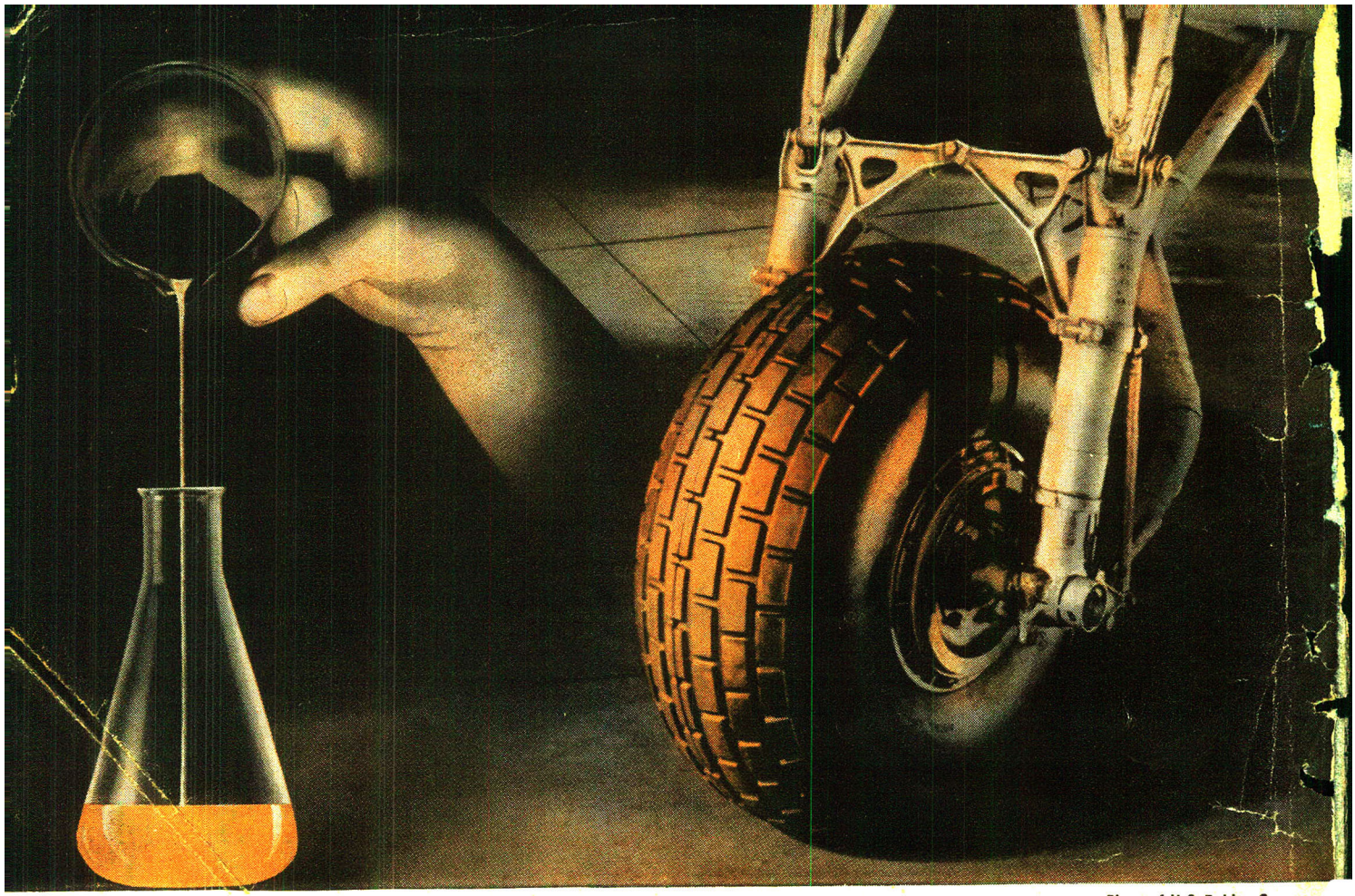
ANALYTICAL CHEMISTRY

JANUARY 1947



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ANALYTICAL CHEMISTRY

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Analytical Edition, Industrial and Engineering Chemistry

A New Name and an Expanded Program—Editorial . . . 1

Measurement of Radioactive Tracers . . . . W. F. Libby 2

Improvements in Polarographic Instrumentation . . . . . G. E. Philbrook and H. M. Grubb 7

Dielectric Identity Test for Plasticizers . . . . . M. A. Elliott, A. R. Jones, and L. B. Lockhart 10

Recording Viscometer for Starches . . . . . C. C. Kesler and W. G. Bechtel 16

Study of Hexabromide Number . . . . . J. P. Kass, W. R. Roy, and G. O. Burr 21

Determination of Degree of Substitution of Sodium Carboxymethylcellulose . . . . . R. W. Eyler, E. D. Klug, and Floyd Diephuis 24

Sampling and Analysis of Boron Trifluoride . . . . . C. F. Swinehart, A. R. Bumblis, and H. F. Flisik 28

Solid Polyethylene Glycols (Carbowax Compounds) . . . C. B. Shaffer and F. H. Critchfield 32

Quantitative Separation of Barium from Strontium . . . . . G. L. Beyer and William Rieman III 35

Determination of Aromatics and Naphthenes in Complex Hydrocarbon Mixtures Containing Olefins . R. M. Love, A. R. Padgett, W. D. Seyfried, and H. M. Singleton 37

Quantitative Determination of Paraffins and Naphthenes in Gasolines by Lamp Method . . . . . S. G. Hindin and A. V. Grosse 42

Analytical Methods for Carotenes of *Lycopersicon* Species and Strains . . . . . F. P. Zscheile and J. W. Porter 47

Colorimetric Determination of DDT in Milk and Fatty Materials . . . . . M. S. Schechter, M. A. Pogorelskin, and H. L. Haller 51

Estimation of DDT in Milk by Determination of Organic Chlorine . . . . . R. H. Carter 54

Colorimetric Method for Determination of Traces of Carbon Dioxide in Air . . . . N. A. Spector and B. F. Dodge 55

Determination of Traces of Fluorine in Organic Compounds . W. B. Huckabay, R. H. Busey, and A. V. Metler 59

Determination of Gallium in Silicate Rocks . E. B. Sandell 63

MICROCHEMISTRY

Micromethod for Determination of Gaseous Olefins . . . Rowena Pyke, Allan Kahn, and D. J. LeRoy 65

Determination of Carbon Monoxide . . . . . J. M. Salsbury, J. W. Cole, and J. H. Yoe 66

Estimation of Types of Penicillin in Broths and Finished Products. . . . . K. Higuchi and W. H. Peterson 68

NOTES ON ANALYTICAL PROCEDURES

Magnetic Rotation of Direct Current Arc in Spectrographic Analysis . . . . . A. T. Myers and B. C. Brunstetter 71

AIDS FOR THE ANALYST 72

The Analyst's Column . . . . . 17 A

Instrumentation . . . . . R. H. Müller 23 A

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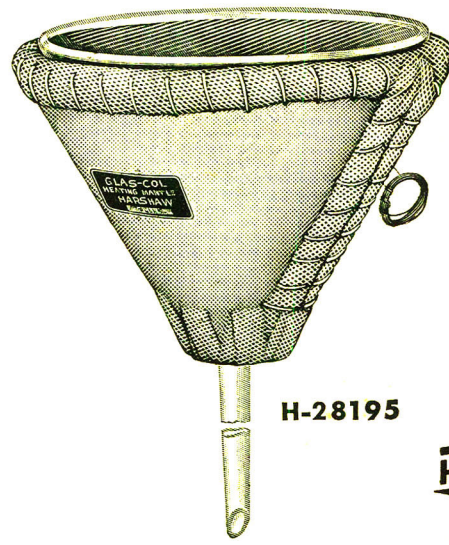

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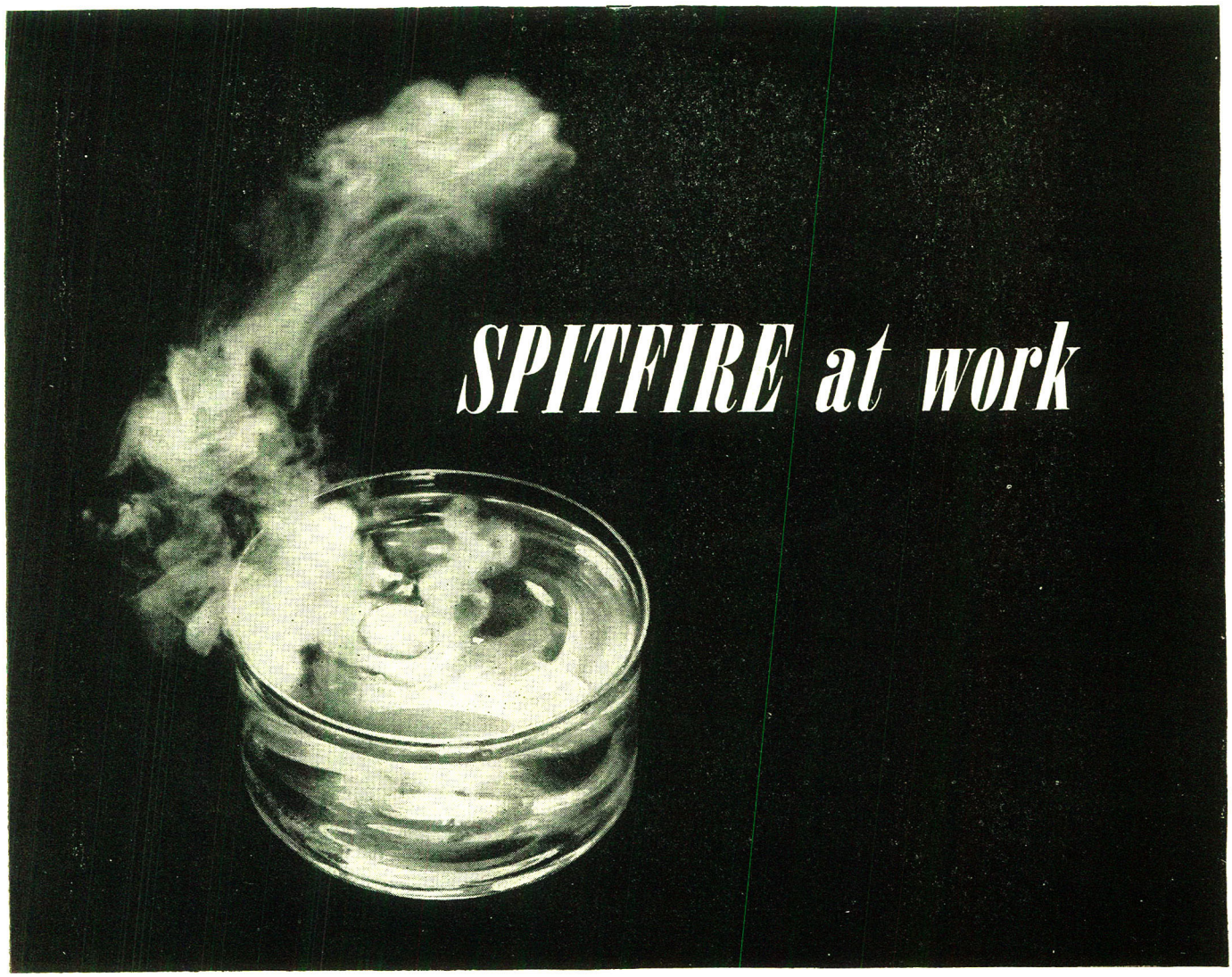

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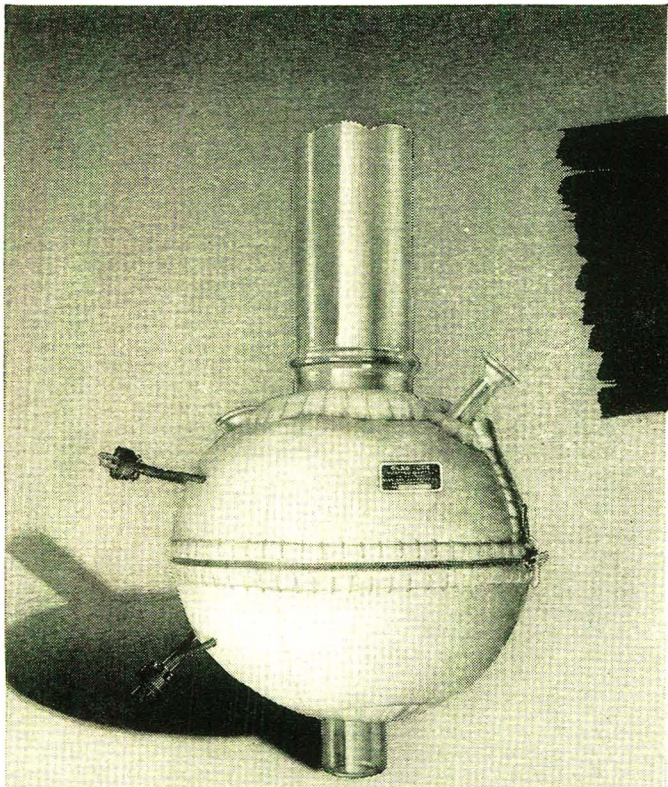

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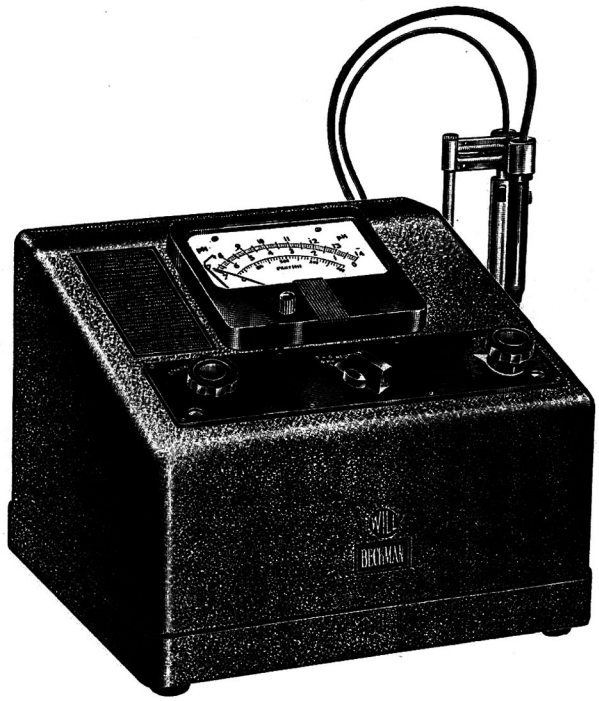

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Completely self-contained. Operates directly from 115 volt 50-60 cycle lines.

This new instrument represents another Beckman achievement in the field of pH measurements. It embodies advances in circuit design to insure the same high operating efficiency, accuracy, simplicity and dependability that characterize the widely-known battery operated Model G and Model M Beckman pH Meters. It is entirely self-contained, light in weight, but ruggedly built. It accommodates standard Beckman Electrodes and reads directly in pH units or millivolts. Only one buffer and only one electrical adjustment are used to standardize the instrument An auxiliary pointer on the meter and a push-button make possible ready checking of asymmetry potential. A few of the many unique features incorporated into the Beckman Model H pH Meter are:

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Rugged Lightweight Construction: The Model H Meter is housed in a cast aluminum case attractively finished in dark gray wrinkled enamel. The net weight is approximately 12 pounds complete. Over all dimensions: 8½″ high, 9½″ deep, 12″ wide.

9681—BECKMAN MODEL H PORTABLE AC pH METER. Complete with Glass Electrode, Calomel Electrode, Electrode Holder, Holder Rod, 50 ml. Pyrex Beaker, 1 pint concentrated Buffer Mixture, pH 7.00, and 100 ml. KCl Solution. For operation on 100–130 Volt 50–60 cycle current. With 5 foot extension cord with fused male plug..... **$180.00**

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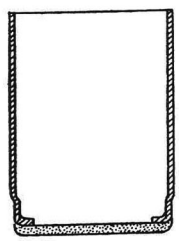

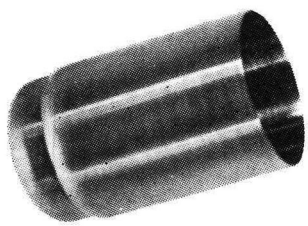

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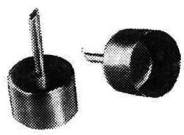
FCF	"F" — fine	1.25
FCE	"E" — medium	1.25
FCD	"D" — coarse	1.25
FCC	"C" — extra coarse	1.25



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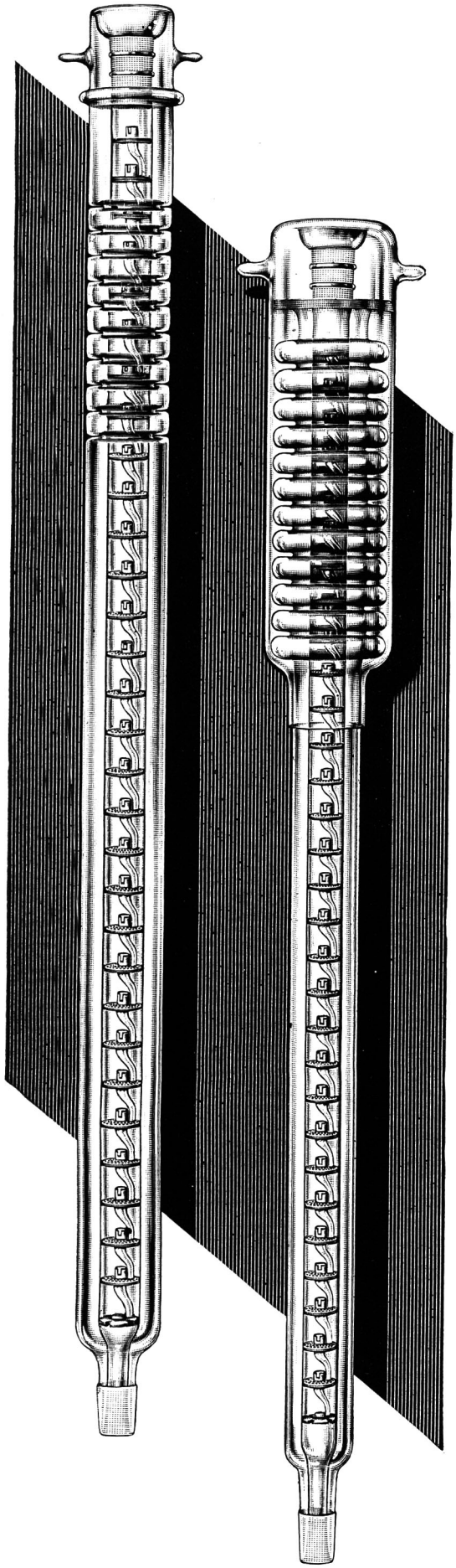

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The improved bubble plate column, described in the November Analytical Edition, has become the accepted column for analytical distillations of hydrocarbon mixtures. Oldershaw columns*, held to the tolerances maintained in our shops, insure uniformity of operation and reproducibility of results.

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the analyst's column

DURING the past year several editorials have highlighted new and expanding activities of this publication, now called ANALYTICAL CHEMISTRY. We intend to continue such discussions in every issue. We have felt for some time that it is appropriate to discuss informally points of view, meetings, new approaches to analysis, and problems of academic and applied analysis. Good editorial comment can crystallize and express opinions held by each analyst and show where improvements can be made.

To some analysts a few of the papers published within the past year and the column on instrumentation may seem a far cry from the type of analysis for which they were trained in college. This is true, but, unless those responsible for analysis in teaching and in industrial laboratories employ these new techniques, they may find other specialized groups becoming analysts. The viewpoint of these groups is too narrow, however, in that they think primarily of the instrument and not of the problems which it can solve. Every analytical group must include those who can use, design, and build such equipment, but, over and above this, there must be supervision of the proper balance for the precision and accuracy of the method for which the instrument is to be used and its relationship to other methods which may not involve instruments.

IT IS encouraging to note that some universities are beginning to appoint new faculty members who have a modern approach to analysis. However, such appointments are rare and at the present writing will not affect the over-all approach to modern analytical techniques which are now used in many industrial laboratories. While qualitative and quantitative analysis have a place in the curriculum, in teaching principles of chemistry and the rudimentary techniques of classical methods, they do not adequately present to the student how modern analysis is now commonly done.

THE principles and physical methods for carrying out routine procedures more automatically are all about us if we will only apply them intelligently. We predict that in the not too distant future such apparatus will be common and that the fallibility of human manipulation and attendant boredom will be largely eliminated.

THE New Brunswick Group of the New Jersey Section of the ACS is collaborating with Rutgers University in sponsoring a series of eight weekly lectures on advanced instrumental methods by authorities in the field. The lectures, tentatively scheduled to begin Feb. 5, and given at the graduate level, are designed for chemists working in near-by industries. This is a highly creditable venture, and we wish it success, with the hope that others may be able to sponsor similar worth-while programs.

PAPERS reporting analytical developments during the war are being released and received in our editorial offices in increasing numbers. Some are strictly war applications developed to solve a particular problem; others are broader in scope and represent new approaches and new techniques for the analyst to use or master. The paper by W. F. Libby, "Measurement of Radioactive Tracers", this issue, page 2, is representative of the broader view. Papers which extend our horizon are always welcome, and ANALYTICAL CHEMISTRY will continue to publish promptly all such worth-while contributions.

ANALYTICAL CHEMISTRY

Published by the American Chemical Society Walter J. Murphy, Editor

A New Name and an Expanded Program

THE *Analytical Edition* of *Industrial and Engineering Chemistry* has a new name, ANALYTICAL CHEMISTRY, a new format, and two new departments, "Aids for the Analyst", and "The Analyst's Column".

Advances in the science of chemistry continue at an ever-accelerating rate. In the field of analytical chemistry, the forward march of knowledge, while perhaps not so spectacular to the lay public as are the contributions in certain other branches, has, nevertheless, been a source of justifiable pride and satisfaction to those who have made possible advancements in every division of chemistry. The analytical chemist is the close associate and collaborator of the research chemist. Indeed, the analytical chemist very frequently is a research chemist in every sense of that term, pioneering in difficult and uncharted fields. Industry cannot function without his services.

Without glory and largely without proper recognition, the analytical chemist has labored assiduously and with great success in a wide variety of fields—industry, medicine, biology, nutrition, nucleonics, to mention but a few. Today the well-trained analyst is almost as much a physicist as he is a chemist. He is expected to be a specialist in many fields of specialization. He needs, and the editors of ANALYTICAL CHEMISTRY will see that he is furnished with, a publication of his own, designed and so edited as to provide all the essential scientific tools.

The present scope of ANALYTICAL CHEMISTRY was discussed in the April 1946 issue, Vol. 18, No. 4, page 218, but it is desirable that we remind our readers that their publication is intended to provide the following:

1. Papers dealing with principles and theory of analytical chemistry.
2. Papers presenting improved or new analytical procedures.
3. Review papers at stated intervals evaluating critical work in given fields during specified periods.
4. Papers providing the evaluation of analytical results or the statistical treatment or interpretation of analytical and test data.
5. Papers reporting on efficient physical equipment, laboratory construction, and layout.
6. Papers discussing the college training of personnel, training programs, organization and operation of analytical laboratories in industry, research foundations, etc.
7. Papers disclosing the development and application of instruments designed for use in the field of analytical chemistry.

"The Analyst's Column", written by Associate Editor Lawrence T. Hallett, is an intimate, newsy, and wholly informal discussion of scientific and nonscientific subjects of special interest to the analyst.

"Aids for the Analyst" provides our readers with a wide variety of valuable hints, mechanical techniques, etc.

The increasingly popular departments, "Notes on Analytical Procedures" and "Instrumentation", the latter prepared by Ralph H. Müller, are being continued.

The editors on this occasion wish to express their deep appreciation to the members of the Advisory Board for their continued interest. Authorization has been given to expand the Advisory Board from nine to twelve members, in order that new fields not yet represented will be more adequately covered. The practice of inviting the officers of the Division of Analytical and Microchemistry to attend Advisory Board meetings will be continued to the end that the close coordination and cooperation between the publication and the division shall be further increased.

ANALYTICAL CHEMISTRY is the publication of the analytical chemist. As such it should meet the changing and expanding needs of its readers and as far as possible anticipate such needs. The continued support and increased interest of authors, reviewers, and readers will make possible a publication second to none in the field of analytical chemistry.

Measurement of Radioactive Tracers

Particularly C^{14}, S^{35}, T, and Other Longer-Lived Low-Energy Activities

W. F. LIBBY, *Institute for Nuclear Studies and Department of Chemistry, University of Chicago, Chicago, Ill.*

The importance to the chemist of the detection of soft beta-radiation is pointed out—the useful longer-lived beta-radioactive isotopes all have soft radiations. An empirical treatment of the absorption of soft beta-radiation is given leading to the range energy relation $l_0 = \frac{1}{150} E^{5/3}$ where l_0 is the range of the most energetic beta-rays in milligrams of aluminum per sq. cm., and E is the upper energy limit in kilovolt units. The absorption at thicknesses less than l_0 is assumed according to experiment to be exponential in character: $I = I_0 e^{-\alpha d}$, where I_0 is the intensity with no absorber, α is the absorption coefficient, and d is the absorber thickness in milligrams per square centimeter. An empirical expression for α is $\alpha = 5/l_0$. This allows a generalized treatment of the problems of absorption and the intensities of radiation from sample layers of various thicknesses. On the basis of this formulation of the problem the relative sensitivities of various counters are discussed, in particular the popular "end window" type, the screen-wall type, and the gas counter.

THERE is a conspiracy in nature against the chemist, in the form of a relation between the rate and energy of radioactive transformations—the longer lived, the softer the radiations. The radioactivities of lives greater than a few weeks almost without exception possess radiations so soft as to require special detection procedures. Table I contains a list of the more useful light chemical tracers with their half-lives and energies and ranges of their radiations in aluminum listed. It is perfectly obvious from this compilation that the average measuring instrument—counter or electroscope—with wall thickness of at least 100 mg. per sq. cm. (0.015 inch of aluminum) will be unsuitable for three of the most useful isotopes in Table I, T(H^3), C^{14}, and S^{35}.

EMPIRICAL TREATMENT OF BETA RAY ABSORPTION

Beta-particles lose energy to absorbers by ionization, and except for the tremendous scattering effects would proceed as alpha-particles do to a rather definite range. The great scattering tendency means that for many experimental arrangements the loss by scattering is at least as large as that due to true absorption. In other words, though a range energy relation exists, the diminution in intensity caused by interposition of a foil of less than the range in, say, a monochromatic electron beam is much greater than it would be for alpha-particles—owing to the larger scattering effect.

Table I. Particularly Useful Radioactive Tracers

Isotope	Half-life	Maximum Energy of Beta-Radiation *Kv.*	Al Range *Mg./sq. cm.*	Half-thickness *Mg./sq. cm.*
T	31 years	9.5	0.23	0.03
C^{11}	20.5 minutes	950	390	54
C^{14}	4700 years (*10*)	140	20	2.8
F^{18}	112 minutes	700	260	36
Na^{22}	3.0 years	580	215	30
Na^{24}	14.8 hours	1400	620	86
Si^{31}	170 minutes	1800	860	120
P^{32}	14.3 days	1690	800	110
S^{35}	87 days	107	13.5	1.9

Figures 1 and 2 show the range energy relation for beta-particles. The data are from experiments with monochromatic electron beams as performed by Schonland, Varder, Ellis, and others (*11*), and described most carefully by Rutherford, Chad-

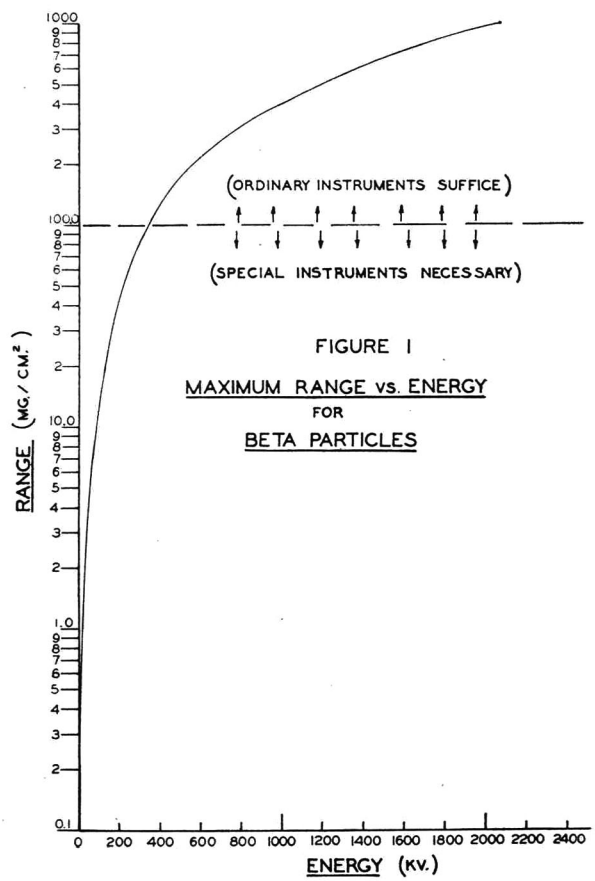
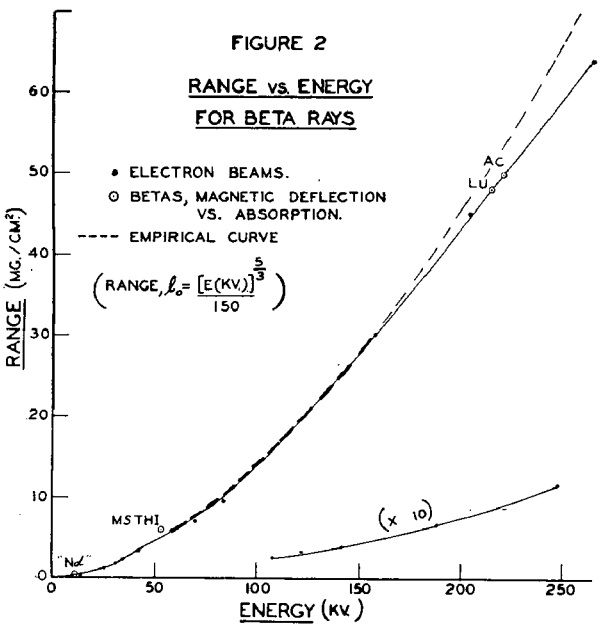


FIGURE 1
MAXIMUM RANGE vs. ENERGY
FOR
BETA PARTICLES

Table II. Directly Measured Range *vs.* Energy Points for Soft Betas

Activity	Energy (Magnetic) *Kv.*	Range *Mg./sq. cm.*	Reference
"Nd"	11	0.29	(8)
T	13	0.23	(1, 2, 6)
MsThI	53	6.0	(7)
S^{35}	107–120	15	(5, 6)
Rb^{87}	132	20	(6)
Lu^{176}	215	48.0	(9)
Ac^{227}	220	(50.0)	(4)



wick, and Ellis (*11*). A few data are given for soft natural beta-emitters, for which the energy limits have been measured magnetically and the absorption limit determined. These fall on the same curve. These points are given in Table II.

The electron beam work showed relatively little dependence on atomic number, so the range values are quoted purely in milligrams of weight per square centimeter, whenever possible aluminum absorbers or substances of similar atomic number being used. The error even with gold is not large, however. It appears that scattering somehow compensates for change in energy loss per centimeter of true path. Figure 2 shows an empirical range energy curve given by

$$\text{Range, } l_0 = \frac{[E(\text{kv.})]^{5/3}}{150} \tag{1}$$

This may be expected to hold only for energies up to 200 kv.

Wilson (*12*) noted early that whereas the absorption of a monochromatic electron beam was far from exponential in character, a typical beta-ray emitter was rather accurately exponential as far as about 90% loss of beam intensity, and he correctly ascribed this paradox to the existence of a range of velocities in beta-emitters, the superposition of such a spectrum of energy values resulting in an approximately exponential absorption curve. It is of real importance that we be able to predict the absorption coefficient from the upper energy limit (the quantity usually available for beta-emitters).

In order to do this we shall assume that the shape of the beta-spectrum is essentially the same for all activities, in so far as it affects the ratio of the absorption coefficient and the range. Then we will expect the absorption coefficient to vary inversely with the range as given by Figures 1 and 2. In other words, if I is the beta-ray intensity where d is the absorber thickness (in mg. per sq. cm.) and α is the absorption coefficient,

$$I = I_0 e^{-\alpha a} \tag{2}$$

Henriques, Kistiakowsky, Margnetti, and Schneider (*3*) give $\alpha = 0.32$ for S^{35}. Calling the maximum range l_0, we then can write as a good approximation for sources of soft betas up to E values of 200 kv.

$$\alpha l_0 = 5 = \alpha \frac{E^{5/3}}{150} \tag{3}$$

This equation will serve to correlate upper energy limits and absorption coefficients (usually taken with essentially flat geometry and close proximity of source and detector to absorber). On this basis we proceed to analyze the problem of detection of beta-activities.

EMPIRICAL THEORY OF SOFT BETA DETECTION

Intensity from Infinitely Thick Layer. Suppose a plane surface to be covered to a depth large with respect to the range, l_0 with a beta-emitting material, which has a specific activity of σ (microcuries per gram). The curie is taken as 3.7×10^{10} disintegrations per second, so the microcurie is 2.22×10^6 disintegrations per minute. What will be the count rate if an area A of this solid be put in a counter with no intervening window?

From a layer of depth l (mg. per sq. cm.) the yield will be (if we neglect back reflection, so only half of the radiation is considered)

$$dI = \frac{A\sigma}{2} e^{-5} \frac{l}{l_0} dx \tag{4}$$

or

$$I_\infty = \frac{A\sigma l_0}{10} \tag{4'}$$

Therefore the count will be 10% of the total disintegrations from a layer of a depth at least equal to the range, l_0 or $\frac{E^{5/3}}{150}$ in milligrams per square centimeter.

Self-Absorption Curve. Consider a given number of millicuries of a soft beta-activity successively diluted with inert material making a thicker layer, always of the same area, A. What will be the count rate without an intervening window for each of the various dilutions?

State all thicknesses in terms of l_0 as unit. Then the initial thickness x_0 contained Al_0x_0 grams at activity σ_0, so

$$\sigma_0 A l_0 x_0 = \sigma A l_0 x \tag{5}$$

where x/x_0 is the dilution ratio. Therefore

$$I = \frac{\sigma_0 x_0}{x} A l_0 \int_0^x e^{-5t}\, dt \tag{6}$$

$$= \frac{\sigma_0 x_0 l_0}{5x} A(1 - e^{-5x})$$

and if I_0 represents the value as $x_0 \longrightarrow 0$

$$\frac{I}{I_0} = \frac{1 - e^{-5x}}{5x} \qquad (x \leqq 1) \tag{7}$$

which is a self-absorption curve of general applicability. This is shown in Figure 3, together with important l_0 values. This Equation 7 obviously should not apply beyond $x = 1$ because the exponential cannot apply then. The new form then will be

$$\frac{I}{I_0} = \frac{1}{5x} \qquad (x > 1) \tag{7'}$$

Actually, Equations 7 and 7′ differ so little that Equation 7 can be used throughout.

Window or Foil Absorption. If a foil or window has thickness a (in terms of the range, l_0)

$$I = I_0 e^{-\alpha a l_0} = I_0 e^{-5a} \tag{8}$$

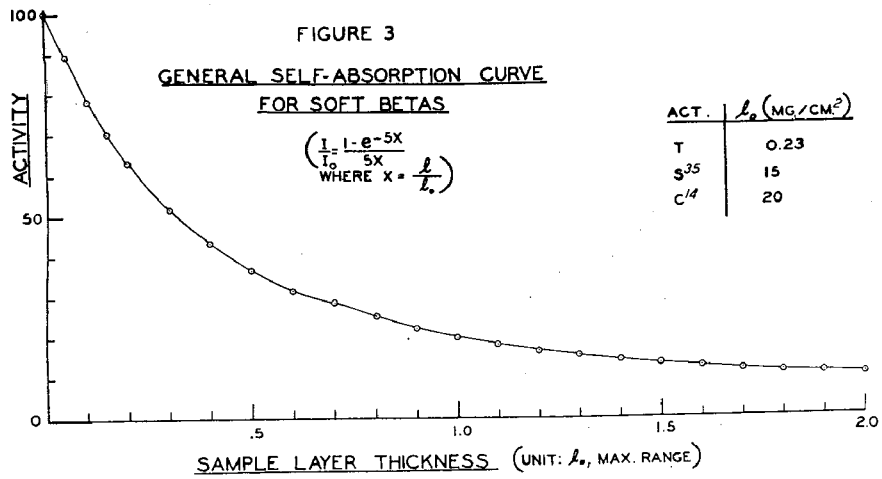


FIGURE 3

GENERAL SELF-ABSORPTION CURVE FOR SOFT BETAS

$\left(\frac{I}{I_0} = \frac{1-e^{-5X}}{5X}\right)$ WHERE $X = \frac{l}{l_0}$

The half-value absorber thickness is given directly by Equation 8 as

$$d_{\frac{1}{2}} = 0.139\ l_0 \qquad (9)$$

In other words, the maximum range will be expected to be 7.2 times the half-thickness. Figure 4 gives the general absorption curve, together with the l_0 values for T, S^{35}, and C^{14}.

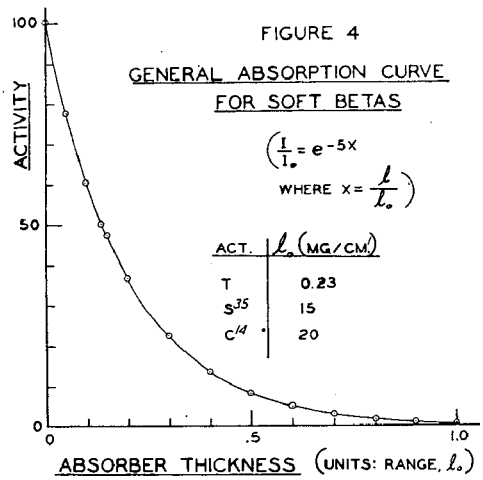


FIGURE 4

GENERAL ABSORPTION CURVE FOR SOFT BETAS

$\left(\frac{I}{I_0} = e^{-5X}\right.$ WHERE $\left.X = \frac{l}{l_0}\right)$

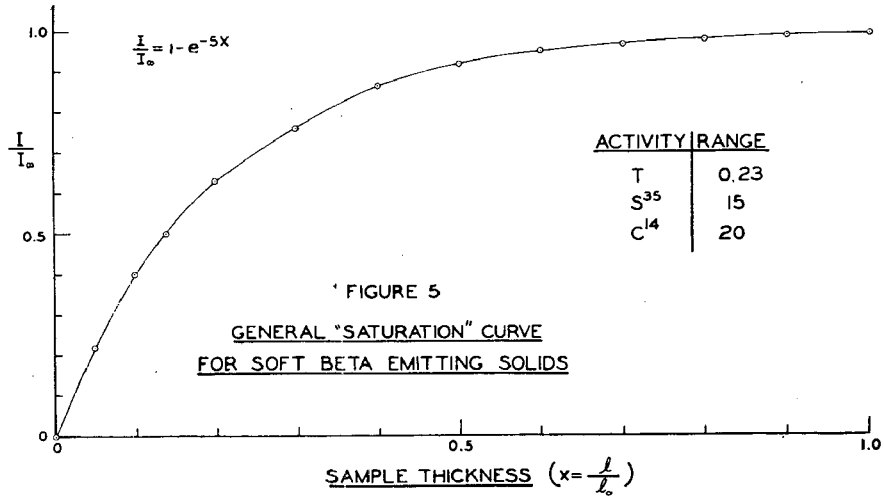


FIGURE 5

GENERAL "SATURATION" CURVE FOR SOFT BETA EMITTING SOLIDS

"Saturation" Curve. Consider the activity from a layer of sample of uniform specific activity, σ, of various thickness, x, in terms of the range, l_0. Its activity will be

$$I = \frac{\sigma A l_0}{2} \int_0^x e^{-5t}\, dt \qquad (10)$$

$$= \frac{\sigma A l_0}{10} (1 - e^{-5x})$$

or

$$\frac{I}{I_\infty} = 1 - e^{-5x} \qquad (10')$$

where I_∞ is the activity for an nfinitely thick layer. The general "saturation" curve for soft betas is given in Figure 5.

THEORY OF DETECTION BY COUNTERS

General Treatment. In order to facilitate the discussion, we shall adopt a definition of sensitivity. We shall define the sensitivity, S, as that limiting dilution of the sample (in grams per microcurie) which will just allow the sample to be measured to 10% (standard deviation) in 10 minutes.

As the counter background will be of the order of the cross-sectional area in square centimeters (measuring count rate in minutes^{-1}), we are free to calculate the sample count rate which will ensure 10% accuracy in 10 minutes by using the Poisson statistics and the counter length L (cm.) and diameter L/α (cm.). The background is proportional to L^2/α (counts per minute) and the total with sample $L^2/\alpha + E$, where E is the sample's count rate. Then the error in E will be

$$\Delta E = \sqrt{\frac{2L^2}{5\alpha} + \frac{E}{5}} \qquad (11)$$

where it has been assumed that equal intervals of 5 minutes be spent with and without the sample. (This approximation has been made to facilitate the calculations and is accurate for the counters of bighest sensitivity.)

Setting ΔE equal to $E/10$ and solving for E, we obtain

$$E = 10\left(1 + \sqrt{1 + \frac{2L^2}{5\alpha}}\right) \qquad (12)$$

as the general expression for the minimum count from the sample for 10% accuracy in 10 minutes' measurement. Figures 6 and 7 present this limiting sample count *vs.* the background and the background *vs.* counter dimensions, respectively.

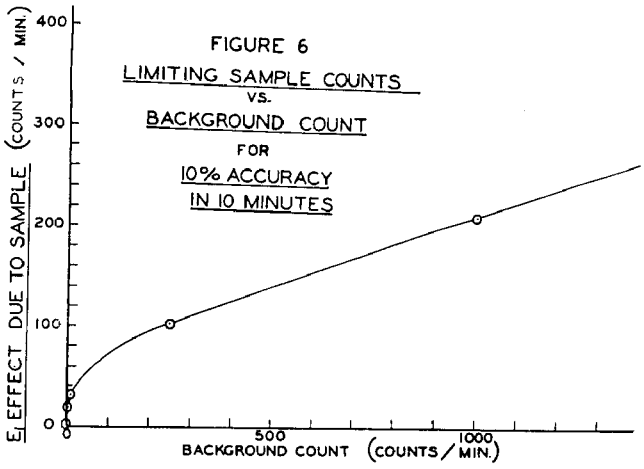
End Window Counter. This popular type of counter is a short, large diameter (small L and α) counter with a thin window at one end; the plane of the window being perpendicular to the axis of the cylinder. It is described by Yankwich, Rollefson, and Norris (*13*), and by Henriques, Kistiakowsky, Margnetti, and Schneider (*3*). Figure 8

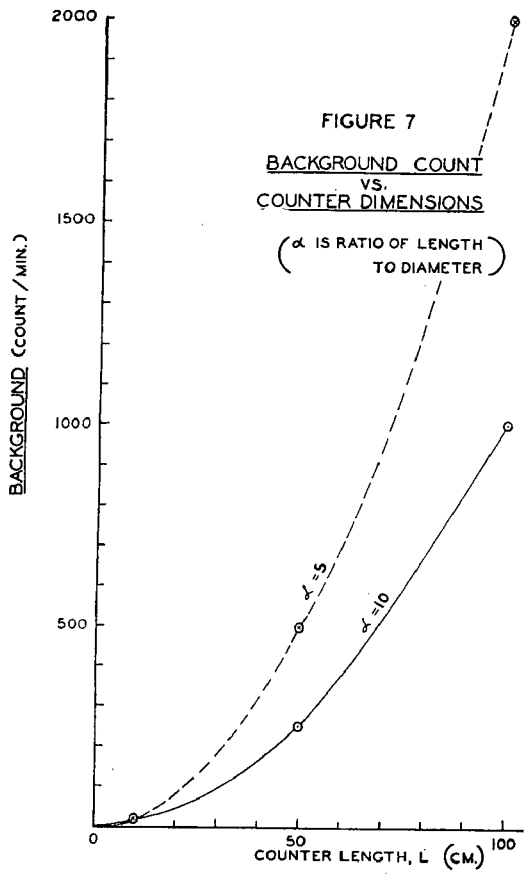
shows the general features of this instrument as described by these authors.

If σ is the specific activity of the sample in microcuries per gram
l_0, the range (mg. per sq. cm.)
w, the window thickness
then the expected count rate (counts per minute) is

$$E = \frac{\pi}{4}\left(\frac{L}{\alpha}\right)^2 \frac{l_0 \times 10^{-3}\,\sigma \times 2.22 \times 10^6}{10} e^{-5w/l_0} \qquad (13)$$

Equating this to Equation 12, we solve for the limiting value of $1/\sigma$ which we have defined as the sensitivity, S.





$$S = 17.4\, l_0 e^{-5w/l_0} \left\{ \frac{\left(\frac{L}{\alpha}\right)^2}{1 + \sqrt{1 + \frac{2}{5}\frac{L^2}{\alpha}}} \right\} \text{(grams per microcurie)} \qquad (14)$$

Similarly, the minimum weight of sample to give an infinitely thick layer is W in

$$W = \frac{\pi}{4}\left(\frac{L}{\alpha}\right)^2 l_0 \times 10^{-3} \text{ (grams)} \qquad (15)$$

Figure 9 presents S *vs.* W values for counters ranging from 1 to 100 cm. in length, and α values of 5 to 10. The top curve is for C^{14} and the second is for S^{35}. T cannot be detected with these instruments.

Screen Wall Counter. This instrument (*6*, *8*) possesses two advantages in sensitivity over the end window design:

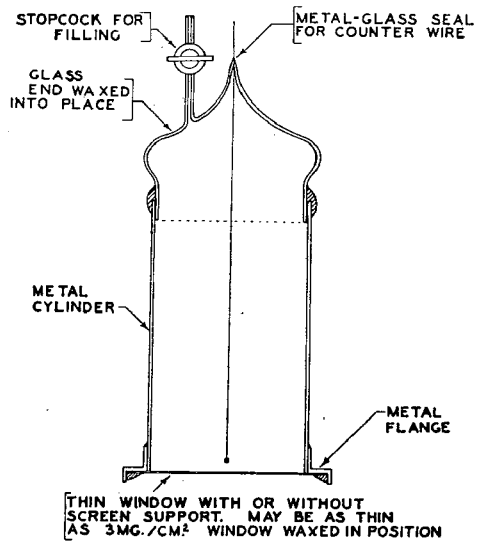
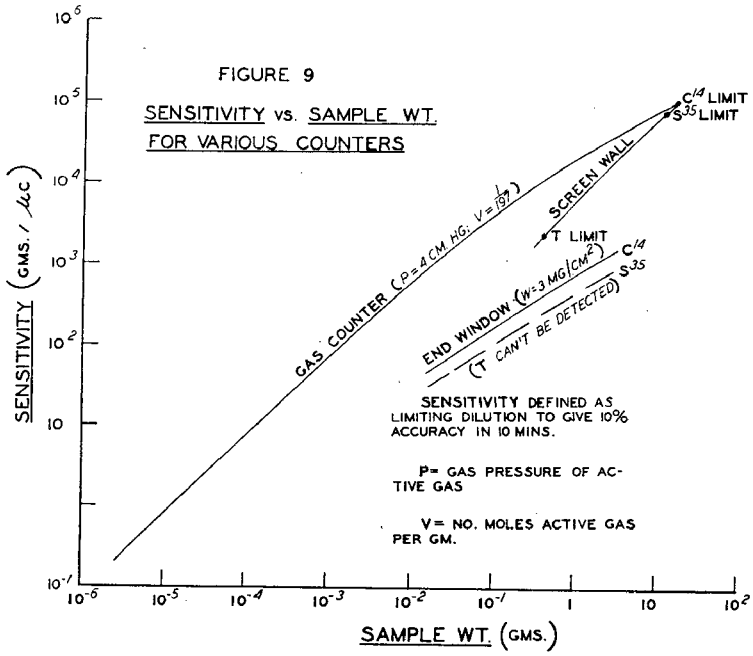


Figure 8. End Window Counter



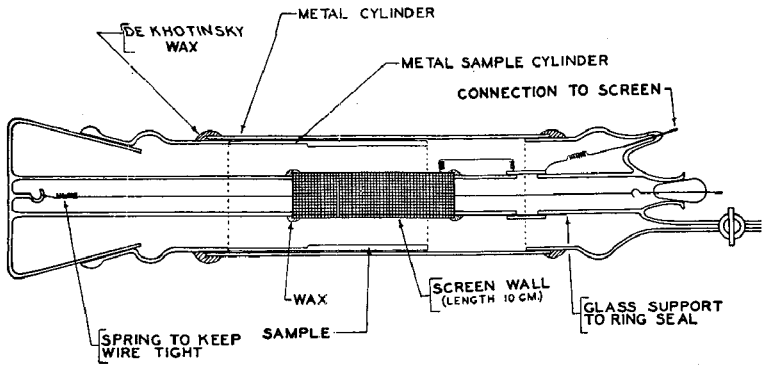


Figure 10. Screen Wall Counter

1. Sample area is $\pi \frac{L^2}{\alpha}$ *vs.* $\frac{\pi}{4}\frac{L^2}{\alpha^2}$
2. No window between sample and counter. (It is recommended that the instrument be operated with "drag in" voltage—i.e., chamber wall negative with respect to screen for maximum sensitivity)

It has the disadvantage that about 20 minutes are required normally to mount and change samples, in contrast to 2 or 3 minutes for the end window design. Figure 10 presents its essential features.

The equations for this counter are

$$S] = 69.1\ l_0 \left\{ \frac{\left(\frac{L^2}{\alpha}\right)}{1 + \sqrt{1 + \frac{2}{5}\frac{L^2}{\alpha}}} \right\} \text{(grams per microcurie)} \quad (16)$$

$$W = \frac{\pi L^2}{\alpha} l_0 \times 10^{-3} \text{ (grams)} \quad (17)$$

They are derived as for the end window type, and are illustrated in Figure 9 for all sizes up to L values of 100 cm. and α values of 5 to 10.

The superior sensitivity of the instrument is obvious from this comparison.

Gas-Filled Counters. One of the most sensitive uses of a counter is the direct introduction of the sample into the counter gas when possible. This, also, is a direct way of obtaining an absolute measure of the radioactivity. The counter can be standardized for absolute sensitivity with the sample filling (or the control dummy filling of the same composition chemically), and the observed sample rate converted directly to curies of activity. The sensitivity is independent of the type and energy of the radiation, providing it produces a few ion pairs per centimeter of path at atmospheric pressure, and providing the physical and chemical characteristics of the gas are such as to make a good counter.

In the use of gas-filled counters it is necessary, of course, to work with a vacuum rack. The pressures of the gas must be measured with due regard to its linear effect on accuracy, and sufficient cognizance must be given to adsorption of absorbable gases on the counter walls, etc.

A convenient construction is shown in Figure 11. It is well to have a plentiful supply of cylinders and glass ends to fit. The construction of a counter takes about 15 minutes if these standard materials are available.

If P be the pressure in atmospheres to which the counter can be filled with the gas being measured. and ν the number of moles of this gas produced by 1 gram of sample, then the basic equations are

$$S = 7.21 \frac{P}{\nu} \left\{ \frac{\frac{L^3}{\alpha^2}}{1 + \sqrt{1 + \frac{2L^2}{5\alpha}}} \right\} \quad (18)$$

and

$$W = 3.17 \times 10^{-5} \frac{P}{\nu} \frac{L^3}{\alpha^2} \quad (19)$$

These are illustrated in Figure 9 for counters of sizes from 1 to 100 cm. in length and α values of 5 to 10.

The principal disadvantage of these counters is the requirement that the gas sample not too seriously damage the counting properties. At pressures of 3 or 4 mm. of mercury this is not a serious restriction, but at the higher pressures required for the maximum S value it is a serious consideration.

For T, hydrogen gas serves. This can be used easily to pressures of 4 or 5 cm. if several centimeters of A be added together with a few millimeters of ethanol. For C^{14}, the alcohols are excellent, of course. Methane is good, as are other hydrocarbons. There seems to be some hope for carbon dioxide.

No sulfur gas has been reported yet.

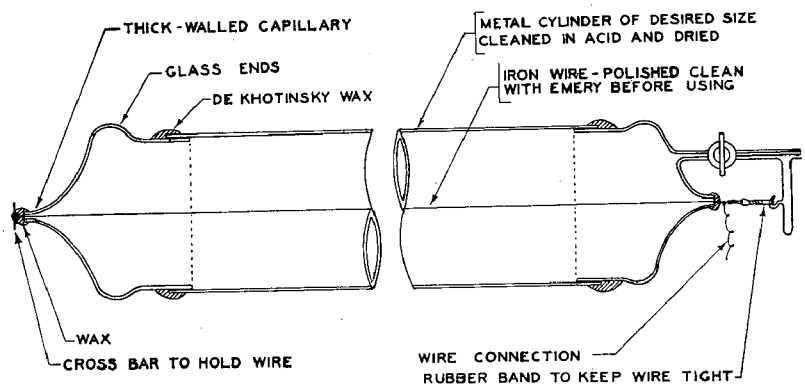


Figure 11. Gas-Filled Counter

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Improvements in Polarographic Instrumentation

G. E. PHILBROOK[1] AND H. M. GRUBB
Standard Oil Co. (Indiana), Whiting, Ind.

The Sargent Model XII polarograph in this laboratory contains a Rubicon taut suspension galvanometer with a sensitivity of 0.003 microampere per mm. at 61-cm. (2-foot) scale distance. This galvanometer is very sensitive to vibration. A vibration-isolating mount constructed for the instrument successfully remedied a vibration problem which according to the makers is the worst they have seen. To make full use of compensation technique some means of damping the excessive galvanometer oscillations at high sensitivity is required. An electrical filter avoids many of the drawbacks of the circuits previously described for this purpose. A polarograph cell has been designed which appears more satisfactory for many routine uses than those described in the literature.

EXCESSIVELY severe vibration from railway traffic prevented the operation of a Sargent-Heyrovský Model XII polarograph equipped with a Rubicon galvanometer. When the instrument stands on a substantial laboratory bench the galvanometer vibrates continuously with an amplitude of 0.5 to 2 mm. Occasional shocks cause deflections of 10 to 15 mm. Mounting the instrument on rubber, slate and rubber, or floating it on mercury increased the instability. A short period pendulum mount appeared to give a very slight improvement. Placing the instrument on a pad of 5 cm. (2 inches) of felt covered with 31.75 kg. (70 pounds) of sheet lead gave sufficient improvement to make 50% of the records usable.

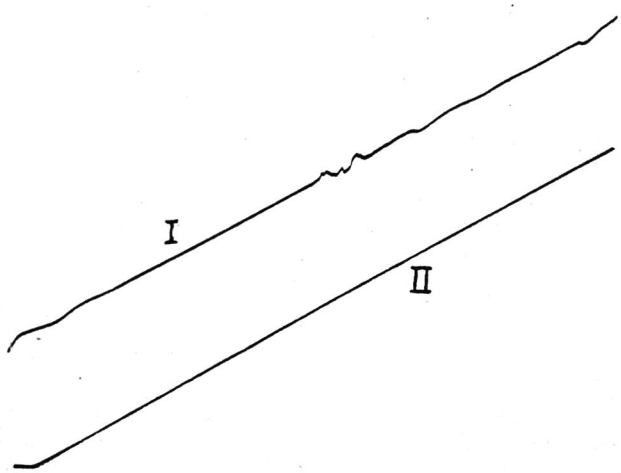

Figure 1. Vibration Records
I. Instrument on laboratory bench
II. Instrument in mount

The system now in use employs four pairs of commercial rubber-in-shear mounts overloaded 300%. The instrument is suspended from these units with its center of gravity close to the plane of the centers of the suspension pairs. This technique reduces pendulum effects to a minimum. A dash pot mounted away from the center of the bed plate, and filled with a very viscous oil, rapidly damps oscillations of the suspension started by manipulation of the instrument. A cam-operated lift plate takes part of the load off the suspension when the instrument is not in use.

[1] Present address, Chemistry Department, University of Georgia, Athens, Ga.

In Figure 1 are shown two vibration records, which were obtained by substituting a resistor for the cell and scanning the voltage range. The first record was made with the instrument resting on a substantial and rigid laboratory bench. The second curve was made under comparable vibration conditions with the instrument in its mounting.

In Figure 2 is shown a schematic cross section of the mount.

The instrument rests on a 0.75-inch plywood bed plate, supported on two U-shaped yokes spaced 11.5 inches on centers from front to back. The yokes are 8 inches deep with an over-all length of 22 inches and are fabricated from 0.25 × 2 inch strap iron. The ends of the yokes are turned down to give a horizontal section 2.75 inches long, which is drilled to take the mounts. A 4-pound Lord plate-form rubber-in-shear mount (Lord Manufacturing Co., Erie, Pa., Catalog No. 102PH4) is bolted to the bottom of each of the horizontal yoke sections. The rubber mounts are on 20-inch centers from side to side and 11.5-inch centers from front to back. The upper rubber mounts of the support pairs are the same as the lower and are bolted to straps of 0.25 × 2 inch flat iron. The yokes are suspended from these upper mounts by 2.5-inch No. 8 machine bolts through the center holes. All straps and yokes are pierced with 1-inch holes opposite the mount centers to clear the bolts and rubber which stretches greatly under the high overload imposed. The straps are supported on a heavy wooden frame fabricated from 2-inch pine with mortised joints. Sections are cut out at the suspension points to clear the suspension members. The front is open and a section is cut out at the right end to clear the camera.

In Figure 3 is shown a vertical view of the mount with the instrument and bed plate removed. The dash pot is 4 inches off center at an angle of 45° to the center lines of the mounts. This location was chosen to damp rotation as well as lateral motion.

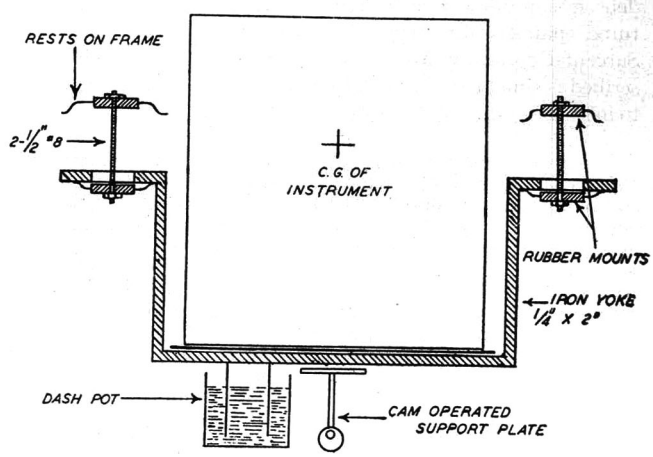

Figure 2. Schematic Cross Section of Polarograph Mount

A 2-inch can open at the bottom and fastened to the bed plate dips into the dash pot, which is filled with a very heavy oil (Pennsylvania steam-refined, viscosity 220 seconds Saybolt at 210° F. or equivalent). The can is immersed 2 inches in the oil. The cam-operated lift plate shown in the center has a vertical rise of 0.25 inch.

GALVANOMETER OSCILLATION DAMPER

Lingane and Kerlinger (*3*) point out that compensation technique is limited by wide oscillations of the galvanometer when the current being compensated reaches a value 10 to 15 times larger than the current being determined, and suggest the use of an electrolytic condenser of fairly high capacity across the Ayrton shunt output to damp these oscillations. To cover a wide range of concentrations several condensers are required, as there is an optimum capacity for each combination of sensitivity and drop time. To overcome this drawback Fill and Stock (*1*) devised an improved circuit in which a condenser was used across the Ayrton shunt output and a variable resistance in series with the Ayrton shunt center tap. This circuit damps effectively over a wide range of sensitivity–drop time values.

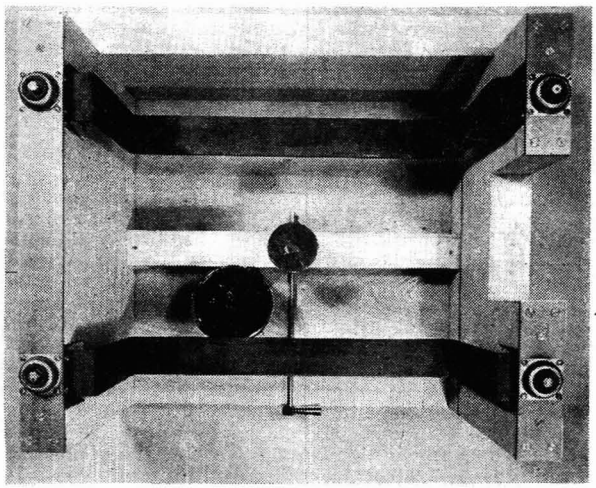

Figure 3. Vertical View of Mount
Instrument and bed plate removed

In both circuits the use of ordinary electrolytic condensers leads to serious difficulty. The majority of electrolytic condensers commercially available contain internal e.m.f.'s of the order of 6 to 60 mv. Such potentials are sufficient to cause full-scale deflections of the galvanometer. While high-capacity paper condensers suitable for such damping circuits have been manufactured commercially, they are too bulky to be installed in the Sargent-Heyrovský Model XII polarograph. The circuit described is similar to that of Fill and Stock but avoids trouble due to internal e.m.f.'s of electrolytic condensers.

