INDUSTRIAL AND ENGINEERING CHEMISTRY

ANALYTICAL EDITION

VOLUME 18, NUMBER 9 ISSUED SEPTEMBER 21, 1946 CONSECUTIVE NUMBER 18

Analysis of Binary Mixtures of Normal Aliphatic Dibasic Acids and Esters

MICROCHEMISTRY

NOTES ON ANALYTICAL PROCEDURES

We acknowledge with thanks the action of J. T. Baker Chemical Co. in releasing the front cover of this issue for editorial purposes.

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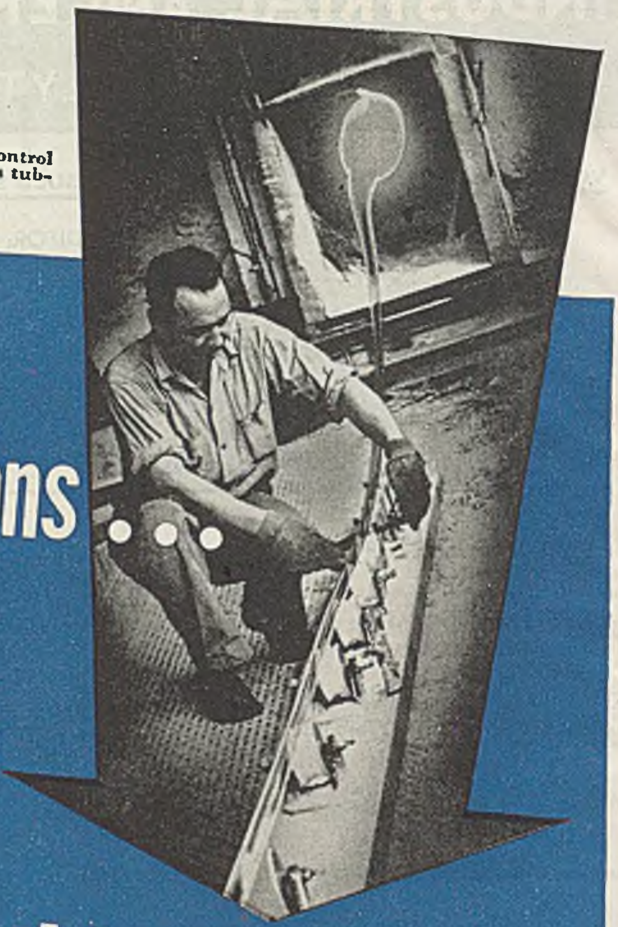
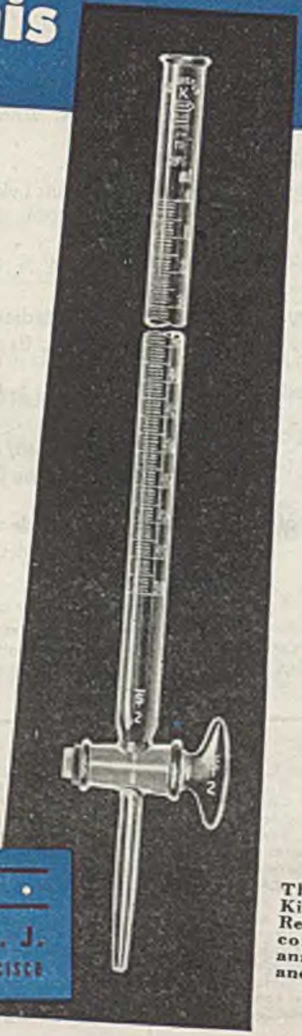


Gauging diameter, a control measure in drawing glass tubing by machine.



The final product — a Kimble Blue Line ⟨EXAX⟩ Retested Burette, sturdily constructed and fully annealed, highly accurate and serviceable.

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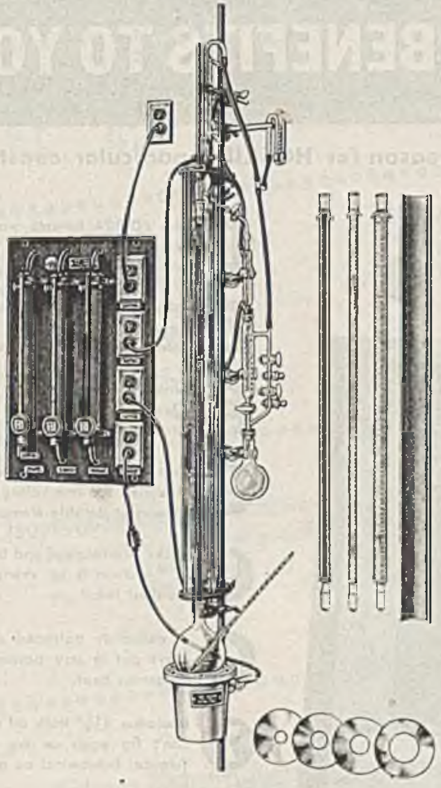
An efficient and versatile laboratory fractionation column assembly with a new method of adiabatic temperature control for complete fractionation of many types of organic liquid mixtures either at atmospheric pressure or under vacuum.



Covered by United States patent No. 2,387,479.

FEATURES:

1. Fractionation efficiency up to 50 theoretical plates.
2. Fractionation charges from 2 cc. to 5000 cc., inclusive.
3. Temperature range from room temperature to 400°C. (752°F.).
4. New precision device for adiabatic temperature control.
5. Atmospheric or vacuum fractionations.
6. Three interchangeable fractionating columns.
7. Improved spiral packing for small column.
8. Rapid fractionation with complete visability.
9. Easily operated with a minimum of experience.
10. Special machined supports for assembling apparatus.
11. Precision control panel for operating the column's "Staggered Dual Heating Unit" and still pot.
12. Special aluminum alloy pot heater with low temperature lag.
13. All metal parts non-corrosive to normal laboratory atmosphere.
14. Rapidly assembled or dismantled.

For additional experimental results, methods of operation, and details, see article, "Efficient and Versatile Laboratory Fractionation Column Assembly," by F. Todd, *Ind. Eng. Chem., Anal. Ed., Vol. 17, page 175, 1945.*

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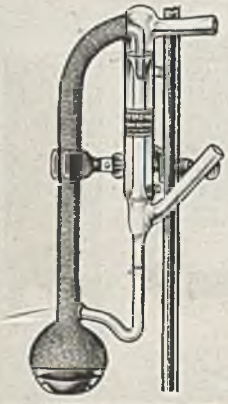

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The TODD HYDRO-VAC PUMP is designed to eliminate serious disadvantages inherent in the ordinary mechanical vacuum pump, such as is generally used by chemical laboratories for the evacuation of distilling apparatus. Since this highly efficient mercury diffusion pump operates on the diffusion principle, it is not damaged by the presence of non-condensable vapors, water, or other corrosive vapors which are frequently evolved during distillation processes. In addition, this pump is a much less expensive piece of apparatus, is more portable, and occupies less table space than a mechanical pump.

OPERATIONAL DATA:

Ultimate vacuum of 0.00001 mm. (0.01 micron).
(with water aspirator forepump)
Ultimate vacuum of 0.000002 mm. (0.002 micron) or better.
(with mechanical forepump)
Calibrated for maximum vacuum.
Maintains 100% of original efficiency on prolonged use.
Not damaged by moisture, non-condensable or corrosive vapors.
Very efficient due to high vapor velocity jet construction.
Rapid evacuation of apparatuses.
Automatic and silent operation.
Requires no maintenance.
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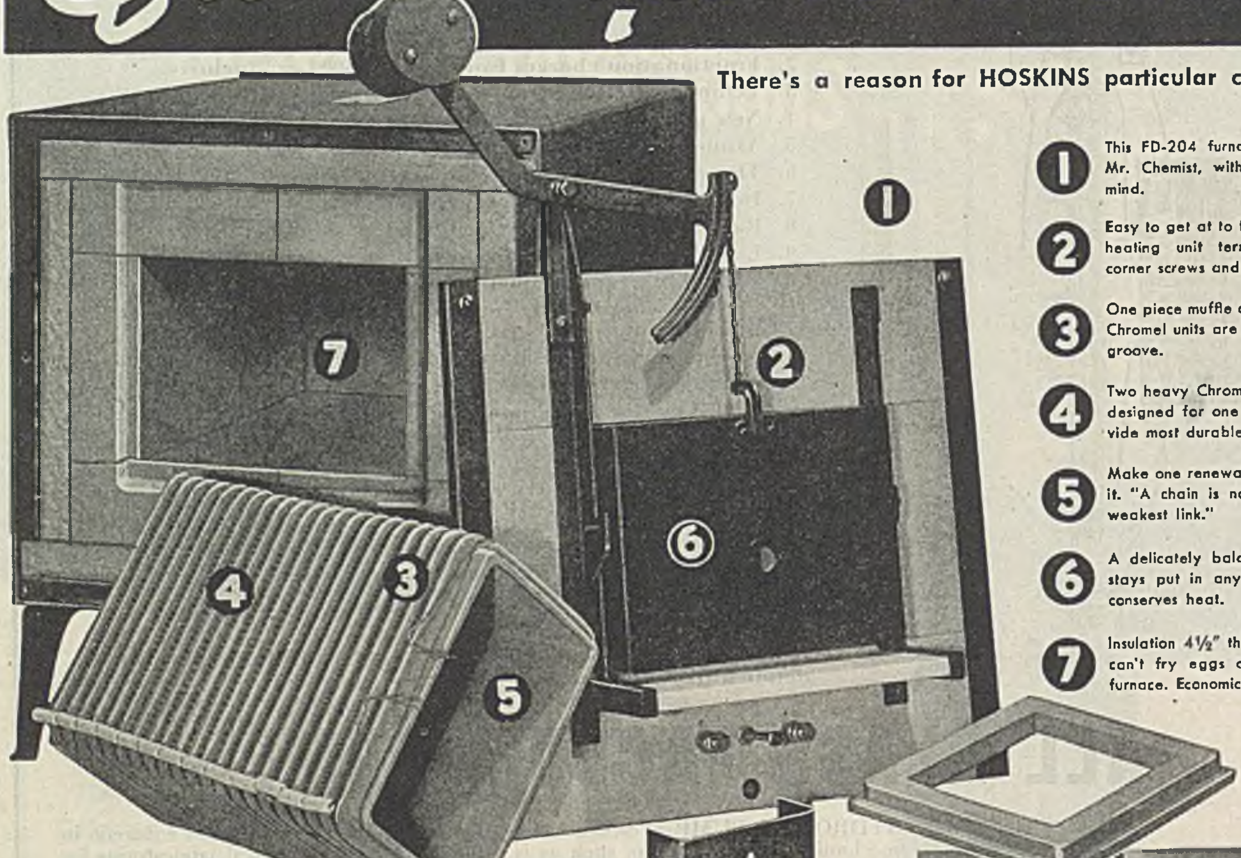


① This FD-204 furnace was designed, Mr. Chemist, with your interests in mind.

② Easy to get at to fix. Loosen Chromel heating unit terminals, remove 4 corner screws and front heat lifts off.

③ One piece muffle around which coiled Chromel units are easily wrapped in groove.

④ Two heavy Chromel coils in parallel, designed for one voltage only, provide most durable element.

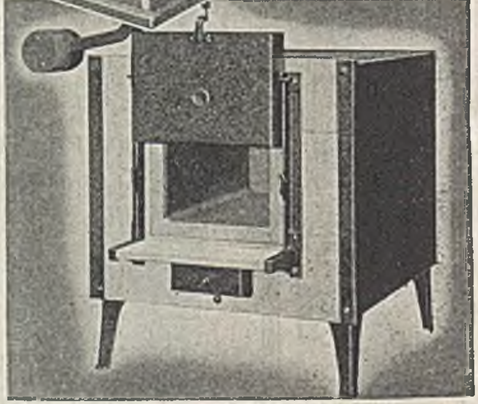
⑤ Make one renewal and be done with it. "A chain is no stronger than its weakest link."

⑥ A delicately balanced sliding door, stays put in any position and thus conserves heat.

⑦ Insulation 4½" thick all around. You can't fry eggs on the top of this furnace. Economical on power.

● Hoskins Laboratory Furnaces are designed around no one feature but with all factors in proper balance to make them of most value to you. These benefits are: durable Chromel elements . . . hard to wear out but easy to renew; a relatively cool furnace case for comfort and economy; a furnace that delivers the goods month in and month out to your complete satisfaction. Buy from your dealer's stock . . . Hoskins Manufacturing Company, Detroit, Mich.

We have a handy little gadget, called a Heating Unit Calculator, that tells how to make coiled Chromel units of 275 to 1,000 watts. Glad to give you one.



This shows the FD-204 assembled. Heating chamber, 7⅜" x 5¼" x 14".

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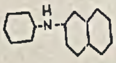
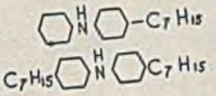


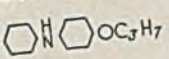
Phenyl B Naphthyl Amine

Distilled—Available in commercial quantities
M. P. 107°
Purity 99.5%
Commercial—Available in commercial quantities
M. P. 106°
Purity 98.0%



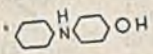
Mixed Mono-and Diheptyl Diphenyl Amines

Available in commercial quantities
Distillation range—145-245 (3.0 mm)
Purity 98%



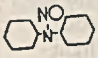
Isopropoxy Diphenyl Amine

Available in commercial quantities
M. P. 78°
Purity 92% min.



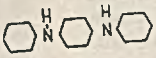
p Hydroxy Diphenyl Amine

Available in commercial quantities
M. P. 15°
Purity 92%



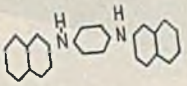
N-Nitroso Diphenyl Amine

Available in commercial quantities
M. P. 62°
Purity 97%



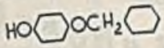
Diphenyl p Phenylene Diamine

Available in commercial quantities
M. P. 144°
Purity 92%



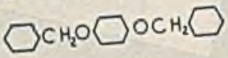
Di B Naphthyl p Phenylene Diamine

Available in commercial quantities
M. P. 230° C
Purity 98%



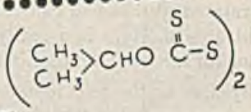
Monobenzyl Ether of Hydroquinone

Available in commercial quantities
M. P. 113°
Purity 90%



Dibenzyl Ether of Hydroquinone

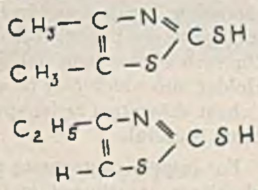
Available in Pilot Plant quantities
M. P. 119°
Purity 85%



$\left(\begin{matrix}CH_3\\CH_3\end{matrix}>CHO\overset{S}{\overset{\|}{C}}-S\right)_2$

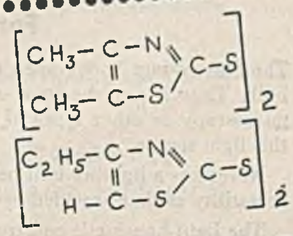
Di Isopropyl Dixanthogen

Available in commercial quantities
M. P. 52°
Purity 98%



Mixed Ethyl and Dimethyl, Mercaptothiazoles

Available in commercial quantities
M. P. 136-153°
Purity Approximately 85% dimethyl and 15% ethyl mercaptothiazoles



Mixed Aliphatic Thiazyl Disulfides

Available in commercial quantities
Liquid

For additional information please write B. F. Goodrich Chemical Company, Department CA-9, Rose Building, Cleveland 15, Ohio.

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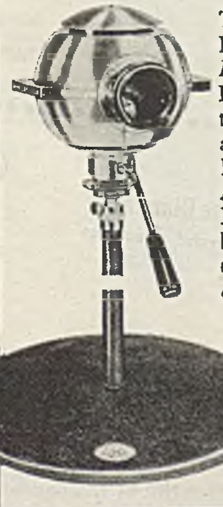
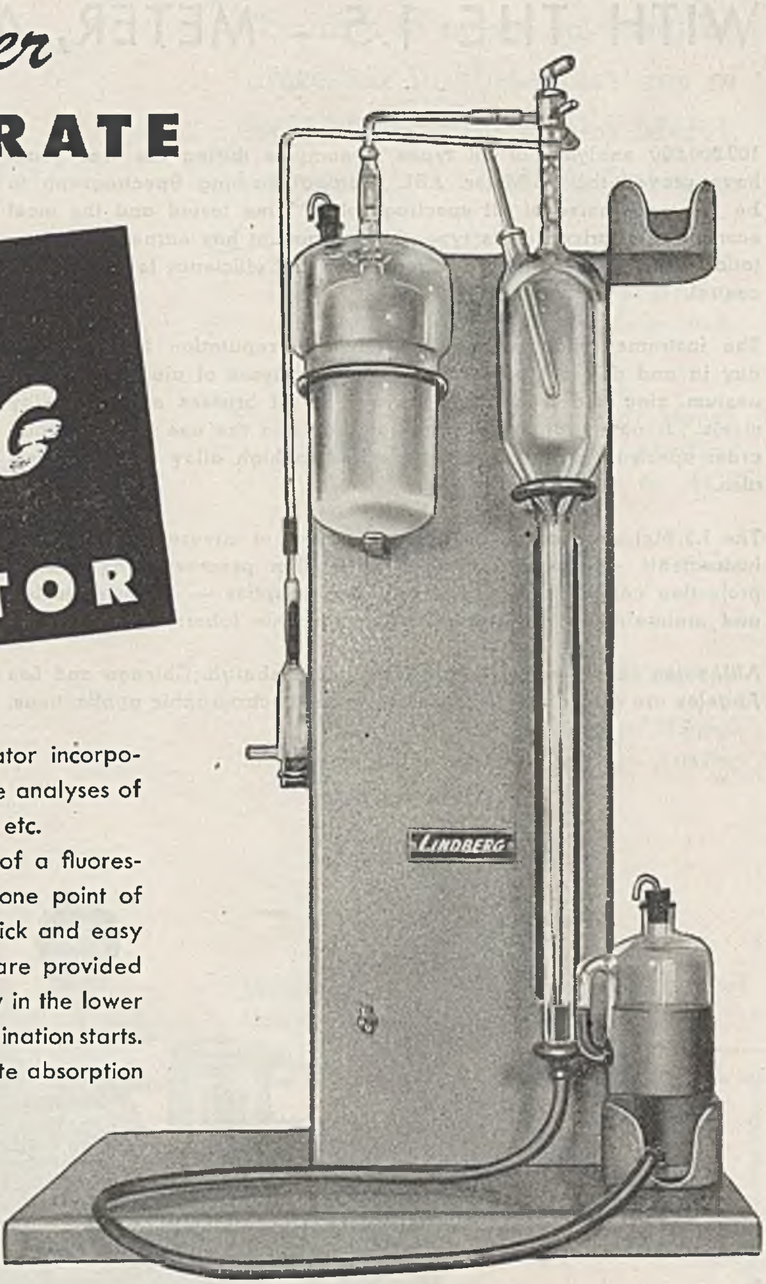


It's Much Easier TO BE ACCURATE WITH THE

New LINDBERG CARBON DETERMINATOR

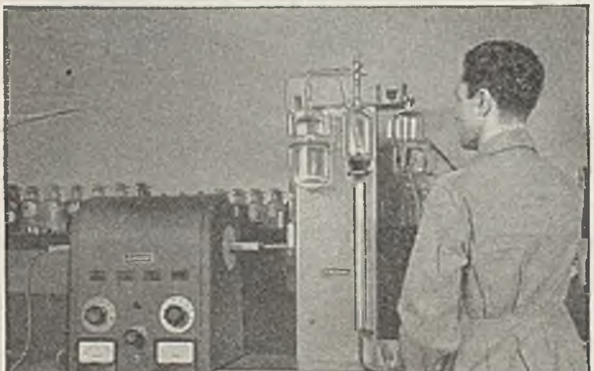


The new Lindberg Volumetric Type Carbon Determinator incorporates features which facilitate faster and more accurate analyses of carbon in iron, steel, heat-resisting steel, stainless steel, etc.

The precisely graduated burette, mounted in front of a fluorescent light for rapid readings, offers an accuracy of one point of carbon . . . or better. The leveling bottle is free for quick and easy leveling. Cups at lowermost and uppermost positions are provided to hold bottle. A conveniently located micrometer screw in the lower cup allows zero adjustment of the meniscus before determination starts.

The contact type absorption chamber permits complete absorption in two passes . . . for many alloys one pass is sufficient. Glass tubing in the chamber assures quick, thorough gas dispersion. Burette is water jacketed and graduated for 1-gram and ¼-gram samples, making the unit adaptable for full range use.

The sturdy stand is attractively finished in glossy grey baked enamel. All glassware is Pyrex to minimize breakage. Panel mounting eliminates the need for clumsy clamps.



Although designed for use with Lindberg Combustion Tube Furnaces, this new Carbon Determinator is easily and quickly adapted for operation with any standard high temperature combustion tube furnace.

See your Laboratory Equipment Dealer today for additional details and prices.

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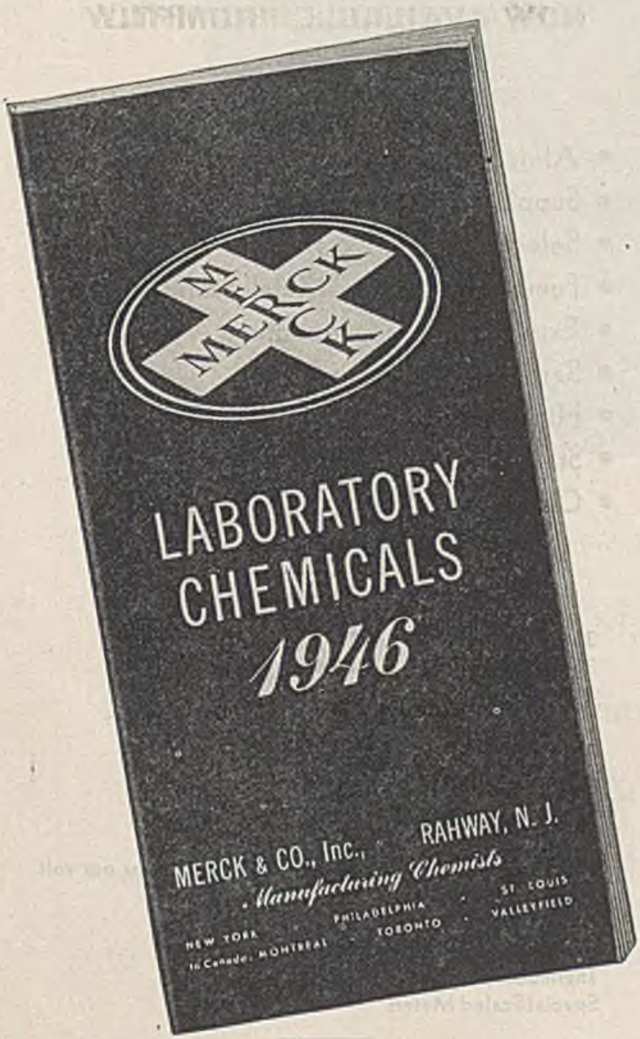
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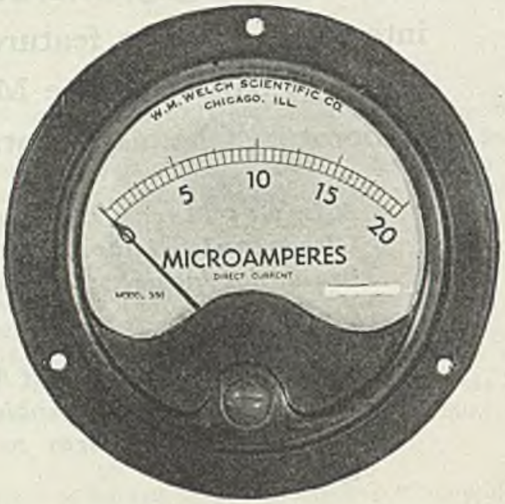
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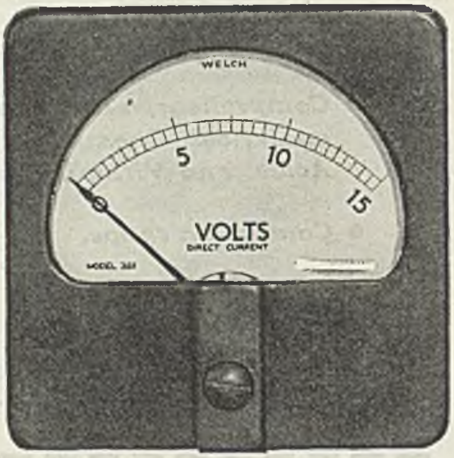
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DIRECT CURRENT
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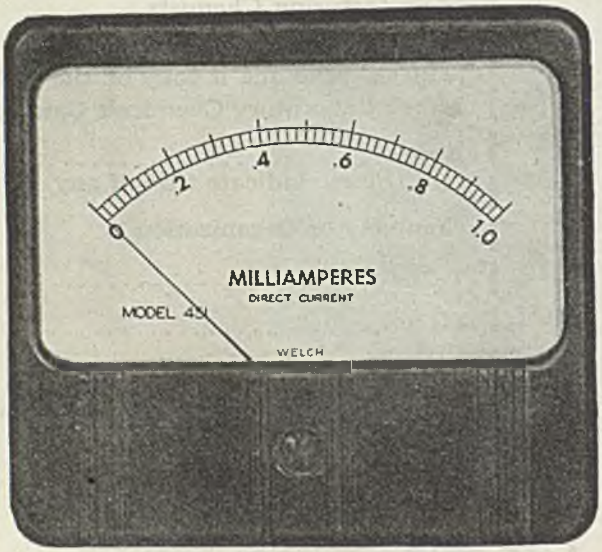
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DIRECT CURRENT
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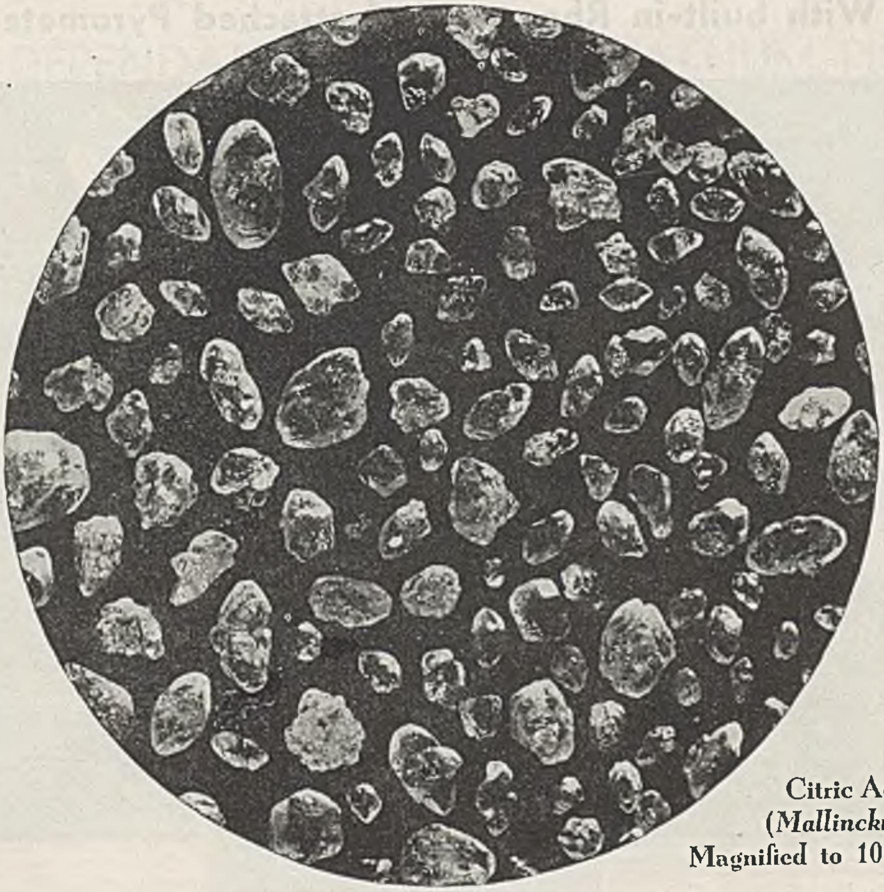
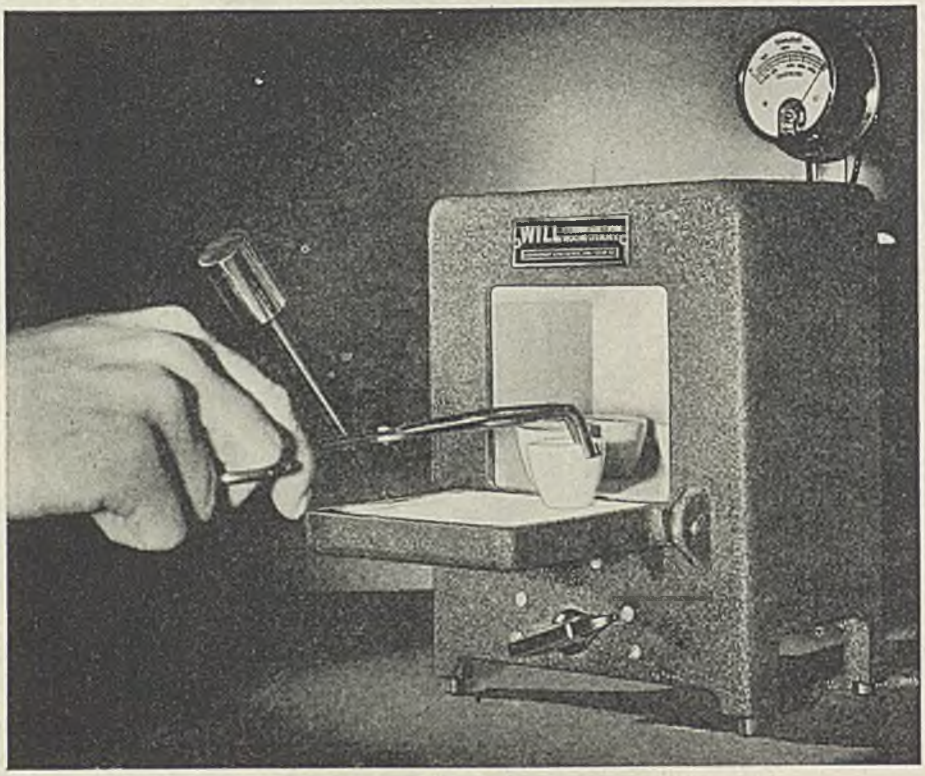


Citric Acid
(*Mallinckrodt*)
Magnified to 10 Diameters

SMALL LABORATORY MUFFLE FURNACE

With built-in Rheostat and attached Pyrometer



8715

SPECIFICATIONS

Dimensions—9¼″ wide, 10½″ deep, 13½″ high.
Muffle Size—4″ x 3¾″ x 3¾″.
Temperature—1850°F. (1000°C.) intermittent; 1500°F. (850°C.) continuous.
Rheostat—"Low," "Medium," "High," and "Booster" Buttons. Snap switch on cord.
Door—Counterpoised, providing 4½″ square platform when opened.
Pyrometer—2¼″ scale, in both Centigrade and Fahrenheit.

