be more valid than titrating to a definite measurable turbidity, which is obviously beyond the true end point. Furthermore, the straight lines drawn through the plotted points after the break have been found to have differing slopes, indicating that titrating to any given turbidity would give values varying by different amounts from the true end point.

The choice of light filter to use in the colorimeter should not affect the determination greatly, since the colorimeter is used only to find the end point. However, a number of Wratten gelatin filters were tested, and filters H No. 45 and C5 No. 47, both transmitting deep blue light, were found to give the greatest change in transmittance for a given unit of turbidity. Filter H No. 45 was arbitrarily chosen for the present method. Use of a deep blue filter has the advantage that in the graphical calculation involved, the intersecting lines are more nearly at right angles than if a less sensitive filter were used.

It was thought that the position of the glass stirrer in the optical cell might have some effect on the results obtained, since the stirrer must be placed at least partially in the light beam because of the dimensions involved. A few tests indicated that small changes in position do not affect the relativity of the transmittance readings, and if the stirrer is left in the same position during a determination, no interference is encountered. It was discovered, however, that extraneous light might cause considerable error, especially when light conditions are changing. To nullify this effect the optical cell and adjacent portions of the apparatus were shrouded with black cloth.

The effects of titration time and time lapse between calcium chloride addition and transmittance measurement were also tested. In the one case, varying the time required to complete the titration from 2 to 8 minutes gave four calcium values of 11.0 for a sample of sodium tripolyphosphate. In the other, varying the time interval between calcium chloride addition and transmittance measurement from 10 to 60 seconds gave values having a total calcium value range of 0.2. Small changes in temperature were also found to be relatively unimportant. A series of titrations in which the initial temperature varied from 20° to 30° C. gave calcium values ranging from 11.1 to 10.9 for the above sample of sodium tripolyphosphate.

EFFECT OF pH. The previously cited work of other investigators and early unpublished data obtained in this laboratory by the visual end point calcium value titration method had definitely shown that pH is an important variable in the determination of calcium value.

In order to determine the effect of pH on the present method, the calcium values of various types of polyphosphates were determined after adjustment of the sample solutions to different pH levels. Also, since pH had been found to decrease during a titration with calcium chloride, the end point pH values were determined on separate aliquots to which the amount of titrant required to reach the end point had been added. Three samples of commercial sodium tripolyphosphate, two samples of commercial sodium "tetraphosphate", one sample of commercial anhydrous tetrasodium pyrophosphate, and one sample of glassy sodium metaphosphate were tested as being representative of the types of material employed in water conditioning. The metaphosphate was prepared by fusing about 25-gram lots of C.P. monosodium orthophosphate in a platinum crucible at 700° to 800° C. for one hour and quenching the hot crucible in ice water after rotating to obtain a thin film of melt on its inside surface. The results obtained are shown in Table I, and the initial pH values are plotted against calcium value in Figure 1. Uncorrected pH values obtained with a glass electrode are used throughout.

Inspection of Figure 1 reveals that determined calcium value is affected by the pH to which the sample solution is initially adjusted in a marked and variable manner. For sodium tripolyphosphate, the calcium value appears to be fairly constant up to a pH of 10.5 to 11.5, in which range a reasonably sharp increase in calcium value occurs. The break does not seem to be limited to a very narrow pH range. The sodium "tetraphosphate" samples both show remarkable increases in calcium value at rather different pH levels. The calcium values of the tetrasodium pyrophosphate and glassy metaphosphate samples are more constant, the latter showing a fairly slow increase with increasing pH.

These findings indicate that for sodium tripolyphosphate, at least, the procedure of adjusting to pH 10.0 gives calcium values in a pH region where pH has little effect. The flat portions of the calcium value–pH curves for tripolyphosphate are not in agreement with results obtained by titrating to the first visual appearance of a turbidity, or by titrating to a given instrumental turbidity. The latter procedures usually give a steady increase in calcium value with increasing pH, and the present flat curves are probably the result of the improved method of locating the end point. The variability of the calcium value–pH data shown illustrates that use of the initial pH value of 10.0 is more or

Table I. Effect of pH on Calcium Values of Various Polyphosphates

| Sample | Calcium Value | pH | | Sample | Calcium Value | pH | |
|---|---|---|---|---|---|---|---|
| | | Initial | Final | | | Initial | Final |
| Sodium tripolyphosphate, sample A | 9.7 | 9.21 | 8.30 | Sodium "tetraphosphate", sample E | 10.3 | 8.99 | 8.00 |
| | 9.7 | 10.00 | 9.40 | | 16.2 | 10.02 | 8.45 |
| | 9.8 | 10.30 | 9.80 | | 16.5 | 10.25 | 8.65 |
| | 9.7 | 10.58 | 10.22 | | 16.7 | 10.50 | 9.15 |
| | 9.8 | 10.79 | 10.55 | | 16.7 | 10.75 | 9.90 |
| | 9.7 | 11.00 | 10.80 | | 16.7 | 11.00 | 10.41 |
| | 11.2 | 11.25 | 11.01 | | 16.5 | 11.50 | 11.35 |
| | 10.9 | 11.50 | 11.32 | | 18.0 | 12.00 | 11.99 |
| | 11.1 | 11.77 | 11.60 | | | | |
| Sodium tripolyphosphate, sample B | 10.2 | 9.28 | 8.40 | Sodium "tetraphosphate", sample F | 9.8 | 7.51 | 6.39 |
| | 10.3 | 10.00 | 9.50 | | 9.0 | 9.01 | 8.42 |
| | 10.3 | 10.36 | 10.00 | | 11.7 | 10.00 | 9.25 |
| | 10.0 | 10.64 | 10.42 | | 11.6 | 10.29 | 9.55 |
| | 10.3 | 10.79 | 10.60 | | 12.5 | 10.56 | 9.78 |
| | 11.1 | 11.10 | 10.90 | | 16.6 | 10.75 | 9.20 |
| | 12.0 | 11.30 | 11.11 | | 18.9 | 11.02 | 9.81 |
| | 12.7 | 11.50 | 11.35 | | 18.9 | 11.31 | 10.92 |
| | 12.4 | 11.78 | 11.62 | | 19.6 | 11.75 | 11.58 |
| Sodium tripolyphosphate, sample C | 10.9 | 9.70 | 8.81 | Sodium metaphosphate glass, sample G | 14.3 | 5.68 | 4.25 |
| | 10.8 | 10.05 | 9.22 | | 14.4 | 9.02 | 7.25 |
| | 10.9 | 10.30 | 9.87 | | 14.5 | 10.09 | 7.80 |
| | 10.9 | 10.53 | 10.19 | | 14.8 | 10.32 | 7.92 |
| | 11.6 | 10.78 | 10.49 | | 15.0 | 10.50 | 8.21 |
| | 11.6 | 11.01 | 10.70 | | 15.0 | 10.79 | 8.30 |
| | 11.7 | 11.28 | 11.05 | | 15.4 | 11.02 | 9.35 |
| | 11.7 | 11.50 | 11.22 | | 16.0 | 11.29 | 9.50 |
| | | | | | 16.7 | 11.50 | 9.50 |
| Tetrasodium pyrophosphate, sample D | 4.9 | 10.30 | 10.19 | | | | |
| | 4.7 | 10.50 | 10.39 | | | | |
| | 4.9 | 10.80 | 10.71 | | | | |
| | 4.9 | 11.19 | 11.11 | | | | |
| | 4.9 | 11.30 | 11.22 | | | | |
| | 4.9 | 11.50 | 11.45 | | | | |
| | 4.7 | 11.75 | 11.71 | | | | |
| | 4.4 | 12.00 | 11.99 | | | | |

less arbitrary, and that no given initial pH will result in calcium values adequately comparing various types of polyphosphates. The calcium value of a given polyphosphate obviously has little meaning unless accompanied by a statement of the pH at which it was determined. In cases where the calcium value-pH behavior is unknown, maximum information is gleaned only from a calcium value-pH curve of the type shown in Figure 1.

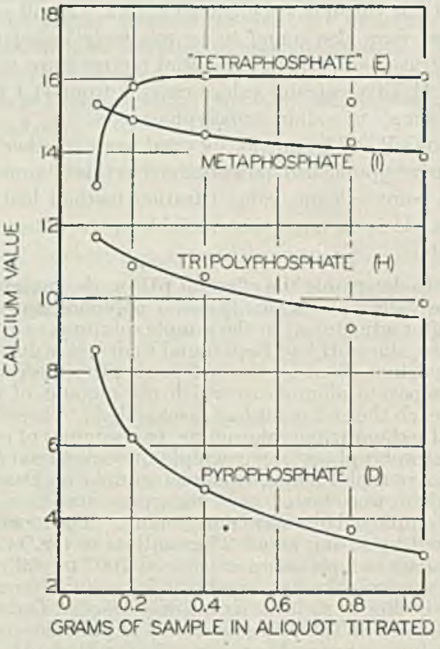

**Figure 2. Effect of Sample Size (Concentration) on Calcium Values of Several Polyphosphates**

During the development of the present method for calcium value, a few determinations were made using a calcium chloride solution that had been adjusted to pH 10.0 in an attempt to eliminate the difference between "initial" and "end point" pH values. However, owing to the difficulty of maintaining the unbuffered reagent at pH 10.0 and because the pH was not constant during titration in any case, it was decided to eliminate this feature in the interest of simplicity.

Effect of Sample Size. Andress and Wüst (*1*) have shown that the calcium value of sodium tripolyphosphate decreases with increasing concentration in the range 3 to 35 grams per liter, the greatest decrease occurring at about 10 to 15 grams per liter. Chwala and Martina (*2*) observed the same general effect for various polyphosphates. The effect of varying sample size on the present method was determined for commercial sodium tripolyphosphate, sodium "tetraphosphate", tetrasodium pyrophosphate, and laboratory prepared glassy sodium metaphosphate. The pyrophosphate and one of the "tetraphosphate" samples used in the pH study were employed. A different laboratory batch of glassy metaphosphate and a different sample of commercial tripolyphosphate were used. The calcium values obtained for different sample sizes of these materials by the present method are shown in Table II and plotted against sample size in Figure 2. Since the method specifies a volume of about 55 ml. at the start of the titration and since about 15 to 20 ml. of titrant may be added, the final concentration using a 0.4-gram sample corresponds to about 5.5 grams per liter in the method as written.

Figure 2 confirms the general effect of concentration on calcium value noted by other investigators. The curves are fairly flat at a sample size of 0.4 gram, indicating that sample size should not affect the precision of the method greatly. The steepest curve in this concentration range is found for tetrasodium pyrophosphate; a sample size difference of 0.1 gram in this case would give a difference in calcium value of about 0.5.

Precision. The precision of the present method for calcium value has been found to vary somewhat, depending on the type of sample being examined. In order to test precision, ten determinations were made by a single experienced analyst on a sample of sodium tripolyphosphate. Treatment of the data (shown in Table III) as outlined by Moran (*4*) gives an $LU_1$ of ±0.4 against an average calcium value of 10.4. $LU_1$ is the symbol for the limit of uncertainty of the method under the best conditions. For data which are statistically normal, this $LU_1$ implies that a single determination has 997 chances out of 1000 of being within 0.4 unit of the average calcium value.

On many samples, duplicate determinations check somewhat better than might be indicated by the above precision. For instance, in determining the calcium values of various polyphosphate mixtures, eight sets of duplicate determinations gave an average difference between duplicates of only 0.05. In other cases, where the end point is not so well defined, duplicate determinations may vary by as much as 0.4. In general, the method has been found capable of precise results on most of the materials tested.

## CONCLUSIONS

The calcium-sequestering ability of sodium polyphosphate water conditioners can be determined with good precision by titration with standard calcium chloride solution, using a filter photometer and graphical computation to ascertain the point at which a precipitate first begins to form. Results should be expressed as grams of calcium sequestered by 100 grams of sample. Increasing concentration decreases calcium value, but small differences in sample size do not greatly influence the precision of the method. Calcium values of different polyphosphates are affected in a marked and variable manner by the pH level to which the sample solution is adjusted before titrating. The precision of the method, in terms of limit of uncertainty under the best conditions, was found to be ±0.4 for sodium tripolyphosphate having a calcium value of 10.4. Precision varies, depending on the type of sample and conditions of determination.

Since the calcium value of phosphate water conditioners varies

**Table II. Effect of Sample Size on Calcium Values of Various Polyphosphates**

| Sample | Calcium Value | | | | |
|---|---|---|---|---|---|
| Sample size, grams | 0.100 | 0.200 | 0.400 | 0.800 | 1.000 |
| Approximate concentration, grams per liter | 1.4 | 2.8 | 5.5 | 11.0 | 13.8 |
| Sodium tripolyphosphate sample H | 11.7 | 10.9 | 10.6 | 9.2 | 9.9 |
| Tetrasodium pyrophosphate, sample D | 8.6 | 6.2 | 4.8 | 3.7 | 3.0 |
| Sodium "tetraphosphate", sample E | 13.1 | 15.8 | 16.1 | 15.4 | 16.1 |
| Sodium metaphosphate glass, sample I | 15.3 | 14.9 | 14.5 | 14.3 | 13.9 |

**Table III. Precision of Method for Calcium Value**

| Calcium Value | Deviation | $(\text{Deviation})^2$ |
|---|---|---|
| 10.27 | 0.17 | 0.0289 |
| 10.32 | 0.12 | 0.0144 |
| 10.39 | 0.05 | 0.0025 |
| 10.32 | 0.10 | 0.0100 |
| 10.59 | 0.15 | 0.0225 |
| 10.49 | 0.05 | 0.0025 |
| 10.49 | 0.05 | 0.0025 |
| 10.52 | 0.08 | 0.0064 |
| 10.61 | 0.17 | 0.0289 |
| 10.39 | 0.05 | 0.0025 |
| Average | | 10.44 |
| Average deviation | | 0.10 |
| Standard deviation, $\sigma$ | | 0.11 |
| $LU_1$, $3\sigma/0.923$ | | ±0.36 |
| Range, 10.61–10.27 | | 0.34 |

with such factors as pH and concentration, the conditions of the determination must be rigidly standardized, and any departure from these conditions should be noted in expressing results. The calcium value obtained may have little connection with water-softening power under conditions of use other than those of the method. Where performance under conditions of actual use is required, the method may be modified, but only with the understanding that the resulting data cannot be compared directly with data obtained by using the method as written.

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# Radioactive Studies

## Analytical Procedure for Measurement of Radioactive Arsenic of 90-Day Half-Life[1]

F. C. HENRIQUES, Jr.[2], and CHARLES MARGNETTI[3]
Harvard University Chemical Laboratories and Medical School, Cambridge and Boston, Mass.

**A procedure for the quantitative radioactive analysis of arsenic of 90-day half-life depends upon the isolation of arsenic metal by reduction with hypophosphite, collection on a Selas filter plate, and measurement of the activity inside the chamber of a Lauritzen electroscope. The utilization of 90-day arsenic rather than the 16-day isotope extends considerably the duration of experimentation following cyclotron bombardment.**

DURING the course of investigations utilizing 16-day $As^{71}$ as a tracer, it was found that an appreciable amount of radioactivity due to 90-day arsenic is also present. This long-lived arsenic (*2*) is known to be either $As^{72}$ or $As^{73}$. It disintegrates into $Ge^{72,73}$ by the capture of a K-shell electron and the emission of a gamma-ray of about 0.05 Mev. Through photon absorption, this gamma-ray may result in the ejection of either a K- or L-shell electron surrounding the germanium nucleus. Such electrons are known as internal conversion electrons and in the case of 90-day arsenic the process is highly efficient. A special procedure has been worked out for the detection of these low energy (approximately 0.05 Mev.) electrons.

Both the 16- and 90-day arsenic isotopes are formed by the deuteron bombardment of germanium. On the basis of a 10-hour bombardment by the M.I.T. cyclotron of Ge and the addition of 50 mg. of carrier $As^{75}$ for separation purposes, it was possible with $As^{74}$ to detect 0.005 microgram and make quantitative radioactive analyses to a 0.1 microgram of arsenic for a period of only 10 to 12 weeks. The procedure described for the detection of the 90-day isotope produced by the same bombardment extended these analyses to a period of about one year.

### DETECTION APPARATUS

Although the usual thin-walled cylindrical Geiger counter (*1*) or the thin mica window helium-filled bell-type counter (*5*) is satisfactory for detection of the 16-day isotope, it is not satisfactory for detection of the internal conversion electron emitted by the 90-day isotope. This is due to the large fraction of these soft electrons that are absorbed by either the window or wall of the above counters. Since it has not as yet proved feasible to make routine radioactive analysis to better than 15% accuracy by placing samples inside counters, recourse is taken to the use of the modified Lauritzen electroscope (*4*).

As in the case of $S^{35}$, the arsenic samples are placed inside the electroscope chamber. In view of the low energy, nearly all the ionization resulting from inelastic collision of the electron with air molecules takes place in the chamber. This is the reason for the much greater sensitivity of the modified electroscope over the thin mica window counters in this particular case. The situation is reversed with the 16-day arsenic isotope, because of the high energy of the emitted particles. Thus, during the early period following the cyclotron bombardment, the concentration of the 16-day isotope is relatively high and the Geiger counter has a greater sensitivity as compared to background than the modified electroscope. This is of little import, however, since during this interval the specific radioactivity is also high.

### ANALYTICAL METHOD

The radioactive determination is made on finely divided arsenic metal. Arsenic in either the +3 or +5 state of oxidation is quantitatively reduced to arsenic metal by alkali hypophosphites in strong hydrochloric acid solutions. The procedure on a micro scale was developed by Polyakov and Kolokolov (*3*). One procedure for obtaining the arsenic initially in the form of arsenate, which is well suited for biological investigations, is to oxidize the sample containing the arsenic by the Carius method. Sufficient nonradioactive (carrier) arsenic is added in the form of $H_2AsO_4^-$ to produce 4 mg. as arsenic metal.

The Carius solution containing 4.0 mg. of arsenic as $H_2AsO_4^-$ is transferred to a 25-cc. beaker and evaporated to dryness to remove the nitric acid. The residue is taken up in 3 cc. of water and 0.1 to 0.2 gram of sodium hypophosphite is added, followed by about 10 to 15 cc. of 7 *N* hydrochloric acid. The solution is then heated on a hot plate until the clearing of the supernatant layer (30 to 45 minutes) signifies that the precipitation is complete.

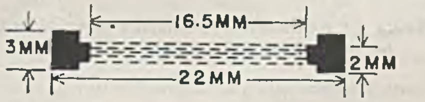

Figure 1. Cross Sections of Filter Crucibles Prepared from Selas Crucible 2001

Effective filtering area, 2.15 sq. cm.

The arsenic precipitate is collected in a manner similar to that used for benzidine sulfate in the radioactive sulfur work (*4*), except that a Selas filter disk (Selas Co., Philadelphia, Pa.) is substituted for the filter paper. The finely divided state of the arsenic metal necessitates the use of these filter disks, which are prepared by cutting off the top of a Selas filter crucible No. 2001. After the filtering areas are immersed in paraffin for protective purposes, the disks are ground to identical size as indicated in Figure 1. The paraffin is then removed with hot ligroin.

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[1] Second article on subject, "Radioactive Studies". The first appeared on page 349, June 15 issue. Succeeding papers appear on pages 417 and 420. The fifth paper will appear in a later issue.

[2] Present address, Radiation Laboratory, University of California, Berkeley, Calif.

[3] Present address, Massachusetts Department of Public Safety, Boston, Mass.

**Table I. Radioactivity Measurements as a Function of 90-Day Arsenic Content of $H_2AsO_4^-$ Using Modified Lauritzen Electroscope**

(Dilution experiments. Concentration of least active sample is taken as unity. Radioactivity measurements are expressed as ratio of net activity to average background.)

| Radioactive Arsenic Concentration, $C_i$ | Radioactive Measurements Observed, $R_i$ | Radioactive Measurements Expected[a], $R_i$ | Average Deviation, % |
|---|---|---|---|
| 250 | 181<br>182 | 181 | 0.3 |
| | Av. 182 | | |
| 200 | 145<br>145 | 145 | 0.0 |
| | Av. 145 | | |
| 125 | 90.2<br>90.6 | 90.6 | 0.2 |
| | Av. 90.4 | | |
| 100 | 73.8<br>72.5 | 72.5 | 0.9 |
| | Av. 73.2 | | |
| 50 | 35.0<br>36.8 | 36.3 | 1.1 |
| | Av. 35.9 | | |
| 25 | 17.5<br>18.2 | 18.1 | 1.4 |
| | Av. 17.9 | | |
| 20 | 14.6<br>15.1 | 14.5 | 2.4 |
| | Av. 14.9 | | |
| 12.5 | 9.27<br>9.14 | 9.06 | 1.6 |
| | Av. 9.21 | | |
| 10 | 7.28<br>7.12 | 7.25 | 0.7 |
| | Av. 7.20 | | |
| 5 | 3.43<br>3.59 | 3.63 | 3.3 |
| | Av. 3.51 | | |
| 2.5 | 1.78<br>1.65 | 1.81 | 5.3 |
| | Av. 1.72 | | |
| 2 | 1.49<br>1.56 | 1.45 | 5.2 |
| | Av. 1.53 | | |
| 1 | 0.70<br>0.64 | 0.73 | 8.3 |
| | Av. 0.67 | | |

[a] $R_i = \frac{C_i\Sigma(R_i/C_i)\log C_i}{\Sigma \log C_i}$. This equation expresses the fact that the accuracy of measurement increases somewhat with concentration of radioactivity.

After the arsenic metal is collected on these disks, it is well washed with a hot reducing solution of 1% sodium hypophosphite in 7 *N* hydrochloric acid followed by absolute ethyl alcohol. Until ready for measurement these disks are kept in a vacuum desiccator.

The radioactive determination is now made by placing the disk containing the arsenic precipitate inside the electroscope chamber by means of the sliding bar device previously described (*4*). After the sample is measured, the arsenic is removed by the reverse flow of hot nitric acid. Alkaline oxidizing agents are to be avoided because of their injurious action on the porous plate.

Since the very low energies of the emitted electrons result in considerable self-absorption, uniformity of the thickness of precipitate over the filter disk area is especially important in quantitative work. Before preparing the disks, the Selas crucibles are selected with this in mind; visual observation of uniformity of precipitate suffices and about 70% of these crucibles pass inspection.

Although the hypophosphite reduction is quantitative (*3*), it cannot be used for gravimetric analysis, since arsenic metal forms an oxide film in moist air. The resulting increase in weight is consistently less than 2% if the procedure described above is strictly followed. This variation in the weight results in a maximum uncertainty of only 0.4% in the radioactive measurements of arsenic precipitates weighing about 4.0 mg. or 1.86 mg. per sq. cm. (Computed from Equation 2.)

### ACCURACY OF RADIOACTIVE ANALYTICAL PROCEDURE AS MEASURED BY LAURITZEN ELECTROSCOPE

The accuracy of the analytical procedure was evaluated by the progressive dilution of the radioactivity, through the addition of known amounts of inactive arsenate ion to an arsenate solution containing 90-day arsenic. Each arsenate solution that was subjected to analysis contained 0.0552 millimole of arsenic (4.0 mg. as arsenic metal). As in the case of $S^{35}$ (*4*), the data are presented in the terms of the following ratio:

$$\frac{(d/t)_s - (d/t)_b}{(d/t)_b} \tag{1}$$

where *d* is the distance traversed by the electroscope fiber in time *t*, *s* indicates the radioactive sample, *b* denotes background, and $(\overline{d/t})_b$ is the average background rate of fiber discharge. The usual distance traversed by the electroscope fiber during measurements is 10 small divisions.

Duplicate experimental determinations are presented in Table I. The concentration of the 90-day arsenic present in the least active sample is arbitrarily taken as unity.

The data indicate that radioactive analysis to 2% can be made on all arsenic samples containing activity greater than about 5 times background by the procedure given above.

### SELF-ABSORPTION OF ELECTRONS BY ARSENIC METAL PRECIPITATE

Unfortunately it is not possible to prepare, as was done for radioactive sulfur (*4*), a correction table for self-absorption of radioarsenic that is nonvarient in time. This is due to the time-dependent ratio of 16-day arsenic to 90-day arsenic. This is not a serious limitation, since in most chemical and biological experiments involving the use of radioarsenic, the weight of the metal precipitate can be predetermined by the addition of carrier in the form of nonradioactive arsenate. If the weight of arsenic metal precipitate cannot be predetermined, it is necessary to have on hand standards of different known weights of precipitate containing equal radioactivity; this activity must of course result from the same bombardment as the radioarsenic being analyzed.

It is found that 4 to 10 mg. (1.86 to 4.65 mg. per sq. cm.) of arsenic give a uniform distribution of metal precipitate on Selas plate. This weight should be kept minimal in view of the high self-absorption.

After about 100 days following cyclotron bombardment, the effective concentration of 16-day radioarsenic is small as compared to 90-day arsenic. Thus from this time on, it would be possible to use a weight correction table for self-absorption. Data for this table have been obtained but are not given here in detail. To within 4%, these data follow the following equation (*4*):

$$I = \frac{K}{\alpha d}\,(1 - e^{-\alpha d}) \tag{2}$$

*I* is the measured radioactivity, *K* is a constant, *d* is the thickness of precipitate in mg. per sq. cm., and $\alpha$ is an exponential absorption coefficient of numerical value equal to 0.79 sq. cm. per mg. of arsenic metal precipitate. Self-absorption is more than 80% complete for a precipitate heavier than 5 mg. per sq. cm. and is equal to 22% for a precipitate of about 2 mg. per sq. cm.

### ACKNOWLEDGMENT

The authors are indebted to J. W. Irvine of the Massachusetts Institute of Technology for suggesting the use of the Selas filtering disk.

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# Analytical Method for Determination of Long-Life Carbon $C^{14}$

F. C. HENRIQUES, JR.[1], AND CHARLES MARGNETTI[2]
Harvard University Chemical Laboratories and Medical School, Cambridge and Boston, Mass.

**A detailed quantitative procedure for the measurement of radioactivity due to long-life $C^{14}$ incorporated into organic compounds is described and evaluated. The method is based on the insertion of carbon dioxide gas into a quartz ionization chamber attached to a Lauritzen electroscope. The assemblage of this detection apparatus is described in detail. The method is especially suitable to biological work, since it will measure $3 \times 10^{-8}$ microcurie of $C^{14}$ diluted with as much as 20 millimoles of ordinary carbon.**

RADIOACTIVE carbon $C^{14}$ of half-life greater than 1000 years is certainly the most valuable of all the radioactive elements for general tracer work. It is usually prepared by the neutron bombardment of the $N^{14}$ present in ammonium nitrate. Radioactive carbon is present in the form of carbon monoxide and carbon dioxide and is ultimately collected as barium carbonate (*8*). Because of the low yield of the $N^{14}$ (*n*, *p*) $C^{14}$ reaction, the production of appreciable quantities of $C^{14}$ of high specific activity by cyclotron bombardment is very costly. However, the utilization of the neutron sources which are now available through the construction of uranium piles will make $C^{14}$ more plentiful.

Ammonium nitrate, subjected to neutron bombardment by the M.I.T. cyclotron staff, was the authors' source of long-life carbon.

Long-life carbon disintegrates into $N^{14}$ by the emission of a beta-particle of maximum energy of about 0.14 Mev. (*8*). Ruben and Kamen (*8*) have outlined a procedure for the radioactive analysis of $C^{14}$, which depends upon the isolation and precipitation of the activity in the form of a carbonate precipitate. The precipitate in milligram quantities is then placed inside a screen-wall counter and a certain fraction of the number of disintegrations is recorded. This procedure is subject to two serious limitations: (1) Geiger counters which are repeatedly subjected to the operations necessary for the insertion of a sample inside the counter are erratic; hence accuracy better than 10 to 15% is not to be expected. (2) Because of the low energy of the emitted particles, self-absorption is an appreciable factor, especially in biological tracer work, where the weight of a carbonate precipitate resulting from the oxidation of 1 gram of tissue is usually in grams. In view of the expense involved in the production of $C^{14}$ of high millicurie strength, this factor must be minimized.

The procedure described was developed with both detection sensitivity and over-all accuracy in mind.

## DETECTION APPARATUS

The ideal solution to the problem would be the insertion of carbon dioxide containing $C^{14}$ inside a Geiger counter; under these conditions at least 90% of the radioactive disintegrations would be counted. One would have, then, a routine analytical method of optimum sensitivity which is applicable to all long-life radiocarbon compounds. Unfortunately this gas is not suitable for proper Geiger counter operation (no measurable plateau and erratic counting rates), and in view of the importance of $C^{14}$ detection, considerable research has been directed toward the solution of this problem.

Recently it has been found (*6*) that the addition of certain contaminating vapors to carbon dioxide markedly improves these counter characteristics, but, as yet, this method cannot be adopted for accurate routine analyses.

It is also possible to introduce the gaseous carbon dioxide into an ionization chamber and to measure the ionization produced by the collisions of the emitted beta-particles with carbon dioxide molecules by means of an auxiliary apparatus. It was decided to measure this ionization with a Lauritzen electroscope (*5*). In view of its sensitivity, simplicity of design, ruggedness, and accu-

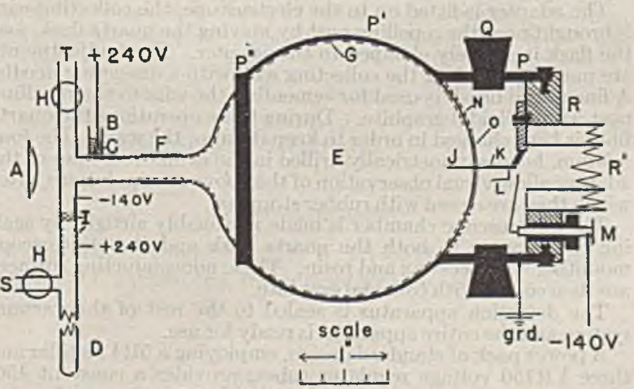

Figure 1. Cross Section of Ionization Chamber, Lauritzen Electroscope Detection Apparatus

*A.* Light source (115-volt 6-watt) for illumination of quartz fiber and scale
*B.* Mercury well
*C.* Tungsten wire providing electrical connection to silvered surface
*D.* Condensing tube
*E.* Quartz flask (ionization chamber)
*F.* Pyrex-quartz graded seal
*G.* Silvered portion of flask
*H.* High-vacuum pressure stopcocks
*I.* Ion trap (very coarse silvered fritted disk and silvered glass tube)
*J.* Ion collecting wire (3-mil tungsten)
*K.* Fiber-repelling post
*L.* Gold-plated quartz fiber
*M.* Electroscope charge button
*N.* Portion of flask coated with colloidal graphite (Aquadag)
*O.* Thin coat of ceresin wax
*P.* Brass adapter
*P'.* Brass straps, 0.25 inch (4 in all)
*P''.* Brass collar provided with screw for cinching straps
*Q.* Rubber-stoppered hole 0.375 inch, in brass adapter (4 in all)
*R.* Lauritzen electroscope frame
*R'.* Electroscope tube containing objective, scale, and eyepiece
*S.* To vacuum system
*T.* To mercury vapor pump

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[1] Present address, Radiation Laboratory, University of California, Berkeley, Calif.

[2] Present address, Massachusetts Department of Public Safety, Boston, Mass.

racy, this electroscope is believed to be better suited for routine analytical work than (*9*) either a sensitive electrometer or a vacuum tube electrometer circuit.

The combination of the ionization chamber and Lauritzen electroscope is shown in Figure 1.

Assembling of Detection Apparatus. The neck of a 200-cc. quartz flask is drawn down and sealed to a quartz-Pyrex graded seal. An L-shaped tungsten lead wire, *C*, is tacked for a distance of 2 mm. along the inside wall of the Pyrex tube and then is sealed in. A minute hole (about 0.13 mm.), for subsequent introduction of the collecting wire, is made in the bottom of the flask, which is then sealed with a thin film of quartz.

After the inside surface is scrupulously cleaned, the interior spherical segment (about 3 cm. in diameter) which is to remain unsilvered is coated with vinyl acetate (Vinylite Resin AYAF, Carbide and Carbon Chemicals Corp., New York, N. Y.). This is done by clamping the flask in a vertical position and then introducing a 3% solution of vinylite in acetone to the requisite depth by means of a long capillary funnel. The excess vinylite solution is removed via the capillary funnel by suction. The remaining acetone is allowed to dry; this leaves a thin protective coating of vinylite over the small spherical segment.

The flask is evacuated with a water pump, and Brashear's silvering solution (*9*) is introduced by means of a stopcock. Removal of the silvering solution and subsequent rinsings are facilitated by use of the water pump. After the silvered surface is well washed with distilled water, the vinylite is dissolved with reagent acetone. Anhydrous reagent ether is used for final rinsing. The silvered surface is now tested for electrical continuity.

After the remainder of the glass apparatus shown in Figure 1 is attached, the outside lower half of the flask is well cleaned and dried. The thin quartz film sealing the hole in the bottom of the flask is pierced by means of a 5-mil tungsten wire. A 3-mil (0.076-mm.) tungsten wire is now introduced into the hole until it projects 8 mm. inside the flask. This ion-collecting wire is sealed in with picein wax.

The external surface of the unsilvered spherical segment is coated with a thin layer of ceresin wax. The remainder of the external surface of the flask is coated with colloidal graphite (Aquadag).

After the external portion of the collecting wire is cut to 3-mm. length (total length 1.3 cm.) the brass adapter is attached to the flask. This adapter is constructed so that when the entire apparatus is assembled the bottom of the flask is 2 mm. from the repelling post of the Lauritzen electroscope.

The adapter is fitted on to the electroscope, the collecting wire is brought near the repelling post by moving the quartz flask, and the flask is securely clamped to the adapter. Final adjustments are made by bending the collecting wire with a dissecting needle. A fine pencil brush is used for cementing the wire to the repelling post with colloidal graphite. During these operations the quartz fiber is kept charged in order to keep it out of the way. The four 9.5-mm. holes symmetrically drilled in the cylindrical sides of the adapter allow visual observation of the above manipulations, after which they are closed with rubber stoppers.

The electroscope chamber is made reasonably airtight by sealing the adapter to both the quartz flask and the electroscope mounting with beeswax and rosin. These nonconducting surfaces are then coated with colloidal graphite.

The detection apparatus is sealed to the rest of the vacuum system and the entire apparatus is ready for use.

A power pack of standard design, employing a 5R4 rectifier and three VR150 voltage regulator tubes, provides a constant 450-volt source required for operating the detection apparatus. A 115-volt pilot light (6-watt) illuminates the quartz fiber and eyepiece scale in spite of the interposition of the auxiliary ionization chamber.

The detection apparatus operates on the following principle:

Let the electroscope mounting, the brass adapter, and the Aquadag surfaces be grounded; let the silvered surface be maintained at a positive voltage; and let the unit, consisting of the gold-plated quartz fiber, the repelling post, and the ion-collecting wire be charged to a negative potential and then be isolated. Then the ion pairs (mainly $CO_2^+$ and $e^-$), produced by the inelastic collisions of beta-particles from $C^{14}$ with gaseous carbon dioxide molecules inside the ionization chamber, are separated by the electric field resulting from the potential difference of the silvered surface and the collecting wire. The subsequent neutralization of the positive ions at the collecting wire makes the repelling post and quartz fiber less negative, and the elastic restoring force of the quartz moves the gold fiber somewhat nearer the repelling post. The rate of this motion is a measure of the amount of radioactivity present.

It is apparent that electrical leakage from the silvered and Aquadaged surfaces will also neutralize the charge on the repelling post. To prevent this the ionization chamber was made of quartz, in view of its high electrical resistance (*7*); as was to be expected (*7*), Pyrex proved to be unsatisfactory. Furthermore the ceresin wax minimized exterior surface conduction due to the absorption of water vapor on the quartz. No increase in "natural" background rate due to volume and surface electric conductivity of the quartz was detectable.

The absolute sensitivity of a Lauritzen electroscope depends upon the elastic force constant of the quartz fiber and the electrostatic capacity of the isolated unit. By connecting the collecting wire to the repelling post this capacity is increased by only about 0.1 mmf., since a wire of small diameter (0.076 mm.) and minimal length (1.3 cm.) is used. Depending somewhat upon the electroscope, the resulting reduction in sensitivity amounts to about 30%. It is suggested that electroscopes to be used for this purpose be ordered with a sensitivity of 5 to 6 divisions per minute per millicurie of radium at 1 meter.

Optimal operating conditions were ascertained by numerous preliminary tests.

With the brass adapter and Aquadaged surfaces grounded, the silvered surface inside the quartz ionization chamber is kept continuously at a potential of +240 volts. Except when measurements are being made, the collecting wire, repelling post, and fiber are held at a potential of −140 volts by means of a simple lock device attached to the electroscope charge button. These potentials are somewhat in excess of that necessary for maximum collection of ions. The continual maintenance of the above voltages is necessary because of the initial flow of polarization current or "soak in charge" into the quartz insulation; about 18 hours were required to attain complete equilibrium (*7*).

When not in use the quartz chamber is left filled with the last gas sample subjected to radioactive analysis. Under no circumstances is the chamber left evacuated more than 15 minutes. There is apparently at least a monomolecular layer of carbon dioxide that is strongly adsorbed by the quartz insulating the collecting wire from the silvered surface, and the orientation of this layer in the electrical field alters slightly the capacity of the measuring unit. This phenomenon is readily recognizable, since longer periods of evacuation will result in a discrete jump of about 3 small divisions of the electroscope fiber to a new position of equilibrium. Surface adsorption is indicated because this phenomenon does not take place with either dry air or hydrogen.

The negatively charged silvered fritted disk, through which the gas enters the ionization chamber, neutralizes the slow-moving polymeric molecular ions which are always present in carbon dioxide owing to cosmic ray bombardment. The presence of these ions in greater than nonequilibrium proportions results in an appreciably increased discharge rate of the electroscope fiber for all samples with activity the order of the background for a period of about 2 hours. The above ion trap enables immediate measurement of all samples. This ion trap proved to be as efficient as those of more usual design (*2*).

The ionization chamber is always filled with about 20 millimoles of carbon dioxide gas; since its volume is 219 cc., this is equivalent to about 2 atmospheres' pressure at room temperature. Under these conditions, the carbon beta-particles encounter sufficient inelastic collisions to produce 97% of the total ionization possible. Further increase in pressure to 3 atmospheres increases the efficiency to nearly 100%.

Sensitivity. Accurate radioactive analysis for $C^{14}$ can be made by utilizing the information given above. Through the cooperation of W. W. Miller of the Massachusetts Institute of Technology, the number of counts per minute (±10%) were determined on 10-cm. mercury pressure of carbon dioxide containing $C^{14}$ within a Geiger counter of 35 cc. detection volume. These data were then compared with that obtained with an identical sample inside the author's detection apparatus. For purposes of comparison, the relative sensitivity will be defined as the dimensionless ratio of measured radioactivity due to the sample to the measured activity due to background radiation; then, these data show that, even if it were possible to operate a 200-cc. Geiger counter

### Table I. Radioactive Measurements as a Function of $C^{14}$ Content of Carbon Dioxide in the Ionization Chamber–Lauritzen Electroscope Detection Apparatus

(Dilution experiments. The $C^{14}$ concentration of the least active sample is taken as unity. Radioactive measurements are expressed as the ratio of the net activity to average background.)

| Relative $C^{14}$ Concentration, $C_i$ | Radioactive Measurements Observed, $R_i$ | Radioactive Measurements Expected[a], $R_i$ | Average Deviation, % |
|---|---|---|---|
| 128 | 83.4 | | |
| | 83.6 | | |
| | Av. 83.5 | 83.2 | 0.4 |
| 64 | 41.8 | | |
| | 41.5 | | |
| | Av. 41.7 | 41.6 | 0.2 |
| 32 | 20.2 | | |
| | 20.7 | | |
| | Av. 20.4 | 20.8 | 1.9 |
| 16 | 10.5 | | |
| | 10.3 | | |
| | Av. 10.4 | 10.4 | 0.0 |
| 8 | 5.20 | | |
| | 5.27 | | |
| | Av. 5.23 | 5.20 | 0.6 |
| 4 | 2.61 | | |
| | 2.66 | | |
| | Av. 2.64 | 2.60 | 1.5 |
| 2 | 1.31 | | |
| | 1.26 | | |
| | Av. 1.29 | 1.30 | 0.8 |
| 1 | 0.68 | | |
| | 0.65 | | |
| | Av. 0.67 | 0.65 | 3.1 |

[a] $R_i = C_i \frac{\Sigma (R_i/C_i) \log C_i}{\Sigma \log C_i}$. This equation expresses the fact that the accuracy of measurement increases somewhat with concentration of radioactivity.

at 2 atmospheres carbon dioxide pressure, it would possess a relative sensitivity no greater than the authors' detection apparatus. Thus an ionization chamber attached to a Lauritzen electroscope is sufficiently sensitive for all investigations utilizing $C^{14}$ as a tracer, so long as there is adequate gas pressure to allow nearly maximum ionization within the chamber.

It is capable of detecting the presence of about $3 \times 10^{-5}$ microcurie of $C^{14}$ in 20 millimoles of carbon dioxide (4 grams of barium carbonate). Surrounding the ionization chamber with a lead cylinder would decrease the minimum detectable quantities of $C^{14}$ to about $2 \times 10^{-5}$ microcurie. This method is of particular advantage in biological work where 20 millimoles of carbon are normally present in approximately 2 to 4 grams of tissue.

With the electroscope used, the discharge rate of the fiber when the chamber is filled with 20 millimoles of nonradioactive carbon dioxide (background) is numerically equal to about 4.3 small divisions per hour. On the basis of 5 division determinations (70 minutes), the maximum variation in background was usually less than 3% and seldom greater than 5%. This variation is somewhat less than that of the Lauritzen electroscope used previously (*4*), since the number of molecules inside the ionization chamber, and thus the measured ionization resulting from each ray, does not depend upon the room temperature and barometric pressure; probably the number of alpha-particles emitted per square centimeter of a silvered quartz flask is less than that of brass [~6 $\alpha$'s per sq. cm. per hour, (*1*)]; and unlike air (30 $\alpha$'s per hour per 100 cc.), the number of alpha-particles emitted from pure carbon dioxide is not measurable (*1*).

## ANALYTICAL PROCEDURE

All organic compounds containing $C^{14}$ are oxidized to carbon dioxide by the standard combustion procedure. The issuing gases are dried with phosphorus pentoxide, and the carbon dioxide is condensed in a trap surrounded with liquid nitrogen. By means of a ground joint, this trap is then joined to an all-glass vacuum system similar in design to that reported in (*3*). The carbon dioxide is transferred to any desired part of the apparatus by means of vacuum distillation, employing liquid nitrogen as the condensing agent. The number of millimoles of gas produced is determined in a calibrated volume connected to a mercury manometer.