The space requirement is approximately 1 × 2 × 2 inches. A resistor (R_1, Figure 4) is placed in series with the low resistance end of the Ayrton shunt and the anode. Two electrolytic condensers (C_1 and C_2, Figure 4) connected back to back are placed in parallel with the anode and the Ayrton shunt center tap. The points at which the resistance and capacitance are inserted are entirely a matter of convenience and the circuit is basically identical with the arrangement of Fill and Stock. Since electrolytic condensers conduct current in only one direction, this arrangement blocks the circuit to continuous direct current flow and the e.m.f. of the condensers is inoperative.

The oscillation damper consists of a simple resistance-capacity filter. The proper circuit values for the authors' instrument were obtained by trial. The damper performed so well that the

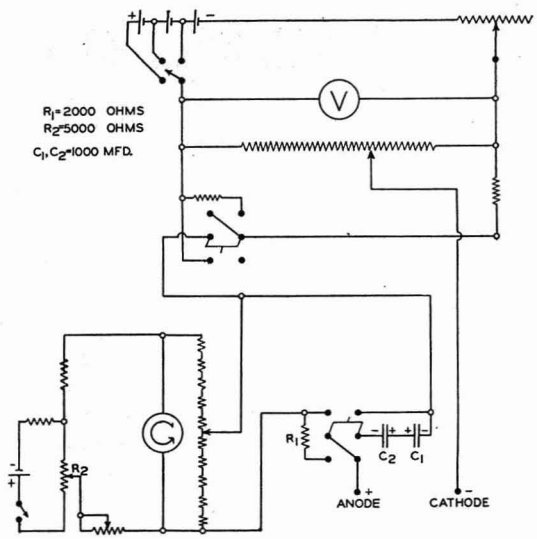

Figure 4. Wiring Diagram for Modified Sargent-Heyrovský Polarograph Model XII

design considerations were worked out and are presented below for those who may wish to add such a circuit to other polarographs.

If it is assumed that the impedance of the galvanometer is equal to its direct current resistance, the resistance arm of the *RC* filter is equal to the sum of the resistance of the galvanometer with its associated Ayrton shunt and the 2200-ohm resistor placed in series. (The actual resistance of most radio-type resistors may deviate 20% from the rated value. This resistor was rated at 2000 ohms.) The resistance of the galvanometer–Ayrton shunt combination varies from about 1 ohm to a maximum of about 300 ohms. The capacity arm of the filter consists of two 1000-mfd. 6-volt electrolytic condensers in series opposing. The effective capacity of two identical condensers used in series in this manner is half that of a single condenser. However, the capacity of an electrolytic condenser is strongly dependent on the applied voltage. Measurement by ballistic methods gave a value of 1250-mfd effective capacity for the pair connected in series at a voltage of 64 mv. This voltage corresponds roughly to normal conditions of use in the damper. If it is assumed that the reactance of the condensers to alternating current of drop frequency is small compared to the resistance in parallel, the damping factor, D, by which the galvanometer oscillations are reduced is given by

$$D = \frac{t}{2\pi RC}$$

where R is the total resistance in ohms, C is the effective capacity in farads, and t is the drop time in seconds. Calculated and observed damping may be compared from data obtained from curves similar to those shown in Figure 5. With the Ayrton shunt set at a sensitivity of 50 (resistance of shunt-galvanometer combination about 20 ohms or a total of about 2220 ohms in the resistance leg of the filter) and a drop time of 3.8 seconds the calculated damping factor is

$$D = \frac{3.8}{2\pi \times 2220 \times 1250 \times 10^{-6}} = 0.22$$

while the observed damping factor is 0.18.

At first glance it may appear that smaller damping factors are desirable. While there is considerable choice in the damping factor employed, this technique has definite limitations. Damping is achieved over a wide range of conditions at the expense of introducing an iR drop in series with the cell. This alters the form of the waves and a correction for this effect must be made in the determination of wave slopes and half-wave potentials.

For small damping factors a second effect can be troublesome. The effect of the damper is to increase the effective period of the galvanometer. If this increase in period is large enough, the galvanometer will lag so far behind the potential changes that

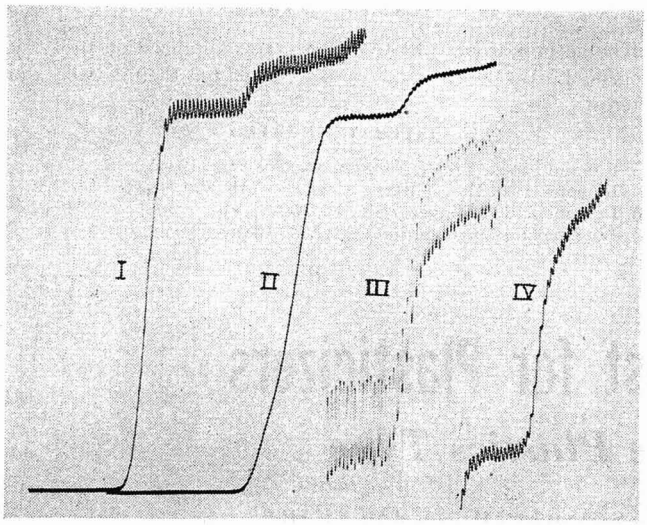

Figure 5. Curves Obtained on Solution 0.005 *M* in Cadmium and 0.0005 *M* in Zinc in 0.1 *N* Potassium Chloride Containing Trace of Hydrochloric Acid

0.001% methyl red
I. Sensitivity 100 undamped
II. Sensitivity 100 damped
III. Zn compensated, sensitivity 20 undamped
IV. Zn compensated, sensitivity 20 damped

waves will show little or no straight portion on the rise or plateau. This trouble can be reduced partially by decreasing the rate of increase of potential to the lowest value which gives satisfactory breaks. The size of damping factor should be selected with the possible uses of the instrument in mind.

This damper has been in use on the authors' instrument for over nine months and has proved extremely satisfactory. It is installed with a double pole–double throw switch to remove it from the circuit if desired. However, it is used on all waves because the reduction of the oscillations on normal waves gives some increase in the precision of measurement.

In order to realize the full advantage of the damper, the compensator which is part of the Sargent Model XII polarograph was somewhat modified.

As originally supplied the compensator voltage control was a 1000-ohm radio-type potentiometer with a 270° rotation. This unit (R_2) was replaced with a 5000-ohm 10-turn (3600° rotation) Helipot (Helipot Corp., 1011 Mission St., South Pasadena, Calif., Catalog No. 680-H). This potentiometer extends the range of the compensator 37% and, more important, avoids the jumpy behavior apparent in the upper 20% of the old compensator voltage range. The original compensator had two shut-off switches. The one on the voltage control was removed and the second was moved from the current control into series with the battery lead. In Figure 4 is shown the circuit diagram for the instrument after all the above modifications were made.

In Figure 5 are shown four curves obtained on a solution 0.005 *M* in cadmium, and 0.0005 *M* in zinc in 0.1 *N* potassium chloride containing a trace of hydrochloric acid. Methyl red (0.001%) was used as a maximum suppressor. Curve 1 was obtained at a sensitivity of 100 without the damper. Curve 2 was obtained at the same sensitivity with the damper in operation. Curve 3 shows the zinc wave at a sensitivity of 20 after compensation without the damper. Curve 4 was obtained with the damper under the same conditions as curve 3.

The small irregularities in curves I, III, and IV of Figure 5 are believed to be due to vibration of the capillary. The cell and capillary are attached to a rigid support which rests on a felt pad. The support is not connected to the wall. A mount for the cell assembly based on the principles used for the instrument does not appear to be practical, because of constructional difficulties. The small irregularities shown do not appear appreciably to affect the results obtained with the instrument.

POLAROGRAPH CELL FOR ROUTINE USE

The polarograph cell for routine use by nontechnical personnel should be constructed from standard items replaceable from stock in case of breakage. As many components as possible should be fixed in place to reduce manual manipulation to a minimum. Accessories not in routine use, such as reference electrodes, should be omitted.

In Figure 6 is shown a cell which the authors believe meets these requirements for most routine uses better than any they have found described in the literature. The construction is evi-

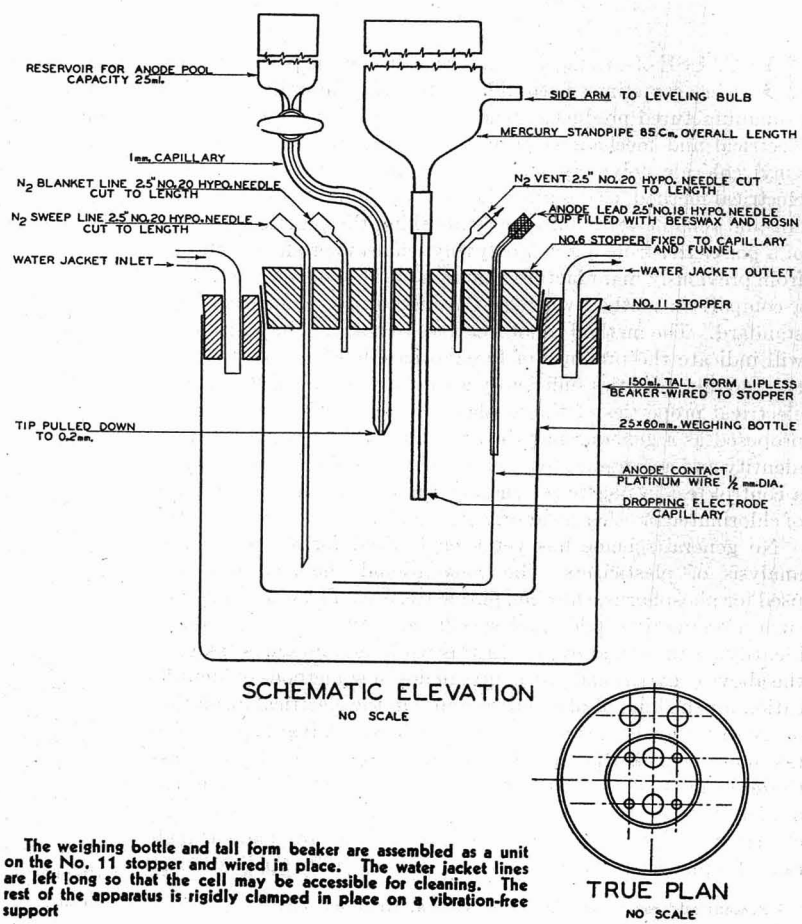

Figure 6. Polarograph Cell

The weighing bottle and tall form beaker are assembled as a unit on the No. 11 stopper and wired in place. The water jacket lines are left long so that the cell may be accessible for cleaning. The rest of the apparatus is rigidly clamped in place on a vibration-free support

dent from the drawing and requires no comment. A standpipe of the type described by Lingane and Laitinen (*4*) is used with this cell. If desired, a silver–silver chloride electrode of the type described by Lingane (*2*) may be used in place of the mercury pool.

This cell has been used for acid, alkaline, and neutral media for several months and no trace of contamination from the stainless steel capillaries has been detected.

This convenient, compact, and rugged cell has proved itself in continuous service for several months on one capillary.

ACKNOWLEDGMENT

The authors would like to express their appreciation to T. H. Rogers, E. W. Thiele, and E. B. Tucker for their advice and interest.

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Dielectric Identity Test for Plasticizers

Polyvinyl Chloride Plastics Type

MYRON A. ELLIOTT, A. RUSSELL JONES[1], AND LUTHER B. LOCKHART
Naval Research Laboratory, Washington, D. C.

A new type of cell and method are described for the rapid determination of the dielectric properties of small samples of plasticizers as a function of temperature. Since these materials have characteristic loss factor–temperature curves that are sensitive to contamination by significant amounts of practically any foreign material, such dielectric data are valuable as an identity or acceptance test. Although the procedure has been applied to some plasticizers in particular, it may be used on nearly all electrically polar organic liquids. The method involves the extraction of a small quantity of the plasticizer from a resin and then the determination of the electrical properties of this plasticizer at a frequency of 10 Mc. as a function of temperature. Each type of plasticizer gave a reproducible curve different from that of the others. Simple qualitative chemical tests were found valuable for confirmation purposes on some types of plasticizers. Refractive index determinations gave useful supplemental information.

BECAUSE of shortages of materials during the past few years, it has sometimes been difficult to maintain uniform quality in manufactured products. One likely cause for variation in the electrical and mechanical properties of plastics made from the vinyl chloride polymers was variation in the plasticizers. The electrical method, as described herein, was found to be a convenient and reliable procedure for establishing the practical identity of a plasticizer from a given polyvinyl chloride product with that from previously manufactured batches of the same product. It is a comparison method whereby the unknown is compared to a standard. The method is not sensitive to traces of impurities but will indicate the presence of foreign materials in a plasticizer if they are in quantities sufficiently great to affect the mechanical or electrical properties of the finished plastic. This method is not proposed as a general analytical tool, but it is recommended for identity and acceptance test purposes. It should also be useful as a control test in plasticizer manufacture and in the manufacture of chlorinated or other polar organic liquids.

No general scheme has yet been devised for the systematic analysis of plasticizers. The conventional chemical tests are used for phosphorus, chlorine, phthalate, etc. Physical properties such as refractive index and specific gravity are also an aid in identifying these materials. In this work, advantage is taken of the above conventional procedures in devising methods of identification for the kind of plasticizers found in the electrical insulation of synthetic resin–insulated Navy cables. Advantage is also taken of a new method which is based on the fact that each plasticizer or mixture of plasticizers shows a characteristic variation of dielectric constant and loss factor (anomalous dispersion) with change in temperature when the measurements are made at high radio frequencies. This method is new only in its application as an identity test for plasticizers and other organic liquids. The anomalous dispersion of the dielectric constant is a well-known phenomenon and is discussed in many publications (*1–4, 6, 9*). Because of the polar nature of plasticizers, electrical methods are well adapted to their characterization. The only problem here is the development of methods that are simple and rapid enough to be used in a routine testing laboratory.

[1] Present address, University of Wisconsin, Madison, Wis.

THEORY

All the plasticizers used with polyvinyl chloride fall into a general class of liquids that are polar but not ionized. When such liquids are placed in an electrostatic field, the molecules tend to become oriented because of electrical interaction between the electric dipoles in the molecules and the field. When this field is alternating, the molecules tend to follow it and so are turned first in one direction and then in the other. If the alternations of the field are sufficiently rapid, the molecules can no longer follow, but remain in a random state. Under these high-frequency conditions the liquid has the low dielectric constant and low loss factor of a nonpolar medium. At intermediate frequencies where the molecules can become partly oriented, the dielectric constant has an intermediate value while the dielectric loss in the liquid is at a maximum or peak. At low frequencies where the molecules become oriented to the maximum extent their thermal motion permits, the dielectric constant reaches its highest value (static value), while the loss factor drops to a low value again.

This anomalous dispersion of the dielectric constant was first observed by Drude in 1897. In 1913 Debye gave the theoretical interpretation of this phenomenon that is generally accepted today. Since the application of the Debye theory to the anomalous dispersion of the dielectric constant of liquids has been given in detail (*1, 2*), it is not necessary to give an outline here.

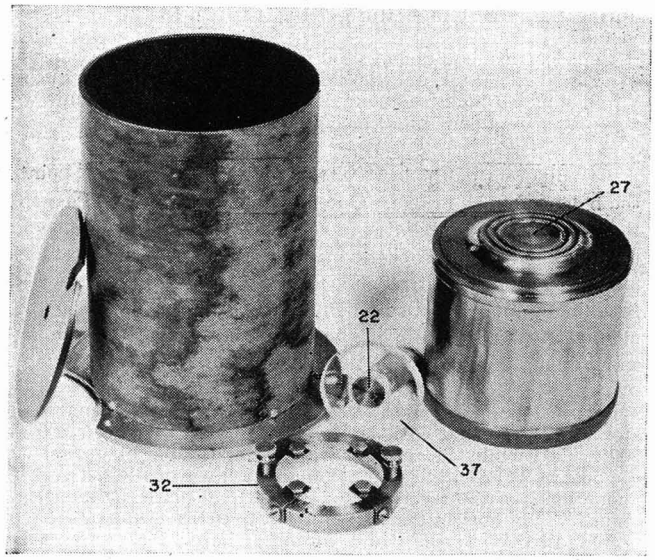

Figure 1. Dielectric Test Cell for Liquids

Reasonable values for the molecular weights of some materials have been obtained from dielectric constant dispersion measurements (*4*, *9*), although the assumptions involved do not always permit quantitative calculations to be made. There is, however, a definite correlation between molecular properties (size, shape, dipole moment, etc.) and electrical properties of the liquid at various temperatures and frequencies. This correlation is the basis for using electrical measurements as an identity test for plasticizers. No attempt is made here to calculate molecular sizes or shapes of plasticizer molecules, but comparisons are made only between the type of curve shown by one plasticizer and that shown by another.

Since the viscosity of the liquid medium in which the molecules are suspended is a function of temperature, it follows that the speed at which these molecules can orient in an alternating field also depends on the temperature. Temperature can therefore be used as the variable to obtain the anomalous dispersion curve while frequency is held constant. The frequency must be such that the anomalous dispersion range of the material under study is covered. Since it is much simpler experimentally to vary temperature than to vary frequency, the data obtained in this work are on the basis of constant frequency (10 Mc.) and variable temperature ($-50°$ to $+50°$ C.).

EXPERIMENTAL

Extraction of Plasticizer. Various methods were tried for the separation of the plasticizer from the synthetic resin insulation. One method depends on dissolving the insulation in hot diisopropyl ketone and precipitating the resin by adding an excess of ethyl alcohol. Details are given below. Another method involves a continuous extraction of the material in a Soxhlet extractor. The following liquids were tried as solvents for the plasticizer: acetone, benzene, hexane, ethyl alcohol, constant-boiling acetone-methanol mixture, and constant-boiling benzene-methanol mixture.

Acetone was observed to dissolve excessive amounts of the resin during the 4-hour extraction period; it was considered unsatisfactory. Benzene and the acetone-methanol mixture also dissolved enough resin during this 4-hour extraction period to necessitate a precipitation of the resin later by the addition of excess ethyl alcohol. An overnight extraction with hexane did not dissolve any resin, but the removal of the plasticizer from the resin was incomplete. The same was true for the alcohol extraction. Whether benzene, hexane, or alcohol is used for the extraction depends on the results desired. If it is desired to remove such materials as lubricants and chlorinated naphthalenes from the synthetic resin insulation, benzene or hexane should be employed. If it is desired to extract as little as possible of these alcohol-insoluble materials, the alcohol should be used for the extraction. The best all-around solvent for the extraction of plasticizer for identity test purposes was found to be the constant-boiling benzene-methanol mixture.

In general, it may be said that any one of the above solvents could be used for the extraction. It is necessary, however, that the same liquid always be used and the conditions of the extraction be kept constant. If any resin is dissolved during the extraction it must be precipitated later with alcohol.

The constant-boiling benzene-methanol mixture (benzene 60%, methanol 40%, boiling point 58° C.) gave satisfactory results for an overnight extraction (20 hours). The plasticizer was 80 to 98% removed, depending on the type of plastic, while no noticeable amount of resin was dissolved. The procedure for extraction using this solvent is as follows:

Place 6 grams of finely chopped (about 20-mesh) sample in a Wiley-Richardson type of extraction apparatus and add 50 ml. of a prepared mixture of 60% benzene and 40% methanol (by volume). Extract for 20 hours and allow to cool. Pour the extract (filter if any precipitate is present) into a beaker and remove the volatile solvent by evaporating on a steam bath. Add about 40 ml. of ethanol and filter if any precipitate is formed. It may be necessary to allow the mixture to stand a few minutes before filtering in order to give the precipitate time to coagulate. Again evaporate the volatile solvent from the plasticizer on a steam bath. This addition of alcohol and second evaporation on the steam bath should be omitted if it is desired to retain any materials in the extract which are relatively insoluble in alcohol. Such materials include lubricants, halowaxes, or other alcohol-insoluble components that may have been extracted.

After the steam bath evaporation has been completed, place the plasticizer (contained in an open, wide-mouthed dish) in a vacuum oven at 110° C. and atmospheric pressure for 0.75 hour. Then evacuate the oven to a pressure of less than 3 mm. of mercury for another 0.75 hour. Remove the plasticizer and place it in a desiccator until the electrical measurements are made. It is important to control the vacuum oven treatment carefully, since too little evaporation will not remove all the solvent, while too much will result in loss of plasticizer and possible fractionation.

Electrical Measurements. The cell in which the liquid was put for electrical measurements is shown in Figures 1 and 2. It is of a new design that requires very little sample (0.3 ml.) and can be cleaned and refilled quickly. Its principal components (see Figure 2) are:

1. Connector to ground terminal of Twin-T circuit
2. Connector to high terminal of Twin-T circuit
3. Ground connecting bar (brass)
5. Base of cell (brass)
6. Cell housing (phenolic plastic)
10. Support for high terminal (polystyrene)
12. Bushing (brass)
15. Collar for bushing (brass)
17. Contact spring (phosphor bronze)
20. Silver-plated phenolic tube, 1.88 cm. (0.75-inch) diameter
21. Brass plug threaded into 20
22. Invar plug threaded into 20 and cemented into 37. Also high electrode. Inorganic cement Insa-lute used.
25. Grounded electrode (gold-plated brass)
27. Cavity holding liquid under test
28. Connecting groove to allow for expansion of test liquid
32. Retainer ring for 37
36. Pressure spring to hold 37 (phosphor bronze)
37. Quartz disk insulator for 22
40. Silver-plated phenolic tube, 10 cm. (4 inches) in diameter
41. Brass ring attached to 40
45. Polystyrene baffles
46. Polystyrene tube, 2.5 cm. (1-inch) diameter
49. Inner wall of dry ice bucket
50. Cell wall (4-inch diameter brass tube)
51. Cover (phenolic)
52 and 56. Thermometer well
55. Thermometer

This particular design of the cell was demanded by a number of conditions. One condition was that the leads between the bridge (Twin-T circuit) and the cell be good electrical conductors (low inductance) at 10 Mc. but poor heat conductors. This was accomplished by using silver-plated phenolic tubes as the leads (20 and 40, Figure 2). The bridge terminals were thereby enabled to remain near room temperature while the cell at the other

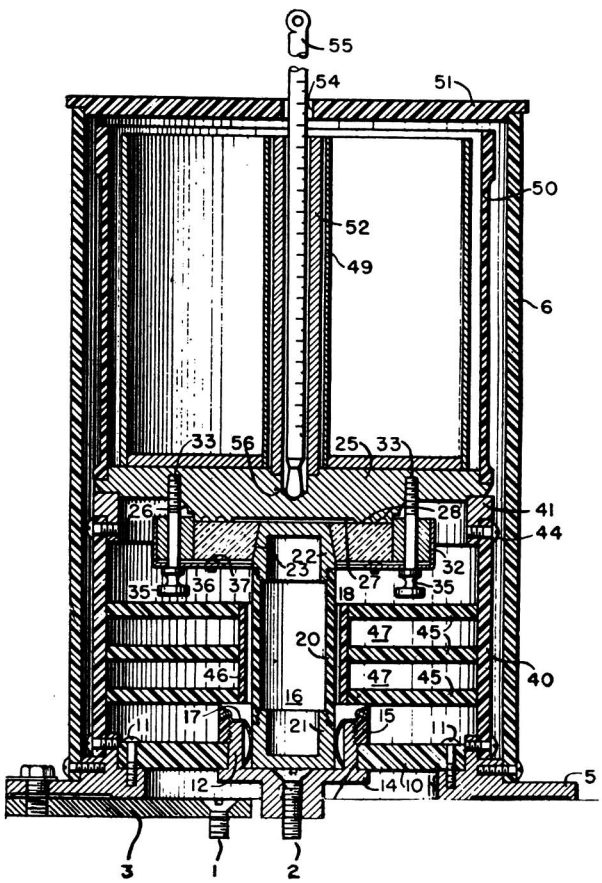

Figure 2. Dielectric Test Cell, Assembled

A dielectric cell of this design is now being manufactured commercially. Information can be obtained from A. B. Wigley, 2431 18th St., N. W., Washington, D. C.

end of the leads was held at −50° C. The following procedure was used to silver-plate the outer surface of the phenolic tube leads:

Two and one-half grams of silver oxide were added to 300 ml. of distilled water and then 10 ml. of concentrated ammonium hydroxide were added with stirring. The phenolic material to be coated was cleaned (slightly roughened) with fine sandpaper, placed in the silvering solution, and boiled 0.5 hour. Small amounts of free aldehyde in the phenolic resin reduce the silver and cause a thin layer of the metal to be deposited on the surface of the tube. Goggles should be worn during the silvering operation and the solution either discarded or the silver precipitated with sodium chloride immediately thereafter, since there is the possibility of silver fulminate formation. The thin silver coating on the tube is next built up to a thickness of about 0.001 inch by silver-plating from a cyanide bath, using low current density. It is desirable at the beginning of this plating operation to wrap the silver-coated tube with a very loose spiral of fine copper wire, so the resistance of the thin silver film will not interfere with the initial plating. This wire must be removed as soon as the plating has been well started.

The circular grooves and connecting paths around the central cup in the brass (grounded) electrode of the test cell are to furnish a channel and space for liquid in the cell to expand or contract during the large temperature changes to which the unit is subjected.

The electrical equipment used in these measurements consisted of a signal generator, a Twin-T impedance measuring circuit, and a well-shielded high-frequency receiver. All measurements were made at a frequency of 10 megacycles in a shielded room.

Two different methods were tried for detecting the null point at the balance of the bridge. One involved beating the signal from the self-contained oscillator in the receiver against the incoming unmodulated signal from the bridge to give an audio note. This method is very sensitive and accurate but somewhat slow and fatiguing if many measurements are to be made. The other method involved the use of a variable audio frequency oscillator and ordinary oscillograph in the manner shown on Figure 3.

In this second method the 10-Mc. current from the signal generator was modulated with an audio frequency (between 700 and 800 cycles) while the receiver was set for normal operation with the beat (CW) oscillator off. Connection was made between the phone jacks of the receiver and the vertical plates of the oscillograph. The horizontal plates of the oscillograph were connected directly to the same audio oscillator that was used to modulate the 10-Mc. signal. Since only audio frequencies enter the oscillograph, there is no difficulty in getting sufficient amplification.

After the variable audio oscillator has been adjusted to the proper frequency and the bridge balanced there appears a crescent-shaped pattern on the oscillograph screen. Any variation in the capacitance balance of the bridge will cause the crescent to become fatter, while any variation in the conductance balance will cause the crescent to tip one way or the other, depending on which way the conductance is off. This ability to distinguish between capacitance and conductance unbalance independently is practically a necessity when measuring the momentary electrical properties of a substance that is changing temperature steadily.

Operation of Test Cell. The plasticizer is extracted from the resin in the manner described above and placed in the cell at room temperature.

The quartz-insulated test electrode is removed from the grounded electrode and, with the grounded electrode face up, 0.2 to 0.3 ml. of plasticizer poured into the test cavity (27, Figure 1). The test electrode, 22, is then slid on in such a manner as to

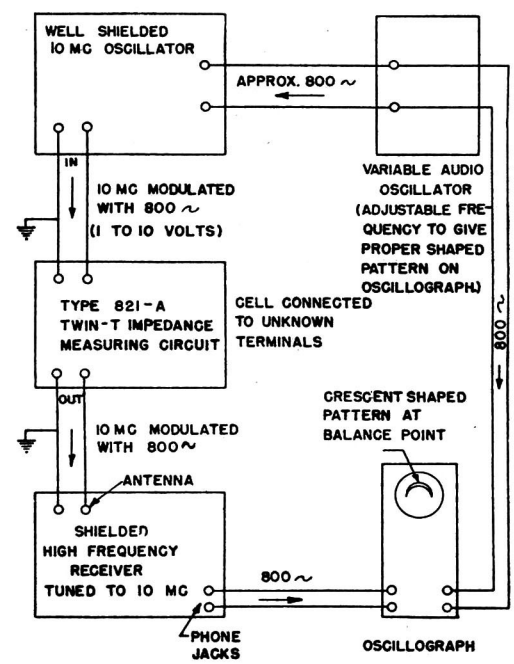

Figure 3. Block Diagram of Measuring Circuit

eliminate air bubbles in the test cavity (observation of bubbles at edge of test electrode may be made through clear fused quartz insulator, 37). The retainer ring, 32, is then screwed down around the test electrode and the whole electrode assembly turned over and inserted into the cell housing mounted on the Twin-T circuit. The capacitance of the cell is measured and the temperature noted. The test electrode on the cell is then removed, a drop or two more plasticizer added, and the electrode replaced. The capacitance is then again measured at the same temperature as before and the values are compared. If they check to within 0.1 micromicrofarad the cell may be considered completely filled.

The cell is next cooled with dry ice to a temperature of 10° C. or more below the peak in the loss factor curve and a measurement made. The approximate position of the peak may be located as the cell is being cooled. Heat is then applied, if necessary, by means of a small electrical heater, so as to warm the cell at a rate of about 2° per minute. Measurements of the capacitance and conductance of the sample are made at frequent intervals during the continuous temperature rise. Because the layer of liquid in the cell is less than 0.02 inch thick, the temperature of the sample lags very little behind that of the surrounding metal electrodes. The cell is so designed that water does not condense in areas where it would introduce errors into the electrical measurements. The temperature of the cell is measured by a thermometer placed in a well in the grounded electrode.

In an actual routine test where an unknown plasticizer is being tested to prove its identity with one previously measured, it is not necessary to measure the electrical properties over the entire temperature range (100° C.) but only to cover a range of about 10° around the peak in the loss factor curve.

The cell is designed to be emptied, cleaned, and refilled in less than a minute (comparable to the Abbe refractometer). After the cell is cooled to its starting temperature, the actual time for the electrical measurement for the 10° temperature range is about 5 minutes. It is estimated that one technician using one cell could obtain the data for 10° range curve on 10 to 15 samples in 8 hours. This does not include extraction of plasticizer.

CALCULATIONS

The dielectric constant of a material is most conveniently measured by taking the ratio of the capacitance of a cell (or condenser) filled with the unknown, to that of the cell filled with air. To do this the stray capacitance of the cell must be known. This is found by calibration with a substance of known dielectric constant, usually pure benzene. The calculations and calibrations for a cell of the type described here are as follows:

Let D_b = dielectric constant of benzene
C_b = capacitance of cell with benzene in
C_a = capacitance of cell with air in
C_s = stray capacitance of cell

Then $$D_b = \frac{C_b - C_s}{C_a - C_s}$$

D_b at 25° C. = 2.272 (*8*)

From direct measurement, C_b for the cell = 17.40 mmf.
From direct measurement, C_a for the cell = 10.54 mmf.

Then $$2.272 = \frac{17.40 - C_s}{10.54 - C_s}$$

and C_s = 5.19 mmf.
Let D_x = dielectric constant of plasticizer (unknown)
C_x = capacitance of cell with plasticizer in

Then $$D_x = \frac{C_x - C_s}{C_a - C_s}$$

$$D_x = \frac{C_x - 5.19}{10.54 - 5.19}$$

For dioctyl phthalate at −2° C., C_x was found to be 28.2 mmf.

Then $$D_x = \frac{28.2 - 5.19}{10.54 - 5.19} = \frac{23.0}{5.35} = 4.30$$

The loss factor is equal to the product of the dielectric constant and the tangent of the loss angle. The tangent of the loss angle is equal to

$$\frac{G_x}{\omega (C_x - C_s)}$$

where G_x = conductance of sample in mhos
$(C_x - C_s)$ = parallel capacitance of sample in farads
$\omega = 2\pi$ times the frequency (6.28×10^7)

$$\text{Loss factor} = \frac{G_x}{\omega(C_x - C_s)} \times \frac{(C_x - C_s)}{(C_a - C_s)}$$

$$= \frac{G_x}{\omega(C_a - C_s)}.$$

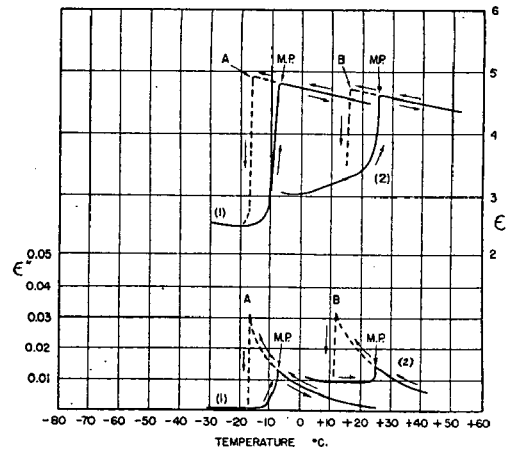

Figure 4. Electrical Properties of Commercial Plasticizers at 10 Mc.

1. Dibutyl sebacate. 2. Dibenzyl sebacate

For the cell use in these experiments

$$\omega (C_a - C_s) = 6.28 \times 10^7 (10.54 - 5.19) \times 10^{-12}$$
$$= 3.36 \times 10^{-4}$$
$$\frac{1}{\omega(C_a - C_s)} = 2980$$

Since the Twin-T bridge reads directly in micromhos, the factor by which the conductance, as read on the bridge, must be multiplied is 2980×10^{-6} or 0.00298 to give the loss factor. This is the conversion constant for the particular cell used here. This constant for any new cell must be determined by calibration with benzene in the manner just described. The conductance of dioctyl phthalate at −2° C. was found to be 381 micromhos in the calibrated cell. The loss factor is then 381×0.00298 or 1.135.

RESULTS AND DISCUSSION OF ELECTRICAL METHODS

On Figures 4 to 6 are curves for loss factor and dielectric constant versus temperature for the nine different plasticizers considered in this work. In order to illustrate the number and location of the experimental points used in drawing the curves, the points are included for one typical curve on each figure.

Figure 4 gives data on two plasticizers that freeze at temperatures considerably higher than the temperatures at which their peaks normally occur. Complete electrical data cannot be obtained on materials that freeze before their peaks are reached unless frequencies considerably higher than 10 Mc. are used for the measurements. For these particular materials it is noted that the liquids supercooled (see Figure 4) until points *A* and *B*, respectively, were reached, then the materials suddenly froze. On warming, the materials were completely melted again at the points marked *M.P.*

Table I. Electrical Properties of Various Plasticizers at 10 Mc.

Plasticizer	Temp. of Loss Factor Peak, ° C.	Height of Loss Factor Peak	Loss Factor at 25° C.	Temp. of Maximum Dielectric Constant, ° C.	Dielectric Constant At maximum	Dielectric Constant At 25° C.	n_D^{25}	Figure No.
Dibutyl sebacate	....	..	0.003	..	..	4.46	1.4399	4
Dibenzyl sebacate	....	..	0.013	..	..	4.61	1.519	4
Dibutyl phthalate	−31.5	1.89	0.05	−13	7.00	6.1	1.4907	5
Dioctyl phthalate	−3.0	1.23	0.34	18	5.15	5.1	1.4848	5
Tricresyl phosphate (commercial)	+9.0	1.57	0.78	27	6.75	6.7	1.5548	5
Methyl acetyl ricinoleate	−28.5	0.53	0.07	−6	4.4	4.1	1.4560	6
Acetylated castor oil	−2.0	0.52	0.24	26	4.0	4.0	1.4684	6
Celluflex (higher aryl phosphates)	+24.5	1.22	1.22	48	5.5	4.5	1.5479	6
Methyl pentachloro ester of corn oil	+36.0	0.94	0.87	71	5.9	4.6	1.5010	6

shows only a single peak, intermediate between the peaks shown by the separate liquids. A summation of the temperature and height of peaks along with the refractive indexes and dielectric constants of all the plasticizers studied is included in Table I.

These plasticizers, whose curves are given, were all of commercial grade, as received from the manufacturer. Dioctyl phthalate samples were obtained from three different large companies. The loss factor curves for these materials were surprisingly close together. The temperature of the loss factor peaks for all of them fell between −2.5° and −3.5° C. with average heights ranging from 1.18 to 1.23. Tricresyl phosphate samples were obtained from two different sources. One sample was water-white, while the other had a brownish-yellow hue. The former had its loss factor peak at 9° C. and 1.57 in height, while the latter had its peak at 9.5° C. and 1.54 in height. Here again the differences are small. The other plasticizer samples were obtained from one source each, respectively.

It is seen on Figures 4, 5, and 6 that the power factor–temperature curves for the various plasticizers differ greatly. Any contamination by appreciable amounts of foreign materials would make a noticeable change in these curves. The only exception to this is the addition of a substance or mixture in which the average time of relaxation of the molecules and their polar properties are the same or very nearly the same as those of the original plasticizer. The chances of this happening in a limited group of

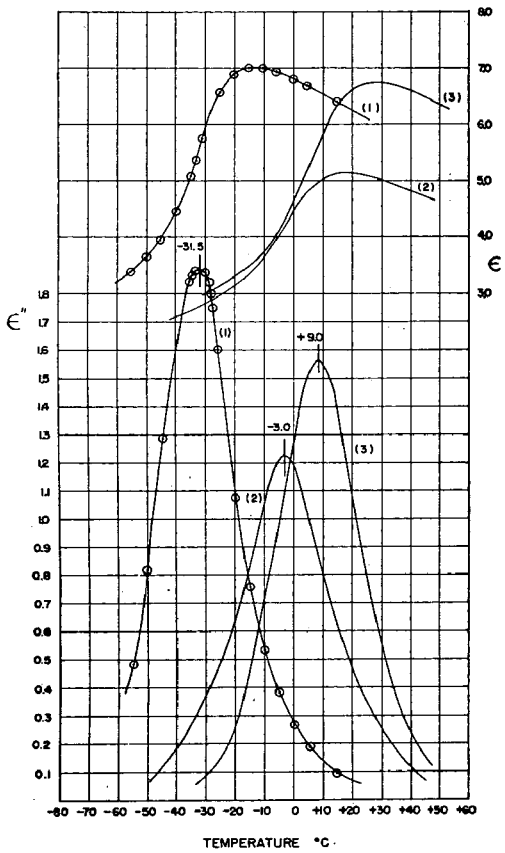

Figure 5. Electrical Properties of Commercial Plasticizers at 10 Mc.

1. Dibutyl phthalate. 2. Dioctyl phthalate. 3. Tricresyl phosphate

It can be seen from dielectric constant curve 2 (commercial dibenzyl sebacate) that the material was not very pure, since it melted over a rather wide range in temperature. The relatively sharp rise in dielectric constant curve 1 (dibutyl sebacate) at −9° to −12° indicates that this material has a sharper melting point than the dibenzyl sebacate and is probably of much higher purity.

The above reasoning cannot be applied to Figures 5 and 6, because the plasticizers shown there did not freeze, but remained liquid at all times. The dielectric constant and power factor curves for these materials are, therefore, the normal curves as shown by all polar liquids when dielectric measurements are made in the anomalous dispersion regions. It is seen that these curves differ greatly for the various plasticizers. This makes it easy to distinguish one from another. It was found that when two plasticizers with different peaks are mixed, the resulting liquid

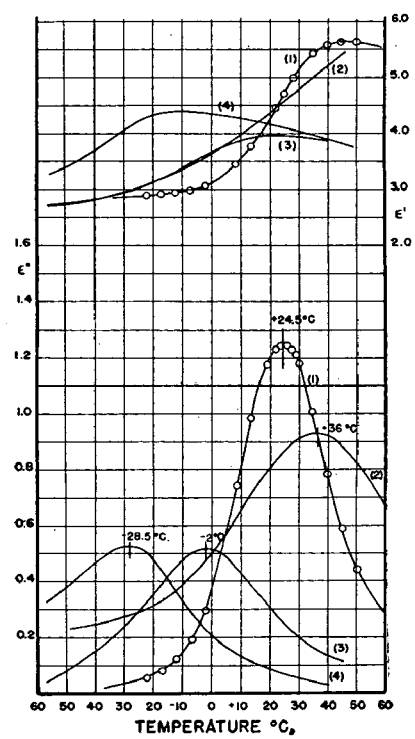

Figure 6. Electrical Properties of Commercial Plasticizers at 10 Mc.

1. Celluflex. 2. Methyl pentachloro ester of corn oil. 3. Acetylated castor oil. 4. Methyl acetyl ricinoleate

materials are not great, but, if these properties were the same, then this new material may be expected to be a plasticizer itself and behave with polyvinyl chloride in a manner similar to the original plasticizer. The chances of a radically different chemical substance being present are made negligible by also requiring identity of refractive index between the unknown and original plasticizer. Three independent quantities are thereby required to be simultaneously equal between the unknown and the original or standard.

The data given in Table II illustrate the reproducibility of curves taken on two plasticizers, before and after they were formulated with a resin. Three different formulations are represented. The data in the column headed "original", were taken on the untreated plasticizers as received from the manufacturer. The data in the "extracted" column were taken on plasticizers extracted from finished polyvinyl chloride insulation (also supplied by the manufacturer), in which the above original plasticizers were respectively incorporated. Each value in the extracted column represents a separate extraction. The only noticeable difference in the loss factor peaks in the two columns is that the peaks occur at a slightly higher temperature for the extracted plasticizer. This is probably due to a small amount of volatile matter in the original plasticizer that was removed by vacuum treatment during the extraction.

ACCURACY AND PRECISION OF ELECTRICAL METHODS

In preparing a plasticizer for an identity test, care must be exercised in separating it from the resin with which it was originally compounded, in order to make sure the plasticizer is free of solvent and other extraneous materials. Serious errors can result if the vacuum-oven evaporation is carelessly made and appreciable amounts of solvent remain.

The curves of loss factor and dielectric constant versus temperature are reproducible to within ±2% in height and ±0.5° C. in temperature. This precision is sufficient for the purpose at hand, since the electric properties of the plasticizers are well spread.

The chief difficulties that may be encountered in obtaining reproducible loss factor temperature curves for plasticizers are:

1. Air bubbles in dielectric cell
2. Variable fractionation of plasticizer during extraction of mixture present
3. Plasticizer contaminated with solvent or resin
4. Change of state (freezing, melting, etc.) of plasticizer

If due care is exercised in the operation of the test and the procedure given under "Experimental" followed, these difficulties cause no serious trouble.

CHEMICAL PROCEDURES

Separation of Plastic into Component Parts. A 5- to 10-gram sample of the plastic material is dissolved in 100 to 200 ml. of hot diisopropyl ketone and filtered through diatomaceous earth (Celite) to remove any insoluble material (fillers, stabilizers, etc.), and the resin is precipitated by the slow addition with vigorous stirring to 400 to 800 ml. of ethyl alcohol (95%). The precipitate is removed by filtration, washed with alcohol, and then redissolved in hot diisopropyl ketone. It is again precipitated with alcohol, dried on a suction filter, and finally dried in a vacuum oven for 3 hours at 65° C. and 3- to 5-mm. pressure. The filtrate from the first precipitation is evaporated to dryness, and the plasticizer is redissolved in methanol and then filtered to remove any residual resin. This filtrate is again evaporated to dryness on a steam bath and finally dried for 3 hours at 110° C. and 3- to 5-mm. pressure in a vacuum oven.

Identification of Resin. The dried precipitated resin is analyzed for chlorine, using any convenient method, and the type of resin identified from the chlorine content. A convenient and reliable method of analysis was found to be that of Elving and Ligett (*5*), whereby the sample is decomposed by heating with potassium in an evacuated sealed tube at 400° C. for 15 minutes. The chlorine may be precipitated and weighed as silver chloride or determined by titration using the Volhard method. The chlorine contents of the resins encountered in this work are as follows:

Polyvinyl chloride	56.7%
Vinylite V (vinyl chloride–vinyl acetate), 95:5	53.9%

Chemical Tests on Plasticizer. Analysis of the plasticizer was simplified to a great extent, since only a limited number of materials were considered to be important plasticizers for these vinyl chloride resins. Thus, only sufficient information was required for differentiation between the various plasticizers actually used. The analytical procedure involved the determination of the plasticizer type (phosphate, phthalate, etc.), the measurement of the index of refraction, the examination of the products of saponification, and a quantitative phosphorus (*7*) or chlorine analysis where indicated. These relatively simple chemical tests were used to obtain general information about the probable composition of unidentified plasticizers.

Table II. Comparison of Average Loss Factor Peak Values of Original and of Extracted Plasticizers

Plasticizer		Original Temp., ° C.	Original Height	Extracted Temp., ° C.	Extracted Height
Tricresyl phosphate		9.5	1.56	10.0	1.57
		9.5	1.59	10.0	1.59
		9.5	1.55	10.0	1.51
		9.5	1.57	10.0	1.58
		9.0	1.60	10.0	1.56
	Av.	9.4	1.57	10.0	1.56
Dioctyl phthalate		−4.0	1.23	−3.0	1.21
		−3.0	1.17	−2.0	1.21
		−3.0	1.20	−2.5	1.20
		−3.0	1.21	−2.5	1.14
		−3.0	1.17		
	Av.	−3.2	1.20	−2.5	1.19

SUMMARY

Plasticizers of the polar type give characteristic and reproducible curves of loss factor and dielectric constant versus temperature at high radio frequencies. Such curves can be obtained over a temperature range of 100° C. in less than one hour, using apparatus requiring not more than 0.3 ml. of plasticizer. In an actual routine identity test the determination of the electrical properties over a range of about 10° C. around the loss factor peak is all that is required. The time necessary to make the measurement is cut correspondingly.

Chemical tests for confirmation purposes are recommended where specific reactions are available. Numerous graphs and tables of data show the variation between different plasticizers.

ACKNOWLEDGMENT

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Recording Viscometer for Starches

C. C. KESLER, *Penick & Ford, Ltd., Inc., Cedar Rapids, Iowa,* AND
W. G. BECHTEL, *Corn Industries Research Foundation, New York, N. Y.*

A continuous recording viscometer for routine and research testing of starch products is described. Variations in cooking procedures which cause errors in viscosity determinations are prevented through automatic control of rate of heating, maximum temperature, rate of stirring, and loss of water by evaporation. Viscosity is measured as the force which the paste exerts against a propeller driven through it at constant speed. A gear differential transmits the force to a dynamometer attached to the pen arm of the recorder. Interchangeable weights on the dynamometer permit measurements in several viscosity ranges with equal sensitivity and without requiring recalibration of the viscometer. Viscosities of one poise or more can be measured throughout any desired length of time, and during both heating and cooling periods. Variations between samples and differences between commercial types of starch may be readily observed. Starches from different sources and of different kinds and degrees of modification give characteristically different curves which are of value in their identification and study.

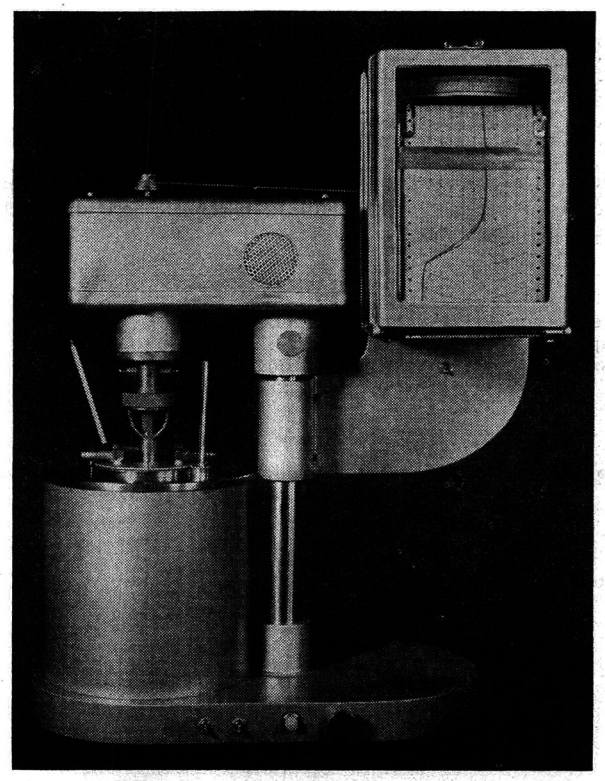
THE most important specification for determining the suitability of starches for various industrial uses is the apparent viscosity of the paste formed when a starch is cooked with water at a definite concentration. Such pastes are mixtures of swollen granules and fragments formed by disintegration of granules, dispersed in a solution of molecules leached from the granules (*11*). They appear to exhibit true viscosity only when the starch concentration is low, below 2% for cornstarch (*4*). In higher concentrations anomalous viscosity is shown and the observed viscosity is a function of the rate of shear (*7*). Various names have been applied to this quantity, such as "viscosity", consistency, and apparent viscosity. However, throughout the starch industry it is called simply viscosity and this usage is followed here.

Starches are used industrially in the concentration range in which they exhibit anomalous viscosity. Therefore, in order to use the viscosity determination to predict their industrial performance adequately, tests must be made on pastes in this same general concentration range and the results will depend on the rate of shear employed. Since the rate of shear depends on the type of construction and dimensions of the viscometer used, only identical instruments will give the same viscosity for any paste (*13*).

Not only must identical instruments be used for all comparative viscosity tests, but the method by which the paste is prepared must be accurately duplicated. When starches are heated with water it is observed that above a definite temperature the granules swell to a large size and the paste viscosity increases to a maximum, after which it generally decreases continuously on further cooking. These changes occur at rates which depend on the variety of starch, its method of manufacture, and the technique used in the preparation of the paste. Any variation in the preparation of the paste will produce a change in observed viscosity. Of especial importance are the rate of heating the paste, the maximum temperature to which it is heated, the stirring rate (*10*), the dimensions of the stirrer, and the stirring motion used. Since starch pastes must be cooked to temperatures near 100° C., loss of water by evaporation will alter the result, as will differences in hydrogen-ion activity (*14*) and the presence of many organic and inorganic substances, including the ions present in hard water (*14*).

The starch-producing and -consuming industries use a number of different kinds of viscometers, and techniques of preparing the pastes vary widely. Even where the same method is used, the maximum paste temperature, stirring rate and motion, the time of cooking, and the time that elapses between transferring the paste to the viscometer and the start of the viscosity test are usually controlled by the operator and are subject to variations from test to test and among different operators. The result has been a lack of agreement in tests performed in different laboratories, which has caused considerable confusion in some of the industries affected (*9*).

A further disadvantage of present methods for the industrial testing of starch is that only a single determination of paste viscosity is usually made. Because the changes in viscosity on cooking occur at varying rates for different starches, a single viscosity determination, even when made by a carefully standardized procedure, is inadequate to characterize a starch completely. This has been shown by Caesar (*6*) and others, and has led to the development of several instruments which either produce a continuous graph of viscosity changes or permit a series of determinations to be made on the same paste. Among such instruments are the consistometer of Caesar (*6*) and the recording viscometer of Bauer (*8*), both of which are designed for very concentrated



Corn Industries Viscometer

[1] Present address, C.I.R.F. Research Fellow, Penick and Ford, Ltd., Inc., Cedar Rapids, Iowa.

pastes, the viscometer of Barham, Wagoner, and Reed (*3*), and the Brabender amylograph (*2*). These have been used for research on starches but none has been extensively used in the starch industry for general testing of products.

OBJECTIVES

The Corn Industries viscometer has been developed with the following main objectives:

To provide a viscometer suitable for the industrial testing of starch products in all laboratories of the corn wet-milling industry.

To include a standardized procedure for preparing pastes, so that all factors such as paste temperature, rate of heating, stirring rate, and evaporation of water will be controlled automatically. This will make the results of tests independent of the skill or technique of the operator.

To obtain automatically a continuous record of all changes in paste viscosity during the period of the test.

To achieve such a degree of sensitivity and precision that the instrument can be used for the control and standardization of starch products and for research.

To measure an extended range of viscosities and yet be sensitive in the lower range of values.

To enable a hot paste test to be made in from 10 to 20 minutes, so that the instrument will be practical in the control laboratory where speed of testing is essential.

To make the instrument rugged, so that it will not be easily damaged.

To make the instrument simple to operate.

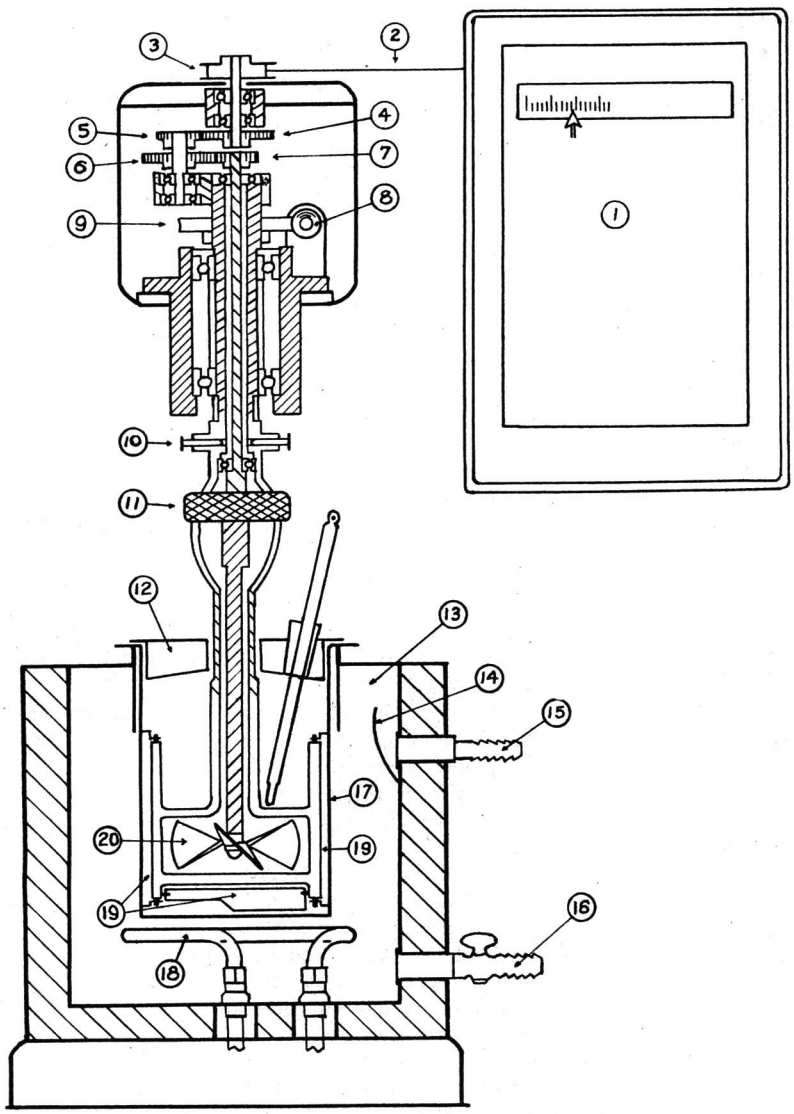


Figure 1. Sectional Drawing of Corn Industries Viscometer

1. Recorder and dynamometer (dynamometer not shown)
2. Cable from viscometer to recorder
3. Cable drum
4, 5, 6, 7. Gears of sun and planet differential
8. Worm, turned by synchronous motor (not shown)
9. Worm gear
10. Spring pins for holding center shaft
11. Coupling to attach stirrer
12. Condenser cover
13. Water bath
14. Baffle to maintain water level
15. Overflow
16. Drain cock
17. Starch beaker
18. Electric heater, 1000 watts, thermostatically controlled
19. Scraper blades
20. Propeller

DESCRIPTION OF VISCOMETER

The construction of the viscometer is shown schematically in Figure 1.

The stirring device consists of two parts. A synchronous electric motor (not shown) drives the outer part or scraper, 19, in a clockwise direction at 24 r.p.m. through worm 8 and worm gear 9. The shaft of the scraper is hollow, and concentric with it is the shaft for propeller 20. The propeller is driven in a counterclockwise direction at 60 r.p.m. by means of the synchronous motor, but the power is transmitted to it through a sun and planet differential which consists of spur gears 4, 5, 6, and 7. The torque to which the propeller is subjected as it turns in a viscous medium such as a starch paste is likewise transmitted through the differential to drum 3, which is attached by cable 2 to a dynamometer (not shown) built into recorder 1.

A standard strip-type recorder chart drive is used, and the pen arm is actuated by the torque on the propeller. This torque is balanced by a dynamometer which consists of a weight arm that moves through an arc. By means of easily interchangeable weights the full scale of the chart reads to 250, 500, 1000, or 2000 gram-cm. The weights may be interchanged even during a test, and without altering the standardization of the dynamometer. This is an advantage over the use of torsion wires, where considerable time is required to change a wire, and where a change of wires requires a recalibration of the instrument. The arrangement used permits the viscometer to cover the wide range of viscosities encountered in various starches, and at the same time makes it sensitive in the range of viscosities of relatively low starch concentration or high degree of modification. By means of a counterpoise in the dynamometer the internal friction of the mechanical parts is balanced. The weight of the counterpoise is adjusted so that the chart reading for water is zero.

In operation, as the shaft which drives scraper 19 is set in motion, the arm upon which planetary gears 5 and 6 are mounted revolves about this shaft. Since gear 4 does not freely rotate because it is connected to the dynamometer, it causes gears 5 and 6 to rotate on their axis as they revolve about the scraper shaft. The rotation of gear 6 drives the propeller counterclockwise through gear 7.

It is possible to uncouple the stirring device at 11, and the head can then be swung to one side to permit the stirrer and starch beaker 17 to be removed. Since the inner shaft to propeller 20 rotates freely, two spring pins at 10 provide a means for holding it during the coupling operation.

When starch is pasted in water in the concentrations used for industrial testing, the paste becomes very thick and convection currents disappear. The paste adheres to the side and bottom of the cooking vessel, and heat transfer through the body of material is very slow. This may be the case, even though the paste

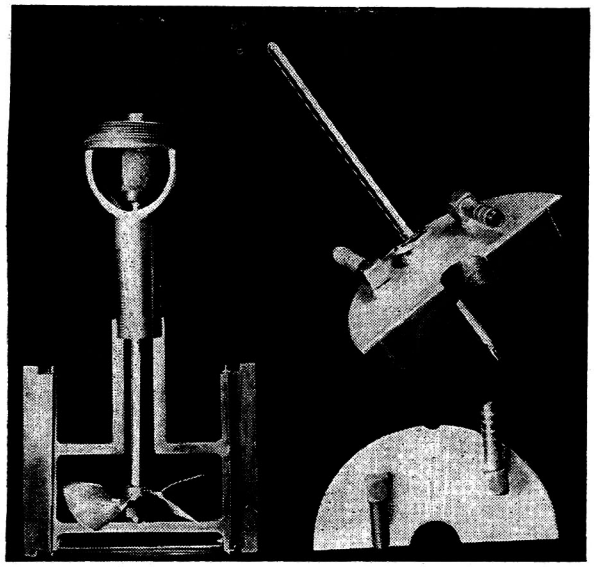


Figure 2. Condenser Cover and Stirring Device

is stirred, for with most stirring methods the layer of paste at the wall is not effectively removed, and this layer has an important insulating effect. It is apparent, since the observed viscosity of a paste depends on the temperature to which it has been cooked, that it is essential to cook all parts of the paste to the same temperature and for the same length of time. This is an important source of error in some of the currently used testing methods for starch, where temperature differentials of 2.5° to 6° C. can be shown to exist between the paste near the wall and at the center. The unique stirring device employed in the Corn Industries viscometer was designed to minimize this temperature differential.

The scraper blades at the side are hinged in such a manner that, as the stirrer turns, the pressure against the blades causes them to swing outward. Similarly the lower blade rests lightly on the bottom of the beaker. This prevents the formation of a thick adhering layer at the wall of the beaker. The construction is shown to advantage in Figure 2. The function of the propeller is to keep the center of the paste agitated, as well as to provide a means of measuring the torque.

The effectiveness of this method of stirring is shown by the fact that temperature differentials between various parts of the paste have not been observed to exceed 0.5° C., and the observed difference when the paste has reached the maximum temperature has been negligible. Another advantage of this stirrer over other types of mechanical stirrers that have been used for cooking and testing starches is that the pastes produced are entirely free from partially gelled lumps, without the necessity of any auxiliary stirring during the gelatinization process.

Heat is supplied to the well-insulated water bath by 1000-watt electric immersion heater. The bath temperature is controlled by an adjustable thermostat with a range of 10° to 150° C. and a temperature differential of ±0.2° C. There is a thermometer in the paste and one in the water bath.

Control of Evaporation. The starch cooking beaker has a capacity of 1 liter. It is of stainless steel, as is the stirrer. The beaker is closed by means of a condenser cover of two sections, shown in Figure 2. The necessity for using a condenser to minimize the evaporation of water is shown by a study of water loss in the Scott procedure (12) for cooking starches for the viscometric test. In this procedure the starch is cooked in a metal beaker which is covered by a watch glass when it is not being stirred. Five closely agreeing tests showed an average water loss of about 5%. Anker and Geddes (2) made a study of the evaporation loss when pastes were tested in a commercial recording viscometer and report losses of 5.0 to 5.5%.