In many laboratories the number of ashings and ignitions is too small to justify the purchase of a standard muffle furnace. To such laboratories we recommend this small electric Muffle Furnace.

The muffle has a capacity of 56.25 cubic inches and is exceptionally long-lived. There are no exposed heating elements and no porcelain lining to crack and break. New muffles cost $8.50 and are interchangeable in one minute's time. The cabinet is a one-piece aluminum casting wire brush finished. The rheostat is a dependable heavy-duty winding on porcelain cores and the pyrometer is sensitive and accurate.

The rheostat has four positions, low, medium, high, and "booster." These positions are set at the factory for 500°, 1000°, 1500° and 1900°F. The settings are adjustable for intermediate temperatures. When the switch is set on the "booster" button the current is not flowing through the rheostat but is entering directly into the muffle and the temperature can be made to rise very rapidly. At 1500 Degrees Fahrenheit the Furnace will stand fairly continuous use. On higher heats it is well to hold such temperatures for as short a time as possible.

8715—MUFFLE FURNACE. Supplied complete with Rheostat and Pyrometer; for 110 volts A. C. or D. C.................................... 50.00

8715A—MUFFLE FURNACE. Similar to No. 8715, with Rheostat but without Pyrometer; for 110 volts A. C. or D. C............................ 33.50

8715B—MUFFLE FURNACE. Similar to No. 8715 but without Rheostat or Pyrometer; for 110 volts A. C. or D. C............................ 25.00

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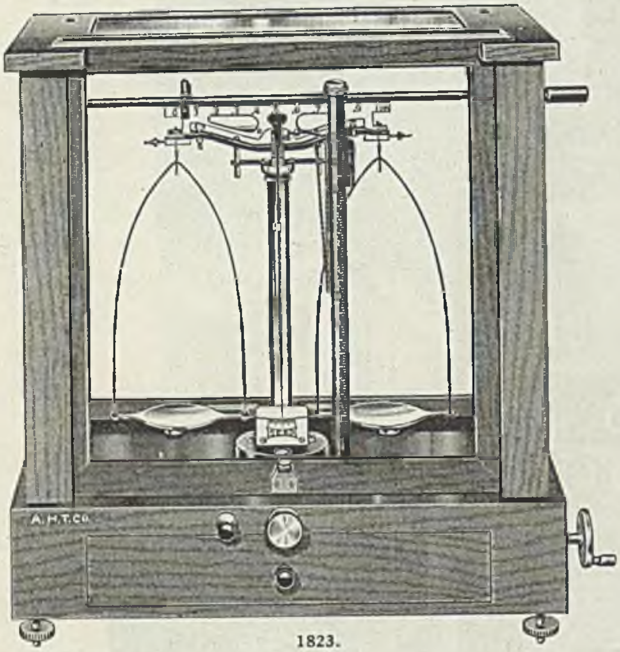
ANALYTICAL BALANCES

AVAILABLE FOR IMMEDIATE SHIPMENT FROM OUR STOCK



1823.

ANALYTICAL BALANCE, CHAIN WEIGHING, "SeKo" No. 356. With notched beam which eliminates the use of all small weights from 0.1 milligram to 1.1 grams. The beam has a channel running its entire length for accurate seating of a rider with flanged center. The combination of channeled, notched beam, flanged rider and cradle-like rider carrier makes rider manipulation easy and positive. The pointer has a blade-like end which aids in overcoming parallax by an apparent thickening of the end when the pointer and the scale are not properly aligned.

Sensitivity — 1/10th mg with full load.
Capacity — 200 grams in each pan.
Case — Of polished mahogany. Overall dimensions 16½ inches long × 18½ inches high × 9½ inches deep.
Beam — Of hardened aluminum, 6½ inches long. Graduated to 1 gram in 0.1 gram notched divisions.
Chain Weighing Device — Replaces fractional weights from 0.1 mg to 100 mg. Chain hangs at one end from an arm on the beam and at the other end from a hook on a movable vernier attached to a graduated column and is manipulated by thumb wheel at right.
Knife Edges and Planes — Of polished agate throughout.
Release and Arrest — The beam has a rigid, three point beam arrest with fallaway action controlled by an eccentric shaft.
Pans — Of aluminum, 2½ inches diameter.
Arches — Of nickel silver, inside dimensions 4⅛ inches wide × 8 inches high.

1823. Analytical Balance, Chain Weighing, "SeKo" No. 356, as above described, without weights but with one 0.5 gram rider..........181.25

ANALYTICAL BALANCE, CHAIN WEIGHING, "SeKo." With graduated notched beam and generally similar to 1823 but of higher sensitivity and with improved beam arrest, plane lateral bearings, and a black plate glass base inside the case.

Sensitivity — 1/20 mg with full load.

Capacity — 200 grams in each pan.

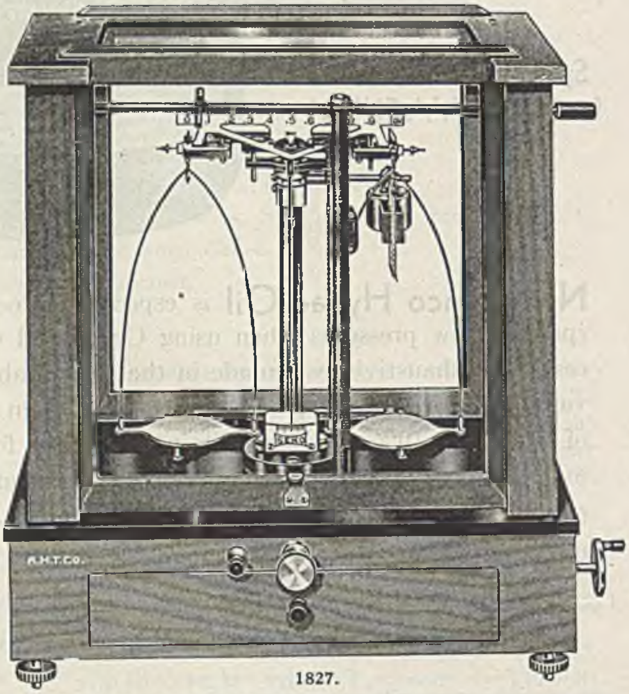
Magnetic Damping Device — Consisting of an aluminum vane suspended by two fine chains from extension arms on the especially designed right stirrup, and a permanent magnet attached at the factory to the central pillar by means of a bracket. The vane moves between the poles of the magnet, thereby setting up eddy currents which check the motion and bring the pointer to rest almost immediately. The damping force can be varied or eliminated completely if desired.

1825. Analytical Balance, Chain Weighing, "SeKo" No. 468, as above described, with one 0.5 gram rider but without magnetic damping device or weights....................237.50

1827. Ditto, "SeKo" No. 472, identical with 1825 but with magnetic damping device.......256.25

10%	*discount in lots of 3*	*singly or 1823, 1825 and 1827, assorted*
12½%	*" " " " 6*	
15%	*" " " " 12 or more*	

More detailed information regarding above Balances sent upon request.



1827.

ARTHUR H. THOMAS COMPANY

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A general method of color grading, based on the I.C.I. system, is described. This method is designed for products in which the colors of all samples of the given product follow a known relationship in color space; only a single number is needed to specify the color of a sample. An example is given of the setting up of a color-grading method for liquid terpene hydrocarbons based on the general principles discussed in the paper. An empirical expression for the locus of chromaticities of a number of representative samples from plant production was first established. Next, the chromaticities of hypothetical standards were selected such that each tenth-grade represented approximately four just perceptible differences. Thirdly, actual physical standards composed of mixtures of color-stable inorganic salts in aqueous solutions were prepared to match as closely as possible the color characteristics of the selected hypothetical standards. Suggestions are given for the use of these physical standards in connection with a photoelectric photometer for grading unknown samples. The use of similar color scales for cellulose plastics and cotton linters is also cited. It is often possible to grade products on the basis of existing color scales. An example is given of the application of the well-known U. S. rosin standards and Gardner standards to the grading of Thanite, a liquid insecticide ingredient.

WHENEVER industry has been confronted with the necessity of providing color specifications of a product, one of two courses has usually been followed: (*a*) an attempt has been made to use an existing color system, or (*b*) a new one has been invented. As a result of (*a*), many materials are now being color-graded on the basis of standards which have color characteristics only approximating those of samples of the corresponding grades. As a result of (*b*), a multiplicity of color-grading systems bearing little or no relationship to one another has come into more or less general use (*4*). Such procedures have some justification from the standpoint of expediency, but they are very apt to increase the confusion which surrounds the already complex subject of color.

Most product color specifications are based on a single-letter or single-number system—e.g., U. S. official rosin standards, Gardner standards, etc. Only those products having color characteristics similar to those of the standards of a given system may be graded by that system. Other specifications are based on a three-number (trichromatic) system—e.g., the Lovibond and Munsell systems. At present, the three-number system most widely recognized is the I.C.I. tristimulus system of color specification (*7, 13*). Practically all classes of products may be graded on the basis of a trichromatic system. However, a three-number specification is inconvenient to obtain and hard to interpret.

It would appear to be a hopeless task to set up a universal single-number color-grading system applicable to all types of colored materials. However, the first step toward alleviation of the confusion attending the large number of existing single-number color scales might very well consist of reducing these scales to a common denominator—i.e., converting them to the universal I.C.I. tristimulus system. A good start has already been made in this direction (*1, 3, 5, 6, 10, 12*). Furthermore, whenever it is necessary to set up a new scale for a given product or class of products, this scale too should be given in terms of I.C.I. data. The method by means of which such a scale can be set up is the subject of this paper. It is presumed in what follows that the reader is familiar with the terminology of the I.C.I. system (*7, 13*).

In order to establish such color scales, one must have access to a means for determining the I.C.I. specifications of the materials under consideration. These can be conveniently calculated from spectral transmittance or reflectance curves.

For the purpose of this discussion, the authors wish to draw a distinction between "color specification" and "color grading". By the term "color specification" is meant the designation of a point in the color solid which corresponds to a plot of the x- and y-trichromatic coefficients and the luminous transmittance or reflectance (Y-tristimulus value) of the sample in question. By "color grading" is meant the designation of the position of a point relative to a scale of grade numbers or letters on a pre-established two-dimensional chromaticity curve or a three-dimensional color (chromaticity-Y) curve. Such a curve is the locus of points representing the colors of a large number of representative samples of the given product for which the grading method has been devised. The following discussion will make this distinction more clear.

Suppose, for example, that we wish to determine the color of a given sample of a certain product. One method might consist of determining three numbers—e.g., I.C.I. X-, Y-, and Z-tristimulus values, or x-, and y-trichromatic coefficients and Y—with respect to some illuminant. Any one set of three such numbers will completely specify the appearance of a uniform sample for any one particular illuminating and viewing condition. However, it is difficult for the average person to visualize a color from such a three-number specification. A specification consisting of but a single number would be much more practical. Such a single-number specification could be used if the colors of all samples of a given product followed a known relationship in color space.

For example, let us assume that the colors of samples of the product we are investigating obey a relationship such as that represented by the space curve AB of Figure 1. Let us further assume that we have arbitrarily set up a sequence of numerical grades (from 0 to 8 on Figure 1) based on equal increments of x-trichromatic coefficient (Δx). Then, a determination of any one of the three coordinates of a sample color determines uniquely a point on the space curve. The position of this point, as read off the numerical grading scale, is taken as the single-number specification which we seek.

Such a procedure of determining a single-number color specification is hereafter referred to as color grading, as opposed to three-number color specification. Color grading, as defined above, can be accomplished only when the plotted product colors lie on, or reasonably close to, an average curve such as AB. If the product colors are widely scattered—e.g., if some samples are of various shades of blue, others green, and still others red—samples cannot ordinarily be graded on a single scale; it is usually necessary to determine a three-number specification for each sample.

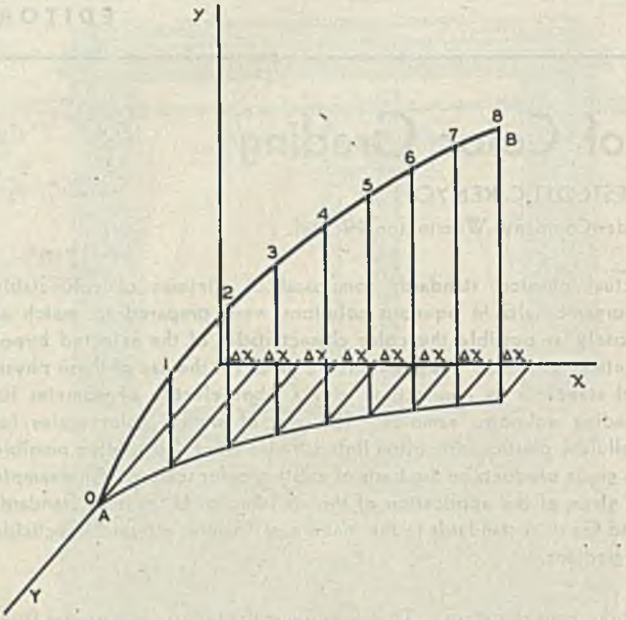

Figure 1. Three-Dimensional Product Locus

It has been found by repeated experiments in this laboratory that the eye has a tendency to neglect reasonably large differences in luminous transmittance during the visual color grading of transparent materials. This is fortunate, because, in some cases, as in the grading of gum rosin, rather large variations in this property occur in samples having the same chromaticities. While some tendency to downgrade samples of low Y value has been observed, this tendency is not so marked as one might expect. In the color grading of refined products, such as those dealt with in this paper, only small differences in Y among samples of the same chromaticity exist. Hence, methods of grading have been developed with the aid of a simple two-dimensional chromaticity diagram (x versus y) instead of a three-dimensional plot such as that of Figure 1. Frequently, however, variations in luminous transmittance or reflectance among samples of the same chromaticity are too large to neglect. In such cases, a notation giving information regarding Y should accompany each single-number grading.

TYPICAL COLOR SCALE

In order to illustrate the foregoing principles, a description will be given of the development of a method of grading a series of liquid terpene hydrocarbons, all of which had been refined by fractional distillation, and samples of which varied in color from practically water-white to dark amber. The first step in the procedure consisted of obtaining a large number of samples from regular plant production. Spectral transmission curves were obtained on these samples, and from the curves the x- and y-trichromatic coefficients and luminous transmittances with respect to Illuminant C were calculated. Representative curves from the set are shown in Figure 2, and trichromatic coefficients and luminous transmittances are given in Table I for the entire set. Figure 3 is a plot of x versus y from the data of Table I. Although there is some spread of the points, they follow a definite locus on the chromaticity diagram.

Table I. x- and y-Trichromatic Coefficients and Luminous Transmittances of Samples of Liquid Terpene Hydrocarbons Refined by Fractional Distillation

(50-mm. cell thickness)

Sample No.	x	y	Luminous Transmittance, Y, %
Illuminant C	0.3101	0.3163	92
1	0.3110	0.3190	90.40
2	0.3111	0.3184	90.67
3	0.3112	0.3197	90.74
4	0.3120	0.3201	90.22
5	0.3128	0.3211	89.21
6	0.3131	0.3222	90.74
7	0.3134	0.3229	90.29
8	0.3135	0.3221	89.37
9	0.3146	0.3246	89.72
10	0.3148	0.3254	90.72
11	0.3155	0.3275	90.34
12	0.3156	0.3268	90.09
13	0.3174	0.3296	89.19
14	0.3185	0.3305	88.04
15	0.3185	0.3310	88.90
16	0.3198	0.3321	88.06
17	0.3206	0.3342	89.67
18	0.3215	0.3359	87.75
19	0.3226	0.3389	89.56
20	0.3239	0.3396	89.07
21	0.3253	0.3400	86.26
22	0.3287	0.3482	88.73
23	0.3299	0.3505	87.90
24	0.3415	0.3678	86.53
25	0.3416	0.3694	86.40
26	0.3487	0.3801	85.50
27	0.3876	0.4190	72.99
28	0.3948	0.4265	74.79
29	0.4487	0.4722	64.09

In order to aid in establishing the position of this locus, it is often helpful, although not always necessary, to rectify the plot—i.e., to select coordinates which will yield a straight line. This has been done in Figure 4 which was plotted from the data of Table II. After coordinates have been selected such that the data plot out in a close approximation to a straight line, the usual methods of establishing the equation of the curve may be applied. In the present case, the equation was found to be

$$y = 0.3701 \log 100\,(x - 0.2236) - 0.0267 \qquad (1)$$

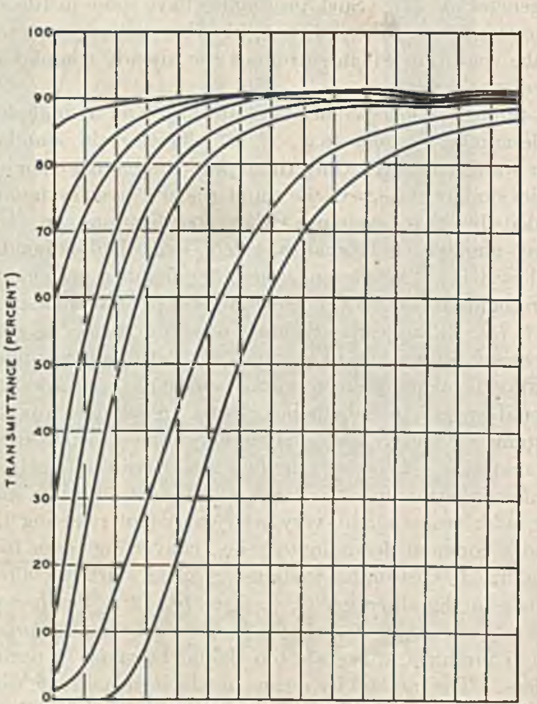

Figure 2. Spectral Transmittance Curves of Typical Terpene Hydrocarbons

Cell thickness, 50 mm.

by the method of averages. General methods of calculating empirical equations may be found in several references (*2*, *11*).

If enough samples are measured to ensure a representative cross section of plant production, and if the manufacturing process is held constant, this equation may be considered as the defining equation of the locus of points representing the colors of samples of the product. However, if at any time the manufacturing process is modified in such a way as to change the character of the color of the samples, a new set of colorimetric data should be obtained, and a new equation calculated.

Once the basic defining equation is established, the next step consists of setting up standards in terms of which routine grading results may be expressed. The spacing of these standards is an entirely arbitrary procedure and depends on the accuracy with which it is desired to grade. Generally, there is no point in establishing fractional grade differences which are less than minimum perceptible differences. Whether or not they are less can be determined by replotting the locus on a uniform chromaticity diagram such as that proposed by Judd (*8*, *9*). Often, however, visual examination of a number of specimens which have small perceptible color differences, and whose chromaticities are known, will be sufficient for the selection of a practical unit of fractional grading.

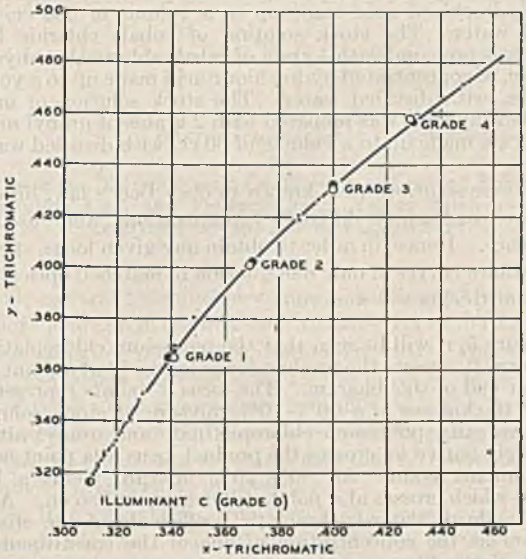

Figure 3. Chromaticities of Terpene Hydrocarbons

- • Terpene hydrocarbons
- ● Arbitrarily chosen hypothetical standards
- ○ Actual working standards

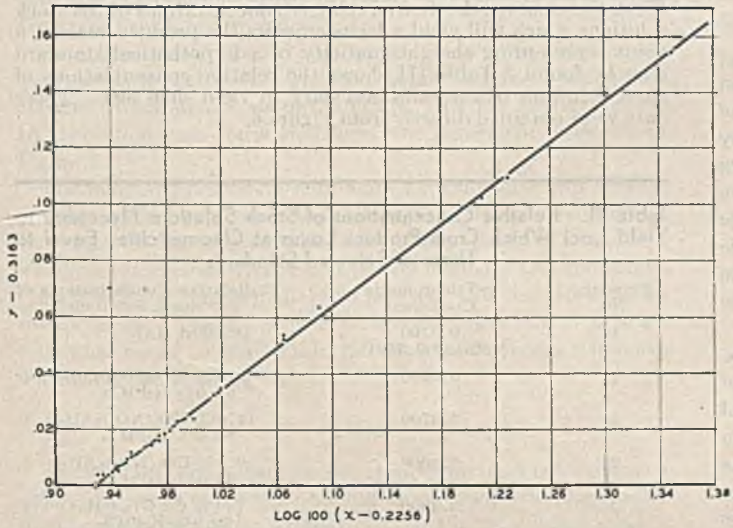

Figure 4. Rectified Plot of Chromaticities of Terpene Hydrocarbons

Table II. Data for Rectified Plot of Chromaticities of Terpene Hydrocarbons

Sample No.	x	$x - 0.2256$	log 100 × $(x - 0.2256)$	y	$y - 0.3163$
Illuminant C	0.3101	0.0845	0.9269	0.3163	0
1	0.3110	0.0854	0.9315	0.3190	0.0027
2	0.3111	0.0855	0.9320	0.3184	0.0021
3	0.3112	0.0856	0.9325	0.3197	0.0034
4	0.3120	0.0864	0.9365	0.3201	0.0038
5	0.3128	0.0872	0.9405	0.3211	0.0048
6	0.3131	0.0875	0.9420	0.3222	0.0059
7	0.3134	0.0878	0.9435	0.3229	0.0066
8	0.3135	0.0879	0.9440	0.3221	0.0058
9	0.3146	0.0890	0.9494	0.3246	0.0083
10	0.3148	0.0892	0.9504	0.3254	0.0091
11	0.3155	0.0899	0.9538	0.3275	0.0112
12	0.3156	0.0900	0.9542	0.3268	0.0105
13	0.3174	0.0918	0.9628	0.3296	0.0133
14	0.3185	0.0929	0.9680	0.3305	0.0142
15	0.3185	0.0929	0.9680	0.3310	0.0147
16	0.3198	0.0942	0.9740	0.3321	0.0158
17	0.3206	0.0950	0.9777	0.3342	0.0179
18	0.3215	0.0959	0.9818	0.3359	0.0196
19	0.3226	0.0970	0.9868	0.3389	0.0226
20	0.3239	0.0983	0.9926	0.3396	0.0233
21	0.3253	0.0997	0.9987	0.3400	0.0237
22	0.3287	0.1031	1.0133	0.3482	0.0319
23	0.3299	0.1043	1.0183	0.3505	0.0342
24	0.3415	0.1159	1.0641	0.3678	0.0515
25	0.3416	0.1160	1.0645	0.3694	0.0531
26	0.3487	0.1231	1.0903	0.3801	0.0638
27	0.3876	0.1620	1.2095	0.4190	0.1027
28	0.3948	0.1692	1.2284	0.4265	0.1102
29	0.4487	0.2231	1.3485	0.4722	0.1559

For example, a number of the samples represented on the chromaticity diagram of Figure 3 were examined visually, and it was decided that two samples having a difference in x-trichromatic coefficients of approximately 0.0030 could easily be distinguished under ordinary north sky illumination. This difference was called one-tenth grade. A Δx of 0.0300, therefore, represents one full grade. Actually it was found, by reference to the Judd uniform chromaticity diagram, that one-tenth grade represents, on the average, approximately four just perceptible differences. However, for our purpose, the grading unit was considered sufficiently small.

The grades increase in numerical value from 0, which represents a water-white sample—i.e., one having a chromaticity equal to that of Illuminant C—to 4, which represents a standard about as dark as any sample encountered in the representative lot. In Figure 3 are shown the positions of these arbitrarily chosen standards on the product locus.

The spacing of standards may be done on the basis of one of the other colorimetric quantities instead of x. Thus, certain materials might better be graded on the basis of equal increments of y, still others on the basis of equal increments of z, excitation purity, or dominant wave length. An even better method of spacing would be based on equal distances on one of the uniform chromaticity diagrams cited above, since equal spacings on these diagrams more closely approximate corresponding estimated visual differences than equal spacings on the I.C.I. diagram.

Through the medium of such data interlaboratory comparisons of color scales could readily be made. Color scales "tailor-made" to fit the products for which they were intended could be set up without fear that the resulting large number of scales would introduce unwarranted complexity. Correspondence between laboratories involving color scale comparisons would necessarily include tables of x, y, and Y values of numbered standards on the scales under discussion. Alternatively, one might use equations such as Equation 1 or plots such as that in Figure 3 for such comparisons.

STANDARDS

The next step in establishing the grading method consists of devising actual physical standards, the chromaticities of which will match as nearly as possible the chromaticities of the arbitrarily chosen hypothetical standards. Physical standards may consist of: (1) specimens of the material itself which are chosen to match in color the hypothetical standards; (2) standards consisting of combinations of colored glasses; or (3) standards composed of mixtures of solutions of organic or inorganic compounds. Any set of standards chosen should have the following characteristics: (1) The spectral transmittance curves should be similar in character to those of the material being graded. (2) The standards should have reasonably permanent color characteristics over a long period of time. (3) Their colors should not be appreciably altered by variations in temperature over the range from 15° to 30° C. (4) They should be easy to prepare.

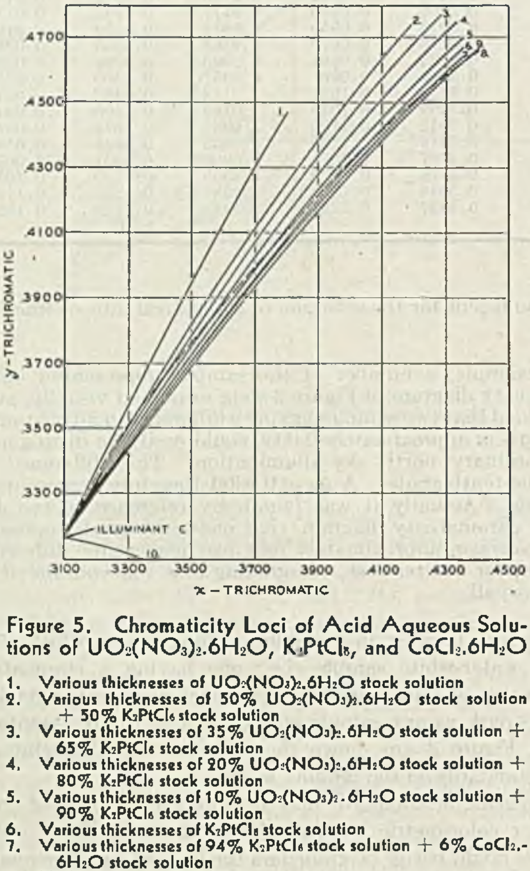

Figure 5. Chromaticity Loci of Acid Aqueous Solutions of $UO_2(NO_3)_2.6H_2O$, K_2PtCl_6, and $CoCl_2.6H_2O$

1. Various thicknesses of $UO_2(NO_3)_2.6H_2O$ stock solution
2. Various thicknesses of 50% $UO_2(NO_3)_2.6H_2O$ stock solution + 50% K_2PtCl_6 stock solution
3. Various thicknesses of 35% $UO_2(NO_3)_2.6H_2O$ stock solution + 65% K_2PtCl_6 stock solution
4. Various thicknesses of 20% $UO_2(NO_3)_2.6H_2O$ stock solution + 80% K_2PtCl_6 stock solution
5. Various thicknesses of 10% $UO_2(NO_3)_2.6H_2O$ stock solution + 90% K_2PtCl_6 stock solution
6. Various thicknesses of K_2PtCl_6 stock solution
7. Various thicknesses of 94% K_2PtCl_6 stock solution + 6% $CoCl_2.6H_2O$ stock solution
8. Hydrocarbon product locus
9. Various thickness of 92% K_2PtCl_6 stock solution + 8% $CoCl_2.6H_2O$ stock solution
10. Various thicknesses of $CoCl_2.6H_2O$ stock solution

Standards prepared from the material itself usually have most of the desirable characteristics enumerated above, except that of permanence. This characteristic may often be improved by sealing the standards in air-tight glass containers under vacuum or in inert atmospheres, and by storing them in the dark. When using such standards, their spectral transmittances should be checked frequently to determine whether any appreciable change in color with time is taking place. If small changes do occur, the nominal value of each of the standards may be adjusted from time to time to compensate for such changes.