This carbon dioxide is transferred to a mixing bulb and the amount of nonradioactive (carrier) gas required to bring the total amount to 20 millimoles is added. The previous sample in the quartz ionization chamber is either transferred to a storage bulb or pumped away. The chamber is then completely evacuated for 5 minutes by means of a mercury diffusion pump. The carbon dioxide is condensed into tube *D* (Figure 1) and allowed to evaporate slowly through the ion trap into the ionization chamber. The electroscope charge button is now released and the discharge rate of the fiber is determined. Samples producing a sufficiently high discharge rate (greater than one small division per minute) are measured in triplicate; others are usually determined in duplicate. When the apparatus is in routine use, a standard sample, which is kept in a storage bulb attached to the vacuum system, is measured at the beginning and the end of the day; background is determined during the noon hour.

The accuracy of this method for the measurement of relative amounts of $C^{14}$ was determined by progressive dilutions with inert carbon dioxide of a standard sample of carbon dioxide containing some $C^{14}$. Depending upon the activity present, each radioactive determination was made either in triplicate or duplicate. Two independent series of dilutions were measured. As in previous investigations (*4*), the data are presented in terms of the following equation:

$$R_i = \frac{(d/t)_s - (d/t)_b}{(\overline{d/t})_b} \tag{1}$$

where $d$ is the distance traversed by the electroscope fiber in time $t$, $s$ indicates the sample, $b$ denotes background, and $(\overline{d/t})_b$ is the average background rate of fiber discharge. The usual distance traversed by the fiber during measurements was 10 small divisions, although no samples were measured for periods longer than about 1 hour.

The experimental determinations for two independent dilution series are given in Table I. The concentration of the least active sample (approximately $5 \times 10^{-5}$ microcurie of $C^{14}$) has been arbitrarily taken as unity.

The data indicate that radioactive analysis to 2% can be made on all carbon samples containing, per 20 millimoles of carbon, activity at least equal to the background.

## ACKNOWLEDGMENT

The authors are indebted to J. W. Irvine of the Massachusetts Institute of Technology for suggesting the use of a silvered fritted disk as an ion trap.

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# Analytical Procedure for Measurement of Radioactive Hydrogen (Tritium)

F. C. HENRIQUES, Jr.[1], AND CHARLES MARGNETTI[2]
Harvard University Chemical Laboratories and Medical School, Cambridge and Boston, Mass.

**A quantitative procedure for the measurement of radioactivity due to $H^3$ depends upon insertion of hydrogen gas in a quartz ionization chamber attached to a Lauritzen electroscope. Radioactive analysis of organic compounds containing $H^3$ is based on combustion to water and the quantitative conversion of this water to hydrogen. A procedure for obtaining tritium water samples of high specific activity is described.**

TRITIUM (radioactive hydrogen) is in certain respects an ideal tracer element. It has a half-life of about 30 years (*7*) and samples of high millicurie strength are easily obtainable. The principal difficulty is in detection. Tritium ($H^3$) disintegrates into $He^3$ by the emission of a beta-particle of maximum energy (*6*) of about 0.015 Mev. This energy is so low that tritium must be detected in the gaseous phase.

Semiquantitative investigations using tritium as a tracer have been made principally by Ruben and co-workers (*8*), who analyzed for radioactivity by introducing hydrogen gas containing $H^3$ into a Geiger counter. Under the best conditions, radioactive analyses by this procedure are limited to about 10 to 15% accuracy because hydrogen is not an ideal counting gas (*1*); and because of the extreme importance of the nature of the cathode surface and traces of contaminants—e.g., mercury vapor—in the mechanism of Geiger counter discharge. It has been the authors' experience that the continual evacuation and refilling of counters are not practical as a routine procedure.

Black and Taylor (*3*) have obtained reproducible counting by introducing hydrogen at low pressure together with three contaminants into a counter. Unfortunately, their method is not adaptable to routine analysis.

Since certain planned investigations using tritium as a tracer necessitated about 2% accuracy, it was decided to employ a quartz ionization chamber attached to the Lauritzen electroscope as a means of analyzing the relative tritium content of hydrogen gas. This detection apparatus has been used successfully for the analysis of long-life carbon as carbon dioxide (*4*).

This paper evaluates this procedure as a general method for the radioactive analysis of compounds containing tritium as a tracer, and describes briefly the method of obtaining tritium samples of high specific activity.

### PREPARATION OF TRITIUM SAMPLES OF HIGH SPECIFIC ACTIVITY

During the production of neutrons by the interposition of a water-cooled beryllium target in the deuteron cyclotron beam, two nuclear side reactions (*2, 7*) take place which lead to the formation of radioactive hydrogen, $H^3$ (tritium, T). These reactions, the first of which gives the greater yield of $H^3$, are:

$$Be^9 + H^2 = H^3 + 2He^4(Be^8) \qquad (1)$$

$$H^2 + H^2 = H^3 + H^1 \qquad (2)$$

A significant fraction of this tritium remains trapped inside the beryllium target, probably as TD gas. The tritium is removed by placing the target in a quartz tube attached to a vacuum apparatus. The tube is evacuated, a predetermined quantity of "carrier" hydrogen is introduced, and the tube is then heated to red heat for about 15 minutes. The hydrogen is now oxidized to water by allowing the gas to come in contact with hot (300° C.) cupric oxide. The water is condensed out into a trap chilled with liquid nitrogen. At the completion of this reaction the degree of vacuum will be the same as before the introduction of the hydrogen, and thus a spark discharge serves as an indicator.

At least 99% of the tritium initially present in the target forms tritiated water by the above process. Both water and hydrogen are the most useful general starting materials for the synthesis of compounds containing tritium. In view of the ease of storage, water was chosen as the end product of the above process, especially since it is a simple matter to convert water quantitatively to hydrogen.

Three samples containing tritium have been prepared. In each case the amount of carrier hydrogen added was sufficient to form 2 millimoles (36 mg.) of water. Two of these preparations were made from beryllium targets obtained through the cooperation of J. G. Hamilton of the Radiation Laboratory, Berkeley, Calif. The authors are indebted to H. W. Fullbright of Washington University, St. Louis, for the beryllium scrapings of numerous targets employed in the preparation of the third sample. As data on the cyclotron bombardment times are not available, the millicurie strength of the water samples cannot be used to compute yield data.

### DETECTION APPARATUS

All radioactive analyses are made on hydrogen gas containing tritium inside a quartz-ionization chamber attached to the Lauritzen electroscope. This apparatus has been used successfully for the detection of long-life carbon as carbon dioxide (*4*). The substitution of $H^3$ for $C^{14}$ necessitated certain minor modifications.

Because of the low molecular weight of hydrogen, the ion trap is not necessary.

The chamber is filled with 10 millimoles of hydrogen, which is equivalent to a pressure of about 1 atmosphere. This quantity of gas is sufficient to ensure the production of all the ionization (mainly $H_2^+$ and $e^-$) which can result from the inelastic collisions of tritium beta-particles with hydrogen molecules.

The potentials of the silvered surface and the unit consisting of the collecting wire, repelling post, and quartz fiber are charged to

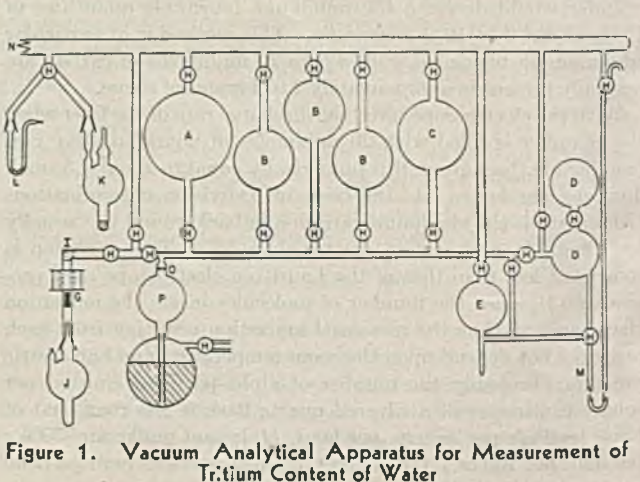

Figure 1. Vacuum Analytical Apparatus for Measurement of Tritium Content of Water

| | |
|---|---|
| *A.* | $H_2$ storage bulb (5 liters) |
| *B.* | Storage bulbs (500 cc.) |
| *C.* | Standard sample storage bulb (1 liter) |
| *D.* | Mixing chamber |
| *E.* | Ionization chamber attached to electroscope |
| *G.* | Induction coil and hammer |
| *H.* | Vacuum stopcock |
| *I.* | Glass wool plug |
| *J.* | Reaction flask in position to break seal |
| *K.* | Reaction flask with Mg-Hg amalgam |
| *L.* | U-tube with water sample containing tritium |
| *M.* | Mercury manometer |
| *N.* | To mercury vapor pump |
| *O.* | Fritted disk medium porosity |
| *P.* | Toeppler pump |

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[1] Present address, Radiation Laboratory, University of California, Berkeley, Calif.

[2] Present address, Massachusetts Department of Public Safety, Boston, Mass.

+125 and −125 volts, respectively. These potentials suffice for total collection of the ions.

Owing to the low ionization efficiency of hydrogen gas, the discharge rate of the electroscope fiber is exceedingly slow when the ionization chamber contains 10 millimoles of nonradioactive hydrogen. Hence to facilitate the measurement of background and "weak" samples, a 20× eyepiece containing a glass scale with 0.0254 mm. graduations is substituted for the standard 6× eyepiece and 0.1-mm. graduated scale.

For this particular detection apparatus, the background rates are numerically equal to about 1.2 and 5 small divisions per hour, respectively, with the 0.1-mm. and 0.0254-mm. graduated scales. On the basis of 1-hour determinations, the variations in this background were identical with that obtained with carbon dioxide (*4*)—namely, a maximum variation that was usually less than 3%, and seldom greater than 5%. An intercomparison of this detection apparatus with a Geiger counter filled with hydrogen containing tritium showed that the relative sensitivity (activity/background) of the ionization chamber is about 40% of that of a counter of identical volume filled to the same pressure. Since tritium is readily obtainable with high specific activity, this reduction in relative sensitivity is trivial. The apparatus is capable of quantitative detection of about $10^{-4}$ microcurie of tritium in 10 millimoles of hydrogen.

In order to compare the dilution factors possible with tritium with respect to those of the more commonly used hydrogen tracer, deuterium, let us consider the tritium sample prepared from targets obtained from Washington University at St. Louis. This sample, as prepared, contained about 1 millicurie of tritium in 2 millimoles of hydrogen; the dilution factor of this particular sample is at least $5 \times 10^7$. This dilution is about 100-fold greater than that possible with 100% deuterium. Since tritium containing considerably more than 1 millicurie total activity could be readily prepared, this factor can still be increased significantly.

## ANALYTICAL PROCEDURE

A general method for the determination of tritium activity is based on the conversion of the hydrogen present in the sample to water by the combustion method and the reaction of this water with magnesium amalgam to form hydrogen. This hydrogen is then introduced into the ionization chamber.

The quantitative formation of water by direct combustion of an organic compound in oxygen is standard. However, instead of absorbing the water vapor, it is condensed in a weighed U-tube chilled with a dry ice–ether mixture. The weight of water formed is then determined by reweighing the U-tube. The weight of water used for the production of hydrogen is about 220 ± 20 mg.; thus if the weight of the water formed by combustion is less than 200 mg., nonradioactive (carrier) water is added dropwise while the U-tube is on the balance; if this weight is greater than 240 mg., the water is well stirred and a rough aliquot is used.

Allen and Ruben (*1*) converted water to hydrogen by reaction with magnesium at 620° C. The addition of mercury to the magnesium turnings lowers the temperature to 400° C. and a Pyrex vessel can be employed.

About 2 grams of magnesium turnings and 3 grams of mercury are introduced into a 250-cc. reaction flask (*K*, Figure 1) and are well mixed. The flask and U-tube containing the water are then attached to a 3-way stopcock by means of ground joints, as indicated in the upper left corner of Figure 1. The water is frozen with liquid nitrogen and this system is evacuated. All the water is vacuum-distilled into the reaction flask; the flask is then sealed off at the indicated constriction. Before placing the flask in an electric furnace, the contents are well shaken in order to disperse the magnesium amalgam throughout the inside surface. One hour at 400° C. suffices for complete production of hydrogen.

Storage bulb *A* contains nonradioactive hydrogen for the purpose of determining background. Storage bulb *C* contains a reference sample of tritium; during routine analysis this standard is measured daily and then toepplered back into *C*. The mixing chamber, *D*, enables the dilution of samples which are too active to measure accurately. The fritted disk, *O*, prevents spillage of the mercury in the Toeppler pump into the remainder of the vacuum system. The mercury manometer, *M*, measures the pressure of the hydrogen gas introduced into the ionization chamber, *E*. Since the volume of the ionization chamber and the manometer were calibrated, the number of millimoles introduced can be calculated.

Table I. Radioactive Measurements as a Function of Tritium Content in Benzene

(Dilution experiments. $H^3$ concentration in least active benzene sample is chosen as unity. Radioactivity measurements are expressed as ratio[a] of net activity to average background measured as hydrogen gas in ionization chamber–Lauritzen electroscope detection apparatus.)

| Relative $H^3$ Concentration, $C_i$ | Radioactive Measurements: Observed, $R_i$ | Expected[b], $R_i$ | Average Deviation, % |
|---|---|---|---|
| 259 | 474<br>479 | | |
| | Av. 476 | 472 | 0.7 |
| 65.7 | 117.4<br>120.7 | | |
| | Av. 119 | 120 | 0.8 |
| 14.6 | 26.6<br>25.8 | | |
| | Av. 26.2 | 26.5 | 1.1 |
| 3.79 | 7.06<br>6.87 | | |
| | Av. 6.97 | 6.90 | 0.9 |
| 1.00 | 1.81<br>1.88 | | |
| | Av. 1.85 | 1.82 | 1.4 |

[a] This ratio includes factor $\frac{w_1 + w_2}{w_1}$ where $w_1$ is weight of water obtained from benzene combustion and $w_2$ is weight of nonactive water added to bring total weight above 200 mg. In each case this factor was about 2 and thus ratios of activities measured as hydrogen to background are $^1/_2$ of the values given in table.

[b] $R_i = \frac{C_i \Sigma (R_i/C_i) \log C_i}{\Sigma \log C_i}$ expresses the fact that the accuracy of measurement increases somewhat with concentration of radioactivity.

The ionization chamber is always filled with 10 millimoles of hydrogen (about 70 cm.). In view of the unavoidable dead space during the toepplering of gas from the reaction flask, *J*, into the ionization chamber, *E*, at least 200 mg. (11 millimoles) of water must be used for conversion to hydrogen.

The relative amount of tritium present in the original sample analyzed is computed from the weight of water formed during the combustion process and any additional carrier water added, together with the discharge rates of the electroscope fiber when the ionization chamber is filled with the hydrogen generated from this water, the reference standard in bulb *C*, and nonradioactive hydrogen, respectively.

The threefold difference in mass between $H^1$ and $H^3$ may result in a considerable difference in reaction rates during any process involving either these atoms or the ions. In order to ensure completion of the chemical reactions in the above analytical procedure, radioactive analyses were made on radiobenzene progressively diluted with nonradioactive benzene. The radiobenzene was prepared by the nickel-catalyzed exchange between TH and the hydrogens of benzene; this method was used by Polanyi and co-workers for the partial deuteration of benzene (*5*).

In order to include in the final computations both the weight of the water produced by combustion and the weight of carrier water required to bring the total weight above 200 mg., about 160 mg. of benzene (about 6 millimoles of hydrogen) were analyzed in each case. These experiments also evaluate the quartz ionization chamber as an apparatus for the determination of relative concentrations of $H^3$.

The data are presented in terms of the following equation:

$$R_i = \frac{\frac{w_1 + w_2}{w_1} \left[ (d/t)_s - (d/t)_b \right]}{(d/t)_b} \qquad (1)$$

where $w_1$ is weight of water resulting from the benzene combustion, $w_2$ is the weight of the carrier water added; *d* is the distance traversed by the electroscope fiber in time *t*, *s* indicates sample, and *b* denotes background. The usual distance traversed by the fiber during measurements was 10 small divisions, although no samples were measured for periods longer than about one hour; at least duplicate readings were made.

The radioactive analyses of duplicate benzene samples are given in Table I. The concentration of the least active tritiated benzene sample (approximately $3 \times 10^{-4}$ microcurie of tritium) has been arbitrarily taken as unity.

The data in Table I indicate that no detectable isotope separation takes place in the analytical procedure given here. Furthermore, radioactive analysis to 2% can be made on organic compounds which contain enough tritium, per 10 millimoles of hydrogen gas, to give an activity at least equal to background.

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# Determination of Hydroperoxides in Rubber and Synthetic Polymers

H. A. LAITINEN AND J. S. NELSON
Noyes Chemical Laboratory, University of Illinois, Urbana, Ill.

**The relative amounts of hydroperoxide in natural rubber or synthetic polymers can be determined by allowing the peroxide to react with ferrous iron in benzene-methanol solution, using o-phenanthroline as a color reagent for the excess ferrous iron. The method gives results reproducible to about 20% on a given rubber solution, but sampling difficulties may cause larger variations on solid samples. The procedure as written is sensitive to 10 or 20 p.p.m. of active oxygen, calculated on the solid polymer and it can be easily made sensitive to 1 p.p.m. by increasing the sample size and compensating for its color. Evidence is presented to show that the results with any ferrous iron procedure are high and have only relative significance.**

FERROUS iron has been used as a reagent for the determination of peroxide by numerous investigators. Yule and Wilson (*12*) estimated peroxide in cracked gasoline by shaking with an acid solution of ferrous thiocyanate and back-titrating the resulting ferric salt with titanous chloride. The method was criticized by Young, Vogt, and Nieuwland (*11*), who used the color of the resulting ferric thiocyanate complex as a basis for a colorimetric determination of peroxide. In this procedure methanol was used as the solvent. Bolland *et al.* (*1*) modified the method to enable rubber samples to be analyzed by changing the solvent to a mixture of benzene and methanol (73% benzene by volume).

For determining peroxide in GR-S (butadiene-styrene copolymer) and other butadiene copolymers it would be desirable to employ a solvent rich in benzene, since these polymers tend towards insolubility upon oxidation. A solvent composed largely of benzene would also improve the sensitivity of the determination, since larger quantities of polymer could be dissolved in a given volume of solvent.

There are several disadvantages inherent in the use of thiocyanate as a color reagent for iron (*10*). The intensity of the color depends upon the concentration of thiocyanate and upon the acid concentration, and varies with the presence of various ions which form complexes with iron. In practice, a large excess of thiocyanate is used to lower the effects of acid and interfering ions and to give a closer approximation to Beer's law. The red color of the ferric thiocyanate complex is somewhat unstable, requiring colorimeter readings to be made without undue delay. The ferrous thiocyanate reagent of Bolland *et al.* (*1*) and Robey and Wiese (*7*) is so unstable that it must be freshly prepared every few hours and stored in the dark.

The advantages of *o*-phenanthroline as a color reagent for iron have been recognized by many investigators (*3*, *8*, *9*, *10*). Its complex with ferrous iron is very stable, its solutions showing no change in color for many months. Beer's law is closely obeyed. The intensity is not so strongly affected by the concentration of excess reagent or of acid, as in the case of the thiocyanate complex. Since large concentrations of inorganic salts are not needed, it should be possible to use a solvent consisting largely of benzene, with only a small amount of methanol. Solutions of ferrous salts in methanol under nitrogen and *o*-phenanthroline in benzene are stable and can be stored indefinitely without noticeable change.

The effects of complexing agents on the oxidation potential of the ferrous-ferric ion system are of interest. Thiocyanate lowers the oxidation potential, making the oxidation of the ferrous ion proceed more readily. This shift is advantageous in making the reagent very reactive toward polymer peroxides but also accounts for its extreme sensitivity to air oxidation. *o*-Phenanthroline has just the opposite effect (*4*); the ferrous *o*-phenanthroline complex is not appreciably oxidized by polymer peroxides, and it is entirely stable with respect to air oxidation. To increase the reactivity with polymer peroxides, uncomplexed ferrous iron was first tried as a reagent. As will be seen below, satisfactory results were obtained under the proper conditions, provided that no antioxidant was present in the polymer. In the presence of antioxidant, incomplete reduction of rubber peroxide was observed. It was found that the addition of phosphoric acid (which lowers the ferrous-ferric oxidation potential) made the reaction proceed satisfactorily even in the presence of antioxidant. Nitric acid was added to prevent a color due to solvolysis of ferric iron.

Farmer and Sutton (*2*) observed that natural rubber forms only peroxides of the hydroperoxide type. In the present investigation, numerous synthetic polymers, including polyisoprene, polybutadiene, and copolymers of isoprene or butadiene with styrene, acrylonitrile, and other vinyl-type monomers, were found to form peroxides which reacted at the same rate as natural rubber peroxides with the text reagent. Since disubstituted organic peroxides failed to react (*2*), this observation is evidence that all the polymers studied form peroxides of the hydroperoxide type.

## PROCEDURE

This method is intended for the determination of relative amounts of hydroperoxides in natural rubber, and various synthetic polymers and copolymers. It is applicable only to hydroperoxides, and except for this limitation it can be used generally for compounds of low molecular weight as well as high polymers.

Preparation of Solutions. *Ferrous Iron Solution.* Remove the dissolved oxygen from 1 liter of methanol by bubbling nitrogen through it for 30 minutes. Dissolve 19.605 grams of ferrous ammonium sulfate hexahydrate, $FeSO_4(NH_4)_2SO_4 \cdot 6H_2O$, in the methanol containing 13.9 ml. of concentrated sulfuric acid to make the solution about 0.25 *M* in sulfuric acid. If stored under an atmosphere of nitrogen, this solution is stable for a long time. For use over a period of a few days, 10-ml. portions can be allowed to stand in air.

Each day a 0.002 *N* working solution is prepared by diluting 2 ml. of the 0.05 *N* solution to 50 ml. with methanol but without adding acid.

*Nitric Acid–Methanol Solution.* Add 1 ml. of concentrated nitric acid to 20 ml. of methanol slowly and with cooling. One milliliter of this solution provides 0.05 ml. of concentrated nitric acid.

*Phosphoric Acid–Methanol Solution.* Prepare a 1 *M* stock solution by adding 6.75 ml. of 85% phosphoric acid (14.8 *M*) to sufficient methanol to prepare 100 ml. of solution. Dilute the 1 *M* solution to 0.04 *M* for use as a working solution; 0.5 ml. of 0.04 *M* solution provides 0.02 millimole of phosphoric acid.

*o-Phenanthroline Solution.* Dissolve 1 gram of *o*-phenanthroline monohydrate in 1000 ml. of thiophene-free benzene.

ANALYSIS OF UNKNOWN SAMPLES. Pipet 1 ml. of rubber solution (containing about 1 gram of polymer per 100 ml. of benzene) into a 50-ml. volumetric flask. Add about 25 ml. of thiophene-free benzene, washing any polymer solution from the sides of the flask. Add 1 ml. of nitric acid–methanol solution and 0.5 ml. of 0.04 *M* phosphoric acid (methanol), shaking well after each addition. Pipet 1 ml. of 0.002 *M* ferrous iron into the flask, shake well, and allow the mixture to stand at least 15 minutes. Add 3 to 5 ml. of *o*-phenanthroline solution and make up to 50 ml. with thiophene-free benzene. Read the transmission value at 508 mμ with a spectrophotometer or use a photoelectric colorimeter provided with a filter showing maximum transmission at 500 or 510 mμ (preferably not 520 mμ), comparing the transmission with that of benzene.

If the transmission value lies between 50 and 70%, calculate the active oxygen content as shown below. Otherwise, estimate the adjustment necessary in sample size required, and repeat the determination. For samples of entirely unknown peroxide content, it is advisable to vary the sample size, using 0.1, 1, and 10 ml. of polymer solution in the preliminary estimation. If a 10-ml. sample is used, or if the sample is highly colored, a diluted benzene solution of polymer should be used instead of benzene for the comparison liquid in the optical measurement.

CONSTRUCTION OF CALIBRATION CURVE. Using a graduated 1-ml. pipet, add the following amounts of 0.002 *N* ferrous iron solution to a series of 50-ml. volumetric flasks: 0.2, 0.4, 0.6, 0.8, and 1.0 ml. Add about 25 ml. of benzene to each flask, washing the walls carefully. Complex the ferrous iron with 3 to 5 ml. of *o*-phenanthroline solution and make up to 50 ml. with benzene. Take colorimeter or spectrophotometer readings relative to benzene.

Compute the optical density of each solution from the equation $D = \log I_0/I$, and construct a graph of optical density against concentration of iron (expressed as equivalents of ferrous iron per 50 ml.). A straight line, corresponding to Beer's law, should be obtained.

### Table I. Effect of Sulfuric Acid on Ferric Complex

| 0.002 *N* Iron Complexed | Concentrated $H_2SO_4$ | Time of Standing | | Transmission | |
|---|---|---|---|---|---|
| *Ml.* | *Ml.* | $t_1$, *min.* | $t_2$, *min.* | $I_1$, % | $I_2$, % |
| 1.0 | 0.00 | 95 | 1200 | 87 | 85 |
| 1.0 | 0.02 | 95 | 1200 | 98 | 97 |
| 1.0 | 0.05 | 95 | 1200 | 99.5 | 98.5 |
| 1.0 | 0.08 | 95 | 1200 | 99.5 | 99 |
| 1.0 | 0.0 | 90 | 360 | 81 | 78 |
| 1.0 | 0.1 | 90 | 360 | 100 | 99 |
| 1.0 | 0.2 | 90 | 360 | 100 | 100 |
| 1.0 | 0.4 | 90 | 360 | 100 | 100 |
| 3.0 | 0.0 | 90 | 1200 | 80 | 80 |
| 3.0 | 0.1 | 90 | 1200 | 99 | 78 |
| 3.0 | 0.2 | 90 | 1200 | 98.5 | 98 |
| 3.0 | 0.4 | 90 | 1200 | 99 | 99 |

### Table II. Effect of Sulfuric Acid on Ferrous Complex

| 0.002 *N* Iron Complexed | Concentrated $H_2SO_4$ | Time of Standing | Transmission |
|---|---|---|---|
| *Ml.* | *Ml.* | *Min.* | % |
| 1.0 | 0.00 | 45 | 34 |
| 1.0 | 0.02 | 45 | 62 |
| 1.0 | 0.05 | 45 | 68.5 |
| 1.0 | 0.08 | 45 | 69 |
| 1.0 | 0.0 | 45 | 34 |
| 1.0 | 0.1 | 45 | 62 |
| 1.0 | 0.2 | 45 | 65 |
| 1.0 | 0.4 | 45 | 69 |

### Table III. Effect of Nitric Acid

| 0.002 *N* Iron Complexed | Concentrated $HNO_3$ | Time of Standing | | Transmission | |
|---|---|---|---|---|---|
| *Ml.* | *Ml.* | $t_1$, *min.* | $t_2$, *min.* | $I_1$, % | $I_2$, % |
| On Ferric Complex | | | | | |
| 1.0 | 0.00 | 15 | 60 | 94 | 94 |
| 1.0 | 0.02 | 15 | 60 | 95 | 95 |
| 1.0 | 0.05 | 15 | 60 | 95 | 95 |
| 1.0 | 0.08 | 15 | 60 | 95 | 94.5 |
| 1.0 | 0. | 960 | .. | 76.5 | .. |
| 1.0 | 0.2 | 960 | .. | 96 | .. |
| 1.0 | 0.5 | 960 | .. | 96 | .. |
| 1.0 | 1.0 | 960 | .. | 98 | .. |
| On Ferrous Complex | | | | | |
| 1.0 | 0.00 | 15 | 60 | 34 | 34 |
| 1.0 | 0.02 | 15 | 60 | 34 | 34.5 |
| 1.0 | 0.05 | 15 | 60 | 34 | 34.5 |
| 1.0 | 0.08 | 15 | 60 | 34 | 34.5 |
| 1.0 | 0.0 | 960 | .. | 34 | .. |
| 1.0 | 0.1 | 960 | .. | 36 | .. |
| 1.0 | 0.3 | 960 | .. | 83 | .. |
| 1.0 | 0.5 | 960 | .. | 95 | .. |

CALCULATIONS. From the calibration curve the amount of iron remaining unoxidized can be read directly. By difference the amount of iron oxidized is determined. Each equivalent of iron oxidized corresponds to one equivalent or 8 grams of active oxygen. The active oxygen content is calculated as parts per million parts of solid polymer. If a polymer is only partly soluble, the concentration of the soluble polymer is determined by evaporation of an aliquot portion of the solution, and the calculation is based on the soluble part only.

$$\frac{(A - B) \times 8 \times 10^6}{C \times V} = \text{micrograms of active oxygen per gram of polymer} = \text{p.p.m. active oxygen}$$

where $A$ = equivalents of ferrous iron taken
$B$ = equivalents of ferrous iron remaining
$C$ = concentration of polymer grams per ml. of benzene
$V$ = ml. of polymer solution used

## DEVELOPMENT OF METHOD

SPECTROPHOTOMETRIC CURVES OF STANDARD IRON SOLUTIONS. A 0.05 *N* stock solution of ferrous iron was prepared by dissolving ferrous ammonium sulfate, $FeSO_4(NH_4)_2SO_4.6H_2O$, in air-free methanol, with sufficient concentrated sulfuric acid added to make the solution 0.25 *M* in acid. The solution was stored under nitrogen and by occasional titration with ceric sulfate was found to be stable indefinitely. A 0.002 *N* working solution was freshly prepared each day by diluting 2 ml. of the stock solution to 50 ml. with methanol.

A 0.1% solution of *o*-phenanthroline in benzene was used as the indicator solution. Various amounts of iron from $2.5 \times 10^{-4}$ to $2.5 \times 10^{-3}$ milliequivalent were treated with 6 ml. of indicator solution, and diluted to 25 ml. with benzene, and the absorption curves were determined with a Cenco-Sheard spectrophotelometer. In agreement with Fortune and Mellon (*3*) for aqueous solutions, the maximum absorption was found at 508 mμ.

Calculation of the optical density at the wave length of maximum absorption and plotting against concentration showed that Beer's law was being closely followed over the concentration range studied.

EFFECT OF ACIDS ON FERROUS AND FERRIC COMPLEXES. Preliminary experiments showed that while the concentration of excess indicator could be varied over wide limits without affecting the absorption at 508 mμ, the acidity of the solution is of considerable importance. If the acidity is too low, the ferric ion shows appreciable absorption, apparently because of partial solvolysis of the *o*-phenanthroline complex. Upon complete oxidation of a solution of ferrous iron, the usual yellow color of ferric iron appeared. When *o*-phenanthroline was added, a deeper yellow color

**Table IV. Effect of Time, Temperature, and Acid on the Reaction of Rubber Peroxides and Ferrous Iron**

| Concentrated $HNO_3$ | Temperature | Time of Reaction | Time after Complexing | | Transmission | |
|---|---|---|---|---|---|---|
| *Ml.* | | *Min.* | $t_1$, *min.* | $t_2$, *min.* | $I_1$, % | $I_2$, % |
| 0.1 | Cold | 5 | 30 | .. | 64 | .. |
| 0.1 | Cold | 10 | 30 | .. | 67.5 | .. |
| 0.1 | Cold | 15 | 30 | 960 | 69 | 64 |
| 0.1 | Cold | 20 | 30 | .. | 69.5 | .. |
| 0.1 | Cold | 30 | 55 | 180 | 69.5 | 68 |
| ... | Cold | 30 | 40 | ... | 64 | .. |
| 0.1 | Hot | 15 | 30 | 960 | 66 | 62 |
| ... | Hot | 15 | 30 | 960 | 67 | 60 |
| 0.1 | Hot | 30 | 30 | 960 | 70 | 66 |
| ... | Hot | 30 | 30 | 960 | 70 | 64 |
| 0.1 | Hot | 60 | 30 | 120 | 70 | 69.5 |

**Table V. Effect of Concentration of Excess Ferrous Iron**

| Polymer Solution | 0.002 *N* Ferrous Iron | Time after Complexing | | Transmission | | Active[a] Oxygen |
|---|---|---|---|---|---|---|
| *Ml.* | *Ml.* | $t_1$, *min.* | $t_2$, *min.* | $I_1$, % | $I_2$, % | *P.p.m.* |
| 0.2 | 1.0 | 10 | 180 | 43.5 | 43 | 2230 |
| 0.4 | 1.0 | 10 | 180 | 51 | 50 | 1730 |
| 0.6 | 1.0 | 10 | 180 | 59 | 57 | 1550 |
| 0.8 | 1.0 | 10 | .. | 67 | .. | 1470 |
| 1.0 | 1.0 | 10 | .. | 70 | .. | 1220 |
| 1.2 | 1.0 | 10 | .. | 77 | .. | 1150 |
| 1.4 | 1.0 | 10 | .. | 83 | .. | 1080 |
| 0.4 | 0.4 | 60 | .. | 86 | .. | 1380 |
| 0.4 | 0.8 | 60 | .. | 61 | .. | 1540 |
| 0.4 | 1.0 | 60 | .. | 51 | .. | 1730 |
| 0.4 | 1.2 | 60 | .. | 40 | .. | 1610 |
| 1.0 | 0.8 | 30 | .. | 82.8 | .. | 1120 |
| 1.0 | 1.0 | 30 | .. | 70.0 | .. | 1220 |
| 1.0 | 1.2 | 30 | .. | 62.5 | .. | 1390 |
| 1.0 | 1.4 | 30 | .. | 47.0 | .. | 1280 |

[a] Calculated as parts of active oxygen (equivalent weight = 8) per million parts of dry polymer.

appeared instead of the usual blue color obtained in aqueous solutions. With a larger excess of acid, absorption at 508 mμ by the ferric complex could be eliminated, but the ferrous *o*-phenanthroline complex then became unstable.

A series of experiments was performed in which conditions were sought that would give the maximum transmission for ferric iron and the minimum for ferrous iron at 508 mμ. In each experiment a known amount of standard ferrous ammonium sulfate in methanol or standard ferric chloride, prepared by dissolving sublimed ferric chloride in methanol, was used. The iron solution, in a 50-ml. volumetric flask, was treated with 25 ml. of benzene. Five milliliters of 0.1% benzene solution of *o*-phenanthroline were added. After addition of the acid being investigated and just sufficient methanol (1 to 2 ml.) to keep the acid in solution, the volume was made up to 50 ml. with benzene. The spectrophotometric transmission value was determined at 508 mμ at different time intervals after complexing, using benzene as a comparison liquid.

The results for sulfuric acid are shown in Tables I and II and for nitric acid in Table III.

Similar data for trichloroacetic acid showed that the ferrous complex was unaffected but that the absorption by the ferric complex could not be removed. Hydrochloric acid prevented absorption by the ferric complex but decomposed the ferrous complex.

Nitric acid is the only acid tried that will remove the absorption by the ferric complex at 508 mμ and yet not affect the ferrous complex. Not more than 0.1 ml. of concentrated acid can be used per 50 ml. of solution. Using this amount of acid, the absorption by the ferrous complex is not affected, and only 5% absorption is found for the ferric complex.

EFFECT OF TIME, TEMPERATURE, AND ACID ON REACTION BETWEEN POLYMER PEROXIDE AND FERROUS IRON. A polymer of relatively high peroxide content was desired.

A laboratory GR-S sample was heated in air at 70° for 2 hours. The polymer was allowed to stand with 100 ml. of benzene for each gram of polymer; the gel was filtered off with a 100-mesh stainless steel screen. The resulting solution contained 0.0088 gram of soluble polymer per ml. Preliminary experiments showed that 1 ml. of this polymer solution gave a convenient extinction value when allowed to react with 1 ml. of 0.002 *N* ferrous iron.

Experiments were run as described in the previous section, using 1 ml. of polymer solution, 1 ml. of 0.002 *N* ferrous iron, and 0.1 ml. of nitric acid, except as noted. The solutions containing ferrous iron, polymer, and acid were allowed to stand various lengths of time at room temperature before the *o*-phenanthroline was added. No oxidation of iron occurred in the presence of the indicator. In certain experiments the mixture was heated to boiling and kept at the boiling point for the desired time. In these instances the acid was not added until after cooling and complexing, as the acid would oxidize the ferrous iron in hot solutions.

The data in Table IV indicate that the reaction between polymer peroxide and ferrous iron is complete in 15 minutes at room temperature if acid is present. No increase in transmission was obtained by heating up to 60 minutes. The final solutions were stable with respect to transmission values for periods of 1 to 2 hours, with only slight effects over longer periods of time. In all cases a more stable color was obtained in the presence of acid.

EFFECT OF CONCENTRATION OF EXCESS FERROUS IRON. To determine whether an excess of ferrous iron is necessary for complete reduction of the rubber peroxides, the same polymer solution and procedure were used as in the previous section, allowing reaction times of 15 and 30 minutes at room temperature. The results are given in Table V.

From Table V it appears that with an increasing excess of ferrous iron a higher apparent peroxide content is in general obtained. As is shown below, this trend is caused by a variable amount of air oxidation of the excess ferrous iron. By limiting the observed transmission range to 50 to 70%, a maximum deviation of around ±20% in apparent peroxide content is allowed, according to Table V. Considering the difficulty of sampling solid polymers and the relative nature of the method, this variation is not serious for following trends in polymer peroxides.

EFFECT OF ANTIOXIDANT. To determine the effect of antioxidant, 2% of phenyl-β-naphthylamine (based on the dry polymer) was added to the polymer solution already studied. With antioxidant present, hardly any oxidation of the ferrous iron occurred either at room temperature or upon heating.

EFFECT OF PHOSPHORIC ACID IN PREVENTING INTERFERENCE BY ANTIOXIDANT. Experiments designed to increase the ease of oxidation of ferrous iron by lowering the ferrous-ferric ion oxidation potential were carried out. Fluoride and phosphoric acid were used as complexing agents. After preliminary experiments, phosphoric acid was adopted to avoid the etching effect of fluorides. The optimum concentrations of phosphric and nitric acids were found by a study of the spectrophotometric absorption at 508 mμ of the ferrous and ferric *o*-phenanthroline complexes in the absence of peroxides. The same procedure was used as for ferrous and ferric complexes above, with the addition of phosphoric acid in the form of a methanol solution. The results appear in Table VI. In each experiment 1.00 ml. of 0.002 *N* ferrous or ferric iron was treated with various amounts of phosphoric and nitric acids, *o*-phenanthroline was added, and the volume brought to 50 ml.

Even small amounts of phosphoric acid exert an adverse effect on the ferrous complex if no nitric acid is present, presumably by pulling the ferrous iron away from the *o*-phenanthroline complex. A small amount of nitric acid, by suppressing the ionization of the phosphoric acid, prevents the interference. Phosphoric acid has a desirable effect on the ferric iron in decreasing the absorption by forming the colorless ferric phosphate complex. From these results it was decided that 0.02 millimole of phosphoric acid and 0.05 ml. of concentrated nitric acid per 50 ml. are the optimum amounts.

To determine whether phosphoric acid prevents the interference by phenyl-β-naphthylamine, the polymer solution containing antioxidant was tried with a reaction time of 20 minutes before adding the indicator. The results are shown in Table VII. A

### Table VI. Effect of Phosphoric Acid

| Concentrated $HNO_3$ | $H_3PO_4$ | Time of Standing | | Transmission | |
|---|---|---|---|---|---|
| *Ml.* | *Millimoles* | $t_1$, *min.* | $t_2$, *min.* | $I_1$, % | $I_2$, % |
| | | On Ferrous Complex | | | |
| 0.0 | 0.00 | 30 | ... | 34 | .. |
| 0.0 | 0.008 | 30 | ... | 40.3 | .. |
| 0.0 | 0.02 | 30 | ... | 43.3 | .. |
| 0.0 | 0.04 | 30 | ... | 44.3 | .. |
| 0.05 | 0.00 | 20 | 180 | 34.0 | 33.0 |
| 0.05 | 0.008 | 20 | 180 | 33.9 | 35.0 |
| 0.05 | 0.02 | 20 | 180 | 34.0 | 35.9 |
| 0.05 | 0.04 | 20 | 180 | 34.5 | 36.5 |
| 0.1 | 0.00 | 25 | 180 | 35 | 36 |
| 0.1 | 0.008 | 25 | 180 | 36 | 39 |
| 0.1 | 0.02 | 25 | 180 | 36 | 39 |
| 0.1 | 0.04 | 25 | 180 | 36 | 39 |
| | | On Ferric Complex | | | |
| 0.05 | 0.00 | 35 | ... | 95 | .. |
| 0.05 | 0.008 | 35 | 120 | 97 | 97 |
| 0.05 | 0.02 | 35 | 120 | 97 | 97 |
| 0.05 | 0.04 | 35 | 120 | 98 | 98 |

### Table VII. Oxidation of Ferrous Iron in Presence of Antioxidant

| Polymer Solution | 0.002 *M* Ferrous Iron | Time after Complexing | Transmission | Active Oxygen |
|---|---|---|---|---|
| *Ml.* | *Ml.* | *Min.* | % | *P.p.m.* |
| 0.2 | 1.0 | 15 | 44 | 2230 |
| 0.4 | 1.0 | 15 | 51.5 | 1770 |
| 0.6 | 1.0 | 15 | 59.2 | 1560 |
| 0.8 | 1.0 | 15 | 67 | 1420 |

### Table VIII. Effect of Air on Colorimetric Peroxide Determination

| 0.002 *N* Peroxide | 0.002 *N* Iron | Iron Used | Recovery | Conditions |
|---|---|---|---|---|
| *Ml.* | *Ml.* | *Ml.* | % | |
| | | *o*-Phenanthroline Method | | |
| 0.50 | 1.20 | 1.14 | 228 | Air saturated |
| 0.50 | 1.00 | 0.73 | 140 | $N_2$ through benzene only |
| 0.50 | 1.00 | 0.65 | 130 | $N_2$ through all reagents before reaction |
| 0.50 | 1.00 | 0.59 | 118 | $N_2$ through all reagents and during reaction |
| | | Thiocyanate Method | | |
| 0.20 | 15 | 0.38 | 190 | Air saturated |
| 0.30 | 15 | 0.56 | 187 | Air saturated |
| 0.50 | 15 | 0.75 | 150 | Air saturated |
| 0.80 | 15 | 0.77 | 96 | Air saturated |
| 0.30 | 15 | 0.55 | 183 | $N_2$ before reaction |
| 0.50 | 15 | 0.72 | 144 | $N_2$ before reaction |
| 0.80 | 15 | 0.74 | 93 | $N_2$ before reaction |
| 0.30 | 15 | 0.18 | 60 | $N_2$ before and during reaction |
| 0.50 | 15 | 0.12 | 24 | $N_2$ before and during reaction |

comparison of the results with those obtained with the same polymer solution in the absence of antioxidant (Table V, first four experiments) shows that very similar data were found in the two cases. The modified method using both nitric and phosphoric acids was also tried on the polymer solution without antioxidant, with very similar results.

The commonly used antioxidants BLE (a complex condensation product of acetone and diphenylamine) and Stalite (an alkylated secondary arylamine) were likewise shown not to interfere in the peroxide determination.

## ABSOLUTE ACCURACY

To check the absolute accuracy of the proposed method, an analysis of a standard peroxide was desired. Benzoyl peroxide and furoyl peroxide, which is much less stable thermally, failed to react noticeably with the reagent even after long standing. On the other hand, *tert*-butyl hydroperoxide reacted as readily as polymer peroxides.