Moisture losses observed in the Corn Industries viscometer when the condenser cover was used as an air condenser were negligible. The losses of water from the beaker which contained 1000 grams of paste were as follows: paste maintained at 94° C. for 25 minutes, loss of water 0.14%; paste maintained at 94° C. for 55 minutes, loss of water 0.21%. The condenser cover is fitted with connections for the circulation of cold water if that is desired.

Technique of Operation. Any viscosity method acceptable as an industrial testing procedure must be rapid. A disadvantage of previously described techniques for the use of continuous-reading viscometers is the long period required to bring the paste temperature to the maximum. Rates of temperature increase from 0.5° to 1.5° C. per minute are common, with the result that a viscosity determination requires from 1 to 2 or more hours. To accomplish rapid testing the water bath of the Corn Industries viscometer is heated to the desired maximum temperature before starting the test. The temperature of the bath may differ for various tests, depending on their purpose, but must be sufficiently high to gelatinize the starch. A temperature between 92° and 96° C. has been found satisfactory. By this procedure the paste reaches its maximum temperature in approximately 15 minutes, and sufficient information for routine testing is obtained within 20 minutes.

To make a determination the metal beaker is placed in the water bath, and the stirring device is attached and started. The starch required for 1000 grams of paste is stirred to a slurry free from lumps in the entire quantity of water needed. The water should be at room temperature. The slurry is poured rapidly into the viscometer and at the same time the recorder is started. The condenser cover is then put in place and the remainder of the test is accomplished automatically.

RELIABILITY OF RESULTS

Precision. An analysis has been made of the degree of precision attained in the maximum value of viscosity shown by replicate determinations. The line width of the graph is approximately 1 mm., and this remains constant with all starches. Readings are made at the center of the line. Two studies were made. In the first, all determinations were made by the same operator. Results of 75 determinations in duplicate show that the precision to be expected is within ±1%.

In the second study a single starch was tested in a number of laboratories by different operators, in order to check the performance of the viscometer over an extended time, and to ascertain whether an inexperienced operator could obtain satisfactory results. Under these conditions the degree of precision shown is approximately ±2%.

Sensitivity. In addition to knowing the precision of the viscometer, it is important to know its sensitivity to small changes in concentration of starch, in order to determine the accuracy required in weighing the starch and measuring water. Several determinations were made to study the sensitivity using a concentration of 5% of unmodified cornstarch, calculated on the basis of dry starch, as the control.

Commercial starches contain variable amounts of moisture. It is frequently desirable to compare them on the basis of the dry starch present, so that the effect of differences in moisture will be eliminated. A change of 0.5 gram in 50 grams of dry starch changed the chart reading 3.5 units; a change of 10 grams of water in 950 grams caused an equal change in chart readings. Since the chart can be read accurately to less than 0.5 unit, this indicates that to avoid errors due to measurement of samples, starch should be weighed to within ±0.05 gram and water should be measured to within ±1 ml.

Effect of Change in Volume. The effect of a change in total paste volume was studied. It seemed unlikely that small changes in volume would affect the results, since the device used for obtaining the viscosity measurement, the propeller, is completely

submerged and is located about midway from top to bottom when 1000 grams of paste are used. The results show that the volume may be varied by as much as 100 ml. without affecting the readings.

CALIBRATION

The viscometer was calibrated in order to determine the viscosity in absolute units corresponding to any torque measured in gram-centimeters. For this purpose National Bureau of Standards oils L-9, M-11, and N-12 of standard viscosity were used. As these are all in the lower range of viscosities measured by the viscometer and no other oils of standard viscosity are available in the required range, they were used to calibrate an Ostwald-Cannon-Fenske viscometer. This was then used to determine the viscosities of a number of corn sirups which covered the entire range of the instrument. The results of the calibration are shown in Figure 3. From the data it appears that there is an approximately linear relationship between the measured torque and viscosity in poises.

Range of Viscosities. The present design of the agitator permits measurement of viscosities up to approximately 55 poises. In terms of starch concentration this covers the range from 3% unmodified tapioca or potato starch or 4% unmodified cornstarch to 6.5% tapioca or 9 or 10% cornstarch. This range can be extended through the substitution of a smaller propeller so that the torque will be less for a given viscosity. For the determination of viscosities of materials which do not require cooking, the outer part of the agitator can be removed entirely, and a disk can be used in place of the propeller.

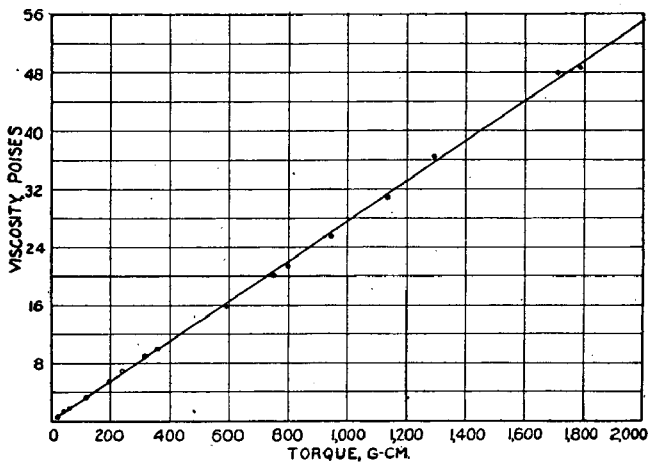


Figure 3. Viscosity in Poises *vs.* Measured Torque

Table I. Relationship of Corn Industries and Scott Viscosities for Batch Samples of Unmodified Cornstarch

Sample	Moisture, %	pH	C.I.[a], Maximum Chart Reading	Scott, Seconds	Scott/C.I.
		Laboratory A			
1	10.7	4.7	51.5	77	1.50
2	8.8	4.8	58.5	83	1.46
3	10.4	4.4	54	83	1.54
4	10.6	4.9	55	85	1.55
5	11.3	4.9	47.5	90	1.89
6	11.3	4.9	59	91	1.54
7	8.2	4.6	59	92	1.56
8	10.0	4.7	61	97	1.59
9	9.7	4.9	65	105	1.62
10[b]	5.2	4.4	96.5	116	1.20
				Av.	1.58
		Laboratory B			
1	6.60	4.7	65	107	1.65
2	9.25	4.7	58	90	1.55
3	10.45	4.8	59.5	95	1.60
4	10.40	4.6	59	94	1.59
5[c]	11.05	4.7	53.5	65	1.21
6	10.65	4.7	65	92	1.42
7	10.30	4.5	55.5	93	1.68
8	9.84	4.5	62.5	105	1.68
9	9.88	4.6	63	111	1.76
10	9.62	4.8	65	102	1.57
11	9.40	4.6	64.5	100	1.55
12	8.16	4.5	70.5	120	1.70
13	12.50	4.8	54	93	1.72
14	9.80	4.8	66	105	1.60
15	...	...	62	104	1.68
				Av.	1.63

[a] Corn Industries viscometer.
[b] Sample 10 has an abnormally low moisture. The Corn Industries chart showed a very rapid fall in viscosity following the maximum. This ratio omitted from average.
[c] Omitted from average.

APPLICATIONS

Data from Charts. The charts used have a scale from 0 to 100 marked at 2-unit intervals. Time is shown at each minute by an arc. Figure 4, a reproduction of a Corn Industries viscosity chart for an acid-modified cornstarch, illustrates the types of information which can be obtained in each test. While the curve shows viscosities at all times during the test, certain points have special significance, and these are marked on the chart for convenience in discussing them.

The recorder is started at *A* when the starch-water slurry is poured into the viscometer. At point *B* the granules have swollen sufficiently to cause a noticeable increase in viscosity, and at *C* the maximum viscosity is reached. This determination was stopped at *D*, representing a total cooking time of 20 minutes.

Investigations of the temperatures at which various starches gelatinize are very numerous. They include determinations of the temperature at which birefringent crosses disappear from the granules and observations of changes in translucency of the paste and the change in viscosity. The problem has been discussed at length by Alsberg and Rask (*1*). Since these types of change do not occur simultaneously, the value found for gelatinization range depends on the method used.

The viscometric chart gives a convenient means of obtaining this quantity from viscosity. According to this method the gelatinization range is the temperature range from *B* to *C*. Gelatinization rate of starches can also be obtained from the chart, and is related to the slope of the curve between *B* and *C*. The first part of the viscosity

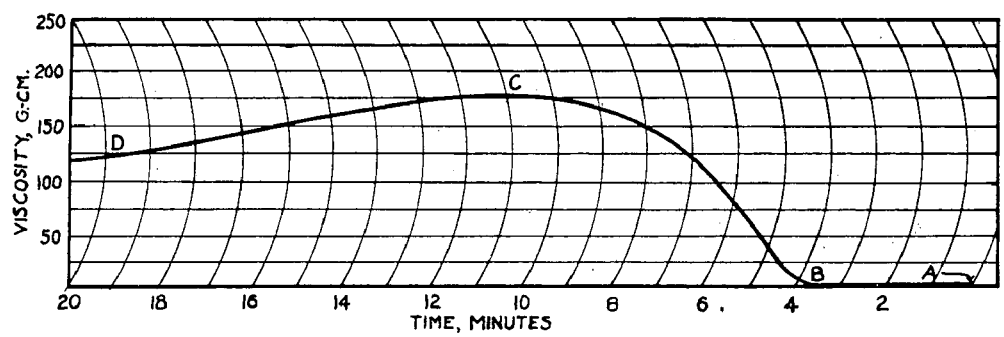


Figure 4. Corn Industries Viscometer Curve of Cornstarch

Alkali fluidity 20, concentration 7%

curve is the resultant between the forces tending to swell the granule and the forces such as granule disintegration and shrinking due to leaching of soluble material from the granules (*10*) which lower viscosity. When the viscosity curve is used for studies of gelatinization range, it must be recognized that it represents an average value of the paste as a whole. At the point of initial viscosity rise some granules have not gelatinized while others are swollen considerably. Similarly at the maximum of the curve most granules are swollen to their greatest size, but some are still swelling and others have begun to shrink and to disintegrate.

The decrease in viscosity or paste breakdown following the maximum is an important quantity which is obtained from the chart. The extent of breakdown is of great significance in comparing various starches and in determining their industrial applications. It is obvious that the factors which affect the viscosity of a paste affect its gelatinization and breakdown as well.

Differences in Batches. The value of the viscometer in the control testing of starches depends on its ability to evaluate differences which exist between production batches of the same product as well as to distinguish products of different types of manufacture. A number of batches of unmodified cornstarch were studied at two laboratories. The maximum of the Corn Industries viscosity curve was compared with the Scott viscosity (*12*), which was the standard test used in these laboratories.

In the Scott method the viscometric test is made on all starches after an equal period of cooking. When the maximum of the curve is selected for a reference point in the Corn Industries test, differences in rate of gelatinization of various samples cause the maximum to appear after different cooking times. There is therefore no reason to expect a direct correlation between the two methods and it is certain that there will not be such a correlation when different starches are tested. The significant point shown in Table I is that the Corn Industries viscometer does distinguish between various batch samples. Nevertheless the ratios of Scott viscosities (the time of flow of 50 ml. of paste through the orifice) to the maximum chart readings on the Corn Industries viscometer do show a rather close correlation for batches of a single kind of starch. The Scott tests were made by trained, experienced operators, while the operators who made the Corn Industries determinations were without previous experience with the instrument.

Degrees of Modification. Figure 5 was prepared from Corn Industries viscometer charts for convenience in comparing the curves. The starches used for illustration are unmodified and certain commercial grades of acid-modified cornstarch, all of which were used at the same concentration and heated to the same paste temperature, 90° C. Where results from starches which vary widely in viscosity are given in the same graph, the curves of lower viscosity do not appear to be widely separated. It should not be inferred from this that the separation on the original charts is poor. Viscosity measurements of pastes of low viscosity are made by use of smaller counterweights on the dynamometer, as described above. By this means the curves for these pastes cover as large a part of the original chart as do those of more viscous pastes where a heavier counterweight is used. It has been found possible to compare starches ranging from unmodified cornstarch to cornstarch of 60 alkali fluidity (*5*) at the same concentration. More highly modified starches require a higher concentration. This is true also when other viscometers are used. By means of the curves the various commercial grades of cornstarch can be readily distinguished and batch differences of modified starches can be detected. Starches differing by a very few units of alkali fluidity give widely differing curves.

Starches from Different Sources. As shown in Figure 6, starches from different sources produce curves which differ widely, not only in viscosity, but in gelatinization rate and range and in the extent of paste breakdown. All starches in Figure 6 were pasted at 5% concentration of dry starch to a temperature of 90° C. It is possible to use the Corn Industries viscosity curves to obtain information by means of which starches from different sources can be identified readily. Not only do such properties vary for starches from different sources, as shown in Figure 6, but similar significant differences are found when the various modified starches from the same source are examined.

For many purposes the analysis of cooking curves is sufficient, but for others a study of the characteristics of pastes during cool-

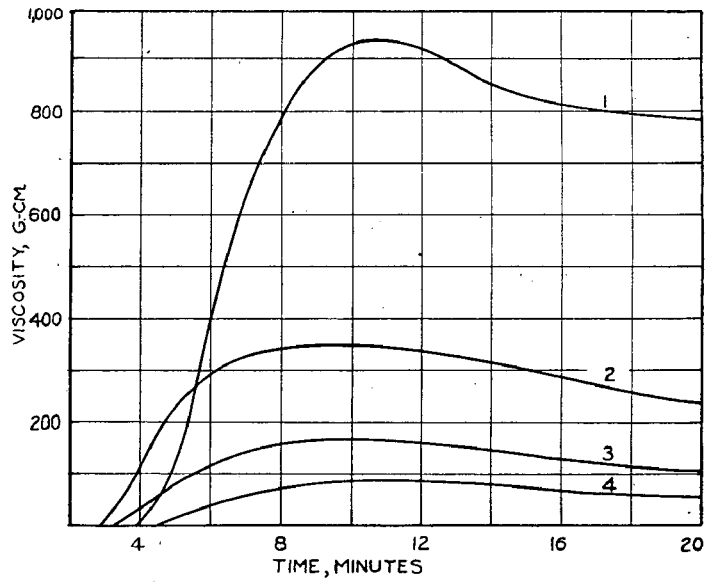


Figure 5. Viscosities of 8% Cornstarch Pastes

1. Unmodified
2. Alkali fluidity 20
3. Alkali fluidity 40
4. Alkali fluidity 60

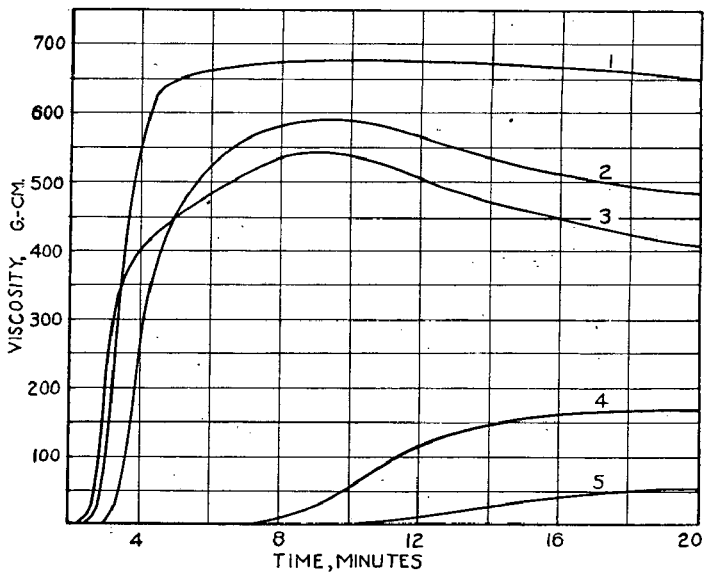


Figure 6. Viscosities of 5% Pastes of Different Varieties of Starch

1. Potato
2. Waxy maize
3. Tapioca (Sando)
4. Corn
5. Wheat

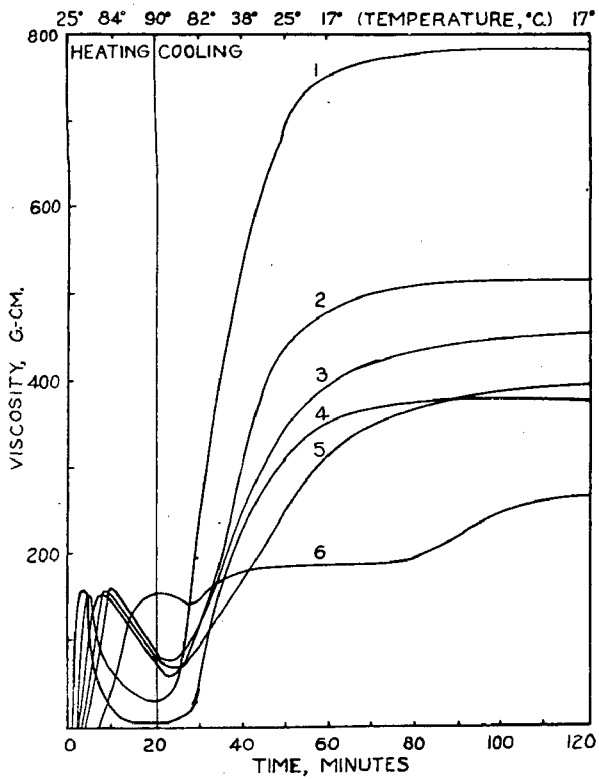


Figure 7. Viscosities of Cornstarches during Cooking and Cooling

1. Acid-modified, alkali fluidity 90, 23.8% concentration
2. Acid-modified alkali fluidity 60, 9.8% concentration
3. Acid-modified alkali fluidity 40, 8.5% concentration
4. Oxidized, 19.7% concentration
5. Acid-modified, alkali fluidity 20, 7.2% concentration
6. Unmodified, 5.0% concentration

ing is required. Figure 7 shows the results obtained when pastes of several modified cornstarches are cooled. In this graph the cooking portion of the curves has been subordinated to show the cooling effects to better advantage. For the purpose of this study the starches used were taken at such concentrations that their maximum viscosities on cooking should be approximately the same. While the differences in gelatinization and breakdown are apparent, the most striking feature shown is the great range in cold paste viscosity. It is evident that the process of acid modification does not diminish the viscosity factors that are involved in the tendency of the paste to gel on cooling to the same degree that it diminishes the factors that cause hot paste viscosity. It appears also, by comparison of curves 1 and 4, which are of starches of approximately equal concentration, that the process of oxidation lowers the gelling tendency of starches more than does the process of acid modification. This figure illustrates a fact of great importance, well known in the starch industry, that it is not possible to predict the cold paste viscosity of a starch from its hot paste viscosity.

ACKNOWLEDGMENT

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Study of the Hexabromide Number

J. P. KASS[1], W. R. ROY, AND G. O. BURR
Department of Botany, University of Minnesota, Minneapolis, Minn.

The problems involved in the determination of linolenic acid by the precipitation of its hexabromide are discussed. Previously reported hexabromide numbers obtained by accepted methods are probably incorrectly high because of insufficient washing of the precipitate. A more adequate procedure gives consistent results and an analytical precipitate identical in appearance with pure hexabromostearic acid. The empirical nature of the hexabromide numbers is emphasized and the specification of experimental procedure is recommended.

THE hexabromide number (the percentage of ether-insoluble, benzene-soluble precipitate obtained under specified conditions by the bromination of the mixed acids of fats and oils) has long been recognized as the distinguishing constant of the vegetable oils containing the 9,12,15-octadecatrienoic linolenic acid, and several methods differing considerably in experimental procedure have been proposed for its determination (*3, 5, 10, 11, 13*). Although this analytical value has proved useful in the characterization of the drying and semidrying oils, especially in the detection of adulteration of linseed, perilla, and soybean oils (*1, 2, 12*), its true relation to the actual concentration of the component linolenic acid has as yet not been satisfactorily established. This uncertainty is due in part to the problems involved in the selection of a pure linolenic acid to serve as the appropriate standard, and in part to the variation of the results with the conditions of the determination.

The more recently developed spectroscopic and thiocyanometric procedures offer two alternative methods for the estimation

[1] Present address, Research Laboratories of Interchemical Corp., New York 19, N. Y.

of linolenic acid. However, the first requires specialized equipment, while the second suffers from the same uncertainties as the determination of linolenic acid by bromination, in addition to requiring an infrequently used unstable reagent. Moreover, neither method can differentiate among the possible geometric or nonconjugated positional isomers of the unsaturated acids. The isolation of the characteristic hexabromostearic acid therefore remains as the only specific means available at present for the qualitative and quantitative identification of linolenic acid.

It is now generally accepted that the hexabromostearic acid precipitated in the determination of the hexabromide number corresponds to only a fraction of the linolenic acid, the remainder of the bromination product remaining in solution as a noncrystallizable oily liquid. Since the ostensibly pure linolenic acid regenerated from the crystalline α-hexabromostearic acid gives on rebromination only 20 to 25% of the theoretical yield of this solid hexabromide—i.e., has a hexabromide number of 55 to 68 compared with the theoretical value of 273—Rollett (*9*) originally postulated the formation in equal amounts of all four of the theoretically possible racemic pairs of stereoisomeric hexabromides, three of which happen to be liquid and only one an ether-insoluble crystalline solid. The linolenic acid content of a mixture would accordingly be equivalent to approximately four times the amount calculated from the hexabromide number, or more accurately, to the ratio of the hexabromide number of the mixture and of the experimentally determined hexabromide number of pure linolenic acid (*9*). Work in this laboratory (*4*) has shown, however, that the proportions of various bromides formed from a single trienoic acid do not necessarily bear any predictable relation to the theoretically possible requirements.

More significantly, Brown and his co-workers (*6, 10*) have demonstrated that the linolenic acid regenerated from the hexabromide is not entirely identical with its natural form isolated by direct crystallization from the untreated acids of linseed or perilla oils, in that debromination appears to induce up to 15% of isomerization to geometric isomers which do not yield solid hexabromides. The most homogeneous sample of linolenic acid obtained to date by the crystallization technique and claimed to be identical with the natural substance was reported to give by an empirical procedure a hexabromide number of 96, compared with hexabromide numbers of 75 to 81 similarly found for the debromination linolenic acid. The correct linolenic acid content of a mixture should be therefore simply obtained from the relation

$$\% \text{ linolenic acid} = \frac{100 \times \text{hexabromide No. of mixture}}{96}$$

provided identical conditions were used in the determination of the experimental hexabromide number and in the determination of the standard value.

Since the various procedures proposed for the determination of the hexabromide number usually do not give concordant results in the hands of different operators, none has been universally adopted; nor is satisfactory duplication achieved with any one method except by strict adherence to arbitrarily selected conditions. The main source of discrepancy appears to lie in the difficulty in freeing the white solid hexabromide from the other oily and colored bromination products of linolenic acid, as well as the ether-soluble solid and liquid unstable tetrabromides of linoleic and the liquid dibromide of oleic acid occurring in mixtures. This is evident in the necessity of drying the precipitate at 60° C., although the pure hexabromide is relatively stable below its melting point, variously given at 178° to 183° C.

The published procedures recommend washing the precipitated hexabromides three or four times prior to drying, with cold ether on a filter crucible as in the Wizöff method (*3, 5*), by centrifugation with ether (*10*), or preferably with ether previously saturated with hexabromide as in the method of Steele and Washburn (*11*). The authors' experience had shown that either the filtration or the centrifugation procedure may produce a white precipitate, as required, but this product usually dried in the oven to a brittle waxy solid, rather than to a fine crystalline powder characteristic of pure α-hexabromostearic acid. In connection with investigations of the isomerism of the unsaturated acids it was considered desirable, therefore, to make a study of the conditions required to obtain an analytical precipitate identical in appearance with the pure compound.

EXPERIMENTAL

Materials. The fatty acids were prepared by the quick-saponification procedure of Moore (*7*), in which the oil or ester was boiled for 3 minutes with about twice its volume of an alcoholic potassium hydroxide solution prepared by dissolving 20 grams of the alkali in 13 ml. of water and diluting with 100 ml. of 95% ethanol. The soap solutions were then cooled quickly by the addition of 4 volumes of water, covered with ether, and acidified with 20% sulfuric acid. The washed and dried ether solution was evaporated under vacuum at a final temperature of 60° C., preferably with a stream of inert gas. No indications of oxidation were ever observed with this simple technique, and the linseed acids retained an iodine value of 179 for some time when stored with the usual precautions.

"Debromination" linolenic acid was prepared from highly purified hexabromostearic acid as described elsewhere (*8*). The "crystallization" linolenic acids were made available through the courtesy of J. B. Brown and represented a sample of debromination linolenic acid recrystallized fourteen times by Matthews (*6*) to be a reported hexabromide number of 96, and two samples of 88 and 84% purity obtained by Shinowara (*10*) by direct low-temperature crystallization of linseed and perilla acids, respectively. Both were reported to have hexabromide numbers of 83, the contaminant presumably being linoleic acid. In contrast to the impure acids, both the pure debromination and crystallization acids showed a pronounced tendency toward oxidation even when resealed in evacuated vials, evident in diminishing hexabromide numbers. Only those results obtained on the first day of exposure of these acids to air will therefore be presented.

Bromination. Since no evidence exists to prove the necessity of brominating in chloroform, the rather cumbersome procedure of Steele and Washburn (*11*) was discarded in favor of direct bromination of the acids in dilute ethyl ether solution chilled in a methanol-ice bath, and filtration on a prepared Gooch crucible. The brominated mixture was allowed to stand in the icebox overnight, and the excess bromine was discharged with amylene prior to filtration. A large excess of halogen did not appear to affect the results, bromination to a distinct and permanent orange color being sufficient. Centrifugation was found to pack the precipitate, and washing was therefore performed as described under each series of determinations.

Table I. Effect of Sample Weight on Hexabromide Number of Linseed Fatty Acids (Iodine Value 179)

(Precipitation in and washing with ether at 0° C.)

Sample Weight	Hexabromide Weight	Hexabromide Number	
		Uncorrected	Corrected[a]
Grams	*Gram*		
0.1010	0.0192	19.0	41.8
0.1352	0.0336	24.8	41.8
0.1678	0.0443	26.4	40.1
0.2000	0.0628	31.4	42.9
0.2050	0.0658	32.1	43.3
0.2081	0.0697	33.5	44.5
0.2083	0.0675	32.3	43.4
0.2166	0.0666	30.7	41.3
0.2198	0.0720	32.8	43.2
0.4069	0.1619	39.7	45.3
0.4523	0.1739	38.4	43.5
1.0491	0.5241	50.2	52.2
1.0726	0.5313	49.5	51.5

[a] Correction of +0.0230 gram for solubility of hexabromostearic acid in total of 100 ml. of ether at 0°.

EFFECT OF WASHING

The inadequacy of the direct washing procedure recommended by the Wizöff method (*3, 5*) is shown by the data in Table I, in which the effect of adsorption of the soluble bromides is made apparent, among other possible factors shown in subsequent work, through the increase of the hexabromide number with the sample

weight. In this series, the samples were weighed into 50-ml. centrifuge tubes, dissolved in 25 ml. of ether, and brominated as described above. The precipitates were filtered with gentle suction onto prepared Gooch crucibles and were finally washed with additional ether, a total of 75 ml. being used for the transfer and washing. Despite the precaution of not allowing the precipitate to dry on the filter during the washing and drying only at 60° as directed, the weighed precipitates were invariably waxy, brittle, and gray. A sample of pure hexabromostearic acid treated identically lost 23 mg., and the weights of the hexabromide precipitates were corrected accordingly. Steele and Washburn (*11*) reported the solubility of pure hexabromostearic acid to be 26 mg. in 100 ml. of ether at 0°.

Substitution of ether previously saturated with hexabromostearic acid (*11*) for pure ether throughout the procedure made no difference in the results, as shown in Table II. In this instance, a negative correction of 18.4 mg. had to be applied, because of evaporation of the solvent from the saturated ether solution during the washing.

In the next series, the precipitates were prepared as before, but they were washed by decantation with 25-ml. portions of hexabromide-saturated ether the designated number of times before being transferred and washed on the Gooch crucible with 75 ml. of cold ether. The supernatant liquids were cautiously siphoned off after the stirred precipitates had been allowed to settle freely for 10 to 15 minutes under a bell jar, the air space of which was saturated with ether vapor. This precedure eliminated the convection currents caused by the rapid evaporation of the ether from the surface, which interfered with the settling of the precipitate.

Table II. Effect of Sample Weight on Hexabromide Number of Linseed Fatty Acids (Iodine Value 179)

(Precipitation in and washing with hexabromide-saturated ether)

Sample Weight	Hexabromide Weight	Hexabromide Number Uncorrected	Hexabromide Number Corrected[a]
Grams	*Gram*		
0.1605	0.0665	41.4	30.0
0.1640	0.0742	45.2	34.0
0.3044	0.1466	48.1	42.1
0.3381	0.1682	49.7	44.2
0.5091	0.2576	50.6	47.0
0.6537	0.3215	49.2	46.3
0.9993	0.5410	54.1	52.3
1.2113	0.6321	52.2	50.6

[a] Correction of −0.0184 gram for deposition of hexabromide from wash liquid.

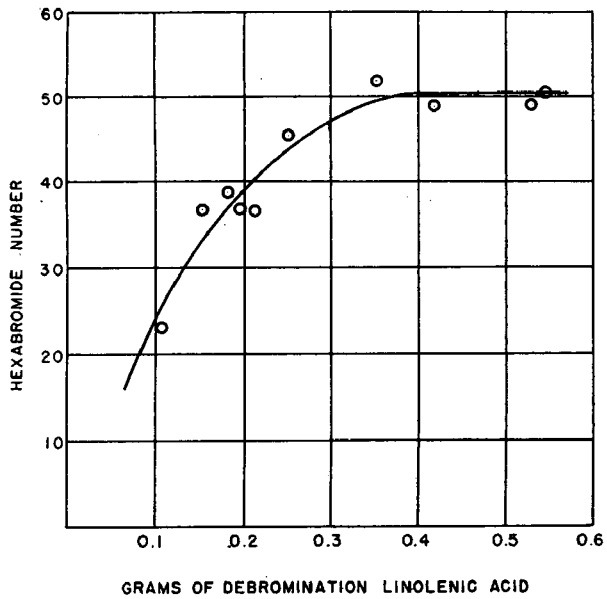

Figure 1. Effect of Sample Size (Concentration) on Hexabromide Number of Debromination Linolenic Acid

Table III. Effect of Washing of Precipitate on Hexabromide Number of Linseed Fatty Acids (Iodine Value 179)

Number of Washings[a] (by Decantation) with Saturated Ether	Sample Weight	Hexabromide Weight	Hexabromide Number Uncorrected	Hexabromide Number Corrected[b]
	Gram	*Grams*		
0	0.9904	0.4581	46.1	48.5
0	1.0272	0.4322	42.2	44.4
3	1.0087	0.3923	38.9	41.3
4	1.0834	0.4100	37.8	40.0
4	1.1294	0.4368	38.7	40.7
8	0.9879	0.2952	29.9	32.2
8	1.0885	0.3224	29.7	31.8
16	0.9620	0.3054	31.7	34.1
16	0.9853	0.3090	31.3	33.3

[a] Precipitation in 25 ml. of ether, all washings with hexabromide-saturated ether followed by transfer and additional washing with 75 ml. of ether at 0°.
[b] Correction of +0.0230 gram for solubility of hexabromide in total of 100 ml. of ether at 0°.

The data, to which was applied the correction factor of 23 mg. for the solubility of hexabromostearic acid in 100 ml. of ether, are given in Table III and show that washing eight times by this procedure is required to remove adsorbed materials completely and to give a constant hexabromide number. The precipitates obtained in this manner were fine white crystalline powders even when dried above 100°, indistinguishable from pure hexabromostearic acid. Identical results were obtained using 75 ml. of hexabromide-saturated ether for the final transfer and washing on the crucible, the correction factor in this case again being −18.4 mg. for the deposition of hexabromostearic acid from the wash liquid. Thus, six determinations using approximately 0.5-gram samples of fatty acids and eight preliminary washings gave hexabromide numbers varying from 32.0 to 33.7, with average and median values of 32.8. This may be compared with the hexabromide number of 42 reported by Bailey and Baldsiefen (*1*) for an average linseed oil fatty acid mixture, and found in the authors' work as well after only the insufficient three or four washings recommended by previous methods.

HEXABROMIDE NUMBER OF LINOLENIC ACID

Using the above procedure of washing the precipitate eight times by decantation before transferring to the weighing crucible with an additional 75 ml. of hexabromide-saturated ether, the hexabromide numbers of the linolenic acids were determined. With quadruplicate samples weighing from about 0.3 to 0.6 gram, corrected hexabromide numbers varying from 49.2 to 51.8 and averaging 50.2 were obtained for the debromination linolenic acid prepared in the authors' laboratory. This is in better agreement with the original data of Rollett (*9*) than with the figures given by Brown and co-workers (*6*, *10*). However, smaller samples gave lower results, as shown in Figure 1. On the assumption that the solubility correction factor used in this work is generally applicable and that the reaction between bromine and the unsaturated acids is complete, no obvious explanation presents itself for the observed concentration effect, which, despite the adequate washing procedure, is apparently even more pronounced with the debromination linolenic acid than with the mixed linseed fatty acids used in the preliminary experiments.

Approximately 0.5-gram samples of the debromination linolenic acid recrystallized fourteen times (*6*) gave an average corrected value of 76.8, while quadruplicate samples of the linolenic acid crystallized to 84 and 88% purity (*10*) gave average values of 65.4 and 66.3, respectively. Calculated to 100% purity, these become 77.6 and 75.4, in good agreement with the hexabromide number of the pure sample of the crystallization acid.

DISCUSSION

The data presented in this paper emphasize the empirical nature of the hexabromide numbers now in the literature. There

can be little doubt that the reported values are higher than would be expected from the actual proportion of the homogeneous solid α-hexabromostearic acid formed on the bromination of linolenic acid. It is therefore suggested that future theoretical studies relating to questions of isomerism among the various unsaturated acids and their bromides take this factor into account and consider hexabromide numbers to be valid only when based on weights of precipitates washed to a constant loss, giving due regard to the concentration effect. However, for analytical purposes, especially for the identification and the detection of adulteration of the various vegetable oils, empirical procedures will obviously remain satisfactory, since these involve only comparisons with firmly established values, erroneous though they may be. It follows that future proposals of standard hexabromide numbers, whether of mixed fatty acids of oils or of pure linolenic acid, should be accompanied by specifications of the experimental method.

On the assumption that the samples of the recrystallized linolenic acid are identical with the natural isomer present in linseed oil and using averaged results, the concentration of linolenic acid in the mixture of linseed fatty acids used in this study is $\frac{100 \times 32.8}{76.6} = 42.8\%$, in line with the currently accepted conception of the composition of linseed oils as determined from empirical thiocyanogen values or ultraviolet absorption data. On the other hand, a similar calculation based on the hexabromide number of debromination linolenic acid gives an obviously impossible high concentration of linolenic acid; the calculated proportion accounts for the total iodine value without allowing for the known presence of oleic and linoleic acids in the mixture.

Comparison of the hexabromide numbers of debromination and crystallization linolenic acids as obtained by the authors' procedure indicates that an even greater degree of isomerization occurs during the debromination of α-hexabromostearic acid than suggested by Brown and co-workers (*6*). Confirmation of the higher hexabromide number of natural linolenic acid thus further requires the modification of Rollett's conclusion (*9*) of the formation in equal proportion of four pairs of *isomeric* hexabromides from that unsaturated acid, his fundamentally correct hypothesis having been based on the observation of the fortuitous behavior of the nonhomogeneous debromination linolenic acid (*4*). Final solution of the exact degrees of isomerization and proportions of bromides formed awaits the unquestionable purification of linolenic acid to proved identity with the natural form and the development of a method for the determination of true hexabromide numbers, since the present study may be claimed to have brought out only correct minimal values, having disregarded such effects noted by Steele and Washburn (*11*) as the increased hexabromide numbers observed in the presence of traces of alcohol or acetone in the solvent.

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Determination of Degree of Substitution of Sodium Carboxymethylcellulose

R. W. EYLER, E. D. KLUG, AND FLOYD DIEPHUIS
Hercules Experiment Station, Hercules Powder Company, Wilmington 99, Del.

THE increasing industrial importance of sodium carboxymethylcellulose has created interest in methods for its analysis. The degree of substitution—i.e., the average number of sodium carboxymethyl groups substituted per anhydroglucose unit—markedly affects the properties of this compound and convenient methods for its determination have therefore become necessary.

Hollabaugh, Burt, and Walsh (*5*) have published a complete review and bibliography on the uses and applications of this product. Brown and Houghton (*1*) in another review described a method for determining degree of substitution of the acid form of carboxymethylcellulose based upon electrometric titration. Another method reported by the same authors (*1*) involves precipitation of the copper or aluminum salts and determination of the metal content of the precipitate. Schmidt, Meinel, Jandebeur, and Simson (*7*) describe a conductometric method for determining carboxyl in cellulose which is of interest in connection with one of the methods discussed in the present paper. Sakurada (*6*) reports three methods for determining substitution, one involving potentiometric or conductometric titration with sodium hydroxide, another requiring ashing the sodium salt, and the third consisting in titration of the free acid with sodium hydroxide. Since none of these procedures fulfilled the need for methods suitable for control purposes and applicable to both purified and unpurified samples of the sodium salt of varying degrees of substitution, the methods presented here were developed.

This paper describes three methods—acid-wash, conductometric and colorimetric—for determination of the degree of substitution of sodium carboxymethylcellulose. With appropriate modifications, however, the methods would be applicable also to the free acid form. Quantitative determination of the amount of carboxymethylcellulose present in admixture with other materials would be possible but would require previous knowledge of the degree of substitution. Each of these methods is best adapted to a certain type of sample, although the applications may sometimes overlap.

ACID-WASH METHOD

This method involves conversion of the sodium salt of carboxymethylcellulose to the acid form by treating with methanol acidified with hydrochloric or nitric acid, removal of the excess acid by

Three methods are described for determining the degree of substitution of sodium carboxymethylcellulose. This material may be converted to its free acid form by treatment with acidified alcohol, freed from excess acid, and the carboxyl content determined by an acidimetric procedure using phenolphthalein indicator. Alternatively, the sodium salt may be dissolved in water containing excess sodium hydroxide, and the solution titrated conductometrically with standard hydrochloric acid solution. In the analysis of purified, dry samples, the use of this latter method results in a considerable saving in time over that required in the former. A third method involving treatment of the carboxymethylcellulose with sulfuric acid to produce glycolic acid, which is then determined colorimetrically using 2,7-dihydroxynaphthalene, is recommended for use with difficultly soluble samples. Possible use of this method in quantitative determination of carboxymethylcellulose in mixtures is suggested. The three methods give comparable results when applied to samples having a degree of substitution ranging from 0.2 to 1.3. The most advantageous application of each method is suggested.

washing with a methanol-water solution, and drying the material. Weighed samples of the free acid are dissolved in distilled water containing an excess of standard sodium hydroxide, and the excess base is back-titrated with standard hydrochloric acid using phenolphthalein indicator. This method differs from those described in the literature in two respects: The carboxymethylcellulose is retained in the solid state during the washing procedure, and an excess of alkali is used to facilitate solution. Results obtained on five samples with various degrees of substitution are given in Table I.

REAGENTS AND APPARATUS. Nitric acid reagent. Add 100 ml. of 70% nitric acid to 1 liter of anhydrous methanol slowly with stirring.

Hydrochloric acid reagent. Add 25 ml. of concentrated hydrochloric acid to a solution of 900 ml. of anhydrous methanol and 270 ml. of distilled water.

Methanol, 70% by weight.

Methanol, 80% by weight.

Hydrochloric acid, 0.5 *N*, accurately standardized.

Sodium hydroxide, 0.5 *N*, accurately standardized.

Pressure filter, with fritted disk, porosity M, Corning Glass Works, Catalog No. 34020; or equivalent filter of other manufacturer.

PROCEDURE. Place about 10 to 15 grams of freshly precipitated sodium carboxymethylcellulose and 200 ml. of the acid reagent in a 500-ml. Erlenmeyer flask, stopper, and shake for 3 or 4 hours. Transfer the acid and carboxymethylcellulose to the filter funnel and remove the acid liquor by suction. Add 100 to 150 ml. of 70% methanol to the filter funnel, break up the mat by stirring, and then attach a 2-liter separatory funnel to the top of the filter by means of a bored rubber stopper to give a tight seal. Place 2 liters of 70% methanol in the separatory funnel and open the stopcock slightly to allow about one drop per second to pass through the filter below. This washing may conveniently be carried on overnight. (Note. Use 80% methanol for washing if the degree of substitution is above 1.0.)

When all the methanol has been delivered to the filter, place the filter on a filter flask and remove the excess solvent by suction. Add 100 to 150 ml. of 70% methanol to the filter, stir up the carboxymethylcellulose mat, and again remove excess methanol by suction. Test this filtrate for neutrality by mixing 5 ml. of the filtrate with 5 ml. of distilled water and adding one drop of methyl red indicator. If the filtrate is acid, continue washing in this same manner until the filtrate is neutral to methyl red, and then remove as much as possible of the wash liquor under strong suction.

Add 150 ml. of anhydrous methanol to the filter, break up the carboxymethylcellulose mat by stirring, stopper, and allow to dehydrate for about one hour. Again remove the methanol under strong suction and then transfer the carboxymethylcellulose to a small beaker. The remainder of the methanol may be removed by drying with a blower or in an oven at 80° C.

Place approximately 2 grams of the washed and dried carboxymethylcellulose in a weighing bottle and dry for 1 hour at 100° C. Weigh by difference (to nearest milligram) into a rubber-stoppered 500-ml. Erlenmeyer flask. Add 15 ml. of 70% methanol, allow to stand a few minutes, and then add 200 ml. of distilled water and 50 ml. of 0.5 *N* sodium hydroxide solution, accurately measured from a buret. Place the flask on a bottle shaker and shake rapidly for 3 to 5 hours to dissolve or disperse the carboxymethylcellulose. Titrate with 0.5 *N* hydrochloric acid using phenolphthalein as indicator.

Calculation.

$$\frac{(\text{Ml. of NaOH} \times N) - (\text{ml. of acid} \times N)}{\text{grams of sample}} =$$

milliequivalents of total carboxyl per gram of sample. Value A

$$\frac{0.162\,A}{1 - 0.058\,A} = \text{degree of substitution}$$

where the constants are derived from the molecular weight of the anhydroglucose unit of cellulose (162) and from the net increase in the weight of the anhydrogluclose unit for each carboxymethyl group substituted (58).

When the hydrochloric acid reagent was used, the sample of carboxymethylcellulose was given three 1-hour steeps, using 100 ml. of fresh reagent for each steep instead of the 3 to 4 hours' shaking period used with a single portion of nitric acid reagent as described above. Either may be used, although the nitric acid procedure is more convenient.

Table I. Degree of Substitution of Typical Carboxymethylcellulose Samples by Various Methods

Sample	Conductometric Found	Conductometric Av.	Acid-Wash-HNO_3 Found	Acid-Wash-HNO_3 Av.	Acid-Wash-HCl Found	Acid-Wash-HCl Av.	Colorimetric Found	Colorimetric Av.
1	1.20	1.19	1.29	1.29	1.33	1.32	1.51	1.38
	1.19		1.29		1.30		1.38	
	1.20		1.30		1.34		1.46	
	1.12		1.30				1.33	
	1.20		1.29				1.35	
	1.17		1.29				1.25	
	1.20		1.28					
	1.23		1.29					
			1.29					
	0.69	0.70	0.70	0.71	0.75	0.75		
	0.71		0.72		0.77			
	0.69		0.72		0.74			
					0.74			
					0.73			
					0.75			
3	0.74	0.72	0.74	0.74	0.74	0.75	0.80	0.77
	0.70		0.73		0.76		0.76	
	0.71		0.74		0.75		0.76	
4	0.54	0.51	0.56	0.56	0.56	0.57	0.55	0.55
	0.50		0.56		0.57		0.55	
	0.50		0.57		0.57			
5	0.17	0.17	0.16	0.17	0.17	0.18	0.19	0.18
	0.17		0.17		0.18		0.18	
	0.17		0.17		0.18		0.17	

CONDUCTOMETRIC PROCEDURE

Early attempts to titrate the sodium carboxymethylcellulose with hydrochloric acid either electrometrically or with use of an indicator were abandoned because an indistinct inflection occurs in the titration curve at the completion of formation of the carboxymethylcellulose free acid. It was found, however, that this same end point could be satisfactorily determined conductometrically. In this procedure, the sodium carboxymethylcellulose is dissolved in distilled water containing a small known amount of standard sodium hydroxide solution. This alkali serves to speed solution and convert any carboxymethylcellulose free acid to the sodium salt. The solution is then titrated con-

ductometrically with standard hydrochloric acid solution. As is shown by Figure 1, three linear segments are obtained which are extrapolated to two intersections. The volume of acid corresponding to the difference between points V_1 and V_2 is a measure of the carboxyl groups in the sample. The titration vessel and the electrode system used are illustrated in Figure 2. Results obtained on five samples covering a range of substitutions are given in Table I.

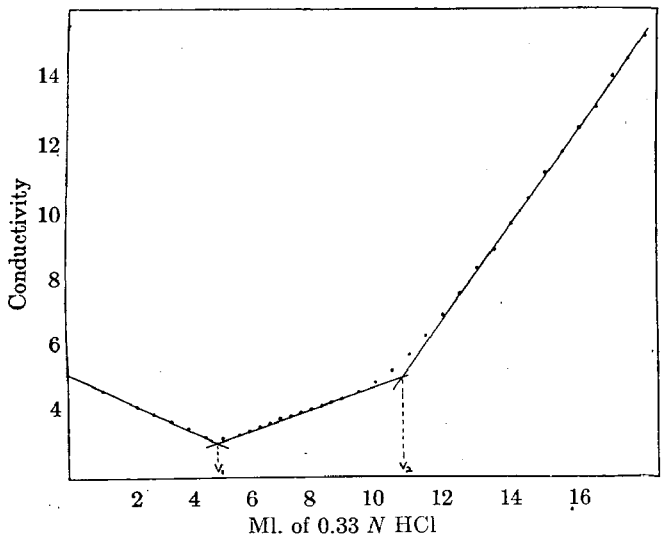

Figure 1. Conductometric Titration of Sodium Carboxymethylcellulose

Reagents. Hydrochloric acid, 0.33 N, accurately standardized.

Sodium hydroxide, 0.5 N, accurately standardized.

Methanol, 70% by weight.

Apparatus. Conductivity cell, made from a 500-ml. Florence flask, indented, 8-mm. side arm for introduction of gas; side neck for electrodes fitted with standard-taper joint (see Figure 2).

Electrodes. Platinum foil electrodes 7 × 7 mm. reinforced at the edges with No. 18 platinum wires and spaced approximately 7 to 10 mm. apart. The two electrodes are separated by sealing into separate glass tubes which are in turn sealed into a standard-taper joint, to fit the side neck of the cell. Contact is made between the electrodes and the lead wires through a few drops of mercury placed in the glass tube. For satisfactory performance the electrodes should be platinized.

Variable-speed motor stirrer.

Buret, 10-ml. capacity, 0.02-ml. subdivisions, with side filling tube. Offset tips are sealed on in place of the straight tips regularly supplied.

Constant-temperature bath maintained at 25° ± 0.2° C.

Iodine flasks, 250 ml.

Conductivity bridge. Leeds & Northrup, Philadelphia, Pa., portable electrolytic resistance indicator, Catalog No. 4960; or Model RC-1, Industrial Instruments, Inc., Bayonne, N. J.; or equivalent.

Procedure. Grind the sample in a laboratory micro Wiley mill or equivalent, using a 20-mesh screen. Weigh roughly about 0.3- to 0.4-gram sample of medium- or high-substituted material or up to 1.0-gram sample of low-substituted material (less than 0.3 degree of substitution) into a glass-stoppered weighing dish. Dry the sample 1 hour in an oven at 100° to 105° C. Remove, stopper, cool in a desiccator, and weigh to the nearest 0.001 gram. Transfer the contents of the weighing dish to a dry 250-ml. iodine flask and weigh the empty bottle to get the sample weight by difference. Add 15 ml. of 70% methanol solution and allow the sample to soak for 10 minutes. Add 200 ml. of carbon dioxide-free distilled water and 3 ml. of 0.5 N sodium hydroxide solution from a buret or pipet. Flush the air from the flask with a stream of nitrogen, stopper immediately, and shake until the sample is dissolved or, if it is low-substituted, until it is dispersed. This will take from 15 minutes to 4 hours depending on the type of sample; low-substituted materials will require longer time. Pour the solution into the conductivity cell and rinse the flask with 3 separate 50-ml. portions of carbon dioxide-free distilled water, adding the washings to the cell. Start the stirrer and nitrogen stream and allow approximately 5 minutes for the contents of the cell to become homogeneous. Stir vigorously but avoid introducing bubbles into the body of the liquid by too rapid stirring.

Determine the resistance of the solution with the conductivity bridge and then titrate with the 0.33 N hydrochloric acid, adding the acid in 0.3- to 0.4-ml. portions. Take a resistance reading after each addition of acid, allowing sufficient time for adequate mixing. After 10 ml. of acid have been added, continue additions in 0.5-ml. portions to a total volume of 16 ml. A total volume of 16 ml. of 0.33 N acid is usually sufficient for a sample having a substitution of 1.2 or less.

Calculate values of the reciprocal of the resistance and plot these against milliliters of hydrochloric acid solution as shown in the sample curve, Figure 1. Ignore the points obtained up to about 25% beyond the second end point and then draw the best straight line from the points between 25 and 75% excess hydrochloric acid. Extrapolate the three linear portions of the curve to obtain the two end-point intersections and determine the volumes of hydrochloric acid solution V_1 and V_2 corresponding to these intersection points.

Calculation. *Total Carboxyl.* The milliequivalents of total carboxyl per gram of sample are measured by the difference between V_2 and V_1.

$$\frac{(V_2 - V_1)\,N}{\text{grams of sample}} = \text{milliequivalents of total carboxyl per gram. Value } A$$

V_1 and V_2 are defined above and N is the normality of the hydrochloric acid used.

Free Carboxyl.

$$\frac{(\text{Ml. of NaOH} \times N) - (V_1 \times N)}{\text{grams of sample}} = \text{milliequivalents of free carboxyl per gram. Value } B$$

V_1 is defined above.

Degree of Substitution.

$$\frac{A \times 0.162}{(1 + 0.022\,B - 0.080\,A)} = \text{degree of substitution}$$

where 0.080 is the net increase (divided by 1000) in the weight of the anhydroglucose unit of cellulose for each sodium carboxymethyl group substituted; and 0.022 is obtained by combining terms containing the constants 0.080 and 0.058 previously defined.

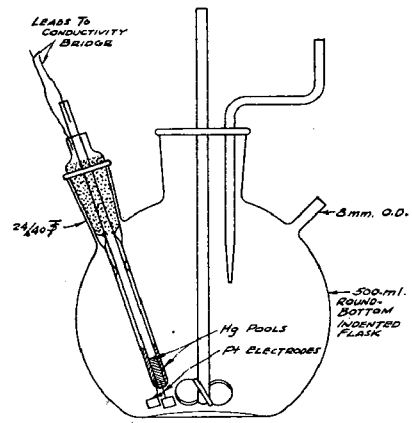

Figure 2. Conductivity Cell and Electrode System

The term 0.022 B may be neglected if the sample is known to be entirely in the sodium salt rather than partly in the free acid form.

COLORIMETRIC METHOD

Chowdhury (*3*) reports that treatment of carboxymethylcellulose with phosphorus triiodide and water yields glycolic acid. Feigl (*4*) describes the use of 2,7-dihydroxynaphthalene as a spot test reagent for glycolic acid; and Calkins (*2*) describes a quantitative procedure for the determination of glycolic and oxalic acids

using this same reagent. In order to avoid possible interference from the iodide ion in the determination of the glycolic acid produced from the carboxymethylcellulose, sulfuric acid was successfully tried as the ether-cleaving reagent to replace phosphorus triiodide and water. Briefly the method involves solution of the sample in sodium hydroxide solution, acidification with sulfuric acid, and heating under reflux to produce glycolic acid. The procedure of Calkins is then used with slight modifications to determine the glycolic acid in an aliquot of the resulting solution. Some aldehydes (especially formaldehyde), glycolic acid, and sodium glycolate will interfere in the colorimetric step in this procedure. Results obtained on four samples of varying degrees of substitution are given in Table I.

Reagents and Apparatus. Sodium hydroxide solution, 6%. Dissolve 30 grams of reagent grade sodium hydroxide in 470 ml. of water.

Dihydroxynaphthalene solution. Dissolve 0.100 gram of 2,7-dihydroxynaphthalene (Eastman Kodak Co. Catalog No. 4408) in 1 liter of 95% sulfuric acid. Allow this solution to stand until the initial yellow color disappears before using. (Usually 5 to 6 hours are required.) Store this solution in a dark cabinet.

Standard glycolic acid solution. Dry some glycolic acid (Eastman Kodak Co. Catalog No. 998) in a calcium chloride desiccator at room temperature overnight. Accurately weigh 0.025 gram of the dried material, dissolve in distilled water, and make up to volume in a 250-ml. volumetric flask. Prepare a fresh solution each time a calibration is carried out.

Spectrophotometer. A Beckman spectrophotometer Model DU was used in this work. A wave length of 540 millimicrons, a slit width of 0.025 mm., and a 1-cm. cell were used.

Procedure. Using a 1-ml. graduated pipet, measure accurately 0.2-, 0.5-, and 1.0-ml. portions of the standard glycolic acid solution into separate 8 × 0.75 inch Pyrex test tubes and add 20 ml. of the dihydroxynaphthalene solution to each with a graduate. Place the test tubes in a beaker of boiling water for 20 minutes. Place the test tubes in a container of cold tap water and allow to cool. Transfer the contents of the test tubes to 50-ml. volumetric flasks, rinse the test tubes with three 5-ml. portions of distilled water, and add the washings to the flasks with the aid of a small funnel. The water should be added carefully with adequate swirling to mix, taking care to prevent the mixing from taking place in the neck of the flask. Caution: Watch for possible spattering of the acid solution. Raising the funnel slightly with the forefinger to provide an air vent during additions to the flask is recommended.

Cool the flasks and contents to room temperature in a water bath, and make up to volume with water, cooling again if necessary. Read the color of the standards with a Beckman spectrophotometer or other convenient photometer against a blank of 20 ml. of color reagent treated in the same fashion as the standards. Plot grams of glycolic acid in the aliquot taken versus photometer reading. The calibration curve should be checked about once each week.

Grind the sample in a Wiley mill, or equivalent, to pass a 20-mesh sieve and mix thoroughly. Weigh 0.06 gram of 0.25-substituted material or 0.035 gram of 0.75-substituted material into a glass-stoppered weighing bottle. Dry in an oven at 100° to 105° C. for 1 hour, remove, stopper, and cool in a desiccator. Transfer the contents of the weighing dish to a dry 250-ml. Erlenmeyer flask with ground-glass joint and weigh the empty dish to get the sample weight by difference. Add 25 ml. of 6% sodium hydroxide solution with a graduate and shake until solution of the sample is complete. Wash down the neck and sides of the flask with 25 ml. of distilled water.

Add 36 ml. of 95% sulfuric acid carefully to the solution with a graduate. The final acid concentration will then be 50%. Attach the flasks to condensers with ground-glass joints and heat under reflux for 3.5 hours on a hot plate. (The temperature of the boiling liquid should be about 125° to 130° C.) Allow the mixture to cool to room temperature, and dilute to 100 ml. with 50% sulfuric acid.

Prepare a reagent blank solution consisting of 25 ml. of 6% sodium hydroxide, 25 ml. of water, and 36 ml. of 95% sulfuric acid and treat in the same manner as the unknown samples.

Pipet 1 ml. of the final cooled and diluted solution into a test tube and add 20 ml. of the color reagent. Heat in boiling water for 30 minutes, then cool and dilute in the same manner as for the standard solutions. Read the per cent transmittancy with a suitable photometer against the reagent blank solution. Read the concentration of glycolic acid corresponding to this reading from the calibration curve.

Calculation.

$$\frac{\text{Grams of glycolic acid in aliquot} \times 100}{\text{grams of sample}} = \text{grams of glycolic acid per gram of sample. Value } A$$

$$\frac{162\,A}{76 - 80\,A} = \text{degree of substitution}$$

where 76 is the molecular weight of glycolic acid and 162 and 80 have been previously defined.

DISCUSSION

Results of replicate determinations on five representative samples by the acid-wash and conductometric methods, and on four samples by the colorimetric method are given in Table I. Each value represents an individual sample carried through the complete procedure given above. Satisfactory agreement between the acid-wash and conductometric methods was obtained throughout the substitution range. The trend toward somewhat lower results by the conductometric method has not been explained. The colorimetric method agrees well with the other two methods when applied to the lower-substituted material, but does not give results of comparable precision when applied to high-substituted material. The precision of the values in Table I is consistent with previous experiences in using these methods over a period of two years.

It has been found that the acid-wash method can be applied to the greatest advantage to unpurified samples. It is also useful for the analysis of purified material unless time is an important factor. The outstanding advantages of the method are its simplicity and the fact that the common impurities are eliminated, thus making the method as written applicable to any sample of doubtful purity.

The shorter analysis time for the conductometric method recommends the procedure for use when several purified samples are to be analyzed in a short time. The method gives high and unreliable results if weak acids and their salts other than carboxymethylcellulose are present.

The analysis time for the colorimetric method is comparable to that for the conductometric method. The method may be used to the best advantage in the analysis of low-substituted samples, since the 6% sodium hydroxide facilitates complete solution of difficultly soluble material. The specificity of the action of sulfuric acid to produce glycolic acid from the carboxymethylcellulose lends itself to the quantitative analysis of samples containing materials which would interfere in other procedures; previous knowledge of the degree of substitution, however, is necessary in calculating the results. The method gives high results when applied to samples containing such interfering substances as formaldehyde, glycolic acid, and sodium glycolate.

SUMMARY

Three methods are described for the determination of the degree of substitution of sodium carboxymethylcellulose. These methods were developed for research and control purposes and for application to purified and unpurified samples with various degrees of substitution. The most advantageous application of each method is suggested.

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Sampling and Analysis of Boron Trifluoride

CARL F. SWINEHART, AUGUST R. BUMBLIS, AND HARRY F. FLISIK

The Harshaw Chemical Company, Cleveland, Ohio

An accurate and safe procedure for weighing samples of boron trifluoride from cylinders, accurate methods for determining common impurities, and a reasonably accurate method for total acidity are described.

OVER a period of several years methods for sampling and analysis of boron trifluoride have been developed in the laboratories of the Harshaw Chemical Company. The usual method of separating boron and fluorine by distillation of methyl borate from calcium fluoride as given by Treadwell and Hall (*10*) is not suitable for process or quality control.

The complex nature of water solutions of boron trifluoride, boric acid, and hydrofluoric acid has been described by Mellor (*7*), Gasselin (*5*), Travers and Malaprade (*9*), and others without reaching definite conclusions as to their composition. Variable and ambiguous titrations are obtained unless steps are taken to promote the completion of the hydrolysis when titrating total acidity or to convert the boron trifluoride to a stable salt when titrating fluosilicate. Methods are here presented for dealing with boron trifluoride, so that regular volumetric procedures can be employed.

PROPERTIES AND HANDLING TECHNIQUE

Boron trifluoride is a colorless gas at atmospheric pressure and temperature. It condenses to a liquid which freezes at −128° C., boils at −99.9° C., and has a density of 3.065 grams per liter at 0° C. and 760 mm. (*4*). Its critical temperature is −12.25° C. at 49.2 atmosphere (*1*). The gas is shipped in high-pressure steel cylinders of two sizes: H-size cylinders of 43,262-ml. (2640 cubic inch) capacity hold 27.2 kg. (60 pounds) of gas at 105.5 to 126.5 kg. per square cm. (1500 to 1800 pounds per square inch) while E cylinders hold 2.7 kg. (6 pounds) of gas at the same pressures. There is no liquid phase in these cylinders at ordinary temperatures and therefore no segregation of gaseous impurities. Boron trifluoride is an "oil-pumped" gas; therefore it, or equipment for it, must not be used with high-pressure oxygen without taking suitable precautions. It can be diluted without reaction with nitrogen, dry air, carbon dioxide, sulfur dioxide, hydrochloric acid, chlorine, and hydrogen.

The gas is very soluble in water, alcohol, ether, amines, etc.; when it is to be introduced into liquids of this type suck-back is a hazard that must be prevented by a vacuum breaker or other features of apparatus design. Mercury, white mineral oil, mineral spirits, and carbon tetrachloride are typical liquids in which the gas has a low solubility and are suitable for use in displacement bottles, manometers, and vacuum breakers.

For the construction of equipment to hold dry boron trifluoride steel tubing or pipe, forged steel fittings, steel-to-steel ground unions, and bar stock valves give the best service. For temporary low-pressure lines malleable iron fittings can be used. Moisture causes the gas to attack steel. Litharge and white mineral oil make a good dope for pipe threads. Copper tubing and brass fittings are satisfactory for low-pressure lines carrying either dry or moist gas. Pyrex, Saran, hard rubber, paraffin wax, polyethylene, and Vistanex are resistant to both the dry gas and its water solutions. Rubber tubing can be used for temporary connections. Booth and Willson (*2*) have described the handling of boron trifluoride in glass laboratory apparatus.