Although glass standards are usually satisfactory, it may be found that because of the limited number of suitable types of glass available, it may be impossible to match the hypothetical standards accurately. Moreover, the calculations involved in determining the relative thicknesses of two or more components necessary to match a given hypothetical standard must be repeated each time it is necessary to replace the standards, unless the glasses for the replacement set are taken from the same melts as used previously. The glass elements must be accurately ground to the calculated thicknesses to avoid error. This means that considerable expense is involved in making up a set.

On the other hand, many liquid standards, especially those made with acid solutions of certain inorganic salts, have excellent color stability and have the great advantage of being easy to prepare. It may be difficult to choose a liquid or combination of liquids having spectral transmittance curves similar to those of the material being color graded. However, in many cases, a sufficiently good approximation may be obtained for practical grading.

In the present example, a series of liquid standards was prepared from acid solutions of the following salts which are known to be color-stable: uranyl nitrate hexahydrate, potassium chloroplatinate, and cobalt chloride hexahydrate. The reason for this choice will be evident from an examination of Figure 5, which shows the loci of points representing the colors of different thicknesses of stock solutions of each of the three salts and of various mixtures of stock solutions of these salts on a chromaticity diagram, together with the product locus of Figure 3.

The stock solution of potassium chloroplatinate was prepared with 1 gram of potassium chloroplatinate plus 50 cc. of concentrated hydrochloric acid made up to a volume of 500 cc. with distilled water. The stock solution of cobalt chloride hexahydrate was prepared with 1 gram of cobalt chloride hexahydrate plus 50 cc. of concentrated hydrochloric acid made up to a volume of 500 cc. with distilled water. The stock solution of uranyl nitrate hexahydrate was prepared with 2 grams of uranyl nitrate hexahydrate made up to a volume of 50 cc. with distilled water.

Since these solutions were known to obey Beer's law, different thicknesses instead of different concentrations were used for convenience. Hence, in order to obtain any given locus, spectral transmittance curves of only one solution in matched optical cells of different thicknesses were run.

In Figure 5, it will be seen that the potassium chloroplatinate locus (curve 6) crosses the product locus (curve 8) at a point near the upper end of the diagram. The locus of points representing different thicknesses of a 90%-10% mixture of stock solutions of the two salts, potassium chloroplatinate and uranyl nitrate, respectively (curve 5), crosses the product locus at a point nearer the illuminant point. An 80%-20% mixture yields a locus (curve 4) which crosses at a point still nearer, and so on. A plot is then made of the x-trichromatic coefficients of the crossing points versus the concentration of one of the constituents, as shown in Figure 6, *a*.

In the case of standards darker than those represented by the crossing point of the potassium chloroplatinate stock solution locus, mixtures of potassium chloroplatinate and cobalt chloride stock solutions were used to give crossing points on the upper part of the product locus. Figure 6, *b*, is a plot of these crossing points versus the concentration of cobalt chloride stock solution. From these curves the desired relative concentrations of the stock solutions which will yield a locus crossing the product locus at a point representing the chromaticity of a hypothetical standard may be found. Table III shows the relative concentrations of stock solutions of the salts necessary to yield such loci. These data were obtained directly from Figure 6.

Table III. Relative Concentrations of Stock Solutions Necessary to Yield Loci Which Cross Product Locus at Chromaticities Equal to Those of Selected Standards

Standard No.	x-Trichromatic Coefficient	Relative Concentrations of Stock Solutions
0	0.3100 (actually 0.3101)	Distilled H_2O
1	0.3400	38.0% $UO_2(NO_3)_2.6H_2O$ + 62.0% K_2PtCl_6
2	0.3700	11.0% $UO_2(NO_3)_2.6H_2O$ + 89.0% K_2PtCl_6
3	0.4000	0.5% $UO_2(NO_3)_2.6H_2O$ + 99.5% K_2PtCl_6
4	0.4300	7.1% $CoCl_2.6H_2O$ + 92.9% K_2PtCl_6

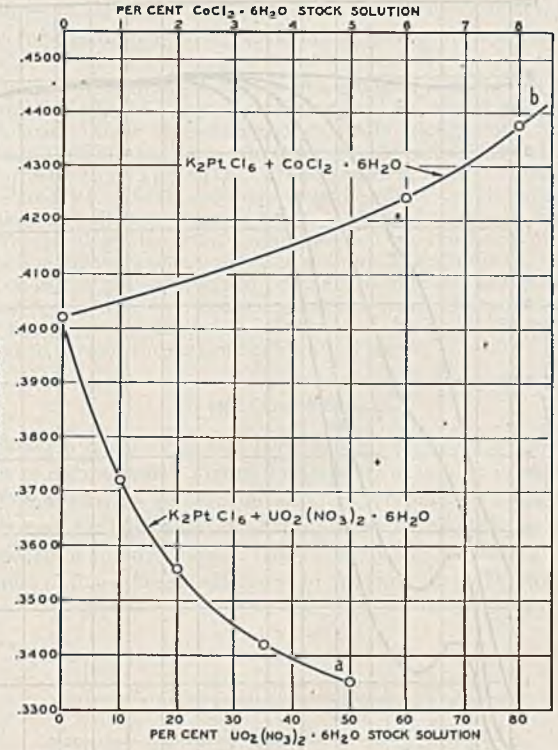

Figure 6. x-Trichromatic Coefficients of Crossing Points of Solution Loci and Product Locus Versus Relative Concentration of One Solution Constituent

Next, spectral transmittance curves of different thicknesses of solutions made up in accordance with Table III were run, and the corresponding chromaticities were computed. The x-trichromatic coefficients corresponding to the different thicknesses of each of these solutions are given in Table IV. The thicknesses, t, corresponding to x-trichromatic coefficients equal to those of the desired hypothetical standards may then be interpolated from the table or from a curve of t versus x.

Since Beer's law holds, solutions of thickness t are equivalent colorimetrically to 5 cm. of solution diluted in the ratio of t parts of original solution to $(5 - t)$ parts of distilled water. Using this relationship, the proper concentrations of the various constituents in 5 cm. of aqueous solution to yield each of the hypothetical standards were determined. These are recorded in Table V. The solutions were then made up in accordance with the compositions listed in Table V, placed in 5-cm. glass absorption cells, and sealed off.

As a final check, spectrophotometric data were obtained on each standard (Table V). The locus connecting these points on a chromaticity diagram should coincide with the product locus. In the actual case considered here, the agreement is shown in Figure 3.

The foregoing procedure represents a considerable expenditure of labor. However, once the standards have been contrived, they may be reproduced with ease at any time. The cells in which the standards were sealed can be made by an experienced glass blower for approximately $1.50 each. In this work, 5-cm. cells were used instead of cells of less thickness, since they are somewhat easier to hold within the required thickness tolerance, which is of the order of ±1%.

FILTERS

The next step in setting up the grading method is to choose a pair of filters to be used on a suitable photoelectric photometer for obtaining quantities proportional to the established grades. Two filters or filter combinations, one of which is selected to yield a photocell response proportional to the X-tristimulus value, and the other of which is selected to yield a photocell response proportional to the sum of the X-, Y-, and Z-tristimulus values, will give, when the ratio of the first to the second is computed, a product proportional to the x-trichromatic coefficient (since $\frac{X}{X + Y + Z} = x$).

However, a pair of filters which would be more desirable from the standpoint of sensitivity and response could be selected from an examination of the spectrophotometric curves of samples of the product. It will be seen from an examination of Figure 2 that from sample to sample, the greatest change takes place in the blue and violet regions of the spectrum, while very little change takes place in the red region. Hence, for maximum sensitivity, one would assume that a ratio of blue to red filter readings would be the most satisfactory. However, most of the commercially available red glasses are of the selenium type. These have high temperature coefficients which make them unreliable for ordinary routine grading purposes. On the other hand, amber (orange) filters can be made up from glasses having negligible temperature coefficients. It will be seen from Figure 2, that while slightly greater changes occur in the orange than in the red region of the spectrum between different samples, the changes are still small compared to those occurring in the blue and violet regions. Amber and violet filters were used with a photoelectric photometer to obtain the calibration curve of Figure 7, in which instrument readings are plotted against the grades of the previously described set of five liquid standards.

Table IV. *x vs.* Thickness for Solutions Made Up in Accordance with Table III

Relative Concentrations of Stock Solutions	Thickness, Cm.	x-Trichromatic Coefficient
38.0% $UO_2(NO_3)_2.6H_2O$ + 62.0% K_2PtCl_6	0	0.3101
	1	0.3435
	1.8	0.3662
	3	0.3941
	5	0.4271
11.0% $UO_2(NO_3)_2.6H_2O$ + 89.0% K_2PtCl_6	0	0.3101
	1	0.3435
	1.8	0.3672
	3	0.3967
	5	0.4349
0.5% $UO_2(NO_3)_2.6H_2O$ + 99.5% K_2PtCl_6	0	0.3101
	1	0.3434
	1.8	0.3673
	3	0.3981
	5	0.4370
7.1% $CoCl_2.6H_2O$ + 92.9% K_2PtCl_6	0	0.3101
	1	0.3414
	1.8	0.3644
	3	0.3943
	5	0.4331

Table V. Calculated Concentrations of Salts in Aqueous Solutions and 5-Cm. Thicknesses to Color Match Hypothetical Standards

Standard No.	x	y	Composition
0[a]	0.3104	0.3182	Distilled H_2O
1	0.3385	0.3646	0.22 gram of K_2PtCl_6 + 2.64 gram of $UO_2(NO_3)_2.6H_2O$ + 10.8 cc. of HCl made up to 1 liter with distilled H_2O
2	0.3629	0.3952	0.67 gram of K_2PtCl_6 + 1.66 gram of $UO_2(NO_3)_2.6H_2O$ + 33.6 cc. of HCl made up to 1 liter with distilled H_2O
3	0.3984	0.4306	1.22 grams of K_2PtCl_6 + 0.12 gram of $UO_2(NO_3)_2.6H_2O$ + 61.1 cc. of HCl made up to 1 liter with distilled H_2O
4	0.4307	0.4589	1.79 grams of K_2PtCl_6 + 0.14 gram of $UO_2(NO_3)_2.6H_2O$ + 96.2 cc. of HCl made up to 1 liter with distilled H_2O

[a] Chromaticity differs from that of Illuminant C because of color of glass cell windows.

Since the grading method was set up on the basis of the I.C.I. system, the use of filters other than those yielding I.C.I. specifications will give rise to grading errors if the samples and standards are not spectrally similar. A method of correcting for such errors is discussed more fully below.

PHOTOELECTRIC PHOTOMETERS

The following basic design features in photoelectric photometers have been found desirable for trouble-free color grading:

An essentially parallel light beam of just sufficient intensity to give adequate sensitivity.

An absorption cell with plane glass windows which should be of reasonable optical quality essentially free from disturbing color in the glass.

A receiver consisting of one or more barrier-layer photocells, the faces of which are illuminated uniformly by the beam of light after it has passed through the sample; (these photocells should preferably be chosen to have high internal dark resistance and low fatigue).

A set of filters, the spectral transmittances of which preferably are so chosen with respect to the spectral sensitivity of the photocell and the spectral distribution of the light source that the photocell response (depending on the filter) is proportional to one of the tristimulus values or to the sum of the three tristimulus values of the sample being measured.

An electrical circuit which offers a low external resistance to the photocells. The circuit preferably should be of the null type—e.g., one in which the desired transmittance readings are obtained from a value of resistance read on a dial or slide wire, or from a calibrated flux-reducing mechanism in the optical path.

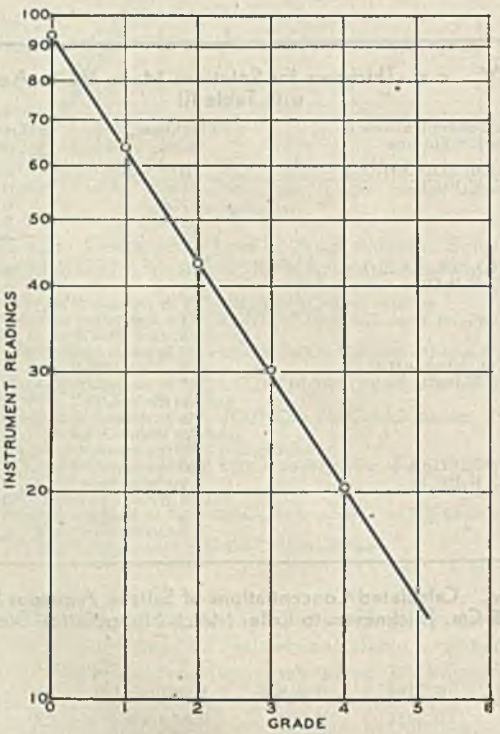

Figure 7. Photometer Calibration Curve

These fundamental characteristics of good design are found in several photometers now available on the market. In the work described in this report, a null-type photometer of the authors' own design was used. This instrument is so constructed that a ratio of one photocell response to another may be read directly from a slide wire.

CALIBRATION

Before unknown samples were graded, a calibration curve was prepared by inserting each of the standards in the light beam in turn, and taking the corresponding readings as described above. These readings were plotted against the actual grades of the standards on a sheet of single-cycle, semilogarithmic paper. It was fortuitous that a straight line resulted, as is shown in Figure 7. This circumstance makes it possible to plot a calibration curve with only two standards. In general, however, such a calibration would be a curve, and it would be necessary to run a complete set of standards each time a calibration was made. With some of the authors' instruments, this is done every few days and takes less than 5 minutes.

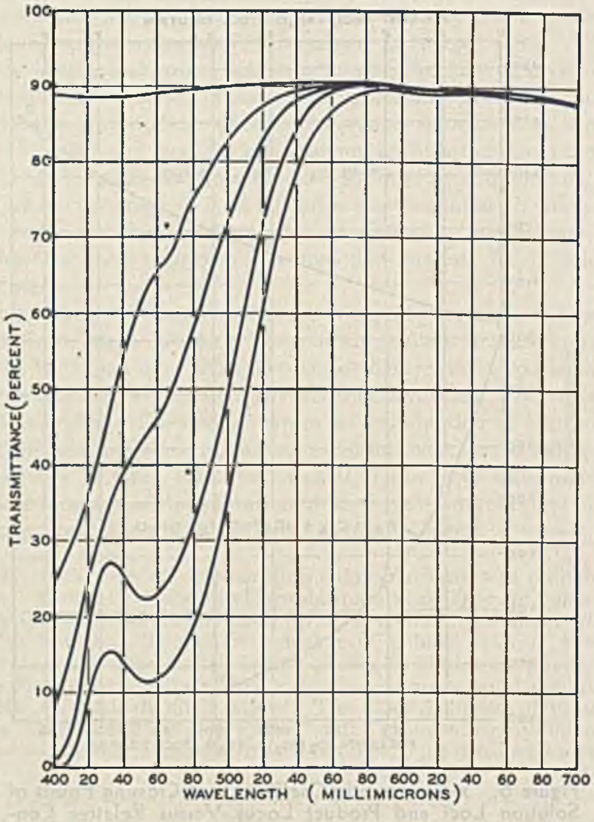

Figure 8. Spectral Transmittance Curves of Working Standards

Slight spectral selectivity of 0 standard due to small amount of color present in glass of cell windows

Samples were graded by pouring them in 5-cm. cells, inserting each of the cells in the light beam in turn, and taking instrument readings. Each reading was referred to the calibration curve, and the grade was read to the nearest tenth grade.

If samples and standards are not spectrally similar, a given sample having the same I.C.I. specifications as one of the standards will not necessarily grade the same as the standard on a photoelectric photometer using a pair of filters other than those carefully designed to yield I.C.I. specifications. However, the standards may still be used to check the calibration of the instrument periodically if the samples themselves are unstable. In such a case, the proper corrections may be computed by (1) calculating grades of a series of samples from I.C.I. data obtained spectrophotometrically and referred to the product locus, (2) calculating grades from photoelectric photometer readings referred to a calibration curve obtained for the photometer with the selected standards, and (3) computing differences in the grades obtained by the two methods. These differences may then be used to correct all readings subsequently made on the photometer.

This procedure will be clarified by describing its application to the grading of terpene hydrocarbons. The spectral dissimilarity between the samples and the inorganic standards may be seen by comparing the transmittance curves of the former (Figure 2) with those of the latter (Figure 8). In order to establish a correction for this dissimilarity, the following procedure was used.

A number of samples selected from a group of those falling near the product locus of Figure 3 were assigned fractional grades by interpolating their spectrophotometrically determined x-trichromatic coefficients between those of the arbitrarily chosen standards listed in Table III. These grades are listed in column 4 of Table VI. Next, readings were obtained on the grading photometer, and were referred to the calibration curve of Figure 7. Fractional grades were again assigned on the basis of this calibration curve, and are listed in column 5 of Table VI. Differences in the grades assigned by the two methods are given in column 6. In the case considered here, these differences were small enough to be neglected. In general, however, they could be used to correct the original calibration curve.

Table VI. Corrections for Spectral Dissimilarity between Terpene Samples and Inorganic Standards

Designation	x	y	Grade Determined from I.C.I. Data	Grade Determined from Photometer Reading	ΔG
6a	0.3133	0.3223	0.11	0.09	−0.02
20a	0.3241	0.3388	0.47	0.51	0.04
23a	0.3351	0.3569	0.84	0.97	0.13
26a	0.3753	0.4110	2.18	2.31	0.13
28a	0.4241	0.4564	3.80	3.94	0.14

OTHER COLOR SCALES

This same scheme has also been applied successfully to other classes of compounds. Figure 9 represents a number of samples of cellulose plastics plotted on an (x, y)-chromaticity diagram. In this case, the agreement of all samples with a single locus is not as good as in the first case. This is partly due to the fact that examples of five different classes of compounds are included in the figure. The agreement is still close enough, however, to allow the same grading scheme to be used for all. Deviations are considered less important than the difficulty in applying and interpreting a three-number (or even a two-number) specification.

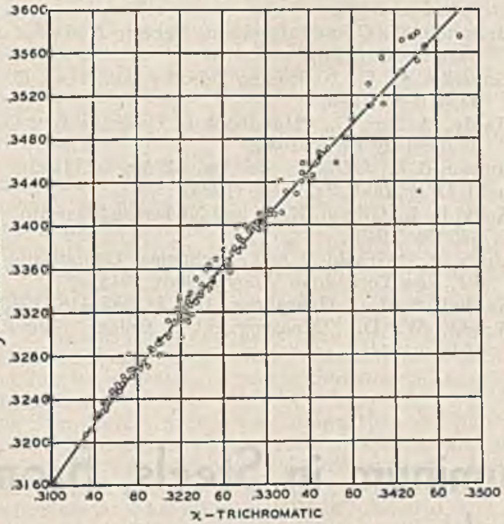

Figure 9. Chromaticities of Cellulose Products

○ Cellulose products samples
● Working standards

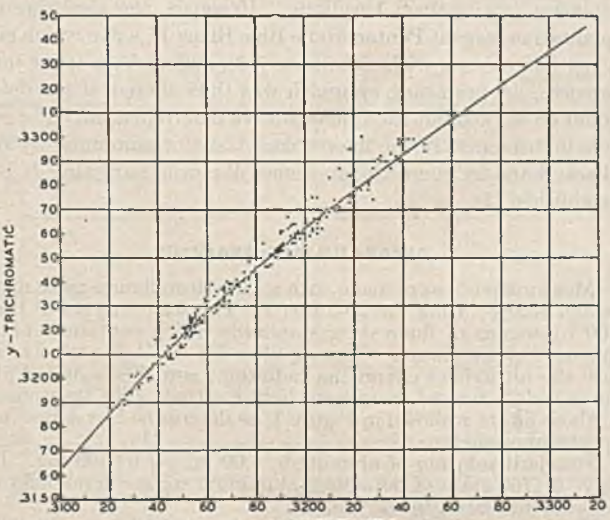

Figure 10. Chromaticities of Cotton Linters

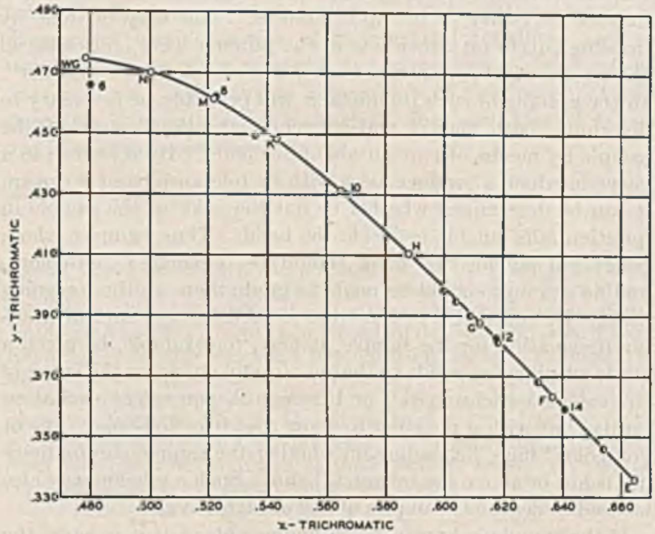

Figure 11. Chromaticities of Thanite Samples, U. S. Rosin Standards, and Gardner Standards

○ U. S. rosin standards
● Gardner standards } Cell thickness, 50 mm.
◐ Thanite samples

Figure 10 is a product locus for cotton linters plotted from the chromaticities of a large number of pressed samples from regular plant production. About the same lack of agreement is evident here as in Figure 9.

Standards were chosen for both classes of products by means of the method described above, and were made of combinations of solutions of the same salts as used for the terpene standards.

Well-known color scales may often be applied without error to certain classes of products. For example, two types of standards whose use is widespread are the glass U. S. rosin standards sponsored by the United States Department of Agriculture (*1*), and the Gardner color standards used rather extensively in the varnish industry (*4*).

The chromaticity plots of a few standards of each of these two types are shown in Figure 11 in order to demonstrate the possibility of applying them to a color grading scheme for commercial grades of Thanite, a liquid insecticide ingredient. The U. S. rosin standards are nearly equally spaced with respect to their x-trichromatic coefficients. It can readily be seen that they may be used for grading the product in question. The Gardner standards down to No. 8 also fall on the locus of the product points, but their lack of equal or even regular spacing indicates that they should be modified to make them more useful in applying or interpreting a color-grading method based on them.

For rough grading these physical standards may often be used visually—e.g., in a Nessler tube. It would not, of course, be valid to use variable thicknesses of a single standard in a Nessler tube unless it had been ascertained previously that Beer's law was obeyed by the mixtures comprising the standards. In the case of Gardner standards, varying the thickness does not correspond to changing the number. This is due to the fact that the standards are not merely dilutions of the darkest standard, but actually have different relative compositions. This condition also holds with the terpene standards discussed above.

SPECIAL CONSIDERATIONS

Very often, a product is encountered in which the chromaticity points of a large number of samples have rather wide dispersion—i.e., the scattering about the locus is large. In such a case, it may be necessary to set up tolerances. This may be done by drawing curves on either side of the product locus, enclosing all the points which, from experience, it is decided are "on-color". In the grading of such products, it will probably be necessary to determine both the *x*- and *y*-trichromatic coefficients of the sample by means of two suitable filter pairs. By reference to a curve in which a product locus with its tolerance band is drawn, it can be determined whether or not the color of the sample in question falls outside or inside the band. Thus, samples whose colors fall outside the band should be designated "off-color", and no attempt should be made to grade them on the foregoing basis. However, if it is desired to establish some sort of grading designation for the sample, it may, for example, be given a grade which corresponds to that of a sample lying on the curve of equivalent *x*-trichromatic, or better still, equivalent excitation purity, but with a notation to show that it is "off-color" low or "off-color" high, depending on whether the sample chromaticity lies below or above the tolerance band. Such a scheme may also be used to designate samples of low or high *Y*-value.

If the sample is known to be fluorescent, or if it is hazy, the color specification which can be most conveniently applied is that which one would normally make visually by means of viewing the sample with the aid of a directed beam of light passing through the sample toward the eye. This same result may be accomplished in a photoelectric instrument by excluding the scattered or fluorescent light from the receiver. This may easily be done by mounting the receiver at a considerable distance from the sample. Sometimes, however, it may be customary to grade samples of a certain product by viewing them with more or less indirect illumination. Such a case occurs when the grader lines up a series of samples on a sheet of white paper near a window. It will often be found that samples graded in this manner will not fall in the same order as if they were graded by direct light from the window, especially if the samples contain varying amounts of haze. Photoelectric grading, to correspond approximately with visual grading by indirect illumination, should be done with the sample very near the receiver. If an integrating sphere is used as the receiver, the sample may be mounted inside the sphere for such a measurement.

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Fluorometric Determination of Aluminum in Steels, Bronzes, and Minerals

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THE absence of specific sensitive reagents for the determination of aluminum is a notable handicap to the analytical chemist. This difficulty is reflected in the laborious procedures required for an accurate gravimetric analysis of small percentages of aluminum in steel (*1*, *6*, *12*) and in the fact that rock analysts usually calculate alumina by difference from the R_2O_3 precipitate (*5*).

The reagent which has found widest use is "aluminon", ammonium aurintricarboxylate (*4*, *8*, *15*). In spite of interference by chromium, iron, beryllium, vanadium, titanium, and gallium, it has been used for colorimetrically determining from 0.04 to 1.5% of aluminum in steel (*2*), and for low percentages in nonferrous alloys (*10*). Ether extraction and mercury cathode electrolysis were used, respectively, as separations in these two procedures.

But the need was still felt for a method, other than spectrographic (*11*), suitable for determining down to less than 0.01% of aluminum in such materials as steels, bronzes, and minerals. A quantitative fluorescence method for aluminum in pure solution using the reagent morin (*14*) was reported subject to several interferences, among them beryllium. However, the very sensitive qualitative reagent Pontachrome Blue Black R, a dye which gives a red fluorescence with aluminum (*13*), suffers from fewer interferences. A promising approach was thus offered, if the details could be worked out for a quantitative determination. The relative interferences in the fluorescence tests for aluminum by Blue Black R and by quercetin, an isomer of morin, have already been established (*3*).

APPARATUS AND REAGENTS

Measurements were made with a Lumetron fluorescence meter, model 402EF, using the 25-ml. cell. The scale was set at 0 and 100 by means of fluorescing standards which contained known amounts of aluminum. Corning filter No. 5874 was used to isolate the ultraviolet energizing radiation, and sheets of red plastic to isolate the red fluorescent light emitted. The transmission of these filters is shown in Figure 1, as determined by a Beckman spectrophotometer.

Standard solution of aluminum, 1.00 ml. = 0.0100 mg. Dissolve 0.1760 gram of potassium aluminum sulfate crystals in water, and dilute to 1 liter.

Weaker standard solution of aluminum, 1.00 ml. = 0.00100 mg. Pipet out 100 ml. of the above solution, and dilute to 1 liter.

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Ammonium acetate solution, 10%. Dissolve 50 grams of the salt in water and dilute to 500 ml.

Pontachrome Blue Black R (Color Index 202), 0.1% solution. This dye is the sodium or zinc salt of 4-sulfo-2-hydroxy-α-naphthalene-azo-β-naphthol. Dissolve 0.50 gram in 500 ml. of 95% ethyl alcohol, and allow to stand a few days before using. This dye may also be purchased under the name Superchrome Blue Black (National Aniline Division of Allied Chemical and Dye Corporation).

Pontachrome Violet SW (Color Index 169), 0.1% solution. Dissolve 0.50 gram in 500 ml. of 95% ethyl alcohol.

Sodium hydroxide solution, 10%. Dissolve 25 grams in 250 ml. of water in a large platinum dish, with the aid of a platinum stirring rod. Store in a ceresin bottle, to avoid aluminum contamination from glassware.

Dilute sulfuric acid, 1 to 9. Pipet 100 ml. of concentrated acid into several hundred milliliters of water in a 1000-ml. volumetric flask, cool, and dilute to the mark.

A rapid fluorometric method is described for the quantitative determination of from 0.001% to somewhat over 1% of aluminum in steels, bronzes, and minerals. This represents a range of 0.0002 to 0.025 mg. of aluminum in a volume of 50 ml. The necessity for special microtechnique is avoided by the use of aliquots of a macrosample; the sensitivity is better than 1 part in 100,000,000. For small percentages of aluminum, this method surpasses other procedures in speed, sensitivity, accuracy, and freedom from interference. The preferred reagent is the dyestuff Pontachrome Blue Black R, which is used at a pH of 4.8 in buffered solution. Excellent results may also be obtained with Pontachrome Violet SW. Electrolysis in a mercury cathode cell serves to eliminate interfering ions. Studies have been conducted on the changes in intensity of fluorescence under variation of experimental conditions such as temperature, time of standing, pH, dye concentration, and aluminum concentration. The probable composition of the fluorescent substance has been established by analysis, after amyl alcohol extraction from aqueous solution.

EXPERIMENTAL

It was necessary first to study the effect on the fluorescence intensity of such variables as pH, amount of dye, amount of aluminum, time of standing, and temperature.

EFFECT OF pH. A series of twenty solutions was prepared in 50-ml. volumetric flasks. To each flask were added 0.050 mg. of aluminum, 5.0 ml. of 10% ammonium acetate as a buffer, 1.0 ml. of 0.1% Blue Black R dye, and quantities of acetic acid or ammonium hydroxide sufficient to give a range of pH from 2.4 to 9.8. The solutions were diluted to the mark, shaken vigorously, and allowed to stand for 2 hours before fluorescence measurements were taken. The pH was measured with the laboratory model Beckman pH meter. Under these conditions, the optimum pH is about 4.8 or 4.9 (Figure 2).

Repetition at the lower level of 0.010 mg. of aluminum gave similar results, except that the peak was considerably narrower.