Since Farmer and Sutton (*2*) have shown natural rubber peroxides to be of the hydroperoxide type, it was of interest to compare the results obtained on rubber peroxides by the proposed method and by the thiocyanate method of Robey and Wiese (*7*), which responds to all peroxides. The same rubber or GR-S solution showed about 20% more peroxide (relative) by the *o*-phenanthroline method than by the thiocyanate method.

Analysis of solutions of *tert*-butyl hydroperoxides standardized by the iodide method of Liebhafsky and Sharkey (*6*), and diluted for colorimetric analysis, showed that both colorimetric procedures gave high results, increasing with decreasing amounts of peroxide in the reaction mixture (compare Table V). However, careful exclusion of oxygen by bubbling the reagents before and during the reaction led to lower results (Table VIII). With use of the thiocyanate method, the rate of reaction between peroxide and iron was found to decrease markedly as the last traces of oxygen were removed. Thus a fading of the thiocyanate color led to low results in air-free solutions. These observations suggest that peroxide catalyzes the air oxidation of iron (induced reaction) and conversely that oxygen catalyzes the peroxide iron reaction. Thus both colorimetric procedures are nonstoichiometric in the presence of air and very slow in its absence. For best results, both should be applied only over a narrow range of peroxide content in the reaction mixture.

If the recommended transmission range of 50 to 70% is used in the proposed procedure (corresponding to a twofold range of peroxide concentration), comparative analyses can readily be made without standardization. For results of absolute significance, standardization by means of *tert*-butyl hydroperoxide is recommended. For larger amounts of peroxides, the iodide method gives stoichiometric results, but titration methods involving ferrous iron again were found to give high results in the presence of air. This observation has also been made by Kolthoff and co-workers (*5*) in the analysis of soap peroxides.

## SENSITIVITY

The procedure as given is sensitive to 10 or 20 p.p.m. active oxygen, calculated on the solid polymer. No particular effort has been made to gain the utmost sensitivity, but much larger sample sizes could be used. The limiting factor is the color of the polymer solution itself, which could be compensated by using a solution of the polymer rather than benzene as the comparison liquid. By this means, less than 1 p.p.m. of active oxygen could be detected, considering the fact that the method gives an abnormal response to very small traces of hydroperoxide.

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# Separation of Calcium from Magnesium

## By Oxalate Method in Samples of High Magnesium-Calcium Ratio

E. R. WRIGHT AND R. H. DELAUNE, Texas Division, The Dow Chemical Company, Freeport, Texas

**By careful control of the relative concentrations of magnesium and oxalate ion, it is possible to achieve acceptable separations of calcium from magnesium by direct precipitation of calcium oxalate in samples containing magnesium-calcium ratios of 20 to 1 or greater. Results which can be achieved with a single precipitation are limited by the solubility of calcium oxalate which increases rapidly with increasing oxalate concentration in hot solutions.**

IN THE analysis of magnesites and magnesium chloride brine concentrates, it has long been recognized that the separation of calcium as calcium oxalate becomes increasingly uncertain as the magnesium content of the sample is increased. This uncertainty is caused by two properties of magnesium oxalate: its complex-forming nature which effectively ties up oxalate ion and makes the precipitation of calcium oxalate slow or incomplete, and its low solubility which causes excessive adsorption and especially postprecipitation of magnesium oxalate.

As a result of a study of the solubility of magnesium oxalate in ammonium oxalate solutions, Bobtelsky and Malkowa-Janowski (*2*) pointed out that both these effects could be ameliorated by adding to the solution a much larger quantity of oxalate ion than normally employed, the additional concentration of oxalate having the effect of forming a soluble complex with magnesium and furnishing sufficient oxalate in excess for the precipitation of the calcium. Additional information is herein presented dealing with the solubility of calcium oxalate, the quantity of oxalate required to prevent precipitation of magnesium oxalate, the best mode of precipitation of calcium oxalate, the amount of error to be expected from coprecipitation of magnesium, and maximum permissible magnesium-calcium ratio.

### REAGENTS

MAGNESIUM CHLORIDE SOLUTION. A solution of magnesium chloride free of calcium was prepared by dissolving pure magnesium metal in hydrochloric acid and diluting so that it contained 16.0% magnesium chloride (4.09% magnesium). A spectrographic analysis showed that this solution contained less than 0.001% calcium and no detectable amount of aluminum, copper, iron, manganese, silicon, or nickel. The solution was stored in a Pyrex, glass-stoppered bottle.

STANDARD CALCIUM SOLUTION. The solutions were made up as needed to contain about 0.8 mg. of calcium per millimeter by dissolving a weighed quantity of Baker's Iceland spar in a slight excess of distilled hydrochloric acid and diluting to known volume. The solutions were standardized according to the procedure shown below, although a good agreement was always obtained between the calcium content as determined and that obtained by assuming the Iceland spar to be a primary standard.

HYDROCHLORIC ACID. Reagent grade hydrochloric acid was diluted with an equal volume of water and distilled from an all-Pyrex still. The resulting solution was approximately 6 *N* in hydrochloric acid.

AMMONIA. Ammonia solutions were prepared 1 liter at a time by passing ammonia gas from a cylinder through a water scrubber, then into cold water in a Vycor flask. The concentrated solution (6 to 9 *N*) so obtained was stored in the Vycor flask, or in some cases in hard rubber bottles.

AMMONIUM OXALATE: For most of the work, ammonium oxalate was purified by a single crystallization from hot water in order to remove insoluble impurities.

In some cases where crystallization did not appear necessary, analytical reagent grade ammonium oxalate monohydrate was used directly. Determinations of the solubility of calcium oxalate were made with ammonium oxalate prepared by crystallizing reagent grade oxalic acid which was then neutralized with ammonia gas.

NITRIC ACID. Analytical reagent grade acid was distilled from an all-Pyrex still and stored in a Pyrex bottle.

### PROCEDURE

STANDARDIZATION OF CALCIUM SOLUTIONS. The required amount (25.00 or 50.00 ml.) of calcium solution was pipetted into a 400-ml. beaker and 5 ml. of 6 *N* hydrochloric acid were added. The solution was diluted to 75 ml., 25 ml. of 5% ammonium oxalate solution were added, and the solution was heated to about 80° C. The calcium oxalate was then precipitated by the dropwise addition of 6 *N* ammonia until the solution became basic to methyl red indicator and about 3 drops in excess. After digestion at 80° C. for about 15 minutes the solution was allowed to cool for an hour, and was then filtered through a tared fritted Pyrex filter (fine porosity) and washed 5 times with cold 0.2% ammonium oxalate solution. The precipitate was dried for a half hour at 180° C., and was ignited for one hour at 475° to 500° C. in a muffle furnace according to the procedure of Willard and Boldyreff (*9*). The resulting calcium carbonate was allowed to cool at least 4 hours in a desiccator containing anhydrous calcium chloride and was then weighed.

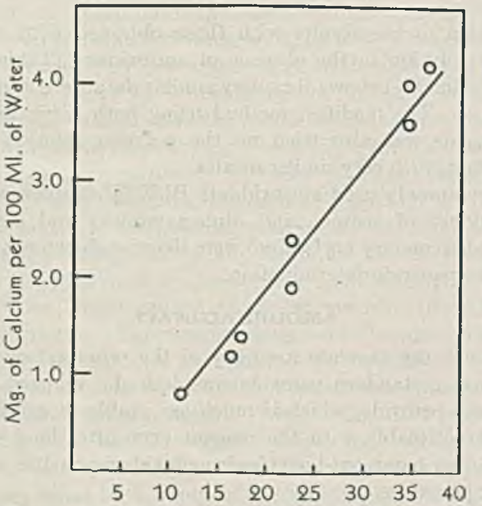

**Figure 1. Solubility of Calcium Oxalate in Ammonium Oxalate Solutions at 95° C.**

Table I. Solubility of Calcium Oxalate in Solutions of Ammonium Oxalate and Other Salts

| Salt Present per 100 Ml. of $H_2O$ at 80–90° C. | Calcium Carbonate Taken | Calcium Carbonate Found | Ca Dissolved |
|---|---|---|---|
| *Grams* | *Mg.* | *Mg.* | *Mg.* |
| 5.0 $(NH_4)_2C_2O_4.H_2O$ | 49.5 | 49.2 | 0.14[a] ± 0.02 |
| 10.0 $(NH_4)_2C_2O_4.H_2O$ | 49.5 | 48.6 | 0.35[a] ± 0.05 |
| 15.0 $(NH_4)_2C_2O_4.H_2O$ | 49.4 | 47.9 | 0.60[b] ± 0.12 |
| 20.0 $(NH_4)_2C_2O_4.H_2O$ | 57.0 | 53.6 | 1.4[c] ± 0.2 |
| 25.0 $(NH_4)_2C_2O_4.H_2O$ | 49.5 | 44.4 | 2.0[a] ± 0.2 |
| 18.0 $H_2C_2O_4.2H_2O$[d] | 56.5 | 53.2 | 1.4[e] |
| 26.0 $K_2C_2O_4.H_2O$ | 68.4 | 63.2 | 2.0[e] |
| 20.0 $NH_4Cl$ | 56.5 | 56.4 | <0.1[e] |
| 20.0 NaCl | 56.5 | 56.8 | <0.1[e] |
| 20.0 KCl | 56.5 | 56.8 | <0.1[e] |

[a] Average of four determinations.
[b] Average of three determinations.
[c] Average of five determinations.
[d] Neutralized with $NH_4OH$.
[e] Average of two determinations.

Precipitation from Magnesium Chloride Solutions. Several modes of precipitation were tried as shown below, the following being adopted finally as the recommended procedure.

The neutral magnesium chloride solution containing the proper amount of calcium and about 1 gram of ammonium chloride is diluted to 100 ml. in a 400-ml. beaker and heated to 80° C. The proper quantity of solid ammonium oxalate monohydrate (from Table III) is then added all at once and the mixture stirred until solution is complete. The precipitate is digested for 0.5 to 1 hour at 80° C., and filtered hot through a tared Pyrex filter. The determination is completed as for standardization of calcium solution.

In many cases a second precipitation was made by dissolving the ignited calcium carbonate in dilute hydrochloric acid, filtering the acid solution through the Pyrex filter from which the calcium carbonate was dissolved, and then continuing by the procedure shown above under standardization of the calcium solutions.

## RESULTS

Solubility of Calcium Oxalate. The fact that the solubility of calcium oxalate increases with oxalate-ion concentration became evident early in the work, and in order to obtain data showing the magnitude of this effect, a number of determinations were made by adding various quantities of solid ammonium oxalate monohydrate to the hot solution containing calcium oxalate monohydrate precipitated by the procedure described above for standardization of the standard calcium solutions. After addition of the solid ammonium oxalate the solutions were digested hot for 1 hour, filtered hot, and washed with cold 0.2% ammonium oxalate. Results are shown in Table I, together with similar determinations made with a few other salts.

In order to provide further corroboration of the general magnitude of this solubility, a number of determinations were made by analyzing for calcium in the filtrate of the ammonium oxalate solutions. For this purpose an all-Pyrex apparatus was employed containing a sealed-in fritted filter, so that the filtration could be made while the apparatus was immersed in a constant-temperature bath at 95° C. Results by this method (Figure 1) provide an approximate check on those values shown in Table I.

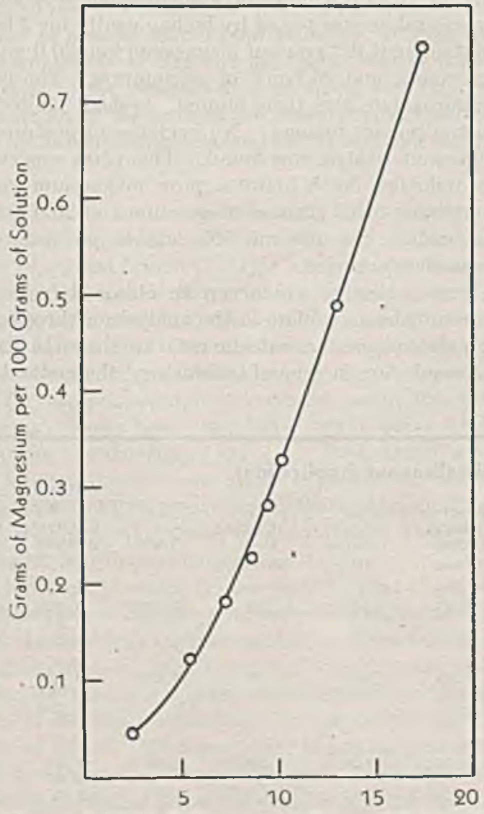

Figure 2. Solubility at 100° C. of Magnesium Oxalate in Ammonium Oxalate Solutions (2)

Table II. Quantity of Ammonium Oxalate Required

| Magnesium | $(NH_4)_2C_2O_4 \cdot H_2O$ | Calcium Carbonate Taken | Calcium Carbonate Found, 1st pptn. | Calcium Carbonate Found, 2nd pptn. | Error, Ca, 1st pptn. | Error, Ca, 2nd pptn. |
|---|---|---|---|---|---|---|
| Grams/100 ml. | at 90° C. | Mg. | Mg. | Mg. | Mg. | Mg. |
| 0.046 | 3.0 | 50.3 | 50.7 | 49.9 | + 0.16 | − 0.16 |
| | 3.0 | 50.3 | 50.5 | 49.7 | + 0.08 | − 0.24 |
| 0.116 | 3.0 | 56.8 | 128.6 | 56.4 | +28.7 | − 0.16 |
| | 3.0 | 56.8 | 142.0 | 56.5 | +34.1 | − 0.12 |
| | 3.0 | 101.0 | 218.4 | 100.3 | +47.0 | − 0.28 |
| | 3.0 | 101.0 | 224.5 | 100.6 | +49.4 | − 0.16 |
| | 5.0 | 56.8 | 60.6 | 56.1 | + 1.5 | − 0.28 |
| | 5.0 | 56.8 | 57.3 | 55.1 | + 0.2 | − 0.28 |
| | 5.0 | 101.0 | 131.2 | 100.4 | +12.1 | − 0.24 |
| | 5.0 | 101.0 | 134.0 | 100.4 | +13.2 | − 0.24 |
| | 7.0 | 50.3 | 50.5 | 49.6 | + 0.08 | − 0.28 |
| | 7.0 | 50.3 | 50.3 | 49.5 | 0.00 | − 0.32 |
| | 7.0 | 101.0 | 101.5 | 100.1 | + 0.20 | − 0.36 |
| | 7.0 | 101.0 | 101.5 | 100.2 | + 0.20 | − 0.32 |
| 0.231 | 5.0 | 56.8 | 86.5 | 58.0 | +11.9 | + 0.48 |
| | 5.0 | 56.8 | 228.5 | 98.1 | +68.7 | +16.5 |
| | 10.0 | 56.8 | 55.8 | 55.3 | − 0.4 | − 0.6 |
| | 10.0 | 56.8 | 55.7 | 55.2 | − 0.4 | − 0.7 |
| | 15.0 | 56.8 | 54.4 | 54.2 | − 1.0 | − 1.0 |
| | 15.0 | 56.8 | 54.0 | 54.1 | − 1.1 | − 1.1 |
| 0.462 | 5.0 | 51.3 | Very | high | Very high | |
| | 10.0 | 51.3 | 712.2 | 238.4 | +264 | + 75 |
| | 10.0 | 51.3 | 518.8 | 341.0 | +187 | +116 |
| | 15.0 | 51.3 | 106.9 | 50.5 | +22.2 | − 0.32 |
| | 15.0 | 51.3 | 91.7 | 49.0 | +16.1 | − 0.9 |
| | 20.0 | 51.3 | 48.7 | 48.7 | − 1.0 | − 1.0 |
| | 20.0 | 51.3 | 47.9 | 47.5 | − 1.4 | − 1.5 |
| | 20.0 | 68.8 | 65.5 | 64.7 | − 1.3 | − 1.6 |
| | 20.0 | 68.8 | 65.9 | 65.6 | − 1.2 | − 1.3 |
| | 25.0 | 51.3 | 45.8 | 45.4 | − 2.2 | − 2.3 |
| | 25.0 | 68.8 | 63.6 | 62.7 | − 2.1 | − 2.4 |
| 1.16 | 25.0 | 56.8 | Very high | | Very high | |
| | 30.0 | 56.8 | 145.0 | 55.7 | +35.3 | − 0.4 |
| | 30.0 | 56.8 | 153.0 | 47.4 | +38.5 | − 3.8 |
| | 35.0 | 56.8 | 43.0 | 42.5 | − 5.5 | − 5.7 |
| | 35.0 | 56.8 | 42.3 | 42.2 | − 5.8 | − 5.8 |

It is evident from these solubility figures that if hot filtration is employed, the solubility error is appreciable and increases rapidly with increasing oxalate concentration.

Quantity of Ammonium Oxalate Required. The solubility at 100° C. of magnesium oxalate dihydrate in ammonium oxalate solutions of concentration up to 20 grams of ammonium oxalate per 100 grams of solution is shown in Figure 2 according to data presented by Bobtelsky and Malkowa-Janowski (2).

The practical significance of these solubility figures was checked approximately as shown in Table II by a procedure which consisted of adding various quantities of solid ammonium oxalate monohydrate to 100 ml. of hot solution containing known quantities of magnesium and calcium. These solutions were digested at 80° to 90° C. for 0.5 to 1 hour and filtered hot. The quantity of precipitated magnesium oxalate drops sharply when sufficient ammonium oxalate is present to equal the solubility requirement shown in Figure 2. In actual practice a further excess of oxalate appears desirable in reducing coprecipitation of magnesium; consequently amounts of ammonium oxalate are recommended as shown in Table III, together with the solubility corrections necessary.

Table III. Recommended Quantity of Ammonium Oxalate

| Magnesium Present | $(NH_4)_2C_2O_4 \cdot H_2O$ Added | Solubility Correction, Ca |
|---|---|---|
| G./100 ml. | G./100 ml. | Mg./100 ml. |
| 0.10 | 7 | 0.20 |
| 0.20 | 11 | 0.35 |
| 0.30 | 15 | 0.60 |
| 0.40 | 20 | 1.4 |
| 0.50 | 25 | 2.0 |

### Table IV. Mode of Precipitation

| Magnesium | $(NH_4)_2C_2O_4 \cdot H_2O$ | Error in First Pptn. (as $CaCO_3$) | | | MgO in Ppt. | | |
|---|---|---|---|---|---|---|---|
| | | Method A | Method B | Method C | Method A | Method B | Method C |
| *Grams/100 ml.* | | *Mg.* | *Mg.* | *Mg.* | *Mg.* | *Mg.* | *Mg.* |
| 0.075 | 1.5 | +1.3 | ... | ... | 1.0 | ... | ... |
| | 3.0 | ... | +0.6 | +0.6 | ... | 0.5 | 0.7 |
| | 5.0 | +0.7 | +0.3 | ... | 0.6 | 0.5 | ... |
| | 6.0 | ... | ... | −0.5 | ... | ... | 0.2 |
| 0.200 | 1.5 | +4.7 | ... | ... | 3.3 | ... | ... |
| | 5.0 | +2.4 | +2.7 | +86.7 | 1.3 | ... | ... |
| | 8.0 | ... | ... | +0.5 | ... | ... | 0.5 |
| | 11.0 | +1.4 | −1.3 | −0.6 | 0.6 | 0.4 | 0.2 |
| 0.400 | 10.0 | +13.5 | +5.3 | ... | ... | ... | ... |
| | 13.0 | −1.1 | ... | +11.6 | 0.7 | ... | ... |
| | 15.0 | −2.2 | −2.6 | −1.4 | 0.9 | 0.1 | 0.3 |
| 0.462 | 20.0 | ... | ... | −3.8 | ... | ... | 0.1 |

Method A, Kolthoff and Sandell (*5*).
Method B, reverse order, addition of sample to hot $(NH_4)_2C_2O_4$ solution.
Method C, addition of weighed quantity of solid $(NH_4)_2C_2O_4 \cdot H_2O$ directly to hot sample.
All determinations made with calcium content of about 50 mg. of $CaCO_3$.
Figures listed are averages of duplicate determinations.

**Mode of Precipitation.** This is the point to which previous investigators have devoted most of their attention in an effort to improve the calcium-magnesium separation. It has been clearly shown (*1, 3, 5, 6, 7*) that in magnesium-calcium ratios (by weight) of 1 to 1 or lower a better separation is attained by slow neutralization of an acid oxalate solution than by addition of oxalate to a neutral solution. In this case, sufficient oxalate according to Figure 2 is not always added and it is necessary to depend upon supersaturation to keep magnesium oxalate from precipitating (*4*).

It was pointed out by Blasdale (*1*) that there is no purpose in the slow neutralization of a sample containing much magnesium because the calcium does not begin to precipitate in this case until the solution is nearly neutral. This observation has been repeatedly confirmed; in fact, it was noted that the neutralization of a hot acid solution containing 20 grams of ammonium oxalate monohydrate and 0.4 gram of magnesium ion resulted sometimes in a heavy precipitation of magnesium oxalate which tended to dissolve as the neutralization proceeded. This behavior is to be expected, since in an acid solution the oxalate-ion concentration is low at first and as it increases during the neutralization a point is reached at which the oxalate-ion concentration is favorable for the precipitation of magnesium oxalate. As the oxalate-ion concentration continues to increase during the neutralization, the precipitated magnesium oxalate goes back into solution, presumably in the form of a complex ion. The exact nature of this complex ion is not clear, but it may contain a mole ratio of oxalate to magnesium as high as 4 to 1, since the mole ratios calculated from the solubilities shown in Figure 2 appear to approach this value as the magnesium content increases.

It was decided, therefore, to investigate three modes of precipitation according to the following scheme. Results are shown in Table IV.

Method A. According to Kolthoff and Sandell (*5*). This procedure consists of the dropwise addition of 6 *N* ammonia to an acid solution containing 1.5 grams or more of ammonium oxalate monohydrate per 100 ml. at 70° to 80° C. until the solution is basic to methyl red indicator. The solution is then allowed to stand without further heating for 1 hour and filtered cold. This procedure was modified in cases where more than 5.0 grams of ammonium oxalate monohydrate was used by maintaining the solution at 70° C. in order to prevent precipitation of ammonium oxalate monohydrate upon cooling.

Method B. Reverse order. The sample was added dropwise from a separatory funnel to a hot solution of ammonium oxalate of such dilution that the final volume would be 100 ml. The precipitate was digested 0.5 hour at 70° C. and filtered hot.

Method C. Solid ammonium oxalate monohydrate was added directly to the hot solution according to the method given under Procedure.

After the first precipitation was completed according to one of the above procedures, the ignited and weighed precipitate of calcium carbonate containing any coprecipitated magnesium was dissolved in hydrochloric acid, and a second precipitation was made (see Procedure). The filtrate from the second precipitation was examined for magnesium by the Titan yellow method (*8*) as a check on the loss in weight between the first and second precipitations.

Conclusions drawn from the results shown in Table IV may be summarized as follows:

Method A results in a somewhat greater coprecipitation of magnesium than method B or C, but gives less precipitation of magnesium oxalate where a deficiency of ammonium oxalate is used.

Method B is somewhat less convenient than method C and does not give results that are much, if any, better than those with method C.

If sufficient ammonium oxalate is present, methods B and C result in negligible coprecipitation of magnesium, about 0.1 to 0.3 mg. of magnesium usually being found with the ignited calcium carbonate. Results are low, however, because of the solubility of calcium oxalate in the concentrated ammonium oxalate solutions.

Method A lends itself to good accuracy without solubility correction in samples containing magnesium-calcium ratios by weight as high as 20 to 1 if 5.0 grams of ammonium oxalate monohydrate are used per 100 ml. of solution, a double precipitation is made, and not more than 0.2 gram of magnesium ion per 100 ml. is present.

The stability toward boiling of a magnesium solution containing excess oxalate was tested by boiling gently for 2 hours a solution containing 0.462 gram of magnesium ion, 20.0 grams of ammonium oxalate and 20.7 mg. of calcium ion. The precipitated calcium oxalate was then filtered, washed, ignited, and weighed in the regular manner. No evidence of postprecipitation of magnesium oxalate was found. This point was checked further by refluxing for 8 hours a pure magnesium chloride solution containing 0.462 gram of magnesium and 20.0 grams of ammonium oxalate per 100 ml. No visible precipitation of magnesium oxalate occurred.

**Applications.** Results which can be obtained by a single precipitation of calcium oxalate in the analysis of three samples containing a high magnesium-calcium ratio are shown in Table V. While these results are in general satisfactory, the method is not

### Table V. Miscellaneous Applications

| Description | Ratio by Weight Mg:Ca | Correction Applied, Ca | Magnesium Present | Volume | $(NH_4)_2C_2O_4.H_2O$ Used | Calcium | | |
|---|---|---|---|---|---|---|---|---|
| | | | | | | Present | Found | |
| | | | | | | | $CaCO_3$[a] method | $KMnO_4$ method |
| | | *Mg.* | *Grams* | *Ml.* | *Grams* | % | % | % |
| Dilute (15%) $MgCl_2$ liquor | 16:1 | 1.4 | 0.43 | 100 | 20 | 0.232[b] | 0.231<br>0.231<br>0.232 | 0.229<br>0.229<br>0.229 |
| Concentrated (34%) $MgCl_2$ liquor | 85:1 | 4.0 | 1.08 | 200 | 50 | 0.099[b] | 0.098<br>0.097<br>0.096 | ...<br>...<br>... |
| B. of S. burned magnesite (standard sample 104) | 22:1 | 1.4 | 0.41 | 100 | 20 | 2.39 | 2.39<br>2.36<br>2.37 | ...<br>...<br>... |

[a] By method shown under procedure, using single oxalate precipitation.
[b] By removal of 90% of magnesium with NaOH, followed by double oxalate precipitation of calcium, then ignition to $CaCO_3$.

always practical because of the large quantity of ammonium oxalate required, and the necessity for applying an accurately known empirical correction due to solubility of calcium oxalate. The calcium oxalate precipitate can be titrated with permanganate with results that check closely those obtained by weighing as calcium carbonate, as shown in Table V.

### CONCLUSIONS

The separation of calcium by precipitation as oxalate from solutions containing much magnesium is limited by the solubility of calcium oxalate, which becomes appreciable in hot concentrated ammonium oxalate solutions, and by the necessity of using large amounts of ammonium oxalate in order to prevent precipitation of magnesium oxalate. By the addition of sufficient ammonium oxalate, up to 0.5 gram of magnesium ion can be held in solution in 100-ml. volume at 80° C.

Coprecipitation of magnesium is small if a large excess of ammonium oxalate is added directly to a hot neutral solution containing magnesium and calcium.

In the range of magnesium-calcium ratios (by weight) of 20 to 1, calcium can be determined with acceptable accuracy by a single precipitation of calcium oxalate using a large amount of ammonium oxalate and an empirical correction for solubility of calcium oxalate, or by double precipitation using not over 5 grams of ammonium oxalate per 100 ml. as precipitant.

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# Systematic Polarographic Metal Analysis

## Determination of Tin, Lead, Nickel, and Zinc in Copper-Base Alloys

JAMES J. LINGANE
Department of Chemistry, Harvard University, Cambridge 38, Mass.

**Procedures are described for determining tin, lead, nickel, and zinc in copper-base alloys. Other minor elements such as antimony, bismuth, iron, and manganese, do not interfere, and two samples suffice for all four determinations. Electrolysis at controlled potential is used to remove copper (and antimony, bismuth, etc.) prior to the determination of lead and tin, and to remove copper, lead, and tin prior to the determination of nickel and zinc. Separate aliquot portions of the solution remaining after removal of copper are used for polarographic determination of lead and tin, the former in 1 *N* sodium hydroxide, and the latter in a supporting electrolyte composed of 4 *M* ammonium chloride and 1 *N* hydrochloric acid. Nickel and zinc are determined simultaneously in the solution remaining after removal of copper, lead, and tin; an ammoniacal supporting electrolyte is used, and small amounts of nickel may be determined accurately in the presence of large amounts of zinc. All four determinations can be completed in about 2.5 hours. Results obtained with several representative Bureau of Standards copper-base alloys agreed very well with accepted values.**

PROCEDURES for the polarographic determination of copper, zinc, lead, iron, and nickel in brass have been described by Hohn (*2*, *3*) and Mnich (*3*, *11*), a method of determining only copper and zinc in such alloys has been discussed by Tyler and Brown (*16*), and a method for nickel in brasses and bronzes was developed by Milner (*10*). Several studies of the polarographic characteristics of tin have been made (*4*, *8*, *9*, *13*, *14*, *15*), but no method for the polarographic determination of this element in alloys has previously been described. In this paper a systematic procedure for the determination of tin, lead, nickel, and zinc in various kinds of copper-base alloys is presented. Other minor elements which may be present in such alloys, such as antimony, bismuth, iron, and manganese, do not interfere, and two samples suffice for all four determinations.

Since the wave of cupric copper precedes that of the other elements concerned, it must be removed. Taking advantage of the fact that the cuprous cyanide complex ion is not reducible at the dropping electrode in basic solution, Hohn (*2*) and Milner (*10*) recommended the reduction of cupric copper by cyanide ion in ammoniacal medium to eliminate its interference in the determination of nickel. This procedure is not applicable when tin and lead are also to be determined, and Milner (*10*) found that the diffusion current of the nickel cyanide complex was influenced by the amount of zinc present.

In the present method copper is removed by electrolysis with a platinum cathode at controlled potential, and lead and tin are directly determinable in the residual solution in the presence of nickel and zinc. Antimony and bismuth are removed with the copper, and iron is finally present in the ferrous state and does not interfere. Nickel and zinc are determined in a second sample after removal of copper, tin, and lead (and antimony, bismuth, etc.) by controlled potential electrolysis. Although, on paper, it might seem that a precipitation method of removing copper would be simpler than controlled potential electrolysis because of the large amount of precipitate that would have to be handled, electrolytic separation is more convenient. Using the automatic apparatus previously described (*6*, *7*), electrolytic separation actually requires less of the operator's time than that involved in processing a precipitate. Furthermore, in a precipitation method errors due to coprecipitation must be considered, and the necessity of introducing relatively large quantities of reagents frequently complicates subsequent polarographic determinations. In electrolytic separations only hydrogen ion in amount equivalent to the metal deposited is introduced, and the preparation of the residual solution for polarographic determinations is thus facilitated.

The solution remaining after removal of copper, which contains the tin in the stannic state, is diluted to a known volume and separate aliquot portions are used for the determination of lead and tin. Nickel and zinc are determined simultaneously in the solution remaining after electrolytic removal of copper, tin, and lead from a second sample. In the ammoniacal supporting electrolyte employed the wave of nickel precedes, and is well separated from, the wave of zinc, which permits the simultaneous determination of the two metals from a single polarogram (Figure 2). The amount of nickel in a copper-base alloy is usually considerably less than the amount of zinc, and accurate determinations of nickel may be made in the presence of a large excess of zinc without difficulty.

## EXPERIMENTAL TECHNIQUE

The electrolytic separations were performed with a platinum gauze cathode 5 cm. high and 5 cm. in diameter, and a platinum gauze anode 5 cm. high and 2.5 cm. in diameter which was mounted inside and coaxially with the cathode. Efficient stirring was provided by a magnetic stirrer consisting of a bar of soft iron sealed in a Pyrex glass shell activated by a rotating magnet mounted on the end of a motor shaft below the 250-cc. beaker which served as the electrolysis cell. (This device is obtainable from A. H. Thomas Co., Philadelphia.) A saturated calomel electrode was used to control the cathode potential, and the tip of the salt bridge was placed as close as possible to the outside surface of the cathode near its middle.

The electrolyses were performed by so adjusting the total e.m.f. applied to the cell that the potential of the cathode versus the saturated calomel electrode attained the desired value, which was maintained as electrolysis proceeded by suitable readjustment (usually decrease) of the applied e.m.f. The electrical circuit used which has been described (*6*, *7*), performs this function automatically and maintains the cathode potential to within ±0.02 volt of any desired value without any attention. Not more than 5 minutes of the operator's time is required for an electrolytic separation with this automatic apparatus, and the total elapsed time is usually less than 45 minutes. A manually operated circuit of the type described by Sand (*12*) can also be used, but it requires constant attention.

When the electrolysis was complete (5 to 10 minutes after the current fell to a small constant value) the stirrer was stopped, the beaker was lowered from the electrodes with the circuit still connected, and the electrodes were washed with a small amount of water from a wash bottle. If lead has been deposited on the cathode the washing should be done quickly with a minimal amount of water, because appreciable amounts of lead are dissolved by prolonged washing (*7*). Since no more than 2 or 3 cc. of the original 200 cc. of solution electrolyzed adheres to the electrodes, and since the accuracy of the subsequent polarographic analysis is of the order of 1%, a single washing of the electrode suffices. The combined residual solution and washings were prepared for polarographic analysis as described below under the separate determinations.

Polarograms were recorded with a Sargent-Heyrovský Model XI polarograph, whose recording galvanometer was calibrated as previously described (*3*). The polarographic cell was placed in a water thermostat at 25° C.

The dropping electrode assembly, including a stop-clock device which automatically measures the rate of flow of mercury, has been described (*5*). Preliminary measurements, in which accurate values of half-wave potentials were desired, were made with the usual H-type cell with saturated calomel anode (*3*). In subsequent determinations of nickel and zinc in an ammoniacal supporting electrolyte a length of lead wire (No. 18) wrapped in the form of a helix directly on the dropping electrode capillary served as anode. The potential of this lead anode in a solution containing 0.2 *M* ammonium ion, 1 *M* ammonia, and 0.1 *M* sulfite ion is about −0.68 volt *vs.* the S.C.E. The anode reaction is $Pb + 2OH^- = Pb(OH)_2 + 2e$, and since lead hydroxide is very insoluble in ammoniacal media no appreciable concentration of lead ion is produced in the solution.

For determination of tin in a supporting electrolyte containing 4 *M* ammonium chloride and 1 *M* hydrochloric acid, and for determination of lead in 1 *M* sodium hydroxide, a silver wire anode wrapped in a helix on the dropping electrode was used (*5*). In 4 *M* ammonium chloride–1 *M* hydrochloric acid the potential of the silver anode is approximately −0.1 volt, and in 1 *M* sodium hydroxide −0.2 volt, *vs.* the saturated calomel electrode.

In the determination of nickel and zinc in ammoniacal medium, sulfite ion (0.1 *M*) was added to the solutions to remove oxygen. In addition to its convenience, sulfite ion removes oxygen more effectively than nitrogen or hydrogen gas. In these determinations a small (10- to 25-cc.) Erlenmeyer flask served as the polarographic cell. The use of sulfite to remove oxygen, and of the lead or silver wire anodes, constitutes the simplest possible technique, and it is very well suited to rapid routine analysis.

Concentrations were computed from the relation $C = i_d/Im^{2/3}t^{1/6}$ millimoles per liter, where $i_d$ is the observed diffusion current (microamperes), $I$ is the diffusion current constant, $m$ is the rate of flow of mercury (mg. per second), and $t$ is the drop time (*4*). The use of this relation, with previously determined values of diffusion current constants, eliminates the calibration of each dropping electrode with known concentrations of the substance being determined. The pertinent diffusion current constants at 25° C. determined in this investigation are summarized in Table I. In using these data it should be borne in mind that the above relation fails when the drop time is less than about 1 second.

## LEAD AND TIN

A suitable size of sample is dissolved in hydrochloric acid with the aid of the minimal amount of nitric acid required to effect complete solution. The solution is diluted and treated with hydrazine dihydrochloride as an anodic depolarizer, and the copper (and antimony) is removed by electrolysis with the potential of the platinum cathode maintained constant at −0.35 volt *vs.* the saturated calomel electrode. In the deposition of 1 gram of copper from a volume of about 200 cc. the initial current was usually about 8 amperes, and it decreased to about 0.02 ampere within about 45 minutes. In agreement with the experience of Diehl and Brouns (*1*) it was found that the deposition of metallic copper on the cathode proceeds slowly at first, and during the initial stage of electrolysis reduction of cupric ion to a chloride complex of the cuprous state appears to be the predominant cathode reaction. Reduction to the cuprous state is almost complete after a few minutes and deposition of metallic copper then proceeds rapidly to completion. Diehl and Brouns (*1*) recommended the use of a 1 to 1.5 *M* hydrochloric acid solution for the separation of copper from tin, but the writer obtained much better deposition when the concentration of hydrochloric acid was kept just large enough to prevent hydrolysis of stannic ion, not over 0.5 *M*. With this minimal concentration of hydrochloric acid the complications observed by Diehl and Brouns (*1*) in more concentrated chloride solution were not encountered, the presence or absence of tin was immaterial, and antimony was completely deposited with the copper. The potential should not be allowed to exceed about −0.4 volts, as otherwise lead and tin may deposit, and it should be at least −0.3 volt to obtain rapid deposition of copper. The solution remaining after the electrolysis, which contains the tin in the stannic state, is diluted to a known volume and separate aliquot portions are taken for the determination of lead and tin.

Lead is determined in 1 *M* sodium hydroxide as supporting electrolyte; in this medium the half-wave potential of the plumbite ion is −0.76 volt *vs.* the saturated calomel electrode and the wave characteristics are excellent (*4*). Since stannic tin does not produce a wave in this solution (*4*), nickel and iron are precipitated, and the half-wave potential of the zincate ion is −1.50 volt,

### Table I. Pertinent Half-Wave Potentials and Diffusion Current Constants

Temperature = 25° C. The half-wave potentials are referred to the saturated calomel electrode. The diffusion current constants correspond to the observed diffusion current in microamperes, when the concentration is 1 millimolar, and when the value of $m^{2/3}t^{1/6}$ is 1 mg.$^{2/3}$ sec.$^{-1/2}$. All solutions contained 0.005% gelatin as a maximum suppressor.

| Metal | Supporting Electrolyte | $E_{1/2}$ Volts | $I$ |
|---|---|---|---|
| Lead | 1 *M* NaOH | −0.76 | 3.40 |
| | 4 *M* $NH_4Cl$ + 1 *M* HCl | −0.52 | 3.52 |
| Tin | 4 *M* $NH_4Cl$ + 1 *M* HCl | −0.25 | 2.84[a] |
| | | −0.52 | 3.49[b] |
| | | | 6.33[c] |
| Nickel | 0.2 *M* $NH_4Cl$ + 1 *M* $NH_3$ | −1.06 | 3.54 |
| | 1 *M* $NH_4Cl$ + 1 *M* $NH_3$ | −1.09 | 3.56 |
| | 3 *M* $NH_4Cl$ + 1 *M* $NH_3$ | −1:12 | 3.33 |
| Zinc | 0.2 *M* $NH_4Cl$ + 1 *M* $NH_3$ | −1.33 | 3.78 |
| | 1 *M* $NH_4Cl$ + 1 *M* $NH_3$ | −1.33 | 3.82 |
| | 3 *M* $NH_4Cl$ + 1 *M* $NH_3$ | −1.36 | 3.94 |

[a] First wave.
[b] Second wave.
[c] Total double wave.

very small amounts of lead can be determined without interference from the other metals. The amounts of nickel and iron present in copper-base alloys are relatively small, and usually the hydroxides of these metals need not be filtered off. Curiously enough it was found that sulfite (0.1 *M*) does not remove oxygen efficiently from sodium hydroxide solutions that contain lead; apparently the plumbite ion inhibits the oxygen-sulfite reaction, and hence nitrogen or hydrogen must be used.

The polarogram of this solution also includes the wave of zincate ion at −1.50 volt *vs.* the saturated calomel electrode, and, provided the amount of lead does not exceed the amount of zinc, this wave might be used for the determination of zinc. However, the characteristics of the zincate wave leave much to be desired and the writer prefers the determination of zinc in ammoniacal medium in conjunction with the nickel determination.

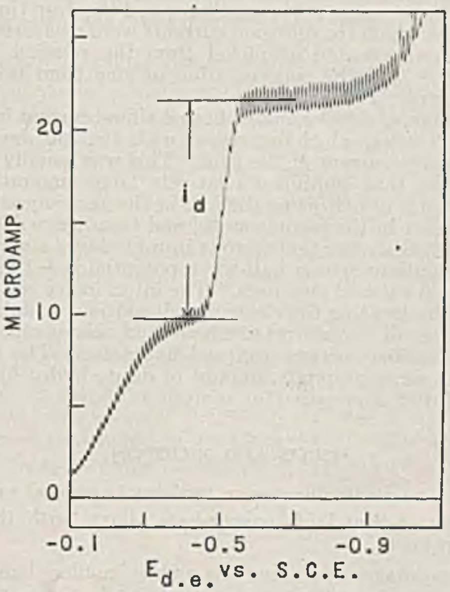

**Figure 1. Typical Polarogram of 2.08 Millimolar Stannic Tin in 4 M Ammonium Chloride, 1 M Hydrochloric Acid, and 0.005 % Gelatin, Showing Method of Measuring Diffusion Current**

Tin is determined in a supporting electrolyte containing 4 *M* ammonium chloride and 1 *M* hydrochloric acid. In this medium stannic tin produces a double wave, corresponding to stepwise reduction first to the stannous state and then to the metal, with half-wave potentials of −0.25 and −0.52 volt *vs.* the saturated calomel electrode (*9*). The first diffusion current is not completely developed before the second wave begins, but the total diffusion current is very well defined (see Figure 1). The height of the first wave is 45% that of the total double wave, instead of 50% as it would be if the diffusion current were completely developed, but this creates no difficulty because the proportion is constant regardless of the concentration of the tin. Hence either the first wave, the second wave alone, or the total double wave may be measured; the diffusion current constants, $i_d/(Cm^{2/3}t^{1/6})$, at 25° are listed in Table I. Since the measurement of either the first wave or total wave requires correction for the residual current, which must be separately determined because the first wave starts from zero applied e.m.f., the writer prefers measurement of the second wave. The half-wave potential of lead in this supporting electrolyte is virtually coincident with that of the second stage of the reduction of the chlorostannate ion, and hence the second wave includes a diffusion current due to lead for which correction must be applied. As the amount of lead in a copper-base alloy seldom exceeds the amount of tin, and usually is less, such a correction is not as objectionable as it might otherwise be.

The method of applying this correction is best illustrated by a typical example. Aliquot samples (50 cc.) were used for each determination and in each case were finally diluted to 100 cc. in the appropriate supporting electrolyte. The observed diffusion current of lead in 1 *N* sodium hydroxide was 2.34 microamperes with $m^{2/3}t^{1/6} = 1.57$, and the diffusion current of the second wave in 4 *M* ammonium chloride–1 *M* hydrochloric acid was 7.10 microamperes with $m^{2/3}t^{1/6} = 1.60$. From the data in Table I the diffusion current constant of lead in 4 *M* ammonium chloride–1 *M* hydrochloric acid is seen to be somewhat larger than in 1 *M* sodium hydroxide, the ratio being $3.52/3.40 = 1.036$. The contribution of lead to the second wave in the former medium was thus $2.34 \times 1.036 \times 1.60/1.57 = 2.47$ microamperes, and the diffusion current due to tin was $7.10 - 2.47 = 4.63$ microamperes. The concentration of lead was $2.34/(3.40 \times 1.57) = 0.438$ millimolar, and that of tin was $4.63/(3.49 \times 1.60) = 0.829$ millimolar.