Standard regulators are not suitably constructed for reducing the pressure from cylinders. A bar stock needle valve, 2, attached to the cylinder valve, 1, as shown in Figure 1 can serve this purpose. The cylinder valve should never be used to regulate flow, since there is a danger of cutting the seat and losing the contents. These valves are flat seated and not intended for regulation of flow.

GENERAL PLAN OF ANALYSIS

Separate samples are taken for water-insoluble and water-soluble gases and the results are combined and calculated to weight per cents in the original gas. For estimating the insoluble gas, principally air, a known volume is absorbed in sodium chloride solution and the undissolved gas measured. For the soluble gases (boron trifluoride, sulfur dioxide, silicon tetrafluoride, etc.) a sample of about 20 grams is absorbed by reaction with chopped ice. After the ice melts, weighed aliquots of the solution are taken for the individual determinations.

PROBABLE IMPURITIES

Judging from the raw materials used and processes employed in the manufacture, the principal gaseous impurities would be air, sulfur dioxide, and silicon tetrafluoride with possibly trace amounts of hydrogen, sulfur trioxide, water, and hydrofluoric acid. Hydrogen would appear with the insoluble gas and be counted as air.

The combined amounts of water (or rather boron trifluoride

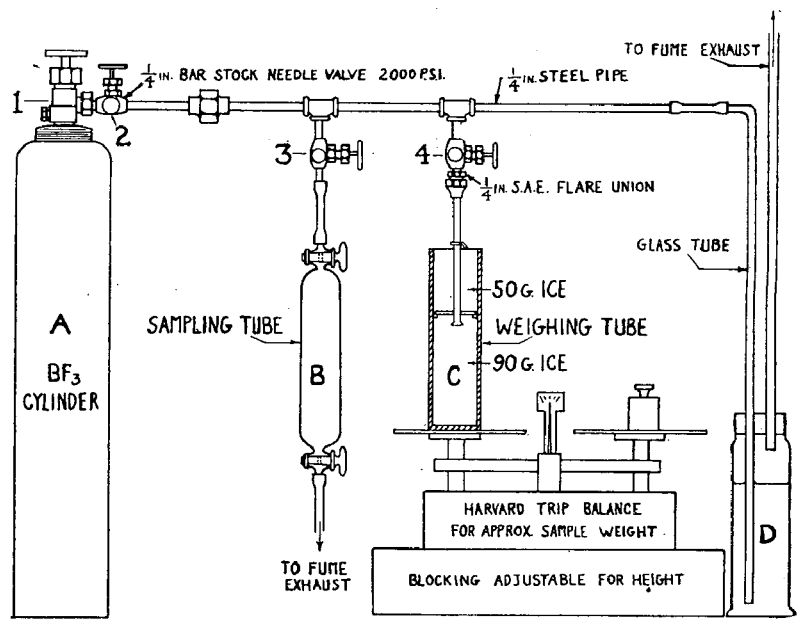

Figure 1. Apparatus for Sampling Boron Trifluoride

Table I. Duplicate Analyses of Some Cylinders of Boron Trifluoride[a]

Sample Cylinders	Sample A		Sample B		Sample C		Sample D		Sample E	
Constituent	Found	Mean	Found	Mean	Found	Mean	Found	Mean	Found	Mean
					Per cent by weight					
Total acidity as BF_3	99.9		98.7		98.2		99.5		99.0	
	100.0	100.0	99.0	98.9	99.0	98.6	99.4	99.5	99.1	99.1
BF_3	99.4		96.5		96.2		99.0		97.8	
	99.3	99.4	96.7	96.6	96.9	96.7	99.0	99.0	97.7	97.8
SiF_4	0.50		2.32		2.39		0.37		1.38	
	0.46	0.48	2.36	2.34	2.37	2.38	0.36	0.37	1.36	1.37
SO_2	0.17		0.39		0.24		0.20		0.27	
	0.16	0.17	0.40	0.40	0.23	0.24	0.19	0.20	0.28	0.28
Air	0.03		0.42		0.25		0.12		0.11	
	0.03	0.03	0.42	0.42	0.26	0.26	0.11	0.12	0.13	0.12
Total		100.1		99.7		99.6		99.7		99.6

[a] Produced by Harshaw Chemical Co., each sample representing a different batch. Samples B and C were made from raw materials unusually high in silica, selected to show applicability of method.

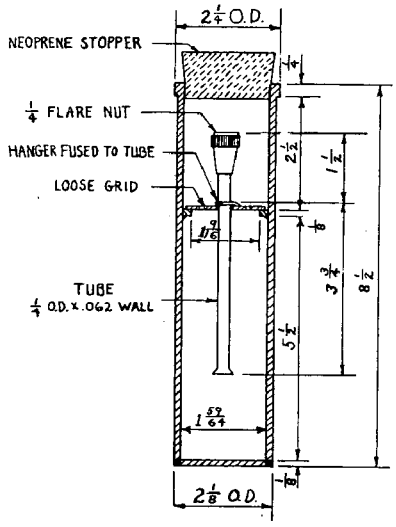

Figure 2. Sample Weighing Tube

Maximum weight of complete assembly 300 grams. Saran construction throughout. All dimensions in inches.

monohydrate), hydrogen fluoride, and sulfur trioxide must be very small, since the dew point of the gas as shipped in cylinders is generally below −40° C. A procedure for estimating sulfur trioxide from the water-soluble gas sample is included, though it is seldom found. Table I shows the distribution of impurities in some samples. The variation in silicon tetrafluoride corresponds to fluosilicate in the raw materials, while sulfur dioxide is formed from sulfuric acid in the process of generation.

SAMPLING

The arrangement of apparatus shown in Figure 1 has been found satisfactory for obtaining a laboratory sample of boron trifluoride from cylinders and storage tanks.

Apparatus. *A* is the container for the original boron trifluoride gas sample. In order to obtain a representative sample of a plant batch, 16 additions of quantities of the gas corresponding to pressure increments of 0.35 kg. per square cm. (5 pounds per square inch) each are run into an E-type cylinder, *A*, from the production system. It is then attached to the manifold as shown in Figure 1. *A* may also be a shipping cylinder in which case the pressure would probably be about 126.5 kg. per square cm. (1800 pounds per square inch). In any case there is no liquid phase to cause segregation in cylinders or storage tanks at ordinary temperatures.

B is a 250-ml. Pyrex sampling tube in which a separate sample is taken for the determination of water-insoluble gas (oxygen, nitrogen, hydrogen, etc.).

C is the Saran sample weighing tube detailed in Figure 2, in which the laboratory sample is weighed for determining water-soluble gases. (Saran weighing tubes can be obtained from The Harshaw Scientific Division, Harshaw Chemical Company.)

This is of the same design as the wax-lined hard rubber tube (*7*) for sampling anhydrous hydrofluoric acid.

D is a trap for limiting the pressure in the manifold. The receptacle is a glass bottle containing carbon tetrachloride, into which dips a glass tube attached to the end of the manifold. The outlet tube serves for guiding vented fumes into a hood.

Procedure. Before taking samples for either water-insoluble or water-soluble gases, flush the entire manifold system for at least 5 minutes with the boron trifluoride to be sampled; then just before attaching *B*, or the Saran delivery tube of *C*, flush out valve 3 or 4 for 15 seconds.

Water-Insoluble Gases. Determine the capacity of the glass sampling tube, *B*, if not already calibrated. After cleaning, dry by sweeping with dry air or preferably by alternately evacuating and admitting dry air ten times—then at atmospheric pressure close both stopcocks.

After sweeping the manifold with the boron trifluoride to be sampled, open valve 3 (Figure 1) for a few seconds, then immediately attach one end of *B* to the rubber tube on valve 3 and to the other end attach a rubber tube for guiding the fumes into a hood. Open in the following order: valve 3, the upper stopcock, and then the lower stopcock. Allow the boron trifluoride to pass through *B* at least 15 minutes. Close the upper stopcock, then the lower stopcock, and then valve 3. Note the temperature of the air around *B*. Disconnect and proceed with the determination of water-insoluble gases as described below.

Water-Soluble Gases. Before taking this sample, set up the Harvard trip balance with *C* as shown in Figure 1. Add enough weights to hold *C* at its highest position on the balance. Loosely couple the Saran delivery tube assembly of *C* to valve 4 adapter, then raise or lower the balance so that the hanger on the delivery tube is in line with the top of the weighing tube. Caution: This adjustment is necessary to prevent suck-back of liquid into valve 4 when the ice melts. Disconnect the Saran delivery tube assembly and dry it by blowing with dry air or by a combination of warming in an oven at 105° C. for a few minutes and blowing with dry air. Dry the neoprene stopper by blotting with a clean cloth. The weighing tube is most conveniently dried by rinsing in alcohol and blowing with air until the odor of alcohol is gone.

Weigh the entire dried weighing tube (Saran delivery tube assembly and stopper) on a torsion balance having a sensitivity of 15 mg. and capacity of 500 grams, using rough weights or an approximate tare weight, and balance exactly. Test the accuracy of this torsion balance for such factors as equality of arms and positioning of weights, and make suitable corrections if the errors are in excess of 20 mg. After thus establishing the weight of the entire weighing tube, do not disturb the tare weights, for succeeding weighings must be made by adding only analytical quality weights. From this point on complete the sampling as quickly as possible.

Place about 90 grams of chopped ice in the bottom part of the weighing tube. Properly insert the Saran delivery tube, so that the perforated disk rests flat on the narrow ledge and the hanger rests over the rim of the weighing tube. Add about 50 grams more of chopped ice to the top part of the weighing tube above the perforated disk. Wipe off any droplets of water on the outside of the weighing tube or on the coupling of the delivery tube. Weigh exactly on the torsion balance, adding only analytical weights. Check this weight immediately after wiping off water condensed on the outside of the weighing tube. Record the weight of ice.

The 90 grams of ice in the bottom serve to absorb the heat of reaction of boron trifluoride and the 50 grams in the top section serve to trap any cloud formed by boron trifluoride contacting water vapor. The ice must not greatly exceed 140 grams. This amount, when melted with 20 grams of sample, will not bring the liquid level above the outlet of the Saran delivery tube. If the setup is exactly as described above, ample clearance is assured.

Absorbing and Weighing Sample. Immediately after flushing the manifold and valve 4 as described above, couple the Saran delivery tube to the adapter on valve 4 and tighten it with pliers. Balance with rough weights, make certain that the delivery tube does not hinder the balance swing, then add a 20-gram weight to overbalance the tube. Carefully open valve 4 and adjust the flow of boron trifluoride, so that no cloud appears over the top of the ice in the weighing tube. During the flow, watch the top of

the weighing tube for the appearance of a cloud in the ice and as soon as noticed reduce the flow. Keep testing the balance to make certain that its swing is not hindered by shifting ice. After the 20-gram weight is slightly overbalanced, close valve 4, disconnect the Saran delivery tube, and carefully drop it into the weighing tube before removing from balance. Tightly stopper the weighing tube without delay.

Weigh on the torsion balance, adding more analytical weights. Record the additional weight over the ice weight as the water-soluble sample weight. Mix thoroughly by careful inversion until all the ice melts, being certain to keep the tube tightly stoppered, so that none of the liquid is lost before the solution becomes homogeneous. Remove the Saran delivery tube and restopper immediately to avoid loss of sulfur dioxide. The diluted acid clinging to the Saran delivery tube is of no consequence, since aliquot weights of the solution are taken for analysis. Proceed with the determination of water-soluble gases as described below.

ANALYSIS

Air. Connect one end of the sampling tube, *B*, to a 500-ml. leveling bulb containing 400 ml. of sodium chloride solution (300 grams dissolved in 1.0 liter of water) and the other end to a gas buret also filled with the sodium chloride solution. Take care to have no air bubbles in these connections. A trace of a wetting agent such as Ultrawet (Atlantic Refining Co.) in the salt solution assists in freeing small air bubbles from the walls of connecting tubes. Clamp *B* in a vertical position and allow the solution in the leveling bulb to run up into *B*, rapidly at first but slowly at the end, lest the impact of the solution break the glass. After absorption is complete, draw the insoluble gas into the buret and record the volume of air and the buret temperature.

Sulfur Dioxide. This must be the first water-soluble constituent determined, because opening the weighing tube for other aliquot samples may result in loss of sulfur dioxide.

In a 250-ml. beaker place 50 ml. of water and exactly 10 ml. of standard 0.1 *N* iodide-iodate solution and weigh on a torsion balance. Place a 50-gram weight on the balance pan, then add the sample to the beaker until slightly overbalanced. Weigh to the nearest 0.5 gram. Immediately back-titrate the excess liberated iodine with standard 0.1 *N* thiosulfate, using starch solution as indicator.

Standardize the iodide-iodate solution against the standard thiosulfate under like conditions, substituting 50 ml. of water for the sample and making acid with 5 ml. of 1 to 1 sulfuric acid.

Calculate the equivalent thiosulfate for the aliquot to grams of sulfur dioxide in the entire water-soluble weight absorbed in *C* by the following equation, which also applies to the other water-soluble gases.

$$\frac{(\text{Ml. of standard solution}) \times (\text{factor } X) \times (\text{grams of ice} + \text{grams of sample})}{\text{grams of aliquot}} = \text{grams of } X$$

$$\text{Factor } X = (\text{normality of standard solution}) \times (\text{milliequivalent weight of } X)$$

$$1 \text{ ml. of } N \text{ thiosulfate} = 0.032 \text{ gram of } SO_2$$

The above procedure is satisfactory for the determination of sulfur dioxide in commercial boron trifluoride. It is accurate when the sulfur dioxide content is below 0.2%. Above this amount some may be lost when opening the sampling tube to remove the delivery assembly and weighing the aliquot.

When the sulfur dioxide content is much above 0.2% a more accurate procedure is to take a separate sample from the cylinder and with the ice add a measured excess of iodide-iodate solution and 5 grams of potassium iodide, then back-titrate the excess liberated iodine as above. By this more accurate procedure an increase of 0.05% over the recommended procedure may be expected when the content is around 0.75%.

Silicon Tetrafluoride. Weigh into a 75-ml. platinum dish 1 gram of reagent sodium fluoride and 5.0 grams of the sample. Add 5 ml. of 0.5 *N* hydrochloric acid and 5 ml. of water. Place the dish on a steam bath and stir with a plastic or platinum rod until the sodium fluoride dissolves. Evaporate to dryness, remove the dish from the steam bath, and add 20 ml. of ethyl alcohol and 10 ml. of carbon dioxide–free water.

The products formed when boron trifluoride is absorbed in ice are complex in behavior and not clearly understood. Gasselin (*5*) writes the equation as follows to account for the alkali consumed before and after the addition of glycerol or mannitol:

$$2BF_3 + 3H_2O \longrightarrow HBF_4 + H_3BO_3 + 2HF \quad (1)$$

This reaction is an oversimplification, since the fluoride ions of hydrofluoric acid are not found in this solution. It acts as if something like an easily hydrolyzed form of fluoboric acid (*5*) were present. In any case, hydrolysis and the buffered behavior seriously interefere with a direct titration of silicon tetrafluoride, the solution of which in water may be represented as follows:

$$3SiF_4 + 3H_2O \longrightarrow 2H_2SiF_6 + H_2SiO_3 \quad (2)$$

Evaporation of the solution with sodium fluoride containing some hydrochloric acid forms a mixture of salts consisting of sodium fluoborate, sodium fluosilicate, sodium acid fluoride, sodium fluoride, and sodium chloride. Assuming Equation 1 for the solution of boron trifluoride, the conversion upon evaporation would be as follows:

$$HBF_4 + H_3BO_3 + 2HF + 4NaF \longrightarrow NaBF_4 + H_3BO_3 + 3NaHF_2 \quad (3)$$

$$H_3BO_3 + 3NaHF_2 \xrightarrow{\text{Heat}} NaBF_4 + 2NaF + 3H_2O \quad (4)$$

$$2NaF + HCl \longrightarrow NaHF_2 + NaCl \quad (5)$$

$$2H_2SiF_6 + H_2SiO_3 + 6NaF \longrightarrow 3Na_2SiF_6 + 3H_2O \quad (6)$$

An excess of sodium fluoride is desirable to allow for variations in original boron trifluoride sample weights. The 1 gram called for in the method is a 33% excess for the 5-gram aliquot of a 20-gram sample in 140 grams of ice. The addition of hydrochloric acid is a convenient way of forming sodium acid fluoride (Equation 5), which aids the completion of the reaction shown in Equation 4. Alcohol is added to prevent partial hydrolysis of sodium fluoborate; sodium fluosilicate does not dissolve in 50% or stronger alcohol. Ethyl alcohol was used in this work. Methyl or isopropyl alcohols are fair substitutes.

Stir and break up the lumps until the salts become disintegrated. Add 5 drops of phenolphthalein indicator and titrate with 0.5 *N* sodium hydroxide to a pink color that remains permanent during 30 seconds of continuous stirring. (Sodium hydroxide should always be used for this titration; if potassium hydroxide is used potassium fluoborate precipitates and occludes some sodium acid fluoride which cannot be conveniently leached out. The sodium hydroxide should be silica-free. It should be stored in a wax-lined bottle or steel drum and not allowed to stand in a glass buret longer than necessary.) Disregard this titration (3.5 to 4.5 ml.) because the acidity is due to acid fluoride with which we have no concern except to neutralize it exactly. Pour the contents of the dish into a 250-ml. beaker. Nearly fill the dish with carbon dioxide–free water (at 25° C.), stir somewhat to aid solution of the insoluble residue, and pour into the beaker. Rinse the dish twice in this manner to dissolve and completely transfer contents to beaker. To the beaker add 10 more drops of phenolphthalein indicator and without delay titrate with standard 0.1 *N* alkali to a faint pink color remaining permanent 15 seconds. (Sodium fluoborate hydrolyzes in aqueous solution to a small extent. No serious error results if a 15-second end point is accepted.) This titration is equivalent to the four fluorine atoms in silicon tetrafluoride plus the reagent blank. Run the blank according to this procedure, substituting 5 ml. of water for the sample.

Calculate to grams of silicon tetrafluoride in the entire water-soluble sample weight absorbed in *C*, using the general equation given above under sulfur dioxide,

$$1 \text{ ml. of } N \text{ alkali} = 0.02600 \text{ gram of } SiF_4$$

EXPERIMENTAL

Because of the difficulty of preparing boron trifluoride free from silicon tetrafluoride, synthetic preparations of standards were made up from reagent hydrofluoric acid and boric acid corresponding to 20 grams of boron trifluoride in 140 grams of water. The proportions used were based on Equation 1. The boric acid used showed no silica when the ammonium molybdate colorimetric method (*3*) was used. The hydrofluoric acid used showed 0.003% of silicon tetrafluoride by the fixation method (*8*), which corresponds to 0.006% based on the 20-gram boron trifluoride preparation.

The calculated amounts of hydrofluoric acid, boric acid, and water were weighed into 500-ml. polyethylene bottles. Five

Table II. Determination of Silicon Tetrafluoride in Synthetic Standards

SiF_4 Present %	SiF_4 Found %	Deviation[a] %
0.006	0.02	0.03
0.006	0.02	0.01
0.006	0.02	0.01
0.11	0.11	0.00
0.11	0.10	0.01
0.21	0.22	0.01
0.21	0.19	0.02
0.51	0.49	0.02
0.51	0.50	0.01
1.01	1.05	0.04
1.01	1.10	0.09

[a] Most of these deviations are within the variations of the reagent blank which is ±0.02 from the average deducted.

standards were thus prepared (Table II). To four of these was added reagent sodium fluosilicate to make standards containing the equivalent of 0.10, 0.20, 0.50, and 1.00% silicon tetrafluoride based on 20 grams of boron trifluoride in addition to the amount introduced through the hydrofluoric acid. The reagent blank for the determinations of these synthetic standards averaged 0.35 ml. of 0.1 N alkali. Individual values of the blank titration were 0.28, 0.32, 0.40, and 0.40, which indicates that a variation of ±0.02% silicon tetrafluoride might be expected.

Sulfur Trioxide. Sulfur trioxide is not likely to be present. If present, it will be very little and may be disregarded in the final calculation.

On a torsion balance weigh 50 grams of the sample into a 400-ml. beaker and dilute to about 100 ml. Add a drop of methyl orange indicator and make slightly ammoniacal. Digest hot several minutes to hydrolyze fluosilicate, filter, and wash moderately with water. To the filtrate add 4 ml. of 1 to 1 hydrochloric acid, precipitate with barium chloride, and determine the sulfate in the usual manner.

Boron Trifluoride. Weigh a glass or platinum weighing bottle half-filled with water on the analytical balance. Add as quickly as possible 50 to 60 drops (3 to 4 grams) of the solution of the sample by means of a dropping pipet, cover the bottle promptly, and reweigh. Carefully wash the sample into a 300-ml. Erlenmeyer flask containing 5 grams of neutral calcium chloride dissolved in 25 ml. of water, add one drop of methyl orange indicator, and titrate with standard 0.5 N alkali to a yellow color. Record this titration and all succeeding titrations. Heat to a gentle boil and digest at about 90° C. for 10 minutes. Titrate the hot solution to an approximate end point. If the sulfur dioxide content is above 0.2% the methyl orange indicator may be destroyed. In such cases the solution should be cooled somewhat and another drop of indicator added before titration.

Repeat the boiling and digestion, until only 1 ml. or less of alkali is required to reach an approximate end point. Boil and digest at 90° C. for 30 minutes. Cool to room temperature and titrate to an exact end point. Repeat the boiling, 30-minute digestion, and cooling until no more acidity develops. The total amount of alkali required is equivalent to sulfur dioxide, silicon tetrafluoride, and boron trifluoride. Calculate to grams of boron trifluoride in the total water sample weight, using the general equation given under sulfur dioxide, and from this value deduct the sum of: grams of sulfur dioxide × 0.706, and grams of silicon tetrafluoride × 0.869 to obtain grams of boron trifluoride,

$$1 \text{ ml. of } N \text{ alkali} = 0.02260 \text{ gram of } BF_3$$

Calculations. The above determinations on the water-soluble gas give the grams of each constituent in the sample. In order to calculate weight percentage of each, a calculated weight of the air (the insoluble gas) must be added to obtain the true sample weight.

The insoluble gas is assumed to be air and the volume measured (over salt solution) is corrected for moisture and temperature in order to have it under the same conditions as the gas in sample tube B.

$$\text{Milliliters of air in } B = \text{ml. measured} \left[\frac{P - p}{P} \times \frac{273 + t'}{273 + t''}\right]$$

t' = temperature of B when sample tube is filled

t'' = temperature of buret when air is measured

p = vapor pressure of 23 weight % sodium chloride solution (6) at t''

P = barometric pressure

The barometric pressure has little effect when the percentage is small. Table III gives approximate values for the factor $\left[\frac{P - p}{P} \times \frac{273 + t'}{273 + t''}\right]$, which are applicable at barometric pressures from 720 to 760 mm.

The ratio of the corrected volume of air in B to the volume of water-soluble gas in B $\left[\frac{\text{ml. of air in } B}{(\text{volume of } B \text{ in ml.}) - (\text{ml. of air in } B)}\right]$ permits the calculation of a weight of air corresponding to the water-soluble sample in C as follows:

$$\text{Grams of air} = L_N(\text{air}) \times \left[\frac{\text{ml. of air in } B}{(\text{volume of } B \text{ in ml.}) - (\text{ml. of air in } B)}\right] \times \left[\frac{\text{grams of } BF_3}{L_N(BF_3)} + \frac{\text{grams of } SO_2}{L_N(SO_2)} + \frac{\text{grams of } SiF_4}{L_N(SiF_4)}\right]$$

L_N ( ) is the density of the respective gases at 0° C. and 760 mm. Substituting these values, the equation becomes

$$\text{Grams of air} = 1.29 \times \left[\frac{\text{ml. of air in } B}{(\text{ml of } B) - (\text{ml. of air in } B)}\right] \times [(\text{grams of } BF_3 \times 0.325) + (\text{grams of } SO_2 \times 0.34) + (\text{grams of } SiF_4 \times 0.21)]$$

True sample weight = water-soluble sample weight + grams of air.

$$\% BF_3 = \frac{\text{grams of } BF_3 \times 100}{\text{true sample weight}}$$

$$\% SO_2 = \frac{\text{grams of } SO_2 \times 100}{\text{true sample weight}}$$

$$\% SiF_4 = \frac{\text{grams of } SiF_4 \times 100}{\text{true sample weight}}$$

$$\% \text{ Air} = \frac{\text{grams of air} \times 100}{\text{true sample weight}}$$

Table III. Correction Factors for Air Volume

Temperature t' of B When Filled, ° C.	Temperature t'' of Buret 19° C.	20° C.	30° C.	40° C.
10	0.99	0.95	0.92	0.85
20	1.02	0.98	0.94	0.88
30	1.06	1.01	0.97	0.91
40	1.10	1.05	1.00	0.94

DISCUSSION OF RESULTS

Table I shows the analysis of some cylinders of boron trifluoride. The variation in silicon tetrafluoride originates in the raw materials, while sulfur dioxide and air result from the process of manufacture.

The sampling procedure developed for anhydrous hydrofluoric acid has been adapted to boron trifluoride.

Procedures for the determination of air and sulfur dioxide are essentially those in common use.

The procedure for silicon tetrafluoride is new, in that after conversion of boron trifluoride to a stable salt the differential hydrolysis of fluosilicate can be titrated. This was found to be reasonably exact, even though a relatively large but constant reagent blank is involved.

Total acidity corrected for sulfur dioxide is essentially a determination of total fluorine which after correction for silicon tetrafluoride is calculated to boron trifluoride. This is permissible, since no appreciable amounts of other acidic gases are to be expected in commercial boron trifluoride. The correction for sulfur dioxide may be uncertain, because of small losses in steps subsequent to the absorption of the sample in ice, especially when the

sulfur dioxide content is in excess of 0.2%. A total boron determination is not usually required for commercial boron trifluoride. However, experiments not reported above have shown that if the heating periods in the presence of calcium chloride solution for total acidity are carried out under a reflux condenser the total boron as boric acid can be titrated as a second step after adding glycerol, invert sugar, or mannitol.

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Solid Polyethylene Glycols (Carbowax Compounds)

Quantitative Determination in Biological Materials

C. BOYD SHAFFER AND FRANCES H. CRITCHFIELD, *Mellon Institute, Pittsburgh, Pa.*

Two methods are described for the quantitative determination of the solid polyethylene glycols (Carbowax compounds) in biological materials. These methods, one gravimetric, the other colorimetric, are based upon a reaction of the polyglycols with the heteropoly acids, silicotungstic and phosphomolybdic. Certain features of this reaction are discussed, and evidence is presented to demonstrate its applicability to the estimation of the polyglycols in plasma and urine.

THE polyethylene glycols are compounds of the general formula

$$HOCH_2(CH_2OCH_2)_nCH_2OH$$

The lower members of this series, diethylene glycol and triethylene glycol, have been familiar industrial chemicals for some years. More recently, there has come into production a series of polyethylene glycols of higher molecular weight, not as separate and distinct compounds, but as mixtures of individual polymers. There are now available in this group four liquids and five solids, the solids being sold under the trade-mark name of Carbowax compounds (Carbide and Carbon Chemicals Corporation). Each product represents a band of molecular weights, the average of which (except in the case of Carbowax compound 1500) is employed in characterizing that particular member of the series. The exception noted is a blend of substantially equal weights of polyethylene glycol 300 and Carbowax compound 1540. The liquid compounds are thus known as polyethylene glycols 200, 300, 400, and 600, and the solids as Carbowax compounds 1000, 1500, 1540, 4000, and 6000.

By their combination of unique chemical and physical properties, the solid polyethylene glycols have become well established in a number of major pharmaceutical applications. In consequence of their widespread use and in anticipation of their future possibilities, an extensive study of their pharmacological properties was initiated in this laboratory several years ago. It was early shown (*5, 6*) that the polyethylene glycols are substances of a very low order of acute toxicity both by mouth and on the skin. Positive information on their absorption, intermediary metabolism, and excretion from the body has been lacking, primarily because no method has been available for their detection and estimation in blood and excreta.

The low order of chemical reactivity of the polyethylene glycols, coupled with the fact that they are actually mixtures, renders the formulation of an analytical method extremely difficult. In the course of a considerable amount of investigation toward this end, the only reaction of any practical analytical significance that they have been observed to undergo is the formation in acid solution of highly insoluble complexes with the heteropoly inorganic acids, such as phosphomolybdic and silicotungstic, in the presence of a heavy metal cation such as barium. No explanation is offered of the mechanism of this reaction, but it has proved useful as a basis for the quantitative determination of the solid polyethylene glycols. Two methods have been devised.

In the gravimetric method, the polyglycol is precipitated in hydrochloric acid solution with silicotungstic acid and barium chloride, and the precipitate is filtered, washed, dried, and ignited at 700° C. in a muffle furnace. The residue, consisting of the mixed oxides of barium, silicon, and tungsten, is weighed. The amount of polyglycol originally present in the sample is calculated from the weight of residue by means of an empirical factor determined from known quantities by this method. This procedure is suitable for quantities of polyglycol of the order of 5 to 100 mg. where an ordinary macroanalytical balance is used.

In the colorimetric modification the polyglycol is precipitated from the sample in a small centrifuge tube by the addition of barium chloride and phosphomolybdic acid. The precipitate is isolated and washed by repeated centrifugation, following which it is digested in concentrated sulfuric acid. The digest is diluted, neutralized, and made up to a definite volume, in an aliquot of which molybdenum is determined. The useful range of this method is of the order of 0.05 to 1.0 mg. of polyglycol at a minimum concentration of 0.01 mg. per ml. Phosphomolybdic is substituted for silicotungstic acid in this case because molybdenum can be determined somewhat more satisfactorily than tungsten.

Owing to the variation in useful range of the two methods, the colorimetric modification has been applied principally to whole blood and plasma, while the gravimetric technique is used almost exclusively for urine.

REAGENTS

Silicotungstic Acid, 10%. Dissolve 10 grams of silicotungstic acid ($4H_2O.SiO_2.12WO_3.22H_2O$) in a small quantity of water and neutralize with 10% sodium hydroxide to a methyl red end point. Dilute to 100 ml.

Hydrochloric Acid, 1 to 4. Dilute 1 volume of concentrated hydrochloric acid to 4 volumes with water.

Barium Chloride, 10%.

Phosphomolybdic Acid, 10%.

Phenylhydrazine Sulfate (for molybdenum determination). Dilute 3 ml. of concentrated sulfuric acid to 60 ml. with water and add 3 ml. of freshly distilled phenylhydrazine. Shake well to dissolve the precipitate and dilute to 100 ml. Store in a brown glass bottle and refrigerate when not in use.

METHODS

Pretreatment of Samples. Filtrates of whole blood or plasma that are completely free from traces of protein are suitable for analysis, provided they are not prepared with tungstic or molybdic acids. In the present work, preference has been given to Somogyi's (*7*) zinc sulfate–barium hydroxide precipitation of plasma proteins. Sulfate will obviously interfere in the gravimetric method, and, while it should theoretically not affect the colorimetric method, it is considered desirable to remove it in this case as well. Despite careful balancing of the zinc sulfate and barium hydroxide solutions, it has been the authors' experience that filtrates of plasma prepared in this manner invariably contain excess sulfate. The latter may be removed by precipitation with barium immediately prior to precipitation of the polyglycol.

In the analysis of urine by the gravimetric method, Fiske's ferric acetate treatment has been found satisfactory for the removal of interfering substances, with the exception of sulfates, from average, normal urines. The procedure is carried out as described by Hoffman (*2*), who states that the basic ferric precipitate removes not only phosphates but also protein, lipoids, and any debris present along with a large part of the urinary pigment. The filtrate from the ferric acetate precipitation must undergo further treatment for the removal of sulfate. For this purpose an aliquot of the filtrate is diluted to 50 ml., 4 ml. of concentrated hydrochloric acid are added, and sulfates are hydrolyzed and precipitated according to Folin's directions (*4*) for the determination of total sulfate in urine. After removal of the barium sulfate by filtration, the filtrate, including washings, is ready for precipitation of the polyglycol contained therein according to the procedure given below.

The experience of handling a large number of control blood and urine samples has demonstrated that these methods of pretreatment are effective in removing substances ordinarily present in the body fluids that might form insoluble products with silicotungstic or phosphomolybdic acids. Specimens from subjects receiving certain types of medication—e.g., cinchona alkaloids—would present individual problems. In some instances, as in the foregoing example, the interference could be removed by ether extraction of the sample. In connection with the question of of interfering materials it seemed desirable to test the reaction of certain metabolites and related substances with silicotungstic acid. It was found that glycine, tyrosine, methionine, cystine, cysteine, choline, creatinine, uric acid, allantoin, phenol, catechol, and hydroquinone in 50-mg. amounts form no precipitate with silicotungstic acid under the conditions of this determination.

Gravimetric Procedure. The sample, freed of interfering materials, is placed in a 600-ml. beaker and 10 ml. of 1 to 4 hydrochloric acid and 10 ml. of 10% barium chloride solution are added. For ease of subsequent filtration it is desirable that the quantity of polyglycol present be less than 0.1 gram. In the case of urine treated according to the above scheme, sufficient hydrochloric acid and barium chloride are already present at the conclusion of the procedure, so that additional quantities of these reagents need not be added. The contents of the beaker are diluted to about 250 to 300 ml. and brought to a boil on a burner or hot plate. At this point the polyglycol is precipitated with 10 ml. of silicotungstic acid added slowly from a pipet. The solution is boiled a few seconds in order to flocculate the precipitate, and the beaker is then covered and set aside for 8 to 12 hours. At the end of this time the precipitate is filtered with suction in a tared Gooch crucible previously ignited at 700° C. for 0.5 hour and cooled in room air. The precipitate is washed thoroughly with a minimum of 200 ml. of distilled water, dried in an oven at 110° C. for several hours, and transferred to a muffle furnace at 700° C. for consecutive 30-minute periods to constant weight. The temperature of ignition is important, as it is the optimal temperature which minimizes incomplete dehydration of the silicon oxide on the one hand and volatilization of tungsten oxide on the other (*8*).

Table I. Recoveries by Gravimetric Method of Carbowax Compounds Added to Human Urine

Carbowax Compound Added	Carbowax Compound 1000 Average recovery in duplicate determinations	Carbowax Compound 1000 Graduated values[a]	Carbowax Compound 6000 Average recovery in duplicate determinations	Carbowax Compound 6000 Graduated values[a]
Mg.	%	*Mg.*	%	*Mg.*
20	100.8	20.1	96.4	19.5
30	99.8	30.2	98.7	29.7
40	101.7	40.3	101.3	39.9
50	101.0	50.4	99.6	50.0
60	100.6	60.4	101.7	60.2
70	99.7	70.5	98.9	70.4
80	100.9	80.6	101.3	80.6

[a] Graduated values obtained by substitution of "Carbowax compound added" in straight-line equations calculated from recovery data by method of least squares.

It is not necessary to boil the solution upon adding the silicotungstic acid, as the precipitate appears to form almost equally as well in the cold. The gravimetric factor will be very slightly different in the latter case. In filtering the precipitate, it is important to prevent the crucible from running dry at any time during the process. If the precipitate is sucked dry it cakes and breaks into fragments, through the crevices of which the wash water channels.

Table I lists the results of a series of known amounts of Carbowax compounds 1000 and 6000 added to urine and recovery by the gravimetric method.

Colorimetric Procedure. Ten milliliters of a protein-free filtrate of plasma from which sulfate has also been removed are placed in an ordinary 15-ml. graduated centrifuge tube, to which are added, in the order given, 1 ml. of 1 to 4 hydrochloric acid, 1 ml. of 10% barium chloride, and 1 ml. of 10% phosphomolybdic acid. The solution must be stirred after each addition with a thin glass rod.

When addition of the reagents has been completed, the tube is allowed to stand for at least 1 hour, during which time a characteristic flocculent greenish precipitate forms by the interaction of the phosphomolybdic acid and any polyglycol present. The tube is then centrifuged at about 2500 r.p.m. for 10 minutes, and the supernatant solution is slowly and carefully drawn off without disturbing the precipitate. For siphoning off this fluid a capillary device such as the one described for washing calcium precipitates (*4*) is very useful. The precipitate and tube are washed with two portions of 0.1 *N* hydrochloric acid. In each washing 3 ml. of the acid are allowed to flow slowly from a pipet down the sides of the tube, so that the walls are washed about their entire circumference. The precipitate is then fragmented with the glass rod and suspended in the acid, following which the rod and the walls of the tube are rinsed down with about 7 ml. of distilled water. The tube is then recentrifuged and the washing process repeated.

After the final centrifugation the liquid is drawn off and the precipitate is transferred quantitatively to a 100-ml. Kjeldahl flask with a minimum amount of water. Three milliliters of concentrated sulfuric acid are next added to the contents of the flask, and the precipitate is digested with nitric and perchloric acids in the usual fashion. At the completion of this process, the sulfuric acid residue is cooled, diluted with about 20 ml. of water, and neutralized with 40% sodium hydroxide to a phenolphthalein end point. At this point, 1 or 2 drops of dilute sulfuric acid are added to bring the mixture just to the acid side of the indicator. The solution is then made up to 100 ml. in a volumetric flask.

Molybdenum is determined in the neutralized, diluted digest as follows (*1*, *3*):

A 10-ml. aliquot followed by 5 ml. of the phenylhydrazine solution is placed in an Evelyn colorimeter tube and the solutions are mixed by swirling. The tube is closed by a clean rubber stopper pierced by a fine capillary and placed in a hot-water bath at 81° ± 2° C. The tube is allowed to remain in the bath exactly 15 minutes, after which it is removed and allowed to cool to room temperature. The transmission of the contents is read in the colorimeter using filter 490, and setting the galvanometer to 100 with a blank carried through all the steps of the procedure. The polyglycol content of the original sample is then read from a standard curve prepared from a series of known quantities carried through the identical procedure. A plot of concentration against extinction is linear within the range of the instrument.

Table II. Recoveries by Colorimetric Method of Carbowax Compounds Added to Rabbit Plasma

Carbowax Compound Added	No. of Determinations	Carbowax Compound 1000 Mean recovery	Carbowax Compound 1000 Range	Carbowax Compound 1000 Graduated values[a]	Carbowax Compound 6000 Mean recovery	Carbowax Compound 6000 Range	Carbowax Compound 6000 Graduated values[a]
Mg. %		%	%	*Mg. %*	%	%	*Mg. %*
10	5	98	92–100	9.5	103	100–108	9.9
20	5	100	100	19.6	100	100	20.1
40	5	98	98	39.8	99	95–102	40.6
60	5	101	100–102	60.0	103	98–105	61.0
80	5	99	96–100	80.2	102	99–104	81.4
100	5	101	100–103	100.4	102	101–104	101.9

[a] Graduated values obtained by substitution of "Carbowax compound added" in straight-line equations calculated from recovery data by method of least squares.

DISCUSSION

Phosphotungstic, phosphomolybdic, or silicotungstic acid will form insoluble complexes with all the Carbowax compounds in acid aqueous solution. In the case of silicotungstic acid, polyglycols 200, 300, and 400 do not react with the formation of insoluble products in dilute acid aqueous solution where hydrogen is the only cation present. In this connection it became of interest to ascertain at what point in the polyglycol series the capacity to form precipitates with barium and silicotungstic acid commences. Therefore, approximately 200-mg. amounts of di-, tri-, tetra-, penta-, and hexaethylene glycols were submitted to the above procedure. It was found that pentaethylene glycol is the lowest member of the series to give this precipitate. This finding, however, does not exclude the possibility that some sort of reaction may take place with the first three glycols that does not involve formation of an insoluble product.

Reaction of Carbowax Compound 4000 with Silicotungstic Acid. Examined microscopically, the turbidity produced by silicotungstic acid with Carbowax compound 4000 in pure, dilute hydrochloric acid solution may be seen to consist of finely divided oily droplets, which, in the course of several hours' standing, coalesce to form a colorless, greasy film on the bottom of the container. If, however, sodium or ammonium ions are introduced into the solution, either by the addition of their chlorides or by previous partial neutralization of the silicotungstic acid with the corresponding hydroxides, a white, flocculent, solid precipitate forms which may be filtered. Although no attempt has been made to determine sodium or nitrogen quantitatively in these precipitates, they are presumed to be the sodium and ammonium salts of the polyethylene glycol–silicotungstic acid complex, since they do not form where these cations, or others except hydrogen, are absent. They, as well as the barium derivative, are referred to hereinafter as "salts" for want of better knowledge of their composition.

Samples of the isolated sodium salt melted at 234–6° C. (Fisher-Johns, uncorrected). Samples of the ammonium salt melted at 179–81°, and analyzed 18.45% carbon, and 62.5% residue after ignition at 700° C. It is assumed that this residue is $SiO_2.12WO_3$. No melting point is reported for the barium salt because it was consistently observed to undergo slight charring at 282–3° C.

Small quantities of the barium salt of the Carbowax compound 4000–silicotungstic acid complex were prepared for elementary analyses by precipitating the polyglycol under the conditions of the analytical procedure set forth above. The precipitates were washed with distilled water by repeated centrifugation and dried in a desiccator at room temperature. Drying was completed in a vacuum pistol at a temperature of 100° C. and a pressure of 0.005 mm. of mercury. The average of replicate analyses showed H = 2.160%, C = 11.685%, and residue = 77.225%. Chlorine was absent. The residue itself, consisting of the mixed oxides of barium, silicon, and tungsten, analyzed an average of 9.265% barium in duplicate determinations, and was carbonate-free. This figure approximates a theoretical value of 8.72% barium for a residue of the proportions $2BaO.SiO_2.12WO_3$.

Accurate interpretation of the composition of the unignited barium derivative from the carbon and hydrogen values reported above is obviously impossible without a knowledge of the exact mean molecular weight of Carbowax compound 4000. This molecular weight has variously been estimated at 3000 (Menzies-Wright) and 3590 (acetyl value). If we accept the former figure as the correct one, we may calculate an almost exact ratio of 1 mole of polyglycol to 4 moles of mixed oxides—i.e., 1 glycol to 4 ($2BaO.SiO_2.12WO_3$).

In the present state of our knowledge it is impossible to say with any certainty whether any water of composition or crystallization remains in the compound under the conditions of drying employed. However, it would seem from the slight discrepancy between the residue value obtained in the elementary analyses, 77.225%, and that which may be calculated from the gravimetric factor, 78.09%, that some water was present in the samples submitted for analysis. This inference is further borne out by the fact that the calculated value for percentage of polyglycol in the compound, based upon percentage of hydrogen found, is higher than that based upon either percentage of carbon, or percentage of residue. If water of composition or crystallization were present, the result based on the hydrogen value would be expected to be high.

Determination of Gravimetric Factors for Different Carbowax Compounds. Samples of all four Carbowax compounds, 1000, 1540, 4000, and 6000, were dehydrated in benzene and stored in a desiccator over phosphorus pentoxide. From these samples standard solutions of 2 grams per liter in distilled water were prepared and aliquots of each were analyzed in quadruplicate by the gravimetric procedure. From the results of the analyses, a gravimetric factor was calculated that defined the amount of each Carbowax compound represented per amount of residue weighed: Carbowax compound 6000, 0.2712; Carbowax compound 4000, 0.2808; Carbowax compound 1540, 0.2487; Carbowax compound 1000, 0.2544.

Variation of Gravimetric Factor among Different Batches of Carbowax Compound 4000. The gravimetric factors listed obviously can apply strictly only to those particular samples of polyethylene glycols under observation. As the Carbowax compounds used industrially are blends of production batches, the proportions of the components of which are varied to maintain constant physical properties, it seemed necessary to indicate the probable limits within which the factor for a given compound may vary, in view of the possible use of this method in estimating these compounds in miscellaneous commercial preparations.

Accordingly, samples were obtained of ten consecutive production batches of Carbowax compound 4000. Eight of these specimens were in the form of fine flakes; the other two resembled hard waxes. Portions of each were crushed and desiccated in vacuo overnight over phosphorus pentoxide, and a stock solution containing approximately 2 grams per liter was prepared for each sample. Aliquots of each stock solution were then submitted to the analytical procedure, and the ratio of ash to Carbowax compound was calculated. These ten examples on ignition produced residues ranging from 3.56 to 3.78 (mean 3.661 ± 0.004) mg. per mg. of desiccated polyglycol.

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Quantitative Separation of Barium from Strontium

GEORGE L. BEYER[1] AND WILLIAM RIEMAN III
School of Chemistry, Rutgers University, New Brunswick, N. J.

Methods are described for separation of barium from strontium by double precipitation of barium chromate and for subsequent determination of barium. Errors of 0.003 millimole or less are obtained with samples containing 1.0 to 0.01 millimole of barium and 10 millimoles of strontium. One-millimole quantities of cadmium, calcium, cobalt, copper, mercuric mercury, magnesium, manganese, nickel, or zinc do not interfere. Beryllium, aluminum, and large quantities of nitrate ion give low results.

THE published methods (*5*) for the quantitative separation of barium from strontium depend on the compensation of errors, and are not applicable to large ratios of strontium to barium. The frequently used method of Skrabal and Neustadtl (*12*) uses a double precipitation of barium chromate. These authors record errors of about 0.002 millimole with samples containing approximately 1 millimole of barium and various amounts of strontium and calcium. The directions given by Skrabal and Neustadtl, when tested by the authors on samples containing 1 millimole of barium and 0 to 5 millimoles of strontium, yielded negative errors of 0.02 to 0.07 millimole. Similar results were obtained at the Massachusetts Institute of Technology (*7*).

Several serious faults of this method were found: The pH of the precipitations was much above the optimum for the separation of barium from strontium, which would lead to large coprecipitation of strontium. The pH of the first precipitation varied from 5.6 to 5.9, and that of the second from 5.8 to 6.2, whereas the optimum pH is 4.6. No chromate was added before the second precipitation. Therefore, little or no excess chromate was present with samples containing no strontium, and loss of barium ensued. The first precipitation was performed in boiling solution, and both precipitations were made rather rapidly. Both these conditions produce loss of barium and excessive coprecipitation of strontium. The method described here decreases or eliminates these sources of error and presents procedures of wider applicability. The barium chromate is determined volumetrically by the iodometric method.

THEORETICAL

The optimum pH for the separation of barium from strontium under given conditions can be calculated with the aid of the equilibrium constants for the reactions concerned.

The general conditions adopted for the determination of one millimole of barium are as follows:

To a volume of 200 ml. are to be added 2.00 millimoles of dichromate ion; the ionic strength of the medium after precipitation is to be 0.090. One millimole of barium is to be determined with a loss of 0.00100 millimole of barium chromate due to solubility in the mother liquor. This barium-ion concentration, 5.00×10^{-6} mole per liter, together with the value (*2*) of the solubility product of barium chromate (1.06×10^{-9}) at this ionic strength, indicates that after precipitation a free chromate-ion concentration of 2.1×10^{-4} mole per liter is necessary to decrease the barium loss to the required value.

The chromate-ion concentration in solution is governed by the following reactions:

$$CrO_4^{--} + H^+ \rightleftharpoons HCrO_4^-$$

$$2HCrO_4^- \rightleftharpoons Cr_2O_7^{--} + H_2O$$

The equilibrium constants of these reactions have been determined by Neuss and Rieman (*8*).

$$\frac{[H^+]\,[CrO_4^{--}]}{[HCrO_4^-]} = 8.9 \times 10^{-7}$$

$$\frac{[HCrO_4^-]^2}{[Cr_2O_7^{--}]} = 0.013$$

By substitution of the known chromate-ion concentration and of the dichromate-ion concentration from the equilibrium constant of the second equation in the equation for the total chromium concentration,

$$[CrO_4^{--}] + [HCrO_4^-] + 2[Cr_2O_7^{--}] = 0.015$$

the hydrochromate-ion concentration may be obtained. Its value is:

$$[HCrO_4^-] = 0.00707$$

The hydrogen-ion concentration required for these conditions may be calculated by substitution in the equilibrium-constant equation for the second ionization of chromic acid, which gives:

$$[H^+] = 3.00 \times 10^{-5}$$

The activity coefficient of hydrogen ion (*6*, *11*) at an ionic strength of 0.090 is 0.84, so that the hydrogen-ion activity is 2.52×10^{-5}. This represents a pH of 4.60. This is the optimum pH for quantitative separation of barium from strontium, under these conditions, since the chromate-ion concentration present is the minimum for satisfactory precipitation of barium and will have the minimum tendency to cause coprecipitation of strontium.

The solubility product of strontium chromate reported by Davis (*3*) is 2.2×10^{-5} at 25° C. It has been calculated that if coprecipitation does not occur under the recommended conditions, 10 millimoles of strontium should cause no error in the determination of 1.0 millimole of barium.

It is realized, of course, that the ionic strength cannot always be adjusted to 0.09 in the analysis of an unknown sample. However, changes in ionic strength cause only minor changes in the equilibrium constants and therefore do not appreciably disturb the method.

REAGENTS

Approximately 0.1 *M* barium chloride was prepared from the reagent-grade salt in 0.01 *M* hydrochloric acid. The concentration of barium ion was determined by precipitation and weighing of barium sulfate; duplicate determinations agreed within 1 part per thousand.

Approximately 0.1 *M* strontium chloride was prepared from the reagent-grade salt whose barium content was 0.005% or less, as indicated by the test recommended by Rosin (*10*). The solution was standardized by precipitation of strontium sulfate with sulfuric acid, and evaporation of the water and excess acid.

Samples of reagent-grade salts of the following ions were weighed and used without further standardization: aluminum, cadmium, calcium, cobaltous, cupric, mercuric, magnesium, manganous, nickelous, and zinc chlorides, and beryllium nitrate.

Solutions of 0.40 *M* sodium dichromate, 1.31 *M* sodium acetate, and 2.0 *M* hydrochloric acid were prepared from reagent-grade chemicals within 5% of the recommended concentrations, since they control the pH of the precipitation.

The buffered wash solution used for most of the washing was designed to avoid appreciable loss of barium. Its composition was as nearly as possible that of the mother liquor after precipita

[1] Present address, Eastman Kodak Co., Rochester, N. Y.

tion—that is, 0.0075 *M* in dichromate ion, 0.0373 *M* in acetic acid, and 0.0328 *M* in alkali acetate. This was prepared by adding 2.23 grams of sodium dichromate ($Na_2Cr_2O_7 . 2H_2O$), 9.63 grams of sodium acetate ($NaC_2H_3O_2 . 3H_2O$), and 3.1 ml. of 12 *M* hydrochloric acid to enough water to make the volume 1 liter. Its pH was 4.60.

The final washing was made with water containing enough sodium hydroxide to raise its pH to 9 or 10.

For the analytical method, 0.1 *N* sodium thiosulfate was prepared and standardized by the usual methods (*9*). One-half per cent solutions of potato starch were preserved with mercuric iodide. Forty per cent solutions of potassium iodide were prepared fresh daily and were kept in subdued light.

PROCEDURES

To a sample containing 0.4 to 1 millimole of barium chloride and 0 to 10 millimoles of strontium chloride in a 400-ml. beaker, add 3.0 ml. of 2.0 *M* hydrochloric acid. Dilute to 185 ml., add 5.0 ml. of 0.40 *M* sodium dichromate, and then with continuous stirring introduce 10.0 ml. of 1.31 *M* sodium acetate through a constricted funnel designed to deliver this quantity in about 2 (±0.5) minutes. During this addition, the pH is raised sufficiently to permit the quantitative precipitation of barium chromate. Heat the suspension to boiling over a gas burner in 3 to 6 minutes and stir occasionally during the heating. When vigorous boiling is reached, remove the beaker from the flame, cool it rapidly to room temperature in a water bath, and allow it to digest for one hour at room temperature.

Pour the cold supernatant liquid through a medium-porosity sintered-glass filter crucible (Corning 30M) of about 30-ml. capacity. Wash the fine, granular precipitate in the beaker three times by decantation with about 20-ml. portions of the buffered wash solution. Transfer the precipitate to the crucible by washing with more of the same solution. Since a second precipitation is to be made, it is not necessary to remove that precipitate which clings to the beaker. Wash the precipitate on the filter with more wash solution, so that the total volume of wash solution used is 150 to 200 ml. Wash the precipitate and the crucible with 30 ml. of the basic wash solution added from a fine-tipped wash bottle.

Transfer the major part of the precipitate back to the beaker with a fine stream of water, applied so that about 10 to 20 ml. are required to remove all loose particles. That part still on the crucible (estimated to be about 0.5%) is not reprecipitated. Cover the crucible and set it aside. Dissolve the precipitate in the beaker by adding 3.0 ml. of 2.0 *M* hydrochloric acid and heating to boiling over a small flame. Cool the solution, dilute to 185 ml., and add 3.75 (±0.1) ml. of 0.40 *M* sodium dichromate. Reprecipitate the barium chromate at room temperature by adding 8.55 (±0.1) ml. of 1.31 *M* sodium acetate through the constricted funnel while stirring. Heat the suspension to boiling, cool, and allow to digest for 1 hour. Repeat the filtration and washing by decantation and wash the precipitate into the crucible containing the untreated residue from the first precipitation. This time, remove the particles clinging to the walls of the beaker by scrubbing with a rubber policeman and washing into the crucible. Wash the contents of the crucible until the washings total 150 to 200 ml. Then carefully wash the precipitate and crucible with a fine stream of alkaline water. No chromate should be detected in the filtrate after 30 ml. of this wash solution have been used. The presence of chromate may be tested by neutralizing a portion of the filtrate and adding silver nitrate.

Transfer the major part of the precipitate with water into a 500-ml. Erlenmeyer flask. Draw 50 ml. of 0.5 *M* hydrochloric acid followed by some water through the filter crucible into the flask. This dissolves the remaining residue. Dilute the solution in the flask to about 150 ml. and determine the chromate present by the iodometric method of Willard and Furman (*13*).

With 0.4- to 0.01-millimole samples of barium, follow the foregoing procedure, but after cooling each precipitate to room temperature, allow it to digest overnight, rather than for one hour.

The pH values of the filtrates, exclusive of the washings, were determined with a Beckman pH meter, laboratory model, although this step is not necessary for the separation.

RESULTS AND DISCUSSION

In addition to the determination of the optimum pH for the separation, a number of other conditions for the most satisfactory separation of barium from strontium have been studied (*1*). Sodium chromate is more soluble than either ammonium or potassium chromate. Accordingly the authors found that potassium and ammonium ions added as reagents were coprecipitated to a large extent when precipitation and digestion were performed at room temperature, whereas sodium ion did not coprecipitate in a measurable amount under these conditions. Therefore, sodium salts were chosen as reagents. However, much less contamination by ammonium ion was observed for samples precipitated at boiling, and it is expected that potassium would behave similarly.

The solubility product of barium chromate increases with rising temperature (*2*), whereas that of strontium chromate decreases (*3*). Therefore, it would be expected that the least coprecipitation of strontium chromate would occur at low temperatures. This was observed experimentally—1 millimole each of barium and strontium on single hot precipitation gave results high by 0.03 to 0.07 millimole, whereas cold precipitation under comparable conditions gave results 0.020 millimole high. However, the precipitates obtained by cold precipitation and digestion are fine-grained, so that filtration and washing are tedious. Larger crystals are produced by precipitation at boiling temperature, but greater coprecipitation of strontium and loss of barium occur. The procedure described combines the advantages of both conditions and produces filterable crystals without considerable increase in coprecipitation. This is accomplished by precipitating the barium chromate at room temperature, heating to boiling for a short time, then cooling and digesting at room temperature. Double precipitation is required for most samples.

Table I gives the results obtained in the determination of 1 millimole of barium in the presence of varying quantities of strontium, in which 1-hour digestion was used.

These results indicate that 1 millimole of barium may be determined with an average error of ±0.003 millimole, or 0.3%, in the presence of 0 to 10 millimoles of strontium. With the larger amounts of strontium, the pH values of the first mother liquors were low because of the hydrogen ions liberated upon the coprecipitation of strontium according to the equation:

$$Sr^{++} + H\dot{C}rO_4^- \longrightarrow SrCrO_4 + H^+$$

Table II summarizes the results obtained when various amounts of barium were determined in the presence of 10 millimoles of strontium, with 1-hour digestion.

From 1.0 to 0.4 millimole of barium can be determined with an average error of 0.003 millimole or less under these conditions. For quantities of barium from 0.3 to 0.1 millimole, however, the results are considerably low.

When overnight digestions were substituted for 1-hour digestions, the results shown in Table III were obtained.

Table I. Results with 0.990 Millimole of Barium

(One-hour digestions)

Sr Taken	Mean Error, Ba	Mean Deviation, Ba	No. of Determinations	Measured pH	
				First	Second
Mmol.	*Mmol.*	*Mmol.*			
	−0.003	0.000	3	4.59	4.60
1.0	+0.002	0.002	2	4.59	4.60
3	+0.002	...	1	...	4.60
5	−0.004	0.002	2	4.43	4.62
6	−0.003	...	1	4.45	4.61
7	−0.005	...	1	4.40	4.61
10	+0.001	0.001	3	4.48	4.62

Table II. Results with 10 Millimoles of Strontium

(One-hour digestions)

Ba Taken	Mean Error, Ba	Mean Deviation, Ba	No. of Determinations	Measured pH	
				First	Second
Mmol.	*Mmol.*	*Mmol.*			
0.990	+0.001	0.001	3	4.48	4.62
0.493	0.000	0.002	4	4.53	4.61
0.396	−0.004	0.001	3	...	...
0.297	−0.009	0.001	3	...	...
0.197	−0.006	0.002	4	4.58	4.61
0.098	−0.012	0.004	2	4.61	4.60

Table III. Results with 10 Millimoles of Strontium

(Overnight digestions)

Ba Taken	Mean Error, Ba	Mean Deviation, Ba	No. of Determinations	Measured pH First	Measured pH Second
Mmol.	*Mmol.*	*Mmol.*			
0.990	+0.009	0.002	3	4.48	4.62
0.493	+0.009	0.001	3	...	...
0.396	+0.001	0.000	4	...	...
0.297	0.000	0.001	4	...	...
0.197	+0.001	0.001	3	4.58	4.60
0.142	−0.001	0.002	4	4.63	4.60
0.098	0.000	0.000	3	4.60	4.61
0.049	+0.002	0.002	2	4.61	4.62
0.020	−0.003	0.001	6	4.61	...
0.010	−0.005	...	1	4.61	...

Samples containing 0.4 to 0.02 millimole of barium were determined within 0.003 millimole. However, 0.5 to 1.0 millimole of barium gave positive errors beyond the acceptable range. This behavior was unexpected, since the equilibrium between precipitate and mother liquor was reached (within experimental error) in 1 hour when 1 millimole of barium and no strontium was taken (Table I). Therefore, for samples containing 0.5 to 1.0 millimole of barium and 10 millimoles of strontium, a considerable change in composition of the precipitate must occur during overnight digestion. Duschak (*4*) has shown that considerable contamination of a pure barium chromate precipitate occurs on long digestion with strontium ion. Apparently, equilibrium in the recrystallization process is reached slowly, so that little contamination occurs during short digestion, but longer digestion leads to greater inclusion of strontium chromate.

Those samples containing 0.02 millimole or less of barium were precipitated only once, since the amount of strontium carried down was very small.

This method has been tested in the presence of a number of cations. One millimole of barium ion and 1 millimole of the metal chloride were mixed, and the solution was analyzed for barium. One-hour digestions were used. The results for cadmium, calcium, cobalt, copper, mercuric mercury, magnesium, manganese, nickel, and zinc were accurate within 0.003 millimole. Beryllium caused a negative error of 0.028 millimole, and the results with aluminum were 0.008 millimole low. The samples containing aluminum produced flocculent yellow precipitates and those with beryllium gave a white turbidity which did not disappear when the solution was acidified and heated after each precipitation. In these cases the hydroxides (or basic salts) may coprecipitate some barium hydroxide, thus preventing the quantitative precipitation of the barium as chromate.

Nitrate ion in large amounts produces low results with 1 millimole of barium. Five millimoles of sodium nitrate gave an error of −0.007 millimole, but 5 millimoles of sodium chloride caused no error. Two millimoles of sodium nitrate gave results within the allowable error. The low results are probably due to the coprecipitation of barium nitrate.

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Determination of Aromatics and Naphthenes in Complex Hydrocarbon Mixtures Containing Olefins

R. M. LOVE, A. R. PADGETT, W. D. SEYFRIED, AND H. M. SINGLETON
Humble Oil & Refining Company, Baytown, Texas

A relatively rapid method of analysis has been developed, utilizing simple equipment, for the determination of naphthenes and aromatics in complex hydrocarbon mixtures boiling in the range of 93° to 149° C. Interfering olefins and diolefins, if present, are removed by bromination and steam-distillation; after fractionation of the steam-distillate, the aromatics and naphthenes are determined in selected fractions from refractive indices before and after extraction with sulfuric acid. The method is accurate to about ±0.3% (absolute) on aromatics and about ±1.0% (absolute) on naphthenes.