CONCENTRATION OF BLUE BLACK R. A series of 15 solutions of 50-ml. volume was made up, each containing 0.050 mg. of aluminum, 0.50 gram of ammonium acetate, 0.10 ml. of glacial acetic acid to give a pH close to the optimum, and amounts of 0.1% dye solution varying from none to 5.0 ml. The solutions were allowed to stand 80 minutes before readings were taken. It is evident from Figure 3 that maximum intensity is achieved by the use of 1.5 ml. Solutions containing more than this amount showed a rapid decrease in fluorescence in those portions furthest from the ultraviolet source, indicating a progressive absorption of the energizing radiation.

TIME OF STANDING. Since it was known that the fluorescence did not attain its maximum intensity immediately after mixing, the change of intensity with time was investigated. A solution was prepared which contained 0.010 mg. of aluminum, 0.50 gram of ammonium acetate, 1.0 ml. of 1 to 24 sulfuric acid, and 1.5 ml. of 0.1% Blue Black R in a volume of 50 ml. The temperature was 24° C. Measurements were made over a period of 1 hour, and another reading was taken after 3 hours. Figure 4 shows that equilibrium was attained in less than an hour. Repetition of the experiment at the higher level of 0.100 mg. of aluminum gave a similar result.

TEMPERATURE. In order to determine whether maximum intensity could be obtained in a shorter time by heating the solution, a solution containing 0.010 mg. of aluminum, 0.5 gram of ammonium acetate, and 0.05 ml. of acetic acid was diluted to 48 ml. and heated to 70° C., and then 1.5 ml. of dye solution were added. Readings of fluorescence were taken during the next 1.5 hours, as the solution cooled gradually down to room temperature. The intensity increases more slowly than that of a solution mixed at room temperature (Figure 5). Repetition at the level of 0.020 mg. of aluminum gave a similar result. The instrument scale was reset arbitrarily for each run, so that readings are not necessarily transferable from one graph to another.

The effect of cooling was studied next. A 50-ml. solution con-

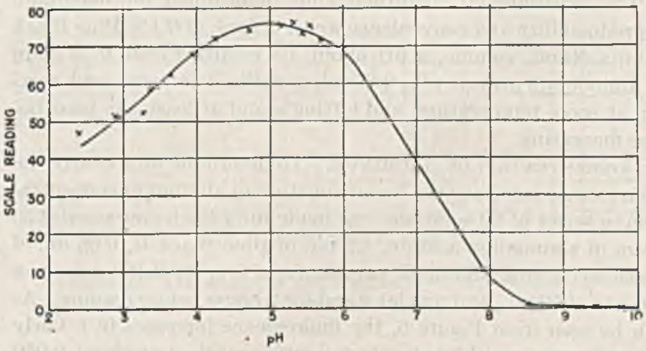

Figure 2. Effect of pH on Fluorescence Intensity.

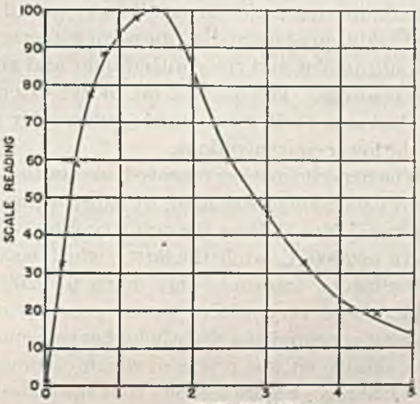

Figure 3. Effect of Blue Black R Concentration on Fluorescence Intensity

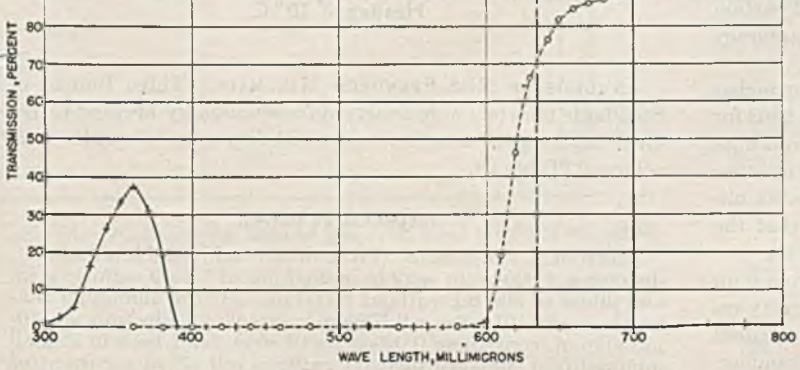

Figure 1. Transmission of Primary and Secondary Filters

Table I. Analysis of Synthetic Standard Steels

Al Present %	Scale Reading	Al Found %
0.000 Standard	0.0	...
0.050 Standard	50.0	...
0.001	1.0	0.001
0.026	24.8	0.025
	26.0	0.026
0.051	51.4	0.051
	49.6	0.050
0.076	78.7	0.079

taining 0.020 mg. of aluminum, 0.50 gram of ammonium acetate, 0.05 ml. of acetic acid, and 1.5 ml. of Blue Black R was allowed to stand several hours, and its fluorescence was measured at room temperature, 25° C. Then it was cooled in ice, and the intensity measured at 10°, 15°, and 20° C. The fluorescence increased slightly at the lower temperatures. The reading was about 2% greater at 10° than at 25° C.

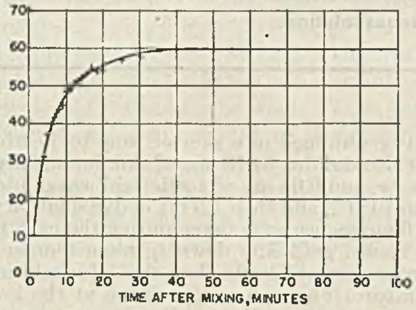

Figure 4. Time Required to Attain Full Intensity of Fluorescence

The experimental conditions thus determined for maximum reproducibility and convenience were: 1.5 ml. of 0.1% Blue Black R in a 50-ml. volume, a pH about 4.8 resulting from 0.50 gram of ammonium acetate plus 0.05 ml. of sulfuric or acetic acid, mixing at room temperature, and letting stand at least one hour before measuring.

Concentration of Aluminum. To determine how nearly the flourescence intensity is a linear function of aluminum concentration, a series of 20 solutions was made up. Each contained 0.50 gram of ammonium acetate, 1.5 ml. of Blue Black R, 0.06 ml. of acetic acid, and aluminum varying from 0 up to 0.100 mg., in a volume of 50 ml., and was let stand for 2 hours before reading. As can be seen from Figure 6, the fluorescence increases in a fairly linear manner until a saturation point is reached at about 0.050 mg. of aluminum, beyond which the intensity remains almost perfectly constant.

The flat portion of this curve is only slightly affected by the aluminum-dye ratio for small increases of dye beyond 1.5 ml. The addition of more dye causes an increase in absorption of both the ultraviolet and the emitted light and gives a reduction in all the readings. The use of 2 ml. of dye extends the useful portion of the curve to 60 micrograms, but greatly reduces the accuracy of the lower concentrations.

The experiment was repeated, except that irradiation by higher energy ultraviolet was used, by substituting Corning No. 9863 for the usual No. 5874 as the primary filter. The former transmits down to 2300 Å., while the latter, which was used for all the other experiments, transmits only down to 3200 Å. The results obtained were very similar to the previous ones, except that the plateau appeared at a slightly higher concentration, 0.060 mg.

A similar set was prepared which covered the range from 0 up to 0.020 mg. Figure 7 shows that the concentration-intensity relation is practically linear up to 0.020 mg. This was repeated several times; greater deviations were noticed in the summer, when room temperature was about 33° C.

To investigate the lower limit of sensitivity, a series covering the range up to 0.001 mg. was prepared. Although a fairly linear graph was obtained, this was not completely reliable because of the rapid decrease in the weak fluorescence during the period of irradiation. However, it was easy even visually to distinguish among solutions containing 0.0004 and 0.0008 mg. of aluminum in the 50-ml. volume. This corresponds to a sensitivity of 1 part in 125,000,000.

Nature of the Fluorescent Substance. To determine if possible the formula of the fluorescent complex, a solution of 5 grams of Blue Black R dyestuff and 25 grams of potassium aluminum sulfate crystals in 300 ml. of water was adjusted to pH about 5.0, by the addition of solid ammonium acetate, and allowed to stand a few hours. It was then extracted with successive 100-ml. portions of *n*-amyl alcohol, and the strongly fluorescent extracts were carefully evaporated to dryness. Analysis of the dried residue indicated that two dye molecules are combined with each aluminum hydroxide molecule. Calculated for $AlOHO_2(C_{20}H_{11}N_2SO_3Na)_2$: C, 56.74%; H, 2.74%; Al, 3.19%. Found: C, 56.64, 58.13%; H, 4.30, 4.58%; Al, 3.19, 3.21%

Analysis of Synthetic Standard Steels. A convenient means for quantitatively determining very small amounts of aluminum in pure solutions had been established by the foregoing work; it still remained to apply the technique to the analysis of actual materials, such as steel. Therefore, varying percentages of aluminum were added to NBS iron 55a, and the resulting synthetic standards were analyzed by Method A, below. Good results were obtained, as shown in Table I.

Analysis of NBS Standard Steels. Several Bureau of Standards steels were analyzed by Method A for acid-soluble aluminum content, which is of greater metallurgical interest than total aluminum. Table II shows the accuracy attained for both high and low percentages. It may be noted that the fluorescence method offers major advantages in the analysis for low percentages, rather than high. Acid-insoluble alumina in steel may also be determined with accuracy (Table III).

Analysis of NBS Standard Bronzes. Several Bureau of Standards copper-base alloys, covering a range of aluminum content, were analyzed by Method B, below. The variability of the results (Table IV) is less than that on the certificates of standardization.

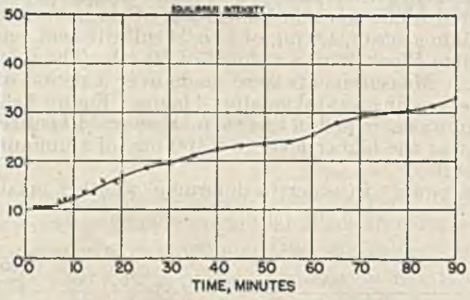

Figure 5. Time Change of Fluorescence after Heating to 70° C.

Analysis of NBS Standard Minerals. Three Bureau of Standards minerals were analyzed for alumina by Method C, below. Again, good accuracy and small dispersion of results were achieved (Table V).

METHODS IN DETAIL

Method A, for Steels. To determine acid-soluble aluminum, dissolve a 1.000-gram sample in 25.0 ml. of 1 to 9 sulfuric acid, and dilute to 500 ml. without filtration. (If the aluminum content is over 0.10%, use a 0.100-gram sample.) Electrolyze a 10-ml. aliquot, containing 0.020 gram of steel, for 1 hour in a small motor-stirred Melaven mercury cathode cell (*7*) at a current of 0.5 ampere or slightly less. Draw off the solution and rinsings into a 50-ml. volumetric flask which contains 5.0 ml. of 10% ammonium acetate plus 1.50 ml. of 0.1% Blue Black R, and dilute to the mark. After at least 1 hour, measure and compare the fluorescence intensity of the solutions and of pure aluminum standards prepared similarly, including electrolysis, and containing the same amounts of acid, buffer, and dye as the unknowns. Inasmuch as the calibration curve is nearly linear, only two standards are required, except in most accurate work.

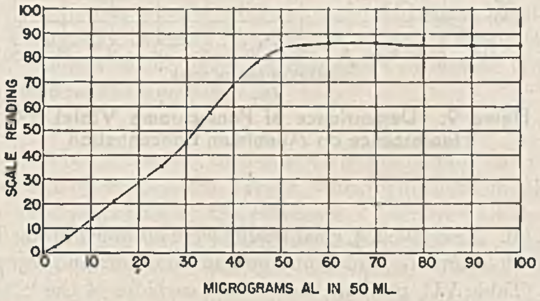

Figure 6. Dependence of Blue Black R Fluorescence on Aluminum Concentration

To determine the acid-insoluble alumina in steel, filter off whatever insoluble residue remains after dissolving a 1.000-gram sample in 1 to 9 sulfuric acid, using a retentive paper, and wash thoroughly with 5 to 95 hydrochloric acid and then water. Ignite in a platinum crucible until all carbon is gone, then add 1 ml. of 1 to 1 sulfuric acid and 5 ml. of hydrofluoric acid. Evaporate down to copious fumes of sulfuric acid, allow to cool, wash down the sides of the crucible with a few milliliters of water, and evaporate and fume strongly again. When cool, transfer to a large platinum dish with 50 ml. of water, and heat until the salts dissolve completely. Add 10% sodium hydroxide solution until alkaline to methyl red, then 1 to 9 sulfuric acid dropwise until barely acid, then an excess of 25.0 ml. of 1 to 9 sulfuric acid. Transfer to a 500-ml. volumetric flask, dilute to the mark, shake well, and pipet out a 10-ml. aliquot for mercury cathode electrolysis. Carry out the remainder of the analysis in the usual manner.

METHOD B, FOR BRONZES. Weigh out a 1.000-gram sample, for materials containing 0.10% aluminum or less; for higher percentages, up to about 1%, use a 0.100-gram sample. Dissolve in 10 ml. of 1 to 1 nitric acid in a 250-ml. beaker, add 20 ml. of 1 to 1 sulfuric acid, and evaporate down to copious fumes of sulfuric acid. Allow to cool, wash down the sides with about 15 ml. of water, and again evaporate to strong fumes. (Each evaporation may be accomplished in a few minutes by heating the beaker over a free flame, with vigorous swirling of the contents.) Cool, dilute with 100 ml. of water, make just neutral to methyl red with 10% sodium hydroxide, and add 25.0 ml. of 1 to 9 sulfuric acid. Dilute to 500 ml., shake well, and pipet a 10-ml. aliquot into the mercury cathode cell. After electrolyzing for an hour, draw off into a 50-ml. volumetric flask containing 5.0 ml. of 10% ammonium acetate and 1.50 ml. of 0.1% Blue Black R, and dilute to the mark. Let stand at least 1 hour, and then measure the fluorescence and compare with that of standards prepared similarly and simultaneously.

Table II. Analysis of Bureau of Standards Steels for Acid-Soluble Aluminum

Steel	Certified Value %	Found %
55a	0.001	0.001 0.001 0.001 0.001
4c	0.022	0.021 0.021 0.024 0.022 0.022 0.021 0.021 0.022
106a	1.07	1.05 1.05 1.12 1.13
106	1.06 (total)	1.09 1.09 1.05 1.05

Table III. Analysis of Bureau of Standards Steel for Acid-Insoluble Alumina

Steel	Certified Value %	Found %
106a	0.011	0.011 0.011 0.011 0.012

Table IV. Analysis of Standard Bronzes for Aluminum

Alloy	Certified Value %	Found %
62	1.13	1.09 1.14 1.11
62a	0.92	0.93 0.93 0.95 0.96
62b	0.97	0.98 0.95 0.95 0.97
63	0.05	0.044 0.051 0.052 0.055
124a	0.006	0.006 0.008

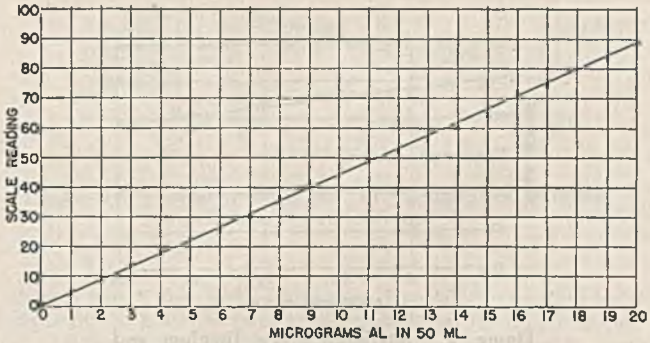

Figure 7. Dependence of Blue Black R Fluorescence on Concentration

METHOD C, FOR MINERALS. For materials consisting largely of silica, such as glass sand or silica brick, the following direct method is suitable. Weigh 0.100 or 0.500 gram of sample (depending on aluminum content) into a 20-ml. platinum crucible, add 2 ml. of 1 to 1 sulfuric acid and 10 ml. of hydrofluoric acid, and evaporate down to copious fumes. Cool, wash down the sides with 10 ml. of water, and again evaporate to heavy fumes. Add to 100 ml. of water in a platinum dish, heat until all salts dissolve, and make just neutral to methyl red with 10% sodium hydroxide. Then add 25.0 ml. of 1 to 9 sulfuric acid, dilute to 500 ml., and electrolyze a 10-ml. aliquot in the Melaven cell for an

Table V. Analysis of Standard Minerals for Alumina

Sample	Certified Value %	Found %
81	0.265	0.268 0.279 0.287
88	0.067	0.063 0.067 0.063 0.062
102	1.96	1.98 2.01 2.03

hour. Complete the determination as described in Methods A and B, and calculate the results as aluminum oxide. The blank on the complete procedure is very small, about 0.0001 mg. of aluminum oxide on the 10-ml. aliquot.

For other types of minerals, it is more convenient to proceed with the ordinary scheme of analysis, and then apply the fluorescence method to the determination of alumina in the R_2O_3 ammonia precipitate. This may be illustrated in the case of NBS dolomite No. 88.

Ignite a 1.000-gram sample at 1100° for 30 minutes, then boil with 40 ml. of 1 to 1 hydrochloric acid. Filter off the small insoluble residue, wash, ignite in a platinum crucible, treat with 5 drops of 1 to 4 sulfuric acid and 5 ml. of hydrofluoric acid, and evaporate to dryness. Then fuse with 0.5 gram of potassium pyrosulfate, dissolve the cooled melt in water, and add this solution to the original filtrate and washings. Add about 10 grams of ammonium chloride and precipitate the R_2O_3 as usual with ammonia, using methyl red indicator. Filter off the hydroxides, wash several times, transfer to a beaker by a jet of water, and dissolve by the addition of 25.0 ml. of 1 to 9 sulfuric acid. Then dilute the solution to 500 ml., pipet out a 10-ml. aliquot for electrolysis, and complete the determination in the usual manner.

DISCUSSION

The mercury cathode separation was chosen as most suitable here for removing iron, copper, etc.; even a little ferric ion destroys fluorescence. Attempts were made to extract the fluorescent complex from the iron solution with amyl alcohol, and also to use sodium hydroxide or cupferron for eliminating the iron, but none of these gave as good results as the mercury cathode.

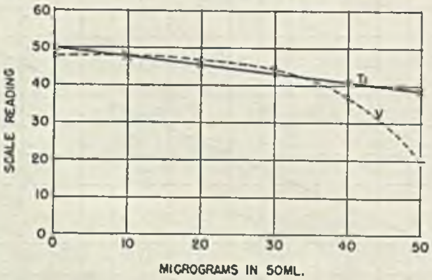

Figure 8. Interference by Titanium and Vanadium in Solutions Containing 0.010 Mg. of Aluminum

Such interferences as iron, copper, chromium, nickel, and cobalt are removed quantitatively by mercury cathode electrolysis. It was of interest to investigate possible interference by titanium, vanadium, and zirconium, which are not so removed and which are frequently found in steel. Varying quantities of these ions were added to fluorescing solutions which contained 0.010 mg. of aluminum. Titanium was found to interfere somewhat, and pentavalent vanadium more seriously (Figure 8), but zirconium, not at all. Nevertheless, good results were obtained in the fluorometric determination of aluminum in titanium and vanadium steels (Table VI), perhaps because the carbides of the latter are insoluble in dilute sulfuric acid.

Table VI. Determination of Aluminum in Titanium and Vanadium Steels

Steel	Gravimetric Analysis	Aluminum Found %
K	0.066% Al, 0.085% Ti	0.064 0.066 0.064 0.063
L	0.051% Al, 0.11% V	0.053 0.053 0.053 0.054

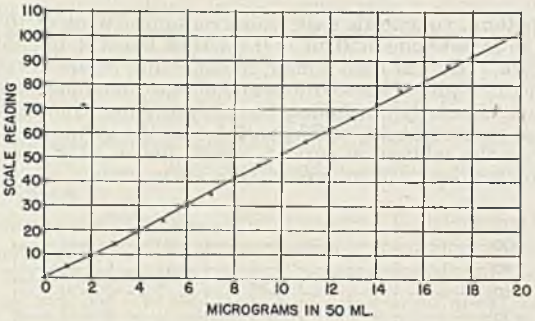

Figure 9. Dependence of Pontachrome Violet SW Fluorescence on Aluminum Concentration

Pontachrome Violet SW has also been suggested (*9*) as a fluorescence reagent for aluminum; it gives an orange fluorescence at 5850 to 6250 Å, compared with the red fluorescence of Blue Black R at 6365 to 7000 Å. In the Violet SW dye molecule, a benzene ring replaces one of the naphthalene rings in Blue Black R.

Detailed investigations of the suitability of Violet SW as a quantitative reagent showed that wider variations in dye concentration could be tolerated, that the dependence of intensity on aluminum concentration was almot perfectly linear (Figure 9), and that accurate results could be obtained for amounts of aluminum as small as a few tenths of a microgram. However, the Violet SW fluorescence required more careful control of pH, and was destroyed by even smaller traces of iron. Therefore, the Blue Black R reagent was chosen for the bulk of this work, although analysis of NBS and synthetic standard steels were completed with good accuracy, using Violet SW.

ACKNOWLEDGMENT

The assistance of Pearl G. Weissler in the preparation of graphs is gratefully acknowledged.

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Quantitative Determination of Some Inhibitors in Polymers by Ultraviolet Light Absorption

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A rapid and accurate method of analysis for inhibitors in polymeric materials employing ultraviolet light absorption has been developed which is especially desirable for inhibitors present in small concentrations. Correction for linear "background" absorption is made without need for direct measurement.

ORGANIC polymeric substances are commonly subject to attack by atmospheric oxygen, which will cause changes in the physical properties of the polymers. Inhibitors are usually incorporated to prevent or retard polymer degradation caused by atmospheric and imposed oxidizing conditions. The use of stabilizers is, therefore, very widespread and is especially important in synthetic rubbers.

Inhibitor concentration is an important factor in estimating the potential stability of a polymer. The concentration requirements for stabilizing polymers of different types will vary with the type of polymer. The use of small concentrations of inhibitor has created an urgent need for a more precise method of inhibitor analysis. Production control requires an easy and rapid method of analysis as well as accurate results, even where higher concentrations of inhibitor are used. *N*-Phenyl-2-naphthylamine (commonly called phenyl-β-naphthylamine) has been used very widely in the stabilization of synthetic elastomers and, therefore, an effort was made to develop the best analytical method for this specific inhibitor. A method of analysis of primary aromatic amines involving titration with standardized nitrous acid (*5*) has been applied to its determination; however, when this method was used to determine the inhibitor present in a polymer in small concentrations, it was found unreliable in the absence of very careful control and expert manipulation. Craig (*2*) estimated the concentration of *N*-phenyl-2-naphthylamine in rubber by isolation of the hydrochloride. An adaptation of this method to Butyl rubber by a turbidimetric measurement of the amine hydrochloride has been used for production analysis but was unsatisfactory unless very careful control was maintained. An oxidative method using ceric sulfate has also been used with somewhat more reliable results. Investigation of rapid physical methods of analysis revealed that *N*-phenyl-2-naphthylamine has a very strong absorption in the near-ultraviolet region (*4*, *6*, *7*) which is very desirable for spectral analysis. Qualitative spectrographic determination of various rubber ingredients, including *N*-phenyl-2-naphthylamine, has been described (*3*). The use of spectrophotometry now appears to be the best method of analysis for *N*-phenyl-2-naphthylamine in polymers.

Since polymers and various blending ingredients are not entirely transparent to ultraviolet light, it is necessary to subtract the "background" absorption (absorption due to materials other than *N*-phenyl-2-naphthylamine) to obtain a true estimation of inhibitor concentration in the polymer. A mathematical adaptation of the method which Wright (*8*) used in infrared spectroscopy in correcting for the background absorption, without actual measurement of the background absorption, was applied to this determination with considerable success. The method can be satisfactorily used with any polymer which can be dissolved in a solvent, or from which the inhibitor can be extracted by a solvent, where the background absorption is linear through the spectral points or wave lengths at which the inhibitor exhibits a maximum and two adjacent minimum absorptions. The correction for linear background absorption by optical density measurements at three wave lengths is outlined below. Although certain forms of this mathematical approach are in use, to the authors' knowledge it has not been previously reported. (Derivation and first application of this equation to polymer analysis was carried out in this laboratory by T. S. Chambers.)

Two assumptions are made: (1) Beer's law is obeyed and (2) the background absorption is linear with wave length over the portion of the spectrum involved. The former assumption has been found valid for the concentrations employed. Knowledge of the system used in the analysis will determine whether the latter is true or is a close approximation which would introduce but little error. Figure 1 is a typical illustration of the absorption of a solution of polymer containing an inhibitor.

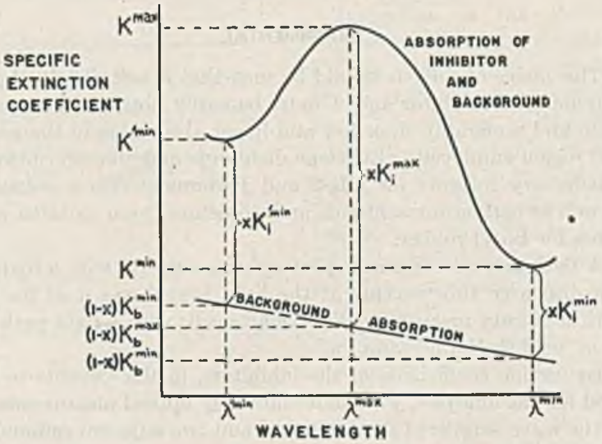

Figure 1. Typical Absorption of Solution of Polymer Containing an Inhibitor

K'^{min}, K^{max}, and K^{min} are observed specific extinction coefficients of the polymer sample being analyzed for inhibitor content. $K_b'^{min}$, K_b^{max}, and K_b^{min} are the specific extinction coefficients of the background and $K_i'^{min}$, K_i^{max}, and K_i^{min} are the specific extinction coefficients for the inhibitor. Let x = fraction of inhibitor in polymer; and $1 - x$ = fraction of polymer or background.

Then

$$K'^{min} = xK_i'^{min} + (1 - x)\,K_b'^{min} \tag{1}$$

$$K^{max} = xK_i^{max} + (1 - x)\,K_b^{max} \tag{2}$$

$$K^{min} = xK_i^{min} + (1 - x)\,K_b^{min} \tag{3}$$

The K's and K_i's are experimentally determined, leaving four unknowns. The value of x can be determined without knowing K_b's if one of the K_b's is known in terms of the others. From Figure 1:

$$(1 - x)K_b^{max} = (1 - x)K_b^{min} + \frac{\lambda^{min} - \lambda^{max}}{\lambda^{min} - \lambda'^{min}}\left[(1 - x)K_b'^{min} - (1 - x)K_b^{min}\right] \tag{4}$$

or

$$K_b^{max} = (1 - n)K_b^{min} + nK_b'^{min} \tag{5}$$

where

$$n = \frac{\lambda^{min} - \lambda^{max}}{\lambda^{min} - \lambda'^{min}} \tag{6}$$

Substitute values of $K_b'^{\min}$ and $K_b^{\min}$ from Equations 1 and 3 in Equation 5:

$$K_b^{\max} = \frac{(1 - n)(K^{\min} - xK_i^{\min}) + n(K'^{\min} - xK_i'^{\min})}{1 - x} \quad (7)$$

Substitute value of $K_b^{\max}$ from Equation 7 in Equation 2:

$$x = \frac{K^{\max} - (1 - n)K^{\min} - nK'^{\min}}{K_i^{\max} - (1 - n)K_i^{\min} - nK_i'^{\min}} \quad (8)$$

Since $K = \dfrac{D}{LC}$

where D = optical density = $\log \dfrac{I \text{ solvent}}{I \text{ solution}}$
L = cell length = 1 cm.
C = concentration of polymer in solution in grams per liter
I solvent = intensity of light through pure solvent
I solution = intensity of light through polymer solution

then

% inhibitor in polymer =

$$\frac{100[D^{\max} - (1 - n)D^{\min} - nD'^{\min}]}{C[K_i^{\max} - (1 - n)K^{\min} - nK_i'^{\min}]} \quad (9)$$

EXPERIMENTAL

The choice of solvent should be such that it will dissolve both polymer and inhibitor and it must be easily obtained in a pure state and preferably show low and linear absorption in the spectral region employed. Ethylene dichloride and chloroform were satisfactory solvents for GR-S and Perbunan. These solvents as well as carbon tetrachloride and iso-octane were suitable solvents for Butyl rubber.

A Beckman quartz prism spectrophotometer (*1*) with a hydrogen discharge tube serving as the light source was used for all optical density measurements. Quartz cells with a light path of 1 cm. held the liquid samples.

Extinction coefficients of the inhibitors, in the solvents to be used for the analyses, were determined by optical measurements at the wave lengths of the maximum and two adjacent minimum absorptions best suited for analytical purposes. Several concentrations were employed and an average extinction coefficient was calculated for the inhibitor at each of the three wave lengths. It is important that measurements of extinction coefficients of inhibitors be made for each instrument, since the exact dispersion, resolving power, actual slit width, photocell spectral sensitivity, and amount of reflected and scattered light of the instrument are factors which affect the optical density measurements.

Since only small samples of polymer were employed, care was exercised to get truly representative results. This was accomplished by milling and refining a sample of rubber from which portions were taken for analyses. Milling was also beneficial in destroying gel in polymers which would introduce error from light reflection. Excessive milling and heating in contact with air were avoided.

An accurately weighed portion of polymer was placed in a glass-stoppered Erlenmeyer flask and a known volume of solvent added from a pipet. Dissolution occurred on standing 1 or 2 days with occasional shaking, or it was accelerated by stirring or heating. A clear sample was removed from any settled insoluble material (centrifuging may be used) and transferred to the quartz cell for optical density measurements. A matched quartz cell containing a solvent control was used as the reference zero optical density. The concentration of inhibitor in the polymer was calculated by means of Equation 9. Using this procedure, only a few minutes are required to determine the inhibitor content of a sample of dissolved polymer.