For percentages of tin and lead between about 0.1 and 10, a 0.5- to 1-gram sample is suitable, and it is convenient to dilute the residual solution after removal of the copper to 250 cc. and take 50-cc. aliquots for the polarographic determinations.

PROCEDURE. Dissolve a 0.5- to 1-gram sample of the alloy in a warm mixture of 6 cc. of 12 *N* hydrochloric acid, 4 cc. of water, and 1 cc. of concentrated nitric acid in a Kjeldahl flask. Dilute to about 50 cc. and boil briefly to remove oxides of nitrogen and chlorine. Transfer the solution to a 250-cc. beaker, add 2 grams of pure hydrazine dihydrochloride, dilute to about 200 cc., and electrolyze with the potential of the platinum cathode at −0.35 volt *vs.* the saturated calomel electrode. Transfer the residual solution to a 250-cc. volumetric flask, cool to room temperature, and dilute to the mark. The final solution will be about 0.4 *N* in respect to hydrochloric acid.

Transfer a 50-cc. aliquot (corresponding to one fifth of the sample) to a 100-cc. volumetric flask, add 24 cc. of 5 *N* sodium hydroxide (or 4.8 grams, 0.12 mole, of the solid) and 2.5 cc. of 0.2% gelatin solution, and dilute to the mark. Transfer a portion of the solution to the polarographic cell in a water thermostat at 25.0° ± 0.2° C., remove dissolved air with nitrogen or hydrogen, record the polarogram, and measure the diffusion current of the lead. Determine the *m*-value of the dropping electrode, measure the drop time at the potential at which the diffusion current was measured, and compute the concentration of lead from the relation $C = i_d/3.40\, m^{2/3}t^{1/6}$ (see Table I).

Transfer another 50-cc. aliquot to a 100-cc. volumetric flask, add 21 grams (0.4 mole) of solid ammonium chloride, 6.6 cc. (0.08 mole) of 12 *N* hydrochloric acid, and 2.5 cc. of 0.2% gelatin solution, and dilute to about 90 cc. Shake until the ammonium chloride is dissolved, warm back to room temperature, and dilute to the mark. Transfer a portion of the solution to the polarographic cell in a water thermostat at 25.0° ± 0.2° C., remove dissolved air with nitrogen or hydrogen, record the polarogram, and measure the diffusion current of the second wave (see Figure 1). Apply the correction for lead, and compute the concentration of tin, as described above.

The concentrations of the components of the supporting electrolytes are not critical, but should be within about 10% of the values specified.

### NICKEL AND ZINC

A sample of the alloy is dissolved, and the copper is removed electrolytically exactly as in the determination of lead and tin. After most of the copper has deposited (about 15 minutes), the potential is increased to −0.70 volt *vs.* the saturated calomel electrode to deposit tin and lead. The initial current at −0.70 volt was usually of the order of 3 to 5 amperes, and ordinarily, it decreased to a constant value of about 1 ampere after about 15 minutes. The current at −0.70 volt does not decrease to zero because hydrogen ion is reduced at this potential. To ensure complete deposition of tin and lead the electrolysis should be continued for about 10 minutes after the current decreases to a constant value. Since tin and lead are precipitated in the ammoniacal supporting electrolyte used for the determination of nickel and zinc it is not essential that they be removed completely; in fact, if the amount of tin and lead present does not greatly exceed the amount of nickel or zinc (whichever is the smaller), they need not be removed at all. A large precipitate of the hydrous oxides of tin and lead is objectionable because it may coprecipitate significant amounts of nickel and zinc.

A systematic study was made of the influence of the concentration of ammonium chloride and ammonia on the nickel and zinc waves; the effect of various concentrations of ammonium chloride at a constant concentration (1 *M*) of ammonia is shown by the data in Table I. Increasing the concentration of ammonium chloride shifts the half-wave potentials of both metals to slightly more negative values, and since the half-wave potential of nickel is shifted more than that of zinc, the separation of the waves is less satisfactory in 3 *M* ammonium chloride than in 0.2 *M*. Even very large changes in the concentration of the ammonium chloride produce relatively small changes in the diffusion current constants, so that the adjustment of the concentration of ammonium chloride is not at all critical. Increasing the concentration of ammonia from 0.1 to 5 *M* at a constant concentration (0.2 *M*) of ammonium chloride also decreases the separation of the waves, but causes only slight changes in the diffusion current constants. The optimum supporting electrolyte is one that contains about 0.2 *M* ammonium chloride and 1 *M* ammonia; in this medium the two waves are so well separated that there is no difficulty in determining nickel in the presence of a fiftyfold or even larger excess of zinc (see Figure 2).

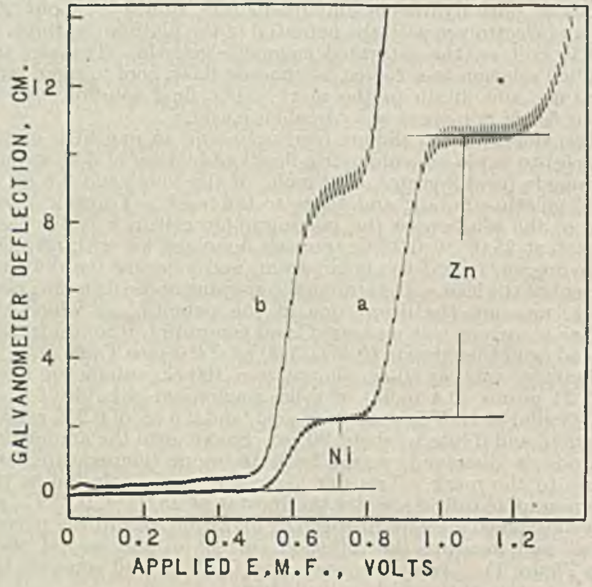

Figure 2. Polarograms of Nickel and Zinc

Obtained in analysis of Bureau of Standards cast bronze No. 52b, containing 0.72% nickel and 2.96% zinc. Supporting electrolyte contained 0.2 *M* ammonium chloride, 1 *M* ammonia, 0.1 *M* sodium sulfite, and 0.005% gelatin. A lead wire anode was used. Curve *a* was recorded with a galvanometer sensitivity of 0.748 microampere per cm., and curve *b* with a sensitivity of 0.187 microampere per cm. to magnify the nickel wave.

Procedure. Dissolve a 0.5- to 1-gram sample, and prepare the solution for electrolysis, exactly as for determination of lead and tin. Electrolyze first at a potential of −0.35 volt *vs.* the saturated calomel electrode, and after most of the copper has deposited increase the potential to −0.70 volt to deposit tin and lead. Continue the electrolysis for about 10 minutes after the current decreases to a constant value. Transfer the residual solution to a 250-cc. volumetric flask and dilute to the mark.

Transfer a 50-cc. aliquot to a 100-cc. volumetric flask, add 8 cc. of 15 *M* ammonia, 1 to 1.5 grams (approximately 0.01 mole) of pure anhydrous sodium sulfite to remove oxygen, and 2.5 cc. of 0.2% gelatin, and dilute to the mark. Place a portion of the solution in a polarographic cell in a water thermostat at 25.0° ± 0.2° C.—e.g., a 15-cc. Erlenmeyer flask if a lead wire anode wrapped on the dropping electrode is used—and record the polarogram. If the amount of nickel is much smaller than that of zinc, a second polarogram should be recorded at an increased sensitivity to magnify the nickel wave to a value large enough for accurate measurement. Measure the two diffusion currents (see Figure 2), the *m*-value of the capillary, and the drop times at the potentials at which the diffusion currents were measured. Compute the concentration of nickel from the relation $C = i_d/3.54\, m^{2/3}\, t^{1/6}$, and the concentration of zinc from the relation $C = i_d/3.78\, m^{2/3}\, t^{1/6}$.

Table II. Analysis of Bureau of Standards Copper-Base Alloys

| Sample and Bureau of Standards Analyses | Polarographic Analyses, % Pb | Sn | Ni | Zn |
|---|---|---|---|---|
| Phosphor bronze 63a<br>Cu 78.48, Pb 8.92, Sn 9.76, Ni 0.32, Zn 0.61, Sb 0.49, Fe 0.52, P 0.58, S 0.11 | 9.04 | 9.84 | 0.32 | 0.60 |
| Cast bronze 52b<br>Cu 88.26, Pb 0.01, Sn 8.00, Ni 0.72, Zn 2.96, Fe 0.034 | 0.02 | 7.82 | 0.70 | 2.96 |
| Ounce metal 124a<br>Cu 85.05, Pb 4.86, Sn 4.81, Ni 0.001 Zn 5.25, Fe 0.004 | 4.84 | 5.00 | .. | 5.29 |
| Brass 37c<br>Cu 70.07, Pb 0.97, Sn 0.96, Ni 0.58, Zn 27.22, Fe 0.17 | 0.92 | 0.97 | 0.59 | 27.8 |

Polarograms of some samples showed a final current increase at about −1.5 volts, which interfered with the full development of the diffusion current of the zinc. This was usually observed with samples that contained relatively large amounts of iron. In the presence of hydrazine the iron in the electrolyzed solution will be present in the ferrous state, and from the work of Voriskova (*17*) it is known that ferrous iron produces a wave in ammoniacal solutions whose half-wave potential is −1.49 volts *vs.* the saturated calomel electrode. The interference can easily be eliminated by treating the electrolyzed solution, or an aliquot of it, with 5 cc. of concentrated nitric acid, and evaporating to dryness to oxidize ferrous iron and hydrazine. The residue is taken up in an appropriate amount of dilute hydrochloric acid, and the solution is prepared for analysis as above.

## RESULTS AND DISCUSSION

The foregoing procedures were tested with several representative Bureau of Standards copper-base alloys, with the results shown in Table II.

With percentages of the various metals smaller than about 5, the polarographic analyses agree with the bureau's values about as closely as the latter are known, and even with larger percentages the agreement is satisfactory. For determining fractions of a per cent of these metals, especially zinc, the polarographic method is probably more reliable than the classical procedures, but it cannot compete with the classical methods, except from the standpoint of convenience, for amounts larger than about 10%. Determinations of the four metals can be completed within about 2.5 hours by the polarographic procedure.

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# Calculation of Specific Dispersion of Pure Hydrocarbons and Petroleum Fractions

M. R. LIPKIN AND C. C. MARTIN, Sun Oil Company Experimental Division, Norwood, Pa.

**An equation is presented for the calculation of specific dispersion of pure hydrocarbons and petroleum fractions from common physical properties, density, refractive index, and approximate molecular weight, which can be estimated from mid-boiling point and density or viscosities at 100° and 210° F. This makes it possible to obtain specific dispersion on a highly colored sample or in a laboratory where no instrument is available for the direct measurement of dispersion. The accuracy of the calculated specific dispersion for petroleum fractions is comparable with the accuracy of measurements obtained on the Abbe instrument, ± 3 units.**

THIS paper continues the general investigation in this laboratory of the interrelationship of physical properties and the relation of these properties to hydrocarbon structure (*4*, *6–12*, *15*, *18*), and is particularly concerned with the calculation of specific dispersion of hydrocarbons from easily determined physical properties. This permits the use of specific dispersion by many laboratories which do not have equipment for experimentally determining specific dispersion, and extends the use of specific dispersion to highly colored samples on which it is difficult or impossible to obtain a direct measurement.

Specific dispersion is the difference between the refractive indices of a sample at two different wave lengths of light divided by the density of the sample. Most literature data are reported in terms of the *F* and *C* lines of hydrogen, although experimentally it is often more convenient to use other wave length combinations (*16*). In this paper specific dispersion, δ, is defined as:

$$\delta = \frac{n_F - n_C}{\text{d}} \times 10^4 \qquad (1)$$

where $n_F$ = refractive index for the *F* line of hydrogen at 20° C.
$n_C$ = refractive index for the *C* line of hydrogen at 20° C.
d = density at 20° C.

For hydrocarbons specific dispersion is a unique physical property because it is nearly constant for paraffins and naphthenes and is variable with the number of double bonds and their position in an unsaturated hydrocarbon molecule (*2*, *3*, *17*). Accurate determination of specific dispersion requires considerable skill and precision apparatus. Moreover, determination of this property on samples which are highly colored is very difficult and often impossible with the instruments available.

The application of specific dispersion to analysis of hydrocarbons has been seriously handicapped by the difficulty in obtaining this measurement. Early investigators attempted to develop atomic constants for the calculation of specific dispersion. More recently Thorpe and Larsen (*17*) have developed a method dependent on a knowledge of structure which limits the calculation to pure hydrocarbons whose structure is known. No correlation has been developed which permits calculation of specific dispersion for petroleum fractions.

In an effort to correlate the physical properties of hydrocarbons, Lipkin and Martin (*11*) have recently developed Equation 2 for the calculation of the sodium *D* refractive index of paraffins and naphthenes at 20° C.:

$$n_{\text{calcd.}} = \frac{69.878\text{d} - 0.4044A\text{d} - 0.797A + 136.566}{5.543\text{d} - 0.746A + 126.683} \qquad (2)$$

where

$A$ = $-10^6$ × the temperature coefficient of density, which is obtained from the approximate molecular weight, Table I (*12*). Molecular weight is obtained from boiling point and density (*15*) or the kinematic viscosity at 100° and 210° F. (*4*).

If double bonds are present, the calculated refractive index will be lower than the observed refractive index and the difference is a linear function of the specific dispersion. The method has the advantage over earlier methods of being applicable to petroleum fractions as well as pure hydrocarbons.

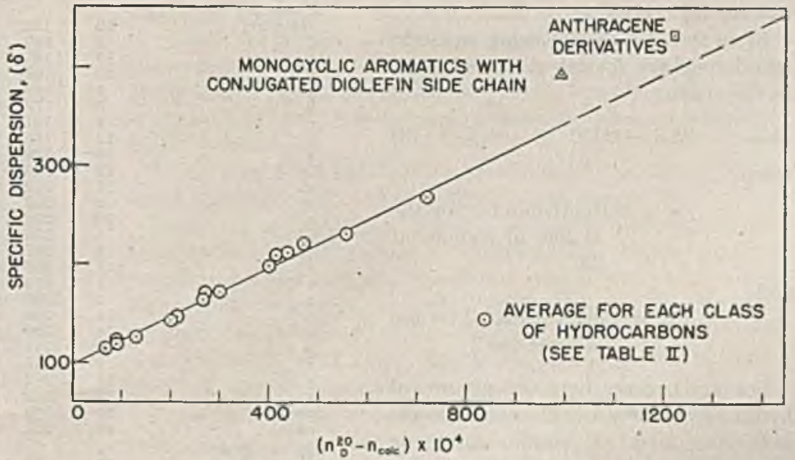

Figure 1

Table I. Effect of Unlike Additivities of Physical Properties on Calculation of Specific Dispersion

| | % Saturate Volume | % Saturate Weight | 50% B.P., ° C. | $d^{20}_4$ | $n^{20}_D$ | δ | Mol. Wt. from B.P.−d | $10^4 \times$ n − $n_{\text{calcd.}}$ | $\delta_{\text{calcd.}}$ | $\delta_{\text{calcd.}} - \delta$ | $\delta_f$[a] | $\delta_{\text{calcd.}} - \delta_f$ |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Saturate | 100 | 100 | 113 | 0.7069 | 1.3988 | 97.9 | 113 | 1 | 98.5 | 0.6 | | |
| Blend | | | | | | | | | | | | |
| 1 | 80.0 | 76.6 | 116 | 0.7376 | 1.4171 | 114.4 | 112 | 59 | 112.8 | −1.6 | 112.1 | 0.7 |
| 2 | 60.0 | 55.2 | 123 | 0.7687 | 1.4357 | 130.2 | 112 | 117 | 127.0 | −3.2 | 126.4 | 0.6 |
| 3 | 40.0 | 35.3 | 130 | 0.7993 | 1.4540 | 144.3 | 112 | 174 | 140.9 | −3.4 | 140.6 | 0.3 |
| 4 | 20.0 | 17.0 | 139 | 0.8312 | 1.4733 | 157.2 | 113 | 235 | 155.9 | −1.3 | 154.0 | 1.0 |
| Aromatic | 0 | 0 | 148 | 0.8629 | 1.4923 | 169.1 | 115 | 293 | 170.1 | 1.0 | | |

[a] Fictitious value calculated from δ of saturate and δ of aromatic assuming volume % additivity.

### Table II. Agreement of Pure Compound Data

(Averaged by Group)

| | No. of Compounds | $10^4 \times (n - n_{\text{calcd.}})$ | $\delta_{\text{calcd.}}$ | $\delta$ | $\delta_{\text{calcd.}} - \delta$ |
|---|---|---|---|---|---|
| Noncyclics | | | | | |
| Olefins | 120 | 86 | 119 | 122 | − 3 |
| Diolefins, conjugated | 21 | 469 | 213 | 219 | − 6 |
| Diolefins, nonconjugated | 8 | 198 | 147 | 142 | 5 |
| Triolefins | 3 | 411 | 199 | 209 | −10 |
| Acetylenes | 9 | 64 | 114 | 113 | 1 |
| Monocyclics | | | | | |
| Aromatics | 47 | 264 | 163 | 163 | 0 |
| Aromatics + olefin side chain | 11 | 436 | 205 | 210 | − 5 |
| Naphthenes + olefin side chain | 5 | 126 | 129 | 126 | 3 |
| Cyclo-olefins | 41 | 88 | 120 | 118 | 2 |
| Cyclo-olefins + olefin side chain | 5 | 210 | 150 | 146 | 4 |
| Cyclodiolefins | 12 | 266 | 164 | 171 | − 7 |
| Cyclodiolefins + olefin side chain | 11 | 394 | 195 | 197 | − 2 |
| Polycyclics | | | | | |
| Alkyl naphthalenes | 20 | 553 | 234 | 231 | 3 |
| Miscellaneous dicyclics | 32 | 296 | 171 | 170 | 1 |
| Miscellaneous tricyclics | 8 | 718 | 274 | 266 | 8 |
| | | Average deviation per compound | | | 7 |
| | | Average deviation per group | | | 4 |
| | | Deviation of average | | | 0 |
| Not averaged | | | | | |
| Aromatics + conjugated diolefin side chain | 4 | 992 | 345 | 393 | −48 |
| Anthracenes | 5 | 1373 | 435 | 506 | −71 |

## DERIVATION OF EQUATION

The difference between the observed refractive index and the refractive index calculated by Equation 2 was plotted against specific dispersion, as shown in Figure 1, for all olefinic, acetylenic, and aromatic type pure hydrocarbons on which specific dispersion data are reported. A best straight line was drawn originating at 98.3 specific dispersion for zero difference in refractive index. The value 98.3 is considered to be the average specific dispersion of paraffin and naphthene hydrocarbons (*2*, *17*).

From this line the following equation was derived for the calculation of specific dispersion:

$$\delta_{\text{calcd.}} = 98.3 + 2450\,(n - n_{\text{calcd.}}) \qquad (3)$$

where

$n$ = refractive index for the $D$ line of sodium at 20°

and

$n_{\text{calcd.}}$ = value calculated by use of Equation 2

For pure hydrocarbons and mixtures of hydrocarbons of nearly the same specific dispersion, such as paraffin-naphthene mixtures or most aromatic extracts, this equation is satisfactory. If $(n - n_{\text{calcd.}})$ is negative the sample can be considered to consist of saturated hydrocarbons and may be assigned a $\delta$ of 98.3.

For mixtures such as ordinary petroleum fractions containing hydrocarbons of appreciably different specific dispersions, Equation 3 will give low results and is modified to include a small additive correction:

$$\delta_{\text{calcd.}} = 98.3 + 2450\,(n - n_{\text{calcd.}}) + C \qquad (4)$$

where $C$ = a small correction term roughly dependent upon the average molecular weight of the mixture. The following table of approximate corrections, derived from the data in Table IV, may be used:

### Correction to Be Used for Petroleum Fractions

| Molecular Weight | $C$ |
|---|---|
| 100 | 2 |
| 200 | 5 |
| 300 | 7 |
| 400 | 8 |

Low results for mixtures are due to the fact that the physical properties used in this calculation and the property calculated are not additive on the same basis. Molecular weight is additive on a mole basis and density on a volume basis in the absence of volume change on mixing. Refractive index is more nearly additive on a volume basis and specific dispersion more nearly additive on a weight basis.

Table I demonstrates this effect of difference in additivities of properties. In this example the authors have blended in various proportions an aromatic stock and a paraffin-naphthene stock of approximately equal molecular weight. When blended these stocks show less than 0.2% volume change on mixing, which is a negligible factor in these calculations. Specific dispersions of the blends calculated by Equation 3 are lower than the experimental specific dispersions, but agree well with fictitious values calculated on a volume basis from the specific dispersions of the paraffin-naphthene stock and the aromatic stock. In most petroleum fractions the situation is further aggravated by the fact that the paraffin-naphthene component is significantly higher in molecular weight than the aromatic component.

It is emphasized that the correction term is only approximate and intended for the types of hydrocarbon fractions normally

### Table III. Agreement of Aromatic Extracts, Pulfrich Refractometer Data

| | Boiling Range, ° C. | 50% B.P., ° C. | $d_4^{20}$ | $n_D^{20}$ | Viscosity, Centistokes 100° F. | 210° F. | $\delta$ | $10^4 \times n - n_{\text{calcd.}}$ | $\delta_{\text{calcd.}} - \delta$ |
|---|---|---|---|---|---|---|---|---|---|
| 6c straight run fraction | 10 | 132 | 0.8611 | 1.4942 | ... | ... | 178 | 339 | 3 |
| d | 2 | 140 | 0.8649 | 1.4969 | ... | ... | 180 | 342 | 2 |
| e | 15 | 145 | 0.8683 | 1.4984 | ... | ... | 178 | 338 | 3 |
| f | 10 | 162 | 0.8652 | 1.4964 | ... | ... | 173 | 314 | 2 |
| g | 4 | 168 | 0.8695 | 1.5000 | ... | ... | 174 | 328 | 5 |
| h | 7 | 173 | 0.8748 | 1.5029 | ... | ... | 174 | 331 | 5 |
| i | 4 | 181 | 0.8757 | 1.5023 | ... | ... | 172 | 316 | 4 |
| j | 12 | 185 | 0.8755 | 1.4998 | ... | ... | 165 | 280 | 2 |
| k | 10 | 198 | 0.8838 | 1.5050 | ... | ... | 167 | 297 | 4 |
| l | 12 | 209 | 0.9141 | 1.5257 | ... | ... | 187 | 376 | 3 |
| m | 17 | 223 | 0.9027 | 1.5134 | ... | ... | 166 | 287 | 3 |
| n | 2 | 233 | 0.9529 | 1.5556 | ... | ... | 217 | 506 | 5 |
| o | 19 | 244 | 0.9384 | 1.5401 | ... | ... | 193 | 400 | 3 |
| p | 1 | 254 | 0.9442 | 1.5460 | ... | ... | 197 | 432 | 7 |
| q | 6 | 257 | 0.9648 | 1.5675 | ... | ... | 232 | 564 | 4 |
| r | 11 | 266 | 0.9550 | 1.5535 | ... | ... | 208 | 457 | 2 |
| s | 7 | 274 | 0.9538 | 1.5527 | ... | ... | 207 | 448 | 1 |
| t | 4 | 280 | 0.9590 | 1.5585 | ... | ... | 215 | 483 | 2 |
| u | 11 | 288 | 0.9583 | 1.5546 | ... | ... | 206 | 443 | 1 |
| v | 14 | 300 | 0.9557 | 1.5497 | ... | ... | 197 | 399 | − 1 |
| w | 8 | 311 | 0.9617 | 1.5523 | ... | ... | 198 | 396 | − 3 |
| x | 7 | 318 | 0.9648 | 1.5527 | ... | ... | 195 | 385 | − 2 |
| y | 21 | 332 | 0.9706 | 1.5561 | ... | ... | 197 | 389 | − 3 |
| z | 18 | 352 | 0.9778 | 1.5619 | ... | ... | 204 | 412 | − 5 |
| 6aa | 80 | 146 | 0.8660 | 1.4943 | ... | ... | 176 | 328 | 3 |
| ba | 90 | 232 | 0.9231 | 1.5330 | ... | ... | 193 | 394 | 2 |
| 23a catalytic fraction | 15 | 136 | 0.8638 | 1.4962 | ... | ... | 180 | 343 | 2 |
| b | 13 | 143 | 0.8739 | 1.5019 | ... | ... | 179 | 353 | 6 |
| c | 1 | 163 | 0.8650 | 1.4973 | ... | ... | 174 | 322 | 3 |
| d | 1 | 168 | 0.8735 | 1.5050 | ... | ... | 177 | 361 | 10 |
| e | 1 | 172 | 0.8774 | 1.5054 | ... | ... | 178 | 349 | 6 |
| f | 2 | 183 | 0.8700 | 1.5003 | ... | ... | 170 | 315 | 5 |
| 7a fuel | 110 | 198 | 0.9115 | 1.5292 | ... | ... | 200 | 431 | 4 |
| 8a | 150 | 185 | 0.8873 | 1.5088 | ... | ... | 177 | 333 | 3 |
| 9a | 80 | 203 | 0.8876 | 1.5064 | ... | ... | 168 | 292 | 2 |
| 24a thermal fuel oil | ... | ... | 0.9617 | 1.5535 | 28.7 | 3.97 | 200 | 381 | −9 |
| b | ... | ... | 1.0212 | 1.6069 | 77.7 | 5.71 | 262 | 669 | 0 |
| c | ... | ... | 1.0471 | 1.6318 | 118.9 | 6.42 | 296 | 813 | 1 |
| d | ... | ... | 1.0617 | 1.6452 | 103.6 | 5.85 | 310 | 891 | 7 |
| 20a straight run oil | ... | ... | 1.0055 | 1.5727 | 235.0 | 8.9 | 195 | 387 | − 2 |
| b | ... | ... | 0.9968 | 1.5606 | 869.1 | 14.9 | 172 | 298 | − 1 |
| c | ... | ... | 0.9661 | 1.5354 | 482.8 | 13.6 | 144 | 169 | − 4 |
| | | | | | | | Average deviation | | 3 |
| | | | | | | | Deviation of average | | 2 |
| | | | | | | | Maximum deviation | | 10 |

Table IV. Agreement of Petroleum Fractions, Pulfrich Refractometer Data

| | | Magnitude Boiling Range, ° C. | 50% B.P., ° C. | $d_4^{20}$ | $n_D^{20}$ | Viscosity, Centistokes 100° F. | Viscosity, Centistokes 210° F. | Av. Mol. Wt. | $\delta$ | $10^4 \times n - n_{\text{calcd.}}$ | $C$ | $\delta_{\text{calcd.}}$ | $\delta_{\text{calcd.}} - \delta$ |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 1 | Straight run gasoline | 125 | 120 | 0.7521 | 1.4199 | ... | ... | 112 | 107 | 26 | 2 | 107 | 0 |
| 2 | Catalytic gasoline | 130 | 108 | 0.7555 | 1.4253 | ... | ... | 104 | 122 | 79 | 2 | 120 | −2 |
| 3 | Thermal gasoline | 180 | 149 | 0.7910 | 1.4429 | ... | ... | 126 | 124 | 80 | 3 | 121 | −3 |
| 4a | Catalytic gasoline cut | 30 | 79 | 0.7183 | 1.4013 | ... | ... | 92 | 103 | 15 | 2 | 104 | 1 |
| 4b | Catalytic gasoline cut | 25 | 107 | 0.7752 | 1.4352 | ... | ... | 101 | 128 | 104 | 2 | 126 | −2 |
| 4c | Catalytic gasoline cut | 25 | 136 | 0.8159 | 1.4628 | ... | ... | 113 | 148 | 192 | 2 | 147 | −1 |
| 4d | Catalytic gasoline cut | 25 | 163 | 0.8388 | 1.4775 | ... | ... | 127 | 154 | 222 | 3 | 156 | 2 |
| 6a | Straight-run fuel cut | 75 | 132 | 0.7603 | 1.4242 | ... | ... | 118 | 107 | 28 | 3 | 108 | 1 |
| 6b | Straight-run fuel cut | 110 | 226 | 0.8143 | 1.4550 | ... | ... | 178 | 116 | 58 | 4 | 117 | 1 |
| 7 | Fuel | 140 | 216 | 0.8506 | 1.4785 | ... | ... | 164 | 140 | 151 | 4 | 139 | −1 |
| 8 | Fuel | 150 | 174 | 0.7718 | 1.4318 | ... | ... | 144 | 108 | 28 | 3 | 108 | 0 |
| 9 | Fuel | 90 | 198 | 0.8364 | 1.4585 | ... | ... | 152 | 106 | 19 | 4 | 107 | 1 |
| 10 | Thermal gas oil | 130 | 267 | 0.8549 | 1.4780 | ... | ... | 205 | 128 | 103 | 5 | 129 | 1 |
| 11 | Thermal gas oil | 120 | 236 | 0.9014 | 1.5079 | ... | ... | 170 | 157 | 229 | 4 | 158 | 1 |
| 12 | Catalytic gas oil | 130 | 266 | 0.8694 | 1.4907 | ... | ... | 201 | 146 | 171 | 5 | 145 | −1 |
| 13 | Catalytic gas oil | 140 | 267 | 0.8613 | 1.4811 | ... | ... | 202 | 130 | 109 | 5 | 130 | 0 |
| 14 | Straight-run gas oil | 140 | 263 | 0.8323 | 1.4652 | ... | ... | 205 | 120 | 70 | 5 | 120 | 0 |
| 15 | Straight-run gas oil | 110 | 283 | 0.8818 | 1.4836 | ... | ... | 215 | 114 | 42 | 5 | 114 | 0 |
| 16 | Lube oil | ... | ... | 0.9173 | 1.5060 | 22.1 | 3.60 | 300 | 128 | 92 | 7 | 128 | 0 |
| 17 | Lube oil | ... | ... | 0.9126 | 1.5028 | 22.4 | 3.69 | 308 | 125 | 78 | 7 | 124 | −1 |
| 18 | Lube oil | ... | ... | 0.9244 | 1.5098 | 46.3 | 5.34 | 332 | 130 | 93 | 7 | 128 | −2 |
| 19 | Lube oil | ... | ... | 0.9253 | 1.5105 | 61.6 | 6.17 | 347 | 129 | 93 | 7 | 128 | −1 |
| 20 | Lube oil | ... | ... | 0.9325 | 1.5152 | 104.7 | 8.0 | 362 | 133 | 107 | 8 | 133 | 0 |
| 21 | Lube oil | ... | ... | 0.9311 | 1.5144 | 150.7 | 9.9 | 387 | 131 | 101 | 8 | 131 | 0 |
| 22 | Lube oil | ... | ... | 0.9390 | 1.5186 | 470.8 | 17.5 | 426 | 132 | 104 | 8 | 132 | 0 |
| | | | | | | | | | | | | Average deviation | 1 |
| | | | | | | | | | | | | Deviation of average | 0 |
| | | | | | | | | | | | | Maximum deviation | −3 |

encountered in the petroleum industry. To obtain a more accurate correction term, it would be necessary to know the magnitude of difference in the physical properties and the relative concentrations of the components. This information is not generally available and would be difficult to obtain.

Table V. Agreement of Petroleum Fractions, Abbe Refractometer Data

(Averaged by Group)

| | No. of Fractions | Mol. Wt. | $\delta$ | $10^4 \times n - n_{\text{calcd.}}$ | $C$ | $\delta_{\text{calcd.}}$ | $\delta_{\text{calcd.}} - \delta$ |
|---|---|---|---|---|---|---|---|
| Petroleum fractions | | | | | | | |
| Kreulen (*5*), gas oils | 11 | 219 | 130 | 113 | 5 | 131 | 1 |
| Fenske (*1*), lube oils | | | | | | | |
| Penna. 180 neutral | 22 | 393 | 115 | 53 | 8 | 119 | 4 |
| Rodessa neutral | 16 | 396 | 107 | 49 | 8 | 118 | 11 |
| Midcontinent neutral 1 | 18 | 380 | 126 | 85 | 8 | 127 | 1 |
| Midcontinent neutral 2 | 18 | 366 | 126 | 89 | 8 | 128 | 2 |
| California neutral[a] | 17 | 303 | 137 | 136 | 7 | 139 | 2 |
| Gulf Coast neutral | 18 | 345 | 130 | 101 | 7 | 130 | 0 |
| | | Average deviation per fraction | | | | | 4 |
| | | Deviation of average per fraction | | | | | +3 |
| Extracts from lube oils | | | | | | | |
| Fenske (*1*) | | | | | | | |
| Bosco neutral extracts | 12 | | 135 | 145 | | 134 | −1 |
| Bosco neutral extracts | 11 | | 96 | −10 | | 98 | 2 |
| Bosco neutral, $H_2SO_4$, $AlCl_3$, and clay-treated fractions | 9 | | 106 | 49 | | 110 | 4 |
| Midcontinent 2 extracts | 4 | | 137 | 166 | | 139 | 2 |
| Midcontinent 2 extracts | 5 | | 92 | 12 | | 101 | 9 |
| Mair and Schicktanz (*13*) | | | | | | | |
| Midcontinent extracts | 7 | | 114 | 48 | | 110 | −4 |
| Midcontinent extracts | 17 | | 99 | −13 | | 98 | −1 |
| Mair and Willingham (*14*) | | | | | | | |
| Midcontinent extracts | 52 | | 175 | 302 | | 172 | −3 |
| Hydrogenated extracts | 15 | | 100 | −12 | | 98 | −2 |
| | | Average deviation per fraction | | | | | 4 |
| | | Deviation of average per fraction | | | | | −1 |

[a] Two fractions obviously in error omitted from tabulation.

## ACCURACY

Table II presents the data on 362 pure hydrocarbons of all types and degrees of unsaturation. The average deviation (without regard to sign) of the calculated specific dispersion is 7 units. Nine compounds have been omitted from this average because of their wide deviation from the average line, Figure 1. These compounds fall into two classes whose specific dispersion is extremely high, the anthracenes and aromatics with conjugated diolefin side chain. The calculated specific dispersions of these nine compounds are lower than the experimental values. The authors intend to make a further investigation of this deviation.

The averages for all other classes, including acetylenes and conjugated diolefins, scatter on both sides of the line as is demonstrated in Figure 1. The groups showing the larger numerical deviations are usually of higher specific dispersion, so that deviations considered on a percentage basis are about the same. Triolefins and other types which polymerize readily, and which are difficult to synthesize and analyze, show the poorest agreement with the equation.

These pure hydrocarbon data are obtained from the sources listed previously (*12*) and from Thorpe and Larsen (*17*).

Table III presents data obtained in this laboratory on aromatic extracts from petroleum. These fractions include straight-run, thermal, and catalytic materials of narrow and wide boiling range, from the gasoline to lube oil boiling ranges. Specific dispersions were obtained on the Pulfrich refractometer and are accurate within ±0.5 unit. The average deviation for 42 fractions is 3 units and the maximum deviation is 10 units.

Table IV presents data obtained in this laboratory on various petroleum fractions containing olefins, aromatics, paraffins, and naphthenes. For these materials it was necessary to calculate specific dispersions using the additive corrections because these fractions are mixtures of different hydrocarbon types. Average deviation for 25 fractions is 1 unit, maximum deviation is −3 units.

Table V shows literature data for 252 petroleum fractions on which dispersions have been determined with the Abbe-type refractometer. The average deviation is 4 units, which is comparable with the experimental accuracy of the data.

Nonhydrocarbons will, of course, affect the calculation, but are probably present in concentrations too small to be significant.

The data in Tables III and IV demonstrate that the specific dispersion of petroleum fractions may be calculated with an accuracy of ±3 units. This is comparable with experimental determination on the Abbe-type instrument which is, according to von Fuchs (*2*), accurate within 3 dispersion units.

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# Determination of Copper in Cast Iron and Steels with Quinaldic Acid

JOHN F. FLAGG and DON W. VANAS, Department of Chemistry, The University of Rochester, Rochester, N. Y.

**The method of Zan'ko and Butenko for the determination of copper in steel by precipitating with quinaldic acid has been investigated and extensively modified. Satisfactory results are obtained only after a reprecipitation of the copper quinaldate. The speed of the method may be increased by making a preliminary separation of copper by internal electrolysis, using an aluminum anode. Spectrographic studies showed precipitates to be of sufficient purity for reliable results. The method, as applied to Bureau of Standards steels, gave an accuracy of about 2 to 3% on samples containing 0.1% or more of copper, but less at lower percentages of copper. The precision is about the same as the accuracy.**

METHODS available for determining copper in cast iron and steel include hydrogen sulfide precipitation (*13*), direct electrolysis (*5, 10, 12, 15*), polarography (*9*), spectrographic methods (*18*), and precipitation with organic reagents. Among the reagents whose use as precipitants for copper has been recommended are salicylaldoxime (*7, 16*), benzotriazole (*2*), α-benzoinoxime (*8, 14, 17*), 5,7-dibromo-8-hydroxyquinoline (*19*), and quinaldic acid (*20*).

The method described in this paper employs quinaldic acid as the precipitant for copper. The method has been studied in some detail in order to obtain a clear picture of the conditions necessary for precipitation, the sources of interference, and, finally, its ultimate accuracy. (Studies were also made using 5,7-dibromo-8-hydroxyquinoline. The extreme insolubility of this reagent in water caused its precipitation, in many cases, along with the copper salt, and its further use was not investigated.)

Quinaldic acid was chosen as the precipitant because of its solubility in water and stability in solution, the definite composition of its salts and their easy filtration, and because information on the behavior of other quinaldates was available (*3*). The method of investigation has been to test the precipitation of copper under conditions similar to those encountered in steel analysis, and then to analyze Bureau of Standards steels.

## MATERIALS AND APPARATUS

Quinaldic acid was prepared by the method of Hammick (*6*) from quinaldine, Eastman No. 216. The product was recrystallized from glacial acetic acid and melted at 156–156.5° (uncorrected). Hammick gives 156° (uncorrected) as the melting point. A 1% solution of the acid in water neutralized to pH 7 with sodium hydroxide was used as a reagent.

Standard copper solutions were prepared by dissolving accurately weighed samples of freshly cleaned pure electrolytic copper foil in dilute nitric acid and diluting to volume.

Ferric salts, for use in making synthetic solutions, were made by dissolving Baker's primary standard iron wire in the appropriate acids. Baker's c.p. iron powder, by hydrogen, was also used and has the advantage of dissolving more rapidly. However, it contains sufficient insoluble material to require filtration of its solutions before use.

Tartaric acid was Merck's reagent grade, fine crystals. Oxalic acid was U.S.P. grade. Hydroxylamine hydrochloride was the Eastman material and was generally dissolved in a small amount of water immediately before use.

All other reagents and chemicals were of the highest purity obtainable. Normax volumetric ware was used throughout. The weighings were performed in a new Seko analytical balance with a sensitivity of 0.2 mg. per scale division and a reliability determined as ±0.03 mg. by the method of Benedetti-Pichler (*1*). A Beckman pH meter with glass electrode assembly, frequently tested against carefully prepared standard buffers, was used for the pH measurements.

## EXPERIMENTAL

A. Double Quinaldic Acid Precipitation. The precipitation of metals from solution with quinaldic acid has been investigated theoretically by Flagg and McClure (*3*). The following procedure was followed to check the reliability of the determination of a small amount of copper from a pure standard solution.

Sufficient standard copper solution to contain 1.008 mg. of copper was pipetted into a 250-ml. beaker and 5 ml. of glacial acetic acid were added. The solution was diluted to 95 ml. and the pH adjusted to 5.5 with dilute sodium hydroxide. The mixture was then heated to 70° to 80° C. and 5 ml. of the 1% quinaldic acid (50 mg.) solution were added slowly. The precipitate was digested 15 or 20 minutes on a steam bath and allowed to cool to room temperature before filtering. After the precipitate was collected on a weighed Pyrex 30F filtering crucible and washed several times with water, it was brought to constant weight at 115–120° C. Two such determinations gave an average value of 1.012 ± 0.009 mg.

The procedure was then repeated, substituting oxalic or tartaric acid for acetic acid. No precipitate appeared in any of several trials using 2 grams of oxalic acid at a pH of 5.5. Two runs in which 2 grams of tartaric acid and a pH of 5.5 were used gave an average value of 1.013 ± 0.003 mg. for the weight of copper. Evidently the complex formed by cupric ion with oxalate is too stable to permit the precipitation of copper quinaldate at this pH.

The high pH value was used because the stability of the complexes formed with oxalate and tartrate increases with increasing pH, so that any interference of these ions with the precipitation of the copper will be magnified. In practice, quantitative precipitation can be obtained under these conditions with a pH as low as 2.6. Obviously, copper can be quantitatively precipitated as the quinaldate in the presence of a large excess of tartrate.

When test analyses were begun on synthetic solutions containing 1 gram of iron (III) and 6 grams of tartaric acid, a difficulty was encountered in the precipitation of large quantities of basic ferric tartrates on neutralization. Experimentation showed that the basic salts do not appear if the iron was originally present as the nitrate or sulfate, but appear only when much of the iron was there as the chloride. Hence, thereafter, the iron for the synthetic mixture was dissolved in a mixture of nitric and sulfuric acids.

The procedure used for the analysis of synthetic mixtures was as follows:

To the pipetted volume of the standard copper solution were added the solution of 1 gram of iron as ferric sulfate and 6 grams of tartaric acid. The solution was brought to the desired pH with concentrated ammonium hydroxide and an excess of quinaldic acid was added after heating to 70° to 80° C. Filtration, etc., were as in the determinations described above. In every case the precipitates were contaminated with ferric quinaldate, as evidenced by their color. Several different wash liquids were tried, but none was successful in removing the contamination.

Results obtained are given in Table I. The amount of iron coprecipitated is seen to vary irregularly with the pH. In runs similar to those reported in Table I the amount of iron in the precipitate was estimated and up to 0.03 mg. was found. Obviously the single precipitation does not give a satisfactory separation of copper from such a large quantity of iron. A double precipitation procedure was then tried on standard steel samples obtained from the Bureau of Standards.

*Recommended Procedure.* A factor weight (1.493 grams) sample of the material is dissolved in 15 to 20 ml. of aqua regia. When the material has dissolved completely, 10 ml. of dilute sulfuric acid (1 to 1) are added and the solution is evaporated to dense white fumes of sulfur trioxide. The residue is taken up in 50 ml. of water and as much dilute sulfuric acid (1 to 4) as necessary to effect solution of the salts. Next the silica and other insoluble material are filtered off on Whatman No. 40 filter paper. After the silica is washed once with water, it is washed with 25 ml. of a solution containing 10 grams of ammonium tartrate, and then once more with water. Concentrated ammonium hydroxide is then added to the combined filtrate and washings until it turns a deep cherry red color. Upon cooling the pH is adjusted to 3.0 ± 0.2 with dilute ammonium hydroxide (1 to 3) or dilute sulfuric acid (1 to 4). The solution is then heated to 70° to 80° C. and 5 ml. of 1% quinaldic acid solution are added per milligram of copper present. Solution and precipitate are digested on the steam bath for half an hour and then allowed to cool to room temperature. The precipitate is collected on the filtering crucible and washed once or twice with cold water.