A SIMPLE and rapid method of analysis for the naphthenes and aromatics boiling in the range of 93° to 149° C. in naphthas containing up to 40% olefinic compounds was required as a result of the construction of Baytown Ordnance Works to produce toluene from petroleum. Most of the toluene produced in the process utilized was made by dehydrogenation of methylcyclohexane. If this method of analysis were to be used as a routine control test for plant operation, the considerations of paramount importance were that it be as rapid as possible consistent with a reasonable degree of accuracy, that it be simple enough for analysts having a high-school education to perform in a routine manner with relatively little training, and that it require the use of no elaborate equipment that might easily get out of adjustment or be broken.

The methods of analysis that appeared promising for routine control were those of Grosse and Wackher (*4*) as supplemented by the Standard Oil Development Company (*3*), of Schneider, Stanton, and Watkins (*7*), and of Faragher, Morrell, and Levine (*2*). The method of Grosse and Wackher was relatively rapid but not satisfactory unless a five-place refractometer with elaborate accessory equipment was used, and the required calculations were rather cumbersome The method of Schneider, Stanton, and

Watkins was relatively rapid and gave accurate results for aromatics, but was not considered accurate enough for naphthenes. Difficulty was encountered with the method of Faragher, Morrell, and Levine in achieving complete removal of olefins, and the aromatic determinations on synthetic samples were low. These considerations led to the development of the present method, which was used successfully for routine control of the operations at the Baytown Ordnance Works for four years. During this time a number of refinements were made to improve its accuracy.

In this method the olefinic compounds are first removed from the hydrocarbon mixture by bromination by the Lewis and Bradstreet modification of the Francis method (*5*), followed by steam-distillation to separate the bromides from the unreacted hydrocarbons. The olefin-free distillate is then separated into fractions of the desired boiling ranges by distillation, and the selected fractions are extracted with 93–94% sulfuric acid to a constant refractive index (n_D^{20}). The aromatic content of the fractions is calculated from the change in the refractive index upon acid extraction, and the naphthene content of the fractions is calculated from the refractive index after acid extraction and the averages of the refractive indices of pure paraffins and of pure naphthenes in the same boiling range as the fraction.

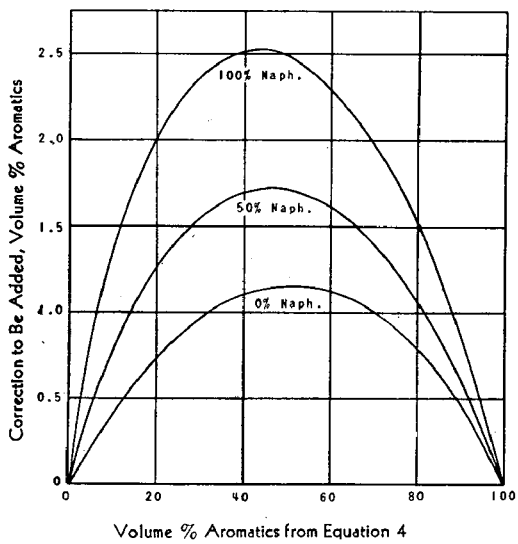

Figure 1. Correction Factor for Calculation of Aromatics

PROCEDURE

Obtain the bromine number of the sample. If the bromine number (centigrams of bromine per gram of sample) is 1.0 or less, the bromination and steam-distillation may be omitted. If the bromine number is between 1.0 and 10.0, charge 700 cc. of sample to a bromination flask equipped with stirrer, reflux condenser, and bottom draw-off tube. For each additional increase of 10.0 or a fraction thereof in bromine number, charge an additional 100 cc. of sample. Immerse the bromination flask in an ice water bath, start the stirrer, and slowly add approximately 1 *N* potassium bromide–bromate solution and 10% sulfuric acid in the ratio of approximately 3 to 1 to the flask until a deep orange color is maintained in the hydrocarbon layer after 2 minutes of agitating without the addition of reagents. Remove the contents of the flask, separate the hydrocarbon layer, and wash first with 10% sodium hydroxide solution containing 1% sodium sulfite and then with water. Measure the volume and temperature of the hydrocarbon sample and charge to the steam-distillation apparatus. This apparatus consists of a 1-liter or 2-liter flask equipped with a steam inlet tube and a fractionating column 2.5 cm. (1 inch) in diameter packed to a height of 20 inches with glass beads or helices.

Steam-distill the sample until small samples of distillate caught in a separatory funnel become heavier than the condensed steam (as evidenced by sinking toward the bottom of the water layer). Discontinue the distillation and measure the volume and temperature of the distillate. Wash the distillate successively with dilute sodium hydroxide solution and water and filter through several thicknesses of filter paper. Correct the volumes of charge to the steam-distillation flask and of the steam-distillate to 15.5° C. (*6*) and calculate the per cent recovered, based on the charge. Determine the bromine number of the filtered distillate and, if it is above 1.0, repeat the bromination and steam-distillation. Over-all recoveries on samples requiring more than one bromination and steam-distillation are obtained by multiplying the recoveries from individual steam-distillations.

Table I. Weighted Refractive Indices of Aromatics in Various Boiling Ranges

Boiling Range, ° C.	Compounds	n_D^{20} Used
93–122	Toluene	1.4969
122–136	Xylenes and ethylbenzene	1.4963
136–149	Xylenes and ethylbenzene	1.4983

Carefully measure 500 cc. of sample or of steam-distillate into a 40-plate fractionating column (total reflux basis), together with 200 cc. of chaser liquid having an initial boiling point of 165° to 175° C. After flooding the column to wet the packing thoroughly, start the distillation and adjust the conditions to obtain the equivalent of 6 to 8 cc. per minute boilup rate in a 0.75-inch column and 5 to 1 reflux ratio. Record the top vapor temperature every 2% and separate and measure the fractions boiling from the initial boiling point to 93°, 93–96°, 96–107°, 107–115°, 115–122°, 122–127°, 127–136°, and 136–149° C. Determine the refractive index (n_D^{20}) on each fraction in the 93° to 149° C. range. Measure approximately 10 cc. of each fraction into a Babcock bottle containing 25 cc. of 93–94% sulfuric acid and shake for 15 minutes in an efficient shaking machine. Add a sufficient quantity of acid to displace all of the hydrocarbon sample into the neck of the bottle and centrifuge the mixture for 15 minutes at 1300 r.p.m. Determine the refractive index (n_D^{20}) of the hydrocarbon sample. Remove the acid layer from the Babcock bottle and repeat the extraction, using fresh 93–94% acid. Continue the extractions until an additional extraction changes the refractive index of the sample no more than 0.0002 unit.

CALCULATIONS

The volume per cent aromatics in each fraction of the hydrocarbon mixture is calculated by the following equation:

$$A = \left(\frac{R_U - R_E}{R_A - R_E} \times 100\right) + C \qquad (1)$$

where A is the volume per cent aromatics in the fraction, R_U is the n_D^{20} of the unextracted fraction, R_E is the n_D^{20} of the extracted fraction, R_A is the n_D^{20} of the aromatics of the corresponding boiling range (Table I), and C is a correction factor obtained from Figure 1.

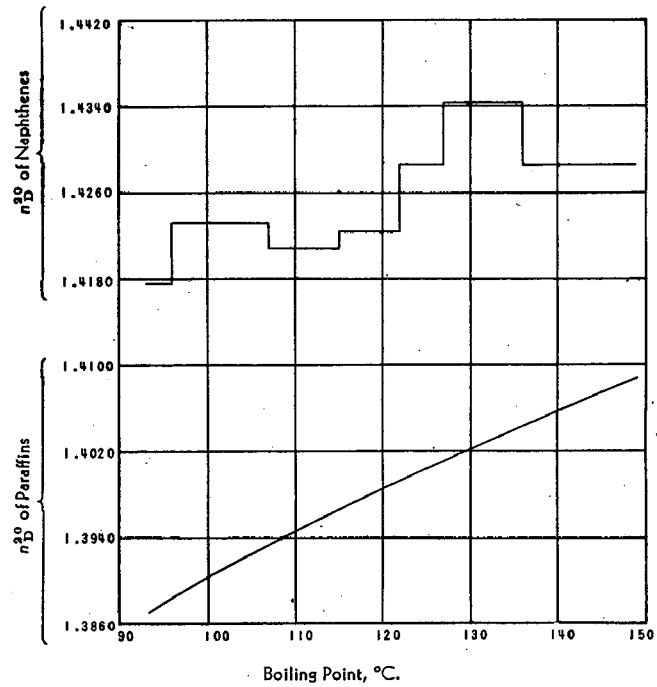

Figure 2. Refractive Indices of Paraffins and Naphthenes

Table II. Development of Correction Factor for Bromination and Steam-Distillation Recovery Calculations

Bromine No. of hydrocarbon charge to bromination	55.1
Volume of hydrocarbon charge to bromination	100.0
Volume of brominated hydrocarbon	107.0
Bromine No. of brominated and steam distilled hydrocarbon	2.1

$$\text{Correction factor} = 1 + \frac{107.0 - 100.0}{(55.1 - 2.1)100} \times \text{bromine No. reduction}$$
$$= 1 + 0.00132 \times \text{bromine No. reduction}$$

Table III. Effect of Degree of Fractionation and Method of Determining Cut Points on the Results of Methylcyclohexane and Toluene Determinations

	115-Plate Column, 30:1 Reflux Ratio, Extraction of 1% Fractions	40-Plate Column, 5.1 Reflux Ratio	
		Extraction of 2% fraction	Extraction of broad fractions, present procedure[a]
Sample 1[b]			
Methylcyclohexane, %	20.7	20.3	20.0
Toluene, %	2.5	2.3	2.4
Sample 2[b]			
Methylcyclohexane, %	...	31.8	31.2
Toluene, %	....	20.2	19.9
Sample 3[b]			
Methylcyclohexane, %	22.7	...	21.8
Toluene, %	10.9	...	10.7

[a] 93°–96°, 96°–107°, and 107°–122° C. fractions analyzed for toluene; 96°–107° C. fraction analyzed for methylcyclohexane.
[b] None of these samples contains unsaturates. Samples 1 and 3 are light naphtha from nonaromatic and aromatic crudes, respectively. Sample 2 was prepared by adding methylcyclohexane and toluene to a light naphtha from an aromatic crude.

The volume per cent naphthenes in each fraction is calculated by the following equation:

$$N = \frac{R_E - R_P}{R_N - R_P}(100 - A) \qquad (2)$$

where N is the volume per cent naphthenes in the fraction, R_P is the average n_D^{20} of the paraffins of the corresponding boiling range and R_N is the average n_D^{20} of the naphthenes of the corresponding boiling range. The average boiling point is calculated from the temperatures taken every 2% during the distillation, and R_P and R_N are then read from Figure 2 or from a table prepared from Figure 2.

After A and N have been determined for each fraction, the toluene content of the charge to the fractionating column is obtained as the weighted summation of the A values of the fractions in the 93° to 122° C. boiling range; in the same manner the methylcyclohexane is obtained from the N value of the 96° to 107° C. fraction, the C_8 naphthenes from the N values of the fractions in the 107° to 136° C. boiling range, and the C_8 aromatics from the A values of the fractions in the 122° to 149° C. boiling range.

The per cent of each component in the original sample (before bromination) is obtained by multiplying the per cent of the component in the charge to the fractionating column by the corrected recovery from the bromination and steam-distillation. The corrected recovery from the bromination and steam-distillation is calculated by the following formula:

$$R_C = R(1 + 0.00132B) \qquad (3)$$

where R_C is the corrected recovery, R is the uncorrected recovery, and B is the bromine number reduction by bromination and steam-distillation.

EXPERIMENTAL

Bromination and Steam-Distillation. Bromination of a sample containing unsaturates results in an increase in volume of the sample. Therefore, the recovery from the bromination and steam-distillation steps should be calculated on the basis of the volume of charge to the bromination and the volume of overhead distillate from the steam-distillation and not from the volume of the brominated sample charged to the steam-distillation and volume of overhead distillate from the steam-distillation. However, in performing the bromination step under routine conditions, it was found that an excessive amount of time would be consumed in effecting complete separation of hydrocarbon from aqueous solutions after the addition of brominating reagents and washing solutions. Therefore, the increase in volume on bromination was determined on typical mixtures containing olefins and a correction factor was developed (Table II) which would allow the calculation of recovery based on the charge to the steam-distillation and overhead from the steam-distillation. This correction factor is shown in the section on calculations.

Effect of Degree of Fractionation and Separation of Narrow and Broad Fractions. The procedure used during the early development work required the analysis of 1% fractions obtained by distillation in a very efficient distillation column at 30 to 1 reflux ratio. This column was shown to have the equivalent of 115 plates when measured in the usual manner with n-heptane and methylcyclohexane. The concentration of a particular naphthene was calculated as the sum of the naphthene contents of the 1% fractions occurring between the low points of the refractive index curves after acid extraction. For example, the methylcyclohexane content of the sample illustrated by Figure 3 was calculated as the sum of the naphthene contents of the 1% fractions occurring between 35 and 70% (93° to 106° C. boiling range). The toluene content was calculated as the sum of the aromatic contents of the fractions boiling between 93° and 122° C.

This procedure was practically valueless as a routine control test because of the excessive time requirements. In an effort to reduce this time requirement to a few hours without seriously reducing analytical accuracy, the present procedure involving the separation, by less precise fractionation, of broad fractions for analysis was developed. The data of Table III show that this modification did not seriously impair accuracy, whereas the time requirement was reduced from several days to 12 to 14 hours.

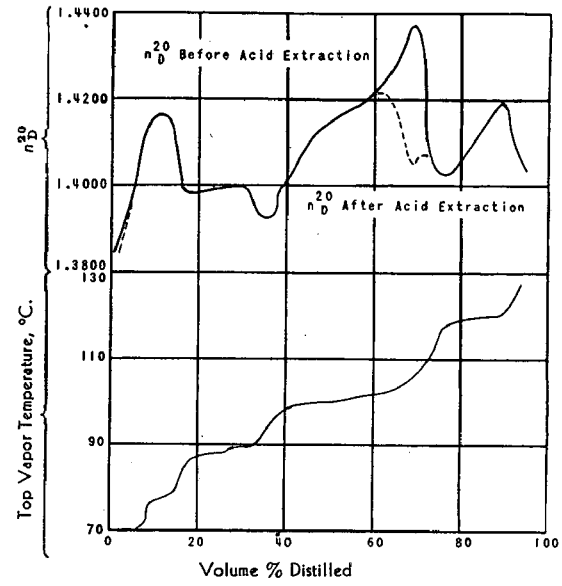

Figure 3. Distillation Curve and Refractive Indices of Typical Naphtha

Effect of Acid Strength. The use of sulfuric acid to remove aromatics from a mixture of hydrocarbons necessitated an investigation of the optimum strength of acid which would completely remove the aromatics with a minimum of extractions and yet would not react with nonaromatic compounds. The data shown in Tables IV and V are typical of the data obtained in this investigation and indicate that an acid strength of 93 weight % is optimum.

Refractive Indices of Hydrocarbons. The values for the refractive indices of pure aromatics and naphthenes were obtained from Doss (*1*) and the values for the pure paraffins are those reported by Ward and Kurtz (*8*). In cases in which more than one of the components was present in a given fraction, the refractive index used in the calculations was computed as a weighted average.

Table IV. Effect of Acid Strength on Extraction of Naphthenes and Paraffins

Composition	Shaking Time, Minutes	H_2SO_4 Strength, Weight %	n_D^{20} before Acid Extraction	n_D^{20} after Acid Extraction
Dimethylhexanes[a]	60	99.4	1.3973	1.3929
	60	96.0	1.3973	1.3968
	60	95.3	1.3973	1.3964
	60	93.0	1.3973	1.3970
	60	92.9	1.3973	1.3973
	60	90.0	1.3973	1.3971
n-Heptane	60	99.4	1.3882	1.3883
85% *n*-heptane, 15% methylcyclohexane[b]	20	93.3	1.3929	1.3929
70% *n*-heptane, 30% methylcyclohexane	20	93.3	1.3980	1.3980
	20	96.0	1.3980	1.3981
	20	99.0	1.3980	1.3981
	20	103.0	1.3980	1.3951

[a] A fraction from product of alkylation of isobutane with butenes.
[b] Relatively impure; n_D^{20} 1.4205.

Table V. Removal of Toluene from a Hydrocarbon Mixture by Successively Extracting with 93% Sulfuric Acid Until a Constant n_D^{20} Is Reached

Toluene	Aromatic-Free Hydrocarbon Distillate	n_D^{20} before Acid Extraction	n_D^{20} after Acid Extraction
0	100	1.4008	1.4008
20	80	1.4190	1.4008
40	60	1.4380	1.4008
50	50	1.4471	1.4008
60	40	1.4569	1.4008
80	20	1.4762	1.4008

The values used for the refractive index of the C_8 aromatics in the 122° to 136° C. fraction and in the 122° to 152° C. fraction were calculated from the values for the pure compounds on the assumption that the compounds were present in the ratios obtained by averaging the ultraviolet analyses of several naphthas, as shown in Table VI. The ultraviolet analyses differed very little from one naphtha to another. The value of n_D^{20} for the 136° to 149° C. aromatics was assumed to be the same as for the 122° to 152° C. fraction in early analyses but was later modified to 1.4983 as a result of experimental values obtained on purified aromatics in the 136° to 149° C. range.

The values for the naphthenes presented a more serious problem because there is a larger number of isomers in a given boiling range than in the case of the aromatics and yet not a sufficiently large number to make a smooth average refractive index curve as in the case of the paraffins. In the 93° to 96° C. range the value is not critical because the naphthene content is used only for correcting the aromatic content. It was assumed that the average of the refractive indices for *trans*-1,2-dimethylcyclopentane and for methylcyclohexane would be sufficiently accurate.

Although three possibilities exist in the 96° to 107° C. fraction, only methylcyclohexane was assumed to be present. This assumption was made on the basis of the analysis of some highly naphthenic naphthas from Coastal crudes in which it was found that the acid-extracted fraction in this boiling range had a refractive index very close to that of pure methylcyclohexane. Ethylcyclopentane and *cis*-1,2-dimethylcyclopentane have considerably lower refractive indices. Pure ethylcyclopentane would be calculated as 90% naphthenes by the use of the curves in Figure 2.

For the trimethylcyclopentanes, the naphthenes present in the 107° to 115° C. range, it was assumed that the 1,1- isomer is not present and that the 1,2,3- and 1,2,4- isomers are present in equal amounts.

In computing the values of the various dimethylcyclohexanes, it was assumed that the various isomers are present in approximately the ratio of the xylenes in Table VI (lower), that there is present twice as much of the trans form as the cis form, and that neither *cis*-1,2-dimethylcyclohexane nor 1,1-dimethylcyclohexane is present in the 115° to 127° C. fraction. The *cis*-1,2-dimethylcyclohexane is outside the boiling range and the structure of 1,1-dimethylcyclohexane makes its presence in significant quantities improbable.

Table VI. Ratio of Aromatics *in Typical* Naphthas as Determined by Ultraviolet Analysis

Compound	Volume Per Cent	Refractive Index
	122°–136° C. Fraction	
Ethylbenzene	52	1.4959
p-Xylene	15	1.4958
m-Xylene	33	1.4971
Weighted average		1.4963
	122–152° C. Fraction	
Ethylbenzene	12	1.4959
p-Xylene	18	1.4958
m-Xylene	46	1.4971
o-Xylene	24	1.5054
Weighted average		1.4987

Table VII. Calculated Distribution of Dimethylcyclohexane Isomers

Dimethylcyclohexane Isomers	n_D^{20}	Volume % of Isomer in 115°–127° C. Fraction	Volume % in Indicated Fraction	
			115°–122 °C.	122°–127° C.
trans-1,4-Dimethylcyclohexane	1.4212	15	28	0
trans-1,3-Dimethylcyclohexane	1.4230	38	72	0
trans-1,2-Dimethylcyclohexane	1.4271	20	0	43
cis-1,4-Dimethylcyclohexane	1.4299	8	0	17
cis-1,3-Dimethylcyclohexane	1.4310	19	0	40

Table VIII. Refractive Indices of Binary Mixtures of Aromatics, Naphthenes, and Paraffins

Composition, %			Actual n_D^{20}	Calculated n_D^{20}	Deviation × 10^4 Calculated from Actual n_D^{20}
Toluene	*n*-Heptane	Methylcyclohexane			
...	0	100	1.4230	...	...
...	9.5	90.5	1.4196	1.4196	0
...	18.2	81.8	1.4168	1.4166	−2
...	33.3	66.7	1.4115	1.4112	−3
...	46.2	53.8	1.4067	1.4067	0
...	50	50	1.4057	1.4054	−3
...	66.7	33.3	1.3997	1.3995	−2
...	82.4	17.6	1.3939	1.3939	0
...	100	0	1.3878	...	...
0	100	...	1.3878	...	...
10	90	...	1.3980	1.3985	+5
20	80	...	1.4087	1.4092	+5
40	60	...	1.4295	1.4306	+11
60	40	...	1.4509	1.4521	+12
80	20	...	1.4727	1.4735	+8
90	10	...	1.4839	1.4842	+3
100	...	...	1.4949	...	...
0	...	100	1.4230	...	...
10	...	90	1.4298	1.4302	+4
20	...	80	1.4360	1.4374	+14
40	...	60	1.4498	1.4517	+19
60	...	40	1.4656	1.4672	+16
80	...	20	1.4795	1.4805	+10
90	...	10	1.4870	1.4877	+7
100	...	0	1.4949	...	...

Many investigators in the past have assumed the absence of the cis form in straight-run fractions and the probable presence of this form in cracked stocks. It is difficult to explain the high refractive indices obtained after acid extraction on certain fractions from highly naphthenic crudes, however, if the cis form is assumed to be absent. Calculation of the distributions of the dimethylcyclohexane isomers on the basis of these assumptions gives the values shown in Table VII. These values were employed to establish the weighted average refractive indices for the dimethylcyclohexanes shown in Figure 2. Iso-propylcyclopentane and *trans*-1-methyl-3-ethylcyclopentane were assumed to be absent by analogy with the methylcyclohexane fraction. Even if present they would have very little effect on the average refractive indices of the fractions in which they occur.

It was assumed that ethylcyclohexane and *cis*-1,2-dimethylcyclohexane are the only naphthenes present in the 127° to 136° C.

boiling range and that they are present in the ratio of 12 to 8, the ratio of ethylbenzene to one third of the *o*-xylene in Table VI, the other two thirds of the *o*-xylene having been assumed to have been formed from *trans*-1,2-dimethylcyclohexane. *cis*-1-Methyl-2-ethylcyclopentane and *n*-propylcyclopentane were assumed to be absent. If they are present, the value for the average refractive index of the naphthenes in this fraction will be lower than shown, and C_8 naphthene contents calculated from Figure 2 will be low.

The value for the naphthenes in the 136° to 149° C. fraction is not critical, as it is used only for the correction of the aromatic content of this fraction. The value shown was calculated on the assumption that only trimethylcyclohexanes were present and that they were present in the same ratio as the corresponding dimethylcyclohexanes. The unweighted average of all values shown for naphthenes in this boiling range in the reference work used (*1*) is 1.4292.

The curve shown for paraffins in Figure 2 is the best average of the points plotted from the data of Ward and Kurtz (*8*).

Correction Factor for Calculation of Aromatic Content. In the early stages of the development of the method it was found that calculation of aromatic contents of synthetic blends by use of the equation

$$A = \frac{R_U - R_E}{R_A - R_E} \times 100 \qquad (4)$$

yielded aromatic contents lower than those known to be present. This was a result of the nonadditivity of the refractive indices of the constituents of the blends. An investigation which was conducted to determine the extent of this error yielded the data shown in Table VIII. These data indicate that the refractive indices of mixtures of toluene and naphthenes deviate from additivity to a greater extent than do mixtures of toluene and paraffins. The refractive indices of mixtures of paraffins and naphthenes, however, were found to deviate to the extent of only ±0.0003 unit. This deviation is almost within the accuracy of the Abbe refractometer (±0.0002) and was, therefore, neglected. Based on these data the correction curves of Figure 1 were constructed.

Table IX. Accuracy of Baytown Ordnance Works Laboratory Procedure

Calculated composition of blend[a]	Base Stock 1	Base Stock 2	Blend I	Blend II	Blend III	Blend IV	Blend V
Methylcyclohexane, %	...	...	5.8	12.8	11.3	3.5	37.1
Toluene, %	...	...	6.6	26.5	23.6	39.5	8.8
Unsaturates, %	...	...	9.9	9.9	19.8	9.9	0.0
Found by analysis							
Methylcyclohexane, %	6.5	16.1	6.0	11.0	9.3	3.4	37.5
Toluene, %	7.3	11.8	6.9	26.6	23.6	39.4	8.6
Unsaturates, %	0.0	0.0	[b]	[b]	20.4	[b]	0.0

[a] Blends I, II, III, and IV prepared from base stock 1, and blend V from base stock 2.
[b] Not determined.

Table X. Reproducibility of Procedure under Routine Laboratory Operating Conditions

	Methylcyclohexane, %					Toluene, %				
	1st	2nd	3rd	4th	Av.	1st	2nd	3rd	4th	Av
Hydroformer feed[a]										
Tank sample	23.9	22.5	23.2	...	23.2	8.6	8.5	8.6	...	8.6
Tank car 1 sample	23.8	22.8	...	...	23.3	8.2	8.9	...	...	8.6
Tank car 2 sample	24.0	22.7	...	...	23.4	8.9	8.3	...	...	8.6
Drum sample 1	24.3	24.0	23.1	24.3	23.9	8.3	8.5	8.6	8.2	8.4
Drum sample 2	23.0	22.7	23.0	...	22.9	8.7	8.8	8.4	...	8.6
Av.					23.4					8.5
Av. deviation					±0.6					±0.2
Typical hydroformer products[b]										
Sample 1	6.1	5.7	...	...	5.9	14.0	13.8	...	...	13.9
Sample 2	7.0	6.8	...	...	6.9	16.1	16.1		...	16.1
Sample 3	4.0	4.0	...	...	4.0	22.0	22.6	...	...	22.3
Sample 4	4.6	4.5	4.6	4.3	4.5	22.8	23.0	23.4	23.3	23.1
Sample 5	2.8	2.7	...	...	2.8	28.8	28.9	...	...	28.9

[a] No unsaturates present.
[b] Contained 3 to 7% unsaturates.

Table XI. Accuracy of Plant Balance for Isolation of Toluene from Hydroformer Product

	Total Stream		Methylcyclohexane		Toluene	
	%[a]	Barrels[b]	%	Barrels	%	Barrels
Charge to system						
Hydro naphtha produced	87.54	8,754	5.0	438	26.0	2,276
Charge to purification plant from inventory	12.46	1,246	16.3	203	32.2	401
Total	100.00	10,000		641		2,677
Products of System						
Light hydro naphtha	16.30	1,630	0.9	15	0.7	11
Heavy hydro naphtha	20.61	2,061	...	...	1.8	37
Hydro naphtha to inventory	2.44	244	5.4	13	26.0	63
Purification plant by-products	36.27	3,627	17.0	617	4.3	156
Charge to product rerun unit to inventory	0.81	81	...	...	97.0	79
Heavy extract	0.57	57	...	...	5.0	3
Slop from product rerun unit	0.05	5	...	...	90.0	5
Toluene	22.95	2,295	...	...	99.5	2,284
Total	100.00	10,000		645		2,638
Error in balance			0.0[c]	4	−0.4[c]	39

[a] Based on charge to system.
[b] Figures are shown on basis of 10,000 barrels of charge and do not represent actual charge to plant.
[c] Correction required in analysis of charge to system, based on charge to system, to balance products with charge.

ACCURACY AND REPRODUCIBILITY

The accuracy of the procedure on synthetic blends is illustrated by the data in Table IX. These data indicate that the values obtained for methylcyclohexane by use of the procedure would, in general, be low. However, in the synthetic blends the deficiency of naphthenes in fractions adjacent to the methylcyclohexane fraction does not allow sufficient compensation for loss of methylcyclohexane to lighter and heavier fractions as a result of inadequate fractionation. (That this is not due to differences in the solubility of paraffins and naphthenes in sulfuric acid is indicated by the data in Table IV.) Fortunately in natural distillates this compensation effect minimized this type of error. Toluene analyses are not affected because the 40-plate column is efficient enough to separate heavier and lighter aromatics from toluene in the presence of other hydrocarbons.

In Table X data on the reproducibility of the method with two types of samples are presented. In Table XI are shown the results of a typical plant balance which was prepared from analyses obtained by this procedure.

Based on these data and the results of a large number of similar determinations and plant balances, it appears that the accuracy of the method is approximately ±0.3% (absolute) on aromatics and ±1.0% (absolute) on naphthenes under routine laboratory operating conditions on the types of naphthas investigated. The method would be somewhat less accurate on samples containing large quantities of compounds that would shift the average refractive index of a class of compounds from the curve of Figure 2 unless the curve were adjusted accordingly.

DISCUSSION

The method of analysis has been entirely satisfactory for the purpose for which it was developed—namely, for a control test which could be performed in a reasonable time by relatively untrained laboratory personnel with reasonably simple standard equipment. It was used for several years at the Baytown Ordnance Works as a routine method for determining the efficiency of the conversion of methylcyclohexane to toluene and C_8 naph-

thenes to C_8 aromatics, but it could not be published heretofore because of wartime restrictions.

The method has certain limitations. It will not reveal such compounds as unsaturated naphthenes, since they are removed in the bromination and steam-distillation step. It will not distinguish between the C_8 aromatics, nor between naphthenes of the same boiling range, such as methylcyclohexane and ethylcyclopentane, nor between the various dimethylcyclohexanes. However, the presence of conjugated diolefins, which are troublesome in other methods of analysis, does not affect the analysis by this method.

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Quantitative Determination of Paraffins and Naphthenes in Gasolines

By the Lamp Method

S. G. HINDIN AND A. V. GROSSE, *Houdry Laboratories, Houdry Process Corporation of Pennsylvania, Marcus Hook, Pa.*

The lamp method for the determination of hydrogen in liquid organic compounds has been applied to the quantitative estimation of paraffins and naphthenes in gasoline fractions. The accuracy of the procedure is independent of isomeric composition of the fraction; it varies from ±1.5 weight % paraffin in the C_5 cut up to ±3.0% in the C_{12} cut. The application and use of the hydrogen-to-carbon ratio in the solution of various analytical problems are suggested.

THE authors have recently described a lamp method (*5*) for the accurate determination of the hydrogen content of liquid organic compounds and mixtures, particularly in saturated hydrocarbons. This paper discusses the application of this technique to the estimation of paraffins and naphthenes in gasolines, after removal of aromatics and olefins by any of the customary procedures, such as absorption by sulfuric acid or a sulfuric acid–phosphorus pentoxide mixture, by silica gel percolation, or by selective solvents.

In view of the expansion of the various catalytic processes in the petroleum industry, the quantitative estimation of paraffins and naphthenes has been assuming ever greater importance—for example, a thorough analysis of the saturate fraction of the charge stock is particularly important in aromatization and isomerization processes.

Up to the present time, the determination of paraffins and naphthenes in gasolines, as exemplified by the so-called "PONA" method for the determination of hydrocarbon class composition, has been based primarily on the measurement of physical properties, mainly density and refractive index, or on derived functions, such as molecular refraction or refractivity intercept (*6–8*) of the saturate fraction, after the aromatics and olefins have been separated or due allowance has been made for their presence.

While such methods are adequate when approximate data are required, and are particularly useful when considerations of sample size and analysis time are important, they are not reliable when there is need for accurate data. The cause of this inaccuracy is twofold: (1) The various isomers of a compound of given empirical (and hydrocarbon class) composition show wide variations in physical properties while average values are used for purposes of analysis, and (2) charge stocks and gasolines both show high concentrations of specific isomers rather than equal amounts of all possible isomers.

As an illustration of the first point, the constants of the five hexanes and the nine heptanes and the major C_6 and C_7 naphthenes are tabulated. Table I includes, in addition, the calculated values for the Lorentz-Lorenz specific refraction, $\left(\frac{n^2-1}{n^2+2} \times \frac{1}{d}\right)$, the Eykman refraction, $\left(\frac{n^2-1}{n+0.4} \times \frac{1}{d}\right)$, and the refractivity intercept, $\left(n - \frac{d}{2}\right)$. As is evident, the calculated "constants" show appreciable deviations from the average, and the maximum percentage deviation is substantial.

The physical constants of the higher hydrocarbons are not so accurately known, but it is possible and even probable that the maximum deviations from the average are even greater.

USE OF HYDROGEN-TO-CARBON ATOMIC RATIOS

As pointed out some time ago (*4*), in a critical analysis of the methods used for estimation of paraffins and naphthenes, "the only unambiguous procedure at present should be based on the determination of the atomic ratio of hydrogen to carbon. The ratio follows directly from the empirical formula of a hydrocarbon and its interpretation involves no further assumptions." Since all paraffins have the empirical formula C_nH_{2n+2}, and all monocyclic naphthenes, C_nH_{2n}, determination of the hydrogen con-

Table I. Constants of Hexanes, Heptanes, and Naphthenes

Hydrocarbon	n_D^{20}	Density	$\frac{n^2-1}{n^2+2}\times\frac{1}{d}$	$\frac{n^2-1}{n+0.4}\times\frac{1}{d}$	$n-\frac{d}{2}$
C_6 Paraffins					
n-Hexane	1.3749	0.6594	0.34706	0.76074	1.0452
2-MeC_5	1.3714	0.6531	0.34750	0.76129	1.0449
3-MeC_5	1.3765	0.6643	0.34582	0.75818	1.0444
2,2-Me_2C_4	1.3688	0.6492	0.34740	0.76078	1.0442
2,3-Me_2C_4	1.3750	0.6616	0.34601	0.75840	1.0442
		Av.	0.34676 ± 0.00067	0.75988 ± 0.00127	1.0446 ± 0.0004
Naphthenes					
Me-cyclo C_5	1.4097	0.7486	0.33075	0.72873	1.0354
Cyclo C_6	1.4262	0.7786	0.32922	0.72724	1.0369
		Av.	0.32999 ± 0.00077	0.72799 ± 0.00075	1.0362 ± 0.0007
C_7 Paraffins					
n-Heptane	1.3877	0.6837	0.34490	0.75738	1.0459
2-Me C_6	1.3849	0.6788	0.34515	0.75764	1.0455
3-Me C_6	1.3887	0.6870	0.34403	0.75559	1.0452
3-Et C_5	1.3934	0.6982	0.34214	0.75195	1.0443
2,2-Me_2C_5	1.3822	0.6739	0.34550	0.75808	1.0453
2,3-Me_2C_5	1.3920	0.6951	0.34258	0.75277	1.0445
2,4-Me_2C_5	1.3816	0.6730	0.34547	0.75796	1.0451
3,3-Me_2C_5	1.3910	0.6933	0.34269	0.75291	1.0444
2,2,3-Me_3C_4	1.3895	0.6900	0.34316	0.75375	1.0445
		Av.	0.34396 ± 0.00117	0.75534 ± 0.00221	1.0450 ± 0.0005
Naphthenes					
Et-Cyclo C_5	1.4198	0.7665	0.33002	0.72826	1.0366
1,1-Me_2C_5	1.414	0.755	0.33098	0.72972	1.036
1,2-Me_2C_5 (cis)	1.4222	0.773	0.32887	0.72603	1.036
1,2-Me_2C_5 (trans)	1.4120	0.752	0.33088	0.72928	1.036
1,3-Me_2C_5 (trans)	1.4087	0.745	0.33164	0.73058	1.036
Me-Cyclo C_6	1.4231	0.7694	0.33104	0.73088	1.0384
		Av.	0.33057 + 0.00077	0.72913 + 0.00133	1.0365 + 0.0007

Table II. Boiling Points of Paraffins at 760 Mm.

	Maximum B.P. ° C.	Hydrocarbon	Minimum B.P. ° C.	Hydrocarbon	Overlap ° C.
C_7	98.42	*n*-Heptane	79.21	2,2-Me_2C_5	None
C_8	125.63	*n*-Octane	99.23	2,2,4-Me_3C_5	None
C_9	150.74	*n*-Nonane	122.28	2,2,4,4-Me_4C_5	3.3
C_{10}	174.04	*n*-Decane	136.8	2,2,5,5-Me_4C_6	13.9
C_{11}	195.84	*n*-Undecane	159.1	2,2,6,6-Me_4C_7 (unknown)	14.9

tent or calculation of the hydrogen-carbon atomic ratio of a saturated hydrocarbon mixture of *n* carbon atoms gives the paraffin and naphthene content immediately. [Although, in theory, bridged rings may occur in the lower boiling gasoline fractions (0,1,3-bicyclohexane boils near 80 °C.), there is, so far, no evidence of their occurrence. Even in the upper end of the gasoline range, where decalin or its homologs may appear, none have, to the authors' knowledge, been shown to be present.] Usually, the molecular weight of the paraffin is derived from the boiling range of the cut under investigation. (In the higher boiling cuts, overlapping may occur as indicated below.)

The calculation of the paraffin-naphthene ratio from hydrogen-carbon data is as follows:

Let x = the experimentally determined H/C ratio of the paraffin-naphthene mixture

a = the H/C ratio of the paraffins boiling in the same range, as calculated from the empirical formula

then $\frac{x-2}{a-2}\times 100$ = weight % paraffins

and $\frac{a-x}{a-2}\times 100$ = weight % naphthenes

Figure 1 indicates the relationship of the hydrogen-carbon ratio of paraffins to their boiling points: all monocyclic naphthenes have, obviously, a hydrogen-carbon ratio of 2.0000.

By the method of Francis (*3*) the boiling points of all paraffins in the gasoline range may be calculated. Thus, the region of overlapping boiling points for the higher paraffins is established: the maximum and minimum boiling points of the nonane, decane, and undecane isomers shown in Figure 1 are based on Table II.

From the practical standpoint, highly branched paraffins are not likely to occur in natural materials; in synthetic materials, attention should be paid to their possible presence, and the accuracy of the lamp method, as shown in Table III modified accordingly.

Table III is a correlation of the hydrogen-carbon ratios of the paraffin homologs in the gasoline range, the differences in the hydrogen-carbon ratio for paraffins and naphthenes, and the accuracy of the lamp method for each fraction.

Since the accuracy of the lamp method, at its present stage of development, is of the order of ±0.03% hydrogen, corresponding to ±0.005 in the hydrogen-carbon ratio, the accuracy in the analysis of the various cuts decreases from ±1.3 weight % with pentanes to ±3.0 weight % with dodecanes, as is shown in the last column of Table III. Actually, the accuracy in the higher ranges is probably better than that indicated here, since volatility losses are reduced; in the absence of pure compound data, however, this point is ambiguous.

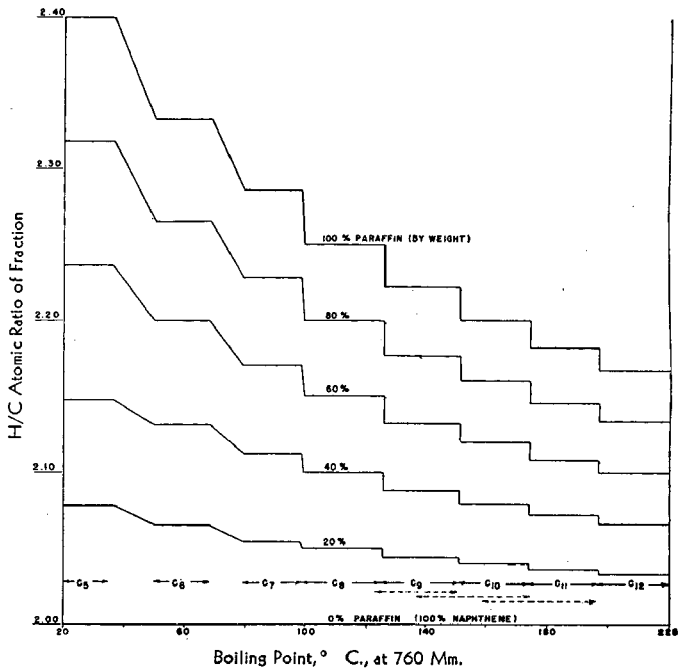

Figure 1

Table III. Hydrogen-to-Carbon Atomic Ratios and Accuracy of Lamp Method

Paraffins	Formula	Molecular Weight (H = 1.0081 C = 12.010)	Weight % H	H/C Atomic Ratio	Difference in Ratio between Paraffins and Naphthenes Δ(P − N)	Accuracy of Lamp Method of Analysis, Weight % (Calcd.)
Pentanes	C_5H_{12}	72.147	16.767	2.4000	0.4000	±1.3
Hexanes	C_6H_{14}	86.173	16.378	2.3333	0.3333	±1.5
Heptanes	C_7H_{16}	100.200	16.097	2.2857	0.2857	±1.8
Octanes	C_8H_{18}	114.226	15.886	2.2500	0.2500	±2.0
Nonanes	C_9H_{20}	128.252	15.721	2.2222	0.2222	±2.3
Decanes	$C_{10}H_{22}$	142.278	15.588	2.2000	0.2000	±2.5
Undecanes	$C_{11}H_{24}$	156.304	15.479	2.1818	0.1818	±2.7
Dodecanes	$C_{12}H_{26}$	170.331	15.388	2.1667	0.1667	±3.0

Table IV Weight Per Cent Paraffins in a Paraffin-Naphthene Mixture of Given Boiling Range as a Function of the Water Number[a]

(Atomic weights: C = 12.010, H = 1.0081, O = 16.0000)

Weight Per Cent of Paraffins

	C_5 Pentanes	C_6 Hexanes	C_7 Heptanes	C_8 Octanes	C_9 Nonanes	C_{10} Decanes	C_{11} Undecanes	C_{12} Dodecanes
	Boiling Range of Cuts							
	5–40° C. 41–104° F.	40–70° C. 104–158° F.	70–100° C. 158–212° F	100–125° C. 212–257° F.	125–150° C. 257–302° F.	150–175° C. 302–347° F.	175–195° C. 347–383° F.	195–215° C. 383–419° F.
0	1.2845	1.2845	1.2845	1.2845	1.2845	1.2845	1.2845	1.2845
1	1.2866	1.2863	1.2860	1.2858	1.2857	1.2856	1.2855	1.2854
2	1.2887	1.2881	1.2875	1.2872	1.2869	1.2866	1.2864	1.2863
3	1.2909	1.2898	1.2891	1.2885	1.2881	1.2877	1.2874	1.2872
4	1.2930	1.2916	1.2906	1.2899	1.2893	1.2888	1.2884	1.2881
5	1.2952	1.2934	1.2922	1.2912	1.2905	1.2899	1.2894	1.2890
6	1.2973	1.2952	1.2937	1.2926	1.2917	1.2910	1.2904	1.2899
7	1.2994	1.2970	1.2952	1.2939	1.2929	1.2921	1.2914	1.2908
8	1.3016	1.2988	1.2968	1.2953	1.2941	1.2931	1.2924	1.2917
9	1.3037	1.3006	1.2983	1.2966	1.2953	1.2942	1.2934	1.2926
10	1.3059	1.3024	1.2999	1.2980	1.2965	1.2953	1.2943	1.2935
11	1.3080	1.3042	1.3014	1.2993	1.2977	1.2964	1.2953	1.2944
12	1.3101	1.3060	1.3029	1.3007	1.2989	1.2975	1.2963	1.2953
13	1.3123	1.3077	1.3045	1.3020	1.3001	1.2986	1.2973	1.2962
14	1.3144	1.3095	1.3060	1.3034	1.3013	1.2996	1.2983	1.2971
15	1.3165	1.3113	1.3076	1.3047	1.3025	1.3007	1.2993	1.2981
16	1.3187	1.3131	1.3091	1.3061	1.3037	1.3018	1.3003	1.2990
17	1.3208	1.3149	1.3106	1.3074	1.3049	1.3029	1.3012	1.2999
18	1.3230	1.3167	1.3122	1.3088	1.3061	1.3040	1.3022	1.3008
19	1.3251	1.3185	1.3137	1.3101	1.3073	1.3051	1.3032	1.3017
20	1.3272	1.3203	1.3153	1.3115	1.3085	1.3062	1.3042	1.3026
21	1.3294	1.3221	1.3168	1.3128	1.3097	1.3073	1.3052	1.3035
22	1.3315	1.3239	1.3183	1.3142	1.3109	1.3083	1.3062	1.3044
23	1.3336	1.3256	1.3199	1.3155	1.3121	1.3094	1.3072	1.3053
24	1.3358	1.3274	1.3214	1.3169	1.3133	1.3105	1.3082	1.3062
25	1.3379	1.3292	1.3230	1.3182	1.3145	1.3116	1.3091	1.3071
26	1.3401	1.3310	1.3245	1.3196	1.3157	1.3127	1.3101	1.3080
27	1.3422	1.3328	1.3260	1.3209	1.3169	1.3137	1.3111	1.3089
28	1.3443	1.3346	1.3276	1.3223	1.3181	1.3148	1.3121	1.3098
29	1.3465	1.3364	1.3291	1.3236	1.3194	1.3159	1.3131	1.3107
30	1.3486	1.3382	1.3307	1.3250	1.3205	1.3170	1.3141	1.3116
31	1.3508	1.3400	1.3322	1.3263	1.3218	1.3181	1.3151	1.3125
32	1.3529	1.3418	1.3337	1.3277	1.3230	1.3192	1.3161	1.3135
33	1.3550	1.3435	1.3353	1.3290	1.3242	1.3202	1.3170	1.3144
34	1.3572	1.3453	1.3368	1.3304	1.3254	1.3213	1.3180	1.3153
35	1.3593	1.3471	1.3384	1.3317	1.3266	1.3224	1.3190	1.3162
36	1.3614	1.3489	1.3399	1.3331	1.3278	1.3235	1.3200	1.3171
37	1.3636	1.3507	1.3414	1.3344	1.3290	1.3246	1.3210	1.3180
38	1.3657	1.3525	1.3430	1.3358	1.3302	1.3257	1.3220	1.3189
39	1.3679	1.3543	1.3445	1.3371	1.3314	1.3268	1.3230	1.3198
40	1.3700	1.3561	1.3461	1.3385	1.3326	1.3278	1.3239	1.3207
41	1.3721	1.3579	1.3476	1.3398	1.3338	1.3289	1.3249	1.3216
42	1.3743	1.3597	1.3491	1.3412	1.3350	1.3300	1.3259	1.3225
43	1.3764	1.3614	1.3507	1.3425	1.3362	1.3311	1.3269	1.3234
44	1.3786	1.3632	1.3522	1.3439	1.3374	1.3322	1.3279	1.3243
45	1.3807	1.3650	1.3537	1.3452	1.3386	1.3333	1.3289	1.3252
46	1.3828	1.3668	1.3553	1.3466	1.3398	1.3343	1.3299	1.3261
47	1.3850	1.3686	1.3568	1.3479	1.3410	1.3354	1.3309	1.3270
48	1.3871	1.3703	1.3584	1.3493	1.3422	1.3365	1.3318	1.3279
49	1.3892	1.3722	1.3599	1.3506	1.3434	1.3376	1.3328	1.3288
50	1.3914	1.3740	1.3614	1.3520	1.3446	1.3387	1.3338	1.3298

	C_5 Pentanes	C_6 Hexanes	C_7 Heptanes	C_8 Octanes	C_9 Nonanes	C_{10} Decanes	C_{11} Undecanes	C_{12} Dodecanes
	Boiling Range of Cuts							
	5–40° C. 41–104° F.	40–70° C. 104–158° F.	70–100° C. 158–212° F.	100–125° C. 212–257° F.	125–150° C. 257–302° F.	150–175° C. 302–347° F	175–195° C. 347–383° F	195–215° C 334–419° F
51	1.3935	1.3758	1.3630	1.3533	1.3458	1.3398	1.3348	1.3307
52	1.3957	1.3776	1.3645	1.3547	1.3470	1.3408	1.3358	1.3316
53	1.3978	1.3793	1.3661	1.3560	1.3482	1.3419	1.3368	1.3325
54	1.3999	1.3811	1.3676	1.3574	1.3494	1.3430	1.3378	1.3334
55	1.4021	1.3829	1.3691	1.3587	1.3506	1.3441	1.3387	1.3343
56	1.4042	1.3847	1.3707	1.3601	1.3518	1.3452	1.3397	1.3352
57	1.4063	1.3865	1.3722	1.3614	1.3530	1.3463	1.3407	1.3361
58	1.4085	1.3883	1.3738	1.3628	1.3542	1.3474	1.3417	1.3370
59	1.4106	1.3901	1.3753	1.3641	1.3554	1.3484	1.3427	1.3379
60	1.4128	1.3919	1.3768	1.3655	1.3566	1.3495	1.3437	1.3388
61	1.4149	1.3937	1.3784	1.3669	1.3578	1.3506	1.3447	1.3397
62	1.4170	1.3955	1.3799	1.3682	1.3590	1.3517	1.3457	1.3406
63	1.4192	1.3972	1.3815	1.3696	1.3602	1.3528	1.3466	1.3415
64	1.4213	1.3990	1.3830	1.3709	1.3614	1.3539	1.3476	1.3424
65	1.4235	1.4008	1.3845	1.3723	1.3627	1.3549	1.3486	1.3433
66	1.4256	1.4026	1.3861	1.3736	1.3639	1.3560	1.3496	1.3442
67	1.4277	1.4044	1.3876	1.3750	1.3651	1.3571	1.3506	1.3452
68	1.4299	1.4062	1.3892	1.3763	1.3663	1.3582	1.3516	1.3461
69	1.4320	1.4080	1.3907	1.3777	1.3675	1.3593	1.3526	1.3470
70	1.4341	1.4098	1.3922	1.3790	1.3687	1.3604	1.3536	1.3479
71	1.4363	1.4116	1.3938	1.3804	1.3699	1.3614	1.3545	1.3488
72	1.4384	1.4134	1.3953	1.3817	1.3711	1.3625	1.3555	1.3497
73	1.4406	1.4151	1.3969	1.3831	1.3723	1.3636	1.3565	1.3506
74	1.4427	1.4169	1.3984	1.3844	1.3735	1.3647	1.3575	1.3515
75	1.4448	1.4187	1.3999	1.3858	1.3747	1.3658	1.3585	1.3524
76	1.4470	1.4205	1.4015	1.3871	1.3759	1.3669	1.3595	1.3533
77	1.4491	1.4223	1.4030	1.3885	1.3771	1.3680	1.3605	1.3542
78	1.4512	1.4241	1.4046	1.3898	1.3783	1.3690	1.3614	1.3551
79	1.4534	1.4259	1.4061	1.3911	1.3795	1.3701	1.3624	1.3560
80	1.4555	1.4277	1.4076	1.3925	1.3807	1.3712	1.3634	1.3569
81	1.4577	1.4295	1.4092	1.3939	1.3819	1.3723	1.3644	1.3578
82	1.4598	1.4313	1.4107	1.3952	1.3831	1.3734	1.3654	1.3587
83	1.4619	1.4330	1.4122	1.3966	1.3843	1.3745	1.3664	1.3596
84	1.4641	1.4348	1.4138	1.3979	1.3855	1.3755	1.3674	1.3605
85	1.4662	1.4366	1.4153	1.3993	1.3867	1.3766	1.3684	1.3615
86	1.4684	1.4384	1.4169	1.4006	1.3879	1.3777	1.3693	1.3624
87	1.4705	1.4402	1.4184	1.4020	1.3891	1.3788	1.3703	1.3633
88	1.4726	1.4420	1.4199	1.4033	1.3903	1.3799	1.3713	1.3642
89	1.4748	1.4438	1.4215	1.4047	1.3915	1.3810	1.3723	1.3651
90	1.4769	1.4456	1.4230	1.4060	1.3927	1.3820	1.3733	1.3660
91	1.4790	1.4474	1.4246	1.4074	1.3939	1.3831	1.3743	1.3669
92	1.4812	1.4492	1.4261	1.4087	1.3951	1.3842	1.3753	1.3678
93	1.4833	1.4509	1.4276	1.4101	1.3963	1.3853	1.3763	1.3687
94	1.4855	1.4527	1.4292	1.4114	1.3975	1.3864	1.3772	1.3696
95	1.4876	1.4545	1.4307	1.4128	1.3987	1.3875	1.3782	1.3705
96	1.4897	1.4563	1.4323	1.4141	1.3999	1.3886	1.3792	1.3714
97	1.4919	1.4581	1.4338	1.4155	1.4011	1.3896	1.3802	1.3723
98	1.4940	1.4599	1.4353	1.4168	1.4023	1.3907	1.3812	1.3732
99	1.4962	1.4617	1.4369	1.4182	1.4035	1.3918	1.3822	1.3741
100	1.4983	1.4635	1.4384	1.4195	1.4048	1.3929	1.3832	1.3750

[a] Water number, grams, of water produced by complete combustion of 1 gram of hydrocarbon.

Table IV was prepared to facilitate calculation of the paraffin and naphthene percentages in the gasoline range. The percentage of paraffins in a fraction boiling in a specified range is given as a function of the experimentally determined water number, w, where w is weight in grams of water produced by combustion of 1 gram of the hydrocarbon being analyzed. It may be derived from the formula of the hydrocarbon, or vice versa. Thus, the water number of hexane (C_6H_{14}) is:

$$w = \frac{7 \times \text{mol. wt. of } H_2O}{\text{mol. wt. of } C_6H_{14}} = \frac{7 \times 18.0162}{86.1734} = 1.4635$$

Table V may be used to convert water number to hydrogen-carbon atomic ratio (for hydrocarbons), and Table VI used to convert hydrogen-carbon ratio into weight per cent hydrogen. A graphical representation of the relationship of weight per cent paraffin to weight per cent hydrogen is given in Figure 2. The

Table V. Conversion of Hydrogen-Carbon Ratios into Water Number and Vice Versa

(w^a = 0.36 to 1.55 and H/C Ratio = 0.50 to 2.50)

H/C Ratio or m/n	0	1	2	3	4	5	6	7	8	9	Av. Δ
0.5	0.3599	0.3668	0.3737	0.3806	0.3875	0.3943	0.4011	0.4080	0.4148	0.4217	69
0.6	0.4285	0.4353	0.4421	0.4488	0.4555	0.4623	0.4690	0.4757	0.4825	0.4892	68
0.7	0.4959	0.5026	0.5093	0.5160	0.5226	0.5293	0.5359	0.5425	0.5491	0.5557	66
0.8	0.5623	0.5689	0.5755	0.5820	0.5886	0.5951	0.6016	0.6082	0.6146	0.6211	65
0.9	0.6277	0.6341	0.6405	0.6470	0.6535	0.6599	0.6663	0.6728	0.6791	0.6856	64
1.0	0.6920	0.6983	0.7047	0.7111	0.7175	0.7238	0.7301	0.7364	0.7427	0.7490	63
1.1	0.7553	0.7616	0.7679	0.7741	0.7804	0.7866	0.7929	0.7990	0.8053	0.8115	62
1.2	0.8177	0.8239	0.8300	0.8362	0.8424	0.8485	0.8547	0.8608	0.8670	0.8730	62
1.3	0.8792	0.8853	0.8913	0.8973	0.9034	0.9095	0.9156	0.9215	0.9276	0.9336	61
1.4	0.9397	0.9457	0.9517	0.9576	0.9636	0.9696	0.9756	0.9815	0.9874	0.9934	60
1.5	0.9994	1.0053	1.0112	1.0170	1.0229	1.0288	1.0346	1.0405	1.0463	1.0522	59
1.6	1.0580	1.0638	1.0696	1.0754	1.0812	1.0870	1.0928	1.0987	1.1044	1.1102	58
1.7	1.1160	1.1217	1.1274	1.1331	1.1388	1.1445	1.1502	1.1558	1.1616	1.1672	57
1.8	1.1729	1.1785	1.1842	1.1899	1.1955	1.2011	1.2068	1.2123	1.2179	1.2235	56
1.9	1.2291	1.2347	1.2402	1.2456	1.2513	1.2569	1.2624	1.2680	1.2735	1.2791	55
2.0	1.2845	1.2900	1.2954	1.3009	1.3064	1.3119	1.3173	1.3228	1.3282	1.3337	55
2.1	1.3391	1.3445	1.3499	1.3553	1.3607	1.3661	1.3715	1.3768	1.3822	1.3875	54
2.2	1.3929	1.3983	1.4035	1.4089	1.4143	1.4195	1.4248	1.4301	1.4354	1.4407	53
2.3	1.4460	1.4513	1.4565	1.4617	1.4670	1.4723	1.4774	1.4826	1.4879	1.4931	52
2.4	1.4983	1.5034	1.5086	1.5138	1.5190	1.5242	1.5294	1.5345	1.5396	1.5447	52
2.5	1.5499										

Proportional Parts

Δ	51	52	53	54	55	56	57	58	59	60	61	62	63	64	65	66	67	68	69
1	5.1	5.2	5.3	5.4	5.5	5.6	5.7	5.8	5.9	6.0	6.1	6.2	6.3	6.4	6.5	6.6	6.7	6.8	6.9
2	10.2	10.4	10.6	10.8	11.0	11.2	11.4	11.6	11.8	12.0	12.2	12.4	12.6	12.8	13.0	13.2	13.4	13.6	13.8
3	15.3	15.6	15.9	16.2	16.5	16.8	17.1	17.4	17.7	18.0	18.3	18.6	18.9	19.2	19.5	19.8	20.1	20.4	20.7
4	20.4	20.8	21.2	21.6	22.0	22.4	22.8	23.2	23.6	24.0	24.4	24.8	25.2	25.6	26.0	26.4	26.8	27.2	27.6
5	25.5	26.0	26.5	27.0	27.5	28.0	28.5	29.0	29.5	30.0	30.5	31.0	31.5	32.0	32.5	33.0	33.5	34.0	34.5
6	30.6	31.2	31.8	32.4	33.0	33.6	34.2	34.8	35.4	36.0	36.6	37.2	37.8	38.4	39.0	39.6	40.2	40.8	41.4
7	35.7	36.4	37.1	37.8	38.5	39.2	39.9	40.6	41.3	42.0	42.7	43.4	44.1	44.8	45.5	46.2	46.9	47.6	48.3
8	40.8	41.6	42.4	43.2	44.0	44.8	45.6	46.4	47.2	48.0	48.8	49.6	50.4	51.2	52.0	52.8	53.6	54.4	55.2
9	45.9	46.8	47.7	48.6	49.5	50.4	51.3	52.2	53.1	54.0	54.9	55.8	56.7	57.6	58.5	59.4	60.3	61.2	62.1

[a] $w = \dfrac{\frac{m}{2}(18.0162)}{12.010n + 1.0081m}$ for C_nH_m: Atomic weight C = 12.010; Atomic weight H = 1.0081

Table VI. Conversion of Hydrogen-Carbon Ratios to Per Cent Hydrogen and Vice Versa

(H = 4.0 to 17.3%, C = 96.0 to 82.7%, H/C-Ratio = 0.50 to 2.50)

$$\%H = \frac{1.0081 \times 100}{1.0081 + 12.010/m/n}$$ For C_nH_m: Atomic weight C = 12.010; Atomic weight H = 1.0081

H/C Ratio or m/n	0	1	2	3	4	5	6	7	8	9	Δ
0.5	4.028	4.105	4.182	4.259	4.336	4.413	4.489	4.566	4.642	4.719	76
0.6	4.795	4.871	4.947	5.022	5.098	5.174	5.249	5.324	5.400	5.475	75
0.7	5.550	5.625	5.699	5.774	5.848	5.923	5.997	6.071	6.145	6.219	74
0.8	6.293	6.366	6.440	6.513	6.587	6.6660	6.733	6.806	6.878	6.951	73
0.9	7.024	7.096	7.168	7.240	7.313	7.385	7.457	7.529	7.600	7.672	72
1.0	7.744	7.815	7.886	7.958	8.029	8.100	8.170	8.241	8.312	8.382	71
1.1	8.453	8.523	8.593	8.663	8.733	8.803	8.873	8.942	9.012	9.081	70
1.2	9.151	9.220	9.289	9.358	9.427	9.496	9.565	9.633	9.702	9.770	69
1.3	9.839	9.907	9.975	10.042	10.110	10.178	10.246	10.313	10.381	10.448	68
1.4	10.516	10.583	10.650	10.717	10.784	10.851	10.918	10.984	11.050	11.117	67
1.5	11.184	11.250	11.316	11.381	11.447	11.513	11.578	11.644	11.709	11.775	66
1.6	11.840	11.905	11.970	12.035	12.100	12.165	12.230	12.295	12.359	12.424	65
1.7	12.489	12.553	12.617	12.680	12.744	12.808	12.872	12.935	12.999	13.062	64
1.8	13.126	13.189	13.252	13.316	13.379	13.442	13.505	13.567	13.630	13.692	63
1.9	13.755	13.817	13.879	13.940	14.003	14.066	14.128	14.190	14.252	14.314	62
2.0	14.375	14.436	14.497	14.558	14.620	14.681	14.742	14.803	14.864	14.925	61
2.1	14.986	15.046	15.107	15.167	15.228	15.288	15.348	15.408	15.468	15.528	60
2.2	15.588	15.648	15.707	15.767	15.827	15.886	15.945	16.004	16.064	16.123	59
2.3	16.182	16.241	16.300	16.358	16.417	16.476	16.534	16.592	16.651	16.709	58
2.4	16.767	16.825	16.883	16.941	16.999	17.057	17.115	17.172	17.230	17.287	58
2.5	17.345										

Proportional Parts

Δ	58	59	60	61	62	63	64	65	66	67	68	69	70	71	72	73	74	75	76
1	5.8	5.9	6.0	6.1	6.2	6.3	6.4	6.5	6.6	6.7	6.8	6.9	7.0	7.1	7.2	7.3	7.4	7.5	7.6
2	11.6	11.8	12.0	12.2	12.4	12.6	12.8	13.0	13.2	13.4	13.6	13.8	14.0	14.2	14.4	14.6	14.8	15.0	15.2
3	17.4	17.7	18.0	18.3	18.6	18.9	19.2	19.5	19.8	20.1	20.4	20.7	21.0	21.3	21.6	21.9	22.2	22.5	22.8
4	23.2	23.6	24.0	24.4	24.8	25.2	25.6	26.0	26.4	26.8	27.2	27.6	28.0	28.4	28.8	29.2	29.6	30.0	30.4
5	29.0	29.5	30.0	30.5	31.0	31.5	32.0	32.5	33.0	33.5	34.0	34.5	35.0	35.5	36.0	36.5	37.0	37.5	38.0
6	34.8	35.4	36.0	36.6	37.2	37.8	38.4	39.0	39.6	40.2	40.8	41.4	42.0	42.6	43.2	43.8	44.4	45.0	45.6
7	40.6	41.3	42.0	42.7	43.4	44.1	44.8	45.5	46.2	46.9	47.8	48.3	49.0	49.7	50.4	51.1	51.8	52.5	53.2
8	46.4	47.2	48.0	48.8	49.6	50.4	51.2	52.0	52.8	53.6	54.4	55.2	56.0	56.8	57.6	58.4	58.2	60.0	60.8
9	52.2	53.1	54.0	54.9	55.8	56.7	57.6	58.5	59.4	60.3	61.2	62.1	63.0	63.9	64.8	65.7	66.6	67.5	68.4

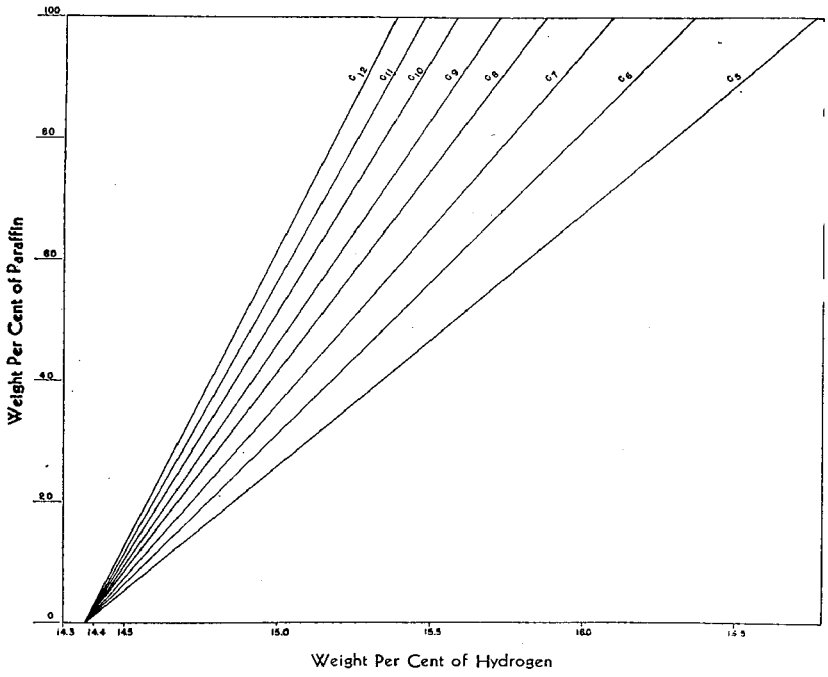

Figure 2

relationship between water number and hydrogen-carbon atomic ratio is, of course, linear.