DISCUSSION

The specific extinction coefficients of *N*-phenyl-2-naphthylamine showed slight variation in numerical value and spectral position with the solvent employed. The evaluation of the coefficients used in calculations in this paper are given in Table I and their use permits simplification of Equation 9 to the following expressions:

Table I. Specific Extinction Coefficients of *N*-Phenyl-2-naphthylamine and Uninhibited Polymers

Wave Length, mμ	Specific Extinction Coefficients, K (l. g.⁻¹ cm.⁻¹) PBN in iso-octane	Butyl rubber in iso-octane	PBN in $C_2H_4Cl_2$	GR-S in $C_2H_4Cl_2$	Perbunan in $C_2H_4Cl_2$
282	49.7	0.01–0.06	54.0	...	...
284	52.0	.....	51.5	0.05	0.03
308	85.6	.01–0.04	85.0	...	...
309	83.5	...	87.0	0.04	0.02
326	13.2	0.01	17.0	...	...
332	15.0	.....	15.0	0.01	0.01

% PBN in Butyl rubber =

$$(D^{308} - 0.6D^{326} - 0.4D^{282})\,\frac{1.73}{C} \quad (10)$$

% PBN in Perbunan and GR-S =

$$(D^{309} - 0.52D^{332} - 0.48D^{284})\,\frac{1.83}{C} \quad (11)$$

where the solvent for Butyl rubber is iso-octane and that for Perbunan and GR-S is ethylene dichloride. Solutions containing about 0.01 gram of *N*-phenyl-2-naphthylamine per liter (or about 0.3 gram of Butyl rubber or 0.05 gram of Perbunan or GR-S per 100 ml.) were most satisfactory for optical density measurements with the Beckman instrument. These solutions have optical densities in the range of 0.1 to 1.0 for the wave lengths prescribed.

The advantage of the ultraviolet absorption method for the determination of *N*-phenyl-2-naphthylamine in Butyl rubber as compared with the turbidimetric determination by precipitated hydrochloride is evident from Table II. An oxidation method involving ceric sulfate oxidation of the inhibitor gave results in good agreement with those obtained by the ultraviolet method.

Table II. Comparison of Methods of Analysis of Butyl Rubber for *N*-Phenyl-2-naphthylamine

Polymer Composition	% N-Phenyl-2-naphthylamine in Polymer: Chemical Methods, Hydrochloride turbidimetric	Chemical Methods, Ceric sulfate	Ultraviolet Method, Corrected for background	Ultraviolet Method, Uncorrected for background
Pure Butyl rubber	0.00	...	0.00	0.01
Pure Butyl rubber + 0.25% PBN[a]	0.22	...	0.24	0.26
Pure Butyl rubber + 2.5% zinc stearate[a]	0.00	...	0.00	0.03
Pure Butyl rubber + 2.5% zinc stearate + 0.25% PBN[a]	0.40	...	0.23	0.26
Butyl rubber (light colored)	0.63	0.35	0.35	0.41
Butyl rubber (dark colored)	0.48	0.00	0.00	0.09
Butyl rubber (dark colored) + 0.25% PBN[a]	0.42	0.25	0.21	0.33

[a] Added on mill.

The calculation of inhibitor content by using only the wave length of maximum absorption gives values listed in Table II as uncorrected for background. This calculation represents the maximum amount of inhibitor that can be in the polymer and is made by Equation 12:

Maximum possible % PBN in polymer =

$$\frac{100K^{308}}{K_i^{308}} = 1.17\,\frac{D^{308}}{C} \quad (12)$$

The uncorrected value does not always agree with that corrected for background absorption but tends to be higher where the background absorption is greater.

The dark-colored Butyl rubber sample in Table II showed no inhibitor present by corrected ultraviolet analysis, while the un-

Table III. Comparison of Different Methods of Analysis of Buna-Type Polymers for *N*-Phenyl-2-naphthylamine

Polymer Composition[a]	% *N*-Phenyl-2-naphthylamine in Polymer: Ultraviolet Method, Corrected for background	Ultraviolet Method, Uncorrected for background	Chemical method, nitrous acid titration of HOAc extract
Unstabilized Perbunan	0.00	0.02	0.00
Perbunan + 1.9% PBN added on mill (A)	1.91	1.99	...
Perbunan (A) milled 10 minutes at 20° C.	1.88	1.96	...
Perbunan (A) milled 10 minutes at 100° C.	1.80	1.96	...
Perbunan (A) aged 4 days, air oven, 85° C.	1.79	1.87	...
Perbunan + 2.0% PBN added on mill (B)	1.98	2.05	1.91
Perbunan commercial product (C)	1.64	1.69	1.65
Perbunan (C) aged 46 days, air oven, 60° C.	1.32	1.42	...
Perbunan, dark colored stock	1.85	2.26	...
Unstabilized GR-S	0.00	0.05	...
GR-S + 0.5% PBN added on mill (A)	0.51	0.54	0.58
GR-S + 1.96% PBN added on mill (B)	1.96	1.99	1.98
GR-S (B) aged 46 days, air oven, 60° C.	0.74	1.24	...

[a] Parenthetical letter refers to specific polymer-inhibitor compositions.

Table IV. Effect of Aging of Buna-Type Polymers on Ultraviolet Absorption and Inhibitor Analyses

Polymer	Aging Conditions	Optical Density: 284 mμ	Optical Density: 309 mμ	Optical Density: 332 mμ	Concn., G./L.	% *N*-Phenyl-2-naphthylamine in Polymer: Ultraviolet Method, Corrected for background	Ultraviolet Method, Uncorrected for background	Chemical method, nitrous acid titration of HOAc extract
Perbunan	Original	0.447	0.732	0.136	0.500	1.64	1.69	...
	50 days, air oven, 82° C.	0.206	0.313	0.076	0.500	0.27	1.05	...
GR-S	Original	0.485	0.805	0.148	0.500	1.81	1.85	1.82
	50 days, air oven, 82° C.	0.360	0.333	0.117	0.500	0.36	0.77	0.43
GR-S	Original solution	0.158	0.878	0.545	0.500	1.96	2.02	...
	Same solution aged 10 days in diffused sunlight at room temperature	0.202	0.716	0.642	0.500	1.11	1.65	...

corrected analysis indicated that inhibitor was still present. Storage stability of this polymer was very poor, indicating that inhibitor was absent.

From a large number of inhibitor determinations on Butyl rubber containing about 0.25% *N*-phenyl-2-naphthylamine, the following probable errors were obtained when corrected for background absorption:

Mean deviation from theoretical	±0.01% PBN
Maximum deviation from theoretical	±0.04% PBN
Mean reproducibility	±0.01% PBN
Maximum deviation from mean	±0.04% PBN

The ultraviolet absorption of GR-S and Perbunan polymers which contain small amounts of such impurities as hydroquinone, soap, fatty acid, persulfate, and mercaptan is very low as compared to that of *N*-phenyl-2-naphthylamine. Since larger amounts of antioxidant are used in the Buna-type polymers (about 2.0%) than in Butyl rubber (about 0.25%), the background absorption of unaged Buna-type polymers is of less significance in determining the inhibitor contents of the polymers by ultraviolet absorption. It is then usually necessary to measure the absorption of a polymer solution only at the wave length of maximum absorption (309 mμ) and calculate the inhibitor concentration by Equation 13.

Maximum possible % PBN in Perbunan or GR-S =

$$\frac{100K^{309}}{K_i^{309}} = 1.15\,\frac{D^{309}}{C} \qquad (13)$$

Even fresh polymers may, however, become contaminated with impurities by milling or improper washing, so that the magnitude of the background absorption is increased, thereby making a background correction necessary if accurate and reproducible results are required. In Table III data are presented illustrating the application of ultraviolet absorption and Equations 11 and 13 to the determination of *N*-phenyl-2-naphthylamine in Buna-type polymers. In certain cases the antioxidant was extracted from the polymers with glacial acetic acid and the extracts titrated with nitrous acid to starch-iodide end points. In these cases special precautions were taken to obtain complete extraction and avoid losses which generally accompany this type of analysis.

Data are also presented in Table III to show the effect of natural and imposed oxidizing conditions on the antioxidant contents of polymers. Ultraviolet analyses of such polymers show not only decreased amounts of antioxidant present in the aged polymers, but also a variation in the two methods of calculation (Equations 11 and 13) which can be accounted for only by assuming that oxidation products of the inhibitor and polymer are contributing to the background absorption.

Inspection of the absorption spectra of highly oxidized Perbunan and GR-S polymers reveal that the characteristic peak absorption of the *N*-phenyl-2-naphthylamine at 309 mμ has been at least partially destroyed, and the absorption has become more linear with wave length than is the case for the absorption of the pure inhibitor. Under such circumstances, application of a background correction results in much more accurate evaluations of the inhibitor contents of the polymers than either measurement of the optical density of the polymer solution at only one wave length, or application of analytical procedures which depend on the reaction of a functional group of the inhibitor. The nitrous acid titration procedure, for example, fails to distinguish oxidation products of *N*-phenyl-2-naphthylamine from the pure inhibitor if amine groups are present in the oxidation products and if these groups will form nitroso derivatives. The work of Rehner, Banes, and Robison (7) has demonstrated that amine compounds may occur in oxidation products of *N*-phenyl-2-naphthylamine.

The changes in ultraviolet absorption and inhibitor content of Perbunan and GR-S polymers due to oxidation promoted by heat and light are further illustrated in Table IV. The more

Table V. Wave Lengths Applicable for Ultraviolet Determination of Inhibitors

Inhibitor	Solvent	Wave Lengths in mμ for Analyses: $\lambda'^{\min}$	$\lambda^{\max}$	$\lambda^{\min}$
Aminox[a]	Ethylene dichloride	246	291	355
Agerite Stalite[a]	Ethylene dichloride	251	286	353
Inhibitor 8567[a]	Iso-octane	246	277	300
N-Phenyl-2-naphthylamine	Iso-octane	282	308	326
N-Phenyl-2-naphthylamine	Ethylene dichloride	284	309	332
N-Phenyl-2-naphthylamine	Chloroform	284	309	332

[a] Aminox, Amine, ketone condensation product. Agerite Stalite, alkylated aromatic amine. Inhibitor 8567, phenolic type.

probably correct analyses are those obtained where background corrections have been made.

This method of analysis has been extended to other inhibitors. It is most reliable where large values for maximum extinction coefficients are encountered. The wave lengths which were used for analyses for certain of these inhibitors in polymers are shown in Table V.

CONCLUSION

A spectrophotometric method of analysis for inhibitors in polymers has been developed. This method corrects for background absorption and has been found to be rapid and more reliable than chemical methods of analyses which were investigated.

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Analysis of Binary Mixtures of Normal Aliphatic Dibasic Acids and Esters[1]

Use of Composition–Melting Point Relations of the Acids

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An empirical method is presented for determining the melting ranges of fused and quenched samples of dibasic acid mixtures. Application to binary mixtures of alternate and adjacent acids containing six to twelve carbon atoms reveals that compositions may be determined within 1 to 5%, depending on the composition of the sample. Approximate data on eutectic temperatures of the systems are included.

MIXTURES of similar dibasic acids often occur in oxidation products from unsaturated fatty acids, and existing methods for their separation and analysis are somewhat unsatisfactory. Crystallizations yield, with difficulty, only small proportions of pure components. The precision of saponification or neutralization equivalent determinations is limited by the 7-unit difference in equivalent weights of adjacent dibasic homologs. Vacuum fractionation of esters gives perhaps the most effective separation, but boiling points of adjacent esters are rather close, and intermediate fractions inevitably remain. Additional composition-property data are desirable for corroborative purposes.

The results of Gantter and Hell (*1*) for melting points of binary mixtures of suberic and azelaic acids indicated that this property might prove useful. The data, though irregular, showed that a marked melting point depression occurred in the system, and hence a considerable range of values was available. The lack of further published information for similar systems appears traceable to the fact that powdered binary mixtures of dibasic acids frequently melt over wide temperature ranges without distinct relation to composition.

An empirical method has now been developed for taking melting points which provides results closely related to composition and affords its determination within a few per cent. This method has been applied to the systems comprising adjacent and alternate pairs of acids containing six to twelve carbon atoms.

PREPARATION OF SAMPLES

Acids used are presented in Table I. One-gram samples of mixtures were prepared by weighing the component acids to 0.2 mg., bringing the mixtures to complete fusion, stirring them during cooling, and powdering the solidified material in a mortar. Portions were introduced into capillary tubes 1.0 to 1.5 mm. in diameter and liquefied by holding the tubes in a stirred and rapidly heated oil bath. Air bubbles, which frequently developed, were dislodged by momentarily removing the tubes and shaking them sharply as with a clinical thermometer. The melted samples were quenched by quickly transferring the capillary tubes to a stream of tap water. Quenched samples were 3 to 5 mm. in height. Approximate melting ranges were observed during the fusion process and allow rapid temperature adjustment in taking the final measurements.

Table I. Dibasic Acids Used for Binary Mixtures

No. of Carbon Atoms	Acid	Capillary M. P., ° C.	Source
6	Adipic	152.0	Eastman product as received
7	Pimelic	103.8–104.3	
8	Suberic	141.4–141.9	Prepared from castor oil acids by oxidation with nitric acid
9	Azelaic	106.6–107.0	
10	[Sebacic	132.8–133.1	Eastman product, recrystallized
11	1,11-Undecanedioic	110.3–110.8	From 12-hydroxystearic acid by method of Hall and Reid (*2*)
12	1,12-Dodecanedioic	128.7–129.0	

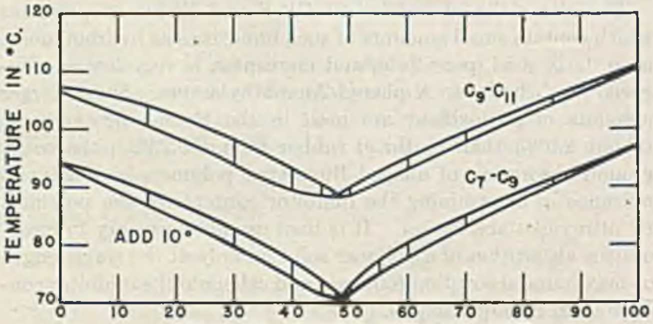

Figure 1. Composition–Melting Point Curves for Binary Mixtures of Odd-Carbon Dibasic Acids

Temperature scale to be shifted as indicated for individual curves

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[1] Second article on this subject appears on page 541.

[2] Present address, F. E. Booth Co., Emeryville, Calif.

Table II. Melting Ranges of Binary Mixtures of Alternate Dibasic Acids

Weight % of Higher Molecular Weight Acid	Odd-Odd		Even-Even		
	$C_7 + C_9$	$C_9 + C_{11}$	$C_6 + C_8$	$C_8 + C_{10}$	$C_{10} + C_{12}$
0	103.8-104.3	106.6-107.0	152.0	141.4-141.9	132.8-133.1
5	101.4-103.1	104.6-106.7	149.4-150.8	139.3-140.5	131.0-132.7
10	99.2-101.4	102.4-105.7	147.1-149.5	137.0-138.8	129.0-131.9
15	97.1- 99.6	100.4-104.1	144.3-147.9	134.2-136.9	127.0-130.9
20	94.5- 97.5	98.4-102.4	141.9-146.2	132.0-134.9	124.9-129.8
25	92.2- 94.9	96.3-100.4	139.5-144.3	129.3-132.7	122.8-128.4
30	89.5- 92.7	94.1- 98.2	136.8-142.1	126.5-130.4	120.6-126.6
35	87.0- 90.0	91.7- 95.9	134.0-139.8	123.7-127.7	117.8-123.6
40	84.3- 87.4	89.4- 93.4	131.1-137.4	120.4-124.6	115.0-120.1
45	81.3- 84.1	88.4- 90.6	127.5-133.8	117.5-120.6	113.1-116.0
50	81.3- 82.5	88.5- 89.7	122.8-129.2	114.5-116.1	112.0-112.7
55	84.9- 87.2	90.7- 92.7	120.0-124.1	112.8-113.7	111.6-112.5
60	87.8- 90.1	93.1- 95.1	119.3-119.7	113.0-114.0	112.3-113.7
65	90.4- 92.6	95.4- 97.4	119.8-120.1	115.3-117.2	114.0-116.8
70	93.0- 94.8	97.7- 99.3	122.2-124.1	118.6-121.6	116.9-120.3
75	95.4- 97.0	99.8-101.4	124.9-128.5	121.2-124.8	119.2-122.9
80	97.9- 99.2	102.0-103.2	127.7-131.9	123.8-127.4	121.2-124.7
85	100.2-101.4	104.1-105.2	130.5-134.8	126.0-129.5	122.0-125.9
90	102.5-103.4	106.1-107.0	133.4-137.8	128.5-131.2	124.9-127.2
95	104.6-105.3	108.2-108.9	137.3-140.2	130.6-132.3	126.8-128.2
100	106.6-107.0	110.3-110.8	141.4-141.9	132.8-133.1	128.7-129.0

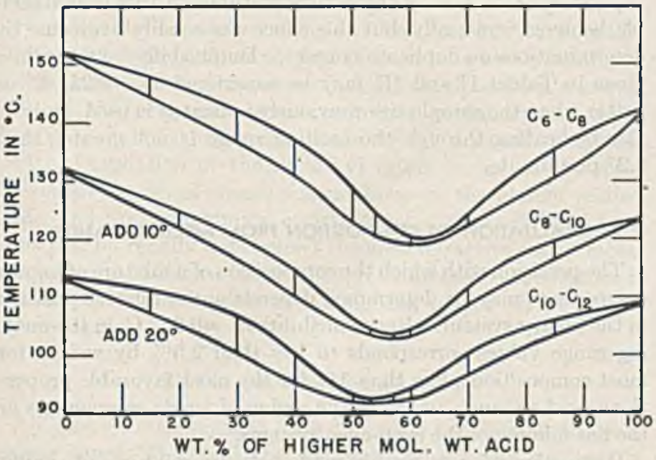

Figure 2. Composition-Melting Point Curves for Binary Mixtures of Even-Carbon Dibasic Acids

Temperature scale to be shifted as indicated for individual curves

DETERMINATION OF MELTING RANGE

Melting ranges were determined in an electrically heated (*7*), mechanically stirred oil bath. The rate of heating was closely controlled by a variable-voltage transformer. Temperatures were read on a 76-mm. immersion thermometer calibrated in degrees and compared with thermometers having calibrations checked by the National Bureau of Standards. Samples were placed next to the bulb of the thermometer and observed through a magnifier while under transverse illumination. Bath temperatures were brought rapidly (3° to 5° per minute) to a few degrees below the expected melting range, and thereafter increased at not over 0.2° C. per minute. The melting range was recorded from the first appearance of clear liquid to the disappearance of the last solid particle. Clear liquid first appeared as a partial meniscus in most cases, though mixtures which were predominantly one-component sometimes began to melt at other peripheral locations. The lower curves shown in the graphs for the individual systems represent empirically reproducible temperatures for the first appearance of clear liquid, and should not be confused with the solidus curves of binary systems having continuous series of solid solutions.

EUTECTIC PHENOMENA

A marked change occurred in the gross appearance of the quenched samples at temperatures below the melting points for all mixtures in a wide central portion of the composition range. The hard waxy surface assumed a soft matte appearance. The temperature of this phenomenon—as observed during the initial rapid heating—was constant within 2° or 3° for all compositions of a binary system that were not grossly crystalline after quenching. The temperatures varied from system to system as shown in Table IV. Microscopical observations showed that the phenomenon actually consisted in the melting of an eutectic mixture.

The occurrence of a constant eutectic temperature over a portion of the composition range apparently places the binary systems in the class characterized by formation of solid solutions of limited solubility (Roozeboom's Type V).

The differences between these eutectic temperatures and those obtained from "thaw-point" (*5*, *6*) measurements (in which the first apparent changes are observed in powdered samples) probably result from the intentional disturbance of equilibria by quenching. The difference between the eutectic temperatures and the melting ranges of the eutectic compositions obtained from the graphs (Table IV) may be partially due to measurement of different stages of melting, but it is more likely that polymorphism of the acids is involved. For example, in the suberic-azelaic system it was found that the melting range at the eutectic composition was 96.7–97.7° C. by the graphical procedure, but the eutectic temperature over a range of compositions was 91.5–92.5° C. by thaw-point measurement or 94–95° C. by heating fused samples slowly. Kofler (*4*) has shown that suberic acid can exist in three forms, and he reported that the transition from Form I to Form III is enantiotropic, occurs at about 90° C., and is very susceptible to superheating or supercooling. Azelaic acid has also been shown to be at least dimorphic. Polymorphism would likely be encountered in binary mixtures of these acids, especially in connection with intentional departures from equilibrium conditions. These phenomena have not been studied further.

COMPOSITION-MELTING POINT DATA

Systems investigated comprise four classes: with (*a*) alternate, even-carbon acids; (*b*) alternate, odd-carbon acids; (*c*) adjacent acids, with the odd-carbon member of higher molecular weight;

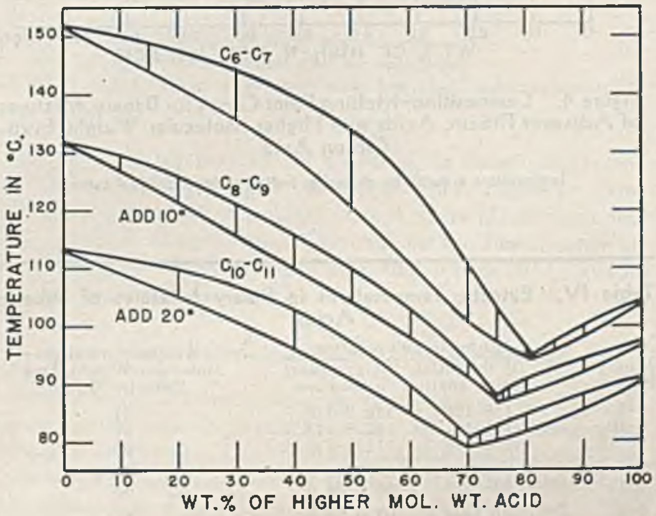

Figure 3. Composition-Melting Point Curves for Binary Mixtures of Adjacent Dibasic Acids with Higher Molecular Weight Odd-Carbon Acid

Temperature scale to be shifted as indicated for individual curves

Table III. Melting Ranges of Binary Mixtures of Adjacent Dibasic Acids

Weight % of Higher Molecular Weight Acid	Odd-Carbon Acid of Higher Molecular Weight			Even-Carbon Acid of Higher Molecular Weight		
	$C_6 + C_7$	$C_8 + C_9$	$C_{10} + C_{11}$	$C_7 + C_8$	$C_9 + C_{10}$	$C_{11} + C_{12}$
0	152.0	141.4-141.9	132.8-133.1	103.8-104.3	106.6-107.0	110.3-110.8
5	149.2-150.9	139.0-140.8	131.0-132.6	100.8-103.6	104.3-105.9	108.3-110.2
10	146.5-149.8	136.7-139.5	129.0-131.8	98.2-102.2	102.2-104.6	106.2-109.3
15	143.8-148.8	133.8-137.8	126.9-130.8	95.8-100.6	100.1-103.1	104.0-108.0
20	141.2-147.5	131.0-135.9	124.8-129.7	94.0- 98.2	98.2-101.3	102.2-106.0
25	138.5-145.8	128.2-133.7	122.7-128.4	93.2- 93.6	96.8- 98.8	101.2-103.6
30	135.7-144.1	125.4-131.0	120.5-126.8	95.2-102.3	96.7- 98.2	100.8-101.6
35	132.5-142.2	122.6-128.4	118.4-124.9	98.4-107.0	99.1-102.5	103.0-105.2
40	129.2-139.8	119.8-125.5	116.3-122.7	102.1-111.1	102.2-106.2	105.2-108.5
45	124.8-137.2	116.8-122.7	113.7-120.0	105.8-114.8	105.2-109.7	107.5-111.6
50	120.5-134.0	113.8-119.7	110.9-117.0	109.3-118.2	108.1-112.9	109.7-114.3
55	115.6-130.3	110.8-116.7	108.0-113.8	112.9-121.3	111.1-115.8	111.8-116.3
60	110.7-124.8	107.7-113.0	104.7-109.9	116.0-124.4	114.0-118.6	114.1-118.2
65	105.6-118.3	104.4-108.7	101.8-105.6	119.2-127.5	116.7-121.2	116.1-119.8
70	100.7-111.1	100.7-103.3	99.0-100.4	122.4-130.2	119.3-123.7	118.2-121.3
75	97.1-103.3	96.7- 97.7	100.2-102.5	125.5-132.7	121.8-126.0	120.0-122.8
80	94.5- 96.1	98.4-100.7	101.8-104.4	128.5-135.1	124.2-128.0	121.9-124.2
85	95.9- 97.0	100.1-102.5	103.5-106.2	131.5-137.2	126.4-129.8	123.8-125.7
90	98.4- 99.9	102.1-104.1	105.4-108.0	134.8-139.0	128.6-131.3	125.7-127.0
95	101.1-102.3	104.2-105.6	107.6-109.5	138.1-140.5	130.8-132.4	127.4-128.2
100	103.8-104.3	106.6-107.0	110.3-110.8	141.4-141.9	132.8-133.1	128.7-129.0

and (*d*) adjacent acids, with the even-carbon one higher. The data obtained are presented graphically in Figures 1 to 4, in which the vertical lines between the curves represent the actual determinations. Melting ranges taken from the graphs at composition intervals of 5% by weight are given in Tables II and III. Approximate eutectic compositions and temperatures from the graphs are collected in Table IV.

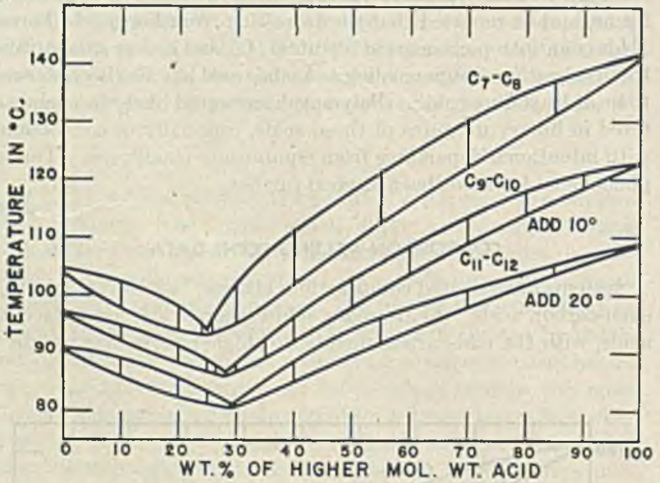

Figure 4. Composition–Melting Point Curves for Binary Mixtures of Adjacent Dibasic Acids with Higher Molecular Weight Even-Carbon Acid

Temperature scale to be shifted as indicated for individual curves

Table IV. Eutectic Temperatures in Binary Mixtures of Dibasic Acids

Binary System	Eutectic Temperature		Weight % of Higher Molecular-Weight Acid in Eutectic Mixture
	By transition during heating	By graphical estimation	
6–8	118–120	119.3–119.7	61
8–10	105–107.5	112.8–113.5	57
10–12	106–108.5	111.6–112.2	53
7–9	78.5–80.5	80.7–81.0	48.5
9–11	82–84.5	88.0–88.5	48
6–7	91.5–94	94.3–94.7	81
8–9	94–95	96.7–97.7	75
10–11	95–98.5	99.0–100.4	70
7–8	91–93	93.2–93.6	25
9–10	92–94.5	96.1–96.8	28
11–12	97.5–100	100.6–101.2	29.5

The eutectic temperatures fall into three groups: (*a*) below 90° for two odd-carbon acids; (*b*) above 110° for two even-carbon acids; and (*c*) between 90° and 105° for adjacent acids. The positions of the eutectics occur on the side of the lower-melting component, and tend to approach a central location as the acids become more nearly alike.

REPRODUCIBILITY OF THE DATA

Melting ranges determined by a single observer on successive samples usually check to ±0.1–0.2° C., and are frequently within 0.1° C. for the upper limit. Three different observers have consistently agreed to ±0.2–0.3° C. for the lower and ±0.1–0.2° C. for the higher temperature. An occasional sample behaved erratically, but this effect was readily overcome by determinations on duplicate samples. Duplicability of the values given in Tables II and III may be considered as ±0.25° C. or better when the sample size previously indicated is used, and the rate of heating through the melting range is not greater than 0.2° per minute.

EVALUATION OF COMPOSITION FROM MELTING RANGE

The precision with which the composition of a mixture of known components may be determined depends on its relative position in the binary system. Reproducibility of ±0.25° C. in the melting range values corresponds to less than 2.5% by weight for most compositions, less than 1% for the most favorable proportions, and as much as 5% in the region of single components or the flat minima of the even-even systems.

Distinction may be readily made between mixtures of similar melting ranges lying on opposite branches of the curve in a known binary system. When the components of a mixture are not definitely known, the possibilities will generally be limited to a very few by the previous history of the material. The approximate eutectic temperature may aid in classifying the mixture, for the two types of alternate-acid systems are usually distinguishable from each other and from those comprised of adjacent acids. Additional evidence obtained from the refractive index (*3*) and saponification equivalent of the methyl esters or neutralization equivalent of the acids will in most cases permit recognition of the components and composition of the mixture. Corroboration may be had by redetermination of the melting range after addition of a significant proportion of one of the pure components.

ACKNOWLEDGMENT

The writers acknowledge the assistance of F. T. Jones, who made the microscopical examination of representative acid mixtures, and of Julia S. Furlow, who checked many of the melting points and eutectic temperatures.