The filtering crucible is placed in an apparatus designed for quantitative recovery of filtrate and the precipitate is dissolved in a few milliliters of hot dilute hydrochloric acid (1 to 1). The crucible is rinsed with several small portions of hot acid and finally with water. To the filtrate 2 grams of tartaric acid and 2 ml. of the quinaldic acid solution are added and the pH is adjusted to about 3 with dilute ammonium hydroxide (1 to 4). The precipitate is digested at 70° to 80° C., cooled and filtered as before, this time on a weighed glass crucible, and washed with cold water. The crucible is dried at 115° to 120° C. for one hour and weighed. The weight of the precipitate in milligrams divided by 100 gives the percentage of copper in the sample.

Table I. Determination of Copper by Precipitation with Quinaldic Acid from Synthetic Mixtures

| Cu Taken | pH | Quinaldic Acid Used | Weight of Precipitate | |
|---|---|---|---|---|
| | | | Theoretical | Actual |
| *Mg.* | | *Mg.* | *Mg.* | *Mg.* |
| 1.01 | 3.4 | 50 | 6.77 | 10.18 |
| 1.01 | 5.8 | 50 | 6.77 | 7.64 |
| 5.04 | 2.4 | 100 | 32.75 | 36.28 |
| 5.04 | 3.7 | 100 | 32.75 | 37.99 |
| 5.04 | 4.5 | 100 | 32.75 | 36.12 |

Table II. Determination of Copper in Standard Steels by Double Quinaldic Acid Precipitation

| B. of S. No. | Type | First Precipitation | Second Precipitation | Averages | B. of S. Certificate Value |
|---|---|---|---|---|---|
| | | % | % | % | % |
| 111 | Ni-Mo | 0.151 | 0.115 | | |
| | | 0.146 | 0.117 | | |
| | | 0.136 | ... | | |
| | | 0.127 | ... | | |
| | | ... | 0.121 | 0.118 | 0.122 |
| 106 | Cr-Mo-Al | 0.162 | ... | | |
| | | 0.166 | 0.140 | | |
| | | 0.156 | 0.139 | 0.140 | 0.142 |
| 101 | 18–8 | 0.075 | 0.066 | | |
| | | ... | 0.055 | 0.061 | 0.055 |
| 5h | Cast Fe | 1.57 | 1.46 | | |
| | | 1.45 | 1.40 | | |
| | | 1.61 | 1.46 | | |
| | | 1.53 | 1.47 | 1.45 | 1.45 |
| 11e | Plain, low C | 0.114 | 0.103 | | |
| | | 0.117 | 0.103 | 1.103 | 0.105 |
| 125 | High Si | 0.081 | 0.067 | | |
| | | 0.066 | 0.055 | | |
| | | 0.070 | 0.052 | 0.058 | 0.066 |
| 30c | Cr-V | 0.092 | 0.092 | | |
| | | 0.110 | 0.106 | 0.099 | 0.099 |
| 55a | Ingot iron | 0.043 | 0.043 | | |
| | | 0.046 | 0.043 | 0.043 | 0.046 |
| 8d | Bessemer | 0.011 | 0.011 | | |
| | | 0.015 | 0.010 | 0.011 | 0.013 |

The values given in Table II were obtained by this method. In most cases the copper quinaldate from the first precipitation was dried and weighed and that value is given also. Perchloric acid digestion was tried because of the difficulty encountered in dissolving the basic salts formed in the sulfuric acid evaporation, particularly since hydrochloric acid cannot be used to aid in redissolving them. However, solutions prepared in this manner tend to give precipitates of basic tartrates similar to those that form when chloride is used. It was found, in general, that it is not necessary to redissolve the basic salts formed in the evaporation quantitatively before filtering in order to obtain good results. The pH meter need not be used in these precipitations. The precipitations may be carried out satisfactorily at a somewhat higher pH, using nitrazine paper for the first neutralization and methyl orange for the second. The Filtrator, obtainable from the Fisher Scientific Company, Pittsburgh, Pa., was found to be most convenient in obtaining quantitative recovery of the filtrate after dissolving the impure copper quinaldate from the first precipitation.

The silica precipitates, reprecipitation filtrates, and copper quinaldate precipitates from several of the analyses reported in Table II were reserved for qualitative spectrographic analysis. The spectrum plates were taken with a Bausch & Lomb large Littrow spectrograph and analyzed in a roughly quantitative manner by the projection method. The results showed definitely that the copper quinaldate precipitates were not contaminated with weighable quantities of any elements. Further, the quantities of copper lost to the silica precipitates and the reprecipitation filtrates are also negligible. Hence it is likely that the favorable results reported in Table II are not the result of compensating errors. The copper quinaldate precipitates were generally free from iron; occasional traces of nickel, zinc, silver, tin, titanium, lead, chromium, cobalt, and manganese were found. Notably absent were the elements silicon, tungsten, vanadium, and molybdenum.

B. Preliminary Separation by Internal Electrolysis. The separation of copper from iron by internal electrolysis using

**Table III. Determination of Copper by Internal Electrolysis from Ferrous Chloride Solution**

| Cu Taken<br>*Mg.* | Time of Electrolysis<br>*Min.* | Cu Found<br>*Mg.* |
|---|---|---|
| 5.04 | 45 | 4.98 |
| 5.01 | 75 | 5.04 |
| 5.01 | 30 | 5.00 |
| 1.00 | 75 | 1.04 |
| 1.00 | 30 | 1.04 |

**Table IV. Determination of Copper in Steels by Quinaldic Acid Precipitation after Separation by Internal Electrolysis**

| B. of S. No. | Type | B. of S. Certificate Value | % Cu Found |
|---|---|---|---|
| 111 | Ni-Mo | 0.122 | 0.120 |
| 11e | Plain, low C | 0.105 | 0.102 |
| 125 | High Si | 0.066 | 0.061 |
| 50a | Cr-V-W | 0.047 | 0.043 |
| 55a | Ingot iron | 0.046 | 0.048 |
| 101 | 18–8 | 0.055 | 0.035 |

an aluminum anode has been described by Lurie and Ginsburg (*11*). An extension of their work by Flagg and Underwood (*4*) indicated that the separation of milligram quantities of copper from 1 gram of iron was at least feasible. The technique is simpler and in general more rapid than external electrolytic methods and appeared to offer a method applicable to steel analysis.

The apparatus used was similar to that of Lurie and Ginsburg (*11*). The cathode was an ordinary platinum gauze electrode, the anode a 23-cm. length of Baker's 99.99% aluminum wire bent into a spiral or simple loop. The electrolysis and preliminary operations were carried out in an electrolysis cell made by cutting a 38 × 300 mm. Pyrex test tube to a length of 13 cm. Test analyses were run from a solution containing 1 gram of iron as ferrous chloride. To the iron solution in the electrolysis vessel were added the pipetted volume of standard copper solution, 1 ml. of concentrated hydrochloric acid, and 1 ml. of concentrated nitric acid. The cell was then immersed in a beaker of water held at 70° to 80° C. by a steam bath and the electrolysis continued for the time indicated. At the end of the run the electrodes were removed with a stream of water playing on the cathode, rinsed in distilled water and acetone, and dried and weighed in the usual manner. Results obtained are shown in Table III.

Analyses of Bureau of Standards nickel-molybdenum steel, No. 111, were then attempted. A 1-gram sample was weighed in the electrolysis vessel and dissolved in aqua regia. Three milliliters of concentrated sulfuric acid were added and the solution was evaporated to fumes. The residue was taken up with about 10 ml. of water, and boiled, and 1.2 grams of hydroxylamine hydrochloride in 10 ml. of water were added to reduce ferric ion to ferrous. Two milliliters of dilute hydrochloric acid (1 to 1) and 2 ml. of dilute nitric acid (1 to 3) were added and the electrolysis was carried out as above.

Six such analyses gave a value of 0.157 ± 0.021% copper as compared with the standard analysis of 0.122%. The poor precision is explained by the possibility of a varying amount of insoluble silica and graphite being occluded in the deposit. A similar effect was noted by MacNeven and Bournique (*12*) in external microelectrolysis and was avoided by filtering before electrolysis. The high results are due to this occlusion and to the presence of small amounts of other metals which can be deposited under these conditions. Their presence was confirmed by spectrographic analysis of three of the deposits, all of which showed fairly strong lines of silver, bismuth, and tin. The combined percentages of these elements would not have to exceed 0.02% to account for the above error. However, it was found that this interference can be eliminated if the deposit be stripped and the copper determined by quinaldic acid precipitation.

*Recommended Procedure.* The deposits are stripped, after dissolving and electrolyzing the sample as described above, with concentrated nitric acid in an apparatus similar to that described by Silverman, Goodman, and Walter (*15*). The solutions are then run into 150-ml. beakers and 5 grams of ammonium acetate are added. The pH is adjusted to 3 to 3.5, but methyl orange may be used with equally satisfactory results. The copper is then determined by precipitating with 50 mg. of quinaldic acid; filtration, washing, and drying of the precipitates are as described in Section A, recommended procedure. Results obtained on several Bureau of Standards steel samples are given in Table IV.

The values obtained are satisfactory in most cases. The 18–8 steel, No. 101, at the point of electrolysis had suspended in the solution large amounts of basic chromic sulfate, which may have prevented complete deposition of the copper. The solution was usually sufficiently acid after the evaporation, so that additional acid was unnecessary. In this case the chloride and nitrate ions necessary to the smooth performance of the electrolysis were added as the sodium salts instead. In the case of readily soluble materials, such as the ingot iron, No. 55a, the evaporation can be omitted entirely, as the acid concentration when solution is complete will be just about that required for smooth electrolysis.

Spectrographic analysis showed that the precipitate is as a rule somewhat less pure than that obtained by a double quinaldic acid precipitation but that the quantities of the elements present are still negligible.

## ADVANTAGES AND DISADVANTAGES

ADVANTAGES. Use of simple and readily available apparatus, an advantage over conventional electrolytic methods; precipitate of definite composition; stable reagent readily soluble in water.

The average cost of materials per duplicate determination is about 3 cents. The reagent can be recovered by dissolving the precipitates with hydrochloric acid, precipitating the copper with hydrogen sulfide, filtering, and recovering the quinaldic acid from the filtrate by evaporation.

DISADVANTAGES. Necessity for reprecipitation, making for a somewhat slower process.

The method is no more accurate than methods previously in general use. In many steels, the accuracy is limited by the small weight of precipitate obtained.

Complete removal of chloride ion is absolutely necessary in the quinaldic acid procedure in order to avoid precipitation of basic ferric tartrate.

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# Determination of Rubber Hydrocarbon by a Gravimetric Rubber Bromide Method

C. O. WILLITS, M. L. SWAIN, AND C. L. OGG, Eastern Regional Research Laboratory, Philadelphia 18, Pa.

**A direct method is given for determining rubber hydrocarbon in extracts from plant tissues, and in rubber crudes, latices, and liquors. The method is based upon the formation of an alcohol-insoluble rubber bromide whose composition varies slightly, depending on the source of the rubber. Gravimetric factors are established for converting weights of rubber bromide to weight of rubber, when the source is guayule, Cryptostegia, or kok-saghyz. Data are presented showing that reasonable variations in time and temperature of bromination and changes in concentration of rubber and brominating solution, within rather wide limits, do not appreciably alter the accuracy of the method.**

DIRECT determination of rubber hydrocarbon in crude rubbers and in latices has been generally considered so inaccurate and unreliable that determination of rubber hydrocarbon by difference has been a common practice. The difference method usually suffices in the analysis of products derived from Hevea rubber, in which the nonrubber constituents have been well characterized or occur in low concentration. In the analysis of natural rubber products obtained from sources other than Hevea, such as guayule, kok-saghyz, and Cryptostegia, the situation is different. The chemical and physical properties of the nonrubber constituents of such products are largely unknown, and in many cases the nonrubber contaminants are present in excessive amounts, sometimes more than 50% of the total. Since the rubber hydrocarbon analysis usually affords the most reliable means for estimating the rubber content of plants and for following the concentration and purification of rubber by mechanical and chemical processes, it appeared desirable to devise or adapt a method which would permit direct determination of this constituent in the presence of relatively large amounts of natural and added contaminants.

Among the methods for determination of rubber in the literature, those which have received the largest amount of study are the gravimetric (*1*, *3*, *5*, *10*, *12*) and volumetric (*7*, *11*, *13*) methods based on the formation of the bromine derivative of rubber. Other methods are the empirical chromic acid oxidation (*4*), the direct alcohol precipitation (*6*), and the nitrosite procedures (*9*, *15*). The gravimetric bromide method showed the greatest promise of adaptability to the determination of rubber hydrocarbon in a wide variety of rubber-containing products. Both the volumetric bromide method and the chromic acid oxidation method are subject to error when the rubber contains material other than rubber hydrocarbon, since any nonrubber compounds capable of reacting with bromine interfere in the volumetric bromide method and any constituents yielding volatile acids on digestion with chromic acid tend to give high results if the chromic acid oxidation method is employed. Estimation of rubber by direct weighing of the hydrocarbon precipitated with alcohol is not applicable to the determination of rubber in impure or dilute solutions. The nitrosite method was not investigated, since it has never met with favor because of the uncertain composition of the reaction products. The gravimetric bromide method was therefore selected for further investigation as a possible and practical means for the direct estimation of rubber hydrocarbon.

The bromine derivative of rubber or the so-called "tetrabromide" was first prepared by Gladstone and Hibbert (*8*), who isolated the compound by evaporating the solvent from a chloroform-rubber solution that had been treated with bromine. Weber (*14*) found that the compound could be more conveniently isolated by precipitation with alcohol. Analysis of his preparation showed a composition in essential agreement with the formula $C_{10}H_{16}Br_4$. The methods devised for determination of rubber hydrocarbon based on the formation of the bromide vary in the choice of (*a*) rubber solvent (carbon tetrachloride, chloroform, or benzene), (*b*) brominating conditions such as time, temperature, and composition and concentration of the reagent, and (*c*) bromide precipitant (alcohol, acetone, or petroleum ether). In several of the methods the bromine in the isolated bromide precipitate is determined and the amount of rubber hydrocarbon calculated by using the ratio of 1 isoprene unit ($C_5H_8$) to 2 bromine.

Several early investigators recognized that this theoretical ratio was not obtained in practice, since formation of the bromide was generally accompanied by liberation of hydrogen bromide, indicating that substitution as well as addition of bromine took place. Hinrichsen and Kindscher (*10*) observed no liberation of hydrogen bromide if the bromination was carried out at 0° C., and proposed a method based on this finding. The volumetric bromide method of Lewis and McAdams (*11*) attempted to evaluate the amount of substitution by titration of the liberated hydrogen bromide and corrected the results accordingly. Bloomfield (*2*) has recently reported that when bromination of rubber is carried out at temperatures below 0° C. in a medium containing a trace of alcohol, substitution of bromine is minimized. A simple adaptation of the bromide method was made by Edison (*5*) and his associates for use in their survey of native American plants as potential sources of natural rubber. In this method, a benzene or carbon tetrachloride solution of rubber is brominated for one hour, the bromide is precipitated with alcohol, washed, dried, and weighed, and the rubber hydrocarbon content is calculated by multiplying the weight of recovered bromide by an empirical factor, 0.285, instead of the theoretical factor, 0.299.

Since conversion of weight of rubber bromide to weight of rubber is based on an empirical factor, it was necessary to establish this factor for rubber from different sources. Effects of variations in conditions were studied to determine the limits within which it is possible to use the established factor.

## EXPERIMENTAL

Samples of rubber bromide for ultimate analysis were prepared by the bromination of benzene solutions of rubber derived from various Cryptostegia, guayule, and kok-saghyz products. Benzene solutions of the rubber of each plant species were obtained as benzene extracts of the acetone-extracted plant tissues, solutions of the resin-containing crude rubber, milled, or extracted from the plants, or extracts of latices or plant liquors prepared from the plants.

Accurately measured volumes of such rubber solutions containing between 2 and 2.5 mg. of rubber per ml. were brominated at room temperature by adding 1 ml. of the brominating solution (see reagents) for every 10 ml. of rubber solution. Bromination was stopped and the bromide precipitated at the end of an hour by the addition of 30 ml. of absolute alcohol for every 10 ml. of the brominated mixture. The bromide was allowed to settle for 2 hours and was then filtered, washed with absolute alcohol, and dried to constant weight at 50° C. in vacuo. The dried precipitates were analyzed for carbon and hydrogen and in some cases for bromine. When the bromide was separated by filtration from the mother liquor immediately after precipitation, the weight and composition of the recovered bromide were the same as those of the bromide separated after standing for 2 hours.

All analyses of carbon, hydrogen, and bromine were made by common microprocedures. Many analyses were made of bromides prepared from resin-free solvent-extracted rubber, crude rubber, and rubber latex obtained from each of the three plant

**Table I. Composition of Rubber Bromides[a] from Three Plant Sources**

| Plant Source | Product from Which Prepared | Bromine, % | Carbon, % | Hydrogen, % | Sum of C + H, % | Total, % |
|---|---|---|---|---|---|---|
| Guayule | Latex dispersion | ... | 25.9 | 3.4 | 29.3 | .. |
| | Crude rubber | ... | 25.3 | 3.5 | 28.8 | .. |
| | Acetone-extracted plant tissue | 69.8 | 25.9 | 3.5 | 29.4 | 99.2 |
| | Av. | | 25.7 | 3.5 | 29.2 | |
| Kok-saghyz | Crude rubber | 69.9 | 25.7 | 3.2 | 28.9 | 98.8 |
| | Acetone-extracted plant tissue | 70.4 | 25.9 | 3.3 | 29.2 | 99.6 |
| | Av. | | 25.8 | 3.2 | 29.0 | |
| Cryptostegia | Crude rubber | 69.2 | 27.0 | 3.4 | 30.4 | 99.6 |
| | Acetone-extracted plant tissue | 69.9 | 26.9 | 3.4 | 30.3 | 100.2 |
| | Av. | | 26.9 | 3.4 | 30.3 | |
| Theoretical composition of $C_5H_8Br_2$ | | 70.12 | 26.34 | 3.54 | 29.88 | |

[a] Each value is average of values obtained in three to eight determinations.

**Table II. Effect of Volume Ratio of Brominating Reagent to Rubber-Benzene Solution on Weight of Rubber Precipitated**

| | Kok-saghyz | | Guayule | |
|---|---|---|---|---|
| Br Solution per 10 Ml. of Rubber-Benzene Solution | Rubber bromide from 20 ml. of rubber-benzene | Wt. of rubber calculated[a] | Rubber bromide from 20 ml. of rubber-benzene | Wt. of rubber calculated[b] |
| *Ml.* | *Grams* | *Grams* | *Grams* | *Grams* |
| 1 | 0.1133 | 0.0329 | 0.1327 | 0.0387 |
| 2 | 0.1124 | 0.0326 | 0.1345 | 0.0393 |
| 3 | 0.1135 | 0.0329 | 0.1348 | 0.0394 |
| 4 | 0.1145 | 0.0332 | 0.1355 | 0.0396 |
| 5 | 0.1159 | 0.0336 | 0.1350 | 0.0394 |
| 6 | 0.1143 | 0.0331 | 0.1363 | 0.0398 |

[a] Gravimetric factor 0.290.
[b] Gravimetric factor 0.292.

sources. The average values in Table I were obtained by three to eight determinations of bromides from each source.

The sums of the averages of the carbon and hydrogen content give the factors for converting weights of rubber bromides to weights of rubber. The factors obtained are as follows:

| | |
|---|---|
| Guayule | 0.292 |
| Kok-saghyz | 0.290 |
| Cryptostegia | 0.303 |

A mean deviation of ±0.003 for each of the three factors was obtained when the carbon and hydrogen data for all the samples were analyzed. In general usage it is not necessary to employ the two factors, 0.292 and 0.290, for guayule and kok-saghyz, respectively, but rather to use the average factor, 0.291, whose mean deviation is within the limits of experimental error.

As an additional test of the variation of the gravimetric factor for rubber in rubber bromide, many of the benzene-rubber extracts obtained in the course of plant analyses were analyzed for rubber both by the bromination procedure and by weighing the rubber film obtained by evaporation. Ultimate analyses showed that the films were 98 to 99% pure. The gravimetric factors were determined by dividing the weight of the rubber film by the weight of the rubber bromide. The average of more than one hundred such determinations yielded the following factors: guayule, 0.292 ± 0.003; kok-saghyz, 0.290 ± 0.004; and Cryptostegia, 0.302 ± 0.003. All are in close agreement with the values obtained by the ultimate analysis of the bromides (Table I). Preliminary experiments have indicated that this method is applicable to Hevea and that the factor 0.291 gives satisfactory results. In addition, test analyses on a sample of GR-S synthetic rubber indicated that reliable results are obtainable using an experimentally found factor of 0.342.

To evaluate variations in time, temperature, rubber concentration, and bromine concentration which would not significantly alter the factor, the weights of bromide recovered from aliquots of rubber-benzene solutions brominated under various conditions were compared. Table II shows the effect of varying the volume ratio of the brominating solution to the rubber-benzene solution.

Although there is a slight increase in the weight of rubber bromide formed with increased amounts of the brominating solution, the weights of rubber, calculated by the factor previously established by ultimate analyses, are fairly constant. Since the variation caused by increasing amounts of brominating reagent is small, the procedure adopted has been to use 1 ml. of reagent for every 10 ml. of rubber-benzene solution, as the gravimetric factors have been established on the basis of this ratio. To change the ratio would necessitate establishing new factors which would be even further from the theoretical value of 0.299.

To show the effect of varying rubber concentration on the amounts of rubber calculated from the bromide with the established factor, a series of 10-ml. aliquots of a rubber-benzene solution was diluted with different amounts of benzene. These were brominated by the addition of 1 ml. of brominating solution for every 10 ml. of the rubber-benzene solutions. Table III shows the results.

It is evident that rubber-benzene solutions containing 0.5 to 3.0 mg. of rubber per ml. of solution can be analyzed by this procedure, with a recovery of 98 to 100%. For solutions containing much more than 3.0 mg. of rubber per ml., low values were obtained.

Aliquots of benzene solutions of rubber from three plant sources were brominated at room temperature (25° ± 2.5° C.) and in a refrigerator at 4° C. for periods ranging from 1 to 24 hours. One milliliter of brominating reagent was used for every 10 ml. of rubber-benzene solution. Table IV shows the results.

The data indicate that reasonable variations in time and temperature of bromination from the one hour and room temperature of the described procedure cause insignificant changes in the amounts of rubber calculated from the bromides. However, prolonged bromination at room temperature results in a gradual increase in the weight of the precipitate; this is presumably due to substitution of bromine. At 4° C. the same phenomenon occurs, but, as would be expected, the rate is slower. When brominations were made at −4° C. in carbon tetrachloride solution containing a trace of alcohol, the gravimetric factors calculated for rubber in rubber bromide formed approached the theoretical value. The proposed method of brominating at room temperature is preferred, however, because of its ease of operation, its adaptability, and the accuracy obtainable.

Results of the carbon and hydrogen analyses of the bromides indicate that the gravimetric factors for converting weights of bromide to weights of rubber vary from one plant source to another. The cause of these variations has not been determined; they may be due to the inherent nature of the rubbers. That the bromide method accounts for all the rubber in a solution is

**Table III. Analysis of Solutions of Different Rubber Concentrations**

| Guayule | | | Kok-saghyz | | | Cryptostegia | | |
|---|---|---|---|---|---|---|---|---|
| Mg. of Rubber per 10 Ml. of Rubber-Benzene Solution | | % Recovery | Mg. of Rubber per 10 Ml. of Rubber-Benzene Solution | | % Recovery | Mg. of Rubber per 10 Ml. of Rubber-Benzene Solution | | % Recovery |
| Added | Found[a] | | Added | Found[a] | | Added | Found[a] | |
| 6.6 | 6.6 | 100 | 5.6 | 5.6 | 100 | 5.4 | 5.4 | 100 |
| 7.9 | 7.8 | 99 | 6.6 | 6.6 | 100 | 6.5 | 6.5 | 100 |
| 9.9 | 9.7 | 98 | 8.2 | 8.2 | 100 | 8.2 | 8.1 | 99 |
| 13.2 | 13.1 | 99 | 10.9 | 10.7 | 98 | 10.9 | 10.8 | 99 |
| 19.8 | 19.6 | 99 | 16.4 | 16.4 | 100 | 16.3 | 16.1 | 99 |
| 29.7 | 29.5 | 99 | 24.6 | 24.5 | 100 | 24.5 | 23.9 | 98 |
| 39.5 | 37.4 | 95 | 32.8 | 31.9 | 97 | 32.6 | 31.5 | 97 |

[a] Gravimetric factors: guayule, 0.292, kok-saghyz, 0.290; Cryptostegia, 0.303. 1 ml. of brominating reagent added for each 10 ml. of rubber-benzene solution.

**Table IV. Effect of Time and Temperature of Bromination on Weight of Rubber Found**

| Time of Bromination | Weight of Rubber Calculated[a] from Bromide Precipitated from 20 Ml. of Solution | | | | | |
|---|---|---|---|---|---|---|
| | Cryptostegia | | Kok-saghyz | | Guayule | |
| | Room temp. | 4° C. | Room temp. | 4° C. | Room temp. | 4° C. |
| *Hours* | *Gram* | *Gram* | *Gram* | *Gram* | *Gram* | *Gram* |
| 1 | 0.0162 | 0.0162 | 0.0276 | 0.0271 | 0.0405 | 0.0402 |
| 3 | 0.0164 | 0.0166 | 0.0282 | 0.0275 | 0.0418 | 0.0408 |
| 6 | 0.0178 | 0.0172 | 0.0284 | 0.0277 | 0.0427 | 0.0414 |
| 24 | 0.0184 | 0.0177 | 0.0285 | 0.0278 | 0.0442 | 0.0427 |

[a] Previously established factors for bromination at room temperature for 1 hour were used.

indicated by the close agreement between the weights of rubber calculated by these gravimetric factors and the weights obtained by evaporation of the pure rubber benzene extracts. This agreement does not preclude the possibility of obtaining high rubber values by the bromide method from impure benzene extracts. However, the possibility is remote that any nonrubber plant materials are present which are soluble in benzene and also form alcohol-insoluble bromine derivatives. Added antioxidants and solution aids have never interfered.

## REAGENTS

Alcohol, A.C.S., absolute
Acetone, A.C.S., analytical reagent grade
Benzene, A.C.S., analytical reagent grade
Trichloroacetic acid, Eastman Kodak Company White Label
Benzene containing 1% trichloroacetic acid
Brominating solution. Dissolve 2 grams of iodine in 100 ml. of carbon tetrachloride, filter through filter paper, and add 5 ml. of bromine to the filtrate.

## ANALYTICAL PROCEDURES

Determination of rubber by the bromide method is useful in evaluating the rubber content of benzene extracts of plant tissues, crude rubbers isolated from plants by mechanical or chemical means, and rubber-containing liquors and lattices.

DETERMINATION OF RUBBER IN THE ORGANIC SOLVENT EXTRACT OF PLANT TISSUE. An organic solvent extract or the rubber film obtained by evaporating an extract may be analyzed by the bromide procedure.

To analyze a rubber film, redissolve it in benzene by stirring and gentle heating, cool, and make to volume in a volumetric flask with benzene. Choose as the final volume of either the extract or the redissolved film one which will contain 0.5 to 3.0 mg. of rubber per ml. Transfer to a beaker an aliquot containing a minimum of 25 mg. of rubber, and add 1 ml. of the brominating solution for each 10 ml. of the aliquot. Cover the beaker with a watch glass and let stand at room temperature for one hour to permit agglomeration of the particles. At the end of the hour stir the brominated mixture thoroughly with a glass rod, taking special care to loosen any precipitate from the bottom of the beaker. Add absolute alcohol, with constant stirring, in the ratio of 30 ml. of alcohol for each 10 ml. of the brominated mixture. Allow the bromide precipitate to settle for at least one hour and then filter with suction, using a tared Gooch crucible with asbestos pad. An ordinary rubber policeman and alcohol may be used in transferring the bromide and in washing the beaker. Wash the bromide several times with alcohol, dry at 50° C. in vacuo under 5-mm. mercury pressure, cool, and weigh. Calculate the rubber content from the weight of the rubber bromide by the following gravimetric factors: 0.290 for kok-saghyz, 0.292 for guayule, and 0.303 for Cryptostegia.

DETERMINATION OF RUBBER IN RUBBER CRUDES. Prepare the analytical sample of the crude rubber by passing it several times through compounding rolls, finally mill it into a thin ribbonlike sheet, and from this cut or tear narrow strips for moisture and for rubber analysis.

Determine the moisture by drying approximately 2 grams of the crude rubber in vacuo at 50° C. to constant weight (12 hours).

Solution of the sample for rubber analysis may be obtained either by heating it in benzene or by allowing it to stand at room temperature in a 1% solution of trichloroacetic acid in benzene. Although the latter method requires 2 to 3 days for solution, it is more convenient in routine analysis, and in general less time-consuming. Since determination of the benzene-insoluble and acetone-insoluble content of the crude rubber is usually required in addition to rubber hydrocarbon, samples of approximately 0.5 grams are recommended.

Cut or tear approximately 0.5 gram of the milled sheet into fine strips, weigh to the nearest 0.1 mg., and place in a tared 70-ml. centrifuge tube. Add 50 ml. of a 1% solution of trichloroacetic acid in benzene, insert a glass stirring rod, lightly stopper the tube with a plug of cotton, and allow it to stand at room temperature for 3 days. To aid in the complete solution of the rubber, stir two or three times a day during the 3-day interval. Centrifuge to separate the benzene-insolubles and decant the benzene-rubber solution into a 200-ml. volumetric flask. Wash the benzene-insolubles and the centrifuge tube twice with 50-ml. portions of benzene, centrifuging after each wash. Add the benzene washes to the benzene-rubber solution and dilute to 200 ml. with benzene. Determine the rubber in a 20-ml. portion of this solution by the bromide method described in the previous section. Calculate the per cent rubber in the crude by the equation:

$$\%\ \text{rubber} = \frac{\text{gravimetric factor} \times \text{weight of bromide (g.)} \times \text{volume of sample (200 ml.)} \times 100}{\text{weight of crude rubber (grams)} \times \dfrac{100 - \%\ \text{moisture}}{100} \times \text{portion used (20 ml.)}}$$

If the percentage of acetone-soluble or resin fraction and the percentage of those materials insoluble in both acetone and benzene are desired, determine the insolubles directly and calculate the acetone-solubles by difference. To determine the insoluble fraction, thoroughly wash the benzene-insoluble residue left in the centrifuge tube with acetone, separate the insolubles by centrifuging, and discard the acetone wash solution. Dry the residue in the tared centrifuge tube for one hour at 110° C. in an air oven, cool, weigh, and calculate the per cent insolubles on a moisture-free basis.

The per cent acetone-soluble fraction is obtained by subtracting the sum of the percentages of moisture-free rubber and insolubles from 100. Since the proposed method is especially suited to the analysis of crude rubber and is applicable to samples containing either large or small amounts of nonrubber nonresin materials, several typical analyses of samples of such rubber from different plants are given in Table V. These show the reproducibility of the method.

DETERMINATION OF RUBBER IN AQUEOUS LIQUORS LOW IN RUBBER CONTENT. Many types of aqueous rubber-containing emulsions having rubber contents ranging from less than 1 to about 5% may be conveniently analyzed for rubber by the bromide procedure. Benzene extracts of the rubber in such emulsions are most easily prepared in the Waring Blendor. The

**Table V. Analyses of Crude Rubber from Different Plants**

| Plant Source | Sample No. | % Rubber | | % Insolubles (Benzene and Acetone) | | Acetone-Solubles[a] (Resins) |
|---|---|---|---|---|---|---|
| Guayule | 5293 | 65.0 | 65.1 | 15.3 | 15.3 | 19.7 |
| | 5319 | 78.6 | 79.2 | 5.3 | 5.3 | 15.9 |
| | 5341 | 68.2 | 68.0 | 10.4 | 10.3 | 21.6 |
| | 5564 | 73.8 | 73.9 | 7.2 | 7.3 | 18.9 |
| | 5568 | 77.4 | 77.5 | 1.8 | 1.8 | 20.8 |
| Kok-saghyz | 7510 | 80.9 | 80.9 | 6.4 | 6.9 | 12.5 |
| | 7520 | 86.2 | 86.1 | 7.2 | 7.2 | 6.7 |
| | 7579 | 77.3 | 76.8 | 8.0 | 8.0 | 15.0 |
| | 8088 | 79.0 | 78.7 | 7.1 | 7.4 | 13.9 |
| | 8227 | 77.5 | 77.5 | 9.7 | 9.9 | 12.7 |
| Cryptostegia | 7726 | 64.5 | 65.3 | 1.1 | 1.0 | 34.1 |
| | 9040 | 87.4 | 87.2 | 5.2 | 5.3 | 7.5 |
| | 9050 | 63.1 | 63.3 | 28.1 | 28.1 | 8.7 |
| | 9054 | 51.3 | 51.2 | 40.5 | 40.3 | 8.4 |
| | 9060 | 84.6 | 84.4 | 5.4 | 5.3 | 10.2 |

[a] Calculated by difference from average of both rubber and insolubles.

persistent emulsions which result when alkali-stabilized rubber liquors are extracted with benzene in the Blendor can be avoided by acidifying the liquor with concentrated hydrochloric acid preliminary to the extraction.

To determine the rubber content, transfer 10 to 50 ml. of the emulsion to a Waring Blendor using a transfer pipet, rinse the pipet several times with water, and combine the rinses with the measured sample, making a total volume of approximately 75 ml. Add sufficient concentrated hydrochloric acid to break the emulsion; usually 5 to 10 ml. are required. Then add about 180 ml. of benzene, churn for 2 minutes, wash the emulsion into a 500-ml. separatory funnel with water, and allow to stand until the aqueous layer appears clear, usually about 8 hours. Draw off and discard the clear aqueous layer.

Transfer the benzene and the interface layers to centrifuge tubes, centrifuge until separation into layers is complete, and transfer the benzene layer to a 400-ml. beaker using a pipet and suction. Rinse the separatory funnel with benzene. Add the rinses to the aqueous residue in the centrifuge tube, mix well, and centrifuge. Again draw off the benzene layer and add it to the original benzene solution in the beaker. Concentrate on a steam bath, transfer, and make to the mark in a volumetric flask of such volume that 20 ml. of the final volume will contain between 10 and 60 mg. of rubber. Transfer a 20-ml. aliquot to a 250-ml. beaker and brominate by the previously described procedure. Should the 20-ml. aliquot of the original solution contain more than 60 mg. of rubber, dilute to the desired concentration and brominate a 20-ml. portion. When the total benzene extract is very low in rubber, it may be reduced to 20 ml. and brominated in its entirety. Calculate the rubber content from the equation:

$$\text{Mg. of rubber/ml.} = \frac{\text{gravimetric factor} \times \text{weight of bromide (mg.)} \times \text{dilution factor}}{\text{ml. of sample}}$$

**Determination of Rubber in Latex or Liquor of High Rubber Content.** When concentrated rubber liquors (containing more than 5% rubber) and latices are being analyzed, complete extraction of the rubber by benzene cannot be achieved by the Waring Blendor method described above. Instead, benzene is added to the sample, the mixture is acidified, and the water is removed by distillation in a Bidwell-Sterling type moisture apparatus. This results in a water-free solution of the rubber in benzene.

Weigh by difference from a glass-stoppered vial that amount of the well-mixed sample which contains less than 1.5 grams of rubber and transfer to a 500-ml. volumetric (boiling) flask equipped with a 24/40 ₸ outer joint. Acidify the sample with concentrated hydrochloric acid to give an acid concentration of about 10%, then add 200 ml. of benzene and attach the flask to a Barrett type Bidwell-Sterling moisture test apparatus provided with a condenser. Boil the mixture until all water is removed (water level in the trap remains constant), and a clear benzene solution is obtained. Remove the flask from the apparatus, cool, and dilute to the mark with benzene. Transfer, with a pipet, a 50-ml. aliquot to a 600-ml. beaker and determine the rubber in this aliquot by the bromide method and the following equation:

$$\% \text{ rubber} = \frac{\text{Gravimetric factor} \times \text{weight of bromide (grams)} \times \text{volume of sample (500 ml.)} \times 100}{\text{weight of sample} \times \text{aliquot (50 ml.)}}$$

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# Determination of Alkyl Disulfides in the Absence and Presence of Mercaptans

I. M. KOLTHOFF, D. R. MAY, AND PERRY MORGAN, University of Minnesota, Minneapolis, Minn., AND
H. A. LAITINEN AND A. S. O'BRIEN, University of Illinois, Urbana, Ill.

**Disulfides are reduced to mercaptans by means of amalgamated zinc and titrated amperometrically with silver nitrate. If the relative amount of mercaptan present is not large, the disulfide is determined by difference by titrating portions of the solution before and after reduction. To determine a trace of disulfide in a mercaptan, the mercaptan is removed before the reduction treatment by precipitation as silver mercaptide.**

BASED upon the reducibility of alkyl disulfides (*1*, *3*, *5*) to mercaptans and amperometric titration of the resulting mercaptans (*4*) a simple method of determination of disulfides has been developed. Experiments were carried out to find suitable conditions for quantitative reduction and for removal of the mercaptan from the disulfide before reduction.

### REDUCTION OF DISULFIDE

Preliminary experiments showed that in order to approach quantitative reduction in a Jones reductor, a temperature of 50° C. was necessary. The zinc amalgam was of a very low concentration (0.02%) in mercury. Under these conditions evolution of hydrogen occurred when an acid solution was passed through the reductor. To prevent difficulties encountered with the counter flow of liquid and gas, the solution to be reduced was made to pass upwards through the zinc in the reductor. A sketch of a reductor with a heating jacket, which is easily constructed and satisfies the above specifications, is shown in Figure 1.

Two different samples of *n*-dodecyl disulfide were used with identical results. At the University of Minnesota, the disulfide was prepared by oxidation of *n*-dodecyl mercaptan with hydrogen peroxide in alkaline ethanol solution, followed by recrystallization from absolute ethanol. The product had a melting point of 32°, in agreement with the value of Collin *et al.* (*1*). At the University of Illinois, *n*-dodecyl disulfide was prepared by the method of Westlake and Dougherty (*6*), in which the Bunte salt prepared from *n*-dodecyl bromide and sodium thiosulfate was oxidized with hydrogen peroxide in aqueous dioxane medium. The crystals which separated upon cooling and standing were extracted with dioxane, and the disulfide was precipitated by the addition of water. The product had a melting point of 34–35°, in agreement with the value of 33.5–34° reported by Fore and Best (*2*). It is not certain whether the low results were caused entirely by incomplete reduction, or partly by the presence of impurities.

Known amounts of *n*-dodecyl disulfide were dissolved in a 0.3 *N* solution of sulfuric acid in 90% ethanol, and 25-ml. portions of the solution, heated to 50°, were allowed to flow through the reductor which was maintained at a temperature of 50°, at such a rate that the disulfide remained in contact with the solution for about 5 minutes. The reductor was washed with 75 ml. of 0.3 *N* sulfuric acid in 90% ethanol, and the mercaptan was determined in the resulting solution after addition of an excess of ammonia corresponding to about 0.25 *M* by the amperometric method of Kolthoff and Harris (*4*). Results obtained with different amounts of disulfide are shown in Table I.

An alternative procedure consisted of adding amalgamated zinc to the acidic disulfide solution (80 ml.) in a 4-ounce screw-cap bottle and rotating it in a thermostat at 50°, usually for 20 minutes. Results with this procedure are given in Table II using 0.3 *N* sulfuric acid and 1 *N* acetic acid in 90% alcohol as the solvent.

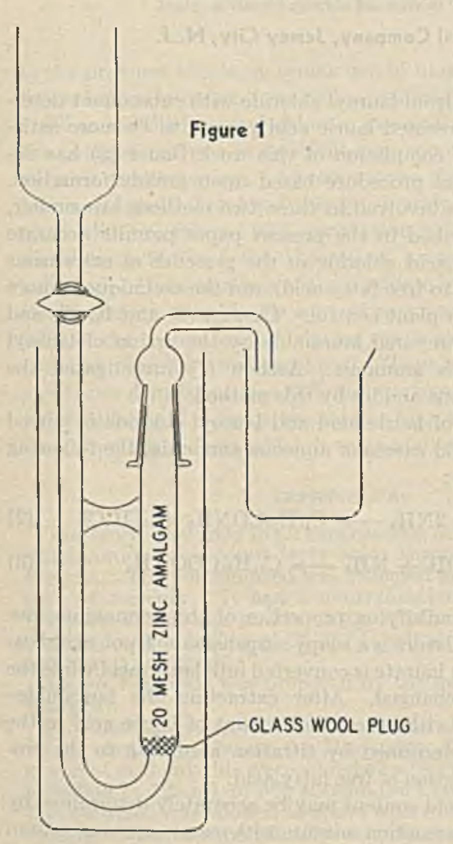

Figure 1

The use of acetic instead of sulfuric acid was found beneficial for small amounts of disulfide (less than 4 mg.). If large quantities of disulfide were present the reduction was slower in acetic acid medium, while with very small amounts (less than 0.3 mg.) the reduction was incomplete using sulfuric acid. Changing the concentration of acetic acid did not appreciably affect the rate or completeness of reduction.

### SEPARATION OF MERCAPTAN FROM DISULFIDE

For the determination of small amounts of disulfide in the presence of large amounts of mercaptan it is necessary to remove the mercaptan, since the mercaptan cannot be titrated with sufficient accuracy to allow the disulfide to be determined by difference. The mercaptan can be removed by adding an exactly equivalent amount of silver nitrate and filtering off the silver mercaptide. An appreciable excess of silver leads to low results for disulfide, since silver mercaptide is precipitated during the reduction step and is not completely reduced to mercaptan. Using the amperometric end point with a sufficiently sensitive galvanometer, it is easily possible to adjust the excess silver concentration to a very small quantity.

Experiments involving the removal of a 1000-fold excess of *n*-dodecyl mercaptan from known amounts of *n*-dodecyl disulfide gave an excellent recovery of disulfide after reduction and titration. Using mixed tertiary mercaptans, some difficulty was encountered in filtration of the silver mercaptide, since the mercaptide mixture was a gummy liquid at room temperature. Working at a temperature of 0° throughout the precipitation and filtration, however, gave satisfactory results.