DISCUSSION OF EXPERIMENTAL DATA

Procedure. The procedure (*5*) consists in burning a weighed amount of sample (usually 1 to 5 grams) in an A.S.T.M. sulfur lamp, in a steam of dry air, and collecting the water formed in a desiccant, $CaCl_2 + P_2O_5$. The % hydrogen is calculated:

$$\% \text{ H} = \frac{\text{weight of } H_2O \text{ collected}}{\text{weight of sample burned}} \times 11.191$$

The precision and accuracy of the procedure, as applied to pure hydrocarbons, are indicated in Table VII.

Analysis of Complex Mixtures. Even in highly complex mixtures such as motor gasolines, where the boiling points of components range from 24° to 215° C., no appreciable fractionation occurs, because the entire body of the liquid rises up the wick and is burned at the tip. The nonfractionation may be easily shown by refractive index measurements (using the Na *D* line, at 20° C.) on the original sample and on some of the same sample that has been partially burned in the lamp. In Table II of a previous paper (*5*) are listed some gasolines and synthetic blends, their boiling ranges, the approximate spread in refractive indices of the components, the refractive index of the original blend, and the refractive index of the sample remaining in the flask after one third to one half of the total has been burned.

To test the accuracy of the procedure with mixtures, synthetic blends, by weight, of *n*-heptane and methylcyclohexane were prepared and analyzed. Table VIII indicates the actual sample composition, the per cent hydrogen on analysis, the composition as calculated from the per cent hydrogen, and the composition based on the refractivity intercept–density relationship.

Although an objection to the use of average paraffin-naphthene data on a selected mixture such as *n*-heptane and methylcyclohexane may be raised, the authors feel that the procedure is valid, inasmuch as closely fractioned cuts may very well show high percentages of specific isomers.

An actual case may be quoted; a close cut, 208° to 215° F. (97.8° to 101.7° C.) analyzed 34.5% naphthene, by weight, using the intercept method (*1*) with average values for all C_7 paraffins and naphthenes. The lamp method indicated 37.3% naphthene, by weight. A later, very much detailed examination of precisely fractionated cuts of the sample showed it to contain more than 90% of *n*-heptane plus methylcyclohexane and gave a value for the naphthene content within 1% of the figure given by the combustion procedure.

Some typical gasoline fractions were analyzed by the lamp method and the results compared with those obtained by the refractivity intercept method (Table IX).

An interesting observation made was that the intercept method apparently yields high values for paraffin percentage. This might well be further studied.

APPLICATION OF LAMP METHOD IN ESTIMATION OF HEAT OF COMBUSTION

In the determination of the heat of combustion of gasolines, the hydrogen content of the gasoline must be accurately known to correct for the weight of water formed. Table X indicates the accuracy and precision of the lamp procedure as applied to gasolines.

APPLICATION OF LAMP METHOD TO ANALYTICAL PROBLEMS

The method may be used in conjunction with other procedures—for instance hydrogenation, bromination—to give novel solutions of many analytical problems. A few of these solutions are given here.

1. The degree of unsaturation of a hydrocarbon mixture may be determined by this means, before and after hydrogenation, as a substitute for the usual bromine absorption. In case of a pure hydrocarbon, hydrogenation is, of course, unnecessary.
2. The hydrogen-carbon ratio may be used to classify olefins as either straight chain or cyclic. To illustrate, the bromine numbers of methylcyclohexene and heptene are, respectively, 166.2 and 162.8. Aside from the usual problems encountered in bromination, the difference in the two values is of the order of

Table VII. Precision and Accuracy

	% H		H/C Ratio	
	Actual	Determined	Actual	Determined
n-Heptane	16.10	16.07 ± .01	2.286	2.281 ± 0.002
Iso-octane	15.88	15.83 ± .04	2.250	2.240 ± 0.008
Cyclohexane	14.37	14.34 ± .03	2.000	1.993 ± 0.006
Methylcyclohexane	14.37	14.34 ± .02	2.000	1.993 ± 0.004
Cetane	15.13	15.13 ± .01	2.124	2.124 ± 0.002

Table VIII. Analysis of Synthetic Mixtures of *n*-Heptane and Methylcyclohexane

Actual Sample Composition, % Paraffins by Weight	Water No.	H/C Ratio	% H	% Paraffin	
				From lamp method	From refractivity intercept
30.8	1.329 ± 0.003	2.081 ± 0.005	14.875 ± 0.035	29.0 ± 2.0	35.3
47.0	1.3565 ± 0.0005	2.132 ± 0.001	15.18 ± 0.01	46.8 ± 0.6	54.6
64.0	1.382 ± 0.004	2.180 ± 0.01	15.465 ± 0.045	63.3 ± 2.6	72.7

Table IX. Analysis of Gasoline Fractions

Gasoline Cut	H	Paraffin by Lamp Method	Paraffin by Intercept Method
° F.	%	%	%
205–250	14.81 ± 0.02	28.9 ± 1.4	35.2
302–347	14.935 ± 0.045	46.3 ± 3.7	52.5
347–392	14.34 ± 0.04	0[a]	10.4

[a] The low value for % H may indicate presence of bicyclic naphthenes. This point is under investigation; it is of particular interest in view of the lack of reliable data on the presence of bicyclics in the high boiling gasoline fractions.

Table X. Analysis of Gasolines by the Lamp Method

Sample	% Hydrogen: By lamp method	% Hydrogen: By standard Liebig combustion, Levin-Uhrig modification	Approximate Composition Weight %: P	O	N	A
Aviation gasoline A	13.71, 13.74	13.6 ± 0.1	35	10	25	30
Aviation gasoline B	13.65, 13.64	[a]	40	10	20	30
Motor gasoline A	13.08, 13.01, 13.10	12.9 ± 0.1	40	10	30	20
Motor gasoline B	13.10, 13.09	[a]	45	10	25	20

[a] These samples were not analyzed.

magnitude of the error in the determination of bromine number. By analyzing for per cent hydrogen (methylcyclohexene = 12.58% H, H/C = 1.7143, and heptene = 14.37% H, H/C = 2.0000), there should be no uncertainty.

This technique may be applied to gasoline analysis:

Determination of H/C ratio

Removal of olefins by the Bond (*2*) method

Determination of H/C ratio of olefin-free material

3. The H/C ratio may be used to measure the diolefin content of an olefin. The advantage of using this procedure is that conjugated or nonconjugated systems would be equally amenable to analysis.

4. Direct analysis for per cent hydrogen would probably be the most direct and most accurate method of following hydrogenation and dehydrogenation reactions.

5. The usual PONA analysis might be varied in this manner:

Determination of H/C ratio

Determination of aromatic plus olefin by sulfuric acid absorption

Determination of H/C ratio of the saturate fraction directly and of the aromatic and olefin fraction by calculation

6. Determination of hydrogen content could be used to analyze mixtures of mono- and dicyclic aromatics. If rings of the phenylcyclohexane or phenylcyclopentane type are encountered, determination of the H/C ratio, followed by analytical hydrogenation, followed by another determination of H/C ratio, could be used to indicate not only the aromatics, but also the weight per cent of naphthene ring.

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Analytical Methods for Carotenes of Lycopersicon Species and Strains

F. P. ZSCHEILE[1] AND J. W. PORTER

Department of Agricultural Chemistry, Purdue University Agricultural Experiment Station, Lafayette, Ind.

Studies on the nutritional importance of tomatoes have necessitated the development of rapid methods for the determination of carotenoids having provitamin A activity. Quantitative absorption curves of the principal carotenoids have in *Lycopersicon* species are presented. Spectroscopic methods for the determination of β-carotene and lycopene are discussed in detail and results compared critically with those obtained by a chromatographic procedure. Sampling and extraction procedures are given and errors of recovery and those due to solvent impurity and carotenoid isomerization are discussed from the viewpoint of practical analysis. The proper application of spectrophotometric methods offers a valuable tool for the rapid analysis of tomato carotenoids.

THE spectrophotometric analysis of tomato fruit carotenes has been of considerable importance in a program conducted at this station for the development of improved strains of tomatoes, genetically constituted to contain much more β-carotene (provitamin A) than the present commercial varieties (*4*). This problem will assume greater significance as the nutritional importance of tomatoes in our national economy becomes more generally recognized and as efforts to improve the vitamin content of tomatoes begin to materialize in commercial production. It is also important in the study of fundamental problems of carotenoid physiology in relation to pigment development in plants.

The complexity of the pigment system has made the analytical problem considerably more difficult than is indicated by earlier methods applied to mixtures of (presumably) all-trans forms (*6*, *7*), partially because of the presence of cis-isomers in some tomatoes (*11*) and in part because of the presence of additional pigments (*10*). However, from the practical viewpoint, after the various components have been identified, the spectroscopic analytical situation with regard to content of β-carotene in the presence of lycopene does not appear so difficult as first suggested by other workers (*5*).

[1] Present address, College of Agriculture, University of California, Davis, Calif.

EXPERIMENTAL

The following procedure has been designed to be as brief and simple as possible, so that it can be applied in a routine manner to hundreds of fresh and canned samples per season.

Sampling. Fresh unpeeled fruits are used. If the fruit and core are large, the core is removed before cutting the fruit into pieces and homogenizing in a Waring Blendor. After about 2 minutes the fruits will be blended into a thick liquid mass which may be accurately sampled by pouring.

Extraction and Separation of Carotenoids. A 20-gram sample, weighed to the nearest 0.1 gram, is poured into a clean Blendor cup and 75 ml. of acetone are added, some of which may be used to rinse the sample from the weighing vessel. Sixty milliliters of hexane (b.p. 65–67° C.) are added and the mixture is blended

for 2 minutes. If the fruits are small, as is characteristic of several species, enough whole fruits to make approximately 20 grams are blended directly in the solvent mixture.

Two phases usually separate rapidly and the blended mixture is filtered on a Büchner funnel. The solid residue left on the filter paper is washed with a few milliliters of acetone, and then a small amount of hexane. Rarely, except with canned samples, will the residue (other than skin flakes) retain an appreciable amount of pigments. Such samples are more completely extracted by shredding the filter cake and paper, blending 2 minutes with 50 ml. of acetone, and refiltering. All filtrates are combined in a 250-ml. separatory funnel. If the hypophase is colorless, it is drained and discarded; otherwise water is added gently before draining. The hyperphase is washed carefully (to avoid emulsions) three times with water. At the last washing any small amount of emulsion is discarded, as its pigment content will be negligible.

Carotenols and chlorophyll are separated from the carotenes by immiscible solvent extraction. The hexane solution is washed once with 20 ml. of 90% aqueous methanol (0.5 minute). All washings are performed by rotating the separatory funnels mechanically. After clearing of the phases (15 minutes to 0.5 hour) the hypophase is drawn off and the hexane phase is washed with 20 ml. of 20% potassium hydroxide in methanol (1 minute). When clear (maximum 0.5 hour) the hypophase is discarded and another washing with 20 ml. of 90% methanol is made (0.5 minute). After drawing off the hypophase, the carotene solution is washed vigorously three times with large quantities of water. The funnel stem is dried before drawing the hexane solution into a 100-ml. volumetric flask. After rinsing the separatory funnel with hexane, the carotene solution is made to volume and placed in the refrigerator until analyzed spectroscopically. These solutions are usually bright and clear and seldom need to be dried over sodium sulfate.

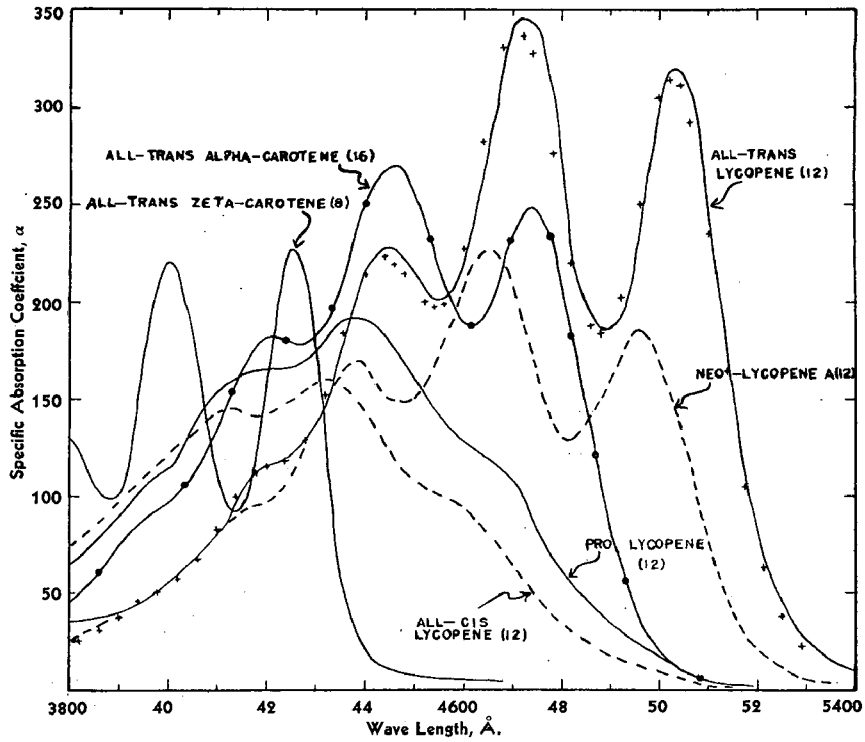

Figure 1. Absorption Curves of Six Carotenes Found in Fruit of *Lycopersicon* Species and Strains (Solvent Hexane)

Crosses indicate all-trans lycopene data from this laboratory

Spectroscopic Analysis. A photoelectric spectrophotometer employing a large Müller-Hilger Universal double monochromator with crystal quartz optics is used. Its performance has been described (*15*, *16*).

Wave length 4875 Å. is used in determining total carotenes (predominantly lycopene, neolycopene A, β-carotene, and neo-β-carotene B). At this wave length the absorption values of all-trans β-carotene and lycopene are nearly equal (180 and approximately 183, respectively). A value of 181 for the specific absorption coefficient has been found most reliable for mixtures which contain small amounts of cis-isomers of these two pigments.

For the lycopene determination wave length 5020 Å. is used. The specific absorption coefficient used for the lycopene fraction is 279 and the difference between this value and the corresponding value of 42 for the β-carotene fraction is 237. The β-carotene fraction content is then obtained by difference.

Equations for the total carotene content and the per cent lycopene are as follows:

From Beer's law (*1*),

$$\text{Total carotene (in micrograms per gram)} = \frac{\log \frac{I_0}{I}\,(4875\text{Å.}) \times \text{dilution factor} \times 10^5}{181 \times \text{length of cell (cm.)} \times \text{sample weight (grams)}}$$

$$\text{Per cent lycopene} = \frac{\dfrac{\log \frac{I_0}{I}\,(5020\,\text{Å.}) \times 181}{\log \frac{I_0}{I}\,(4875\,\text{Å.})} - 42}{237} \times 100$$

In work involving diverse types of fruits, it is advisable to determine the absorption ratio

$$\frac{\log \frac{I_0}{I}\,(4875\text{ Å.})}{\log \frac{I_0}{I}\,(4375\text{ Å.})}$$

The ratio for lycopene (0.94) is nearly the same as for β-carotene (0.88). Deviations indicate the presence of appreciable quantities of carotenes other than the aforementioned two. When such samples are encountered it is necessary to chromatograph an aliquot to determine the β-carotene content more accurately.

Chromatographic Analysis. When results of greater accuracy for β-carotene are needed, the carotene fraction (20 ml.) is chromatographed on a column ((magnesia–Super Cel, 50–50)) 4 cm. long and 16 mm. in internal diameter (adsorptive powdered magnesia No. 2641, Westvaco Chlorine Products Corp., Newark, Calif.). After adsorption of the carotene, the column is washed with a small amount of hexane and then with 10% acetone in hexane until the β-carotene is completely eluted. The eluate is washed twice with water, made to 25-ml. volume, and analyzed spectroscopically at 4360 and 4780 A. (*1*).

DISCUSSION

Sampling. In preliminary studies, sections and equatorial slices of ripe, large fruits (Indiana Baltimore) were analyzed for carotene. A variation of 25 to 50% was found. Carotene contents of sections from fruits which appeared equally ripe differed by 16%; slices from corresponding fruits differed by 40%. Ellis and Hamner (*3*) have reported greater precision in their analyses of median slices, but their error is still greater than that found when several fruits are blended. The use of whole fruits reduces the precision error to about ±5%.

Extraction and Separation of Carotenoids. The skin pigments of tomatoes are not completely extracted by acetone and hexane, but are removed with hot alkali. Their absorption curves are not characteristic of carotenoids and presumably they can be ignored from the provitamin A standpoint. They are alkali-soluble and cannot be transferred to hexane.

The separation of carotenols and chlorophyll from β-carotene

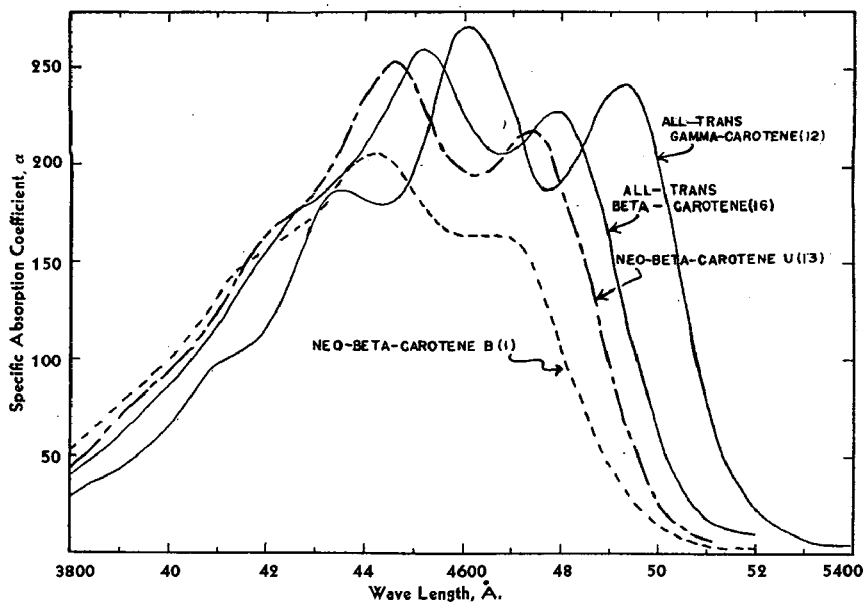

Figure 2. Absorption Curves of Four Additional Carotenes Found in Fruit of *Lycopersicon* Species and Strains (Solvent Hexane)

could probably be accomplished by chromatography of the hexane solution after washing it free of acetone. However, this method might involve considerable difficulties in the determination of both β-carotene and lycopene in a tomato extract. The latter pigment is of considerable importance from the consumers' standpoint, even though it has no vitamin A activity. Adaptation of the chromatographic method to routine analysis of a wide variety of tomato fruit types would probably require more experience to avoid serious losses than would be necessary in the use of immiscible solvent extraction methods.

Neither alkaline methanol solution (10 to 20% potassium hydroxide) nor aqueous methanol or acetone (5 to 25% water) extracted lycopene from hexane solution. β-Carotene is not appreciably removed from hexane by the procedure described in this paper. In recovery experiments known amounts of β-carotene (equivalent to the amount, 2 to 6 micrograms per gram fresh weight, occurring in commercial tomatoes) were added to tomato fruits in the Blendor cup before extraction by the solvent mixture. Recovery was 80 to 90%.

Analytical data on the total carotenoids of canned samples indicate no appreciable loss of pigments due to the canning procedure. The samples were heated at 100° C. for 0.5 hour after sealing in the cans.

Spectroscopic Analysis. Figures 1 and 2 present quantitative absorption curves of the ten most abundant carotenes found in fruits of *Lycopersicon*, including cis-isomers. The parts of the data taken from work of Zechmeister and co-workers were obtained with a Beckman spectrophotometer (*2*). Data from this laboratory were observed with the Müller-Hilger double monochromator spectrophotometer (*15*, *16*). Comparisons indicate excellent agreement between the two instruments in the spectral regions discussed. Of these ten pigments, γ-carotene, ζ-carotene, prolycopene, and all-cis lycopene are present in appreciable quantities in only a few strains of *Lycopersicon*. α-Carotene occurs very rarely. Neo-β-carotene U has been observed only in canned samples in the authors' experience. Those special cases require different analytical treatment and can be detected by the study of relative absorption values at appropriate wave lengths or by chromatography.

In Figure 1 some discrepancies are evident between the writers' data for all-trans lycopene and corresponding data from Zechmeister's work (*12*). Absorption values for several preparations of lycopene differed by only 1 to 2%, but the spectra of all preparations were shifted 10 to 20 Å. toward the blue with respect to Zechmeister's curve. Wave-length drum errors were eliminated by use of the mercury arc, but the possibility remains that the solutions were slightly isomerized, though great care was exercised to avoid isomerization. Values at the cis-peak agreed very well with Zechmeister's value of 26 (*12*). A relatively large uncertainty (±6.4%) in the absorption coefficients at the highest maxima for all-trans lycopene was noted by Zechmeister *et al.* (*12*). These comparisons indicate the extreme difficulty in preparing solutions of pure lycopene in the all-trans form and it is well known that this carotenoid isomerizes in solution very rapidly. Moreover, the absorption changes in isomerization are more marked with lycopene than with most other carotenoids.

In Figure 3 are presented together the curves for the pigments which occur abundantly in *Lycopersicon* fruits from the majority of sources and therefore are of most analytical interest. β-Carotene and lycopene and the isomers included in Figure 3 are also of

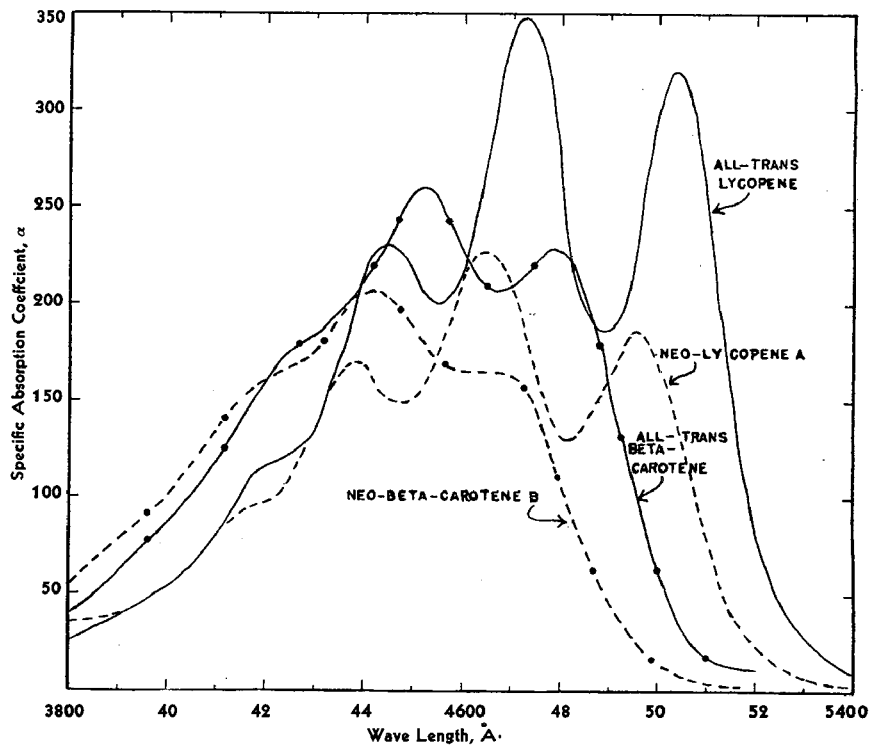

Figure 3. Absorption Curves of Carotenes Most Commonly Found in Fruit of *Lycopersicon* Species and Strains (Solvent Hexane)

Table I. Effect of Small Amounts of Polar Solvents on Absorption Values of Lycopene in Hexane Solution

Wave Length, Å.	Log $\frac{I_0}{I}$ Control	Sample through analysis	Acetone, Ml. 0.1	Acetone, Ml. 1.0	Acetone, Ml. 10.0	20% KOH in Methanol, Ml. 0.1	20% KOH in Methanol, Ml. 0.5	Methanol, Ml. 0.1	Methanol, Ml. 0.5	Ethanol, Ml. 0.1	Ethanol, Ml. 0.5	Ethanol, Ml. 1.0
5020	0.913	0.924	0.933	0.922	0.881	0.920	0.935	0.930	0.925	0.913	0.916	0.929
5000	0.906	0.918	0.906	0.890	0.854	0.909	0.926	0.915	0.910	0.906	0.901	0.917
4880	0.564	0.568	0.570	0.575	0.614	0.569	0.580	0.571	0.575	0.566	0.567	0.579
4780	0.819	0.826	0.832	0.851	0.905	0.830	0.842	0.832	0.840	0.833	0.828	0.849
4540	0.605	0.611	0.610	0.615	0.630	0.611	0.623	0.614	0.617	0.609	0.607	0.623
4430	0.673	0.685	0.684	0.678	0.666	0.684	0.691	0.680	0.681	0.676	0.675	0.688
4360	0.558	0.565	0.564	0.553	0.528	0.566	0.576	0.567	0.567	0.568	0.557	0.570
4330	0.483	0.490	0.489	0.480	0.466	0.489	0.500	0.490	0.490	0.489	0.483	0.494
4250	0.370	0.376	0.376	0.374	0.378	0.376	0.383	0.373	0.379	0.374	0.370	0.382

most practical importance from the nutritional and commercial viewpoints. In special cases other carotenes may be of more analytical importance but are not considered here.

The analytical situation presented in Figure 3 is further complicated because of the probable occurrence of cis-isomers in most samples. Certain assumptions regarding the extent of isomerization must be made in order to arrive at a practical solution of the problem.

In the tomato analyses made in this laboratory for component composition it is assumed that β-carotene is isomerized to neo-β-carotene B to the extent of 18%. This figure is close to that found in numerous vegetables (*1, 14*). Likewise, lycopene is assumed to be 20% isomerized to neolycopene A (see above values of absorption coefficients for the lycopene and β-carotene fractions).

The final hexane solutions of the carotene fraction should be studied within a few days after preparation. In contrast the absorption of the β-carotene fraction (chromatographically separated) at 4360 Å. remains unchanged for several weeks at +4° C.

Analyses based upon this system are sufficiently accurate for a practical breeding program unless the absorption ratio

$$\frac{\log \frac{I_0}{I}\,(4875\text{ A.})}{\log \frac{I_0}{I}\,(4375\text{ Å.})}$$

is less than 0.85 or greater than 0.94. When such samples are found, the β-carotene content can be checked by chromatography. Identification of other carotenes (*10*) may be accomplished by chromatography and spectroscopy.

Since small quantities of polar solvents may remain in the final hexane solution prepared for spectroscopic analysis, the effect of such traces on the spectroscopic properties of lycopene was studied. Results for pertinent wave lengths are tabulated in Table I. The indicated amounts of polar solvents were added to 25 ml. of a hexane solution of lycopene. Absorption values presented correspond to uniform quantities of pigment, since corrections have been made for volume changes.

The data in Table I indicate that large amounts of polar solvents cause considerable changes in absorption values. The solutions containing 0.1 ml. of polar solvent per 25 ml. of total solution have spectroscopic properties similar to the solution which was subjected to the entire analytical procedure. Good agreement (1 to 2% difference) between values for the latter solution and control solution was found. No greater error should be expected in the case of other carotenes.

Chromatographic Analysis. In chromatographic analysis with magnesia, recovery of β-carotene, in quantities of 2 to 6 micrograms per gram fresh weight, varied from 80 to 90%, regardless of whether lycopene was present. Characteristic curves of the β-carotene fraction usually indicated only β-carotene and a small amount of its isomers. Occasionally a sample was found which had a considerable amount of ζ-carotene. When this occurred the value for β-carotene obtained at 4360 Å. was too high.

In the most important analyses it is a good precaution to check the spectroscopic results with those obtained by the chromatographic method. In a series of 18 such checks (reported in Table II), made on widely diverse *Lycopersicon* types, the average deviation of the spectroscopic result for β-carotene from the result by chromatography was 8%; the maximum deviation was 24%. Disagreements between the two methods were much less serious in many series of analyses of fruits with similar genetic background. The series of Table II represents extremes encountered in the authors' studies. Two other checks disagreed more seriously, but this was expected because each had an abnormal absorption ratio (4875 Å./4375 Å.).

All the abnormal absorption ratio values in Table II occurred in the samples in the lower range of β-carotene contents (below 10 micrograms per gram).

Table II. Comparison of Spectroscopic and Chromatographic Analysis for β-Carotene

Sample	Content of β-Carotene Fraction: Chromatographic	Spectroscopic[a]	Difference	Difference[b], %	Absorption Ratio[a], 4875 Å./4375 Å.
	Micrograms per Gram Fresh Weight				
1	90.0	82.6	−7.4	8.2	0.86
2	83.6	76.9	−6.7	8.0	0.84
3	67.5	59.3	−8.2	12.1	0.81
4	57.9	54.5	−3.4	5.9	0.83
5	55.1	55.0	−0.1	0.2	0.88
6	53.2	53.1	−0.1	0.2	0.81
7	50.4	50.3	−0.1	0.2	0.80
8	49.6	52.0	+2.4	4.9	0.87
9	48.2	55.6	+7.4	15.3	0.84
10	23.9	24.3	+0.4	1.7	0.88
11	18.7	18.7	0.0	0.0	0.89
12	14.7	16.4	+1.7	11.5	0.87
13	12.1	13.1	+1.0	8.0	0.86
14	10.0	15.4	+5.4	(54.0)[c]	0.98
15	8.5	7.6	−0.9	10.6	0.92
16	7.5	8.2	+0.7	9.3	0.89
17	7.5	5.7	−1.8	24.0	0.89
18	5.4	4.3	−1.1	20.4	0.92
19	4.3	4.0	−0.3	7.0	0.87
20	3.5	13.3	+9.8	(280.0)[c]	0.39

Average deviation, 8.2%
Maximum deviation, 24.0%

[a] Calculated from light absorption values obtained for carotene solutions before chromatographic analysis.
[b] Calculated as per cent of chromatographic result.
[c] Omitted from average.

In no case was the disagreement between methods sufficient to alter the course of the genetic work based upon these analyses. In critical work where small differences are important and where the numbers of analyses are small, a complete check of methods, including plotting of characteristic absorption curves, should be performed. For survey work involving large numbers of samples and where only large differences are significant, as in breeding work, the spectroscopic method by itself is considered adequate, providing chromatographic checks are made on the most significant and most diverse results.

Biological Implications. Among the pigments discussed, β-carotene is of predominant nutritional interest because of its

activity as provitamin A. Of lesser importance are neo-β-carotene B, neo-β-carotene U (in canned samples), γ-carotene, and α-carotene. Lycopene and its isomers are inactive and ζ-carotene has recently been found inactive (*9*). Results of several biological assays (rat-growth tests), recently conducted on canned tomato samples of widely different β-carotene contents, indicate that the content of β-carotene is at present the best index of provitamin A activity, but that other carotenoids may increase this activity of *Lycopersicon* fruits.

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Colorimetric Determination of DDT in Milk and Fatty Materials

MILTON S. SCHECHTER, MILTON A. POGORELSKIN, AND H. L. HALLER

U. S. Department of Agriculture, Agricultural Research Administration, Bureau of Entomology and Plant Quarantine, Beltsville, Md.

A procedure has been developed for the determination of DDT as such in foodstuffs containing considerable amounts of fatty matter such as milk, butter, and animal fat. Although the method is not rapid, it permits the detection and determination of DDT in milk in quantities as low as 1 p.p.m.

RECENT articles (*11, 13, 16, 17, 21*) have focused attention on the possible danger to the public health from contamination of such products as milk, butter, eggs, meat, and fats when farm animals consume DDT-treated feed. Pharmacological investigations (*21*) have shown that ingested DDT accumulates as such in the fatty tissues of experimental animals and can be excreted in milk. Some of the DDT is metabolized to bis(*p*-chlorophenyl) acetic acid (*3, 20*), which is excreted in urine (*5, 7, 20*). Telford's (*16*) and Telford and Guthrie's (*17*) DDT-feeding experiments on goats and rats, using rather high dosages, indicate that such milk may become toxic enough to kill other animals drinking it. In order to evaluate some of these factors, the Bureau of Entomology and Plant Quarantine started an investigation of the contamination of these foods as a result of feeding DDT-treated crops to farm animals.

The problem of analyzing these foodstuffs is complicated considerably by the presence of large amounts of fatty matter which accompany the DDT in organic solvent extracts—for example, about 4 grams of butterfat will be extracted with the DDT from each 100 grams of milk. Any attempt to detect 0.1 mg. of DDT in 100 grams of milk (equivalent to 1 p.p.m.) by any of the published methods of analysis (*1, 4, 6, 12, 13, 15, 19*) is likely to encounter difficulty because of the large amount of interfering fatty matter. The Schechter-Haller colorimetric method (*10, 12*), although having the advantage of oxidizing a considerable amount of extraneous matter during the nitration, cannot be used on samples containing more than a few tenths of a gram of fatty matter because of the danger of an uncontrollably violent nitration. Attempts to nitrate 0.5 gram or more of butterfat containing DDT led to violent nitrations, and even when the nitration was carefully carried out to prevent a violent reaction, the results obtained were low or negative. Neither Woodard *et al.* (*21*) nor Ofner and Calvery (*7*) mentioned this difficulty when they used the method in pharmacological investigations, probably because there was enough DDT present so that very small samples could be used.

In order to detect very small amounts of DDT, it is necessary to find some method of removing extraneous material and concentrating the DDT. Attempts to concentrate the DDT by chromatography were not successful. Low-temperature precipitation of the fat by cooling a solution with solid carbon dioxide gave rise to difficulties in filtration. Saponification of the fat and use of the unsaponifiable portion would eliminate most of the fatty matter but would, at the same time, convert DDT to its dehydrochlorinated derivative. Such a procedure might be useful if one were not interested in whether the DDT was present as such or had decomposed to its dehydrochlorinated derivative. The method of Stiff and Castillo (*14, 15*) has this disadvantage.

In the authors' experiments it was highly desirable to establish incontrovertibly the presence of DDT as such and to estimate its concentration. The observation of the solubility of fats and the insolubility of DDT in concentrated sulfuric acid led to the development of the procedure described in this article for eliminating all but a small residue from fatty materials. This residue probably consists mostly of hydrocarbons. A search of the literature disclosed similar methods for the determination of oil deposits on

Table I. Recovery of DDT Added to Milk

DDT Added	DDT Found Uncorrected for blank	DDT Found Corrected for blank	Recovery Corrected for Blank
P.p.m.	*P.p.m.*	*P.p.m.*	*%*
0 (blank)	0.35[a]	...	...
0 (blank)	0.38[a]	...	...
1.00	1.27	0.90	90
1.00	1.30	0.93	93
5.00	5.60	5.23	105
5.00	5.40	5.03	101

[a] Calculated as DDT; the characteristic blue color was not produced.

leaves (*9*) and of diphenyl in oranges (*2*, *18*). The relationship to the refining of petroleum with sulfuric acid is also interesting to note.

APPARATUS AND REAGENTS

Some of the apparatus and reagents are described by Schechter *et al.* (*12*); it is advisable to use test tubes 25 × 200 mm. or larger for the nitrations.

Separatory funnels, 500-ml. capacity, should be prepared in the same manner as the 125-ml. separatory funnels mentioned by Schechter *et al.* (*12*) and should be dry when used.

Centrifuge and centrifuge bottles with rubber caps.

Sodium sulfate–sulfuric acid. Dissolve 100 grams of C.P. anhydrous sodium sulfate (oven-dried) in 1 liter of C.P. concentrated sulfuric acid (sp. gr. 1.84) with the aid of heat, and cool to room temperature. Sodium bisulfate is probably formed in the solution.

Fuming sulfuric acid–concentrated sulfuric acid. A mixture of equal volumes of fuming sulfuric acid (20 to 30% sulfur trioxide) and concentrated sulfuric acid (sp. gr. 1.84).

Sodium bicarbonate solution, 5%.

Technical acetone, technical chloroform, and Skellysolve B (a petroleum fraction, boiling at 60° to 70° C.). These solvents should be redistilled before using.

It is advisable to have all apparatus rinsed several times with redistilled technical acetone and dried. The acetone may be saved and recovered.

PROCEDURE

To 100 grams of milk which has been thoroughly mixed before sampling add an equal volume of 95% ethanol. Divide the solution equally between two 200-ml. centrifuge bottles. When the concentration of DDT is higher than 5 p.p.m., it is advantageous to take a correspondingly smaller milk sample. Where larger bottles are available, the sample need not be divided. Add 50 ml. of Skellysolve B to each bottle, cover the bottles with rubber caps, shake vigorously, and centrifuge at 2000 r.p.m. for 15 minutes. Pour the contents of both bottles into a 500-ml. separatory funnel.

After the layers have separated, drain the lower layer in equal portions directly into the same centrifuge bottles. Drain the upper Skellysolve B layer through a 5-cm. tightly packed plug of cotton held in a glass Gooch crucible holder into a 500-ml. Erlenmeyer flask with a standard ground-glass joint. Extract the solution in each centrifuge bottle in the same manner as before with two successive 25-ml. portions of Skellysolve B and a final 50-ml. portion centrifuging for about 10 minutes each time; return the lower layers from the separatory funnel to the centrifuge bottles and filter the upper layers through the plug of cotton into the Erlenmeyer flask. After the last extraction, rinse the separatory funnel with 50 ml. of Skellysolve B, which is also run through the plug of cotton into the Erlenmeyer flask. Add a glass bead to the Erlenmeyer flask and recover the Skellysolve B from the milk extract by distillation on the steam bath, using an all-glass apparatus. While the flask is being heated, insert a tube connected to a vacuum line to remove the last traces of solvent.

Quantitatively wash the residue from the distillation into a 500-ml. separatory funnel with 150 ml. of chloroform. For the analysis of butter or fat, substitute for this residue a 5-gram sample or an extract thereof from which the solvent has been removed. Place 100 ml. of chloroform in a second 500-ml. separatory funnel, and extract the chloroform solutions successively with (1) 50 ml. of sodium sulfate–sulfuric acid, (2) 50 ml. of sodium sulfate–sulfuric acid, (3) 50 ml. of fuming sulfuric acid–concentrated sulfuric acid, and (4) 50 ml. of sodium sulfate–sulfuric acid. If this last wash is not light in color, it is advisable to use still another sodium sulfate–sulfuric acid wash. Drain each acid wash (lower layer) from the first funnel into the second funnel and finally into a 250-ml. cylinder. The extraction in the second funnel is used to minimize the loss of DDT by the slight emulsification of chloroform in the acid washings. The funnels should be shaken vigorously each time and then allowed to stand for 10 to 15 minutes before draining off the acid layer. In the rare case where an emulsion forms and does not separate in 30 minutes, the mixture may be centrifuged and poured gently back into the separatory funnel. It is well to keep a small beaker under each funnel and to have a wet cloth handy to wipe any acid which may drip.

After the acid extractions are completed, filter the chloroform from the first funnel and then from the second funnel through a 5-cm. tightly packed plug of cotton in a glass Gooch crucible holder into a third 500-ml. separatory funnel. Pipet off any chloroform which has risen to the surface from the combined acid washings in the cylinder and run it through the plug of cotton. Rinse the two funnels and the cotton with chloroform, using about 50 to 100 ml. Add enough 5% sodium bicarbonate solution (about 40 ml.) to the combined chloroform filtrate so that it will remain alkaline when tested with litmus paper after vigorous shaking. After allowing about 10 minutes for a reasonably clear separation, filter only the chloroform layer through a 5-cm. plug of tightly packed cotton in a glass Gooch crucible holder into a 500-ml. Erlenmeyer flask with a standard joint. Wash the sodium bicarbonate solution remaining in the funnel with two successive 30-ml. portions of chloroform, which are also run through the cotton into the Erlenmeyer flask. If the filtrate is not clear, filter again.

Add a glass bead to the Erlenmeyer flask and recover the chloroform on the steam bath, using an all-glass system, until only about 10 ml. of solution are left. Wash this quantitatively into a large test tube (25 × 200 mm. or larger) with acetone, add a glass bead, and cautiously evaporate the solvent on the steam bath, removing the last traces by inserting a tube connected to a vacuum line. Nitrate the residue with 5 ml. of nitrating mixture and complete the analysis as described by Schechter *et al.* (*12*).

Since there will still be some interference from the small amount of raffinate from the butterfat, it is advisable to make spectrophotometric measurements at 600, 620, and 640 millimicrons (a Beckman quartz spectrophotometer was used) and average the results. Below 600 millimicrons there may be enough interference to cause rather high results, so that it may be impossible to calculate the amounts of *p,p'*-DDT and *o,p'*-DDT and add them to obtain the total DDT. Consequently, it is desirable to use as a standard a sample of the same DDT as was used in the feeding experiment. If it is not available, DDT of the same type and grade may be used.

DISCUSSION

The method of extracting the milk differs from a similar procedure described by Olson *et al.* (*8*) in that a centrifuge is used to break emulsions rapidly and Skellysolve B is used rather than a mixture of Skellysolve B with ether. In the present procedure it is not necessary to wash the extract with water to remove ethanol, since Skellysolve B alone does not extract ethanol along with the butterfat.

Chloroform is used for the sulfuric acid treatment, because it gives the least trouble with emulsification in the presence of butterfat. The addition of sodium sulfate to the sulfuric acid also seems to aid in preventing emulsification. If solvents other than chloroform are used or if sodium sulfate is not added to the sulfuric acid, emulsions of the consistency of mayonnaise may form. The mixture of fuming sulfuric acid–concentrated sulfuric acid removes material from the chloroform solution of butterfat which is not removed by the sodium sulfate–sulfuric acid washes. The use of straight fuming sulfuric acid containing 20 to 30% of sulfur trioxide has been found to give low results, probably by sulfonation and removal of the DDT. Phosphoric acid (85%) has been tested in this extraction procedure in place of the sulfuric acid but it does not seem to be so satisfactory.

With the amounts of reagents described, persistent emulsions which do not break in 20 minutes will be formed only rarely. If an emulsion is formed, it may be centrifuged or, preferably, the analyses repeated using a smaller sample. If larger samples must be used and emulsions are as a consequence regularly encountered, one or two preliminary extractions of the chloroform solu-

tion with sodium sulfate–concentrated sulfuric acid using gentle shaking is advisable.

Biological tissues may be treated with sodium sulfate as described by Smith and Stohlman (*13*) or Ofner and Calvery (*7*). After evaporation of the solvent used for extraction, the residue may be dissolved in chloroform and submitted to the sulfuric acid extraction procedure described above.

p,p'-DDA, or bis(*p*-chlorophenyl)acetic acid, when put through the sulfuric acid treatment, is removed and does not interfere in the analysis for DDT. If *p,p'*-DDA is to be determined in biological tissues, it should first be separated from the sample by utilizing its acidic properties. It can be extracted from an ether solution of the sample (or extract thereof) with sodium bicarbonate solution, which should be separated, acidified, and extracted with fresh ether. Evaporation of the ether will give a residue containing the *p,p'*-DDA. This can usually be nitrated directly and determined by comparison with *p,p'*-DDA standards run by the Schechter-Haller colorimetric procedure (*12*). If traces are to be determined and interferences are encountered, the residue instead of being nitrated directly can be submitted to a modified sulfuric acid treatment. The modification consists in omitting the fuming sulfuric acid–concentrated sulfuric acid and the sodium bicarbonate washes and using only four sodium sulfate–sulfuric acid washes and one wash with 40 ml. of water. Duplicate determinations on 1.00 mg. of *p,p'*-DDA using this modification have given recoveries of 95 and 91%.

Table II. Analyses of Milk, Butter, and Fat for DDT

Sample, ID No.		DDT	Sample, ID No.	DDT
		P.p.m.		*P.p.m.*
Milk	10,004	3, 3	Milk 10,187	21, 21
	10,038	4, 4	10,188	20, 20
	10,109	15, 15, 18	10,198	21, 24
	10,110	14, 15, 16	10,199	25, 26
	10,141	19, 20	10,197 (blank)	0.4[a], 0.4[a]
	10,142	20, 20	Butter 10,200	456, 456
	10,151	22, 23	10,201	530, 534
	10,152	20, 20	Fat from steak, 10,380	178, 179
			Lean meat from steak, 10,380	4, 4

[a] Calculated as DDT; the characteristic blue color characteristic was not produced.

The application of the sulfuric acid treatment prior to the nitration of the sample may eliminate interfering substances if they are soluble in sulfuric acid or easily sulfonatable. For example, a 5.0% solution of DDT in Velsicol NR-70 (chiefly tetramethylnaphthalene) when analyzed by direct nitration gave values of 10.5 and 10.7%, whereas when the sample was put through the sulfuric acid treatment described under Procedure, values of 5.2 and 5.1% were obtained.

RESULTS

The procedure was first tested on technical DDT and dehydrochlorinated *p,p'*-DDT[1,1-dichloro-2,2-bis(*p*-chlorophenyl)ethylene] to determine the percentage recovery of these materials in the absence of butterfat. When 1.00 mg. of technical DDT was dissolved in 150 ml. of chloroform and carried through the described treatment, 100% recovery was obtained in duplicate runs. When 1.00 mg. of dehydrochlorinated *p,p'*-DDT was treated in the same manner, it was recovered to the extent of 97 and 99% in duplicate runs. Since dehydrochlorinated *p,p'*-DDT is evidently not removed by the sulfuric acid treatment, its presence to any appreciable extent in a sample may be detected by its effect on the absorption spectrum of the developed color. Dehydrochlorinated *p,p'*-DDT gives a red color in the Schechter-Haller colorimetric test (*12*), with an absorption spectrum different from that of the blue color of DDT. *o,p'*-DDT and its dehydrochlorinated derivative likewise would be expected to be unaffected by the sulfuric acid treatment. Any *p,p'*-DDA[bis(*p*-chlorophenyl)acetic acid] which is not removed by the sulfuric acid washes will be removed in the sodium bicarbonate wash of the chloroform solution and hence will not interfere in this determination.

The complete procedure, starting with the extraction of the milk sample, was tested by adding known amounts of technical DDT to the milk. To 100 grams of milk 0.1 mg. of technical DDT in acetone was added to give 1 p.p.m., and to 100 grams of milk 0.50 mg. of technical DDT in acetone was added to give 5 p.p.m. The results of these analyses together with the analyses of the original milk without any DDT added (blank analyses) are given in Table I. The procedure when applied to milk containing as low as 1 p.p.m. of DDT gave an easily discernible characteristic blue color. The blank milk, to which no DDT was added, gave only a yellow color.

Table II shows the results of analyses of milk, butter, and fat samples for DDT content. These samples came from cows which were given DDT-treated feed, except ID 10,197, which came from a control cow that did not receive any DDT. The results are in duplicate or triplicate and have been rounded off to the nearest whole number except for the blanks. Some of the deviations may have been due to inadequate mixing and sampling of the milk, which in many instances had separated on standing. The blue color, characteristic of DDT, was developed in all cases except for the blank milk, ID 10,197.

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Estimation of DDT in Milk by Determination of Organic Chlorine

R. H. CARTER

United States Department of Agriculture, Agricultural Research Administration, Bureau of Entomology and Plant Quarantine, Beltsville, Md.

THE use of DDT as an insecticide on forage and truck crops such as alfalfa, clover, and pea vines, which may be used as feed for livestock, particularly for beef and dairy cattle, has created a need for methods of determining DDT in milk or meat products from these animals.

Methods for the determination of small amounts of DDT occurring as insecticidal residues have been reviewed by Cristol and Haller (*1*). These methods are based on the determination of total or hydrolyzable organic chlorine or on a colorimetric determination (*3*).

The method herewith presented describes a procedure for estimation of DDT in milk and butter samples by determination of the total organic chlorine. This method is rapid, simple, and reasonably sensitive, but it is not specific for DDT. It is possible that other halogen-containing organic insecticides, fungicides, and herbicides, such as Spergon (tetrachlorobenzoquinone), 2,4-dichlorophenoxyacetic acid (2,4-D), *p*-dichlorobenzene, and benzene hexachloride, may also be taken up and stored in milk and meat products. Milk samples analyzed were taken from cows on diets containing DDT, and the presence of DDT in the milk was confirmed by the modified Schechter-Haller colorimetric test (*2*).

REAGENTS

Ethyl alcohol, 95%. Ethyl ether, C.P. Petroleum ether (Skellysolve B). Isopropanol, commercial, 99%.

Sodium, metallic. Silver nitrate, C.P., 0.05 or 0.025 *N* solution. Benzene, commercial, C.P.

Table I. Percentage Recovery of Known Amounts of DDT Added to Milk

Added	Found	Recovery
Mg.	*Mg.*	%
0.00	0.00	
16	15.4	96.2
20	20.1	100.5
50	48.5	97.0

PROCEDURE

Mix 200 ml. or 200 grams of well-homogenized milk with 200 ml. of ethyl alcohol in a separatory funnel. Extract with 250 ml. of mixed solvent (75% ethyl ether, 25% Skellysolve B) by gentle shaking. Use gentle agitation rather than violent shaking during the first extraction to prevent formation of stable emulsions. After separation of the two layers, draw off the aqueous layer and extract three times more with 100-ml. portions of the mixed solvent. Shake vigorously for 5 minutes in each of the last three extractions. Discard the aqueous phase. Combine the solutions from the four extractions in an Erlenmeyer or other suitable flask and evaporate the solvent on the steam bath. Remove the last traces of water by addition and distillation of two 50 ml. portions of benzene.

To the residue in the flask add 150 ml. of isopropanol and approximately 6 grams of metallic sodium cut into small pieces. Reflux for 2 hours with moderate boiling. Add 25 ml. of ethyl alcohol and allow to stand for a few minutes to react with all remaining metallic sodium. Dilute with 100 ml. of water poured through the condenser. Transfer the liquid to a 600-ml. beaker and evaporate most of it on the steam bath. Make up to a volume of approximately 400 ml. with water, warming if necessary to put the soap in solution. Make acid with sulfuric acid to break up the soap and precipitate the fatty acids. Cool with ice or tap water and filter. Wash the precipitate twice with water.

Table II. Amounts of DDT Found in Milk from Cows Receiving DDT in the Diet[a]

Calculated from Total Organic Chlorine	Calculated from Colorimetric Determination[b]
P.p.m.	*P.p.m.*
1.5	3
2	3
4	3
3	4
15	15
17	19
16	22
23	23
25	25

[a] Blanks less than 0.2 by both methods.
[b] Determinations made by M. S. Schechter (*2*).

Combine the aqueous filtrate and washings and extract twice with 100-ml. portions of the mixed solvent (ether–Skellysolve B). Make the aqueous solution alkaline to phenolphthalein with 2 *N* potassium hydroxide. If the volume is in excess of approximately 300 ml., it should be concentrated by evaporation.

Make the solution acid with nitric acid, adding a slight excess, and determine chloride ion by any of the standard procedures. In their investigations the authors have determined the chloride content by electrometric titration with standard silver nitrate. The Volhard procedure is also applicable. Calculate the amount of DDT by multiplying the amount of chlorine by 2.

Recovery of known amounts of DDT added to milk has been 95% or more, as shown in Table I.

Determinations of organic chlorides in milk from cows on a DDT-free diet showed less than 0.2 p.p.m. of chlorine present. In milk from cows receiving DDT in the diet, the chlorine from organic chlorides ranged from approximately 1 to 12 p.p.m. Colorimetric determinations (*2*) have confirmed the presence of DDT in these samples in the amounts indicated by the total-chlorine determinations. These results, shown in Table II, represent the average analyses on several samples; the differences between individual determinations were not significant.

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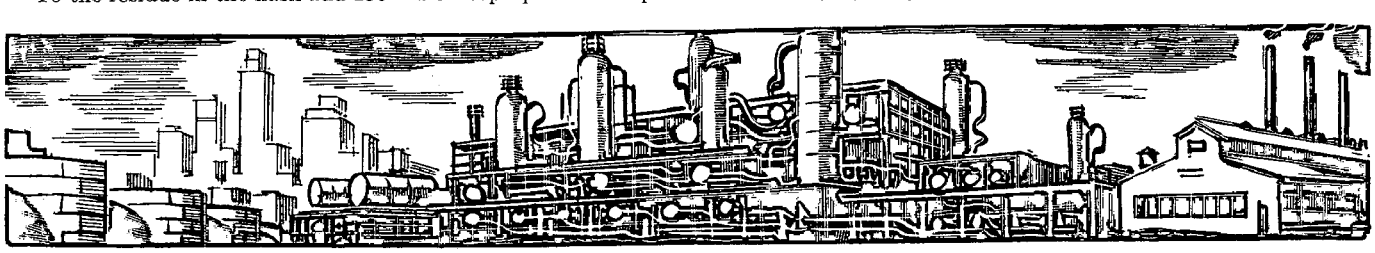

Colorimetric Method for Determination of Traces of Carbon Dioxide in Air

NORMAN A. SPECTOR[1] AND BARNETT F. DODGE
Yale University, New Haven Conn.

A colorimetric method for determining traces of carbon dioxide, using a Lumetron photoelectric colorimeter, depends on the decrease in color intensity of a solution of sodium hydroxide colored with phenolphthalein indicator. The alkalinity of the solution decreases as it absorbs carbon dioxide from the gas sample to be analyzed and consequently the depth of color decreases. The change in the amount of light which the solution transmits is made a measure of carbon dioxide concentration. The precision and sensitivity of the method are functions of the carbon dioxide concentration as well as the volumes of the gas sample and absorbing solution. In general the precision increases with increase in carbon dioxide concentration being measured, with the use of larger gas samples and, within limits, with the use of smaller volumes of absorbing solution. The accuracy of the results is considered to be of the same order as the precision. A 1-liter gas sample is sufficient to determine a carbon dioxide concentration in air of 0.0010% (10 p.p.m.) with a precision of 10%—i. e., ±0.0001%.

THE motive underlying the development of this analytical method was its application to the removal of carbon dioxide from atmospheric air. Such removal is essential to the proper functioning of many processes, and the evaluation of absorption coefficients indicating the performance of equipment for this service requires a rapid and accurate determination of traces of carbon dioxide in the inlet and exit air streams.

This paper presents the development of a method for accurately determining traces of carbon dioxide in air over the concentration range from 0.0315%, usually found in atmospheric air, down to 0.0005%. For this range ordinary gas analysis apparatus cannot be used and the gravimetric methods previously available required large volumes of gas and were too long and tedious. Analytical methods reported in the literature were reviewed, and from this group a colorimetric method which gave promise of being accurate and relatively simple was singled out for further investigation and development. The method is quick and accurate, requires a relatively small gas sample, and utilizes apparatus which is readily available.

ANALYTICAL PROCEDURE

Principles of the Method. A standard solution of sodium hydroxide is prepared and colored with phenolphthalein indicator. As this solution absorbs carbon dioxide from a gas sample the alkalinity is reduced, thus decreasing the intensity of color of the original solution. This change in color is made a measure of the carbon dioxide content of the gas sample. The extent of change in color is shown by means of a photoelectric colorimeter which measures the light transmission of the solutions. Thus, if the standard solution transmits 10% of the light by some arbitrary 100% standard, a solution which has absorbed carbon dioxide will by the same standard transmit more light, the increase in light transmission being related to the carbon dioxide absorbed from a gas sample.

The method requires that a known volume of standard solution and gas sample be brought into intimate contact, so that the solution absorbs all the carbon dioxide in the gas sample. This may be accomplished by means of bubblers or by drawing a gas sample into a holder containing a measured amount of solution, and then shaking the contents thoroughly.

[1] Present address, Chemical Engineering Department, The M. W. Kellogg Co., 225 Broadway, New York 7, N. Y.

Apparatus and Solutions. A Lumetron photoelectric colorimeter, Model 402E, manufactured by the Photovolt Corporation, New York, N. Y., was used for the light transmission measurements. The instrument reads directly in per cent transmission. A 100-mm. cell was used with this instrument, requiring a solution volume of 80 cc. and providing a light path 100 mm. long.

Preliminary tests showed that a monochromatic (narrow band) filter having its transmission peak at a wave length of 515 millimicrons was most sensitive to the changes in color intensity of phenolphthalein in alkaline solution. The basis for selecting this filter may be explained as follows.

A solution of a definite color does not transmit equally well all wave lengths of light. Usually there is a narrow band of wave lengths in which certain specific wave lengths are almost entirely transmitted, and other wave lengths are almost entirely absorbed (Figure 1). Since the color intensity limits of this method are the original color of phenolphthalein in sodium hydroxide solution (transmission = x %) and a colorless solution (transmission = 100%), the maximum range and sensitivity of this determination is (100 − x)% light transmission. It is therefore-

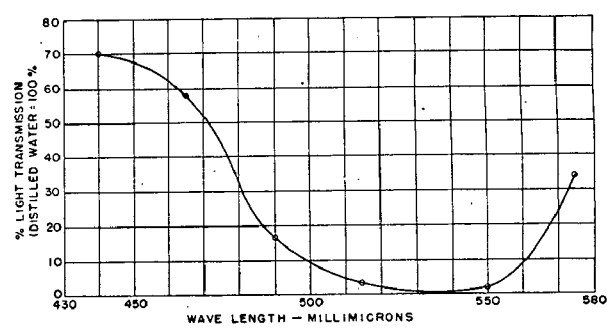

Figure 1. Relative Transmission of Light by a 0.0001 *N* Sodium Hydroxide Solution Colored with Phenolphthalein

obvious that for optimum range and sensitivity the initial transmission value, x, of the colored sodium hydroxide standard solution should be as low as possible. However, even the darkest solution of sodium hydroxide obtainable by adding considerable quantities of phenolphthalein transmits a very large percentage of the light from a standard light bulb source. Hence, it is ap-

parent that the light transmission of the solution can be greatly reduced only by using light of a wave length which is inherently but slightly transmitted by the solution.