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Use of Refractive Indices of Dimethyl Esters

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Measurements on purified dimethyl esters of dibasic acids having from six to twelve carbon atoms show that their refractive indices bear linear relations to change in temperature and to weight percentage of the composition of binary mixtures. A change of 0.0001 index unit corresponds to 3 to 6% change in composition of the mixtures, thus approaching by a simple and rapid measurement the accuracy obtainable by saponification equivalent determinations.

MEASUREMENT of refractive index presents a convenient and rapid means for following the progress of a fractional distillation, and extends the information furnished by the observed distillation temperatures. When careful fractionation yields only single components and intermediate binary mixtures, a close estimate of composition may be obtained from a knowledge of the composition-index relations of binary mixtures. This procedure is nicely applicable in the analysis of dibasic acids. Distillation of the dimethyl esters is one of the most satisfactory ways of separating mixtures of the closely related acids, and the approximate compositions of the individual fractions can be readily determined through refractive index measurements, as is shown in this paper. Further corroboration is possible by determination of the melting ranges (*3*) of the recovered acids.

PREPARATION OF METHYL ESTERS

All esters were prepared from the acids reported in the preceding paper (*3*) except the C_{12} ester, which was fractionally crystallized from an original methyl ester distillation fraction. Properties of the esters are presented in Table I.

Table I. Properties of Esters Used in This Investigation

No. of Carbon Atoms in Acid	Boiling Point of Ester, ° C.	Melting Point of Ester, ° C.	
		This work	Literature values
6	71.4– 72.0 (0.2 mm.)	...	...
8	114.0–114.4 (4.7 mm.)	...	...
9	128.0–128.7 (5.2 mm.)	...	...
10	141.9–142.2 (6.0 mm.)	26	26.4 (*4*)
11	123.0–124.5 (2 mm.)	17	20.3 (*7*)
12	...	30.9–31.3	31 (*2*)

MEASUREMENT OF REFRACTIVE INDEX

Measurement of refractive index was performed with an Abbe-type refractometer which could be read to 0.0001 index unit. Temperatures reported for index readings were controlled to ±0.05° C. by rapid circulation of water from a constant-temperature bath through the prism jackets of the refractometer. All determinations were made on esters which had been freshly distilled or stored under reduced pressure to avoid errors caused by dissolved gases.

TEMPERATURE-INDEX RELATIONSHIPS

Indices were measured at 5° intervals in the range from 25° to 50° C. for all temperatures at which the esters were liquid. The expected straight-line relationships were found, and are expressed by the following equations, in which t represents degrees Centigrade:

Dimethyl adipate	$n_D^t = 1.4205 - 0.00040_5(t - 40)$
Dimethyl suberate	$n_D^t = 1.4262 - 0.00039_5(t - 40)$
Dimethyl azelate	$n_D^t = 1.4284 - 0.00039_5(t - 40)$
Dimethyl sebacate	$n_D^t = 1.4307 - 0.00039(t - 40)$
Dimethyl 1,11-undecanedioate	$n_D^t = 1.4329 - 0.00038_5(t - 40)$
Dimethyl 1,12-dodecanedioate	$n_D^t = 1.4345 - 0.00038(t - 40)$

The index values are in agreement with those given by Karvonen (*4*), and the temperature increments are of the same magnitudes as those found by Mattil and Longenecker (*5*) for monobasic methyl esters and for synthetic glycerides.

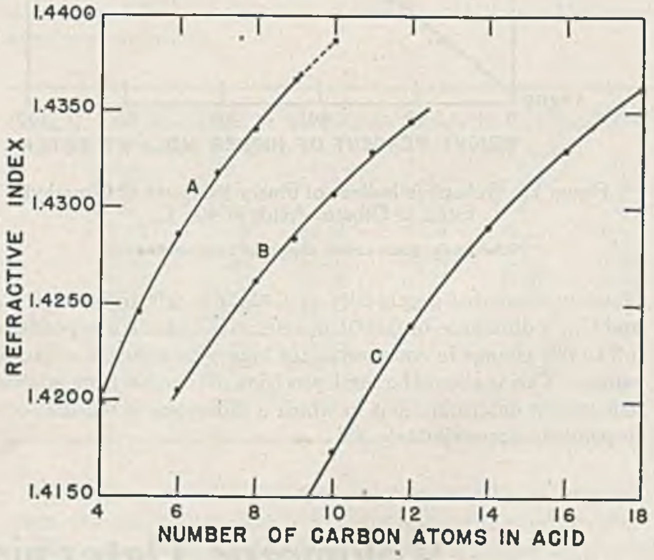

Figure 1. Refractive Indices of Methyl Esters of Normal Monobasic and Dibasic Aliphatic Acids

A. $N_D^{20.0}$ of dimethyl esters of dibasic acids, from Karvonen (*4*)
B. $N_D^{40.0}$ of dimethyl esters of dibasic acids, this investigation
C. $N_D^{40.0}$ of methyl esters of monobasic acids, from Mattil and Longenecker (*5*)

For any single temperature the indices of the homologous esters are represented by a smooth curve as shown in Figure 1. Corresponding indices for monobasic methyl esters (*5*) are included for comparison, as are those of Karvonen for the dibasic esters at 20° C. (value for methyl sebacate is calculated from 28° C. by the equation presented above).

COMPOSITION-INDEX RELATIONSHIP IN BINARY MIXTURES

Several series of binary mixtures were prepared which represented various possible types, and their refractive indices were measured at 40° C. The composition-index relation could be represented by a straight line in all cases when the composition was expressed as weight percentages, as shown in Figure 2. The relation was nonlinear for molecular percentages. Here again the results are in accord with those of Mattil and Longenecker for monobasic methyl esters.

As the difference in indices of adjacent homologous esters varies from about 0.0030 between C_6 and C_7 ($n_D^{40.0}$ for dimethyl

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[1] Second article in series; first appears on page 538.

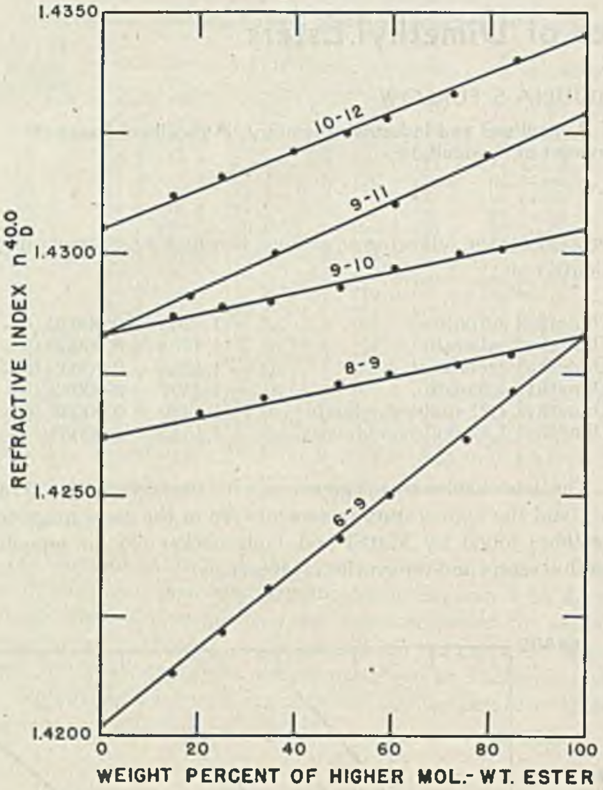

Figure 2. Refractive Indices of Binary Mixtures of Dimethyl Esters of Dibasic Acids at 40° C.

Numbers designate carbon content of component acids

pimelate estimated graphically as 1.4235) to 0.0016 between C_{11} and C_{12}, a difference of 0.0001 in refractive index corresponds to a 3 to 6% change in composition in binary mixtures of adjacent esters. This is about the same precision obtainable from equivalent weight determinations in which a difference of 0.2 unit corresponds to approximately 3%.

INTERFERENCES

One possible source of error is the presence of dissolved gases. If the liquid dimethyl esters are exposed to the atmosphere, the refractive index will drop several fourth-place units over a period of a day or so. Original values can be obtained following redistillation or degassing, but are not achieved by the use of desiccants. This type of error can be avoided readily by making index determinations promptly after distillations, or by storing the liquid esters at reduced pressures.

Methyl esters of monobasic acids such as myristic or palmitic may be present in products from oxidative cleavage (*1*) of unsaturated acids from various sources, although they would normally be removed by partitions prior to analysis of the dibasic acids. If any remained, they would interfere with the determination of composition by means of refractive index. Methyl myristate, for example, distills (*6*) in the temperature range between dimethyl sebacate and undecanedioate, but has a refractive index almost as low as dimethyl azelate (Figure 1). In such a case the calculated composition would indicate too large a proportion of the lower molecular-weight component. However, the apparent composition derived from determination of the saponification equivalent would be in error in the opposite direction. Accordingly, agreement between the results obtained by the two methods would confirm the absence of monobasic esters and enhance the validity of the analysis.

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Volumetric Determination of Magnesium in Magnesium Carbonate Ores

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IN DETERMINING the magnesium content of carbonates, many investigators have used a measured excess of standard alkali to precipitate magnesium hydroxide and have determined the excess with a standard acid. The outstanding difference in the methods is in the indicators used: Kolthoff (*3*) used phenolphthalein and dimethyl yellow; Pierce and Geiger (*5*) used trinitrobenzene and bromophenol blue; and Willstätter and Waldschmidt-Leitz (*7*) used thymolphthalein. Most of the methods employed more than one indicator and specified the use of carbonate-free standard alkali solution. In many investigations the emphasis seemed to be on the saving of time rather than a high degree of accuracy.

The chief objectives of this investigation were (1) to develop an accurate routine method for the volumetric determination of magnesium that could be carried out in a reasonable length of time and would not require carbonate-free standard alkali, and (2) to find a single indicator that could be used for all the neutralizations required in the procedure.

THEORETICAL

In selecting a single indicator for this investigation two conditions had to be satisfied: The iron and aluminum, which are the most common impurities found in carbonate ores, should be completely precipitated as the insoluble hydroxides at the end point, and the indicator should show the true equivalence point when standard alkali which contains carbonates is neutralized by standard acids.

Blum (*1*) states that the precipitation of aluminum hydroxide begins at pH 3 and is complete at or before pH 7 and recommends the use of methyl red as the indicator. Since ferric hydroxide is completely precipitated under the same conditions, aluminum and iron can be removed quantitatively at the methyl red end point. There should be no postprecipitation of magnesium hydroxide if the neutralization is carefully carried out.

At the methyl orange end point (pH 4) the absorption of carbon dioxide shows no decrease in the effective normality of a standard alkali solution (*6*); therefore, methyl red (pH 4.2 to 6.3) should

Table I. Effect of Calcium

	Gravimetric Pyrophosphate Method, Prepared MgO	Proposed Volumetric Method	
		Prepared MgO	Prepared MgO + $CaCO_3$
	%	%	%
1	98.15	98.36	98.36
2	97.93	98.05	98.36
3	98.44	98.36	98.05
4	98.67	98.36	98.05
5	...	98.05	98.05
6	...	98.36	98.36
7	...	98.05	98.36
8	...	98.05	98.36
Av.	98.30	98.20	98.24

show the true equivalence point when 0.5 *N* sodium hydroxide which contains carbonate is titrated with a standard acid.

Manganese, which is often found as an impurity in carbonate ores, is not precipitated as manganous hydroxide at the methyl red end point and could be oxidized to insoluble manganese dioxide by sodium peroxide in alkaline solution.

Time could be saved by decomposing and fuming the ore with sulfuric acid. This would dehydrate the silica and remove excess calcium as insoluble calcium sulfate.

EXPERIMENTAL

Using methyl red as the indicator, the acid titer of 0.5 *N* carbonate-free sodium hydroxide solution was determined before and after air was drawn through the alkali for 10 hours. There was no appreciable change in the titer, indicating that methyl red would show the true equivalence point when carbonates are present in 0.5 *N* sodium hydroxide solution. A double indicator titration (phenolphthalein and methyl red) showed that 0.4 mg. of carbon dioxide had been absorbed per milliliter.

To determine the accuracy of the proposed method the purity of some prepared calcium-free magnesium oxide was determined. The oxide was prepared by igniting magnesium nitrate, C.P., Baker's analyzed, which had been recrystallized from water five times. No calcium was found in the final product.

The purity of the prepared magnesium oxide was determined gravimetrically by the conventional pyrophosphate method (*2*) and volumetrically by the proposed procedure, using 0.200-gram samples. To study the effect of calcium the volumetric determinations were repeated, using mixtures of 0.200 gram of prepared magnesium oxide and 0.200 gram of precipitated calcium carbonate (Table I).

The method was then used on Bureau of Standards samples 1A, 88, and 104, and three limestone samples from Thorn Smith, Detroit, Mich. Since Bureau of Standards sample 104, burned magnesite, showed a high magnesium oxide content, a 0.100-gram sample was used. The results of these determinations are recorded in Table II.

SPECIAL REAGENTS

Sodium hydroxide solution, 0.50 *N* standardized by using sulfamic acid, LaMotte, as the primary standard (*6*) and 1% methyl red solution as the indicator.

Sulfuric acid solution, 0.25 *N* standardized using 0.50 *N* sodium hydroxide solution.

Methyl red indicator solution (*4*), 1%.

PROCEDURE

Weigh into a beaker 0.500 gram of the carbonate ore and cover it with water. Slowly add 10 ml. of 6 *N* sulfuric acid, boil until the ore is decomposed, and carefully evaporate until all the sulfuric acid has been expelled. Take up the residue in about 25 ml. of hot water, boil for 2 or 3 minutes to ensure complete solution of all soluble salts, and filter, washing the residue four or five times with hot water. This residue is composed of acid-insoluble substances such as silica and calcium sulfate. Dilute the filtrate to about 100 ml., neutralize with 6 *N* sodium hydroxide, and add about 0.5 gram of sodium peroxide with stirring. Boil for about 20 minutes or until the excess sodium peroxide is removed. (If manganese is not present in the ore, the peroxide treatment may be omitted.) Acidify with 6 *N* sulfuric acid and boil for a few minutes to ensure the complete solution of all salts. Add 3 or 4 drops of 1% methyl red indicator solution and carefully adjust the acidity to the methyl red end point, using 0.50 *N* sodium hydroxide and 0.25 *N* sulfuric acid. Boil for a few minutes and filter into a 250-ml. volumetric flask, washing the residue of insoluble hydroxides four or five times with hot water. Just acidify the filtrate with 0.25 *N* sulfuric acid and add exactly 25 ml. of 0.50 *N* sodium hydroxide. After thorough mixing, cool the contents of the flask to room temperature, dilute to exactly 250 ml., and pour into a large beaker.

After the precipitate of magnesium hydroxide has settled (20 to 30 minutes), decant the supernatant liquid through a quantitative filter into a 250-ml. volumetric flask containing 50 ml. of distilled water until the total volume is exactly 250 ml. Transfer the solution to a large beaker, add one drop of methyl red solution, and titrate with 0.25 *N* sulfuric acid to the end point. The titration can be speeded up by adding a drop of phenolphthalein solution before the final titration is made: At the phenolphthalein end point the color change is from red to yellow, occurring 10 to 15 drops from the methyl red end point.

DISCUSSION

The results in Table I show that the volumetric values are consistent and the average is in good agreement with that obtained for the pyrophosphate gravimetric determinations. The maximum difference was 0.74% in the four pyrophosphate determinations and 0.31% in the eight volumetric determinations. Appreciable amounts of calcium had no effect on the determinations.

The values for the ore determinations also show good consistency and the averages are comparable with the certified magnesium oxide values.

Table II. Determination of Magnesium Oxide in Carbonate Ores

	Bureau of Standards			Thorn Smith		
	1A (2.19%)	88 (21.48%)	104 (85.67%)	1 (11.64%)	2 (13.27%)	3 (14.14%)
	%	%	%	%	%	%
1	2.19	21.38	85.00	11.75	13.31	14.25
2	2.19	21.44	85.62	11.69	13.31	14.19
3	2.25	21.38	85.31	11.63	13.31	14.25
4	2.25	21.44	85.00	11.63	13.37	14.13
5	2.19	21.50	85.31	...	...	...
6	2.25	21.38	85.31	...	...	...
7	2.25	21.38	85.31	...	...	...
8	2.19	21.50	85.62	...	...	...
9	2.25	21.50	85.31	...	...	...
10	2.25	21.38	85.31	...	...	...
Av.	2.23	21.43	85.31	11.68	13.32	14.20

The differences can be attributed to unavoidable experimental error, for one drop of 0.25 *N* sulfuric acid corresponds to about 0.06% of magnesium oxide for a 0.500-gram sample of ore and about 0.31% for a 0.100-gram sample. The maximum difference in the Bureau of Standards determinations on the three ores was 0.29% for sample 104. The volumetric determinations showed a maximum difference of 0.62% for the same ore, but 0.100-gram samples were used which represented a difference of only 2 drops of 0.25 *N* sulfuric acid in obtaining the final end points.

Methyl red is the single indicator that is used for all the neutralizations throughout the procedure. As it shows the true equivalence point in the presence of carbonates, it is not necessary to use carbonate-free standard alkali for the determinations. Common impurities such as iron and aluminum are completely removed as the insoluble hydroxides at the methyl red end point.

Manganese can be removed by oxidizing it to the insoluble dioxide with sodium peroxide in alkaline solution.

The determination can be carried out in less than 4 hours, and the time is shortened if manganese is not present, since the peroxide treatment is not necessary. If the precipitate of magnesium hydroxide is small, the final filtration can be carried out without allowing the precipitate to settle, thus speeding up the determination. For samples of high magnesium content the same result can be accomplished by using samples smaller than 0.500 gram or by using aliquots of the solution obtained from a 0.500-gram sample; however, accuracy is sacrificed for speed. Time is also saved by using sulfuric acid to decompose the ore and dehydrate the silica.

SUMMARY

The proposed volumetric method for the determination of magnesium in carbonate ores involves removal of most of the calcium as the sulfate, precipitation of magnesium hydroxide with excess standard alkali, and titration of the excess with a standard acid. When methyl red is used as the indicator, 0.50 *N* sodium hydroxide solution that is not carbonate-free can be satisfactorily used. Any indicator having the same pH range as methyl red could be used, but methyl red was selected because it is used in many laboratories as an acid-base indicator. Common impurities such as iron and aluminum are removed as insoluble hydroxides at the methyl red end point and manganese can be removed by oxidizing it to insoluble manganese dioxide with alkali peroxide.

This method gives results that are comparable with those obtained with the conventional gravimetric pyrophosphate method. It does not require as much time as the pyrophosphate method and should be useful for the routine analysis of magnesium carbonate ores.

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Analysis of Oil-Soluble Petroleum Sulfonates

Extraction-Adsorption Method

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A relatively simple extraction-adsorption method for the analysis of oil-soluble petroleum sulfonates is described. The method is applicable to the analysis of sodium and other metal sulfonates and is free of lengthy operations and emulsion difficulties. Procedures are included for the determination of mineral oil, sulfonic acid soap, water, carboxylic acid soap, free alkali, and inorganic salts.

PETROLEUM sulfonic acids are produced by the treatment of petroleum distillates with sulfuric acid in refining processes or by the treatment of petroleum stocks with oleum in the manufacture of medicinal white oils. Some of the sulfonic acids formed remain in the oil layer, and the others are found dissolved in the acid layer. The former type is frequently referred to as "mahogany" acids, while the latter is termed "green" acids. Following the sulfonation process, the "acid oil" layer is separated from the sludge containing the water-soluble green acids and neutralized with caustic, and the crude mahogany soaps are extracted with dilute alcohol.

The crude mahogany soaps obtained in this manner consist principally of approximately equal quantities of sulfonic acid soaps and mineral oil, with minor amounts of water, carboxylic acid soaps, free alkali, and inorganic salts. For the purpose of evaluating these mixtures it is desirable to determine their compositions, particularly the sodium sulfonate contents. Archibald and Baldeschwieler (*2*) have described a procedure of analysis involving a rather tedious extraction of the mineral oil with petroleum ether from a suspension of the sample in 50% aqueous isopropyl alcohol. This procedure is very lengthy and does not include a method for determining carboxylic acid soap content. More recently, an adsorption method for separating and estimating the constituents has been described by Koch (*3*). This method involves separation of the sulfonate soaps from the mineral oil by passing a petroleum ether solution of the material through a column of Attapulgus clay. The mineral oil and petroleum ether pass through the clay, and the solution is collected, the petroleum ether evaporated, and the mineral oil weighed. The sulfonate soap is eluted from the clay with methanol and the weight obtained by evaporating the methanol from the resulting solution. This is very rapid but is not satisfactory when applied to materials containing appreciable quantities of water or inorganic salts. Experience in this laboratory has shown that the elution of the sulfonate soaps with methanol is incomplete, leading to low values for this component.

During 1944 an extensive program of cooperative testing of methods for the analysis of petroleum sulfonates was conducted by the A.S.T.M., as a result of which, a method has been proposed (*1*) which covers the determination of mineral oil, sodium sulfonate, carboxylate soap, inorganic salt, and free alkali contents, combining weight and specific gravity. The method involves multiple extractions of an aqueous isopropyl alcohol suspension of the sample with petroleum ether. The mineral oil passes into the petroleum ether phase and is thus isolated. The alcohol phase is then subjected to a number of rather lengthy manipulations to separate the sodium sulfonates and carboxylates from the remaining constituents. Although the method yields fairly accurate and precise data, the manipulations involved are both tedious and time-consuming; a complete analysis requires about 4 days.

In view of the recognized shortcomings of the A.S.T.M. and Archibald-Baldeschwieler methods with regard to time consumption, and Koch's adsorption method with regard to inapplicability in the presence of inorganic salts and water as well as incomplete recovery of the adsorbed sulfonates, an attempt has been made by the authors to devise a method of analysis which is free of these objections.

This paper presents a new method in which the sulfonic acids, carboxylic acids, and mineral oil are separated from the inorganic salts by extracting an acidified aqueous suspension of the sample with chloroform. The inorganic salt content is calculated from the sulfated residue obtained from the aqueous phase, making correction for the alkali residue contributed by the sulfonate, carboxylate, and free alkali. A portion of the residue obtained from the chloroform extract is titrated potentiometrically for strong and weak acids to determine the respective equivalents of sulfonic and carboxylic acids present. Another portion of the chloroform-soluble residue is neutralized and the mineral oil isolated by adsorbing the sulfonates and carboxylates on Attapulgus clay. A schematic diagram of this method of analysis is shown in Figure 1.

APPARATUS AND MATERIALS

The percolation apparatus of Koch has been modified somewhat to permit the use of pressure and subsequently a more rapid rate of flow through the adsorbent.

The modified percolator is shown in Figure 2. It was found that a pressure of 351 to 703 kg. per square meter (0.5 to 1 pound per square inch) forced the liquid through sufficiently rapidly. The adsorbent used was the same as that recommended by Koch (30- to 60-mesh Attapulgus clay which has been calcined at 487° C., obtained from the Attapulgus Clay Company, 260 South Broad St., Philadelphia, Pa.).

Inverted-rim beakers of the type described by the A.S.T.M. (*1*) were used for evaporations where there was danger of loss due to "creeping" over the sides.

The chloroform and petroleum ether used were of c.p. quality.

A Precision-Shell (*4*) titrometer was used for the electrometric titration of strong and weak acids.

PROCEDURE

Separation of Organic and Inorganic Constituents. Introduce approximately 10 grams of sample weighed to the nearest centigram into a 100-ml. beaker, add 25 ml. of chloroform, and stir to dissolve or disperse the sample.

Transfer quantitatively to a 250-ml. separatory funnel, rinsing the beaker and stirring rod with an additional 25 ml. of chloroform. Rinse the sampling beaker with 50 ml. of 6 N hydrochloric acid and add this solution to the separatory funnel. Shake the separatory funnel and contents vigorously, venting frequently. Rinse the sampling beaker with 50 ml. of acetone and add this to the separatory funnel. Mix intimately once more and allow the two phases to separate. Draw the chloroform extract (lower phase) into a weighed, inverted-rim beaker. Extract the aqueous phase three more times with 25-ml. portions of chloroform and combine the chloroform extracts in the inverted-rim beaker.

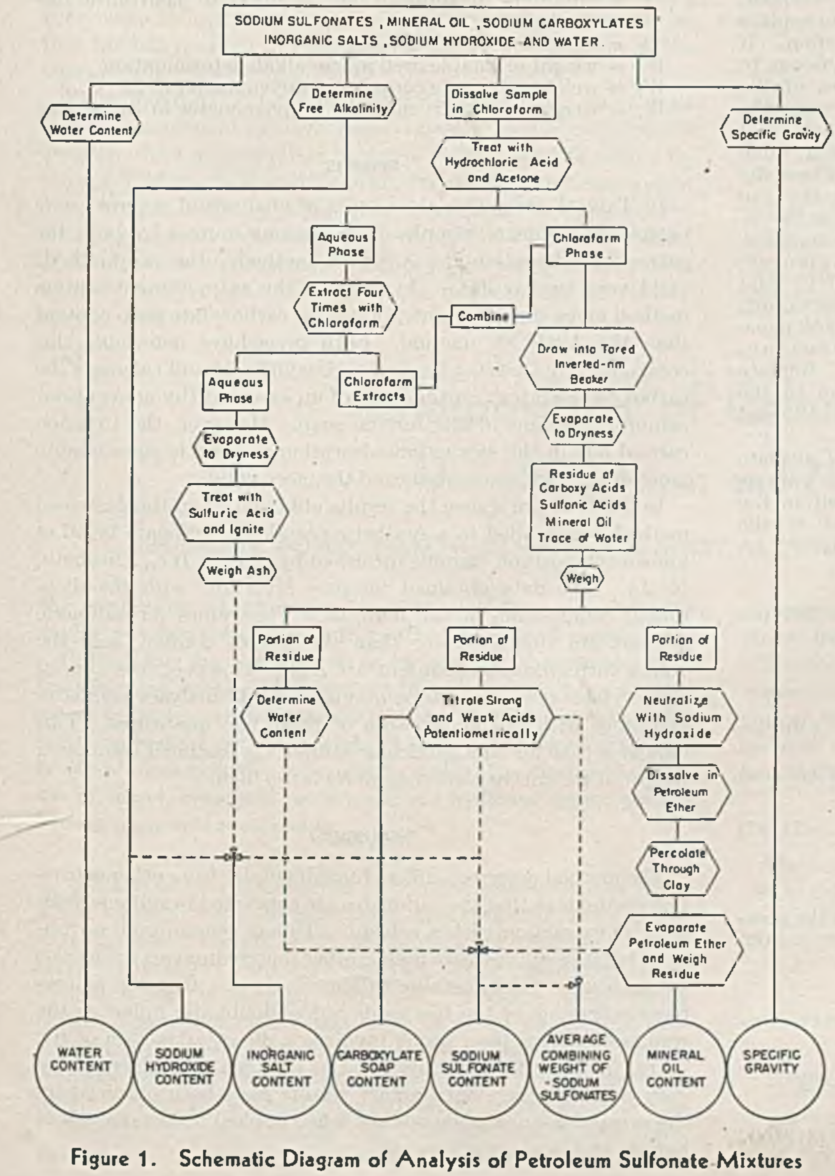

Figure 1. Schematic Diagram of Analysis of Petroleum Sulfonate Mixtures

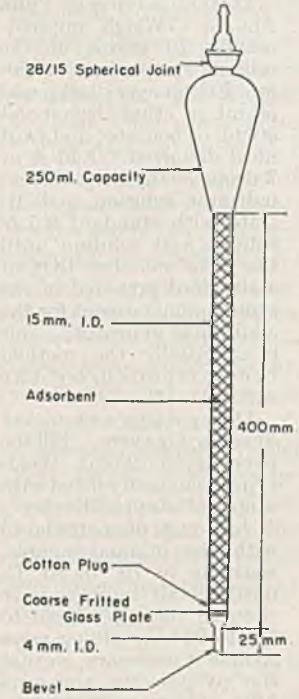

Figure 2. Special Pressure Adsorption Column

Evaporate the combined chloroform extracts to dryness on a steam bath, heating for 15 minutes after the disappearance of the odor of chloroform. Cool to room temperature and weigh the beaker and contents.

Determination of Free Salts. Draw the aqueous layer obtained above into a weighed, ignited platinum dish and evaporate to dryness on a steam bath. Add approximately 2 ml. of 36 N sulfuric acid and rotate the dish in such a manner as to moisten all the residue with the acid. Heat carefully (to prevent spitting) over a small flame until fuming ceases. Repeat this treatment with 1 ml. of sulfuric acid. When fuming ceases, heat in a muffle furnace at 800° ± 50° C. to constant weight.

Determination of Sulfonate and Carboxylate Soaps. Determine the number of equivalents of strong and weak acids present in 100 grams of the chloroform extract by electrometric titration (A.S.T.M. D664-44T) of an accurately weighed 1- to 2-gram sample. Also analyze this residue for water content by the Karl Fischer method. (Place 20 ml. of anhydrous pyridine and 10 ml. of anhydrous ethyl ether in a 100-ml. glass-stoppered volumetric flask and titrate to the red-brown Fischer end point. Weigh 0.5 to 1 gram of sample in a glass weighing boat, slide the boat into the flask, and swirl until the sample is completely dissolved. Titrate the solution with Fischer reagent to the original red-brown end point. For the preparation and standardization of the Fischer reagent, see A.S.T.M. procedure D268-44T, issued under the jurisdiction of Committee D-1.)