**Table I. Reduction of *n*-Dodecyl Disulfide in Jones Reductor**

| Disulfide Taken<br>*Mg.* | Disulfide Found<br>*Mg.* | Reduction<br>% |
|---|---|---|
| 40.0 | 38.3 | 95.8 |
| | 38.4 | 95.0 |
| | 38.3 | 95.8 |
| 20.0 | 19.1 | 95.2 |
| | 19.0 | 94.8 |
| | 19.1 | 95.2 |
| 10.0 | 9.05 | 95.5 |
| 4.00 | 3.90 | 97.6 |
| 2.00 | 1.96 | 98.0 |

**Table II. Reduction of *n*-Dodecyl Disulfide in Bottles**

| Disulfide Taken<br>*Mg.* | Time<br>*Min.* | Disulfide Found<br>*Mg.* | Reduction<br>% |
|---|---|---|---|
| | Using Sulfuric Acid | | |
| 15.6 | 20 | 14.9 | 95.5 |
| 4.52 | 60 | 4.29 | 94.9 |
| 3.12 | 20 | 3.03 | 96.8 |
| 3.01 | 20 | 2.89 | 96.1 |
| 0.752 | 60 | 0.700 | 93.1 |
| 0.312 | 20 | 0.202 | 65.0 |
| 0.301 | 60 | 0.250 | 82.9 |
| | Using Acetic Acid | | |
| 4.52 | 20 | 3.48 | 76.9 |
| 4.52 | 60 | 4.20 | 93.0 |
| 3.01 | 20 | 2.81 | 93.3 |
| 3.01 | 60 | 2.94 | 97.7 |
| 1.51 | 20 | 1.49 | 98.6 |
| 0.752 | 10 | 0.738 | 98.2 |
| 0.752 | 30 | 0.720 | 95.8 |
| 0.752 | 60 | 0.704 | 93.6 |
| 0.301 | 10 | 0.304 | 101 |
| 0.301 | 20 | 0.307 | 102 |
| 0.150 | 10 | 0.179 | 119 |
| 0.150 | 10 | 0.188 | 125 |

### DETERMINATION OF DISULFIDE IN PRESENCE OF MERCAPTAN

A. JONES REDUCTOR METHOD. DETERMINATION BY DIFFERENCE. *Preparation of Amalgamated Zinc.* Etch 100 grams of 20-mesh granulated zinc by stirring with 6 *N* hydrochloric acid for one minute. Add 27 mg. of mercuric chloride, and after stirring for a minute, wash the zinc with distilled water. One hundred grams of zinc are sufficient for a reductor of a convenient size.

Incomplete reduction is encountered if the reductor is not completely cleaned by acid rinsing. A 10 *N* sulfuric acid solution was found to be satisfactory for the rinsing. The reductor should be checked before every run or series of runs by reducing a standard disulfide solution and determining the amount reduced. If the reduction remains slow the reductor should be filled with freshly prepared zinc amalgam.

*Reduction of Disulfide.* Using 90% ethanol–10% water 0.3 *N* in sulfuric acid as the solvent, allow the solution at 50° to run through the reductor at such a rate that the disulfide remains in contact with the zinc for about 5 minutes. Wash the reductor with 75 ml. of the solvent.

*Determination of Mercaptan.* Neutralize the solution with concentrated ammonium hydroxide, using litmus paper as an indicator. Add 2 ml. in excess, and titrate amperometrically with silver nitrate. If mercaptan was present initially, titrate a second portion of the solution without reduction. The difference is a measure of disulfide present.

B. BOTTLE METHOD. REMOVAL OF MERCAPTAN. For the determination of a trace of disulfide in mercaptan, dissolve a 0.1- to 0.2-gram sample of mercaptan in 80 ml. of absolute ethanol and add concentrated ammonium hydroxide (1.2 ml.) until the solution is about 0.25 *M* in ammonia. Titrate the solution amperometrically with 0.05 *N* silver nitrate to a very slight excess of silver. A highly sensitive current-measuring instrument such as a wall-type galvanometer is recommended. If necessary, adjust the excess silver by the addition of 0.005 *M* mercaptan in alcohol and 0.002 *N* silver nitrate until the excess of silver, as indicated by the current, corresponds to about 0.1 ml. of 0.002 *N* reagent.

Filter the solution without suction and wash the precipitate thoroughly with small portions of alcohol. Add 5 ml. of glacial acetic acid. Add 10 to 20 mg. of amalgamated zinc prepared as described in Procedure A to the solution in a 4-ounce screw-cap bottle and rotate in a 50° thermostat for 20 minutes.

Filter the solution again, taking care that no small pieces of zinc amalgam pass into the filtrate. Add 7 ml. of concentrated ammonium hydroxide and titrate with 0.002 *N* silver nitrate to the usual amperometric end point.

### ACCURACY AND SENSITIVITY

The accuracy of the method is limited by the degree of reduction of the disulfide by the amalgamated zinc. Using either method the results are about 5% low if the amount of disulfide is in the optimum range. The results are reproducible to 2% relative on a given sample in the optimum range.

Method B has proved successful in detecting 0.05% disulfide in mercaptan and in making quantitative estimation of disulfide in amounts from 0.1 to 1% or more.

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# Higher Aliphatic Acid Chlorides

## Estimation of Yield in the Preparation of Lauroyl Chloride

ROBERT R. ACKLEY AND GIULIANA C. TESORO, Onyx Oil & Chemical Company, Jersey City, N. J.

**A titration procedure for estimation of yield in the preparation of lauroyl chloride has been found equally applicable for other fatty acid chlorides containing 12 to 18 carbon atoms. Using this procedure, the effect of the ratio of lauric acid concentration to thionyl chloride concentration on the yield of lauroyl chloride was determined. The titration method is applicable to the determination of fatty acid chloride content in reaction mixtures or in distilled products. By the use of this procedure, it was found that undistilled acid chlorides prepared from the corresponding fatty acids and thionyl chloride are sufficiently pure for most synthetic work.**

IN THE course of an investigation of derivatives of higher fatty acids it was necessary to prepare relatively large quantities of lauroyl chloride. When the acid chloride was prepared by the action of thionyl chloride on lauric acid and the yield determined by distillation, it was found significantly lower in the case of reactions involving 1 mole of lauric acid than in identical experiments employing only 0.1 mole of the acid. During the distillation of larger runs, large amounts of hydrochloric acid were evolved.

Among other explanations for lowered yield and evolution of acidic fumes, it seemed possible that the reaction of lauroyl chloride with unreacted lauric acid might take place:

$$C_{11}H_{23}COCl + C_{11}H_{23}COOH \longrightarrow (C_{11}H_{23}CO)_2O + HCl \quad (1)$$

The conditions of distillation (flask temperature approximately 130° C. at 2 mm. of mercury) might favor this reaction. It is apparent, further, that if the initial conversion amounts to 90%, the unconverted acid is capable of reaction with a sufficient quantity of acid chloride to reduce the apparent yield on distillation to 80%, the anhydride remaining behind in the residue. Ketene formation, followed by polymerization, may also be a yield-reducing factor. The polymerized products would not be distillable. An experiment in which the reaction mixture was refluxed under vacuum for a prolonged period showed that the amount of acid chloride present was reduced during the heating period. If small quantities of acid chloride are involved, distillation may be carried out with sufficient rapidity to minimize yield-reducing side reactions.

The high yields obtained when small quantities are involved, together with the demonstrated reduction of yield during slow distillation, suggested the probability that lauric acid chloride could be prepared in sufficiently high yield to make distillation unnecessary. In order to prove this, it was necessary to develop an analytical procedure independent of distillation or prolonged heating.

Several derivatives of lauroyl chloride were prepared which might lend themselves to quantitative recovery. Quantitative separation of these derivatives from unreacted fatty acid was difficult, however, and an indirect method based upon the formation of amide from lauroyl chloride with subsequent determination of the unreacted lauric acid proved to be more satisfactory. Since the completion of this work Bauer (*2*) has described an analytical procedure based upon anilide formation. While the principles involved in these two methods are similar, the procedure described in the present paper permits accurate estimation of fatty acid chloride in the presence of extraneous matter (in addition to free fatty acid) and the technique is more readily adaptable to plant control. Caspari (*3*) and Krafft and Stauffer (*4*), have prepared lauramide by the action of lauroyl chloride on aqueous ammonia. Aschan (*1*) investigated the preparation of various amides by this method.

When a mixture of lauric acid and lauroyl chloride is stirred rapidly into a tenfold excess of aqueous ammonia, the following reactions take place:

$$C_{11}H_{23}COCl + 2NH_3 \longrightarrow C_{11}H_{23}CONH_2 + NH_4Cl \quad (2)$$

$$C_{11}H_{23}COOH + NH_3 \longrightarrow C_{11}H_{23}COONH_4 \quad (3)$$

Because of the emulsifying properties of the ammonium laurate, the reaction mixture is a soapy suspension. Upon acidification, the ammonium laurate is converted into lauric acid while the amide remains unchanged. After extracting the lauramide-lauric acid mixture with ether, the amount of lauric acid in the mixture may be determined by titration according to the procedure for determination of free fatty acid.

The total lauric acid content may be accurately determined by saponification of the reaction mixture with excess aqueous sodium hydroxide, followed by acidification, extraction, and titration. The total content of lauric acid determined by this procedure was found to be in excellent agreement with the known lauric acid content based upon the amount of lauric acid employed and the total weight of the reaction mixture.

From the above determinations, the per cent of free fatty acid and the per cent of total fatty acid are obtained. Using these data the per cent yield and per cent purity of the lauroyl chloride can be calculated.

Using this procedure, when a reaction mixture resulting from the action of thionyl chloride upon lauric acid was heated at 150° C. and 5 mm. of mercury, the apparent conversion was found to decrease from an initially determined value of 96 to 85% after 2 hours.

The applicability of this procedure for studying the effect of varying the proportion of thionyl chloride to lauric acid on the yield of lauroyl chloride was determined by a series of experiments in which the reaction mixtures were analyzed by this method (Table I and Figure 1).

The values found for yield are apparently independent of the relative proportions of lauric acid and lauroyl chloride, whereas

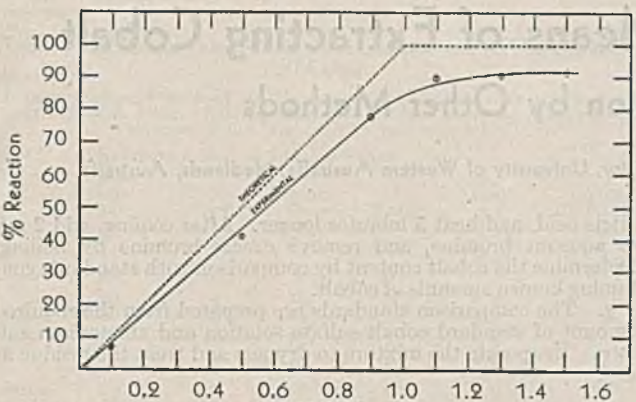

Figure 1. Effect of Varying Proportion of Thionyl Chloride

Moles of thionyl chloride per mole of lauric acid

in the presence of a large proportion of unreacted lauric acid the lauroyl chloride present cannot be distilled quantitatively.

When distilled lauroyl chloride was analyzed by this method, the composition was in excellent agreement with that found by chloride determination. A product from the reaction of 1 mole of lauric acid and 1.2 moles of thionyl chloride, when analyzed prior to distillation, showed 96% conversion to lauroyl chloride. By distillation, 90% of the theoretical amount of distillate was collected. Upon analysis of the distillate by chloride determination, however, the chloride content was found to amount to only 92% of the calculated. A similar result was obtained when the titration procedure was employed. Thus, the actual percentage yield after distillation was 83% and the free lauric acid content of the distilled acid chloride was no less than that of the undistilled reaction mixture from which it was obtained.

## EXPERIMENTAL

The lauric acid used in all experiments was obtained by careful fractionation of coconut fatty acids through a 25-cm. Widmer column. The portion used was collected at 145° to 150° C. at 3 mm. of mercury. It had a neutralization equivalent of 199.5 (theoretical 200) and melted at 43–47° C. The thionyl chloride was the fraction boiling at 72–76° C., obtained by distillation of a commercial product.

Lauroyl chloride was prepared by the method of Ralston and Selby (*5*).

A. DETERMINATION OF UNREACTED LAURIC ACID (FREE FATTY ACID) IN CRUDE OR DISTILLED ACID CHLORIDE. Ten grams of acid chloride were added slowly with cooling and strong agitation to 125 ml. of 6% ammonium hydroxide. The suspension obtained was allowed to stand with intermittent stirring and cooling at room temperature for 20 minutes. Hydrochloric acid, 10 *N*, was then added dropwise with stirring and cooling until the methyl orange end point was reached.

One hundred and fifty milliliters of a 2 to 1 mixture of ethyl ether and ethanol were added, and the mixture was transferred to a 500-ml. separatory funnel, the reaction vessel being washed with repeated small portions of ethanol. The aqueous layer was withdrawn, and the extracted material washed repeatedly with 50-ml. portions of saturated sodium chloride solution until the last washing became alkaline to phenolphthalein on the addition of a single drop of 1 *N* sodium hydroxide.

Table I. Preparation of Lauroyl Chloride

(With varying amounts of thionyl chloride, % reaction)

| Lauric Acid | $SOCl_2$ | FFA in Crude Product | | TFA in Crude Product | | Yield of Crude Product | | Reaction | |
|---|---|---|---|---|---|---|---|---|---|
| | | Calcd. | Found | Calcd. | Found | Calcd. | Found | Theoretical | Experimental |
| *Mole* | *Mole* | *Grams/10 grams* | | *Grams/10 grams* | | *Grams* | | *%* | *%* |
| 0.5 | 0.05 | 8.9 | 9.3 | 10.0 | 9.9 | 101 | 100 | 10 | 7 |
| 0.5 | 0.25 | 4.7 | 5.6 | 9.6 | 9.4 | 105 | 104 | 50 | 41 |
| 0.5 | 0.45 | 0.9 | 2.0 | 9.3 | 9.1 | 108 | 108 | 90 | 78 |
| 0.5 | 0.55 | 0.0 | 0.9 | 8.9 | 9.0 | 114 | 112 | 100 | 90 |
| 0.5 | 0.65 | 0.0 | 0.7 | 8.3 | 8.0 | 126 | 120 | 100 | 91 |
| 0.5 | 0.75 | 0.0 | 0.6 | 7.7 | 7.6 | 139 | 130 | 100 | 92 |

The solvent solution was transferred to a 500-ml. flask, and the separatory funnel washed with 100 ml. of ethanol in small portions. The extract, together with the combined ethanol washings, was titrated to the phenolphthalein end point with 1 *N* sodium hydroxide.

B. DETERMINATION OF TOTAL LAURIC ACID (TOTAL FATTY ACID) IN CRUDE OR DISTILLED ACID CHLORIDE. Ten grams of acid chloride were added with cooling and stirring to 125 ml. of 10% sodium hydroxide solution. The resulting soapy solution was allowed to stand at room temperature for 20 minutes, and acidified to methyl orange as before with 10 *N* hydrochloric acid.

DETERMINATION OF YIELD OF LAUROYL CHLORIDE BY DISTILLATION AND BY TITRATION. Lauroyl chloride was prepared by the reaction of 1.2 moles of thionyl chloride and 1.0 mole of lauric acid. The total weight of the crude reaction mixture was 224 grams. This crude product was analyzed by procedures A and B, giving 4% free fatty acid, 89% total lauric acid, a percentage yield of 96%, and a lauroyl chloride content of 92%.

One hundred and ninety grams of the reaction mixture (84% of the total weight) were distilled from a Claisen flask, 165 grams of distillate being collected at 105–115° at 2 mm. of mercury. If the distillation produced practically 100% lauroyl chloride, the theoretical yield would be 218.5 × 0.84 or 183. Therefore 165 grams correspond to an apparent percentage yield of 90%. Analysis of the distilled product by the method described above gave 7% free fatty acid, and 91% total fatty acid. This is equivalent to 92% lauroyl chloride content and the percentage yield after distillation becomes 83%. It is evident that the crude reaction product, lauroyl chloride content 92%, contains the same percentage of lauroyl chloride as the product obtained by distillation. It appears from these results that distillation of the crude reaction products is not advantageous, since the quality of the product is not changed and the yield is decreased by 13%.

A chloride determination of the distilled product gave 14.9% chlorine. This value, compared with the calculated value of 16.3%, indicates a lauroyl chloride content of 91%. This is in close agreement with the result obtained by the titration method (92% lauroyl chloride content).

EFFECT OF PROLONGED HEATING OF LAUROYL CHLORIDE. Lauroyl chloride was obtained in 96% yield by the action of 1.2 moles of thionyl chloride on 1.0 mole of lauric acid. Analysis of the crude product by procedures A and B indicated a lauroyl chloride content of 92% (TFA = 89%; FFA = 4%).

One hundred and eighty grams of reaction mixture were maintained at 150° C. and 5 mm. of mercury for 2 hours, then again analyzed by procedures A and B; the lauroyl chloride content was found to be 84% (TFA = 91%; FFA = 14%), the apparent percentage yield after heating being 85%. The decrease in percentage yield as indicated by this experiment was comparable with that observed during a distillation carried out under similar conditions.

## DISCUSSION

The precision of the titration method, as indicated by a large number of duplicate determinations, is ±1%.

The titration method does not differentiate clearly between acid chloride and acid anhydride, as the latter, if present, is also capable of reaction with ammonia to form amide. If the acid chloride is to be employed in acylation reactions, however, this is not serious. Further, it is obvious that a reaction mixture which shows 96% acid chloride by titration must contain a minimum of 92% acid chloride and a maximum of 8% anhydride.

This procedure has been applied to the determination of yield of both saturated and unsaturated aliphatic acid chlorides containing 12 to 18 carbon atoms. Oleic acid chloride and saturated acid chlorides containing up to 16 carbon atoms can be analyzed by this procedure, giving results of the same accuracy as those obtained with lauric acid chloride. In the analysis of stearic acid chloride, stearic acid and stearamide tend to crystallize from ether at room temperature, but it was found that this did not significantly influence the ease of removal of excess mineral acid or the accuracy of the results.

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# Thiocyanate Complex as a Means of Extracting Cobalt

## Before Its Microdetermination by Other Methods

N. S. BAYLISS AND R. W. PICKERING, Department of Chemistry, University of Western Australia, Nedlands, Australia

THE colored complex of cobalt with nitroso R salt forms the basis of several analytical procedures for the microestimation of cobalt. Particularly in the case of biological samples, some separation of cobalt from other metals is a necessary preliminary to its estimation. Sylvester and Lampitt (*7*), for example, effected this preliminary separation by precipitating the cobalt (together with iron and copper) with $\alpha$-nitroso-$\beta$-naphthol. Marston and Dewey (*2*) used dithizone extractions at pH 5 and pH 8, the first to separate other heavy metals and the second to extract cobalt.

Since few metals other than cobalt react with ammonium thiocyanate to form a complex salt that can be extracted with organic solvents, ammonium thiocyanate suggested itself as a useful reagent to effect a preliminary separation of cobalt. The blue complex, $(NH_4)_2Co(SCN)_4$, is itself used for the colorimetric estimation of cobalt (*5*, *8*), but the color is not intense enough to be used for the small amounts of cobalt in biological samples. Iron, nickel, copper, and zinc as well as cobalt form complex thiocyanates that are at least partly extracted by organic solvents. However, the iron complex is not very soluble in solvents containing ether (*3*). Furthermore, nickel, copper, and zinc do not interfere with the final estimation of cobalt as the nitroso R salt complex (*2*).

The present investigation had a twofold object: to determine the best conditions (solvent composition, pH, and ammonium thiocyanate concentration) for extracting the cobalt thiocyanate complex, and to determine whether the extract could be used for the estimation of cobalt as the nitroso R salt complex. The authors were led finally to the following recommended procedure, which was used for all the cobalt recoveries described below, except for the obvious modifications required for investigating the effect of varying the conditions of the extraction.

The work reported was carried out during 1939 and would have been completed by a series of actual tests on biological samples but for the outbreak of the war. It is unlikely that the cobalt project will be resumed, but the authors believe that the results obtained will be sufficiently useful to other workers to justify publication.

### RECOMMENDED PROCEDURE

*a.* Dissolve the sample (containing, for convenience, 10 to 20 micrograms of cobalt) in hydrochloric acid, so that the resulting solution contains an excess of about 5 ml. of 6 *M* hydrochloric acid.

*b.* Add 20 ml. of 60% ammonium thiocyanate. The solution will normally be colored red at this stage owing to iron in the sample or in the reagents. Buffer the solution by adding 1 *M* ammonium citrate until the red ferric thiocyanate just disappears. Dilute with water to 50 ml. and add 4 ml. of ether to saturate the solution.

*c.* Extract the buffered aqueous solution with three successive 20-ml. portions of a mixture of 35% amyl alcohol and 65% ether. Cobalt enters the nonaqueous phase as $(NH_4)_2Co(CNS)_4$, while the extraction of ferric iron is prevented by the ammonium citrate.

*d.* Shake the combined extracts with two 20-ml. portions of 2 *M* ammonium hydroxide, thus returning the cobalt to the aqueous phase.

*e.* Evaporate the combined ammonia extracts to dryness. Add 20 ml. of 6 *M* nitric acid to destroy thiocyanate, and evaporate to dryness. Neutralize the resulting ammonium hydrogen sulfate by adding 2 *M* ammonium hydroxide and evaporate to dryness.

*f.* From this point the procedure is essentially that of Marston and Dewey (*2*). To the residue add 5 ml. of water, 5 ml. of ammonium citrate, and 0.5 ml. of nitroso R salt reagent. Heat the solution on a water bath for 5 minutes, add 5 ml. of concentrated nitric acid, and heat 5 minutes longer. After cooling, add 2 ml. of aqueous bromine, and remove excess bromine by boiling. Determine the cobalt content by comparison with standards containing known amounts of cobalt.

*g.* The comparison standards are prepared from the required amount of standard cobalt sulfate solution and ammonium sulfate. Evaporate the mixture to dryness and treat the residue as in *f*.

### REAGENTS

AMMONIUM THIOCYANATE SOLUTION, 60%. Dissolve 420 grams of ammonium thiocyanate in 280 ml. of water. Thoroughly extract the solution with a 0.1% solution of dithizone in chloroform, and remove the excess dithizone by washing with chloroform, and the excess chloroform by washing with amyl alcohol. The proper pH for the dithizone extraction may be found by adding ammonia to the ammonium thiocyanate until, on adding cobalt to a small sample of the solution, the cobalt is easily extracted again with dithizone.

AMMONIUM CITRATE, 1 *M*. Dissolve 210 grams of citric acid in 400 ml. of water, add 200 ml. of concentrated ammonia, and cool the solution. Add more ammonia until the solution is alkaline to phenolphthalein. Adjust the volume to 1 liter, and purify the solution as above with dithizone.

AMMONIUM SULFATE, 10%. Dissolve 100 grams of ammonium sulfate in 900 ml. of water. Purify the solution with dithizone as before.

AMMONIUM HYDROXIDE, 2 *M*. Redistill concentrated ammonia in Pyrex and dilute to the required extent.

HYDROCHLORIC ACID, 6 *M*. Dilute concentrated hydrochloric acid to the required extent and distill in Pyrex.

NITRIC ACID, CONCENTRATED. Twice distill pure nitric acid in Pyrex.

BROMINE, 0.2 *M*. A saturated solution of bromine (analytical reagent grade) in water.

NITROSO R SALT REAGENT. A 1% solution in water.

STANDARD COBALT SOLUTIONS. Solutions of cobalt sulfate in water containing 1 and 2 micrograms of cobalt per ml.

Table I. Effect of Solvent Composition, Using Ferric Thiocyanate as Indicator

(Volume of aqueous phase in each case was 50 ml., and it contained 10 micrograms of cobalt, 20 ml. of 60% ammonium thiocyanate, 5 ml. of 6 *M* hydrochloric acid, and sufficient ammonium citrate just to discharge red color of ferric thiocyanate. Solvent phase had a volume of 20 ml.)

| Composition of Solvent, Amyl Alcohol | Cobalt Recovered after Single Extraction |
|---|---|
| *% by Volume* | % |
| 31 | 81 |
| 33 | 83 |
| 34 | 86 |
| 36 | 85 |
| 37 | 82 |
| 39 | 75 |

### OPTIMUM COMPOSITION OF SOLVENT

Grahame and Seaborg (*1*) have stated that the partition coefficient of $(NH_4)_2Co(SCN)_4$ between amyl alcohol and an approximately 20% aqueous solution of ammonium thiocyanate is about 10. Rosenheim and Huldschinsky (*5*) recommended a mixture of ether and amyl alcohol in the ratio 25 to 1 for the separation of cobalt and nickel. Since the use of ether has the advantage that the solubility of ammonium thiocyanate in the nonaqueous phase is lowered, it was decided to study different mixtures of amyl alcohol and ether to find the optimum composition. Preliminary trials indicated that the best extraction of cobalt was from aqueous solutions buffered to a pH of between 3 and 4. A series of solvent mixtures was then tested with aqueous solutions buffered with ammonium citrate to be just acid to

Table II. Effect of Thiocyanate Concentration and pH on Extraction of Cobalt

(Aqueous phase contained 20 micrograms of cobalt in each case and was saturated with ether. Solvent phase in each case consisted of 20 ml. of a mixture of 35% amyl alcohol and 65% ether.)

| | Reagents Added to Aqueous Phase | | | | | |
|---|---|---|---|---|---|---|
| | Ammonium thiocyanate, 60% | Hydrochloric acid, 6 *M* | Ammonium citrate, 1 *M* | Water to make | Apparent pH of Aqueous Phase | Cobalt Recovered after Single Extraction |
| | *Ml.* | *Ml.* | *Ml.* | *Ml.* | | % |
| eries I | 10 | 1 | 10 | 60 | 5.4 | 0 |
| | 10 | 2 | 10 | 60 | 4.8 | 5 |
| | 10 | 3 | 10 | 60 | 4.1 | 16 |
| | 10 | 4 | 10 | 60 | 3.4 | 32 |
| | 10 | 5 | 10 | 60 | 2.8 | 27 |
| Series II | 20 | 2 | 10 | 60 | 4.8 | 59 |
| | 20 | 3 | 10 | 60 | 4.1 | 72 |
| | 20 | 4 | 10 | 60 | 3.4 | 85 |
| | 20 | 5 | 10 | 60 | 2.8 | 84 |
| Series III | 20 | 2 | 4.1 | 65 | 4.0 | 78 |
| | 20 | 4 | 9.0 | 65 | 3.8 | 81 |
| | 20 | 6 | 13.9 | 65 | 3.8 | 87 |
| | 20 | 8 | 18.6 | 65 | 3.7 | 83 |
| | 20 | 10 | 22.7 | 65 | 3.7 | 88 |

bromophenol blue (pH = 3). In each case the aqueous solutions were saturated with ether (4 ml. in 50 ml. of aqueous solution) before adding the extracting solvent. The best extraction, as determined by following the analytical procedure outlined above, was obtained with a solvent containing about 35% of amyl alcohol by volume.

After the method of using ferric iron as an indicator had been developed (see below), a further test was made of solvents in this composition range. The result is shown in Table I. It was confirmed that about 34% amyl alcohol is the optimum composition, 86% of the cobalt being removed from the aqueous phase in a single extraction.

The authors used in each case a single extraction with definite volumes of aqueous phase and extracting solvent. This was done deliberately to make it possible to calculate approximate partition coefficients if necessary, and to ensure strictly comparable results. When the results are applied in an analytical method, it is easy to determine how many extractions are needed for a desired recovery. Using optimum conditions of 86% recovery in one extraction, it is seen that two successive extractions would remove 98%, and three extractions 99.7%, of the cobalt in the aqueous phase.

The concentration of ammonium thiocyanate in the aqueous phase was 24%, and the partition coefficient for the complex thiocyanate under these conditions is about 15. While the extraction efficiency is not unduly sensitive to variations in the composition of the solvent, the authors' optimum composition is far from that recommended by Rosenheim and Huldschinsky (*3*).

### EFFECT OF pH AND THIOCYANATE CONCENTRATION

Experiments to study the effect of varying the pH and the thiocyanate concentration in the aqueous phase are outlined in Table II, Series I and II.

In each case the aqueous phase contained 20 micrograms of cobalt in 60 ml., and was saturated with ether before shaking with the extracting solvent. The pH was varied by altering the amount of hydrochloric acid present, and was measured after the cobalt had been removed by the extracting solvent. A quinhydrone electrode was used, and no attempt was made to correct for the salt effect resulting from the very high electrolyte concentration. The pH values are therefore "apparent" values only, and have relative, if not absolute, significance. The cobalt recovered in a single extraction was determined by carrying out the analytical procedure outlined above.

A pH in the neighborhood of 3.4 is seen to be the best, and a comparison of Series I and II shows the expected marked effect of altering the thiocyanate concentration. The extraction is reasonably good in Series II, where 60 ml. of aqueous phase contain 20 ml. of 60% ammonium thiocyanate. Using half this concentration as in Series I, the amount extracted is too small to be useful in an analytical method.

### SUPPRESSION OF FERRIC IRON AND USE AS INDICATOR

Ferric iron is invariably present at much greater concentration in biological samples than is cobalt, and it is also normally present in small quantities in reagents that have been purified with dithizone, which does not form an iron complex. It is therefore necessary to suppress the ferric thiocyanate complex in order to prevent interference with the cobalt determination. Sodium pyrophosphate has been suggested for this purpose (*6*); but the authors found ammonium citrate more effective. It was also noticed, in the experiments comprising Series I and II, that the addition of ammonium citrate as a buffer caused the red color of the ferric thiocyanate complex (resulting from the iron in the authors' reagents) to disappear at a point very close to the optimum pH for the extraction.

Series III, Table II, records experiments performed to find whether ferric iron could be used as an indicator. Solutions containing 20 micrograms of cobalt were treated with ammonium thiocyanate and varying amounts of hydrochloric acid. Ammonium citrate was then added in each case until the red ferric thiocyanate had just disappeared. The volumes were made up to a convenient, uniform value; and the cobalt was extracted and determined as before. In each case the extraction was good, so that the cobalt in the aqueous phase could be removed practically quantitatively by two or three extractions. The use of ferric iron as an indicator is therefore possible, and it has an advantage over organic indicators in that the latter are carried through the procedure and may interfere with the final color comparison.

### REMOVAL OF THIOCYANATE

Ammonium thiocyanate is slightly soluble in the mixture of ether and amyl alcohol, and if it is still present when the excess nitroso R salt is being nitrated, there is a violent reaction between the nitric acid and the thiocyanate, with the formation of a yellow precipitate which is probably isoperthiocyanic acid (*4*). Using the solvent of optimum composition for the extraction, the authors found that 6 *M* nitric acid removed the thiocyanate satisfactorily in stage *e* of the procedure described above. With more concentrated acid, the reaction was too violent.

### CONCLUSIONS

In the extraction of the cobalt thiocyanate complex from aqueous solutions containing ammonium thiocyanate and small quantities of cobalt, the most suitable mixture of ether and amyl alcohol is one containing 35% by volume of amyl alcohol, providing the aqueous phase is first saturated with ether.

If the aqueous phase of volume 50 ml. contains 10 to 20 micrograms of cobalt, and if the ammonium thiocyanate concentration is at least 20%, 86% of the cobalt can be removed by a single extraction with 20 ml. of the above solvent if the pH is in the region of 3.5. This corresponds to a partition coefficient of 15 between the solvent phase and the aqueous phase. Two extractions would therefore remove 98%, and three extractions 99.7%, of the cobalt in the aqueous phase.

If the aqueous phase of volume 50 ml. contains 5 ml. of 6 *N* hydrochloric acid, the addition of ammonium citrate until the red color of ferric thiocyanate just disappears not only prevents interference by iron, but at the same time gives the correct pH for the optimum extraction of the cobalt thiocyanate complex, thus dispensing with the need for an organic indicator.

The cobalt thiocyanate complex can be back-extracted from the organic solvent by 2 *M* ammonia, yielding a residue which, after destroying the thiocyanate with 6 *M* nitric acid and neutralizing the resulting ammonium hydrogen sulfate, can be used for the estimation of cobalt by the nitroso R salt method of Marston and Dewey.

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# Small Glass Center-Tube Fractionating Column

E. A. NARAGON AND C. J. LEWIS

Beacon Research Laboratory, The Texas Co., Beacon, N. Y.

**An improved small glass center-tube fractionating column which can be easily reproduced is described and construction details are given. The fractionating section, which is surrounded by a silvered vacuum jacket, is 30.5 cm. long and consists of an 8-mm. inside diameter outer tube and a 6.5-mm. outside diameter center tube. Above the fractionating section a distributor is used which distributes the reflux from the head half to the outer tube and half to the center tube. The column is equipped with an automatic take-off valve. It has an efficiency of over 75 theoretical plates with an H.E.T.P. of less than 0.4 cm.**

THERE is always a need in the laboratory for a fractionating column which is capable of efficiently separating small quantities of close-boiling liquids. To be of practical value such a column must have a low operating holdup, must be easily reproduced from readily available materials, and must be easily operated with a minimum amount of attention. A center-tube column previously described (*5, 6*) was found to fill all these conditions except that it is not easily reproduced.

This article deals with a fractionating column that is similar to the one previously described but includes several improvements in design and construction technique which make it easily reproduced and increase its operating efficiency. The improvements include a reflux distributor, a method of accurately spacing the center tube, and an automatic take-off system. It has an efficiency under conditions of total reflux of over 75 theoretical plates with an H.E.T.P. of less than 0.4 cm. for a 30.5-cm. (1-foot) fractionating section. The column can be used not only for micro work but for work involving larger quantities of liquid.

## CONSTRUCTION

The following procedure was used to construct the column shown diagrammatically in Figure 1.

A tube of 6.5 ± 0.1 mm. outside diameter was carefully selected for straightness and uniformity from stock. Capillary tubing was used, since it was found to be more satisfactory in meeting these requirements than either regular tubing or rod. One end of this tube was drawn down and sealed to an 8-mm. ball. Troughs which were made by cutting 7-mm. outside diameter tubing in half with a glass saw were sealed on opposite sides of the ball just below the horizontal center and tilted downward at an angle of 15° from the horizontal. The ends of the troughs were cut at an angle of 30° from the vertical and at right angles to the length. Slots of 1 × 3 mm. were cut into the ends of the troughs. Glass projections to be used for supports were sealed to the tube just below the ball. This assembly was made to fit within 25-mm. outside diameter tubing with a clearance of approximately 1 mm. between the wall and the ends of the troughs and projections with the ball centered.

The bottom of the 6.5-mm. outside diameter tube was drawn down to 2-mm. outside diameter and left extended for 5 cm. (2 inches) with a small needle eye at the end. The length of the tube between the drawn-down ends was 30.5 cm. The tube was wrapped at a 6-mm. pitch with copper wire, which had been stretched to an approximate outside diameter of 0.75 mm., making use of the needle eye and the glass projections to hold the ends of the wire. A 30.5-cm. length of Ace Trubore tubing (Pyrex) of 8 ± 0.01 mm. inside diameter was flared out slightly at both ends. A 25-mm. outside diameter tube was sealed to one end of it. The tube with the wire wrapping was inserted through the large tube into the Trubore tubing by rubbing the wire down carefully with fine emery cloth to obtain a snug fit without any binding. The wire was loosened from the needle eye and cut back to the Trubore tubing. The end of the center tube was drawn down to eliminate the needle eye and was bent over to the side. An 18-mm. outside diameter tube was sealed to the other end of the Trubore tube, care being exercised to avoid constricting the annular space. The bent end of the center tube was sealed to the 18-mm. tube. A drip tip was ring-sealed above the ball with a clearance of about 2 mm. between the tip and the ball. The glass projections were sealed to the wall.

The jacket, bottom drip tip and joint, head assembly, and thermowell, which had a thin wall at the bottom, were added in the order named. The column was annealed. During the annealing, air was drawn slowly through the column to ensure even heating and prevent differential stresses. The copper wire was removed with aqua regia and nitric acid. The meniscus in the annular space was tested for flatness as a check on the uniformity of the spacing by raising and lowering a leveling bulb which was connected to the bottom of the column and contained first water and then a hydrocarbon.

The following evacuation procedure was used after silvering the jacket. The column was placed in an oven and sealed to a system comprising a liquid air trap, a two-stage fractionating pump (Distillation Products Co.), and a Welch Duo-Seal pump. Evacuation was started. The temperature of the column was brought up slowly to 300° C. while air was drawn through the annular space. The evacuation was continued at 300° C. until the pressure was down to $10^{-6}$ mm. of mercury. The heat was then cut back and the column allowed to cool to approximately 125° C. Evacuation was continued at this temperature until a pressure of $4 \times 10^{-7}$ mm. of mercury or lower was obtained as measured by an ionization gage unit (Type HG-200, Distillation Products Co.) and then the column was hermetically sealed. The finished column was allowed to cool slowly to room temperature. It was insulated with 1-inch magnesia pipe lagging.

The critical dimensions in the column are those pertaining to the distributor and to the annular clearance between the center tube and the outside tube. The 2-mm. clearance between the drip tip and ball of the distributor gives a liquid contact which spreads the reflux to the column evenly across the ball, with the result that approximately half of it flows down the troughs to the outside wall and the remainder flows down the center tube. The clearance and slots at the ends of the troughs permit a liquid contact to the outside wall. It is not necessary to use Trubore tubing for the outside tube to obtain the desired annular clearance if sufficient care is exercised in selecting a tube of uniform diameter from stock. For general use, however, Trubore tubing is recommended. A head assembly half the size of the one shown

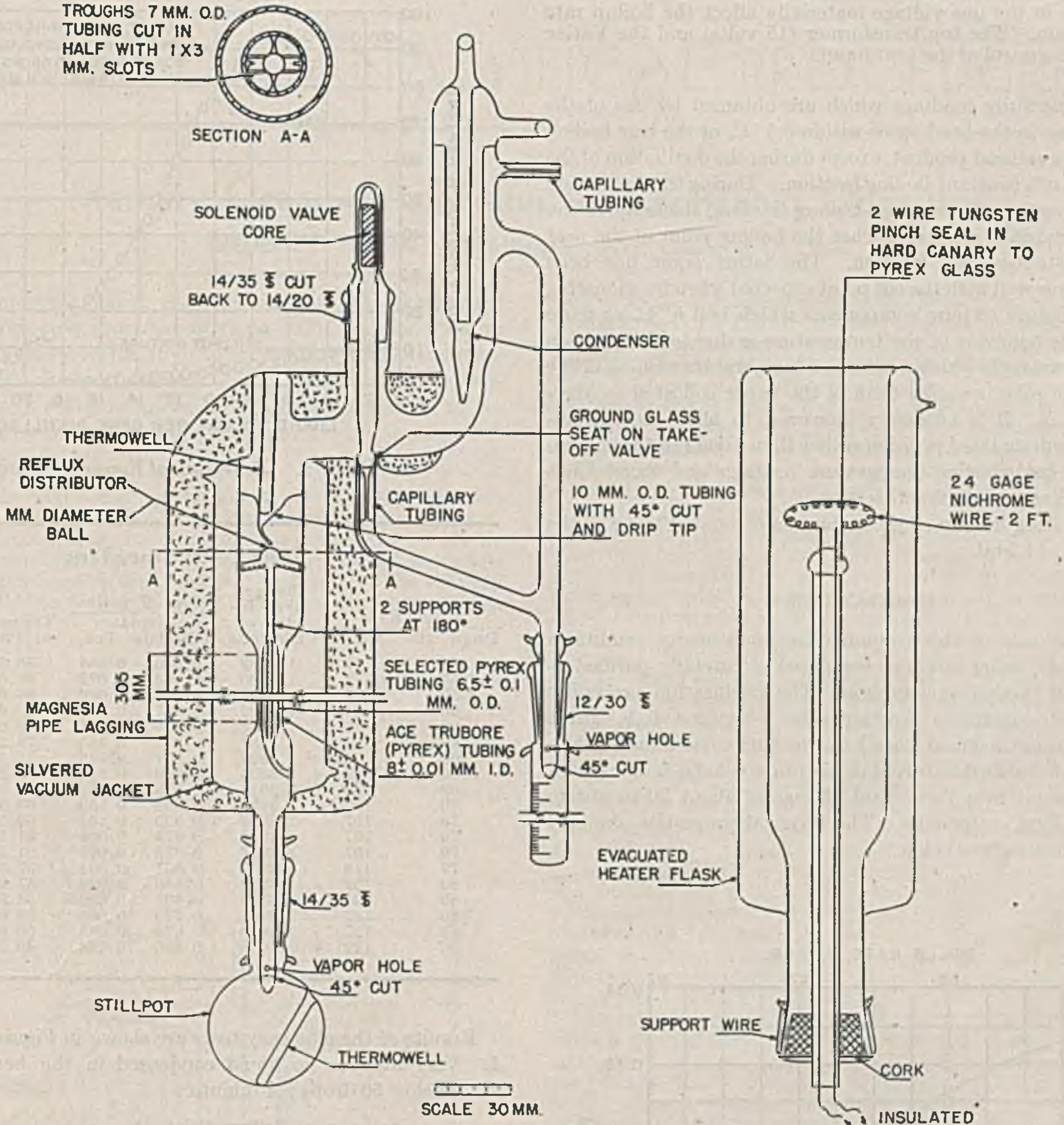

Figure 1. Diagram of Fractionating Column

in Figure 1 has been found to be satisfactory on an otherwise duplicate column.

The spherical end of the take-off valve was made in a brass mold. The female impression was made with a ball bearing attached to a rod. The ground surface was obtained with FFF Carborundum and polished with cerium oxide.

An iron-constantan thermocouple was cemented in the thin-walled thermowell by the method suggested by Baker (*1*), using Technical B copper cement obtained from the Weinbaum Dental Supply Company (220 West 42nd St., New York, N. Y.). This cement gives good heat conductivity to the thermocouple and permits accurate temperature readings.

The evacuated (unsilvered) heater flask was constructed as shown in Figure 1.

### OPERATION

The operation of the column requires a minimum amount of attention after it has been started and equilibrium conditions have been reached. It consists of periodically measuring the temperatures in the head and still pot, the boilup rate, and the volume or weight of the distillate. Various fractions are collected by changing the product receiver as desired. The take-off rate being slow, the product receiver does not have to be changed often and, therefore, very little of the operator's time is required for this operation. The still-pot temperature is measured, since it gives an early indication of a cut point and warns of the need for increasing the heat input to the still pot so as to maintain the boilup rate constant.

In starting the column the sample is pipetted or weighed into the still pot. Boiling chips are added. A hydrocarbon-insoluble grease or any other suitable grease is applied to the ground joint at the base of the column and the still pot is put in place and held with small springs hooked to the glass projections. A thermocouple is inserted into the thermowell of the still pot. The heater flask is raised around the still pot and insulated at the top by use of glass wool. The heater element within the heater flask is raised to within 12 mm. of the still pot. The heat is turned on and adjusted so that a boilup rate of approximately 80 drops per minute into the still pot is obtained within a half hour. After refluxing at this rate for one hour, the heat input is adjusted to give the desired boilup rate which is maintained constant. Except for the lower boilup rates, 3 to 4 hours then are usually required to reach equilibrium. After equilibrium is reached the electric timer, which is used in conjunction with a solenoid to operate the take-off valve, is adjusted and started to give the desired take-off rate.

Heat input to the column is controlled through a constant-voltage regulator, a toy transformer, and a Variac in series. Use of the constant-voltage regulator is recommended, since small fluctuations in the line voltage materially affect the boilup rate in the column. The toy transformer (15 volts) and the Variac permit close control of the heat input.

The temperature readings which are obtained by use of the thermocouple in the head agree within 0.5° C. of the true boiling point of the overhead product, except during the distillation of the last portion of a constant-boiling fraction. During the distillation of the last portion of a constant-boiling fraction, the temperature increases gradually until it reaches the boiling point of the next higher constant-boiling fraction. The latter point has been found to agree well with the cut point expected when fractionating a known mixture of pure components which boil 6° C. or more apart. This behavior of the temperature is due to the position of the thermocouple which results in a temperature reading of the reflux to the column rather than of the vapor collected as overhead product. It is necessary, however, to have the thermocouple in its designated position rather than higher in the column in order to get constant-temperature readings and thereby follow the progress of the fractionation.