By the use of colored glass filters substantially monochromatic light of various wave lengths can be isolated from the light bulb source. The transmission of various light wave lengths by a sodium hydroxide solution colored with phenolphthalein was measured by the author and the data of Figure 1 were obtained This curve shows a very low transmission at 515 millimicrons, and a monochromatic light filter having its transmission peak at this wave length was selected because of ready availability. It is apparent that this choice of filter gives a maximum range and sensitivity to this method.

The color temperature of the light source depends on the lamp temperature. For convenience in routine work, the lamp temperature adjustment can be made by noting the galvanometer deflection with only the filter in place. The temperature of the light source was arbitrarily maintained at its maximum reproducible value as indicated by the galvanometer deflection. Slight changes in the temperature of the light source because of line voltage fluctuations introduced no detectable error.

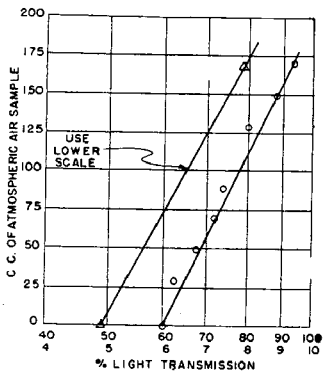

Figure 2. Change in Light Transmission of a Standard Sodium Hydroxide Solution Colored with Phenolphthalein Due to Absorption of Carbon Dioxide from Atmospheric Air

130 cc. of solution used. Runs 1 to 7

The method requires that a small amount of neutralization shall cause a considerable change in pH of the absorbing solution and consequently in the color of the indicator. Hence, the sodium hydroxide must be very dilute. Good results were obtained using as the absorbing solution 0.0001 *N* sodium hydroxide colored with sufficient phenolphthalein indicator, so that the light transmission of this standard was of the order of 10% as against a reading of 100% light transmission for distilled water. Solutions stronger than 0.0001 *N* were tried but their sensitivity to traces of carbon dioxide was poor. Weaker sodium hydroxide solutions are very sensitive to small amounts of carbon dioxide, as is to be expected in view of the small quantities required to neutralize them. Solutions of sodium hydroxide more dilute than 0.0001 *N* can be used to gain extra sensitivity, provided extreme caution is exercised in guarding against contamination of the standard solution. They require frequent recalibration to check on the effects of possible contamination by atmospheric carbon dioxide.

General Method of Analysis and Calibration. The analysis requires that all the carbon dioxide in a known volume of gas sample be absorbed in a fixed volume of the standard solution. The solution is then transferred to the Lumetron where the light transmission is measured. The amount of carbon dioxide required to produce the measured light transmission in the volume of solution used is found from an empirical calibration curve, and knowing the gas sample volume, the carbon dioxide concentration is easily calculated.

Extreme care must be taken to prevent contamination of the sample solution by carbon dioxide from the atmosphere. Commercial nitrogen made from liquid air or some other source of carbon dioxide–free gas must be used to purge all the vessels before they are used for this analysis. Atmospheric air can be used as a gas mixture of known carbon dioxide concentration, provided it is taken from the open air and not from the laboratory. The calibration curve is readily obtained by using a calibrated gas holder as an absorption chamber. In general, the carbon dioxide contained in different volumes of air is absorbed by a fixed amount of absorbing solution and the transmissions are measured. This determines a calibration curve of transmission values versus absolute amount of carbon dioxide as contained by the samples of air and can be used for any size of air sample. For different volumes of absorbing solution the individual calibration curves must be determined.

CALIBRATION AND RESULTS USING AIR

Apparatus and Solutions. The absorption vessel may be any ordinary gas-sampling tube of accurately known capacity (in this case 300 cc.) fitted at the top with a three-way stopcock and at the bottom with a two-way stopcock and graduated so that the volume of solution and the volume of gas in it can be read. A sodium hydroxide solution approximately 0.0001 *N* is made up in a large carboy and colored with phenolphthalein until its transmission is approximately 10%. The lamp temperature is set to give a maximum reproducible deflection of the galvanometer scale through a 100-mm. cell filled with distilled water. The carboy should be fitted with a soda-lime tube and siphon for delivery of the solution.

Method of Calibration. The absorption tube is first purged with commercial nitrogen which is free of carbon dioxide, and then connected to the siphon of the colored sodium hydroxide standard and a volume of this solution allowed to enter. The volume of solution required is that of the absorbing solution to be used plus the volume of air to be taken (in most cases 100 cc. of solution and 50 to 200 cc. of air are used).

One end of the tube is connected to the gas sample and by running out sodium hydroxide through the other end air is sucked in until the predetermined volume is obtained. After a few minutes of vigorous shaking, the carbon dioxide is absorbed by the solution, the color of which is decreased. The absorption vessel is then vented to the atmosphere through a soda-lime absorption tube and the solution is drained into a colorimeter test cell previously purged with nitrogen. The sample is then placed in the colorimeter and the per cent light transmitted by this solution determined, using as a standard 100% light transmission by clear distilled water. Other standards of light transmission can be used; two other standards tried were such that the original colored sodium hydroxide solution showed a light transmission of 50 and 60%, respectively. Transmissions obtained using a standard of 100% light transmission by clear distilled water are designated as "absolute transmission", whereas the other standards give "relative transmission" values.

The carbon dioxide content of air has been determined by many investigators and has been found to remain approximately constant at a value of 0.031%. Several check determinations were made by the author using a barium hydroxide absorption

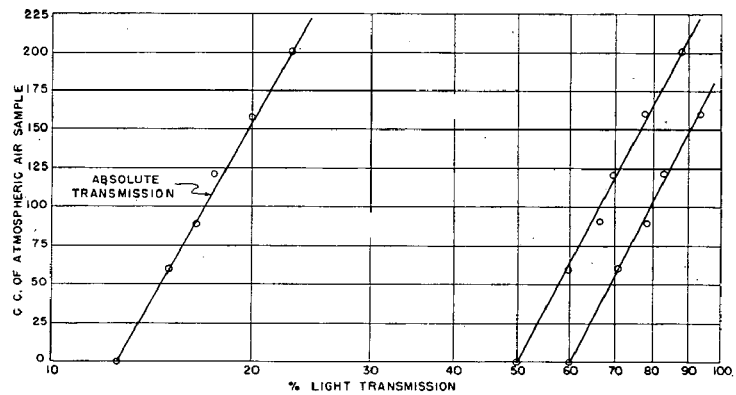

Figure 3. Change in Light Transmission of a Standard Sodium Hydroxide Solution Colored with Phenolphthalein Due to Absorption of Carbon Dioxide from Atmospheric Air

100 cc. of solution used. Runs 9 and 13 to 19

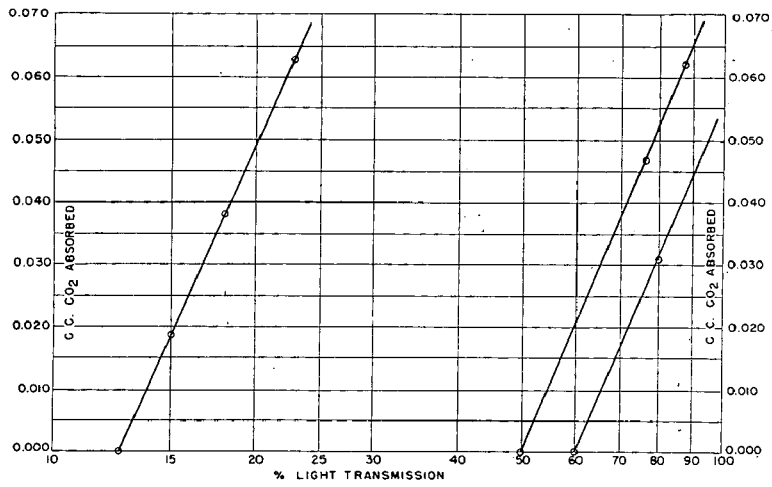

Figure 4. Change in Light Transmission of a Standard Sodium Hydroxide Solution Colored with Phenolphthalein Due to Absorption of Carbon Dioxide

Data from plot of Figure 3. 100 cc. of solution used

method and the literature findings were substantiated by results which showed the carbon dioxide content of clean air to be essentially constant and equal to 0.0315%. Thus, knowing the percentage of carbon dioxide in air, the carbon dioxide in a given volume of air can be calculated. In this way it is very easy to construct an empirical graph of light transmission versus quantity of carbon dioxide, and to use this graph to convert transmission values to percentages of carbon dioxide in a measured gas sample. For every new standard solution of sodium hydroxide made up, a new calibration curve should be determined.

No detectable absorption of carbon dioxide from the gas sample takes place at the gas-liquid interface during the addition of the absorbing solution. This was determined by adding the absorbing solution in the manner described, draining the solution without mixing it further with the gas sample, and measuring its transmission. Nor is any detectable contamination by atmospheric carbon dioxide caused in venting the gas holder to the atmosphere through a soda-lime absorption tube when drawing the solution from the holder. This was also determined by running a blank check.

Calibration Results. Calibration curves are shown for two different conditions: 130 cc. of absorbing solution and 150-mm. cells, and 100 cc. of absorbing solution and 100-mm. cells. Absolute and relative transmission values were obtained in most cases. The calibration data are presented in Table I, and the results plotted in Figures 2, 3, and 4.

Table I. Calibration Data

Lamp temperature = 22 divisions on galvanometer. All gas volumes at 80° F. and atmospheric pressure.)

Run No.	Volume of Air Sample	CO_2 in Air Sample	Absolute Transmission	Relative	Transmission
	Cc.	*Cc.*	%	%	%
	150-Mm. Cells and 130 Cc. of Absorbing Solution				
0	0 (standard solution)	0	4.9	50	60
1	170	0.05355	7.9	77	93
2	130	0.04095	6.5	..	79.8
3	90	0.02835	..	..	73.3
4	50	0.01575	..	..	67.4
5	150	0.04725	..	..	88.0
6	70	0.02205	..	..	71.2
7	30	0.00945	..	..	62.0
8	150 cc. of air drawn through soda-lime scrubber	0	..	..	60.0
	100-Mm. Cells and 100 Cc. of Absorbing Solution Used				
10	0 (standard solution)	0	12.5	50.0	60.0
9	200	0.06300	23.1	88.5	...
13	60	0.01890	15.0	59.9	71.6
14	60	0.01890	14.8	59.5	71.4
15	60	0.01890	15.0	60.1	71.8
16	120	0.03780	17.4	69.4	82.8
17	160	0.05040	19.9	78.4	94.2
18	90	0.02835	16.6	66.3	79.1

INTERPRETATION AND DISCUSSION OF RESULTS

Graphical Approach. Because it was expected that the data would conform to an exponential function such as the Beer-Lambert law, the results were plotted on semilog coordinate paper. It is obvious from Figures 2, 3, and 4 that the data fall on a straight line. The straight-line calibration is a great advantage, since only two points are needed to determine the curve, and one of these points can be taken as the absolute or relative transmission value of the blank standard sodium hydroxide solution. Thus, the calibration of a new standard solution becomes a very simple matter.

Precision and Sensitivity. Generally speaking, the absolute transmission values are most reproducible on the colorimeter, since these values have the highest ratio of galvanometer deflection to slide-wire travel.

In runs 13, 14, and 15 (Table I), the absolute transmission values for three successive determinations of the same amount of carbon dioxide differ at most by 0.2% transmission. Referring to the absolute transmission calibration curve of Figure 4, it is evident that over the range being considered, an error of 0.2% corresponds to 4 cc. of air or its carbon dioxide equivalent of 0.00126 cc.

Assuming now that the gas sample to be analyzed were to be 1 liter of air containing 10 p.p.m. of carbon dioxide, the total carbon dioxide absorbed would be

$$(1000)\,(0.000010) = 0.010 \text{ cc. of } CO_2$$

Hence, the precision of this determination would be

$$\frac{0.00126}{0.010} \times 100 = 12.6\%$$

or, an error of 1.26 p.p.m. of carbon dioxide when measuring a gas sample containing 10 p.p.m. of carbon dioxide. Obviously this error can be reduced by running a larger sample for analysis of air having this carbon dioxide content. A 1-liter sample of air having a carbon dioxide content higher than 10 p.p.m. gives a determination which is more precise than 12.6%.

Color Stability. The likelihood that the standard might tend to change color upon storage, thus limiting the utility and accuracy of a given calibration with time, was also investigated. Obviously the necessity of recalibrating the standard at too frequent intervals would seriously limit the utility of this method of analysis. A hint that the calibration of the standard might be independent of the initial color and light transmission is first obtained from the results of runs 1 to 7, as plotted in Figure 3. Here the calibration curve obtained when the instrument is arbitrarily set to give a blank standard transmission of 50% is parallel to the calibration curve based on absolute transmission. Since the net effect of resetting the instrument to give a 50% initial blank standard reading is the same as though the standard itself had decreased in color intensity, any change in the color standard should merely result in shifting the whole calibration curve parallel to the original calibration. These conclusions are substantiated by the data obtained in subsequent runs.

The actual stability of color of the sodium hydroxide standard was checked two weeks after the initial tests with the same

Table II. Calibration Data

(Lamp temperature = 22 divisions on galvanometer. All gas volumes at 80° F. and 1 atmosphere)

Run No.	Volume of Air Sample	Volume of CO_2	Absolute Transmission
	Cc.	*Cc.*	%
	(100-Mm. Cells and 100 Cc. of Solution Used in All Runs)		
	Blank standard solution		11.0
20	200	0.0630	20.5
21	100	0.0315	14.5

standard, in order to discover whether any fading or darkening of the standard solution had occurred, and if so, what effect this change would have on the calibration of the solution. The absolute standard transmission was checked, and the calibration curve was again determined by runs 20 and 21. The calibration data appear in Table II and Figure 5.

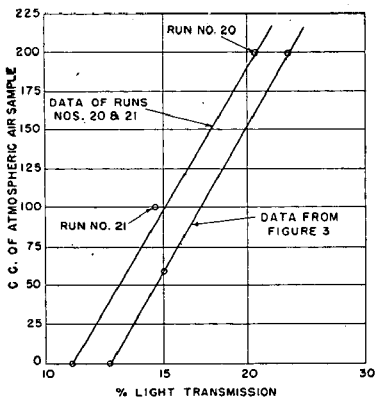

Figure 5. Relationship of Calibration Curves for Standard Sodium Hydroxide Solutions of Different Initial Blank Transmission Values

From these data it is apparent that the color of the sodium hydroxide standard is not completely stable. The solution darkened slightly on standing and transmitted only 11.0% light *vs.* distilled water, whereas the original solution transmitted 12.5%. The conclusions previously reached concerning the effect of lightening the color of the standard are found by the data of runs 20 and 21 to be equally valid for an increase in color. This is shown graphically in Figure 6. The new calibration curve lies parallel to the original one, but shifted slightly toward the darker region.

Summarizing, the calibration curve of a given standard is a straight line over the range investigated. Furthermore, the slope of this line remains constant when the blank standard transmission is artificially changed by resetting the colorimeter or the blank standard itself deepens in color upon storage. Thus, one calibration suffices to define all calibrations with a given standard, all other calibration curves for this standard being defined by the intercept of the blank standard and the slope of the original calibration curve.

APPLICATION OF THE METHOD

The method of carbon dioxide determination presented in this report was used to determine the carbon dioxide content of air produced by a packed tower scrubbing carbon dioxide from atmospheric air. The sodium hydroxide solution used was approximately 0.00005 *N* and the calibration curve of this solution is shown as Figure 6.

Table III. Determination of Carbon Dioxide

	Sample 1	2	3
Run A-15			
Volume of air sample, cc.	493	493	493
Volume of absorbing solution, cc.	100	100	100
Transmission of blank standard absorbing solution, %	7.7	7.7	7.7
Transmission of absorbing solution after reaction with air sample, %	9.8	10.3	9.9
Carbon dioxide in air sample from Figure 6, cc.	0.00945	0.0115	0.0101
Carbon dioxide in air sample, %	0.00192	0.0023	0.00205
Carbon dioxide in air sample, p.p.m.	19	23	21
Run A-19			
Volume of air sample, cc.	493	493	493
Volume of absorbing solution, cc.	100	100	100
Transmission of blank standard absorbing solution, %	8.5	8.5	8.5
Transmission of absorbing solution after reaction with air sample, %	9.8	9.5	9.6
Carbon dioxide in air sample from Figure 6, cc.	0.00536	0.00410	0.0048
Carbon dioxide in air sample, %	0.00109	0.000835	0.000975
Carbon dioxide in air sample, p.p.m.	11	8	10

The air sample was collected in a 600-cc. calibrated gas holder equipped with stopcocks at both ends. Since the scrubber was operating under a slight vacuum, it was necessary to draw the sample from the tower through the gas holder by suction. The air sample was drawn through the holder for some 10 to 15 minutes before the gas holder was sealed off at each end by closing the stopcocks. In this way the holder was purged and the sample collected.

The results obtained are summarized in Table III.

The main advantages of this method of analysis are (1) small gas sample required, (2) speed, and (3) precision. This method is both precise and sensitive, while requiring but 0.5 liter of gas sample. Its accuracy is estimated to be of the same order as the precision. This is a great improvement over most methods, which require gas samples of from 2 to 20 liters before any comparable accuracy is obtained. The barium hydroxide absorption-titration method formerly used required at least 10 liters of gas sample. A determination by this method requires approximately 15 minutes, whereas the time required to draw and analyze a sample by the barium hydroxide method was of the order of 2 hours.

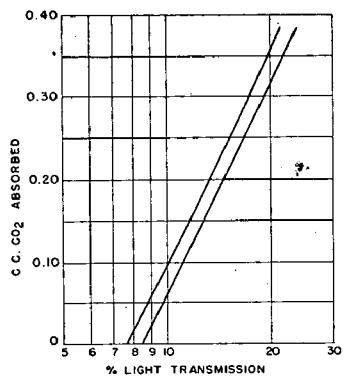

Figure 6. Calibration Curves for Runs A-15 and A-19

The precision of this method is demonstrated by the results of the reported runs. For run A-15 a 493-cc. volume of gas sample was sufficient to determine the carbon dioxide content as 21 ± 2 p.p.m. The percentage error of the determination is only $\frac{2}{21} \times 100 = 9.5\%$. At lower carbon dioxide concentrations the precision is still excellent. The same size of gas sample was used in run A-19 to determine a carbon dioxide concentration of 9.7 ± 1.3 p.p.m. maximum deviation. This represents a percentage error of 13.5%.

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Determination of Traces of Fluorine in Organic Compounds

W. B. HUCKABAY, R. H. BUSEY[1], AND A. V. METLER
Field Research Department, Magnolia Petroleum Company, Dallas, Texas

A method is described for determining very small amounts of fluorine when present as organic fluoride in mixtures of other organic substances. The sample is vaporized and burned from a jet, and the combustion is completed by passing the products over hot platinum in the presence of oxygen. After collection in an absorption tower, the fluorine is determined volumetrically by a combination of conventional methods. Results are superior to those obtained by other current methods, in that the decomposition of the fluoride is more complete than when the material is simply burned from a jet. The sensitivity of the method is limited only by the size of the sample. Data are presented for samples of known fluorine content. The general method of decomposition is directly applicable to analogous cases where the sample contains traces of organic compounds of the other halogens and possibly sulfur. Data are shown for organic bromides.

THE determination of fluorine and other halogens in compounds containing an appreciable percentage of halogen has been described (*6, 18*).

Pyrolysis of the methyl chlorides in methane has been accomplished by McBee (*12*) and others, who mixed the sample with excess air and passed this mixture through a clay tube at 1000° C. The issuing gas was then passed through a sodium carbonate absorber solution. Winter (*18*) used an apparatus similar to the burner employed in the A.S.T.M. method for sulfur (A.S.T.M. Designation D90-41T), and this has been adapted to simple halide compounds by others (*15*). A similar decomposition method described by Matuszak and Brown (*14*) uses a specially designed absorber chimney. Cadenbach (*4*) has described a method in which the sample is vaporized or decomposed in a stream of hydrogen, then burned, and collected in a silver apparatus.

McVicker (*13*) volatilized organic fluorides in a stream of oxygen and passed this mixture through a silica tube packed with granular silica. The combustion products are absorbed in sodium hydroxide. For nonvolatile samples he used sodium in liquid ammonia decomposition in the presence of an inert solvent such as ether or butanol (*16*). The fluorine was then determined gravimetrically as calcium fluoride, lanthanum fluoride, lead chlorofluoride, or phenol fluostannate; colorimetrically in the presence of alizarin and zirconyl nitrate; and volumetrically by titrating with ferric chloride using ammonium thiocyanate indicator, or thorium nitrate with sodium alizarin sulfonate indicator (*13*). Hubbard and Henne (*11*) used a similar decomposition but determined fluoride by titrating with cerous nitrate at 80° C. using methyl red and bromocresol green indicator. Grosse, Wackher, and Linn (*9*) used a platinum-copper decomposition tube in an electric furnace where the sample was vaporized in the tube with an oxygen-air mixture, decomposed, and absorbed in an alkaline solution.

All the above methods have been developed for the analysis of pure organic compounds where the percentage of halogen is high, but are not easily applicable to organic mixtures containing very small amounts of halogen. Such concentrations are found in the complex mixtures of organic fluorides resulting from side reactions in the alkylation of butane-butene mixtures using hydrogen fluoride as the catalyst (*7*). The alkylation is accompanied by the formation of organic fluorine compounds which are difficult to decompose. Some of these may be vaporized directly through a flame without being decomposed completely. Values shown by Winter (*18*) using the flame method are low. Brauns (*3*) states that several organic fluorides are difficult to decompose. Others, no doubt, have encountered similar difficulties. The method described is presented in the hope that it may be useful to others interested in determining small amounts of halogens or sulfur.

Table I shows a comparison of the results of analyses obtained in a procedure essentially the same as that described by Matuszak and Brown and by the procedure herein described on samples of heavy alkylate produced using hydrogen fluoride as catalyst. Alkaline absorber solutions were used in both procedures. The absorber chimney used in the lamp method was extracted at length with warm dilute sulfuric acid and the extract distilled according to the method of Gilkey, Rohs, and Hansen (*8*). No titrable fluorine was detected in these washings. After a number of determinations the inner surfaces of the chimneys were thoroughly scraped and the scrapings analyzed. No fluorine was found.

The method described in this paper has been used by the authors for over 3 years and results from hundreds of analyses have shown a high degree of accuracy and precision. This method is superior to previous methods in that the original products of the combustion of the sample are finally passed over hot platinum in the presence of oxygen, ensuring complete oxidation of the sample and conversion of all the fluorine to an absorbable form.

After absorption, fluoride is determined in the absorber solution by the method of Willard and Winter (*17*), using the sodium alizarin sulfonate indicator of Armstrong (*2*) and the half-neutralized monochloroacetic acid buffer of Hoskins and Ferris (*10*).

REAGENTS AND SOLUTIONS REQUIRED

Thorium Nitrate Solution. 0.01 *N* thorium nitrate is prepared by dissolving 1.38 grams of thorium nitrate tetrahydrate in 1 liter of water. 0.003 *N* thorium nitrate is prepared by dissolving 0.41 gram of thorium nitrate tetrahydrate in 1 liter of water.

Standard Sodium Fluoride Solution. 0 01 *N* sodium fluoride is prepared by dissolving 0.4200 gram of C.P. sodium fluoride in 1 liter of water.

Buffer Solution, 9.4 grams of C.P. monochloroacetic acid and 2.0 grams of C.P. sodium hydroxide dissolved in 100 ml. of water.

Table I. Comparison of Results on Hydrogen Fluoride Alkylate

Sample No.	% Fluorine	
	This method	Lamp method
1	0.98	0.75
	1.00	0.68
		0.71
2	0.085	0.062
	0.082	0.059
		0.0
3	0.048	0.032
	0.047	0.035
	0.044	0.029
4	0.004	0.003
	0.006	0.002

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

Freshly prepared buffer has been found to require a smaller amount of thorium nitrate solution than buffer which has stood for 4 months or longer.

Indicator Solution, 0.05% aqueous solution of sodium alizarin sulfonate.

Permanent Blank. The permanent blank recommended by Eberz, Lamb, and Lachele (*5*) is made from very dilute soluitions of cobaltous nitrate and potassium chromate.

Distilled Water. Fluoride-free distilled water must be assured. There are instances where simple distillation has not given water which is sufficiently free of fluoride (*2*).

0.1 *N* sodium hydroxide, 0.1 *N* hydrochloric acid, and phenolphthalein indicator.

Activated charcoal.

Oxygen.

Methane or natural gas substantially free from sulfur compounds.

Sodium hydroxide, C.P. pellets.

Calcium chloride, anhydrous, 4-mesh.

Calcium sulfate, anhydrous, 4-mesh.

DESCRIPTION OF APPARATUS

The apparatus is shown in Figure 1. The combustion chamber, *A*, is a 1-liter three-necked Pyrex flask with standard-taper ground joints. This flask furnishes the combustion space where methane and sample vapor burn from the jet of the vaporizer, *B*. The vaporizer is specially made, with a methane inlet, one standard-taper ground joint to accommodate the weight pipet, and another to fit into the combustion flask into which also extends the outlet jet (Figure 2). A heater for this vaporizer is wound with Nichrome wire (approximately 22 B. and S.) such that the power load is approximately 500 watts. The weight pipet is L-shaped with a stopcock on one end and a ground joint on the other (Figure 3). The drying tube, *C*, is packed with a 1 to 1 mixture of 4-mesh calcium chloride and calcium sulfate supported by a wad of glass wool. Air enters the drying tube and its rate of flow is regulated by the stopcock, *M*, and measured by the flowmeter, *L*. The alkali scrubber, *E*, is packed with sodium hydroxide pellets supported by a wad of glass wool. The oxygen enters at *H* and passes through the alkali scrubber with the dried air into the combustion flask. The adapter, *N*, is used to join the flask to the silica combustion tube. A preheater rests on this adapter. The combustion tube, *D* may be made of Vycor or fused silica (55 × 1 cm. outside diameter).

The internal components of the tube are arranged from left to right (Figure 4). From the left end to the middle, three flat spirals made of platinum wire are placed about 6 cm. apart. A roll of platinum gauze 5 cm. long is placed at the center. Next, 8-mesh lumps of platinized activated silica are packed against the platinum gauze. This should fill the rest of the hot portion of the tube. It is held in place by a flat spiral and a single platinum wire braced against the end of the tube (activated silica is impregnated with 1% platinum chloride solution and ignited at 250° C.).

At the end of the combustion tube, another adapter carries the combustion gases through a rubber stopper into the flask, *J*, and thence through the fritted-glass scrubber, *F*, and spray trap, *I*, where the suction is applied. The suction should be very dependable, and if possible, both a water jet aspirator and an electric pump should be available with a means of switching quickly from one to the other in case of water-pressure or power failure.

The furnace is a Pregl-type microcombustion furnace, which preferably is equipped with a pyrometer, thermocouple, and rheostat for regulating the input voltage. The vaporizer heater is operated from a variable autotransformer, since even regulation of heating is required from room temperature to approximately 400° C. The preheater is controlled by a variable resistance or may be placed in series with the furnace. If the furnace has a resistance of 28 ohms and the preheater 14, the two may be placed in series directly across the 110-volt alternating current line to give the correct temperature in both places.

DETAILS OF ANALYTICAL PROCEDURE

The furnace is brought to 600° to 800° C. and 25 ml. of distilled water are added to the gas absorber. The suction is adjusted until the air passing through the absorber pushes bubbles up to approximately 2.5 cm. (1 inch) of the suction trap tube. The flow of oxygen is then adjusted to a slight excess over the suction. This is most conveniently measured by a flowmeter which is connected to the drying tube. The stopcock on the air inlet is closed, the vaporizer is removed, and its space is plugged with a cork.

Liquid samples boiling from 30° to 200° C. may be pulled into the weight pipet by applying suction on a piece of rubber tubing attached to the stopcock end of the pipet. The pipet and sample are weighed to 1 mg. and then placed in the ground joint of the vaporizer in such a position that none of the sample is introduced. (If only light liquid samples are to be decomposed, a simplified type of vaporizer may be used in which the jet preheater coil is not included.) With the vaporizer out of the combustion flask, a source of methane is attached, a flow is started and allowed to purge for a few minutes, and then the gas is lighted. The methane flow is adjusted until the yellow flame is about 4 cm. high. The vaporizer is then placed in position in the combustion flask, and the oxygen rate is decreased until it is just smaller than that of the suction. Water will condense on the inner surfaces of the flask and front part of the tube, owing to the combustion. This

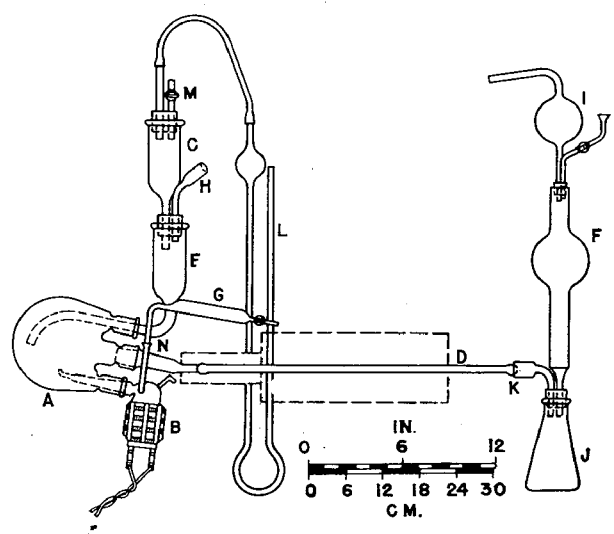

Figure 1. Apparatus

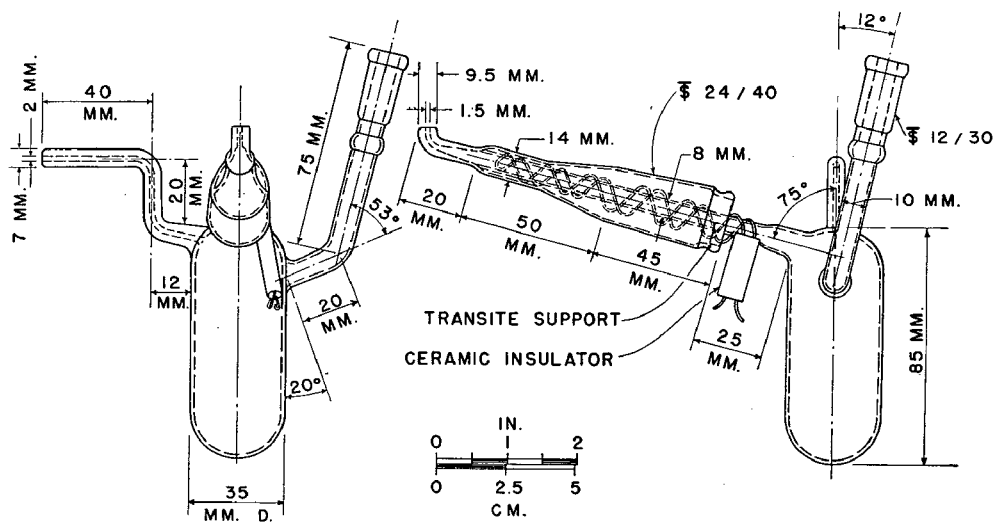

Figure 2. Vaporizer

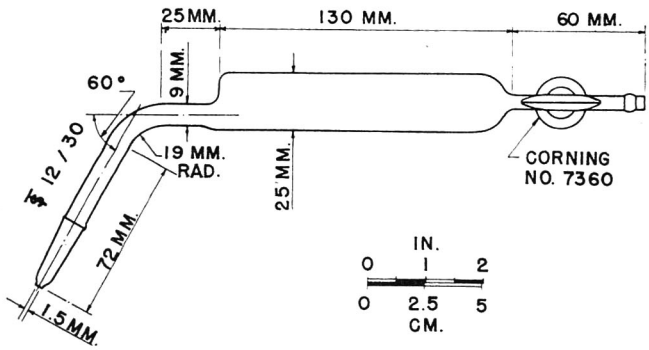

Figure 3. Weight Pipet

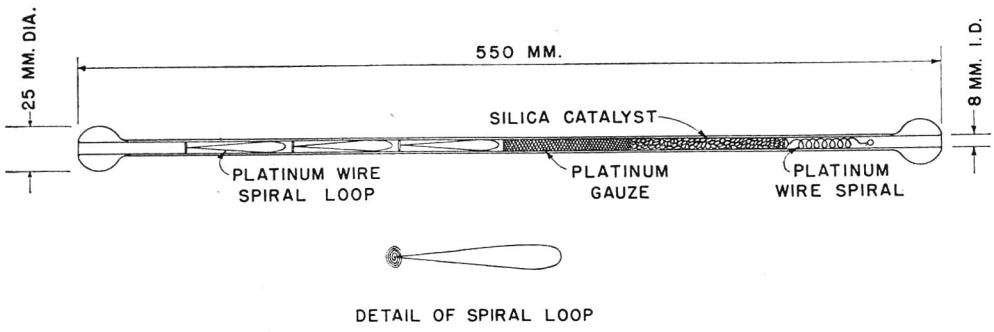

Figure 4. Detail of Combustion Tube Packing

water should be vaporized off by flaming the surfaces. The methane is adjusted until the flame is about 1 cm. high. The pipet is rotated through an angle of 180°, the stopcock is opened, and the sample is allowed to flow into the vaporizer. The heat to the vaporizer is increased slowly until the flame grows to about 3 cm. high. Throughout the entire decomposition of the sample, the flame is kept from 2 to 4 cm. high by regulating the temperature of the vaporizer. The preheater will prevent condensation of water in the adapter and combustion tube after the combustion has been started.

After all volatile components of the sample have been driven out of the vaporizer, in some cases a tarry residue will remain. When the heater has been maintained at its maximum temperature for 5 minutes and no more sample is being vaporized, the methane is cut off and the pipet is removed and weighed. The difference between the initial weight and this weight will give the true weight of the sample. Air is allowed to sweep through the vaporizer for a few minutes and then oxygen is introduced through a ground joint inserted in place of the pipet. If the residue left behind in the vaporizer is appreciable, the semioxidized vaporized material will issue from the jet and be carried to the hot furnace where the oxidation is completed. The oxidation should be continued for 5 minutes after the last visible residue has disappeared. The suction line is disconnected from the gas absorber assembly, allowing the absorber solution to drain into the collection flask. The absorber assembly should be washed with distilled water and the solution and washings combined.

If the sample contains more than 0.0020% fluorine, 0.05 to 0.10 gram of activated charcoal is added to decolorize the absorber solution (*1*), which is then warmed on a hot plate for 5 to 10 minutes, and filtered into a volumetric flask. When the solution is at room temperature, it is diluted to a measured volume, and 25-ml. aliquots are taken for titration. To the aliquots in 125-ml. conical flasks are added 25 ml. of 95% alcohol, 1 ml. of buffer, and 3 drops of indicator (*10*). Standard thorium nitrate is added from a 5-ml. microburet until the color matches the permanent blank (*5*), the titer of which has been previoulsy determined. The total quantity of fluoride ion titrated should not exceed 0.6 mg. (*2*).

If the fluorine content is 0.002% or less, the absorber solution is made alkaline with 0.1 *N* sodium hydroxide, using phenolphthalein as indicator, and is concentrated on a hot plate (*2*). The extent of the concentration will depend on the fluorine content. Samples containing from 0.0002 to 0.0010% are concentrated to 15 ml. This concentrate is neutralized with 0.1 *N* hydrochloric acid and titrated as above.

In cases where samples may contain some organic sulfur compounds, the hydrofluosilicic acid in the absorber solution must be separated from the sulfuric acid. This separation may be accomplished by the use of the distillation process of Gilkey, Rohs, and Hansen (*8*). The first five samples in Table II were treated this way.

The foregoing discussion covers the procedure for liquid materials which boil over the range 30° to 200° C. With minor changes, the procedure can be used also for the analysis of gaseous samples, for high-boiling liquids, or solids or samples made up of more than one phase or state.

When a gas sample is to be analyzed, the sample container, which should be equipped with valves at both ends, is fixed in a vertical position above the vaporizer. Connection from the lower end of the container to the vaporizer is made through a Hoke needle valve and into a ground joint which will fit into the vaporizer in place of the weight pipet. The link between the needle valve and container should be of copper tubing, and the link with the vaporizer is best made of neoprene tubing and should be as short as possible. Sample weight is determined by weighing the sample container before and after entry of sample. The rate of entry of sample is regulated by the needle valve, and decomposition is conducted in a manner analogous to the one already described.

For the decomposition of heavy liquids and solids, the procedure is modified.

Heavy liquids are drawn directly into the vaporizer and the weight of the sample is determined from the weight of the vaporizer before and after filling, or they may be weighed and introduced from the weight pipet as usual. Solids are dissolved in some volatile organic solvent, which is free from both fluorine and sulfur, and introduced in the same manner. The vaporizer is heated by the vaporizer heater and the jet preheater is kept at incipient red heat throughout the determination. After the main portion of the sample has been vaporized, a tarlike residue will remain. This residue is broken down by passing oxygen slowly through the methane inlet. The decomposition of the sample is complete 5 minutes after the last trace of the residue disappears. The remainder of the procedure has already been discussed.

Four such assemblies have been combined into a multiple unit as shown in Figure 5, supported in a cabinet of Transite. The various controls are supported in an accessible position on front panels. Small windows of safety glass are provided for observation of the combustion process, and doors provide access to the trains for manipulation. This cabinet forms a barrier around the combustion units in case of accidental extinguishment of the flame by failure of any of the services to the equipment. Explosion of the combustion chamber may be prevented by closing the oxygen and suction valves and cutting off the vaporizer heater current.

When this multiple assembly is used, four analyses may be completed in 2 hours when the fluorine content is relatively high. The time will be proportionally longer up to 8 hours when the fluorine content is of the order of 0.0001%.

DISCUSSION OF METHOD AND RESULTS

Standard samples were made of *p*-fluorotoluene, α-fluoronaphthalene, and fluorobenzene by introducing a weighed amount of the compound into a weighed amount of acetone or iso-octane. The purity of the standard compounds was determined by analyzing samples by the "etch method" (*3*), peroxide bomb, and

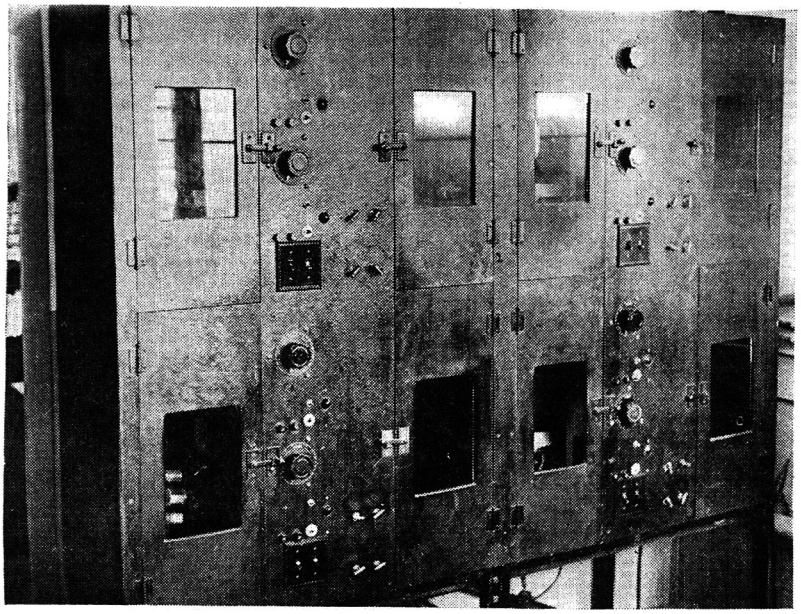

Figure 5. Multiple Unit

Table II. Analysis of Pure Substances for Fluorine Content

Compound	B.P. °C.	Fluorine, Etch Method %	Fluorine, Peroxide Bomb %	Fluorine, NH_3-Na %	Fluorine, Theory %
p-Fluorotoluene	117	17.2	17.4	...[a]	17.3
α-Fluoronaphthalene	212	13.5	13.1	13.2	13.0
Fluorobenzene	85	19.5	...[a]	...[a]	19.8

[a] Method not suited for this compound.

sodium–liquid ammonia process (*16*) and were all found to contain the theoretical amount of fluorine within 2%. The results of these purity analyses may be seen in Table II.

Analytical data obtained on samples containing known fluorine content are shown in Table III. Since the results are stated to only three significant figures, no correction is necessary for the purity of the compounds used. The number of times each individual sample was analyzed is shown in column 4. Column 5 contains an average of these determinations, and the theoretical per cent fluorine is shown in column 6. Average error is the difference between theory and the average of the determinations on each sample. Average deviation is determined by taking the difference between each of the separate analyses and their average. The error for samples containing from 0.26% to 0.01% fluorine ranges from 0 to 46 parts per thousand with an average of 22 for the eight samples considered. Samples containing from 0.005 to 0.001% fluorine have an average error of 69 parts per thousand for 6 separate samples. The average deviation in the range 0.26 to 0.01% fluorine is 40 parts per thousand for samples 1 through 8, and 64 parts per thousand for samples containing 0.005 to 0.001% fluorine. For samples containing less than 0.001% fluorine, both the error and deviation are somewhat higher.

Table IV shows typical analyses of organic bromine compounds. The decomposition is conducted according to essentially the same procedure as described with the modified absorption solution mentioned below. The absorber solution was analyzed gravimetrically, using silver nitrate, or by any of the standard methods for halide ions.

Organic bromides used in the samples shown in Table IV were Eastman Kodak "highest purity" grade, refractionated in a 100-plate column. Analysis of the compounds indicated that they were better than 99% pure.

SOURCES OF ERROR

In the case of a sample containing 0.0005% fluoride, the titer will be approximately 0.5 ml. of thorium nitrate (0.01 *N*) when a 25-gram sample is burned. (The end-point error is ± 0.05 ml., hence ±10% error is involved.) Increased accuracy can be attained by burning additional 25-gram samples, combining absorber solutions, and evaporating to a suitable volume. Some question might arise about the use of water as absorbing medium. The authors have compared results using water with those obtained when an alkaline solution is used and have found that the absorption is essentially complete with water alone. When the apparatus is used for decomposing organic compounds of the other halogens, it is necessary to use 2 *N* caustic solution. Small amounts of oxyhalogen compounds which may be formed are reduced in this solution by adding an excess of sodium nitrite.

Traces of sulfate in the titrating solution cause high results. When sulfur-containing compounds are present in the inlet gases

Table III. Analysis of Synthetic Samples Containing Fluorine

Sample No.	Compound[a]	Solvent[a]	No. of Detns.	Fluorine Found %	Fluorine Theory %	Average Error %	Average Deviation %
1[b]	A	D	3	0.257	0.266	−0.0090	0.0035
2	B	D	3	0.221	0.224	−0.0030	0.0030
3	B	E	2	0.0475	0.0503	−0.0028	0.0018
4	A	E	1	0.0488	0.0502	−0.0014	....
5[c]	B	E	2	0.0259	0.0252	0.0007	0.0010
6	A	E	2	0.0261	0.0254	0.0007	0.0015
7	B	E	2	0.0103	0.0103	0.0000	0.0010
8	A	E	2	0.0102	0.0102	0.0000	0.0002
9	B	E	2	0.0047	0.0052	−0.0005	0.0000
10	A	E	2	0.0059	0.0061	−0.0002	0.0008
11[d]	B	E	2	0.0027	0.0027	0.0000	0.0001
12	A	E	2	0.0019	0.0019	0.0000	0.0001
13	B	E	2	0.0009	0.0011	−0.0002	0.0000
14	A	E	2	0.0011	0.0010	0.0001	0.0001
15	C	D	1	0.0017	0.0021	−0.0004	....
16	C	D	2	0.0005	0.0004	0.0001	0.0001
17	C	D	1	0.0002	0.0001	0.0001	....

[a] A, *p*-fluorotoluene. B, α-fluoronaphthalene. C, fluorobenzene. D, acetone. E, iso-octane.
[b] One burning of sample with two distillations, samples 1 through 4.
[c] Scrubber solutions titrated directly without distillation, samples 5 through 10.
[d] Concentrated scrubber solution treated with activated charcoal prior to titration, samples 11 through 17.

Table IV. Analysis of Synthetic Samples Containing Bromine

Sample No.	Compound[a]	Solvent[a]	No. of Detns.	Bromine Found %	Bromine Theory %	Average Error %	Average Deviation %
1	B	E	3	0.1116	0.1112	0.0004	0.0009
2	A	F	2	0.1082	0.1088	−0.0006	0.0008
3	B	E	1	0.1050	0.1055	−0.0005	....
4	B	F	3	0.0523	0.0522	0.0001	0.0005
5	D	F	4	0.0460	0.0450	0.0010	0.0010
6	C	F	3	0.0265	0.0267	−0.0002	0.0003
7	B	F	2	0.0130	0.0120	0.0010	0.0010
8	D	F	2	0.0021	0.0018	0.0003	0.0003
9	C	F	3	0.0052	0.0052	0.0000	0.0001
10	C	F	3	0.0002	0.0001	0.0001	0.0001
11	..	E	3	0.0000	0.0000	....	....
12	..	F	3	0.0000	0.0000	....	....

[a] A, ethyl bromide. B, isopropyl bromide. C, *n*-butyl bromide. D, *n*-propyl bromide. E, acetone. F, iso-octane.

used for the combustion, sulfate which is formed in the absorber may be eliminated by a distillation (*8*), or the total titer may be corrected by determination of the sulfur (*14*). Throughout the work described in this paper, no interfering sulfur compounds were encountered.

CONCLUSION

A method for the determination of trace amounts of fluorine present in organic substances involves a unique combination of certain features of previously published methods, resulting in a more complete decomposition of certain types of samples than was available heretofore. With some minor modification of the procedure the method may be used for the determination of the other halogens.

Experimental data show the precision and accuracy of this method over the approximate ranges of 0.0001 to 0.25% fluorine and 0.0001 to 0.1% bromine.

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Determination of Gallium in Silicate Rocks

E. B. SANDELL, *School of Chemistry, University of Minnesota, Minneapolis, Minn.*

THE following method for the determination of trace quantities of gallium in silicate minerals and rocks is based on the fluorescence reaction of gallium with 8-hydroxyquinoline (*4*), in which gallium hydroxyquinolate is extracted with chloroform from an aqueous solution of pH 2.6 to approximately 3.0. With the exception of indium and scandium, no metal hydroxyquinolate imparts a fluorescence to the chloroform phase in this pH range. The fluorescence produced by these metals is much weaker than that given by gallium. At pH 3 the indium fluorescence is about 1/500 as strong as the fluorescence of an equal weight of gallium, and that of scandium is about 1/40,000 as strong. At pH 2.6 the fluorescence intensity of indium is much less, being approximately 1/10,000 of gallium. However, a number of metals form hydroxyquinolates which dissolve in chloroform to give colored (but nonfluorescent) solutions. These colored hydroxyquinolates absorb ultraviolet and visible radiation and interfere with the gallium reaction. The metals thus interfering are ferric iron, quinquevalent vanadium, cupric copper, and sexivalent molybdenum. It has been shown that the interference of iron and vanadium can be prevented by reduction with hydroxylamine hydrochloride. Titanium hydroxyquinolate is insoluble in chloroform under the conditions and produces an emulsion.

The difficulties arising from the presence of the elements mentioned can be overcome in a simple way by isolating gallium by extracting its chloride with ether before applying the fluorescence reaction. In this way it is possible to determine gallium with a sensitivity and accuracy not inferior to any spectrographic method yet described (cf. *3*).

ETHER EXTRACTION

From the standpoint of trace analysis it is fortunate that the distribution of gallium chloride between ethyl or isopropyl ether and 6 *N* hydrochloric acid is independent of the gallium concentration. The value of the partition coefficient for ethyl ether–6 *N* hydrochloric acid is approximately 17 (*2*, see also *5*, *6*). In the present work pure ethyl ether has been used in preference to technical grade isopropyl ether because the latter was found to give a stronger blank fluorescence.

It is desirable to separate gallium from the bulk of the iron in the ether extraction. The acidity can then be adjusted in a simple way for the subsequent fluorometric determination by evaporating the ether, taking up the residue in dilute acid, and buffering with potassium hydrogen phthalate. In this process only minimal amounts of iron may be present, for otherwise the residue will not give a clear solution in the dilute acid. Moreover if the bulk of the iron is separated, less reliance need be placed on the final reduction of iron with hydroxylamine hydrochloride. The extraction of iron can be prevented by reducing it to the ferrous state. Finely divided silver is a suitable reducing agent for the purpose; it seems to be preferable to mercury, whose use has been suggested for the same purpose (*5*). In order to keep volumes as small as possible, most of the iron is reduced by adding the silver to the solution and shaking; the reduction is then completed by passing the solution through a very small column of silver after making up to volume. There is always a little air-oxidation of the ferrous iron, with subsequent extraction of the ferric chloride by the ether, but this small amount does not lead to any difficulty.

Traces of copper and vanadium may be extracted by the ether, but they do not cause any error, in the quantities likely to be encountered in igneous rocks (see Table I). Molybdenum is extracted, however, and produces low results if present in significant amount. Its amount in igneous rocks rarely if ever rises to 0.001%, so that it is not likely to cause trouble in the method. The presence of an appreciable quantity of molybdenum would be revealed by a yellow coloration of the chloroform. So long as the chloroform extract is not appreciably colored (it should be almost colorless, like the chloroform in the comparison solution) the presence of molybdenum can cause no significant error.

Indium will not interfere, for it is not extracted by ether from the hydrochloric acid solution. Even if it were, however, its amount in igneous rocks is so small (*1*) that it could not give a perceptible fluorescence in the final step of the procedure.

Table I. Fluorometric Determination of Gallium in Silicate Rocks after Ether Extraction

Sample	Ga Present	Ga Added	Ga Found	Ga Recovered	
	P.p.m.	*P.p.m.*	*P.p.m.*	*P.p.m.*	%
Solution[a]	10	8	18	8	100
Solution[b]	10	10	21	11	110
Solution[c]	10	12	21	11	90
Solution[c]	10	40	48	38	95
Diabase[d]	19	10	27	8	80
Diabase	19	16	33	14	88
Diabase	19	50	67	48	96
Dunite[e]	0.5	10	9	8.5	85
Dunite[f]	0.5	10	9.5	9.0	90
Dunite	0.5	10	10	9.5	95
Dunite	0.5	10	9	8.5	85
Peridotite[g]	2	5	7	5	100
Composite of mediosilicic rocks + 0.012% Mo	14.5	..	14.5	14.5	100
Composite (No. 1) of subsilicic rocks + 0.4% Cu	12.5	..	11.5	11.5	92
Composite (No. 2) of subsilicic rocks + 0.15% V	13	..	13.5	13.5	104

[a] Composition in mg. (as sulfates and chlorides): Al_2O_3 48, Fe_2O_3 38, MgO 25, CaO 25, Na_2O 10, MnO 0.6, TiO_2 3, P_2O_5 1.2, Cu 0.08. Solution evaporated to dryness and excess sulfuric acid fumed off. Residue taken up in 6 *N* hydrochloric acid, calcium sulfate filtered off, and solution further treated as described in procedure.
[b] Calcium omitted from mixture.
[c] Composition same as [a]. Evaporated to dryness with 2.5 ml. of hydrofluoric acid and excess sulfuric acid.
[d] Percentage composition: SiO_2 52.7, Al_2O_3 14.5, Fe_2O_3 7.4, FeO 5.6, MgO 3.7, CaO 8.0, Na_2O 3.2, K_2O 1.1, TiO_2 1.8, P_2O_5 0.25, MnO 0.24, Cu 0.024, Ni 0.004, Co 0.0024, Mo 0.0002.
[e] Percentage composition: SiO_2 42.0, Al_2O_3 0.4, Fe_2O_3 0.8, FeO 6.8, MgO 48.4, CaO 0.06, Na_2O 0.0, K_2O 0.0, TiO_2 trace, P_2O_5 trace, MnO 0.11.
[f] Comparison solution was a blank carried through procedure.
[g] Percentage composition: SiO_2 44.4, Al_2O_3 3.0, Fe_2O_3 0.7, FeO 7.6, MgO 40.8, CaO 2.6, Na_2O 0.2, K_2O 0.0, TiO_2 0.14, P_2O_5 0.41, MnO 0.13, NiO 0.31.

FLUOROMETRIC COMPARISON

The ether extract is evaporated to dryness after the addition of a little aqueous sodium chloride solution to make more certain the complete solution of gallium chloride later. The residue is dissolved in dilute hydrochloric acid, hydroxylamine hydrochloride is added, and the pH of the solution is brought to 3.1 (calculated) by the addition of potassium hydrogen phthalate. The mixture is allowed to stand until iron has been reduced to the ferrous state and 8-hydroxyquinoline solution is then added. The gallium hydroxyquinolate is extracted with 2 ml. of chloroform. In this volume of chloroform, 0.05 microgram of gallium shows a very faint but certain fluorescence in the near ultraviolet when comparison is made against a blank, provided the eye of the observer is dark-adapted.

The determination is made visually by comparison against a standard series or by fluorometric titration—i.e., by adding standard gallium solution to a comparison solution with thorough shaking until the two chloroform phases show equal fluorescence intensities. The visual comparison is sufficiently precise for the purpose and only small volumes of chloroform are required. No difficulty is experienced in distinguishing between two chloroform solutions differing in gallium concentration by 10% if the amount present is greater than 0.5 microgram (in 2 ml. of chloroform). With a little practice one can detect differences of 7 and perhaps 5% if the fluorescence intensity is not too weak.

Under the conditions described in the procedure the blank was found to correspond to 0.1 microgram of gallium or 1 p.p.m. of sample. The fluorescence of the blank is not due to gallium, because omission of 8-hydroxyquinoline still results in a faint fluorescence. No doubt a trace of some organic compound derived from the ether is responsible for this fluorescence. It would be more correct in principle to use a blank solution as a comparison solution to which known amounts of gallium are added. This seems to be unnecessary in most cases, because the blank is very small, but might be advisable when the gallium content of the sample is very low, as in dunites.

Table I shows that there is a tendency for the recoveries to be slightly low. This is not unexpected, for a small amount of gallium (perhaps a few per cent) no doubt escapes extraction and there may be slight losses in the course of the operations. It is believed that the application of a correction factor of +10% is justified. If the values in the table are increased by this amount, the recoveries are within 10% of the theoretical, with one exception.

It appears that there is no interference from the major or minor constituents of igneous rocks.

APPARATUS

Glass-Stoppered Tubes, 1.8 × 15 cm., flat-bottomed, 25-ml. capacity.

Funnel with Silver Column. Place a plug of glass wool at the bottom of the stem of a buret funnel (stem diameter preferably 8 mm.), and fill the stem loosely to a depth of 15 mm. with powdered silver. The column should allow the passage of 5 to 7 ml. of solution per minute without suction. Since only a small amount of ferric iron has to be reduced by the silver column, it may be used for many reductions before replacement. After use rinse it with 1 to 1 hydrochloric acid and water and then dry.

Microburet, graduated to 0.01 ml., for measuring the standard gallium solution.

Ultraviolet Lamp. A source supplying radiation in the near ultraviolet is satisfactory. A Westinghouse type G-5 lamp serves well.

REAGENTS

Hydrochloric Acid, 1 to 1. Dilute concentrated hydrochloric acid (density 1.18) to twice its volume with water.

Silver Powder. Prepare by reducing silver nitrate with metallic copper. Wash well with dilute sulfuric acid and then water, and dry. The powder should be finely divided. If necessary sift out the larger grains.

Ethyl Ether. Use only the analytical reagent or purified grade, treated daily as follows: Shake 65 ml. (enough for four extractions of gallium) in a separatory funnel with 25 ml. of 1 to 1 hydrochloric acid to which has been added 0.05 gram of sodium hydrogen sulfite. Separate the phases. Do not wash the ether phase but rinse out the stem of the funnel by pouring a little 1 to 1 hydrochloric acid into the funnel and drawing it off. The ether thus purified must not give a yellow color when shaken with a little titanium sulfate in sulfuric acid solution.

Sodium Chloride, 10 grams in 100 ml. of water.

Hydroxylamine Hydrochloride, 20 grams in 100 ml. of solution.

Potassium Hydrogen Phthalate, 0.20 *M*, 20.41 grams of salt in 500 ml. of solution.

8-Hydroxyquinoline, 0.10%. Dissolve 0.10 gram in a little water containing 0.6 ml. of 6 *N* acetic acid and dilute to 100 ml.

Chloroform, analytical reagent.

Standard Gallium Solution. A convenient concentration is 0.0005% gallium. The solution should be 0.05 *N* in hydrochloric acid.

PROCEDURE

To 0.25 gram of 100-mesh rock powder in a platinum dish add 2 ml. of 6 *N* sulfuric acid and 3 ml. of hydrofluoric acid. Evaporate to dryness and fume off the excess sulfuric acid, avoiding decomposition of ferric sulfate. Take up the residue in 0.5 ml. of 6 *N* sulfuric acid and 1 or 2 ml. of water, evaporate to dryness, and again fume off the sulfuric acid. Treat the residue with 10 ml. of 1 to 1 hydrochloric acid, warm the covered dish gently, and stir at intervals to bring all soluble material into solution. After 0.5 hour, or when it is judged that all soluble matter has been dissolved, filter off any calcium sulfate or other insoluble matter on a small (5-cm.) fine filter paper and wash with 5 ml. of water containing a few drops of hydrochloric acid. Catch the filtrate and washings in a 25-ml. volumetric flask. (If the sample contains appreciable amounts of chromite or other mineral not decomposed by hydrofluoric acid, the residue should be treated appropriately to complete the decomposition.)

Add 0.5 gram of silver powder to the volumetric flask and swirl the solution until most of the ferric iron has been reduced, as shown by the almost complete disappearance of the yellow color. Depending upon the amount of iron and the fineness of the silver, from 1 to 5 minutes will be required. Then add 8 ml. of concentrated hydrochloric acid and dilute with water to 25 ml. After mixing for 1 minute, run the solution through the funnel containing dry silver powder in its stem and collect a little more than 10 ml. Without delay transfer 10.0 ml. of the solution to a small separatory funnel which has been rinsed with 1 to 1 hydrochloric acid and proceed with the ether extraction.

Extraction of Gallium Chloride. Add 8 ml. of ether to the separatory funnel and shake for 20 or 30 seconds with the usual precautions. When the layers have separated, drain the aqueous phase into another separatory funnel (rinsed with 1 to 1 hydrochloric acid) and shake with 5 ml. of ether. Draw off and discard the acid layer and combine the second ether extract with the first, rinsing the funnel with 1 ml. of ether. Separate any small amount of aqueous solution present and shake the ether vigorously for 10 seconds with 1 ml. of 1 to 1 hydrochloric acid. Drain off the aqueous layer as sharply as possible and shake the ether again with another 1-ml. portion of 1 to 1 hydrochloric acid. Discard the hydrochloric acid washings. After the second portion of acid has been separated, add a few drops of 1 to 1 hydrochloric acid to the funnel and draw it off without shaking to rinse out the stem of the funnel.

Run the washed ether into a 50-ml. beaker containing 0.5 ml. of sodium chloride solution and rinse the funnel with 1 or 2 ml. of ether. Cover the beaker with a watch glass and evaporate the ether at a low temperature. Remove the cover glass and allow all the water to evaporate; the walls of the beaker must be dry. Cool and add 2.00 ml. of 0.200 *N* hydrochloric acid to the dry residue. With the aid of a stirring rod distribute the acid over the lower walls of the beaker. When the residue has dissolved, transfer the solution to a flat-bottomed glass-stoppered tube and wash the beaker and cover glass with small portions of water totaling about 3 ml. Add 1 ml. of hydroxylamine hydrochloride solution, mix, and then add 6.0 ml. of potassium hydrogen phthalate solution. After mixing, allow the solution to stand at room temperature for 20 minutes. At the same time prepare a comparison solution of the same composition (or if preferred a series of standards) and dilute to the same volume as the sample solution.

Fluorometric Comparison. To sample and comparison solutions add 0.25 ml. of 8-hydroxyquinoline solution, mix by inversion, and then add 2.0 ml. of chloroform. Shake the sample tube vigorously for at least 30 seconds, allow the chloroform to settle, and note the intensity of the fluorescence of the latter when the tube is held vertically above an ultraviolet source in a dark room. The strength of the fluorescence serves as a guide for the initial amount of gallium to be added to the standard tube. After each addition of standard gallium solution to the comparison tube shake well for 30 seconds. When the fluorescence of the chloroform in the comparison tube is almost as strong as that in the sample tube, shake the latter for 0.5 to 1 minute, and after each addition of gallium to the comparison solution shake both tubes for about 0.5 minute. When both chloroform layers show the same fluorescence intensity shake for 1 minute to be certain that distribution equilibrium has been reached and again compare. It is permissible to make the final adjustment by adding a small quantity of gallium to the sample solution if necessary. If the fluorescence appears too strong for good comparison, more chloroform may be added to each tube.