Determination of Mineral Oil. Weigh approximately 2 grams of the chloroform extract to the nearest milligram into a 100-ml. beaker. Add sufficient 0.5 N alcoholic sodium hydroxide solution to neutralize completely the strong and weak acids present (this volume is readily calculated from the data obtained by titration above), then add 0.1 ml. in excess. Evaporate the alcohol on a steam bath. Add 25 ml. of petroleum ether and stir to dissolve the sample completely. Transfer this solution quantitatively to the 250-ml. reservoir of the percolation apparatus (Figure 2), rinsing the beaker and stirring rod with an additional 25 ml. of petroleum ether. Apply a pressure of 0.5 to 1 pound per square inch at the top of the percolator and force the solution through the 40-cm. column of adsorbent clay. Force an additional 150 ml. of petroleum ether through the column in similar fashion. Collect the solution which passes through the clay in a weighed, inverted-rim beaker and evaporate to dryness on a steam bath, heating for 15 minutes after disappearance of the odor of petroleum ether. Heat for 15-minute intervals at 110° C. until the weight loss between successive heatings is less than 1 mg.

Determination of Water. Determine the water content of the original sample by A.S.T.M. Method D95-40 or, if the free alkali content is low, by the Karl Fischer method.

Table I. Comparison of Analyses by Extraction-Adsorption and A.S.T.M. Methods

Constituent	Sample A					Sample B				Sample C				Sample D		Sample E	
	Extraction-Adsorption Method				A.S.T.M. method	Extraction-Adsorption Method			A.S.T.M. method	Extraction-Adsorption Method			A.S.T.M. method	Extraction-adsorption method	A.S.T.M. method	Extraction-adsorption method	A.S.T.M. method
	Run 1	Run 2	Run 3	Av.		Run 1	Run 2	Av.		Run 1	Run 2	Av.					
Mineral oil, %	42.6	42.0	43.0	42.5	43.0	36.4	36.8	36.6	36.1	36.2	37.2	36.7	36.2	53.6	53.2	54.8	55.0
Sodium sulfonate, %	46.0	45.8	45.5	46.0	46.1	54.6	55.8	55.2	55.1	50.6	49.9	50.2	50.7	36.8	37.4	32.2	32.0
Sodium carboxylate, %	0.8	1.1	1.2	1.0	0.3	1.0	0.7	0.8	0.2	1.5	1.0	1.2	0.5	3.0	2.4	0.6	0.8
Sodium hydroxide, %	0.0	0.0	0.0	0.0	0.0	0.2	0.2	0.2	0.2	0.3	0.3	0.3	0.3	0.0	0.0	0.9	0.9
Water, %	4.0	4.0	4.0	4.0	4.0	6.1	6.1	6.1	6.1	7.8	7.8	7.8	7.8	5.3	5.3	7.0	7.0
Inorganic salts, %	7.0	6.8	7.0	7.0	7.3	1.6	1.4	1.5	1.3	3.4	3.6	3.5	4.4	2.4	2.5	4.0	4.5
Total, %	100.4	99.7	100.7	100.5	100.7	99.9	101.0	100.4	99.0	99.8	99.8	99.8	99.9	101.1	100.8	99.5	100.2
Combining weight of sodium sulfonate	487	474	471	477	470	571	531	551	542	560	543	552	566	473	493	413	416

DETERMINATION OF FREE ALKALI. Weigh approximately 10 grams of the original sample into a 250-ml. Erlenmeyer flask, add 50 ml. of ethyl alcohol and 50 ml. of benzene, and swirl until dissolved. Add 6 or 7 drops of thymolphthalein indicator solution and titrate with standard 0.5 N sulfuric acid solution until the color matches that of a standard prepared in the same manner except for the addition of indicator. This is essentially the method recommended by the A.S.T.M. (*1*).

DETERMINATION OF SPECIFIC GRAVITY. Fill the pycnometer (25-ml. Weld-type pycnometer fitted with a special stopper having a 4- to 5-mm. diameter bore) with the original sample, warming to 70° or 80° C. until all air bubbles have risen to the top. Cool to 15° to 20° C., adding more sample if necessary, so that the pycnometer remains full. Insert the stopper, pressing slowly into place with a turning motion. If the sample is too viscous to permit insertion of the stopper, carefully warm the neck of the pycnometer and the stopper with a small Bunsen burner. Place the pycnometer, with the cap in place, in a bath at 25° ± 0.1° C. After 25 minutes, remove the pycnometer, cool to 15° to 20° C., and remove any excess sample by wiping with a cloth moistened with a benzene-alcohol mixture. Replace the cap and weigh to the nearest milligram. Record the sample weight.

CALCULATION. Calculate the quantities of various components present in the sample by means of the following equations:

Mineral oil content, per cent $= \frac{(A)(D)(100)}{(C)(W)}$

Inorganic salt content, per cent =

$$\frac{(100)(B) - (71)(A)(E + e)}{W} - \frac{(71)(G)}{40}$$

(The value 71 is the combining weight of sodium sulfate.)

Sodium sulfonate content, per cent =

$$\frac{(A)(100 + 22E)}{W} - X - \frac{A}{W}[Y + (312)(e)]$$

(The numerical value 312 is the assumed average combining weight of the carboxylic acids. The value 22 converts from the strong acid to the sodium salt.)

Carboxylate soap content, per cent $= \frac{(A)(e)(334)}{W}$

(The value 334 is the assumed average combining weight of the carboxylate soaps.)

Combining weight of sodium sulfonate $= \frac{(F)(W)}{(A)(E)}$

Free alkali content, as sodium hydroxide, per cent $= \frac{(V)(N)(4.0)}{W_1}$

Specific gravity 25°/25° C. $= \frac{W_s}{W_c}$

where

A = weight of chloroform-soluble organic residue, grams
C = weight of organic residue used for mineral oil determination
D = weight of mineral oil found
W = weight of original sample taken for analysis
B = weight of sulfate ash obtained from aqueous residue
E = strong acids, equivalents per 100 grams of organic residue
e = weak acids, equivalents per 100 grams of organic residue
G = free alkali content, per cent
X = mineral oil content of sample, per cent
Y = water content of organic residue, per cent
F = sodium sulfonate content, per cent
V = milliliters of sulfuric acid required to neutralize free alkali
N = normality of sulfuric acid
W_1 = weight of sample used in free alkali determination
W_s = weight of sample contained in pycnometer at 25° C.
W_c = weight of water contained in pycnometer in calibrating

RESULTS

In Table I are shown the results of analyses of several crude petroleum sulfonate samples from various sources by both the extraction-adsorption and A.S.T.M. methods; the two methods yield very similar data. In general, the extraction-adsorption method gives slightly higher values for carboxylate soap content than the A.S.T.M. method. Both procedures determine this component by titrating the free carboxylic acid and calculate the carboxylate content on the basis of an assumed (by convention) combining weight of 334 for the soap. However, the titration carried out in the extraction-adsorption method is considerably more direct and hence is believed the more valid.

In Table II are shown the results obtained when the described method was applied to a synthetic petroleum sulfonate blend of known composition (sample furnished by Stanco, Inc., Elizabeth, N. J.). The data obtained compare favorably with the theoretical composition of the material. The values for sulfonate content are slightly lower than the known content, and the values for carboxylate content are high. However, the sum of carboxylate and sulfonate contents in both analyses compares favorably with the known sum of these two quantities. This indicates that for this particular sample the assumed combining weight of the carboxylate soap (334) is too high.

DISCUSSION

The method described differs fundamentally from other extraction methods in that the sulfonates are converted to sulfonic acids prior to extraction with a solvent. This is generally an advantage, because sulfonates of metals other than sodium may thus also be analyzed. Such metallic sulfonates do not alter the chloroform extraction of the free acids but undoubtedly influence the results of any method which involves a direct extraction of the soaps, in that the distribution ratios between the solvents may vary considerably. Satisfactory results have been obtained by the extraction-adsorption method when applied to the analysis of barium and calcium sulfonates.

Table II. Analysis of Synthetic Sulfonate Sample[a] by the Extraction-Adsorption Method

Constituent	Data Obtained Run 1	Run 2	Av.	Known Composition
Mineral oil, %	50.1	50.1	50.1	49.6
Sodium sulfonate, %	39.5	39.1	39.3	40.6
Sodium carboxylate, %	4.3	4.3	4.3	3.0
Sum of sulfonate and carboxylate, %	(43.8)	(43.4)	(43.6)	(43.6)
Sodium hydroxide, %	0.0	0.0	0.0	0.0
Water, %	3.9	3.9	3.9	3.6
Inorganic salts, %	3.3	3.2	3.2	3.1
Total analysis, %	101.0	100.6	100.8	99.9
Combining weight of sodium sulfonate	465	456	461	...

[a] Sample furnished by Stanco, Inc., Elizabeth, N. J.

Considerable difficulty with emulsion formation has resulted when other extraction methods have been used in analyzing petroleum sulfonate mixtures. The function of the acetone in the method described is to break the emulsion which forms between the chloroform and dilute acid layers. Isopropyl alcohol was tried first as a demulsifying agent and although it broke the emulsions quickly, the results were erroneous, owing to formation of sulfonic acid esters with the alcohol. For this reason a demulsifier was sought which was unreactive toward the free sulfonic acid and at the same time sufficiently volatile to be readily evaporated on a steam bath. Acetone fits these requirements very well; it has proved very satisfactory and in all instances thus far has resulted in instant and complete separation of the aqueous and chloroform phases.

By employing the chloroform extraction procedure, an analysis may be completed in 2 days' elapsed time. This is considerably less than the 4 days required in this laboratory for an analysis by the A.S.T.M. method, and there are fewer manipulations (weighings, extractions, etc.) than in the A.S.T.M. method, so the handling time per determination is appreciably less. In control analyses, where the combining weight of the sodium sulfonate is known from previous experience, the method may be further shortened by eliminating the adsorption step, calculating the sulfonate content directly from the strong acid titration of the chloroform-soluble residue, and obtaining the mineral oil content by difference. This is a distinct advantage over other extraction methods, which permit no such short-cut modifications.

The method described is inapplicable, without sacrificing accuracy, to the analysis of materials containing volatile oils. The composition of samples of this type can be approximated by application of the procedure described, elution of the sulfonates from the Attapulgus clay with methanol to recover the adsorbed sulfonates and carboxylates, and evaporation of the methanol to obtain the weight of sulfonate and carboxylate. The mineral oil content is then determined by difference. Generally this procedure leads to sulfonate values low by 0.5 to 2%, and mineral oil values high by a corresponding amount, owing to incomplete recovery of sulfonate from the clay.

Although chloroform extraction can be applied to green acid soaps as well as mahogany acid soaps, the chloroform extract from green acid soaps is insoluble in petroleum ether and hence the sulfonates and carboxylates cannot be separated from mineral oil by the adsorption procedure described. For this reason attempts to apply the method to green acid sulfonates have been unsuccessful.

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Composition of Cellulose Esters

Use of Equations and Nomographs

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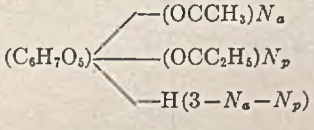
The composition of cellulose esters in terms of the number of ester groups per anhydroglucose unit may be determined readily from analytical data by calculations or by reading from nomographs. Equations and nomographs are given for cellulose acetates, propionates, butyrates, acetate propionates, and acetate butyrates. By either method the per cent acetyl and per cent propionyl or butyryl in any of these cellulose esters can be easily converted to the number of acetyl, propionyl, or butyryl, and hydroxyl groups per anhydroglucose unit or vice versa.

METHODS for the analysis of cellulose esters, such as those reported from this laboratory, give results in terms of per cent "apparent acetyl" (*2*, *6*), per cent acetyl, propionyl, or butyryl (*7*), and per cent hydroxyl (*5*). From the viewpoint of structural organic chemistry, however, it is desirable to express the composition of these esters in terms of the numbers of substituent groups per anhydroglucose unit. This information is required for certain calculations, such as that of unit molecular weight. Some equations for this purpose have been published by Gloor (*3*), by Malm, Genung, and Williams (*5*), and in a Navy specification (*8*). Simpler equations have been derived and are presented here for the cases of cellulose acetates, acetate propionates, and acetate butyrates.

Nomographs have been constructed by means of which this conversion from per cent acyl to number of groups per anhydroglucose unit of cellulose can be made very rapidly for the cases of cellulose acetates, propionates, butyrates, acetate propionates, and acetate butyrates.

EQUATIONS

The equations given below are based on the general formula for the anhydroglucose unit of a cellulose ester, such as an acetate propionate.



$$(C_6H_7O_5)\begin{cases}-(OCCH_3)N_a\\-(OCC_2H_5)N_p\\-H(3-N_a-N_p)\end{cases}$$

The following terminology is used:

a = weight per cent of acetyl
p = weight per cent of propionyl
b = weight per cent of butyryl

h = weight per cent of hydroxyl
N_a = number of acetyl groups per anhydroglucose unit
N_p = number of propionyl groups per anhydroglucose unit
N_b = number of butyryl groups per anhydroglucose unit
N_h = number of hydroxyl groups per anhydroglucose unit

and the unit molecular weight of a cellulose acetate propionate is

$$M.W. = 159 + 43N_a + 57N_p + 3 - N_a - N_p$$
$$= 162 + 42N_a + 56N_p \qquad (1)$$

These calculations assume only three replaceable hydroxyls per anhydroglucose unit. This assumption is valid for most ordinary cellulose esters. It is not strictly true in cases of very degraded and low-viscosity celluloses and their derivatives because the number of hydroxyl groups on the ends of the chains may be significant.

Case of Cellulose Acetate. Weight per cent acetyl, which may be found by analysis, is 100 times the weight of an acetyl group, 43, times the number of such groups, and divided by the unit molecular weight:

$$a = \frac{4300N_a}{162 + 42N_a} \qquad (2)$$

Solving Equation 2 for N_a gives

$$N_a = \frac{3.86a}{102.4 - a} \qquad (3)$$

$$N_h = 3 - N_a \text{ by assumption} \qquad (4)$$

$$h = \frac{1700(3 - N_a)}{162 + 42N_a} = \frac{1700N_h}{288 - 42N_h} \qquad (5)$$

Weight per cent acetyl and weight per cent hydroxyl can be converted readily one to the other using the equations:

$$h = \frac{44.8 - a}{1.42} \qquad (6)$$

$$a = 44.8 - 1.42h \qquad (7)$$

which were derived from Equations 5 and 3.

Case of Cellulose Acetate Propionate. Equations for weight per cent acetyl and propionyl are as follows:

$$a = \frac{4300N_a}{162 + 42N_a + 56N_p} \qquad (8)$$

$$p = \frac{5700N_p}{162 + 42N_a + 56N_p} \qquad (9)$$

Solving Equations 8 and 9 simultaneously gives:

$$N_a = \frac{3.86a}{102.4 - 1.006p - a} \qquad (10)$$

$$N_p = \frac{2.91p}{102.4 - 1.006p - a} \qquad (11)$$

$$N_h = 3 - N_a - N_p \text{ by assumption} \qquad (12)$$

$$h = \frac{1700N_h}{162 + 42N_a + 56N_p} \qquad (13)$$

The corresponding equations for cellulose propionates would obviously be Equation 9, omitting the term $42N_a$ in the denominator, Equation 11 omitting the a term, and Equations 12 and 13 omitting the N_a terms.

Case of Cellulose Acetate Butyrate. The equations for weight per cent acetyl and butyryl are:

$$a = \frac{4300N_a}{162 + 42N_a + 70N_b} \qquad (14)$$

$$b = \frac{7100N_b}{162 + 42N_a + 70N_b} \qquad (15)$$

Solving Equations 14 and 15 simultaneously gives:

$$N_a = \frac{3.86a}{102.4 - 1.009b - a} \qquad (16)$$

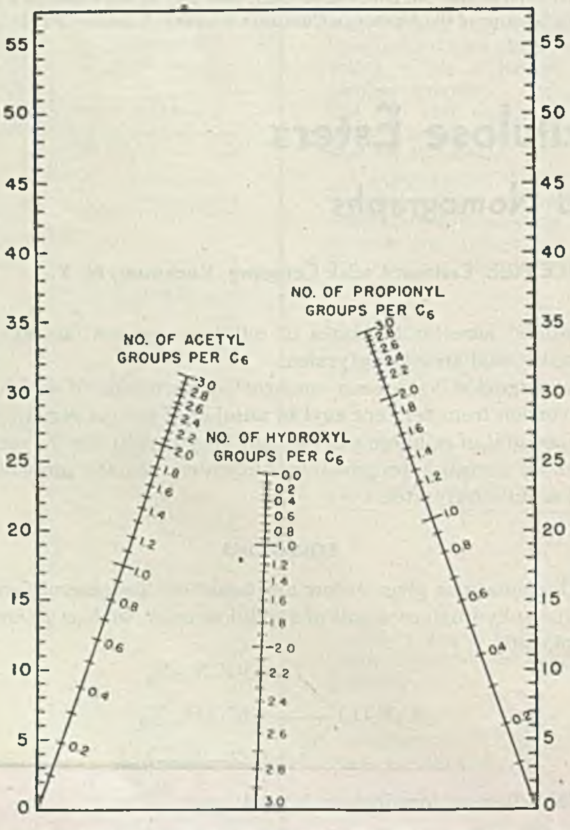


Figure 1. Nomograph for Converting Per Cent Acetyl and Per Cent Propionyl in Cellulose Acetate Propionate to Number of Acetyl and Propionyl Groups per Glucose Unit of Cellulose

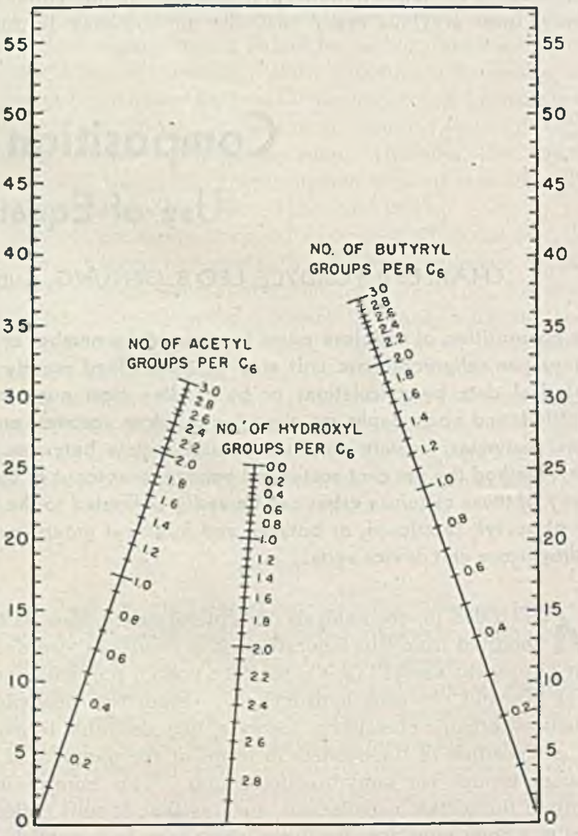


Figure 2. Nomograph for Converting Per Cent Acetyl and Per Cent Butyryl in Cellulose Acetate Butyrate to Number of Acetyl and Butyryl Groups per Glucose Unit of Cellulose

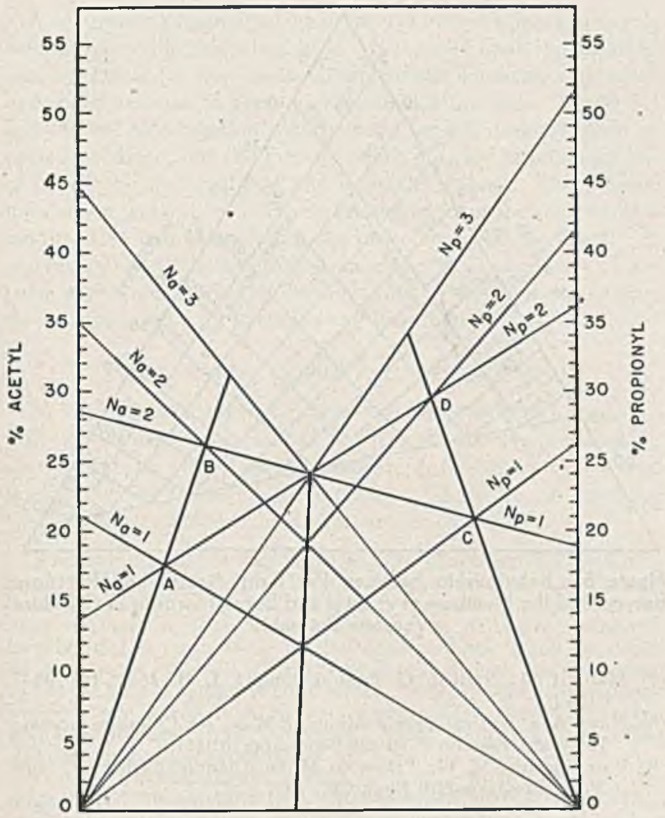


Figure 3. Construction of Nomographs

$$N_b = \frac{2.33b}{102.4 - 1.009b - a} \qquad (17)$$

$$N_h = 3 - N_a - N_b \text{ by assumption} \qquad (18)$$

$$h = \frac{1700N_h}{162 + 42N_a + 70N_b} \qquad (19)$$

The corresponding equations for cellulose butyrates would be Equations 15, 17, 18, and 19, omitting the a and N_a terms, since both are zero in this case.

Derivation of Equations for Cellulose Acetate Propionates. The derivation of Equations 10 and 11 from Equations 8 and 9 is shown below to illustrate the method used to obtain the equations for the numbers of ester groups.

$$a = \frac{4300N_a}{162 + 42N_a + 56N_p} \qquad (8)$$

$$p = \frac{5700N_p}{162 + 42N_a + 56N_p} \qquad (9)$$

Equation 9 is solved for N_a and is then substituted in Equation 8 and solved to obtain the following expression for N_p:

$$N_p = \frac{162}{\frac{5700}{p} - \frac{42 \times 5700a}{4300p} - 56} \qquad (20)$$

$$N_p = \frac{162}{\frac{5700}{p} - \frac{55.7a}{p} - 56} \qquad (21)$$

The numerator and denominator of Equation 21 are divided by the smallest factor, 55.7, and are multiplied by p to give

$$N_p = \frac{2.91p}{102.4 - 1.006p - a} \qquad (11)$$

The equation for N_a derived in the same way is

$$N_a = \frac{162}{\frac{4300}{a} - \frac{56 \times 4300p}{5700a} - 42} \qquad (22)$$

Table I. Data for Construction of Nomograph

N_a	N_p	% Acetyl	% Propionyl
1	0	21.1	0
2	0	35.0	0
3	0	44.8	0
0	1	0	26.1
0	2	0	41.6
0	3	0	51.8
1	2	13.6	36.1
2	1	28.5	18.9

$$N_a = \frac{3.86a}{102.4 - 1.006p - a} \qquad (10)$$

NOMOGRAPHS

Nomographs for converting per cent actyl to the number of groups per anhydroglucose unit have been prepared (Figures 1 and 2). By this means per cent acetyl and per cent propionyl or butyryl in cellulose acetates, propionates, butyrates, acetate propionates, and acetate butyrates can be easily converted to the number of acetyl, propionyl, or butyryl, and hydroxyl groups per anhydroglucose unit.

To use these nomographs lay a ruler across the per cent acetyl value on the left scale and per cent propionyl or butyryl value on the right scale and read the number of acetyl, propionyl, or butyryl, and hydroxyl groups from the intersections with the corresponding scales of the nomograph.

Nomographs suitable for this purpose can be constructed by methods such as those of Davis (*1*) or Van Voorhis (*9*), or by the graphical method described below. Figure 3, which applies to cellulose acetates, propionates, and acetate propionates, demonstrates the method of construction used.

Lines were drawn from 0% propionyl to the points on the acetyl scale corresponding to N_a = 1, 2, and 3 and from 0% acetyl to the points on the propionyl scale corresponding to N_p = 1, 2, and 3. The data used are shown in Table I. The line showing the number of hydroxyl groups was then drawn from the intersection of the lines $N_a = 3$ and $N_p = 3$, through $N_a = 2$ and $N_p = 2$, then $N_a = 1$ and $N_p = 1$ to the base line.

The two lines located by substituting $N_a = 1$ and $N_p = 2$ and also $N_a = 2$ and $N_p = 1$ in Equations 8 and 9 were drawn next. The line showing the number of acetyl groups was established by drawing a line from the left origin through A, the intersection

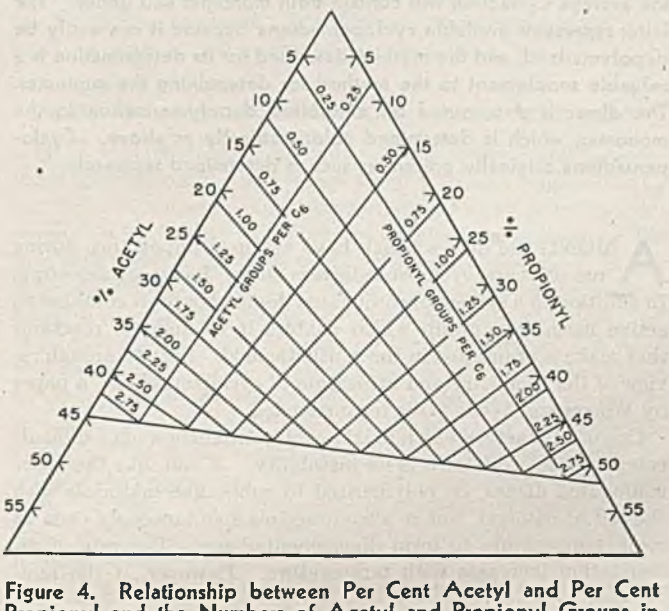


Figure 4. Relationship between Per Cent Acetyl and Per Cent Propionyl and the Numbers of Acetyl and Propionyl Groups in Cellulose Acetate Propionates

of lines $N_a = 1$ and ($N_p = 2$ and $N_a = 1$), and B, the intersection of lines $N_a = 2$ and ($N_p = 1$ and $N_a = 2$), to the line where $N_a = 3$. The line for the number of propionyl groups was drawn in the same way through points C and D.

The scales for the number of acetyl groups and hydroxyl groups were further subdivided by calculations using Equation 2 or by plotting the number of acetyl groups against per cent acetyl, and reading from this graph the acetyl values corresponding to the desired values of N_a. A straightedge was placed across these acetyl values and 0% propionyl, and the points of intersections of the acetyl and hydroxyl scales were marked. The scale for the number of propionyl groups was subdivided in the same way by using data from a corresponding graph, or by substituting values of N_p in an equation for per cent propionyl corresponding to Equation 2.

Triangular Charts. Malm, Fordyce, and Tanner (*4*) have correlated physical properties such as solubilities, melting points, specific gravities, and moisture absorption of these cellulose esters with their acyl contents by means of triangular diagrams. These properties can also be correlated with composition in terms of numbers of acetyl and propionyl or butyryl groups per anhydroglucose unit by means of Figures 4 and 5.

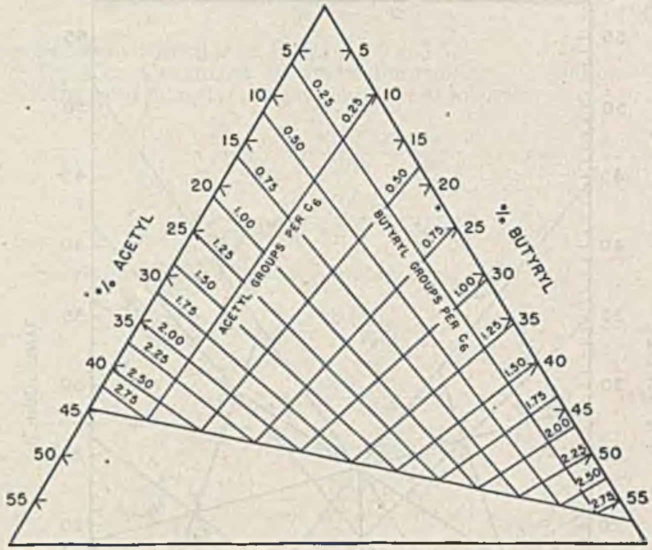


Figure 5. Relationship between Per Cent Acetyl and Per Cent Butyryl and the Numbers of Acetyl and Butyryl Groups in Cellulose Acetate Butyrates

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Determination of Cyclopentadiene and Dicyclopentadiene

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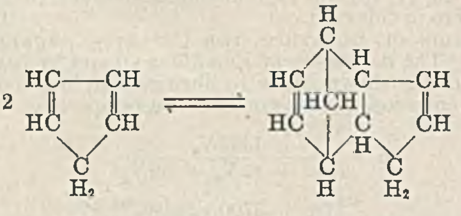
Cyclopentadiene in a C_5 fraction is determined by condensation with benzaldehyde to highly colored phenylfulvene, the intensity of the color of which is a measure of the cyclopentadiene present. None of the materials normally associated with it in hydrocarbon samples interferes. Oxidation inhibitors must be absent. Since cyclopentadiene dimerizes rapidly even at ordinary temperatures, the average C_5 fraction will contain both monomer and dimer. The latter represents available cyclopentadiene because it can easily be depolymerized, and the method described for its determination is a valuable supplement to the method for determining the monomer. The dimer is determined by controlled depolymerization to the monomer, which is determined colorimetrically as above. Cyclopentadiene originally present as such is determined separately.

AMONG the dienes which have assumed importance during recent years, cyclopentadiene is one of the most interesting. In addition to a system of conjugated double bonds, it contains an active methylene group which enables it to undergo reactions that make it of interest in the synthetic field. For a thorough review of the chemistry and utilization of cyclopentadiene, a paper by Wilson and Wells (*5*) is recommended.

One of the factors which makes cyclopentadiene such a difficult compound to work with is its instability. It can, like the other conjugated dienes, be polymerized to rubberlike materials with the aid of catalyst, but it also dimerizes spontaneously even at room temperature to form dicyclopentadiene. The rate of dimerization increases with temperature. However, if the temperature is raised to about the boiling point of dicyclopentadiene (170° C.), the reaction is reversed and the dimer reconverts to the monomer. This means that to know the amount of cyclopentadiene originally present in the sample, it is necessary to determine both the monomer and the dimer. Methods for determining cyclopentadiene are virtually nonexistent. Those which are mentioned in the literature are not specific for cyclopentadiene and are applicable only if no other dienes are present.