The operating holdup of the column is estimated to be of the order of 1.0 to 1.5 ml.

### EFFICIENCY TESTS

Efficiency tests of this column were made under conditions of total reflux, using mixtures composed of carefully purified *n*-heptane and methyl cyclohexane. The purification procedure consisted of separately fractionating *n*-heptane (C.P. grade from California Chemical Corp.) and methyl cyclohexane (white label grade from Eastman Kodak Co.) in a column under conditions equivalent to a theoretical platage of about 30 to obtain constant-boiling center cuts. The physical properties obtained on these cuts are given below.

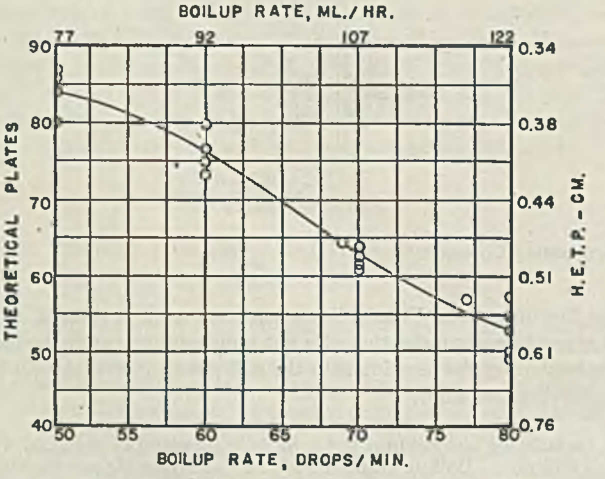

Figure 2. Efficiency Tests

Analyses of the *n*-heptane–methyl cyclohexane mixtures were made using the refractive index *vs.* mole fraction *n*-heptane data of Bromiley and Quiggle (*2*). Analyses of the distillate samples were obtained directly. Analyses of the still-pot mixtures which ranged from 20 to 40 ml. in volume were obtained by back-calculating from the analyses and volumes of the charge to the still pot and of the distillate samples, assuming no holdup in the column. The charge to the still pot was analyzed, measured, and changed periodically to make certain that cumulative errors did not invalidate the efficiency values. This method gave slightly lower efficiency values than would be obtained by direct analyses of the still-pot mixtures but was more convenient. Fenske's (*4*) formula (relative volatility = 1.07) was used for calculating the efficiencies in terms of theoretical plates.

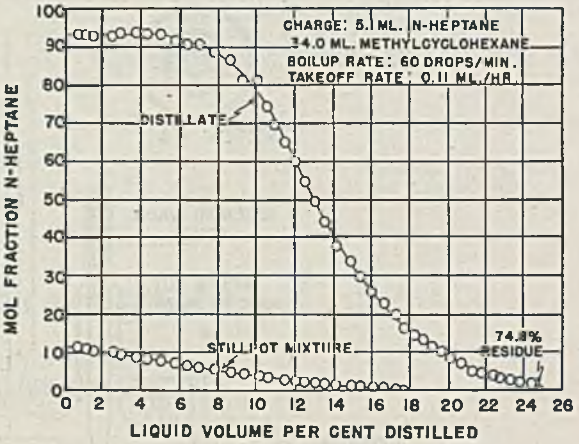

Figure 3. Distillation of Known Mixture

Table I. Efficiency Tests

| Boilup Rate | | Refractive Index of Distillate | Mole Fraction *n*-Heptane | | Theoretical Plates | H.E.T.P., Cm. |
|---|---|---|---|---|---|---|
| Drops/min. | Ml./hr. | | Distillate | Pot | | |
| 50 | 77 | 1.3888 | 0.970 | 0.084 | 86.5 | 0.35 |
| 50 | 77 | 1.3890 | 0.963 | 0.072 | 86.0 | 0.35 |
| 50 | 77 | 1.3890 | 0.963 | 0.080 | 84.0 | 0.36 |
| 50 | 77 | 1.3892 | 0.957 | 0.089 | 80.0 | 0.38 |
| 60 | 92 | 1.3888 | 0.970 | 0.121 | 80.0 | 0.38 |
| 60 | 92 | 1.3887 | 0.972 | 0.165 | 76.5 | 0.40 |
| 60 | 92 | 1.3892 | 0.957 | 0.118 | 75.5 | 0.40 |
| 60 | 92 | 1.3894 | 0.950 | 0.115 | 73.5 | 0.42 |
| 69 | 106 | 1.3916 | 0.878 | 0.083 | 64.5 | 0.47 |
| 70 | 107 | 1.3899 | 0.934 | 0.159 | 63.5 | 0.48 |
| 70 | 107 | 1.3900 | 0.930 | 0.161 | 62.5 | 0.49 |
| 70 | 107 | 1.3916 | 0.878 | 0.099 | 61.5 | 0.49 |
| 70 | 107 | 1.3917 | 0.875 | 0.097 | 61.5 | 0.50 |
| 77 | 118 | 1.3932 | 0.827 | 0.091 | 57.0 | 0.54 |
| 80 | 122 | 1.3928 | 0.840 | 0.098 | 57.0 | 0.54 |
| 80 | 122 | 1.3938 | 0.807 | 0.096 | 54.5 | 0.56 |
| 80 | 122 | 1.3961 | 0.730 | 0.069 | 53.0 | 0.58 |
| 80 | 122 | 1.3979 | 0.675 | 0.065 | 50.0 | 0.60 |
| 80 | 122 | 1.3928 | 0.840 | 0.154 | 49.5 | 0.62 |

Results of the efficiency tests are shown in Figure 2 and Table I. Very little or no liquid condensed in the head at boilup rates below 50 drops per minute.

| | Boiling Point at Pressure of 750 Mm. Hg, ° C. | Refractive Index at 20° C. | |
|---|---|---|---|
| | | Observed | Literature (*3*) |
| *n*-Heptane | 97.8 | 1.3878 | 1.3877 |
| Methyl cyclohexane | 100.2 | 1.4233 | 1.4230 |

### DISTILLATION OF KNOWN MIXTURE

The distillation of a known mixture of *n*-heptane and methyl cyclohexane was carried out at a boilup rate of 60 drops per minute into the still pot with a continual take-off rate averaging 0.11 ml. per hour. Samples of the distillate were taken every 2 hours and were analyzed by the refractive index data of Bromiley and Quiggle (*2*). Analyses of the still-pot mixtures were made by back-calculating as previously described. Results of this distillation are shown in Figure 3.

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# NOTES ON ANALYTICAL PROCEDURES

## Mercury Cleaning Apparatus for Continuous Operation

FREDERIC E. HOLMES, 6515 Blueridge Ave., Cincinnati 13, Ohio

THE present contribution is concerned with the mechanical means of bringing about thorough agitation and fine division of mercury in contact with any chosen cleaning solutions rather than with the chemical process itself. The apparatus consists of as many units, arranged in series, as are needed to accommodate the desired number of reagents and washes. A single unit is shown in Figure 1.

Each unit is prepared for operation in the following manner. In order to prevent escape of solution, a small amount of mercury is introduced into the outlet trap through the outlet by means of a funnel and short piece of rubber tubing, and a few drops are also placed in the inlet cup and trap. The solution reservoir is filled to within about 100 ml. of its capacity with the desired cleaning solution and connected with the unit by rubber tubing as shown. The air inlet is connected by pressure tubing to a source of air under pressure. Cleaning solution is poured in through the splash trap until the level reaches about halfway between bottom and top of the pump tube. The connections to the solution reservoir are freed of air by pinching the rubber tubing. Air under pressure is admitted cautiously through the air inlet until it is bubbling freely from the top of the ascending tube at *J* in the solution chamber. Mercury is then allowed to flow into the inlet cup of the first unit, and the rate of flow is adjusted to the desired rate of cleaning.

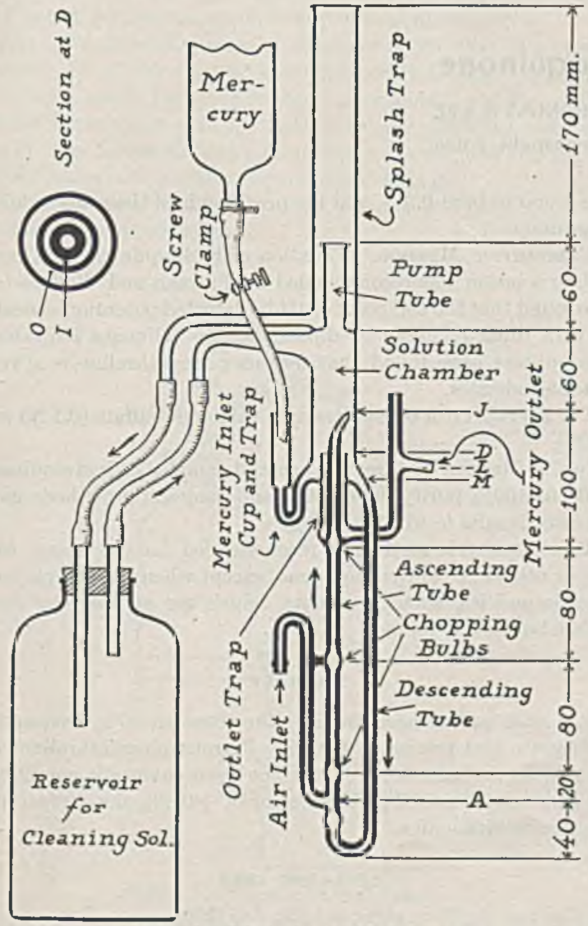

Figure 1. Single Unit of Apparatus

| | |
|---|---|
| Splash trap and solution chamber | 25–28 mm.* |
| Outlet trap (part surrounding ascending tube) | 15–16 mm.* |
| Ascending and descending tubes | 9 ± 0.5 mm.* |
| Inside diameters (bore) | 3–3.5 mm. |
| Pump tube | 15 mm. |
| Vertical distance, *D* to *L* | 11–13 mm. |
| Vertical distance, *D* to *M* | 20–22 mm. |
| Inside diameter of chopping bulbs | 9–11 mm. |

Dimensions are outside diameters except as noted. * Calculated for desired ratio of delivery to recirculation.

Air entering the ascending tube at *A* makes the column of fluid above this point lighter than in the descending tube and produces a rapid flow in the direction indicated by the arrows. Mercury entering the solution chamber through the inlet trap flows into the descending tube at *M* in large drops interspersed with solution from the chamber and thence down this tube to the ascending tube. The bulb below *A* retains enough mercury to act as a valve, retarding backward flow and favoring normal flow. Above *A*, the mercury is broken into smaller droplets by the air. The chopping bulbs in the ascending tube promote division, coalescence, and redivision of the mercury, thus frequently renewing the surface exposed to action of the solution and greatly extending its area. During their progress upward in this tube, these fine droplets are falling in relation to, and through, the more rapidly moving solution and air. Air, solution, and mercury are ejected into the solution chamber from the jet at *J*. The air passes out through the pump tube, carrying solution over with it and maintaining circulation of the solution between reservoir and solution chamber. The mercury impinges on the wall of the chamber and falls back in a shower of droplets to the dividing point, *D*, where a small part enters the top of the outlet trap. The larger portion falls to the bottom of the chamber and reenters the cleaning cycle.

The ratio of mercury delivered from the outlet to that recirculated is approximately proportional to the areas of the annular space between the outside of the ascending tube and the top of the outlet trap and that between the top of the trap and the wall of the solution chamber, indicated by *I* and *O*, respectively, in the insert. The ratio is fixed in the construction of each unit. A ratio of approximately 1 to 5 has been used.

Adjustments during operation are not critical within a wide range. Normal function is maintained by rates of flow of air from that of a "lazy" stream of bubbles to that which produces vigorous action and maximum turbulence. The limiting factor is back-pressure in the ascending tube. The rate of flow of mercury may be from the minimum obtainable to as much as 8 kg. per hour attained in one unit tested. Because of this wide range in rate of performance, each unit of the series will accommodate varying amounts delivered from the preceding unit, and no elaborate balancing of adjustments is required.

Air under pressure may be obtained from the usual laboratory system or from a pump delivering at a pressure of 700 grams per sq. cm. (10 pounds per square inch). Each unit requires a separate valve in a line carrying full pressure, so that the unit having lowest back-pressure cannot steal air from the others. In order to use one pump or one outlet of the laboratory air supply for several units, a metal manifold having a sufficient number of metal valves is suggested. If this is made of large pipe capped at one end, it can be filled with cotton or other material to serve as a filter to remove oil and dirt from the air.

To prevent escape of cleaning solution when a unit is not in use, the pressure tubing may be disconnected at the metal valve and the free end raised and hung on the supporting frame by means of a pinchclamp.

Batch operation of single units of a similar design, using successive changes of cleaning solution, has been tested over a period of two years at Wright Field, Dayton, Ohio, and at Bushnell General Hospital, Brigham, Utah, and proved convenient and satisfactory for processing very small amounts of mercury. A single unit of the present apparatus may be used similarly when economy of space is more important than the advantages of simultaneous multiple operations.

The advantages of the apparatus are fine division of mercury and prolonged contact with the solution, elimination of fine orifices which tend to become clogged with dirt, automatic operation requiring little attention, relatively small size, light weight, adaptability to few or many simultaneous cleaning operations and to very small and very large capacity requirements, and small holdup.

Cleaning solutions that have been used satisfactorily in this type of apparatus are 10% lactic acid, 5% sodium hydroxide, 5% sulfuric acid, 3 to 10% nitric acid, and water, usually in the order named when more than one is used. Control of operations has been based on such criteria as speed of coalescence of droplets, freedom from blemish of the mercury surface, freedom from stain on glass surfaces in prolonged contact with the mercury, and clean appearance during distillation. More specific data have not been sought. It has been assumed that quality of product is inversely related to its rate of flow.

Figure 1 is drawn to scale, except that some diameters are slightly exaggerated for printing. Operable models can be made within a wide range of dimensions and proportions.

Ascending tubes have been used having inside diameters up to 4 mm. and lengths up to 600 mm. The descending tube should have the same inside diameter as that of the ascending tube; greater bore results in unstable operation, and smaller bore yields little if any advantage. The bore of the jet should not be tapered to less than half that of the rest of the ascending tube; if too small, the back pressure is excessive. The ascending and descending tubes should be built as close to each other as possible to avoid collection of excessive amount of mercury in the horizontal part of the loop. A slight funnel-like expansion of the top of the descending tube favors normal flow. A slight constriction at the bottom of the pump tube is intended to improve pumping action.

The side tubes for connection with the solution reservoir are separated horizontally sufficiently to avoid difficult glass blowing and excessive fragility. The one carrying the return to the solution chamber is slightly funnel-shaped and inclined to provide for return of mercury droplets to the chamber. The mercury inlet cup and trap and the mercury outlet are actually in a plane perpendicular to that of the ascending and descending tubes and air inlet. The length of the splash trap may be increased for alkaline or soapy solutions, or caprylic alcohol may be used to break any foam. Any convenient bottle is suitable for the solution reservoir.

Units of this apparatus may be obtained from Harshaw Scientific Company, Cincinnati, Ohio.

# Assay of Hydroquinone

**I. M. KOLTHOFF AND THOMAS S. LEE**
**University of Minnesota, Minneapolis, Minn.**

A COMPARISON has been made of the iodometric and cerometric titrations in the assay of hydroquinone.

Iodometric Method. In this method an excess of standard iodine solution is added to a solution of the hydroquinone and the excess iodine is back-titrated (*1*, *4*, *5*, *6*). The sources of error have been studied systematically with the following results:

1. In order to have the oxidation of hydroquinone go to completion the pH of the solution must be greater than 6. Many authors (*1*, *5*, *6*) recommend a solution of sodium hydrogen carbonate (pH 8.4) as a suitable reaction medium.
2. If the reaction is carried out in a hydrogen carbonate solution, the solution should be protected from air to prevent air oxidation of hydroquinone (*3*). The back-titration of excess iodine must be made with arsenious acid, not with sodium thiosulfate.
3. Another source of error, not discussed in the literature, is that iodine reacts to some extent with quinone to form an orange or brown colored product. From a number of experiments it was concluded that the back-titration of iodine must be made relatively quickly in order to reduce the extent of reaction of iodine with quinone to a minimum. The orange or brown compound formed also obscures the end point.

The following procedure, taken from the Laboratory Manual of the Rubber Reserve Company and modified slightly, was found to give results almost identical with the procedure recommended by Kolthoff (*4*).

*Procedure.* Accurately weigh a sample of 0.15 to 0.2 gram and transfer it to an Erlenmeyer flask. Add 25 ml. of water, dissolve the hydroquinone, and add 5 grams of solid carbon dioxide and 2 grams of sodium hydrogen carbonate. Cover the flask with a small watch glass and swirl the flask intermittently until the dry ice has disappeared. Then warm the solution to room temperature but not above. Do not allow the sample to stand any length of time at this point. Add 1 ml. of starch indicator and titrate immediately with 0.1 *N* iodine solution to the starch-iodine end point. Add just 1 ml. of iodine solution in excess and back-titrate with 0.05 *N* arsenious acid solution to a light yellow color.

The error in both Kolthoff's procedure and that given above was found to be +0.3%, and the precision is of the same order of magnitude.

Cerometric Method. Titration of hydroquinone with ceric sulfate solution was recommended by Furman and Wallace (*2*), who found that the end point could be detected potentiometrically or with diphenylamine or diphenylamine sulfonate indicators. The authors have found that ferrous phenanthroline is a very suitable indicator.

The average error of ten titrations with ceric sulfate (0.1 *N*) was 0.02%.

In the titration of three commercial samples of hydroquinone of 96 to 100% purity, iodometric and cerometric methods gave the same results to within ±0.3%.

The cerometric method is recommended for the assay, routine or otherwise, of hydroquinone, except when the sample contains impurities, such as oxalate, which are oxidized by ceric sulfate but not by iodine.

## SUMMARY

The ceric sulfate procedure for the titration of hydroquinone is accurate and precise to 0.02%. Ferrous phenanthroline can be used as an indicator. Under the most favorable conditions the iodometric method gives an error of +0.3%, due to reaction of quinone with iodine.

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# Constant-Level Feeder for Thermostatic Baths and Continuous Evaporators

M. S. TELANG, Laxminarayan Institute of Technology, Nagpur University, Nagpur, India

VARIOUS forms of useful constant-level devices for thermostatic baths at elevated temperatures have been described (*2–14, 16–23*). Such devices may be broadly classified into three groups: (1) The common form of constant-level attachment not employing the siphon principle, but working in combination with an overflow arrangement. To attach this form to the bath, it is necessary to drill a hole in the bath. (2) Devices depending upon the siphon principle in combination with an overflow arrangement, requiring no drilling of hole to attach to the bath. (3) Devices using siphon system in accordance with the principle of the Mariotte bottle, eliminating drilling of any hole in the bath vessel.

Objections to the first type have been pointed out by Wilde (*20*). Devices of the second type have certain advantages, but require a thermostat in a place easily accessible to a water tap and drain. They waste water, sometimes even hot water, and for this reason, they consume more of the gas or electricity used for heating in conjunction with thermoregulators. If the tap water is not soft enough, these devices cannot be run with distilled water to avoid scale formation in the bath. Some of these devices involve a lot of glass blowing. In many cases, it is necessary to pay periodic attention to adjustment of water flow.

The third type eliminates the defects of the first two types; however, reservoirs must be frequently refilled, though attempts have been made by some authors to minimize refilling. The present paper deals with the third type, simplifies the construction of older forms, indicates improvements over previous forms, and discusses both advantages and disadvantages.

The device is shown in Figure 1. Clamps and other supports are not shown in the diagram.

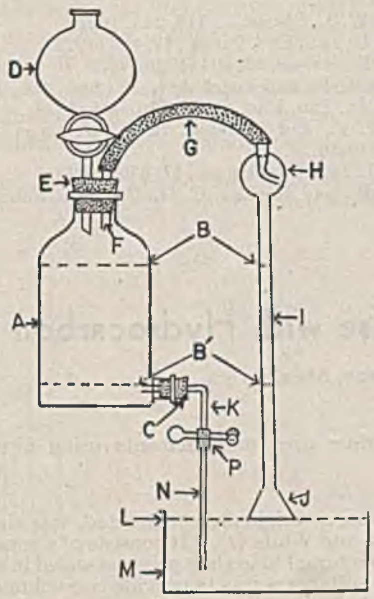

Figure 1. Constant-Level Feeder

$A$. Aspirator bottle, of any convenient size. $B$. Water level at beginning. $B'$. Water level at end. $C$. Single-holed rubber stopper to fit bottom tubulature outlet of $A$. $D$. Separatory funnel of any size. $E$. Double-holed rubber stopper to fit mouth of $A$. $F$. Connecting glass tube, 6-mm. diameter. $G$. Rubber tube. $H$. Splash head such as that of Kjeldahl's apparatus. $I$. Long stem of funnel $J$ fused or connected by short rubber tube to $H$. Rim diameter of $J$ 5 cm., diameter of $I$ 6 mm. $K$. Delivery tube, 3-mm. diameter. $L$. Actual level of water in thermostatic bath $M$, coinciding with rim of $J$. $N$. Feed tube of glass, 3-mm. diameter. $P$. Pinchcock and short rubber tube connecting $N$ and $K$.

$A$ serves as the water reservoir, $D$ being the refiller. $N$ is the feeder to the bath. $G$, being flexible, permits adjustment of level $L$ in $M$. The splash head, $H$, prevents carrying over water from $M$ back into $A$. The limb, $HIJ$, can be regarded as a balancer of pressure in $A$ and consequently as a level controller in $M$. Funnel $J$ is necessary, as otherwise, even if the level falls below $L$, a column of water remains suspended in $I$, owing to surface tension effects, and will throw the feeder out of action.

To start working, the lower end of $N$ is immersed well below level $L$ which, in turn, is adjusted to a predetermined height by the position of the rim of $J$. $P$ is closed and $A$ is filled with water through $D$. While filling $A$, $P$ should be closed, as otherwise the water level in $M$ rises above $L$ by draining through $N$. Extra pressure produced by compression of air enclosed in the space above the water leveli n $A$ during filling through $D$ will be relieved by the escape of air bubbles through $F$ and ultimately through $J$. If filling of $A$ is stopped by closing the tap of $D$ and if $P$ is then opened, a slight readjustment of the levels of water in both $A$ and $M$ takes place and water rises in tube $I$ until it is the same as in $A$ as shown at $B$. If the water is cold at first, the level in $M$ stands a fraction of a centimeter above $L$. As heating and evaporation progress, the level falls to $L$ and remains practically constant throughout. Whenever the level falls very slightly below $L$ owing to continued evaporation, the water seal at the rim of $J$ is broken and air bubbles escape into $A$ through $HIJ$. The pressure of air enclosed above water in $A$ thus increases slightly, thereby driving more water through feeder $N$ until the level in $M$ rises again to $L$ and reaches the mouth of $J$. This process continues as long as there is a water head available in $A$. When the water becomes hot, the water in the balancer may rise a little higher than in $A$, owing to diminution in density of water at elevated temperatures.

Operation is an application of the principle of the Mariotte bottle. The flow of water from $A$ depends jointly upon the head of water and the pressure of air enclosed in $A$. Since the pressure of air in $A$ is controlled by the balancer limb, $HIJ$, it is evident why the flow of water from $A$ into $M$ should stop when the mouth of $J$ is sealed by water reaching level $L$.

The above arrangement is a modification of Gerdel's device (*7*), which has the following defects: To refill, the stopper of the reservoir bottle must be removed or a separatory funnel attached through the stopper by boring a fourth hole in it; this leads to an undesirable state of congestion. Siphoning continues during refilling if done through a separatory funnel, and thus raises the level of water in the bath. At the boiling temperature, some water is carried from the bath back into the reservoir, owing to the increased frequency of air bubbles rising in the balancer limb. This may not be a serious defect so far as the thermostatic bath is concerned, but if all the distilled water in the reservoir is not used up by the bath, the water remaining will be rendered unfit for other purposes, owing to contamination with the water in the bath. At elevated temperatures, air dissolved in water is expelled and air bubbles accumulate at the head of the siphon, hindering or stopping the siphoning operation. These defects are eliminated in the improved device here described.

The advantages of this arrangement are obvious. It can be made of materials readily available in a good laboratory. It feeds water to the bath only when necessary, eliminating wastage of hot water. It can be set up in any desired place. It avoids any damage to vessels, especially those of glass or stoneware. It can be worked even at the boiling temperature. Any desired water level in the bath can be obtained quickly by adjusting the position of the rim of $J$. The device and the bath are entirely independent of each other, hence substitution of either is possible. As there is no continuous flow of water, adjustment of flow needs no attention. Dissolved air expelled from hot water in the bath has no place to accumulate to obstruct siphoning operation, as the flow of water depends mainly upon the hydrostatic head. There is no complicated glass blowing, as the equipment needed is of standard type. It can be used with any quality of water, being specially suitable for distilled water. Refilling of the aspirator bottle is necessary; but this is not serious if an aspirator bottle of large capacity is chosen. For a thermostatic bath of normal size (*13*), refilling may be necessary once a day. If a metal tank reservoir is available, so much the better.

Continuous Evaporators. Evaporators may be of various types (*1*), but they are either open pans or closed bodies employing vacuum. They may be of the small-scale laboratory size or the larger size used in industry. The essential features of a laboratory-size continuous open evaporator are described in the present paper; results referring to a vacuum evaporator will form the subject matter of a future paper.

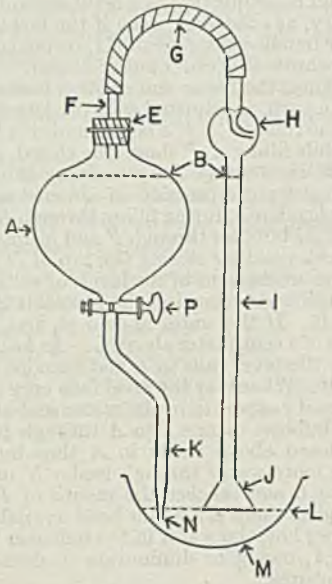

Figure 2. Feeder for Continuous Evaporator

Literature on the subject of constant-level feeders for continuous evaporators, particularly laboratory or pilot-plant size, is rather scanty. A device for maintaining a constant level during continuous evaporation in the determination of total dissolved solids in water recently described (*15*) has to be specially made to given specifications, and so does not permit the choice of materials ordinarily available in a laboratory.

If an evaporating basin is substituted for a thermostatic bath, the arrangement in Figure 2 can be readily understood. If a separatory funnel is substituted for an aspirator bottle, the liquid to be evaporated can be completely drained, especially when a measured volume of liquid is placed in it. In order to accommodate the arrangement properly, the stem of the separatory funnel is bent as shown, and drawn out to a narrow tip of about 3-mm. diameter. Air bubbles that may remain in the stem of the separatory funnel may be expelled by pinching a rubber tube temporarily attached at the tip.

If a rubber connection is undesirable, *H* and *I* may be joined by fusion, as the liquid splashes right up to the splash head, *H*. The apparatus is simple and easily constructed and can give satisfactory service even in analytical work.

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# Adsorption Apparatus without Stopcocks for Use with Hydrocarbon Gases

C. B. WENDELL, Jr., G. L. Cabot, Inc., Boston, Mass.

THE development of the Brunauer, Emmett, and Teller low-temperature adsorption isotherm method for determining the surface area of finely divided substances (*2–7*) has led to widespread acceptance and use of this procedure in many laboratories. The validity of the method has been further established by the work of Harkins and Jura (*8*, *9*, *10*), whose approach to the problem involves precision calorimetry and makes no assumption as to the effective cross-sectional area of the adsorbate. Their measurements yield surface area values in excellent agreement with those of the Brunauer-Emmett-Teller method.

### APPARATUS FOR INERT GASES

The Brunauer-Emmett-Teller method has been used in the author's laboratory for the past five years for determining the surface area of a variety of fine pigments. During this period, an apparatus which is accurate and reasonably foolproof in operation has been developed. Figure 1 shows the apparatus employed for surface area measurements using nitrogen as the adsorbate.

The apparatus, as originally constructed, was similar to that used by Benton and White (*1*). It consists of a constant-volume buret with two internal blue glass pointers sealed in the constant-volume arm at suitable points to provide two volume figures, one approximately twice the other, for versatility in operation. Conventional mercury reservoirs are used to control the mercury levels in buret *J* and manometer *I*.

The usual 120° three-way stopcock first used on the gas buret was unsatisfactory. This particular design of stopcock has such a short distance between each two of the three side arms that it frequently leaks under high vacuum conditions. To overcome this difficulty, stopcock *D* (fabricated by Eck and Krebs, New York, N. Y., shown in detail in Figure 2) was employed. This cock has very little dead space in the bore, yet has a full 180° between the two side arms. Figure 2 also shows a special adsorption cell, *C*, designed to reduce operating time when a series of samples of the same density is to be measured. Since the dead space in this cell remains constant as long as samples of the same

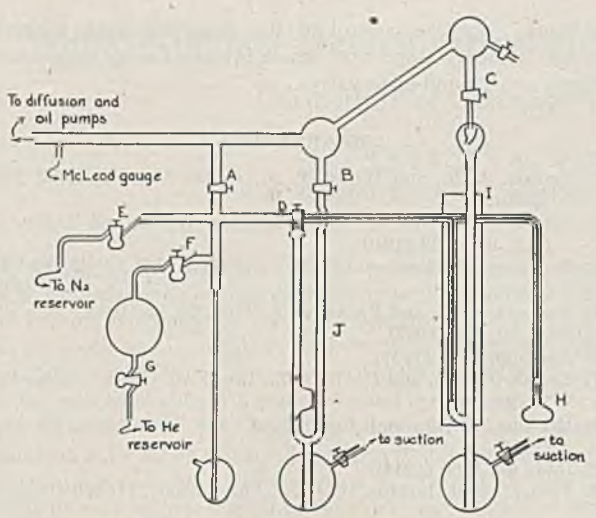

Figure 1. Apparatus for Inert Gases

weight and density are used, a series of measurements may be made under these conditions with a single helium dead space calibration. A considerable gain in time is thus effected over the conventional "seal on and off" type of cell. The ground joint is at least 5 to 7.5 cm. (2 to 3 inches) from the surface of the liquid nitrogen bath; however, conduction by the glass necessitates a water jacket on the female member of the joint to prevent the grease from freezing. The long capillary tube on the lower part of the male joint member effectively reduces dead space to a minimum.

### APPARATUS FOR HYDROCARBONS

Some months ago, it was decided to extend adsorption studies to a number of hydrocarbon gases. Because of the effect of these gases on stopcock grease, an apparatus with no stopcocks in contact with the adsorbate gas was indicated. Since apparatus of this type described in the literature left much to be desired for the author's purposes, the apparatus pictured in Figure 3 was finally designed and constructed. Considerable experience has been gained with this apparatus in conjunction with a study of the heats of adsorption of various gases on fine pigments. The results will be discussed in a forthcoming paper.

The apparatus, aside from the usual mercury cutoffs operated by reservoirs *K*, is essentially similar to that shown in Figure 1 except for the unique controls, *A* and *B*. These controls (shown in detail in Figure 2) were developed to solve the problem of confining a volume of gas in buret *J* and varying its volume with the buret mercury level independent of the levels in the inlet and outlet tubes. By making use of Pyrex hypodermic syringes, *b*, and ground-glass valves, *a*, positive control of the gas is obtained with no contact of the gas with grease. (Medical Center brand syringes were used, manufactured by Becton, Dickinson and Co., Rutherford, N. J.) In each case, the piston of the hypodermic syringe is connected to the ground-glass valve by means of glass toggle joints, *c*, which permit enough freedom of movement in the male sections of the ground-glass valves so that the valve can be tightly seated in the female section. The syringes proper are greased, but since mercury from the reservoir always covers the toggle-joint connection, no contact between gas and grease is permitted. Thus, the valves connected to the syringe pistons may be operated manually, preferably by thumbscrews of proper design. The valve in the left-hand arm of unit *B* is of the simple floating type.

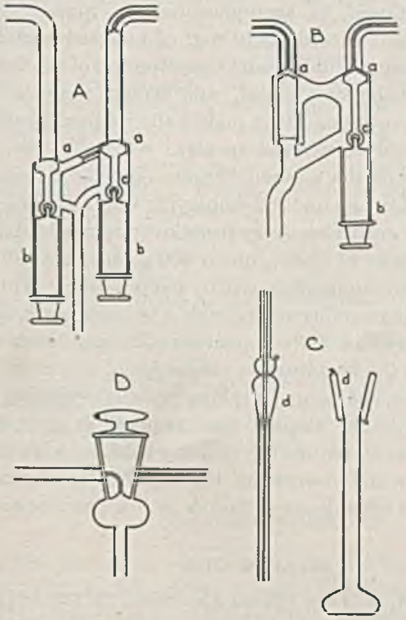

Figure 2. Detail of Stopcock

Operation of these units is simple and positive. With all mercury levels lowered, the entire apparatus is evacuated to the desired working pressure. Buret *J* is then filled with gas as follows: The right-hand valve of *B* being closed by means of the thumbscrew, the mercury control cock of *B* reservoir is opened to the atmosphere. This places a pressure of about 660 mm. on both valves. After the mercury level in the buret is raised to about the center of the U-tube, *J*, and the mercury in *A* to slightly above the higher toggle joint, the desired quantity of gas may be taken into the buret from either the helium or hydrocarbon reservoir. The mercury level in unit *A* is then raised to point *L*, and both valves are closed tightly by means of the thumbscrews. Now the pressure on the gas in the buret may be varied at will (between 0 and about 550 mm.) with no resultant change in the mercury levels of *A* and *B*. Hence the mercury level in buret *J* may be adjusted to touch the desired pointer and the pressure read off the right arm of the buret which is calibrated in millimeters.

With the buret filled, the transfer of known amounts of gas from buret to adsorption cell involves manipulation of unit *B* only. After raising the mercury level in manometer *I* to shut the cell unit off from the line, the control stopcock on the reservoir of *B* is cautiously cracked to suction until the mercury level in *B* proper falls to slightly below the bottom of the floating valve in the left arm. This valve is now open but the right-hand valve is still closed by the pressure maintained on it by the thumbscrew. Manipulation of the thumbscrew will now admit suitable amounts of gas to the adsorption cell. To close control *B* in order to measure the volume of the gas remaining in the buret, the control

Table I. Reproducibility of Results

| Pressure Difference (Buret) *Mm.* | Pressure Reading (Cell) *Mm.* | Calculated Cell Volume *Ml.* | |
|---|---|---|---|
| *T* = 22.8° C. | | | |
| 70 | 96.8 | 26.71 | |
| 152 | 211.1 | 26.60 | Cell I |
| 229.5 | 318.3 | 26.64 | |
| *T* = 23.3° C. | | | |
| 64.3 | 121.3 | 19.51 | |
| 112.0 | 212.0 | 19.48 | Cell II |
| 169.3 | 320.3 | 19.48 | |

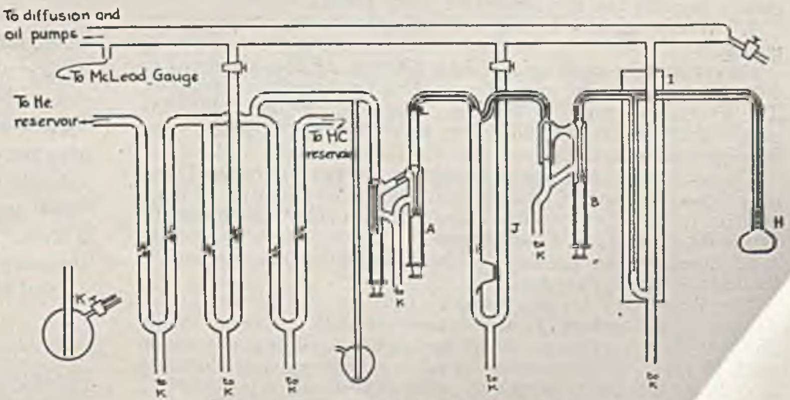

Figure 3. Apparatus for Hydrocarbons

cock of *B* reservoir is again opened to the atmosphere, the rising mercury forcing all of the gas trapped in *B* either into the buret or into the adsorption cell where it will be measured in either case.

The reproducibility of results obtained with this apparatus has been found to be fully equal to that of the apparatus shown in Figure 1, and is well within 1%, as illustrated by the data in Table I, which were taken during the calibration of the apparatus, using two cells of different size. The agreement of the data shows clearly how accurately the transfer of small amounts of gas may be accomplished with this apparatus.

ACKNOWLEDGMENT

The writer wishes to express his appreciation to Ralph A. Beebe and Johnathan Biscoe for their helpful suggestions concerning the development of this apparatus.

## SUMMARY

A high-vacuum apparatus without stopcocks has been designed which permits efficient handling of hydrocarbon gases in adsorption work. Positive control of the gases has been achieved through "mercury stopcocks" which involve simply hypodermic syringes and ground-glass valves.

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# Rapid Qualitative and Quantitative Determination of Barbiturates from Postmortem Specimens

PAUL VALOV, Toxicological Laboratory, Los Angeles County Coroner's Department, Los Angeles, Calif.

A METHOD is described for the separation of barbiturates from postmortem specimens by extraction with aqueous sodium hydroxide. Proteins are coagulated with sodium tungstate upon acidification with sulfuric acid and, following filtration, the filtrate is extracted with ether. Evaporation yields the barbiturates usually in crystalline form ready for qualitative and quantitative determination. The yield is complete. The elapsed time required is 90 minutes.

The prevalent use of barbiturate drugs has resulted in a steady increase in the number of postmortem cases in which barbiturate is the issue. The introduction in this laboratory of the method described below has resulted in large savings in time and reagents.

## PROCEDURE FOR EXTRACTION OF BARBITURATE FROM BLOOD AND VISCERA

1. Measure 60 ml. of blood (or minced viscera), 410 ml. of distilled water, and 10 ml. of 10% sodium hydroxide into a 1-liter flask. Shake 5 minutes.
2. Add 60 ml. of 10% sodium tungstate. Add slowly 60 ml. of 0.67 *N* sulfuric acid with continuous shaking, and acidify with 18 *N* sulfuric acid until acid by Universal indicator paper.
3. Filter to collect 450 ml., extract with an equal volume of redistilled ethyl ether, and shake 5 minutes. Separate from the water phase and evaporate.

The relatively large volume of ether prevents emulsions, which occasionally occur with smaller quantities of ether. The evaporation is normally performed in distillation equipment. The ether is recovered and re-used in later extractions. This procedure permits the attainment of lower blanks.

4. Weigh, deduct blank, and calculate milligrams per 100 grams.

Determination of Blanks. Add 250 mg. of phenobarbital to 60 grams of liver and extract according to preceding directions. The average recovery is 253 mg., representing the barbiturate plus blank. Extract in the same way 60 grams of liver. The average residue is 3 mg.

The established average of foreign matter per 60 grams of liver may be subtracted in the quantitative determination of high positive cases. Low positive cases call for a colorimetric quantitative determination of barbiturate.

5. Identify the presence of barbiturate by the customary Zwikker-Koppanyi method.

The Rotondaro (*1*) method may be employed for final purification of the residue, in which case the color effects with the Zwikker-Koppanyi reagents will be brighter. This is not necessary, however, as the presence of a few milligrams of barbiturate may be established conclusively without Rotondaro purification.

## DISCUSSION

The distinctive feature of this method is the extraction of a small quantity of tissue with sodium hydroxide which brings the barbiturate directly into solution, separating it simultaneously from fats and oils. The coagulation of proteins yields a clear solution, substantially purified, so that the final ether extraction is rapid and complete. The final residue is usually crystalline, ready for qualitative and quantitative determination. Melting points can also be established after sublimation. Secanol residues and, sometimes, nembutal are noncrystalline, but the latter also becomes crystalline after evaporation of added water. In practice, the following residual quantities of ingested barbiturates are encountered: for secanol, up to 3 mg. per 100 grams of liver; for nembutal (pentobarbital), up to 16 mg., and for phenobarbital, up to 39 mg.

Cases are very rare where barbiturate is accompanied by other substances extractable by ether from an acid medium (such as salicylic acid, sedormid, or acetophenetedin). Since therefore any abnormal weight exceeding 40 mg. of ingested barbiturate per 100 grams of tissue would attract the attention of the toxicologist, it could not be overlooked, and would indicate interference of the above type. This makes the method practically specific for commonly used barbiturates.

The advantages of the method become obvious if it be contrasted to the customary method employing ethyl alcohol. Primarily, in order to ensure recovery from low positive barbiturate cases, large quantities of tissue, up to 400 grams, are subjected to four alcohol extractions, followed by evaporation. This procedure, besides being cumbersome, yields a gummy paste, formed by heating the fatty and oily components of human tissue which are extracted with the barbiturate. Subsequent water and ether extractions yield a final noncrystalline residue requiring additional purification. The elapsed time required is from 2.5 to 3 days. Endeavors to reduce the time by working with smaller amounts of tissue and decreasing the number of consecutive alcohol extractions often leads to failure in low positive cases.

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# Micro-Kjeldahl Determination of Nitrogen in Gramicidin and Tryptophan

## Comparison of Gunning-Arnold-Dyer and Friedrich Methods

LAWRENCE M. WHITE AND GERALDINE E. SECOR
**Western Regional Research Laboratory, U. S. Department of Agriculture, Albany, Calif.**

WORK at this laboratory on the modification of gramicidin through reaction with formaldehyde (*6*) required a simple and reliable micromethod for the determination of nitrogen in this antibiotic and in certain of its derivatives and components.

Hotchkiss and Dubos (*3*) reported that the Dumas combustion method was unreliable with gramicidin and that consistent results were obtainable with the Kjeldahl method only when the sample was given a Friedrich pretreatment with hydriodic acid prior to the usual digestion (*9*). Other workers (*2, 11*) have also used the hydriodic acid reduction method for the determination of nitrogen in gramicidin.

The need for the hydriodic acid pretreatment was attributed (*3*) to the failure of the Kjeldahl method to show more than 88 to 95% of the total nitrogen of pure tryptophan, which constitutes up to 40% of the gramicidin molecule. Van Slyke, Hiller, and Dillon (*12*) reported that, with pure tryptophan, the Kjeldahl method gave variable results averaging about 90% of the theoretical. Since the experimental work for the present paper was completed, Miller and Houghton (*8*) have reported 92.8% recovery of nitrogen from tryptophan solutions with a digestion time of 2 hours and 97.7 to 100.7% recovery for a 7-hour digestion. The presence of half of the nitrogen of tryptophan in the indole ring may explain the difficulty experienced in obtaining a quantitative yield of nitrogen from this compound.

Experience with the Gunning-Arnold-Dyer method as described by Clark (*1*) led the authors to believe that the nitrogen of tryptophan could be completely recovered by this method without recourse to the time-consuming and tedious Friedrich hydriodic acid pretreatment. This paper reports a comparison of the nitrogen contents of several samples of gramicidin and *l*-tryptophan and their derivatives as determined by the two methods.