Run a blank through the entire procedure. See the above discussion for the application of a correction factor.

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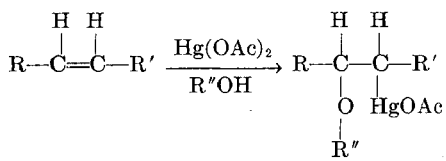
Micromethod for Determination of Gaseous Olefins

ROWENA PYKE, ALLAN KAHN, AND D. J. LEROY, *Department of Chemistry, University of Toronto, Toronto, Canada*

Two new procedures are described for the determination of gaseous olefins in the presence of paraffins, using the Blacet-Leighton gas analysis microapparatus.

IN CONNECTION with research on the photosensitized reactions of the lower hydrocarbons the authors have had frequent occasion to analyze small amounts of gas for olefins and paraffins. While it is relatively easy to separate a gas sample into fractions having the same carbon number (*4*), it is much more difficult to make a precise analysis of these fractions in terms of olefin content. The only method so far suggested for use with the Blacet-Leighton gas analysis apparatus (supplied by the Arthur H. Thomas Company, Philadelphia, Pa.) is that of Blacet, MacDonald, and Leighton (*3*), who used a sintered-glass bead containing fuming sulfuric acid, essentially an adaptation of the well-known macromethod.

In the search for a more satisfactory reagent, various attempts were made to utilize the reaction between olefins and mercuric acetate to form mercurials. In an alcoholic solution the following reaction takes place:



In aqueous solution the corresponding hydroxy mercurial is formed. Since both types of mercurial are relatively nonvolatile, the method would appear to be satisfactory. In the case of the alkoxy derivatives, a nonvolatile alcohol must be chosen which does not dissolve paraffins to any appreciable extent. On the other hand, water is satisfactory because of its small affinity for paraffins and the fact that it can be readily removed from the remaining gas with fused potassium hydroxide or phosphorus pentoxide (*2*). A more serious difficulty is the slowness of the reaction in most cases, although this can be overcome by the use of catalysts (*1*, *5*).

ALKOXY MERCURIAL METHOD

Satisfactory results were not obtained when glycerol was used as the alcohol. The rate of absorption was increased by using hydrogen peroxide as a catalyst, but some oxygen was liberated at the same time. Although success might have been achieved with other catalysts, it was decided to use ethylene glycol instead of glycerol.

A good absorbent was finally obtained using boron trifluoride ethyl etherate (Eastman Kodak Co.) as a catalyst. A paste was

Table I. Analysis of Ethylene-Ethane Mixtures by Alkoxy Mercurial Method

(Absorption time, 10 minutes)

Volume of Sample, Cu. Mm.	Ethylene Theoretical, %	Ethylene Determined, %	Difference, %
46.67	0.00	0.20	+0.20
48.44	10.06	10.14	+0.08
48.81	19.59	19.56	−0.03
49.36	30.18	30.19	+0.01
52.30	39.00	39.04	+0.04
49.27	49.57	49.55	−0.02
51.20	60.54	60.56	+0.02
50.56	69.68	69.72	+0.04
51.84	79.77	79.56	−0.21
52.14	88.82	88.84	+0.02
		Mean	±0.07

Table II. Analysis of Olefin-Paraffin Mixtures by Hydroxy Mercurial Method

(Absorption time 10 minutes)

Mixture	Volume of Sample, Cu. Mm.	Olefin Theoretical, %	Olefin Determined, %	Difference, %
Ethylene-ethane	54.53	0.00	0.02	+0.02
	65.56	9.99	10.50	+0.51
	51.44	25.36	25.33	−0.03
	91.56	30.59	30.36	−0.23
	55.37	49.67	49.75	+0.08
	84.58	57.35	57.11	−0.24
	88.70	66.25	66.21	−0.04
	53.13	74.54	74.52	−0.02
	81.42	84.86	84.57	−0.29
			Mean	±0.18
Propylene-propane	50.12	10.79	10.68	−0.11
	48.12	20.94	20.90	−0.04
	48.91	30.47	30.49	+0.02
	50.05	40.03	39.96	−0.07
	51.90	50.24	50.22	−0.02
	50.11	60.59	60.61	+0.02
	50.04	69.16	69.28	+0.12
	48.83	79.49	79.58	+0.09
	49.85	90.16	90.12	−0.04
			Mean	±0.06
Butene-2-butane	71.96	0.00	0.26	+0.26
	78.55	12.64	13.50	+0.86
	80.06	27.24	27.02	−0.22
	81.09	39.02	39.44	+0.42
	83.47	47.75	47.74	−0.01
	84.06	58.97	58.40	−0.57
	81.51	72.93	72.94	+0.01
	80.60	84.86	84.62	−0.24
			Mean	±0.32

made from 3 cc. of powdered mercuric acetate (General Chemical Co.) and 2 cc. of a 1% solution of boron trifluoride ethyl etherate in ethylene glycol (Eastman Kodak Co.), and was then applied to the standard platinum loop absorbent holder. Table I gives typical results obtained with this absorbent on ethylene-ethane mixtures. A test for complete absorption was made in each case, a fresh bead being used for this purpose.

Attempts to use this absorbent with propylene-propane mixtures were unsuccessful, owing to the absorption of propane. The results were considerably better when "beads" previously saturated with propane were used, but this procedure was not considered satisfactory for a routine method.

HYDROXY MERCURIAL METHOD

Beads made from mercuric acetate and water gave good results with propylene-propane mixtures, but absorption was extremely slow. The rate of absorption could be increased considerably by the addition of benzoyl peroxide, but other gaseous products resulted from the reaction. There was a volume increase even in pure propane.

Since nitrates have been used as catalysts for reactions of this type (*5*), a series of absorbents was tried using mercuric nitrate for this purpose. The data in Table II were obtained with an absorbent made from 3 cc. of powdered mercuric acetate, 1.5 cc. of water, and approximately 1 gram of mercuric nitrate (Merck). Water vapor was removed with fused potassium hydroxide beads. The test for complete absorption was made as before.

There is relatively little difference between the two methods in the case of ethylene-ethane mixtures, but the greater versatility of the hydroxy mercurial method recommends its use in most instances.

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Determination of Carbon Monoxide

A Microgravimetric Method

JASON M. SALSBURY[1], JAMES W. COLE, AND JOHN H. YOE
Cobb Chemical Laboratory, University of Virginia, Charlottesville, Va.

A microgravimetric method, accurate to about 2%, is described for low concentrations (0.002 to 0.1%) of carbon monoxide in air. The gas is drawn over Hopcalite at 195° C. and the carbon dioxide thus formed is absorbed in microabsorption tubes containing Ascarite, the volume being measured with a flowmeter and stop watch. From the weight of carbon dioxide absorbed in the tubes the percentage of carbon monoxide is calculated.

VARIOUS methods for the determination of low concentrations of carbon monoxide in air have been reported (*1-4*). Many of them are based on oxidation, but none involves direct weighing of the oxidation product, carbon dioxide. During the course of a problem involving a search for new carbon monoxide detectors and the devising of instruments for carbon monoxide determination, a microgravimetric method was developed for analyzing low concentrations of this gas. The method is based on the oxidation of carbon monoxide by air in the presence of Hopcalite and subsequent absorption of the carbon dioxide in tubes filled with Ascarite. From 0.002 to 0.1% carbon monoxide in air may thus be determined with an accuracy of about 2%.

[1] Present address, American Cyanamid Co., Stamford, Conn.

APPARATUS

A diagrammatic sketch of the apparatus is shown in Figure 1.

Purification Train. For Air. Outside air is drawn successively through calcium chloride, charcoal, and soda-lime mixture (Chemical Warfare Service mixture), purified silica gel (dry), a moisture indicator (cobalt chloride on silica gel), Hopcalite (room temperature), purified silica gel (dry), calcium chloride, soda-lime, Ascarite, and finally calcium chloride. The purified air then enters the catalyst chamber.

For Carbon Monoxide in Air. The air containing carbon monoxide is purified by successive passage through calcium chloride, charcoal, and soda-lime mixture (CWS mixture), soda-lime, Ascarite, calcium chloride, purified silica gel (dry), and the cobalt chloride moisture indicator. The gas then enters the catalyst chamber.

Microabsorption Tubes. Four microabsorption tubes are used

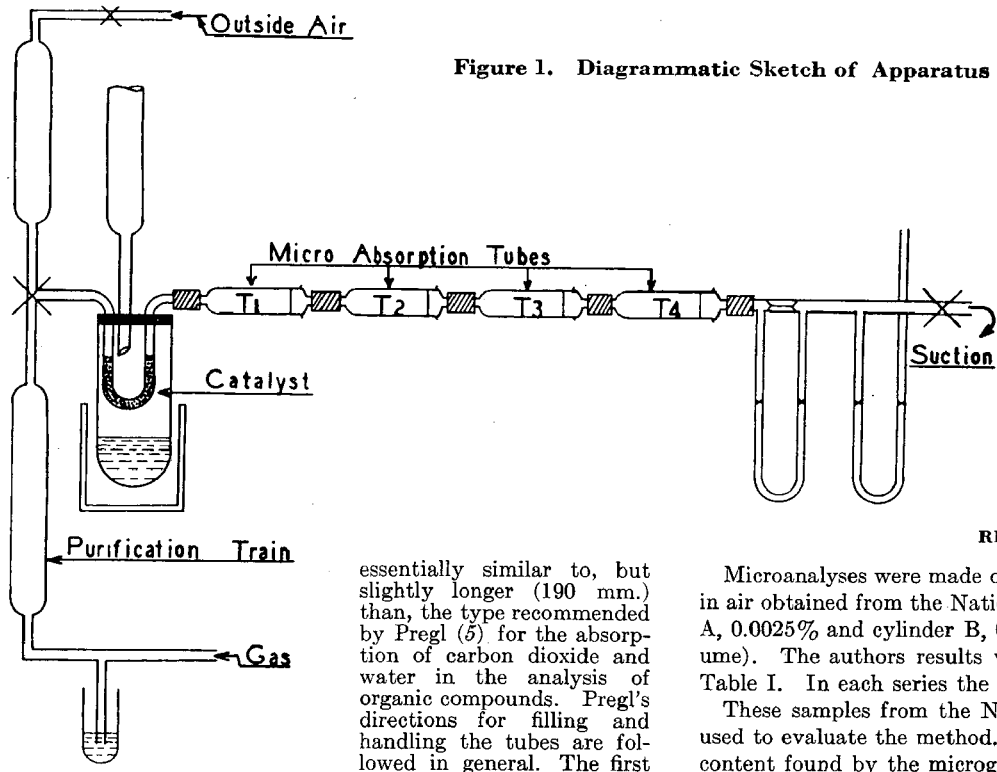

Figure 1. Diagrammatic Sketch of Apparatus

essentially similar to, but slightly longer (190 mm.) than, the type recommended by Pregl (*5*) for the absorption of carbon dioxide and water in the analysis of organic compounds. Pregl's directions for filling and handling the tubes are followed in general. The first tube is packed very tightly with Dehydrite, saturated with carbon dioxide, and flushed with purified air at 100 ml. per minute. The second tube contains Dehydrite for one third of its length and 12- to 20-mesh Ascarite for two thirds. The third tube contains successively Dehydrite ($^1/_5$ of length), 12–20 Ascarite ($^3/_5$), and Dehydrite ($^1/_5$). This is mainly a safety tube. The fourth or control tube contains equal lengths of Dehydrite and 12–20 Ascarite. Small wads of cotton are placed at the ends of each tube and between the absorbing sections. The tubes should be refilled every two weeks. The ground joints of each tube are sealed with Krönig's cement and the tubes are connected in the train with "aged rubber tubing". In weighing, the tubes are wiped and allowed to stand 10 minutes in the microbalance instead of 5 as recommended by Pregl. The need for two absorption tubes for carbon dioxide is evident from the results with 10 liters of air containing 0.008% carbon monoxide:

Weights of Absorption Tubes	Tube 2	Tube 3	Tube 4
Weight after absorption of CO_2, mg.	9.961	6.025	6.650
Weight before absorption of CO_2, mg.	8.586	5.998	6.643
Gain in weight, mg.	1.375	0.027	0.007
Gain in weight of control, mg.	0.007	0.007	
Gain in weight due to CO_2, mg.	1.368	0.020	

PROCEDURE

Outline of Method. Air containing carbon monoxide is purified, dried, and then passed over Hopcalite at 195° C. to oxidize the carbon monoxide to carbon dioxide. Following the Hopcalite are microabsorption tubes containing Dehydrite and Ascarite; next is a flowmeter connected to a suction source. The volume of gas or air passed through the tubes is calculated from the flowmeter readings.

Conditioning of Hopcalite. The Hopcalite is heated in a bath of boiling decahydronaphthalene (technical, boiling point 195° C.) and purified air is drawn through for at least 30 minutes; then 1 liter of the gas to be analyzed is drawn through, followed by 500 ml. or more of purified air. The Hopcalite is then ready for use. This conditioning of the catalyst before the actual analysis is essential. Table II shows that a very low value for the expected carbon monoxide concentration is obtained when the Hopcalite is not conditioned. So long as either air or the gas to be analyzed continues to pass through the Hopcalite, no further conditioning is necessary; however, if it stands more than 5 minutes without air or gas flowing through it, conditioning appears to be necessary to eliminate a low value for the next analysis.

Typical Run. When the Hopcalite is ready for use, the second, third, and fourth absorption tubes are weighed on a microbalance; then all four tubes are connected as described above and attached to the exit end of the catalyst chamber. Each tube is covered with a piece of wet flannel. (This cools the tubes during a measurement and allows the air in them to expand after they are disconnected and taken to the balance room, thus preventing room air from entering.) The gas to be analyzed is drawn through the purifying train, the Hopcalite, the microabsorption tubes, and finally through a flowmeter. The rate of flow may be any constant value between 25 and 100 ml. per minute. The system is flushed immediately with a measured volume of purified air (see tables), the tubes are weighed, and from their gain in weight the per cent of carbon monoxide is calculated.

RESULTS

Microanalyses were made on two samples of carbon monoxide in air obtained from the National Bureau of Standards (cylinder A, 0.0025% and cylinder B, 0.0080$_2$% carbon monoxide by volume). The authors results with these samples are recorded in Table I. In each series the analyses were made consecutively.

These samples from the National Bureau of Standards were used to evaluate the method. In Table I the carbon monoxide content found by the microgravimetric method was within 1% of the bureau's value on the sample of 0.0025% and within 2% on the sample of 0.0080% carbon monoxide.

Next a sample of carbon monoxide in air containing about 0.1% carbon monoxide was prepared. Microanalyses of this mixture gave the values in column 4 of Table II.

Table I. Microanalyses of N.B.S. Samples of Carbon Monoxide in Air

Volume of Gas *Liters*	Volume of Air *Liters*	Rate of Flow *Ml./min.*	CO Concentration Found %	Comments
		Cylinder A (0.0025% CO)		
20.00	1.00	100	0.0024$_2$	Hopcalite conditioned
20.00	1.00	100	0.0026$_3$	Hopcalite conditioned
		Av.	0.0025$_2$ ± 0.0001$_0$	
		Cylinder B (0.0080$_2$% CO)		
Series I				
12.00	1.00	100	0.0079$_6$	Hopcalite conditioned
10.10	1.00	100	0.0078$_4$	
Series II				
10.00	1.00	100	0.0079$_5$	Hopcalite conditioned
10.00	1.00	100	0.0078$_7$	
10.00	1.00	100	0.0073$_8$	Not included in average
		Av.	0.0079$_1$ ± 0.0000$_5$	

Table II. Microanalyses of 0.1% Carbon Monoxide in Air

Volume of Gas *Ml.*	Volume of Air *Ml.*	Rate of Flow *Ml./min.*	CO Concentration Found %	Comments
		Series I		
1000	500	25	0.068$_8$[a]	Hopcalite not conditioned
1000	500	25	0.095$_5$	
1000	500	25	0.091$_6$	
		Series II		
1000	500	25	0.099$_7$	Hopcalite conditioned
1000	500	25	0.098$_0$	
2000	1000	50	0.102$_2$	
		Series III		
2000	1000	50	0.102$_3$	Hopcalite conditioned
2000	1000	50	0.105$_2$	
2000	1000	50	0.097$_3$	
2000	1000	50	0.102$_3$	
4000	2000	100	0.100$_3$	
		Av.	0.099$_4$ ± 0.003$_3$	

[a] Not included in average value.

Table III. Microanalyses of 0.01% Carbon Monoxide in Air

Volume of Gas *Liters*	Volume of Air *Liters*	Rate of Flow *Ml./min.*	CO Concentration Found %	Comments
			Series I	
10.00	1.50	100	0.0133_4	Hopcalite conditioned
10.00	1.00	100	0.0129_6	
16.70	1.00	100	0.0135_4	
9.50	1.00	100	0.0140_0	
			Series II	
15.00	1.00	100	0.0134_1	Hopcalite conditioned
			Series III	
13.80	1.00	100	0.0138_0	Hopcalite conditioned
10.00	1.20	100	0.0134_5	
		Av.	$0.0135_0 \pm 0.0002_4$	

The carbon monoxide–air mixture was then diluted with enough carbon monoxide–free air to yield an estimated 0.013_7% carbon monoxide in air. Microanalyses of this sample gave an average value of 0.0135_0% carbon monoxide as is shown by the data recorded in Table III.

ACKNOWLEDGMENT

The authors wish to thank Charles H. Lindsley for his interest in this work and for helpful suggestions and criticisms. Thanks are also due the National Bureau of Standards for supplying standard samples of carbon monoxide–air mixtures.

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Estimation of Types of Penicillin in Broths and Finished Products

A Microbiological Method

KIYOSHI HIGUCHI AND W. H. PETERSON, *Department of Biochemistry, University of Wisconsin, Madison, Wis.*

A method for the estimation of the relative amounts of three penicillins in a mixture by means of a microbiological differential assay is described. *Staph. aureus* 209-P, *Bac. brevis*, and Organism E are used in the procedure. Assays on various known mixtures and recoveries of penicillins added to broths were carried out. Data on several assays of commercial products are presented. The possible presence of unknown penicillins in penicillin preparations is discussed.

THE term penicillin today denotes a number of closely related compounds, at least four of which are well recognized: G (benzylpenicillin), X (*p*-hydroxybenzylpenicillin), F (Δ^2-pentenylpenicillin), and K (*n*-heptylpenicillin) (*2*). These compounds differ not only chemically, but also in antibiotic properties (*1, 4, 5, 7, 9*). Since present methods of penicillin production usually yield mixtures, much effort is being devoted to devising methods for estimating the relative amounts of each penicillin in a given product. Partition chromatography has been successfully used in the quantitative fractionation of penicillin mixtures (*6*). Another procedure is that of counter-current distribution (*3*). These methods seem particularly advantageous in the detection of unknown penicillins because they are essentially separation procedures. These physical methods have been reportedly used on quantities of 25 mg. and more, which limits their application.

Schmidt *et al.* (*8*) showed that penicillins F and X elicited different responses from *Bac. subtilis* NRRL B-558 than from the standard assay organism, *Staphylococcus aureus* NRRL B-313. By determining ratios among these responses, an indication of the composition of a mixture of penicillins could be obtained. The present method is an extension of the principle of ratios to three penicillins and three test microorganisms.

EXPERIMENTAL

This paper describes a microbiological differential assay method with which an estimation of the relative amounts of three different penicillins in a mixture is possible. Theoretically, the method can be extended to mixtures of more than three penicillins, but the consequent increase in errors makes its practical application difficult.

Crystalline penicillins G, X, F, and K were used as standards. The three organisms used in the assay were selected after a preliminary survey of about sixty gram-positive bacteria. The responses of the organisms to the different penicillins in a liquid medium were studied (Table I), and on the basis of their differential responses and growth characteristics *Staph. aureus* 209-P, *Bac. brevis*, and an unidentified spore-forming lactic, called E, were chosen for the assay purposes. Comparisons on a weight basis of the effects of the various penicillins on the assay organisms are given in Table II. The inhibition values are calculated from the data in Table I and column 3 in Table II. For example, 0.025 unit per ml. of penicillin G is required to inhibit *Staph. aureus*, but since one unit equals 0.6 microgram then $0.025 \times 0.6 = 0.015$ microgram is the weight of G required for inhibition. Likewise, $0.06 \times 1.11 = 0.067$ microgram per ml. of X is required to inhibit the growth of *Bac. brevis*. This latter value represents the largest quantity of any of the penicillins required to inhibit any of the three assay bacteria. The penicillin required in the least amount for any of the three organisms is K; only 0.011 microgram per ml. is needed to stop the growth of *Staph. aureus*. However, in order to compare the results obtained in this paper with previous results, all data are expressed in terms of the standard unit, which is the activity equal to 0.60 microgram of

Table I. Concentrations of Penicillins Required to Inhibit Growth

Organism	Penicillin G	Penicillin X	Penicillin F	Penicillin K
	Unit/ml.	*Unit/ml.*	*Unit/ml.*	*Unit/ml.*
S. aureus	0.025	0.025	0.025	0.025
S. albus	0.05	0.05	0.05	0.05
S. lactis	0.09	0.04	0.13	>0.11
Organism E	0.03	0.015	0.05	0.09
B. vulgatus	0.10	0.05	...	0.20
M. flavescens	0.05	0.02	...	0.05
B. coagulans	0.03	0.015	0.06	0.11
B. brevis	0.03	0.06	0.08	0.13

Table II. Comparison of Penicillin Activity on a Weight Basis

Penicillin	Units/Mg. (9)	γ/Unit	Requirement for Inhibition of *Staph. aureus*, γ/ml.	*Bac. brevis*, γ/ml.	Organism E, γ/ml.
G	1667	0.60	0.015	0.018	0.018
X	900	1.11	0.028	0.067	0.020
F	1550	0.65	0.016	0.052	0.039
K	2300	0.43	0.011	0.053	0.038
Dihydro F(?)	1700	0.59	0.015	0.036	0.040

Table III. Composition of Assay Broth Media

Organism	Difco Yeast Extract *G./l.*	Bacto Peptone *G./l.*	Glucose *G./l.*	Armour Beef Extract *G./l.*	KH_2PO_4 *G./l.*	K_2HPO_4 *G./l.*	pH
Staph. aureus	3	6	2	1.5	...	...	6.3
Organism E	3	6	2	...	5.0	0.5	6.0
Bac. brevis	3	6	.	...	...	...	6.6

sodium penicillin G (*10*). Any figure can be easily expressed on a weight basis by means of a simple calculation.

METHOD

Cultures. The assay organisms are carried as streaks on 0.3% yeast extract, 0.2% glucose agar slants. The media described below are used for growing the inoculum as well as for use in the assay. The *Staph. aureus* and *Bac. brevis* inoculums are grown for about 15 hours at 37° C. Incubation at 45° C. is required for Culture E.

Media. The compositions of the three media are given in Table III.

Apparatus. Approximately 300 tubes of uniform dimensions (18 × 150 mm.) in suitable racks are used.

A pipetting machine to deliver 10-ml. aliquots saves time in setting up the assay.

An instrument for turbidity readings is required. An Evelyn photoelectric colorimeter with a 660-mμ filter is satisfactory.

Several 0.1-ml. micropipets are required for diluting and adding the penicillin standards.

Standards. Pure crystalline penicillins G, X, F, and K are required. For a standard 0.6 microgram of pure sodium penicillin G is taken as one unit, and one unit of the other penicillins is the amount required to give an equal inhibition of *Staph. aureus* 209-P in broth cultures. The penicillin standard solutions are made up in distilled water saturated with chloroform and kept in the refrigerator. Ten milligrams of penicillin G are accurately weighed out on a microbalance and made up in 100 ml. of distilled water. This solution is equal to 166.7 units per ml. Similar solutions based on their activities in units per milligram are made for the other penicillins. At each assay dilutions to 10 and 2.5 units per ml. are made from these solutions with sterile 0.3% yeast extract water.

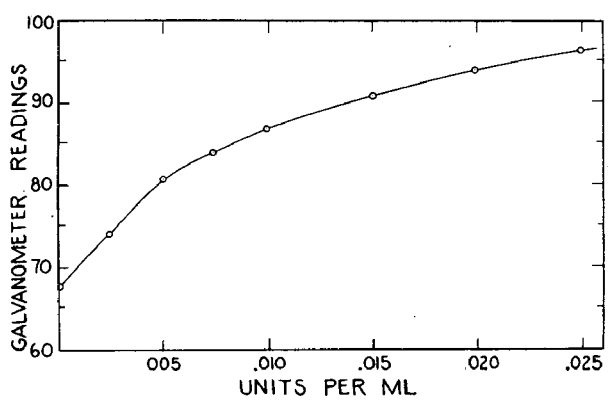

Figure 1. Response of *Staphylococcus aureus* to the Penicillins

Assay Procedure. By means of the pipetting machine, racks of tubes are filled with 10 ml. of the respective media for the three organisms. The tubes are plugged and autoclaved for 10 minutes at 6.8-kg. (15-pound) pressure.

Staph. aureus **Assay.** To a series of tubes prepared as described above, graded amounts of penicillin G are added in duplicate with a micropipet to give 0.005, 0.0075, 0.010, 0.015, 0.020, and 0.025 unit of penicillin per ml. of medium. The 2.5 unit per ml. dilution of the standard G is used. A similar set of tubes is made up for each of the other penicillins. However, the range need include only the 0.010, 0.015, and 0.020 unit per ml. levels, since it is only necessary to standardize these penicillins from the curve obtained by plotting penicillin G concentrations against turbidity readings. The unknowns are likewise added to duplicate tubes at approximately these levels. The curves for penicillins G, X, K, and dihydro F(?) are not always identical with the G curve but, since no consistent differences among the penicillins were found in numerous assays with *Staph. aureus*, the method of averaging the concentration as calculated from three levels of inhibition (at approximately 0.01, 0.015, and 0.02 unit per ml.) has been used. The tubes are inoculated by the additions of one drop of inoculum, prepared as previously described, and then incubated for approximately 15 hours at 37°. Measurements of bacterial growth are made by means of turbidity readings in the photoelectric colorimeter with a 660-mμ filter. When the galvanometer deflections are plotted against concentrations of penicillin G, the standard curve is obtained (Figure 1).

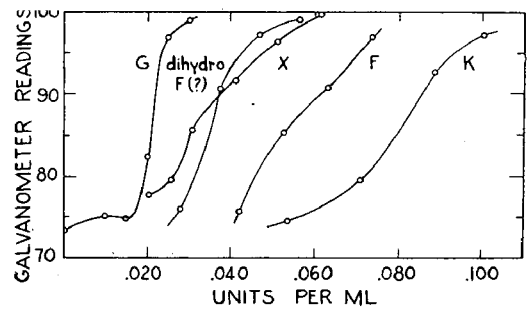

Figure 2. Response of *Bacillus brevis* to the Penicillins

Bac. brevis **Assay.** The general procedure is the same as for *Staph. aureus*, except that there will be a separate curve for each penicillin. The curves for penicillins X, F, K, etc., are plotted after determining the exact concentration of each based on the aureus assay. The levels of the penicillins used must be carefully considered because of the steep nature of some of the curves. For penicillin G, the range lies between 0.015 and 0.030 unit per ml.; for X, 0.02 and 0.06; for F, 0.04 and 0.09; and for K, 0.05 and 0.13. To avoid too great volume changes, penicillins other than G are added from the 10 unit per ml. dilutions of the standards. Figure 2 indicates that the lower levels of the penicillins give no inhibition of the organism and it is necessary to have several points on the steep part of the curve. About 10 tubes at five levels in duplicates are used for penicillin G. Similar numbers are used for the other penicillins. For the addition of the unknowns, unless one has an approximate idea as to the forms of the penicillin present, the dilutions should cover all possible ranges from 100% G to 100% K. Mixtures of other known penicillins will lie between these points in their effect on *Bac. brevis*.

Organism E Assay. All procedures are the same as for the other two organisms, except the penicillin levels. The steep portion of the curve for this bacterium with penicillin G lies between 0.015 and 0.03 unit per ml.; for X 0.0075 and 0.020; for F 0.03 and 0.06; and for K, 0.04 and 0.10. This organism requires approximately 45° C. for optimum growth; therefore incubation is done in a thermostatically controlled water bath for 15 hours. Figure 3 shows the curves obtained with the various penicillins.

Calculations. From the curves plotted from the turbidity readings for each organism the ratios of the activity of the various penicillins is obtained with respect to penicillin G.

Table IV. Results of Assays of Known Mixtures

	Mixture	Penicillins G %	X %	F %	K %
1.	Calculated	53	..	47	..
	Found	60	..	40	..
2.	Calculated	33	..	..	67
	Found	36	..	..	64
3.	Calculated	17	83	..	..
	Found	18	82	..	..
4.	Calculated	..	..	8	92
	Found	..	..	8	92
5.	Calculated	35	33	..	32
	Found	33	36	..	31
6.	Calculated	35	34	..	31
	Found	33	33	..	34
7.	Calculated	31	..	31	38
	Found	40	..	32	28
8.	Calculated	50	0	..	50
	Found	49	<1	..	50

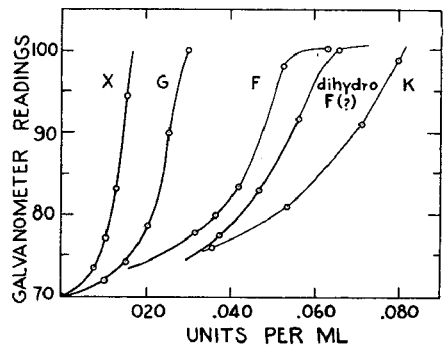

Figure 3. Response of Organism E to the Penicillins

For example, it is evident that with organism E one unit of penicillin X is approximately 1.8 times as potent as one unit of penicillin G; F is only 0.53 times as active as G; dihydro F (?) is 0.43 times as active; and K is only 0.31 times as active as G. These figures are expressed as G/X, G/F, G/dihydro F, and G/K, respectively. Assuming linearity we can add up the effects of a mixture of penicillins as follows:

$$G + 1.80\,X + 0.53\,F + 0.43 \text{ dihydro F} + 0.31\,K = \text{total effect}$$

expressed as G with organism E. The letters G, X, etc., represent the amount of the designated penicillin present.

Similarly, with *Bac. brevis*, the total effect can be expressed as follows:

$$G + 0.55\,X + 0.34\,F + 0.50 \text{ dihydro F} + 0.20\,K = \text{brevis response measured as G}$$

Staph. aureus would necessarily respond as follows:

$$G + X + F + \text{dihydro F} + K = \text{aureus response}$$

Because only three equations have been set up, only mixtures of three penicillins can be considered. In the use of the ratios G/X, G/F, etc., it is desirable to obtain these values at the points on the curves where the unknown sample lies.

Sample Calculation on a Known Mixture of Penicillins G, X, and K. A known mixture of penicillins containing 35 units of G, 33 units of X, and 32 units of K was differentially assayed. Expressed as penicillin G, the mixture showed 100 units with *Staph. aureus*, 106.8 units with organism E, and 56.6 units as measured with *Bac. brevis*. The average G/X and G/K values at the levels of inhibition observed with the "unknown" were such as to give the following equations:

$$G + 1.79\,X + 0.293\,K = 106.8 \text{ (organism E)}$$
$$G + 0.50\,X + 0.175\,K = 56.6 \text{ (\textit{Bac. brevis})}$$
$$G + X + K = 100 \text{ (\textit{Staph. aureus})}$$

Solving the three simultaneous equations for G, X, and K, the values are:

Found: G = 33; X = 36; K = 31
Calculated: G = 35; X = 33; K = 32

Assays of Known Mixtures and Commercial Samples. Numerous assays were run on known mixtures. The results were in general good (Table IV). The errors are greatest on those mixtures of three penicillins which include F. As can be seen from the example given, penicillin F has an effect on brevis and organism E intermediate to that of G and K. Hence, there is a greater tendency for large errors.

As a further check on the many factors involved in the assay, pure penicillins were added to fermentation broths and recoveries made with the method (Table V). Rather good recoveries were obtained.

In Table VI are given results of assays of several commercial products. In general, those samples low in G in each group were made prior to recent attempts to increase the G level. The significance of large negative values is discussed below.

DISCUSSION

The assay is based on several assumptions.

Staph. aureus 209-P is taken as the standard organism by which the unit is defined for all penicillins. The effect of 0.6 microgram of sodium penicillin G is taken as the value of one unit.

The effects of the penicillins in mixtures on the assay organisms are additive. This has been found to be the case in many tests.

The method as now developed is applicable only to mixtures of three penicillins which are known to be present. In cases of more than three penicillins, separation into groups of not more than three by solvent extraction or other means must be employed before the method is applied. No unknown penicillin or other antibiotics may be present if correct results are to be obtained. To extend the method to a new form of penicillin, suitable curves must be developed from the effects of the pure substance on the assay organisms. Some evidence of the presence of penicillins other than those considered in the assays has been obtained—the large negative values for X obtained in certain preparations are good indications of this. Furthermore, a crystalline product having the elementary composition of dihydro F has recently been isolated by one of the commercial producers and kindly made available for testing. It is unique in that it is more potent for *Bac. brevis* than for Organism E. When certain Q176 penicillins are differentially assayed as mixtures of G, F, and K, nega-

Table V. Recoveries of Penicillins Added to Fermentation Broths

	Samples	Penicillins G %	X %	K %
I.	Broth from culture Q176 in synthetic medium	14	3	83
	With added G to give theoretically	61	1	38
	Found	61	1	38
	With added G and K to give theoretically	40	1	59
	Found	37	−2	65
II.	Q176 broth	6	29	65
	Added X to give theoretically	3	65	32
	Found	0	59	41
III.	Q176 broth	77	0	23
	Added K to give theoretically	37	0	63
	Found	37	1	62

Table VI. Assays of Commercial Penicillins on the Assumption That They Were Mixtures of G, X, and K

Commercial Company	No.	G %	X %	K %
A	1	48	51	1
	2	74	0	26
B	1	44	−3	59
	2	93	−9	16
C	1	62	10	28
	2	48	16	36
	3	94	−1	7
	4	101	−3	2
D	1	46	−2	56
	2	67	1	32
E	1	41	−5	64
	2	45	−3	58
	3	80	0	20
	4	88	1	11

tive values are obtained for F. However, it is possible that dihydro F (?) is present, in which case the absurd negative values can be explained. Even though in practical applications it is not always possible to have samples which are limited to those with known types and numbers of penicillins, the results of assays on these preparations are of value in giving an indication of their composition.

ACKNOWLEDGMENTS

The crystalline penicillins were kindly supplied by Abbott Laboratories, Chas. Pfizer and Co., Inc., Commercial Solvents Corporation, Heyden Chemical Corporation, Northern Regional Research Laboratory, Squibb Institute for Medical Research, and Upjohn Company.

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NOTES ON ANALYTICAL PROCEDURES . . .

Magnetic Rotation of the Direct Current Arc in Spectrographic Analysis

A. T. MYERS AND B. C. BRUNSTETTER

Bureau of Plant Industry, Soils, and Agricultural Engineering, Agricultural Research Administration, U. S. Department, of Agriculture, Beltsville, Md.

EXCITATION by the electric arc is probably the most widely used and the most satisfactory of the three methods commonly employed for analytical spectroscopy (*1*). A serious disadvantage of the direct current arc is its instability, due primarily to its inclination to wander irregularly from one point to another over the surface of the electrode (*3*). In a work program to improve the constancy and reproducibility of the direct current arc for quantitative analysis, the authors controlled arc wandering to a limited extent by using pointed upper electrodes. Inasmuch as arc wandering still occurred in a variable manner from sample to sample, the solution seemed to be rotation of the arc.

Jaycox and Ruehle (*2*), who used a system of mechanical rotation of the direct current arc in spectrographic analysis, say that rotation causes the inherent wanderings of the arc to become more rapid and regular, and better reproducibility of spectrograms can thus be obtained. The device described by these authors consists of a motor mounted below the lower electrode, connected to it by an insulated shaft which mechanically rotates the electrode at 600 r.p.m. during the sample exposure. Gibb (*1*) also recommends a system of mechanical rotation of the arc at 600 r.p.m.

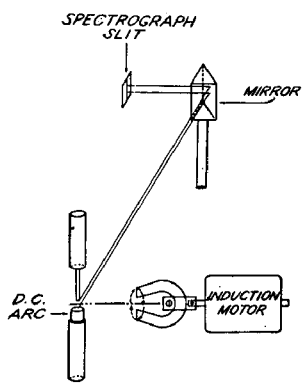

Figure 1. Magnet Mounted on Induction Motor in Position to Rotate the Direct Current Arc

The authors use a strong permanent horseshoe magnet (Alnico 78326-B Little Giant) to rotate the arc magnetically. The magnet is placed as shown in Figure 1, so that it rotates on the shaft of a small induction motor, with the horizontal axis passing through the middle of the arc. The magnet is placed 2 to 2.5 inches away from the arc and rotated at 600 r.p.m.

The direct current arc burns 0.125-inch carbon upper electrodes and 0.3125-inch carbon lower electrodes. The latter are machined with a cavity to hold the samples and standards, which is 0.25 inch in diameter and 0.156 inch deep, with a cavity wall thickness of 0.011 inch. The authors use 22 to 24 amperes at a voltage of about 140 to 150.

The authors have used this method of rotating the arc magnetically for a year or more and have in general observed better reproducibility of their spectrograms; moreover, the lower electrode cavity wall burns down in a more uniform way. It is possible that under other conditions of excitation—e.g., with lower amperages—even more benefit might be seen in the routine use of this arc rotation. This method of rotating the arc is convenient and easy and even if a consistent improvement in reproducibility of only 2 to 5% is realized it is well worth including in the development of improved quantitative techniques. A visual difference between no rotation and magnetic rotation is easily observed on the wall image of the arc.

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AIDS FOR THE ANALYST . . . . .

Factors Affecting Constancy of Analytical Weights. Archibald Craig, Mars, Pa.

Most brass weights are coated with gold, rhodium, or lacquer. Both gold and lacquer are subject to wear; rhodium makes an excellent coating, and apparently chromium is at least as good. Unfortunately, most of the chromium-plated weights now in use have other and unnecessary defects, notably lead filling. Weights made entirely of noncorroding alloys require no coating.

Two-piece weights have cavities in which is placed enough loose metal to bring the weight up to standard. Since lead is soft and has a high density, a larger mass can be put into a weight cavity than of any other base metal. This gives a greater tolerance in the preliminary lathe work and makes fewer rejections necessary.

Unfortunately, lead oxidizes rapidly and is converted into a basic carbonate. Weights filled with it may gain more than they lose by wear, particularly if kept for standards. Since the material is added to correct for irregular lathe work, some weights need little or no addition and others are packed full. Weight changes, therefore, are irregular.

When such a set is corrected, it may be possible to replace the lead with tin or brass, but one or two weights in a set are likely to be too light, and the lead has to be retained or the correction made by an outside addition. Tantalum, which also has a high density, is so hard that its use is practical only for manufacturers.

For these reasons, the best American makers have for several years used either tin or brass as added material. Tin is easily cut and rammed into the cavity, has nearly the same density as brass, and is equally resistant to corrosion.

Cheap German weights containing lead were formerly imported in great numbers, as not many buyers were aware of their defect. Since the war started, some American makers have undertaken to supply the demand for cheap weights, for the most part using lead as added material. Great pains have been taken to give them a fine surface finish, and their defective interiors have been generally overlooked.

There are several causes of variability in weights aside from added material, but they are all very small in comparison with that due to lead.

Lacquered weights have a tendency to gain on standing; a one-piece 20-gram weight coated with the lacquer used for hardware gained 0.10 mg. in one year. A set of two-piece weights coated with Bakelite and containing tin in 5 years gained 0 to 0.03 mg. over the Bureau of Standards certificate value. A rhodium-plated one-piece 20-gram weight showed no change after 5 years, while a one-piece stainless steel 20-gram weight gained 0.02 mg. in the same time. Rhodium-plated two-piece weights sometimes show a gain of a few hundredths gram after several years' standing. These gains are negligible in weights used for analysis, as loss from wear exceeds them.

On the other hand, lead in the interior of a weight will gain much more rapidly and continuously. The lead may be completely converted to a white powder, and the mass increase, amounting to several milligrams, is as much as 20% over the original lead added. When a weight shows a gain of more than 0.25 mg., lead is always present.

Formerly, the National Bureau of Standards accepted weights containing lead for certification, and many sets 5 or 10 years old have gained so much that the certificates are valueless so far as the gram weights are concerned. The bureau has made the following requirement in regard to lead adjusting material.

Effective July 1, 1945, new or reconditioned weights which contain lead adjusting material will not be accepted for test under any of the recognized classes of standard weights, except Class C weights in use before the effective date may still be tested even though they contain lead adjusting material.

If inspection reveals prohibited adjusting material in new or reconditioned weights the bureau will not be obligated to readjust the rejected weights to the values they had before inspection.

Explosion in Determination of Cobalt as Potassium Cobaltinitrite. D. B. Broughton, M. E. Laing, and R. L. Wentworth, Division of Industrial Cooperation, Massachusetts Institute of Technology, Cambridge, Mass.

In carrying out an analytical procedure involving precipitation of cobalt as potassium cobaltinitrite, a violent explosion was recently experienced.

The procedure was carried out, as described in various quantitative analysis texts, by adding a solution of potassium nitrite to a solution of cobaltous nitrate buffered with sodium acetate and acetic acid. After standing warm, overnight, the precipitate of potassium cobaltinitrite was filtered out. Since the filtrate contained a little colloid which had passed the filter, it was heated further over a low flame to coagulate the colloid. In this period, evaporation reduced the volume of the filtrate by about one half. The liquid then turned purple and exploded violently. The flask was shattered, and the wire gauze on which it had rested was bent into a hemisphere.

Presumably, the only constituents in the filtrate were sodium acetate, acetic acid, sodium nitrite, sodium nitrate, and a trace of cobalt.

The experiment has been repeated several times, and explosions invariably result, even when the filtrate is apparently clear and free from colloid. Mixtures of sodium acetate, acetic acid, and sodium nitrite, in the absence of cobalt, do not explode.

It is possible that the purple color appearing on heating the filtrate represents the formation of a new nitro- or nitritocobalt complex, formed from traces of cobalt, and that this material exploded on continued heating.

This procedure (omitting evaporation of the filtrate) is described throughout the literature, without mention of hazard. It appears advisable to avoid prolonged heating and evaporation of these solutions and to discard immediately if a blue or purple coloration appears.

Drying Glassware with Alcohol and Ether. Frederic E. Holmes, 6515 Blueridge Ave., Cincinnati 13, Ohio.

The old idea persists that glassware can be rendered absolutely dry by rinsing with alcohol and then ether. In the clinical laboratory the remark is often heard, "Hemolysis of the blood cannot be due to moisture: the pipet was rinsed with alcohol and ether." As a matter of fact, the chilling produced by drawing air over a glass surface wet with ether usually results in deposition of a film or fine "fog" of moisture on the glass. If a pipet is set aside at this point, a visible droplet of water may collect. However, if air is passed over the glass surface for only a few seconds or a minute or two, depending upon conditions, the thin film of moisture is evaporated. Some criterion other than the mere rinsing with alcohol and ether must be used to determine when the glass is dry.

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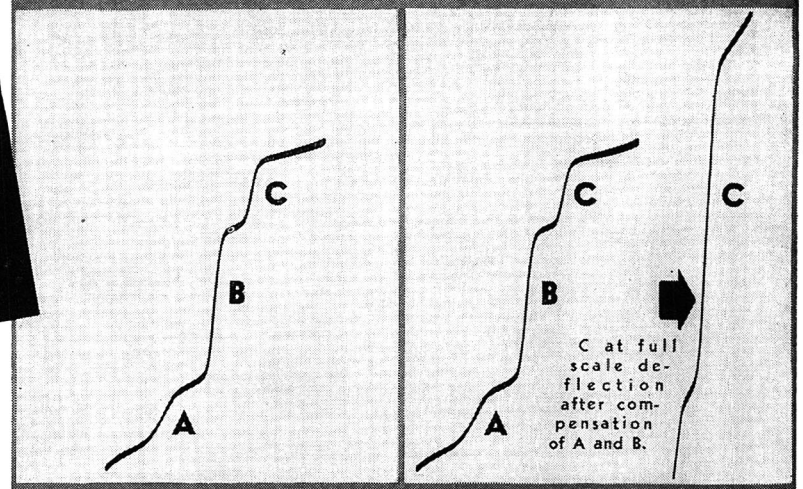

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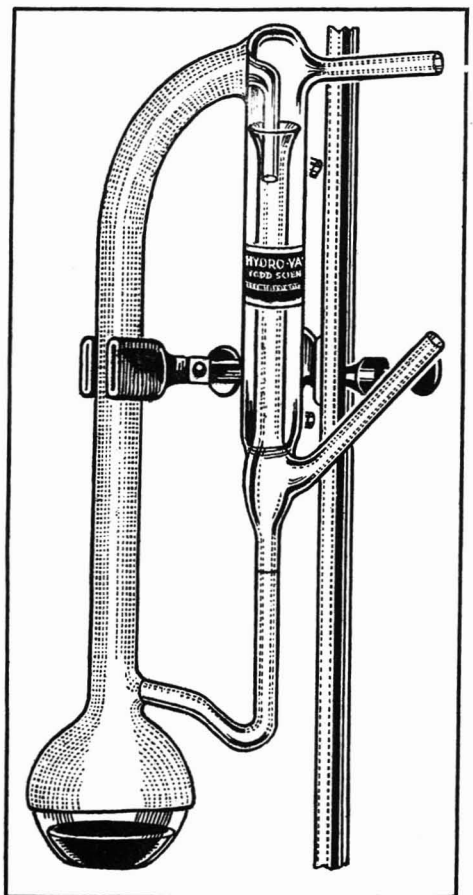

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INSTRUMENTATION

Instrumentation is defined as it applies to analysis and a brief classification of its several aspects is presented

by ***Ralph H. Müller***

DURING the past year the editor of this column has attempted to interpret current developments in various fields in the light of their interest and utility for the analyst. In approaching the assignment for the next year it has seemed desirable to define instrumentation as it applies to analysis and to attempt a brief classification of its several aspects. In trying to do this, we can hope for little more than a nod of limited approval, because any degree of unanimity on these questions could be achieved only through an extended forum or discussion.

We believe it is important to distinguish between instrumental aids to analysis and instrumental methods of analysis. The latter is achieved by an instrument or machine which furnishes the analytical information directly. There are very few examples in practice—the Quantometer in spectrographic analysis, some mass spectrometers, the ebulliometer, and possibly the recording polarograph. The true instrumental method of analysis requires no reduction of data to normal pressure and temperature, no corrections or computations, no reference to correction factors nor interpolation on nomographic charts. It indicates the desired information directly on a dial or counter and if it is desired to have the answer printed on paper—that can be had for the asking. It is strange and difficult to comprehend why the last few steps have not been taken by the analyst in bringing his instruments to this stage of perfection. They are minor details, the absence of which in his motor car, office equipment, or telephone he would not tolerate for a moment. Recently, we were taken to task by one of America's distinguished chemists for emphasizing these distinctions. "All a matter of applied physical chemistry", he explained patiently, "and therefore not particularly new." We are obtuse enough to feel that physicochemical techniques bear the same relationship to instrumental analysis as the violent oxidation of hydrocarbons does to the modern motor car.

Improvement of Existing Techniques

It is often thought that instrumentation is primarily concerned with the complicated techniques of mass spectrometry, infrared, and the electron microscope, but there are countless techniques involving ordinary as well as electrometric titrations, conductance, dielectric constants, simple distillations, extractions, and the like which are monotonous and time-consuming. They are just as important in the laboratory as the more difficult techniques. This class of operations awaits the instrument designer and the solution of each problem requires no particular help from the chemist. His work was done long ago in establishing the fundamental principles and limits of precision, and in exhausting the application possibilities. What is now required is the means for rendering these operations completely automatic. This simple phase of instrumentation elicits no particular enthusiasm from the chemist. It promises nothing new in the final results and it affords him no information which he could not obtain before. That is as it should be. It is a job for the engineer, the electronics expert, and the instrument designer. Their responsibility will be discharged when they have designed mechanized equivalents for these relatively simple tasks.

The economic consequences of such mechanization can be expected to be important in large laboratories. Present practices require some degree of chemical training on the part of the operator unless the determination is purely repetitive. This is to be contrasted with the operation of certain highly complex instruments such as spectrophotometers or recording infrared assemblies, which require even less operator skill or comprehension, because these devices are semiautomatic.

We cannot refrain from comment on some of the simple devices and tools of the laboratory. They concern instrumentation in a very indirect way, but there are times when one must use ring stands, tripods, clamps, and holders in connection with more complicated equipment. There have been notable improvements in these simple devices, but there are few laboratories without the inevitable collection of rusty clamps and rods from which one must, on occasion, erect non-Euclidean monstrosities to hold up apparatus. One wonders where the Victorian foundries in which these impedimenta are cast are to be found in these United States. It is to be hoped that we may simply acknowledge Torquemada as the rightful inventor of chemical hardware, and having discharged our indebtedness to the design improvements of Lavoisier, Liebig, and Bunsen, turn the problem over to a mechanical engineer. The engineer would be greatly assisted in his task by an ignorance of chemistry and its practices. With no initial handicaps, he might accomplish something worthy of American technology. If we hereby offend the purveyors of such equipment, we hasten to add that it is purely intentional.

Complex Techniques

The instrumental problems associated with mass spectrometers, spectroscopy, infrared, electron diffraction, and microscopy may be expected to find their most intensive development in large industrial laboratories and among a few instrument companies. There are sufficient demands in industry to warrant funds for special development projects and these are usually justified by the extent to which their successful solution increases production or improves a product. There will continue to be isolated examples, more we hope, where developments of this sort emanate from university laboratories. The pulsed mass spectrometer from the University of Pennsylvania is an example which we were happy to discuss in a previous column. If our observations are correct, we conclude with reluctance that the initiative has long since passed to the large industrial laboratories for this type of research and development. This would be no particular cause for concern, were it not for the reasons which encourage the research.

In any well administered industrial laboratory, the proposed instrumental development will be quite definitely related to something which is directly useful in the company's business. Even under such relatively restricted incentives, there can be a fair amount of progress if we consider similar developments to other industrial laboratories. The instrument company engages in research and development work primarily to meet a definite scientific or technological need—a type of measurement which has been performed with the crude improvisations of the research laboratory and now requires that degree of refinement and perfection which will yield a true instrument. Neither of these agencies can afford long-range instrumental developments for what might be called "the fun of it". At least it would be a highly unprofitable or hazardous policy and could easily prove fatal for an organization of limited resources. The academic investigator who is interested in such problems faces difficulties of another nature—usually inadequate facilities, or the very considerable budget which such work requires. Yet, is it not true that many of our most useful developments in other fields have come from an unfettered urge to follow a "hunch" or random idea? There is no reason to believe that instrumentation would suffer from some degree of relief from the necessity of proving its worth in advance.

INSTRUMENTATION

Training in Instrumental Analysis

We have made a few observations on this subject in the past and more detailed suggestions elsewhere [*Instruments*, 19, 261 (1946)]. In some respects, the problem becomes progressively more difficult. Since teaching is one of our duties, we may be permitted a few observations on this subject. Before doing so, we wish to set our credentials in the proper light. During the past year many industrial and academic readers of this column have asked us to recommend graduate students for responsible positions in analytical laboratories, presumably under the impression that we "practice what we preach". There is no institution in which what we have been discussing is taught, or for which the facilities are adequate. Some departments have acquired expensive commercial equipment in order to acquaint their students with modern methods. In a few instances, the acquisitions have become museum pieces. With such equipment there is always the danger that the student will learn a few techniques which will be obsolete by the time he is ready to use them elsewhere.

With respect to instrumentation, it would seem best to follow the practices which are used in sound teaching of chemistry itself —to stress fundamentals and to teach basic techniques. For instrumental analysis, this might well include basic theory and experiments in optics and in electrical and electronic measurements. The customary general courses in physics must furnish the background, but as a rule, it will be necessary to select and correlate isolated portions of this subject for extensive review and amplification for the needs of the analyst. The principles of instrumentation have been well defined and classified. As a well organized field of science and technology its rules can be learned in a reasonable time and their relationship to modern analytical practice can be explained and illustrated by specific examples. As we see it, it is simply a matter of a few cardinal principles, a few selected topics in physics, some electronics, and an elementary knowledge of mechanisms. The correlation, for our purpose then requires the judgment and instinct of the analyst in appraising their utility.

Although this supplementary training for the analyst consists entirely of nonchemical subjects and therefore seems to be quite remote from the rest of his chemical training, it is interesting to note that instrumental analysis cuts across the arbitrary barriers which have been established in the teaching of analysis. Analytical chemistry has usually implied inorganic analysis; and organic analysis, and later, microanalysis were originally set up as necessary adjuncts to organic chemistry. A new instrumental method is likely to be equally applicable to the analysis of vitamins or nonferrous alloys. One is likely therefore to come to the conclusion that the analyst in the near future will be well trained in (1) the fundamental chemistry of organic and inorganic analysis and (2) the broad principles of instrumentation. With the latter, he will be able to understand and use existing instruments, but what is more important, he will be able to perceive new needs and possibly aid in their design and development.

We believe that the teachers of analysis cannot continue to neglect this responsibility. The notion that one can relegate these duties to his physics or engineering colleagues is untenable. They have their own problems and they must be forgiven if they regard them as more important than ours. A very interesting and instructive suggestion for "increasing the productivity of research" has been made by Paul E. Klopsteg [*Science*, **101**, 569 (1945)] in which he envisions a division of "instrumentology" within a university. As such it would function as a service and advisory center on instrument problems for the various science departments. He has explained how this group could save the individual research man precious time and effort by assuming that part of his burden for which he is not particularly well trained. Presumably this idea could be extended to the assumption of some of the teaching needs which we have been discussing.

Important Developments

Our journal appears in this issue under a new title and its editors have given much thought and effort toward its continued improvement. It is gratifying and stimulating to witness the many important and fundamental contributions which are appearing in its pages. From our little corner it is equally exciting to witness the important developments which are coming from industrial, academic, and institutional laboratories. There is still much to be done and some of the isolated efforts to improve our instruments may well serve to accelerate a more general effort in this direction. It may even be in order to make the customary seasonal resolutions to do better.

INDEX TO ADVERTISERS

American Platinum Works	17 A
Amersil Co., Inc.	33 A
Applied Research Laboratories	11 A
Atlas Electric Devices Co.	30 A
Baker & Adamson Div.	36 A
Baker Chemical Co., J. T.	2 A
Bausch & Lomb Optical Co.	34 A
Central Scientific Co.	5 A
Chemical Rubber Co.	29 A
Coleman Instruments, Inc.	30 A
Coors Porcelain Co.	32 A
Dietert Co., Harry W.	27 A
Eimer & Amend	16 A
Fisher Scientific Co.	16 A
Fish-Schurman Corp.	32 A
Gardner Laboratory, Inc., Henry A.	31 A
General Chemical Co.	36 A
Glas-Col Apparatus Co.	8 A
Goodrich Chemical Co., B. F.	10 A
Greiner Co., Emil	21 A
Harshaw Chemical Co.	4 A
Hellige Inc.	26 A
Hevi-Duty Electric Co.	22 A
Hoskins Manufacturing Co.	12 A
Kimble Glass Co.	7 A
Klett Manufacturing Co.	25 A: 28 A
Laboratory Equipment Corp.	20 A
LaMotte Chemical Products Co.	26 A
LaPine & Co., Arthur S.	27 A
Lindberg Engineering Co.	24 A
Mallinckrodt Chemical Works	13 A
Martin & Co., H. S.	15 A
Merck & Co., Inc.	6 A
Micro Metallic Corp.	14 A
New York Laboratory Supply Co., Inc.	33 A
Palo-Myers, Inc.	30 A
Perkin-Elmer Corp.	20 A
Photovolt Corp.	28 A
Precision Scientific Co.	35 A
Rubicon Co.	32 A
Sargent & Co., E. H.	19 A
Schaar & Co.	20 A: 29 A
Scientific Glass Apparatus Co., Inc.	25 A
Schleicher & Schuell Co., Carl	31 A
Tech Laboratories	27 A
Thermo Electric Mfg. Co.	29 A
Thomas Co., Arthur H.	18 A
Tracerlab, Inc.	26 A
Ultra-Violet Products, Inc.	28 A
Welch Scientific Co., W. M.	31 A
Will Corp.	9 A

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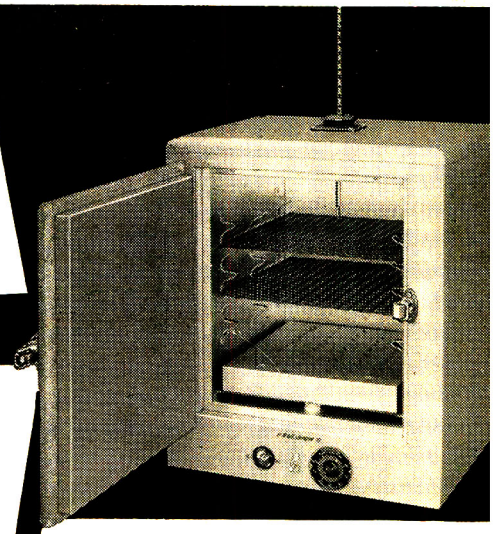

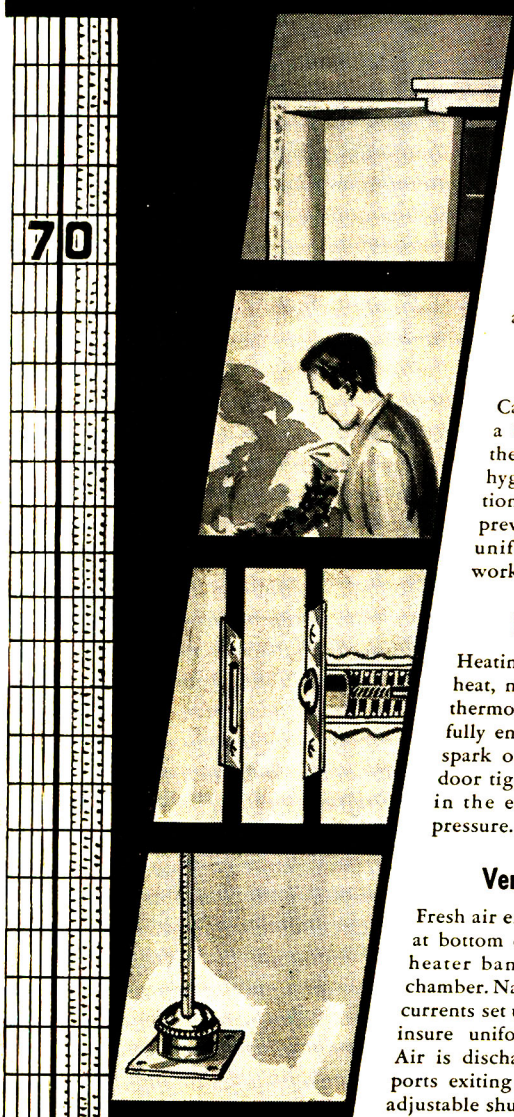

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Heating elements operate at BLACK heat, not incandescence, Hydraulic thermostat has silver contact points fully enclosed—absolutely no open spark or arcing. Safety latch pulls door tightly shut, but springs open in the event of sudden interior pressure.

Ventilation Control

Fresh air enters through intake part at bottom of oven, passes through heater bank, then into working chamber. Natural gravity convection currents set up air-flow patterns that insure uniform heat distribution. Air is discharged through ceiling ports exiting through a vent with adjustable shutter.

RECORDED PROOF OF CONTROL ACCURACY!

Reproduced at left is a typical temperature control chart produced by a recording thermo-couple showing accuracy of Model 16 Thelco Oven. Note straight band, proving thermostatic control accuracy and uniform width of band indicating temperature uniformity throughout working chamber — **FEATURES NEVER BEFORE OFFERED IN A LOW PRICED OVEN.**

Having a temperature range from 35 to 180°C., the "Precision" Thelco No. 16 Laboratory oven can be used for baking, drying, conditioning, preheating and many other applications in every laboratory. Particularly useful as a general purpose oven to handle the overflow capacity in large laboratories. The extremely low price of this unit plus its ruggedness and wide field of applications makes it an "unusual value" for limited budgets. Write for four page Bulletin giving complete details on Model 16 and other "Precision" Thelco units.

STANDARD EQUIPMENT

Working chamber 11x11x11". Overall dimensions 16½" wide, 16" deep, 25" high. Includes 2 latticed metal shelves adjustable for height on three sets of brackets to permit pulling half-way out; thermometer holder; ventilating shutter, hazard-safe door latch, Neon pilot lamp, cord and plug. For A.C. single phase, or D.C. Wattage, 300. Specify 115 or 230 volts.

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