### METHODS

A 5- to 7-mg. sample is weighed by difference into a 30-ml. Kjeldahl flask and digested in the presence of a 5- to 6-mm. glass bead with 1.5 ml. of concentrated sulfuric acid, 500 mg. of potassium sulfate, and 40 mg. of mercuric oxide. The digestion is carried out as described by Clark (*1*) for the Gunning-Arnold-Dyer method for a minimum of 1 hour or until the digest is clear and colorless for 0.5 hour. After cooling, a drop of ethyl alcohol is added and the mixture is again heated until it is colorless. The digests must be boiled vigorously during the later stages of the digestion; otherwise low results may be obtained. (With the samples described in this paper the total time of heating was usually 80 to 85 minutes.) Distillation of the sample is carried out according to Clark's method, but the ammonia is received in 5 ml. of 2% w/v boric acid containing 1% v/v of the mixed indicator of Ma and Zuazaga (*7*). The absorbed ammonia is titrated with 0.01 *N* hydrochloric acid in a final volume of 25 ± 2 ml. The acid is standardized by the determination of nitrogen in acetanilide (N.B.S. standard sample 141) and/or cystine (N.B.S. standard sample 143). Blank determinations are made daily and other usual precautions are taken.

The authors' modification of the Friedrich method varies from that described by Clark (*1*) in the same particulars as does their modification of the Gunning-Arnold-Dyer method and, in addition, they use red phosphorus with the hydriodic acid as prescribed by Pregl and Roth (*9*).

### DISCUSSION OF RESULTS

*l*-Tryptophan from two sources was analyzed without purification; 3,4,5,6-tetrahydro-4-carboline-5-carboxylic acid was prepared from tryptophan and formaldehyde according to the directions of Jacobs and Craig (*4*). The remainder of the samples used in this study were kindly supplied by H. S. Olcott and co-workers of this laboratory, who will report on their preparation and significance elsewhere. All results have been corrected for moisture.

The percentages of nitrogen found by the Gunning-Arnold-Dyer method in a number of samples of gramicidin, tryptophan, and their derivatives are compared in Table I with those found by the Friedrich method. These data show that there was no significant difference between the results obtained by simple digestion and those obtained by longer pretreatment for any of the samples.

**Table I. Nitrogen Analyses of Gramicidin and Tryptophan and Their Derivatives**

| Compound | Gunning-Arnold-Dyer Digestion % *N* | | Friedrich Digestion % *N* | |
|---|---|---|---|---|
| *l*-Tryptophan (Merck), 13.5 to 13.8% | 13.6 | 13.6 | 13.6 | 13.7 |
| *l*-Tryptophan (Eastman 2025), theory 13.7% | 13.5 | 13.6 | 13.8 | 13.8 |
| *N*-acetyl tryptophan, theory 11.4% | 11.3 | 11.4 | 11.3 | 11.4 |
| *N*-benzoyl tryptophan, theory 9.09% | 9.03 | 9.05 | 8.97 | 8.98 |
| *l*-Tryptophan, HCHO-treated[a], theory 12.96% | 12.9 | 12.9 | 12.8 | 12.8 |
| Gramicidin (33% tryptophan, m.p. 208° C.) | 14.2 | 14.3 | 14.2 | 14.2 |
| Gramicidin (37.5% tryptophan, m.p. 225° C.) | 14.5 | 14.5 | 14.4 | 14.5 |
| | 14.5 | 14.6 | .. | .. |
| Gramicidin, HCHO-treated | 13.4 | 13.4 | 13.2 | 13.4 |
| Gramicidin, HCHO-treated, crystalline | 13.3 | 13.4 | 13.3 | 13.3 |

[a] 3,4,5,6-Tetrahydro-4-carboline-5-carboxylic acid.

The recoveries of nitrogen by simple digestion from *l*-tryptophan and its acetyl and benzoyl derivatives were between 98.5 and 100%. Very slightly higher recoveries of nitrogen in tryptophan can be obtained if the digestion is prolonged 30 minutes over that prescribed by Clark. With the longer digestion, recoveries ranged from 99 to 100%. More prolonged digestion was without effect. It may therefore be assumed that the recovery is equally good for gramicidin, since *l*-tryptophan is the only component of this material that has been reported to give low nitrogen values.

Nitrogen in the carboline ring might be expected to be resistant to oxidation. However, analysis of 3,4,5,6-tetrahydro-4-carboline-5-carboxylic acid showed a nitrogen recovery of 99.5% by the simple digestion.

The exact nature of the product obtained on treatment of gramicidin with formaldehyde has not yet been established. However, it is doubtful that the nitrogen occurs in a linkage different from that present in other samples used in this study.

The complete recovery of nitrogen from the indole ring of tryptophan is in accord with the findings of Clark (*1*), Kaye and Weiner (*5*), and Shirley and Becker (*10*), who demonstrated the applicability of mercury as a catalyst to similar refractory nitrogen-containing rings, such as pyridine, quinoline, purine, pyrimidine, thiazole, and pyrole. Working with solid samples the authors have been unable to confirm the results of Miller and Houghton (*8*), who recovered only 92.8% of the nitrogen in tryptophan solutions after a 2-hour digestion with mercuric oxide. The authors found, for example, 92.7% recovery after 35 minutes of total digestion; 97% after 55 minutes; 99.4% after 85 minutes (regular digestion); and 100% after 115 minutes.

### SUMMARY

Mercuric oxide has been shown to be a suitable catalyst for the microdetermination of nitrogen in tryptophan (indole and amino nitrogen) and its acetyl and benzoyl derivatives. By its use the recovery of nitrogen from the carboline ring is complete. With mercuric oxide as a catalyst, nitrogen may be determined in gramicidin and in the gramicidin-formaldehyde reaction product without the customary pretreatment with hydriodic acid.

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# Method for Purifying Beta-Picoline and a Test for Purity

GEORGE RIETHOF AND SIDNEY G. RICHARDS
Pittsburgh Coke & Chemical Co., Pittsburgh, Pa.
AND
SIDNEY A. SAVITT AND DONALD F. OTHMER
Polytechnic Institute of Brooklyn, Brooklyn, N. Y.

BETA-PICOLINE, an important raw material for the manufacture of nicotinic acid, is not usually available in purity higher than 90 to 95%; and this is made from a commercial picoline fraction containing about 30% β-picoline. The boiling point range of the 90 to 95% material is 143–5° C., and the usual impurities consist of γ-picoline and 2,6-lutidine. Further fractional distillation does not increase the purity, since the boiling points of all fall in a very narrow range. The α-picoline and the other lutidines boil at temperatures sufficiently removed to allow separation by fractional distillation.

A suitable chemical method was desired which would allow quantitative separation of γ-picoline and 2,6-lutidine from β-picoline and qualitative demonstration of even very small traces of these impurities in a given sample of β-picoline.

γ-Picoline and 2,6-lutidine may be converted to pyrophthalones (*1*, *2*). β-Picoline does not react. For purifying 1000 grams of approximately 95% β-picoline, 250 grams of phthalic anhydride and 250 grams of acetic anhydride are boiled together under reflux for 4 hours. The mixture is cooled and poured into 5000 cc. of distilled water and then made strongly alkaline with sodium hydroxide solution (concentrated) added slowly. A dark brown precipitate of the pyrophthalones is filtered off. When the filtrate is distilled an azeotropic mixture of β-picoline and water comes over at 97° C. The distillate is dried with solid sodium hydroxide, which separates two layers: picoline above the aqueous sodium hydroxide. The latter is drawn off, and solid sodium hydroxide is added again, until no further separation into two layers is effected.

The picoline is separated from the solid sodium hydroxide and distilled, and the fraction distilling at 143–4° C. is collected. The entire procedure is repeated, starting with the addition of phthalic and acetic anhydrides, until the mixture of the impure β-picoline and the two anhydrides give no yellow color on heating. It is usually necessary to repeat this three times.

### TEST FOR PURITY

One hundred grams of β-picoline, purified as above until no yellow coloration developed, were added to 25 grams of phthalic anhydride and 25 grams of acetic anhydride. Several such mixtures were boiled under reflux for 10 minutes after adding small amounts, down to 0.008 gram, of substantially pure 2,6-lutidine.

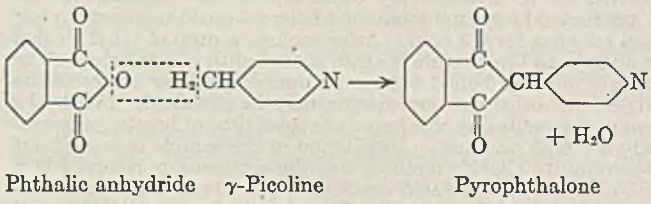
The yellow coloration developed in all cases, decreasing in intensity with smaller amounts of lutidine. The sample containing 0.008 gram of 2,6-lutidine was a pale yellow, showing that as little as 0.01% of this material could be detected.

The same results were obtained when the procedure was repeated using γ-picoline as the impurity.

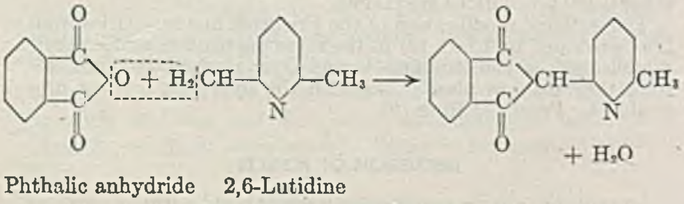
These tests using varying amounts down to almost infinitesimal traces of 2,6-lutidine and γ-picoline, which are the most common impurities of β-picoline, show conclusively the extreme sensitivity of this method of purifying and testing β-picoline. Furthermore they show that β-picoline so purified is substantially free of the impurities normally associated with it.

### DISCUSSION

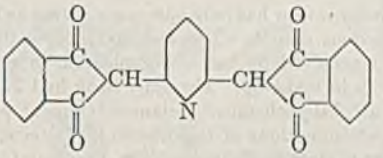
The phthalic anhydride reacts with the methyl groups of picolines when present in the 2 and 4 positions to give yellow pyrophthalones, but no reaction occurs with the picoline having a methyl group in the 3 position. The condensation takes place as follows:



With the 2,6-lutidine, the condensation reactions may be represented as follows:



With a large excess of phthalic anhydride and acetic anhydride, both methyl groups react as follows:



The pyrophthalone compounds are yellow dyes, the properties of which have been described by Hewitt (*1*).

This formation of pyrophthalones may be traced to the presence of 4-picoline or 2,6-lutidine, or both; and it has been recognized that a methyl group in position 2, 4, or 6 is necessary for condensation with carbonyl groups. Two hydrogen atoms from the picoline and one oxygen atom from the phthalic anhydride are released to form water.

However, the methyl group in the 3 position is entirely unreactive and therefore no color develops. The β-picoline may be considered absolutely free of its isomers and homologs when there is no appearance of color following this treatment.

Pure β-picoline is extremely hydroscopic and precautions should be taken to keep it absolutely dry.

Slight traces of any of the usual impurities in a sample of β-picoline will be detected by the appearance of yellow color on refluxing with phthalic anhydride and acetic anhydride. Therefore, if no color develops, the picoline may be considered free of these impurities. The sensitivity of the method and long color stability allow for color comparison as the purification procedure is repeated; and it is possible that a quantitative colorimetric method may be developed for particular conditions, such as the control of manufacture or use where the same impurities are commonly present in about the same relative amounts.

This method serves a twofold purpose—purification of β-picoline and qualitative analysis of β-picoline for its common impurities.

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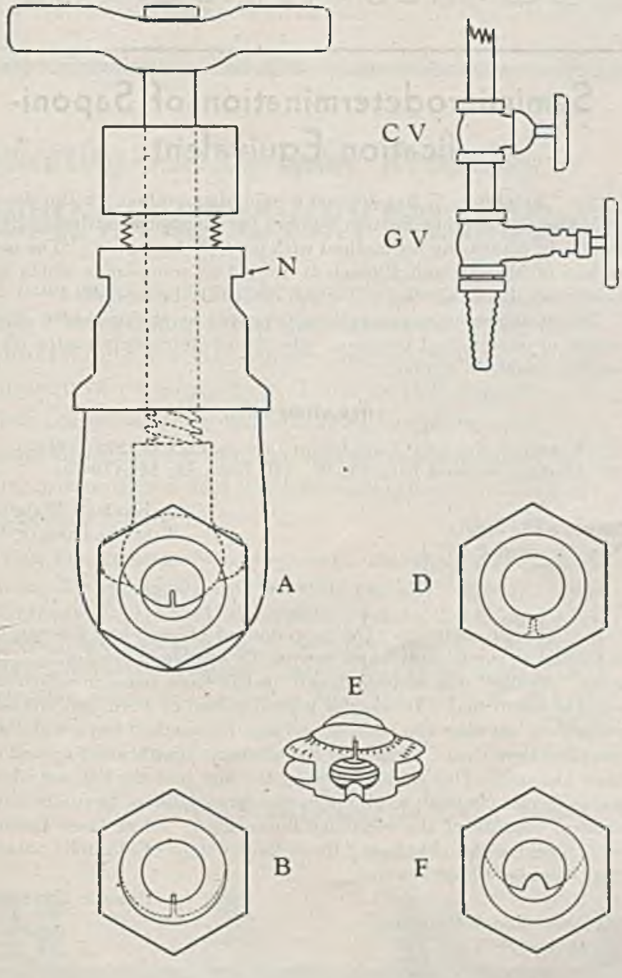
(2) Riethof, George, U. S. Patent, application pending.

# Modified Gate Valve for Control of Water Flow

G. ROSS ROBERTSON, University of California, Los Angeles, Calif.

LABORATORY workers have long deplored the fact that a water faucet, adjusted to low rate of flow, often shuts off the stream spontaneously. This treacherous habit unfortunately is a special failing of the "compression" valve, a device conceded to be the most satisfactory faucet yet developed. In the new arrangement shown in the figure, the regular compression valve, *CV*, with washer, is retained for leakproof on-and-off service. Adjustment to low rate of flow is delegated to a second device, the modified gate valve, *GV*.



In the standard commercial gate valve, *A*, a brass gate normally rises and falls across the water stream with rotation of the left-hand-threaded shaft and wheel handle. As shown in the separate view of the gate, *E*, a narrow slot is cut in the extreme edge of the gate. This slot permits the passage of a small but very definite and constant stream—for example, at adjustment *B*. The stream is precisely adjustable between values fully double that at *B* down to position *D*, where the stream is reduced practically to zero flow. At the same time it is possible to open the gate to full flow as needed. The modified gate valve thus has a much wider range of usefulness than a needle valve which might serve at position *GV* to provide a small stream.

Since it is unnecessary and undesirable to have a narrow slot on both sides of the gate, the lower side (as of gate in position *E*) is cleared for unrestricted flow with a wide slot, whose operating position is seen at *F*, which merely shows the opposite threaded end of valve *A*. In steady service of one kind from day to day—for example, to a reflux condenser—little or no adjustment of *GV* is required, and thus undue wear is obviated.

MECHANICAL SPECIFICATIONS. A standard plumbers' brass gate valve, usually $^3/_8$ or $^1/_4$ inch ("iron-pipe-size") is selected, choice being based on maximum width of the annular ground contact surface of the gate. Such maximum width permits maximum length of slot with limit shown in *D*. The slot is cut with a fine jewelers' saw; a blade 0.31 mm. in width was found to be satisfactory. The resulting slot is of suitable width for use with water pressure of 60 pounds per square inch, or approximately 4 kg. per sq. cm. It should be noted that the opposite and supposedly identical contact faces of a gate are often of varying annular width, or overlap. The wider, with the greater overlap, is selected for the narrow slot, *B*, and the narrower, also cut with the saw, for *F*.

Since this mechanical alteration requires disassembling of the gate valve, inexperienced workers are warned that nut *N* must not be opened while the valve is closed, lest the interior mechanism be sprung and the valve ruined. Instead, the gate is first screwed out about half way. The valve is now fastened securely in a vise, with vise jaws pressing upon the two threaded mouths of the device. Nut *N* may then be started without mechanical damage, and the parts separated by finger contact only.

# BOOK REVIEWS

**Official and Tentative Methods of Analysis.** 6th edition. xii + 932 pages. Association of Official Agricultural Chemists, P. O. Box 540, Benjamin Franklin Station, Washington, D. C., 1945. Price, $6.25.

Ever since it was founded in 1884 the Association of Official Agricultural Chemists has devoted itself almost exclusively to studies in the field of methodology. Beginning with the standardization of methods for the analysis of commercial fertilizers, the scope of its work has expanded continuously to meet the ever-increasing needs of its members who are now concerned with the enforcement of laws and regulations relating to commercial fertilizers, stock feeds, food, drugs, cosmetics, insecticides, fungicides, caustic poisons, and other articles; or who are engaged in research in these and related fields.

Each succeeding edition of the association's text, which has come to be known by the short title "Methods of Analysis, A.O.A.C.", represents the elimination of obsolete or little-used methods, revisions and improvements of other methods, and the addition of many new procedures.

The 6th edition is notable for new chapters on cosmetics, gelatin, dessert preparations and mixes, enzymes, and extraneous materials in foods and drugs. A chapter on vitamins assembles under one head methods for vitamin assays previously scattered throughout the book under other titles. A mechanical improvement in the form of presentation is the use of Arabic numerals to designate chapters, with decimals for the subheadings therein. A special effort has been made to have the "selected references" cited at the end of each chapter show, as far as possible, the original work upon which the methods are based.

It is pertinent to note that these methods have acquired an added significance in recent years, since many of them are being incorporated in standards for food products promulgated under authority of the Federal Food, Drug and Cosmetic Act. This gives legal status to the procedures thus cited.

Laboratory workers in this country who are engaged in official work within the scope of the association's activities, and who comprise the active membership of the association, will welcome this new edition as an indispensable laboratory guide. So also will workers in like fields in foreign countries, among whom this text has come to have wide recognition and acceptance.

E. M. Bailey

**Quantitative Organic Microanalysis.** Edited by *Julius Grant.* 4th English ed. Based on the methods of Fritz Pregl. vii + 238 pages. The Blakiston Co., 1012 Walnut St., Philadelphia, Pa., 1946. Price, $5.00.

The third English edition of Pregl's classical book, published in 1937, was, like its two predecessors, simply a literal translation of the corresponding German edition. It was evidently felt that the Pregl text was sacrosanct.

Now comes Dr. Grant, with what is stated to be not just another and better translation, but rather something between that and a new and original treatise on organic microanalysis.

This seems to the reviewer to be a proper development. With all the great respect due to Pregl, there is no sense in continuing to pretend that he wrote the last word in organic microanalysis. The fact that he wrote the first words is sufficient to ensure him enduring fame. It is to be hoped that the next author to build upon the base established by Pregl will be even more emancipated than is Dr. Grant from an obligation to classicism.

Indeed, the reviewer's only real criticism of Dr. Grant's book is that he did not give nearly enough recognition to the hundreds who have followed Pregl. There was a time, not too many decades ago, when it would have been heresy to write a book on general analytical chemistry that was not described in the flyleaf as based on Fresenius. We have long since got over that; and yet Fresenius' fame as a pioneer has not dimmed. So let it be with Pregl!

The book under review has only 238 pages of text as compared with 271 in the previous edition. Despite this, more actual text is provided; this is achieved by better organization of material and by space economies in make-up. The older book had 27 chapters; the present, seven: Microchemical Balances, General Microanalytical Technique, Determinations of the Elements, Determinations of the General Groups, Determinations of the Physical Constants, Miscellaneous Physical Methods, and Calculations of the Results of Microanalyses.

The author has made a real attempt to discriminate among alternative methods, giving first place to those he believes to be the best, even though they originated outside the Pregl school. But, as stated earlier, the reviewer believes that this policy might have been pursued even more vigorously.

Specific mention should be made of Chapter III, wherein the sections of the determinations of the metals have been gratifyingly expanded. The book is modernized by brief mention, in Chapter VI, of the new techniques of electrometry, polarography, radioactive indicators, and ultraviolet fluorescence analysis. This is all to the good, as far as it goes; but it is hoped that the next edition will go much further. The indexes are much improved, and it is noted that the tables of gravimetric factors have been recalculated to take account of changes in atomic weights.

For the benefit of those not familiar with other editions of Pregl, we quote from Dr. Grant's Preface: "The needs of the beginner in microanalysis have been borne prominently in mind, although a background of knowledge of ordinary organic analysis is assumed."

This book is strongly recommended to all who have occasion to practice, teach, or study quantitative organic microanalysis.

B. L. Clarke

# CORRESPONDENCE

## Semimicrodetermination of Saponification Equivalent

Sir: Ketchum (*1*) has devised a semimicromethod for the determination of the saponification number (or the saponification equivalent). In comparing his method with ours (*2*) he states: "The procedure of Marcali and Rieman is limited to compounds which are readily soluble in alcohol and which can easily be saponified."

This statement is not correct, as is proved by the successful application of our method to eleven oils (*2*), of which only castor oil is readily soluble in alcohol.

LITERATURE CITED

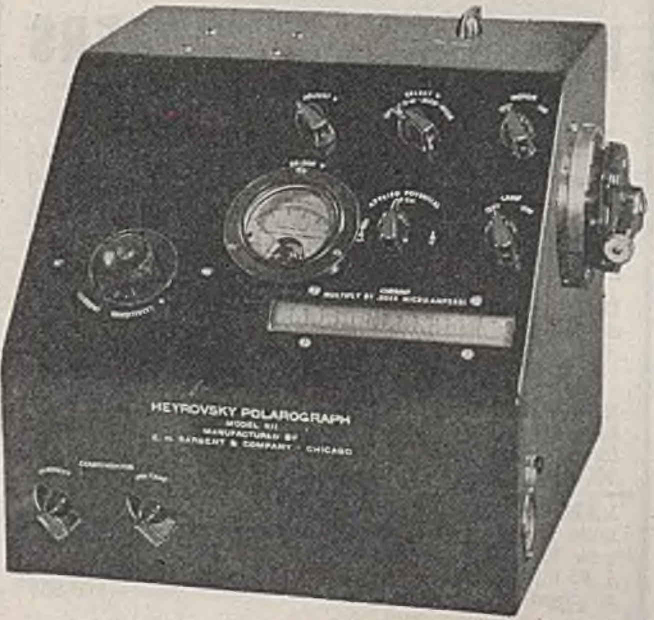
(1) Ketchum, D., Ind. Eng. Chem., Anal. Ed., 18, 273 (1946).
(2) Marcali, K., and Rieman, W., III, *Ibid.*, 18, 144 (1946).

Kalman Marcali
William Rieman III
Rutgers University
New Brunswick, N. J.

* * *

Sir: In the sentence, "The procedure of Marcali and Rieman (*3*) is limited to compounds which are readily soluble in alcohol. . .", the word "readily" was employed only in the loose sense in which the word is often used. It was not a good choice of word, but the sentence does not alter the main theme that my method has a wider application than theirs, because of the solubility limitations imposed by their method. This is illustrated by the fact that the ketones which were successfully analyzed by my procedure could not be run by their method because of the solubility limitations. When these ketones were mixed with only twenty times their weight of alcoholic potash they would not open the ring.

Donald Ketchum
Eastman Kodak Company
Rochester, N. Y.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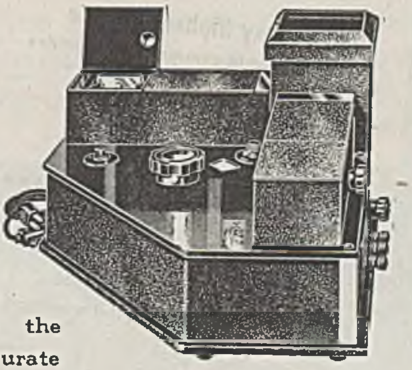

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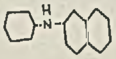

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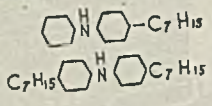

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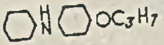

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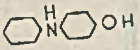

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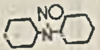

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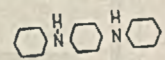

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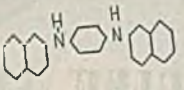

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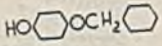

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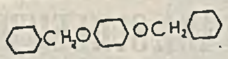

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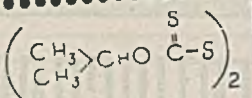

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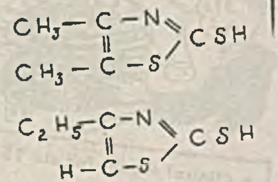

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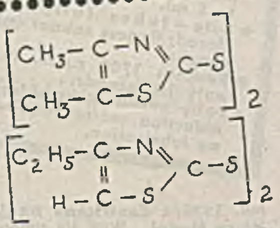

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# Current Developments in

# INSTRUMENTATION IN ANALYSIS

### Discussed by Ralph H. Müller

In the January column we predicted extensive applications of the newer nuclear techniques to the analysts' problems. We are happy to announce the organization of Tracerlab, Inc., of 55 Oliver St., Boston, Mass., which will manufacture instruments, make radioactivity analyses, and offer consultation services in the various phases of radioactive tracer research. This organization includes physicists, organic and inorganic chemists, electronic engineers familiar with modern circuit design and production methods used in radar development, and business personnel familiar with production methods. This staff is supplemented by an impressive list of consultants on nuclear physics, chemistry, and medicine. Tracerlab is now in the process of constructing a chemical laboratory for the analysis and compounding of radioactive tracers and is currently engaged in the design of a printing interval timer and a sample changer for automatic routine measurement of radioactive samples.

## *Instruments for Indicating Radioactivity*

Two instruments which are representative of Tracerlab's offerings are here described in the belief that they offer interesting and important possibilities for the analyst. An instrument for the qualitative indication of radioactivity is illustrated in Figure 1. This is a line-operated Geiger counter-amplifier system which indicates the presence of radioactive material by the "blinking" of a small neon lamp mounted on the front panel. This unit is designated as a Blinker. A similar unit, known as the Squawker, is available and, as the name implies, produces an audible signal in the presence of an active preparation. Either of these units will be recognized as very useful tools or aids during the execution of routine analytical procedures, in which precipitates, filtrates, etc., are to be examined for the presence of the tracer.

The quantitative instrument known as the Autoscaler is shown in Figure 2. It is a line-operated device which (1) supplies the high potential for a Geiger-Müller tube, (2) counts the impulses from this tube, and (3) measures the time required for the reception of a given number of impulses. Describing the functions in this order, the two controls at the bottom of the panel select the high voltage for the counter. The knob to the left sets the threshold voltage and its setting is checked by an aural monitor. The knob to the right of this brings the potential to the operating point in 10-volt increments to 100 volts above threshold. The high voltage supply is continuously variable between 700 and 2000 volts. This and all other power supplies in the instrument are electronically regulated.

Impulses from the Geiger counter are fed to a preamplifier, a 2-stage amplifier, and then a multivibrator which triggers the first of a series of twelve "scale of two" counter circuits. The latter can be selected by the switch shown in the upper left of Figure 2 to provide a predetermined number of impulses from 2 to the second power to 2 to the twelfth power—i.e., 4 to 4096 in integral powers of 2. The statistical error involved in the measurement of an average counting rate by timing a finite number of random impulses is determined by the total number of impulses timed. In the Autoscaler predetermined counts of 128, 256, 512, 1024, 2048, or 4096 correspond to fixed probable errors of approximately 6, 4, 3, 2, 1.5, and 1%. Consecutive scaling units are interconnected with buffer stages and each stage is connected to a small neon lamp, the blinking of which appears through the plastic inserts in the scale selector dial. Monitoring features are provided ahead of the scaling circuits by a cathode follower stage which can feed an oscilloscope for examination of the amplified pulses and a loudspeaker for aural monitoring. Calibration of the Autoscaler on any range is easily effected by switching the amplifier input to a 60-cycle multivibrator.

Measurement of the time interval required for the accumulation of the selected number of impulses is accomplished by an output amplifier and cathode follower stage which actuates the clutch of the timer. The latter with its reset button is shown in the upper right of Figure 2.

Additional features which may be mentioned are:

1. The interruption of the scaling circuit when the timer is stopped.
2. The over-all resolving time of the input amplifiers and scaling circuits is less than 5 microseconds; therefore random impulses up to 200,000 per minute can be counted with losses no greater than 1%.

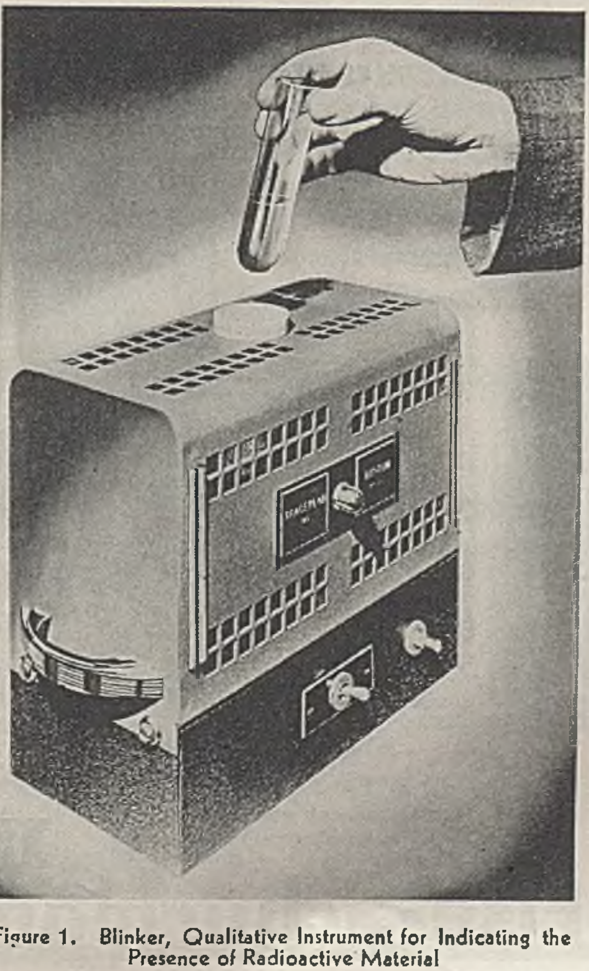

Figure 1. Blinker, Qualitative Instrument for Indicating the Presence of Radioactive Material

# *Instrumentation*

Figure 2. Autoscaler

3. Complete elimination of nonessential controls. Tube matching or selection is unnecessary.
4. Provision of a function switch permitting scaling circuit and timer to run continuously. A relay is actuated, the contacts of which are connected to external binding posts. These may be used to photograph the timer dial or actuate other control circuits.
5. Automatic "cleaning" of the scaling circuit at the beginning of each counting run.
6. A preamplifier containing either a Neher-Pickering (standard) or classical type of quenching circuit is also furnished. It is contained in a $1^3/_8 \times 3$ inch cylindrical housing which is connected to the main chassis by a 7-foot cable. Test leads for connection to the Geiger tube are 12 inches long. Other counter tube mountings to accommodate a thin window beta-ray counter are available.
7. A choice of five interchangeable precision timers is available; the standard model provides a maximum totalized time per revolution of 6000 seconds.

The Autoscaler is contained in a cabinet $10^1/_2 \times 19 \times 14$ inches with standard relay rack panel construction.

## *Electron and Nuclear Counters*

In addition to the references which we listed in the January column we wish to recommend the recent monograph by S. A. Korff, "Electron and Nuclear Counters—Theory and Use", D. Van Nostrand Co., New York, N. Y., 1946. Two thirds of this useful book is devoted to the properties and characteristics of counters. Additional chapters discuss errors and corrections and most of the more important electronic circuits which are needed in nuclear work. Instrumentation of a high order is essential in this field and the extraordinary progress in nuclear physics and chemistry is largely due to the skillful and uninhibited development of new devices and circuits.

With the ominous beating of that metronome at Bikini still reverberating in our ears, we recall that some 10,000,000 words will be written in describing the fourth atomic bomb drop. We are interested only in the 10 or 20 thousand words which will be required to tell the role of instrumentation in that test. They will contain 90% of the useful, irrefutable information.

If we were to recommend an installation for a blast furnace, guaranteed to read temperature, pressure, gas composition and other variables twenty-four times a second, print the answer on film and deliver it to the superintendent by air mail, while the president of the company viewed the whole proceedings in his air-conditioned office, we would be called insane—not the first time, thank you. Yet a few drone planes accomplished a more remarkable data-gathering mission than this on the morning of July 1, 1946. It is comforting, for those who have been annoyed with instruments and their difficulties, to know that on occasion they can be made to operate themselves and thus remove one more barrier to better knowledge.

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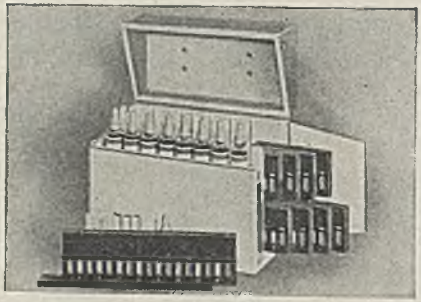

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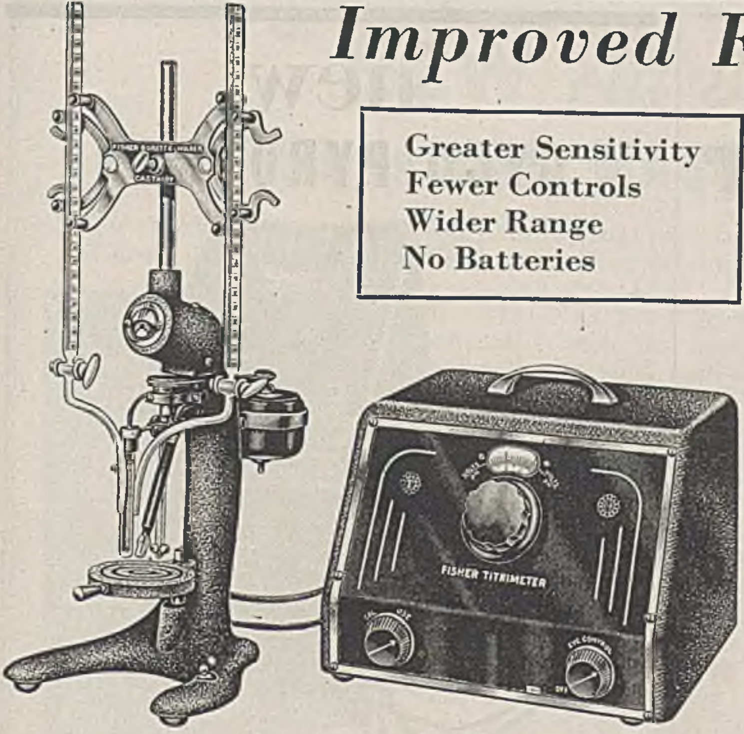
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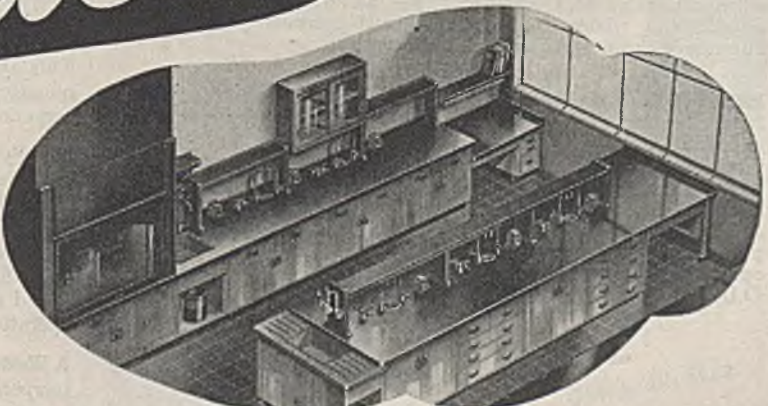

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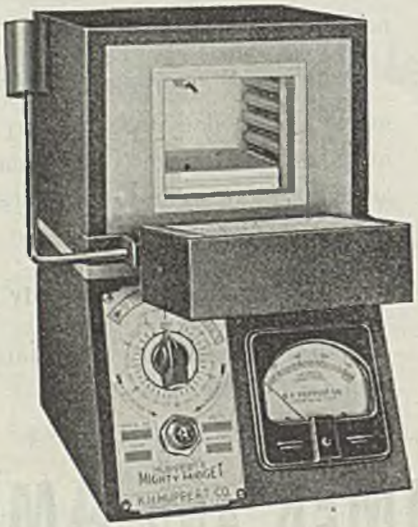

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The Pyrotran is provided with a heavy-duty rubber covered input cable, and has twin plug outlet receptacles for connecting both a hemispherical jacket and cover or two hemispherical units at the same time and at the same power. A red signal light shows when transformer is in operation. An easily replaceable fuse is provided to protect the instrument. Each Pyrotran is fully insulated and is tested to five times the maximum working voltage to insure safe operation.

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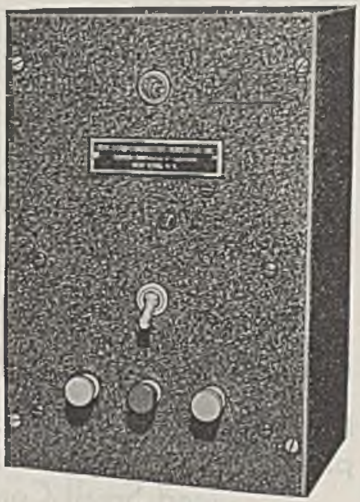


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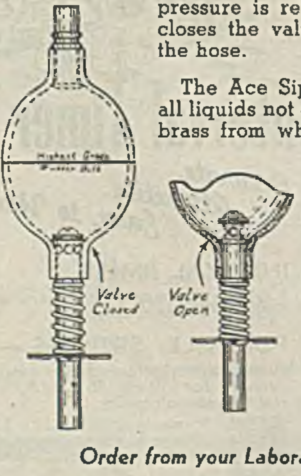

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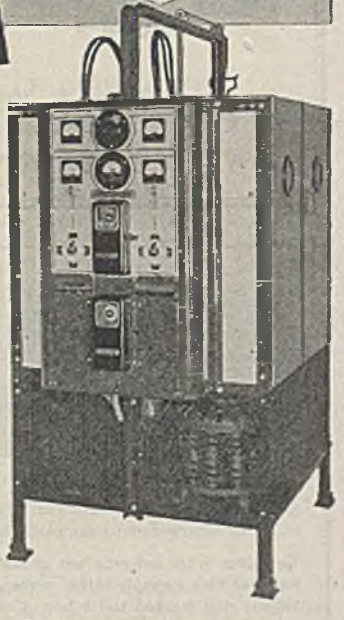

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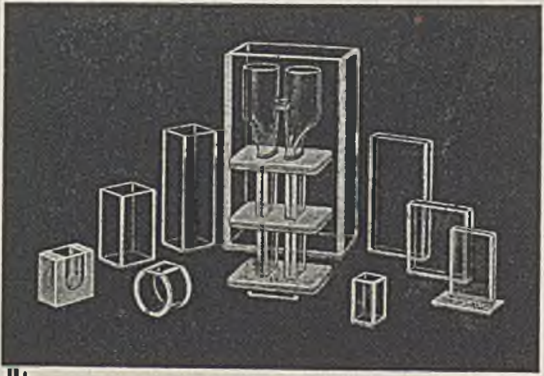

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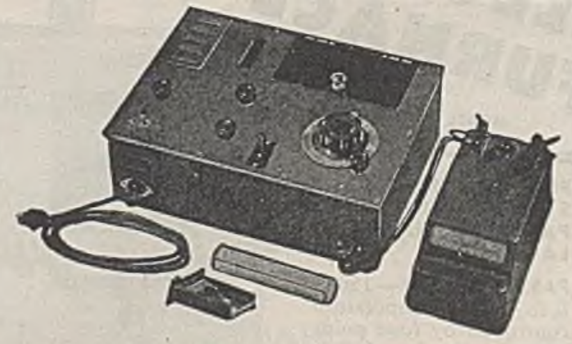

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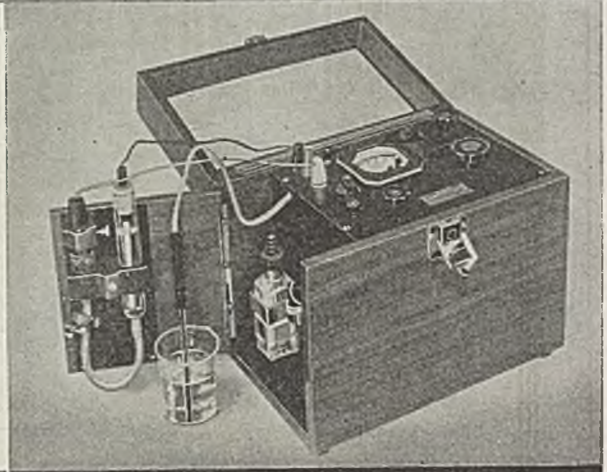

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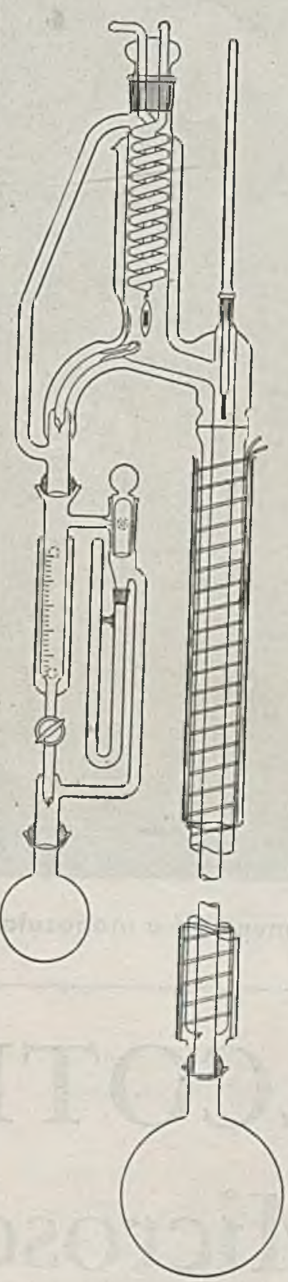

with magnetic reflux control, vacuum jackets and *flat ground joint* between column and distilling head. Flat ground connection, * held securely by newly developed clamp, is vacuum tight and eliminates freezing or sticking. Solenoid-activated "clapper" permits accurate regulation of reflux ratio. Column which can be furnished in various lengths is provided with electric winding and protective jacket. This Still has compact, efficient head with very small holdup and can be used over wide range of temperatures from below 25 deg. C to well above 200 deg. C. Supplied with clamp for flat ground joint, solenoid and six feet of rubber-covered cord. Fraction Cutter for use with the above Still incorporates vacuum manometer for use at pressures below 150 mm Hg. and novel control stopcock for simplified operation. Liquid jacketed calibrated receiver prevents evaporation of low boiling distillates.

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Distilling Apparatus

Smith-Nester design for macro or micro ammonia distillations and steam distillations in general. Compact, sturdy, requires no rubber tubing. Consists of one liter steam generator flask (heated by gas flame), sparger, spray trap and very efficient condenser. Can also be supplied for use with rubber stoppers instead of interchangeable ground glass joints.

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