A recent paper by Sefton (*2*) describes a method for determining cyclopentadiene by means of its heat of reaction with maleic anhydride. The author states that his method is not specific for cyclopentadiene, but he expects little interference, since other dienes of the same boiling range react much more slowly.

Since cyclopentadiene is a conjugated diolefin, it has a very strong ultraviolet absorption spectrum. Pickett, Poddock, and Sackter (*1*) have made a careful study of this spectrum, but have not used it for the determination of this compound. Since cyclopentadiene has a characteristic ultraviolet absorption spectrum, it could be determined rather accurately by ultraviolet spectrometry if not too many interfering materials such as aromatics and conjugated diolefins were present. Infrared spectrometry could likewise be used satisfactorily.

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A colorimetric method which is specific for cyclopentadiene has been developed in this laboratory. It is based upon the observation by Thiele (3) that cyclopentadiene will condense with aldehydes and ketones to form highly colored fulvenes. Ward (4) has utilized this reaction with acetone for the determination of cyclopentadiene, but the method is not entirely satisfactory because of the instability of the dimethylfulvene. The present method, in which benzaldehyde is used to form the fulvene, is a modification and extension of the procedure used by Ward. It can be applied to the determination of cyclopentadiene in C_5 fractions which contain no inhibitor. None of the compounds normally associated with it causes any interference.

PREPARATION OF PURE CYCLOPENTADIENE

In conducting this investigation it was necessary to have available pure cyclopentadiene. It can be conveniently prepared by depolymerizing pure dicyclopentadiene, but it cannot be stored because of its tendency to dimerize. Therefore, it must be freshly prepared each time and used immediately.

A technical grade of dicyclopentadiene (Eastman Kodak Company) was vacuum-distilled from a Claisen flask, and the fraction boiling at 82° C. at 50 mm. of mercury pressure was sufficiently pure without further treatment. As the distillate consisted largely of the endo form of dicyclopentadiene (melting point 32° C.), water at 32–33° C. was circulated through the condenser to prevent its plugging with crystals. The distilled dicyclopentadiene was stored in a brown bottle under nitrogen. It remained sufficiently pure for about a month but had to be redistilled after that period of time.

The dicyclopentadiene purified in this manner was then depolymerized by cracking in a still equipped with a 60-cm. (24-inch) tube packed with short lengths of glass rod which served as a rough fractionating column. It was provided with an air jacket to prevent excess heat loss. Before the distillation was started, the entire system was flushed with nitrogen introduced through a side arm in the flask. The flow of nitrogen was then stopped and the flask heated to the boiling point of dicyclopentadiene (about 170° C.) where depolymerization began. The rate of heating was so adjusted that the overhead vapor temperature was 40–41° C., and the distillate was caught in a receiver cooled with dry ice. A higher vapor temperature would indicate that the rate of heating was so high that dicyclopentadiene was being carried over. The heating was discontinued before the flask became dry to avoid any possible explosion from peroxides.

Occasionally the distillate was cloudy because of traces of moisture or high polymers which accumulated in the condenser, but it could be easily clarified by passing it through filter paper. This cyclopentadiene was sufficiently pure for use without any further treatment. The purity was found to be 99.1% by reaction with maleic anhydride and 100.5% by hydrogenation.

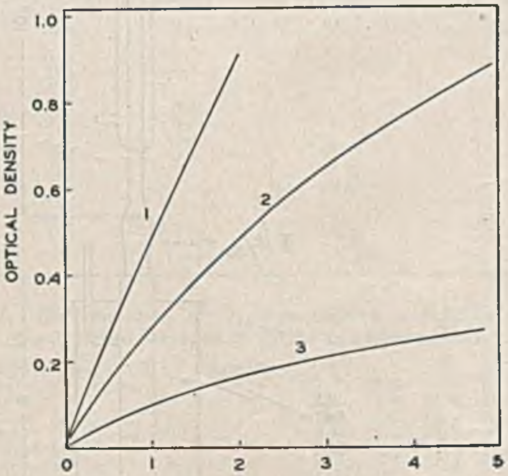

Figure 1. Calibration Curves for Various Filters

Maximum transmission, Å. 1. 4075. 2. 4250. 3. 5000

Table I. Colors and Characteristics of Fulvenes Formed from Cyclopentadiene and Various Aldehydes and Ketones

Compound	Color and Characteristics
Acetone	Yellow color becoming darker
Benzophenone	Unstable, dark red color, slow reaction
Acetophenone	Unstable, light red color
Cyclopentanone	Dark emulsion
Salicylaldehyde	Green emulsion
Anisaldehyde	Yellow color turning red
Citronellal	Yellow color becoming darker
Vanillin	Yellow precipitate
Benzaldehyde	Stable yellow to red color

Table II. Stability of Color of Phenylfulvene

Elapsed time, min.	0	15	30	60	120
Optical density	0.372	0.366	0.366	0.372	0.366

SELECTION OF REAGENT FOR DETERMINING CYCLOPENTADIENE

It is always desirable, of course, to have a method which is specific for the determination of a particular compound, and the Thiele fulvene reaction as used by Ward (4) appeared to be good in this respect. However, the dimethylfulvene formed by the reaction of cyclopentadiene with acetone was unstable and its color changed rapidly. Therefore, a number of other aldehydes and ketones were tested in regard to suitability of the color and stability of the fulvene. As the results in Table I indicate, phenylfulvene, the condensation product of cyclopentadiene and benzaldehyde, was the most promising. Its yellow-to-orange color is well suited to colorimetric work, and its stability, as indicated in Table II, is good. The absorption curve of phenylfulvene, as determined on a Beckman quartz spectrophotometer, shows an absorption peak of 3475 Å.

A photoelectric colorimeter, the Fisher electrophotometer, was used in developing the colorimetric method. To increase the selectivity or sensitivity, filters were used to isolate a certain region of the spectrum for measuring the optical density of the phenylfulvene solutions. Filters with maximum transmission regions below 4000 Å. could not be used with the electrophotometer because they transmitted too small an amount of energy to which the photocells were sensitive. As the wave length of the light transmitted by the filter increased, the sensitivity decreased, but there was a corresponding increase in the permissible concentration of cyclopentadiene. This is illustrated in Figure 1 by the calibration curves shown for three filters. As a compromise between sensitivity and a more extended range of concentration, the No. 2 filter was used. It will permit the determination of as much as 5 mg. of cyclopentadiene in the aliquot.

STUDIES ON THE DEPOLYMERIZATION OF DICYCLOPENTADIENE

Since cyclopentadiene is known to dimerize readily, sometimes spontaneously, the average sample, though originally a C_5 cut, will contain some dicyclopentadiene. For all practical purposes this represents available cyclopentadiene because of the ease with which it can be depolymerized to the monomer. It was apparent, therefore, that it would be necessary to have a method for determining dicyclopentadiene. Numerous chemical and physical methods were investigated for this purpose, but none was satisfactory. The depolymerization of dicyclopentadiene to cyclopentadiene was, therefore, investigated as a possible means for determining the dimer. This procedure would be satisfactory if the depolymerization could be made quantitatively, because the colorimetric method for cyclopentadiene had proved to be accurate. An investigation of the depolymerization reaction was carried out in an attempt to find conditions under which it could be made quantitative.

The depolymerization step is, of course, employed in the preparation of pure cyclopentadiene, but there no attempt is made to carry out the reaction in a quantitative manner. However, from the experience gained in this work, it was possible to predict some of the conditions which would have to be fulfilled: (1) The depolymerization must be carried out rapidly enough so that the cyclopentadiene is removed from the heated portion of the reaction chamber before it has a chance to redimerize at the elevated temperature. (2) The rate of heating must be slow enough so that no dicyclopentadiene distills without depolymerization. (3) Some material which has a boiling point a few degrees above the depolymerization temperature of dicyclopentadiene must be used as a chaser to sweep all the cyclopentadiene completely into the cold portion of the apparatus. (4) Some high-boiling material to serve as bottoms should be used to minimize the danger of explosion if any peroxides are present.

A compromise was necessary if the first two of these conditions were to be satisfied; so various temperatures and rates and means of heating were investigated. The one which finally proved most satisfactory involved the use of an electric heater with exposed element and built-in rheostat (Precision Scientific Company 550-watt heater). The rate of heating could be controlled easily, and the depolymerization vessel could be placed directly on the heating element to obtain rapid heat transfer. Likewise, the entire vessel was heated, so that only a small amount of refluxing took place.

During the investigation to find the best conditions for depolymerization, the apparatus used in this work underwent considerable evolution. In Figure 2 is shown the form which was finally selected. The 25-ml. Erlenmeyer flask is sealed directly to the side arm and condenser, so that the cyclopentadiene vapors have only a short distance to travel before reaching the cool portion of the apparatus. The small $^5/_{20}$ standard-taper joint is used in rinsing out the condenser after a determination. Marks were placed at the 5- and 10-ml. points on the receiver, so that it was possible to judge more accurately the rate at which the distillate was collected.

The third and fourth conditions listed above were satisfactorily fulfilled through the use of decalin (decahydronaphthalene) as a chaser and a mineral oil of 100 Saybolt viscosity at 100° F. as bottoms. Of the materials studied, decalin was most satisfactory in regard to boiling point and stability. The exact properties of the mineral oil used as bottoms are not critical as long as its initial boiling point is well above the boiling range of the decalin used as a chaser.

DETERMINATION OF CYCLOPENTADIENE

Scope. This method is intended for C_5 fractions (18° to 50° C.) to which no oxidation inhibitor has been added. Higher boiling fractions, with the exception of dicyclopentadiene which forms from the monomer on storage, must be absent.

Apparatus. A photoelectric colorimeter, such as the AC Model Fisher electrophotometer with the appropriate cells and light filters.

An assortment of pipets, volumetric flasks, and 50-ml. Erlenmeyer flasks is required for making dilutions.

Reagents. 3% solution of alcoholic potassium hydroxide, filtered.

20% by volume solution of U.S.P. or similar grade benzaldehyde in 95% ethanol. This solution must be protected from unnecessary contact with air because the benzaldehyde is easily oxidized to benzoic acid.

Dicyclopentadiene, Eastman 80% technical grade.

Ethanol, both 95% and absolute.

Pentane, c.p.

Procedure. It is first necessary to make a standard calibration curve from pure cyclopentadiene, which is prepared from redistilled dicyclopentadiene in the manner previously described. The cyclopentadiene must be used immediately to prepare standard dilutions in c.p. pentane, and even these dilute solutions should not be used after they are more than an hour old. These solutions should be of such concentrations that they are distributed evenly throughout the range which can be covered by the particular instrument and filter used. Equal volumes of the standard cyclopentadiene solution, 3% alcoholic potassium hydroxide solution, and 20% alcoholic benzaldehyde solution are mixed and allowed to stand for 3 minutes before the optical density or per cent transmission is determined. The exact volumes of these solutions used depend entirely upon the amount of the final mixture required to fill the cell of the colorimeter. The blank or reference cell of the colorimeter is filled with the same solutions, except that the benzaldehyde solution is omitted and an equal volume of absolute ethanol is used instead. The calibration curve is prepared by plotting the optical density or per cent transmission against the weight of cyclopentadiene for each of the standard dilutions.

The unknown samples are treated in the same manner as the known samples which were used in preparing the calibration curve. A measured amount of the sample is diluted to the proper concentration with pentane. The sample can be measured either by weighing or by using a known volume if the density is known. A blank solution should again be prepared from equal volumes of the pentane dilution of the sample, 3% alcoholic potassium hydroxide, and absolute ethanol. The reading obtained on the unknown sample is referred to the standard calibration curve to obtain the amount of cyclopentadiene present.

Since samples containing dienes usually contain peroxides, such samples should be distilled only in presence of oxidation inhibitors and of "bottoms" in the still pot. Neglect of these precautions may cause explosions. Samples containing cyclopentadiene require special care in handling, since cylopentadiene has been observed to dimerize spontaneously, sometimes explosively.

DETERMINATION OF DICYCLOPENTADIENE

Scope. This method is intended for the determination of dicyclopentadiene in the C_5 fraction. This is dicyclopentadiene which has been formed by the dimerization of some of the cyclopentadiene originally present in the sample. Other higher molecular weight compounds and oxidation inhibitors should be absent.

Apparatus. Depolymerization apparatus as shown in Figure 2. Electric heater with built-in rheostat similar to Precision Scientific Company 550-watt heater.

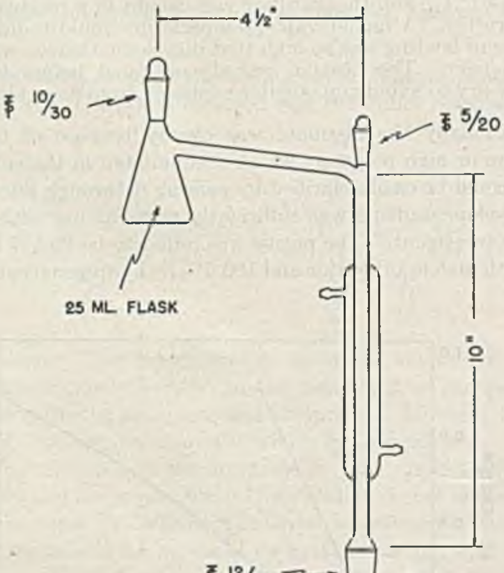

Figure 2. Apparatus for Quantitative Depolymerization of Dicyclopentadiene

Assortment of pipets and volumetric flasks.

Boiling stones.

Reagents. Mineral oil of approximately 100 Saybolt viscosity at 100° F.

Decalin (decahydronaphthalene).

Pentane, c.p.

Ethanol, both 95% and absolute.

Procedure. A 5-ml. portion of the hydrocarbon sample containing the dicyclopentadiene, 5 ml. of decalin, 5 ml. of the mineral oil, and a boiling stone are added to the 25-ml. Erlenmeyer flask of the depolymerization apparatus shown in Figure 2. If the amount of sample available is less than 5 ml. it should be brought to this volume by the addition of pentane. The electric heater is placed so that the flask rests on the heating coil, and the receiver is surrounded by an ice bath. The heat is applied slowly, so that about 20 minutes are required to distill approximately 5 ml. of C_5 hydrocarbon. The heat should then be increased so that the dicyclopentadiene is depolymerized, and decalin distills slowly. The distillation of the 5 ml. of chaser should require not less than 40 minutes of actual distilling time (not just refluxing). When 10 ml. of distillate have been collected, the heater should be turned on high for one minute, and then the distillation stopped. Some of the mineral oil will crack and an additional milliliter or two of distillate will be collected during this time. Under no circumstance should the distillation be carried to dryness, because peroxides may be present.

At the conclusion of the distillation, the condenser should be rinsed by pouring 2 to 3 ml. of 95% ethanol through the small $^{5}/_{20}$ joint, and then the entire contents of the receiver are transferred to a 100-ml. volumetric flask and made to volume with absolute ethanol. Aliquots of this solution are analyzed for cyclopentadiene by the colorimetric procedure previously described.

Table III. Colorimetric Determination of Cyclopentadiene in Pentane Solutions

Milligrams of Cyclopentadiene Present	Milligrams of Cyclopentadiene Found
0.16	0.18
0.32	0.32
0.64	0.65
0.80	0.82
0.96	1.00
1.20	1.26
1.28	1.30
1.60	1.60
2.40	2.46
3.20	3.22
3.60	3.66
4.00	3.98
4.60	4.64

Table IV. Determination of Cyclopentadiene in Presence of Organic Sulfur Compounds

Cyclopentadiene Found	Cyclopentadiene Present	Ethyl Mercaptan Present	Thiophene Present	Methyl Sulfide Present
Mg.	*Mg.*	*Mg.*	*Mg.*	*Mg.*
0.8	0.8	..	..	..
2.4	2.4	..	..	..
4.0	4.0	..	..	..
0.8	0.8	2.0	..	..
2.4	2.4	6.0	..	..
4.1	4.0	10.0	..	..
0.8	0.8	..	2.6	..
2.4	2.4	..	7.8	..
4.1	4.0	..	13.0	..
1.6	1.6	..	..	17.0
3.2	3.2	..	..	34.0
1.6	1.6	1.4	1.7	5.6

Table V. Determination of Cyclopentadiene and Dicyclopentadiene in the Presence of Other C_5 Hydrocarbons

Composition of sample (% by weight)					
Pentane	73.2	73.8	47.3	23.9	66.5
Pentene-2	9.9	9.9	19.7	18.9	9.8
Piperylene	4.2	6.3	10.3	19.9	4.7
Isoprene	3.9	1.9	9.9	19.6	5.1
Cyclopentadiene	2.5	4.9	7.3	11.8	6.1
Dicyclopentadiene	6.3	3.2	5.4	5.8	7.8
Found (% by weight)					
Cyclopentadiene	2.5	4.9	7.6	11.8	5.9
Dicyclopentadiene	6.2	3.2	5.2	5.6	7.7

Table VI. Change in Cyclopentadiene Content of Sample on Storage

Composition of original sample (% by weight)

18.8% cyclopentadiene
14.2% dicyclopentadiene
67.0% C_5 fraction of fluid catalytically cracked naphtha

Weight % found after days	0	2	3	4	5	6	7	9	12	16	30
Cyclopentadiene	18.8	16.1	14.3	12.5	11.5	10.6	9.6	8.0	6.5	5.6	2.9
Dicyclopentadiene	14.2	17.4	18.7	20.5	21.5	22.4	23.4	25.0	26.5	27.4	30.1
Total (as cyclopentadiene)	33.0	33.5	33.0	33.0	33.0	33.0	33.0	33.0	33.0	33.0	33.0

Dicyclopentadiene is determined as the difference between the total cyclopentadiene thus determined and the cyclopentadiene present as such in the original sample.

Accuracy of Methods. The colorimetric method for determining cyclopentadiene appears to be capable of a rather high degree of accuracy. The results of a series of analyses on samples made from pentane and cyclopentadiene are shown in Table III. Here the maximum error is 0.06 mg. of cyclopentadiene, and the average error is 0.03 mg. or 0.3% on the basis of the original sample. As far as has been determined at the present time, the method is specific for cyclopentadiene, and certainly none of the materials which would normally be associated with it in a hydrocarbon sample causes any interference. Some of the sulfur compounds, ethyl mercaptan, methyl sulfide, and thiophene, were tried and found to be without effect (Table IV).

The only additional step involved in the determination of dicyclopentadiene is, of course, the depolymerization reaction. This reaction can be carried out quantitatively if sufficient care is exercised, and the dicyclopentadiene can be determined accurately. In Table V are given the results of analyses made on samples containing both the monomer and dimer blended with other C_5 hydrocarbons. Isoprene and piperylene were present in each of these samples, and, since the results were still accurate, it is apparent that these other conjugated C_5 dienes do not interfere.

Additional proof of the accuracy and precision of the method, as well as an indication of the need for the method for dicyclopentadiene, is shown in Table VI. The sample was prepared by adding a known amount of cyclopentadiene and dicyclopentadiene to the C_5 fraction of a fluid catalytically cracked naphtha, which was found by analysis to be free of cyclopentadiene. This sample was stored at room temperature in a dark bottle and portions of it were analyzed after various periods of time. After only 2 days a very appreciable change had occurred, and after 30 days practically all of the cyclopentadiene had dimerized. It will be noticed that in each of these analyses, with the exception of the one on the second day, the total of the monomer and dimer was 33.0% or exactly the theoretical amount. This rigorous test of the accuracy and reproducibility of the methods indicates that they are entirely reliable.

ACKNOWLEDGMENT

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Rapid Photometric Determination of Iron and Copper in Red Phosphorus

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Photometric methods for the determination of iron and copper as colored complexes with 1,10-phenanthroline and diethyldithiocarbamate, respectively, can be adapted to the rapid determination of traces of iron and copper in red phosphorus with a precision of 2 p.p.m. for either component in the range 0 to 50 p.p.m. Interference from aluminum is minimized by addition of ammonium citrate. For solution of red phosphorus, oxidation with a bromine–carbon tetrachloride mixture is recommended in the analysis for iron, whereas oxidation with nitric acid is recommended in the analysis for copper.

THE stability of red phosphorus toward atmospheric oxidation is decreased markedly by traces of iron and copper. The critical stability requirement involved in certain uses of red phosphorus reflects a need for precise, and preferably rapid, methods for the determination of contaminative iron and copper. Several methods for the determination of traces of iron and copper have been published, but none is specifically applicable to the analysis of red phosphorus. Yoe and Sarver (*6*) have prepared a bibliography of organic reagents for the determination of iron and copper. From a comparison of several photometric methods for iron, Woods and Mellon (*5*) have recommended the 1,10-phenanthroline method (*2*) for general application. Haywood and Wood (*3*) have used the color of the cupric diethyldithiocarbamate complex as a basis for the determination of copper in ferrous materials that had first been dissolved in a mixture of phosphoric and sulfuric acids.

In the present work, conditions were established for dissolving red phosphorus preparatory to its photometric analysis for iron as the ferrous 1,10-phenanthroline complex and for copper as the cupric diethyldithiocarbamate complex. The methods of Fortune and Mellon (*2*) and of Haywood and Wood (*3*) were adapted to the formation of the respective colored complexes. The influence of interfering ions and of other factors on the development of color was studied.

Red phosphorus dissolves in dilute nitric acid to form a solution of mixed acids of phosphorus. On evaporation of the solution to small volume and addition of concentrated nitric acid, the lower acids of phosphorus are oxidized to a mixture of ortho-, meta-, and pyrophosphoric acids. Pyro- and metaphosphoric acids do not affect the determination of copper but do affect development of color in the determination of iron. Although both of these acids can be hydrolyzed to orthophosphoric acid, the iron extracted from the glass vessel during the oxidation step is additive in the iron analysis. Nitric acid thus is a suitable solvent for the determination of copper but not for the determination of iron.

A solution of bromine in carbon tetrachloride reacts smoothly with red phosphorus to form crystals of an addition compound of phosphorus pentabromide and carbon tetrachloride (*4*). Upon the addition of water and subsequent evaporation of the carbon tetrachloride, the phosphorus pentabromide hydrolyzes to orthophosphoric and hydrobromic acids. The hydrobromic acid is decomposed by nitric acid. This method for dissolution of the sample obviates the disadvantages involved in the use of nitric acid as the solvent in an iron determination.

Many samples of commercial red phosphorus yield a yellow to brown solution. The objectionable color is bleached by the action of potassium chlorate on the hot sirupy solution of phosphoric acid.

In the analysis of red phosphorus that has been coated with hydrous alumina (aluminated) to increase its stability, the aluminum precipitates as the phosphate and interferes with the determination of both iron and copper. Ammonium citrate prevents precipitation of the aluminum and can be used without special precautions in the copper determination. In the iron determination, however, tests similar to those of Cowling and Benne (*1*) confirmed their observation that the citrate ion markedly retards the formation of the ferrous 1,10-phenanthroline complex. In tests with 30 mg. of aluminum hydroxide per gram of phosphorus, a 1 to 1 molar ratio of citric acid to aluminum hydroxide proved effective. A slightly greater amount of citric acid is specified in the procedure to take care of normal variations in samples of red phosphorus. Increase of the additions of reducing and color-forming reagents over the amounts used by Fortune and Mellon (*2*) eliminates most of the interference by the citrate.

APPARATUS AND REAGENTS

Filter photometer, Fisher AC electrophotometer fitted with 425-mμ blue and 525-mμ green filters and with 2- and 5-cm. absorption cells.

Nitric acid, 70%, redistilled.

Bromine–carbon tetrachloride mixture, 1 volume of bromine to 3 volumes of redistilled carbon tetrachloride.

Citric acid, 10 grams of the monohydrate per 100 ml. of solution.

Hydroxylamine hydrochloride, 10 grams per 100 ml. of solution.

1,10-Phenanthroline, 0.1 gram per 100 ml. of solution.

Colloid, 1.0 gram of gum acacia dissolved in 100 ml. of boiling water, filtered, and diluted to 200 ml. Prepare fresh daily.

Sodium diethyldithiocarbamate, 0.2 gram per 100 ml. of solution, stored in a dark bottle.

Standard iron solution, 1 ml. ≎ 0.01 mg. of iron. Dilute to 1 liter a 100-ml. aliquot of a solution containing 0.7021 gram of ferrous ammonium sulfate hexahydrate and 5 ml. of sulfuric acid per liter.

Standard copper solutions. Dissolve 0.2500 gram of pure copper in nitric acid and dilute to 1 liter. Dilute 100 ml. of this stock solution to 1 liter for standard solution A (1 ml. ≎ 0.025 mg. of copper). Dilute 200 ml. of solution A to 1 liter for standard solution B (1 ml. ≎ 0.005 mg. of copper).

Potassium chlorate, reagent grade.

Indicator. Alkacid test paper (manufactured by Fisher Scientific Company).

DETERMINATION OF IRON

PREPARATION OF CALIBRATION CURVES. To a series of 100-ml. volumetric flasks add 0 to 28 ml. of the standard iron solution in 2-ml. increments. To a second series of the flasks add, from a microburet, 0 to 5.00 ml. of the standard iron solution in 0.20-ml. increments. Into the contents of each flask mix 1 ml. of hydroxylamine hydrochloride solution, and allow the mixture to stand for 15 minutes. Add 5 ml. of 1,10-phenanthroline solution, and adjust the pH to 6 by dropwise addition of dilute ammonium hydroxide. This is best accomplished by touching a drop of the solution on a stirring rod, to a piece of Alkacid test paper. Dilute each solution to the mark, mix it thoroughly, and allow 1 hour for color development. Read the color intensity on a photometer equipped with a 525-mμ (green) filter. For the solutions in the first series, which represent 0 to 280 p.p.m. of iron on the basis of a 1-gram sample of red phosphorus, use 2-cm. cylindrical cells; for those in the second series, which represent 0 to 50 p.p.m. of iron, use 5-cm. rectangular cells. Plot color intensity versus p.p.m. of iron.

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Blank Determinations. Determine the iron content of each new preparation of bromine–carbon tetrachloride mixture. Dilute 1 volume of phosphoric acid of known iron content with 19 volumes of distilled water, and measure 44.0 ml. of the solution from a buret into each of six 250-ml. beakers. Add the same quantities of bromine–carbon tetrachloride mixture and other reagents that are used in a regular analysis of red phosphorus, and put the blanks through the same analytical procedure. Subtract the iron content of the phosphoric acid from the total iron found to obtain the blank on the bromine–carbon tetrachloride mixture. Subtract the average blank thus obtained from the total iron found in the analysis of red phosphorus to obtain the true iron content of the red phosphorus.

When a large excess of hydroxylamine hydrochloride is used in the determination of iron in aluminated red phosphorus, run a separate blank on this reagent. To 10 ml. of the hydroxylamine hydrochloride solution add 5 ml. of 1,10-phenanthroline solution and adjust the pH to 6 by dropwise addition of dilute ammonium hydroxide. Dilute the solution to 100 ml., mix thoroughly, and allow 1 hour for color development. Use three-tenths of the iron found as a correction in the analysis of aluminated red phosphorus.

Procedure. Weigh 1.00 gram of red phosphorus into a dry 250-ml. beaker. Successively add 75 ml. of carbon tetrachloride, 75 ml. of distilled water, and 15 ml. of nitric acid. Place the mixture under a hood, and add 20 ml. of bromine–carbon tetrachloride solution, from either a buret or a pipet equipped with a suction bulb, at a rate that will not cause violent reaction. Stir the mixture until formation of yellow crystals of $PBr_5.2CCl_4$ ceases. Then nest the 250-ml. beaker and its contents in a 400-ml. beaker with the lips of the beakers divergent. In the air bath thus formed the mixture can be evaporated with fair rapidity and without bumping.

Evaporate the liquid on a hot plate at medium temperature until frothing and evolution of dense brown fume occur at a volume of 5 or 6 ml. If the liquid is colored, add a few potassium chlorate crystals and continue the heating until decolorization ensues. Avoid prolonged heating lest the beaker be attacked.

Dilute the solution to 100 ml. with distilled water, cover with a Pyrex watch glass, and boil at a rate that will decrease the volume to about 30 ml. in 45 minutes. Transfer the solution to a 100-ml. volumetric flask, rinse the beaker five or six times with 5-ml. portions of distilled water, and add the washings to the flask. Dilute the solution to 70 ml. The remainder of the procedure depends upon whether the original sample of red phosphorus was aluminated.

If the original sample was unaluminated, add 1 ml. of hydroxylamine hydrochloride solution to the flask. After 15 minutes add 5 ml. of 1,10-phenanthroline solution, and adjust the pH to 6 by dropwise addition of ammonium hydroxide. Dilute the solution to the mark, mix it thoroughly, and allow the color to develop for 1 hour. Read the color intensity on a photometer with a 525-mμ (green) filter. If color intensity indicates more than 50 p.p.m. of iron, use 2-cm. cylindrical cells; if less than 50 p.p.m., use 5-cm. rectangular cells. Read the iron content from the appropriate calibration curve. Correct for the blank on the reagents.

If the original sample was aluminated, add 4 ml. of hydroxylamine hydrochloride solution to the solution of dilute orthophosphoric acid in the 100-ml. volumetric flask. After 15 minutes add 1.0 ml. of citric acid solution, shake the mixture thoroughly, and cool it to room temperature. Add 10 ml. of 1,10-phenanthroline solution, and adjust the pH to 6 by dropwise addition of ammonium hydroxide. Dilute the solution to the mark, mix it thoroughly, and allow 2 hours for color to develop. Read the color intensity and determine the iron content as described for unaluminated red phosphorus.

Factors Affecting Color Development. The presence of orthophosphoric acid narrows the pH range for maximum color development. At the optimum pH of 6 ± 1, however, quantities of orthophosphoric acid equivalent to as much as 2 grams of red phosphorus are without effect.

The conditions specified in the procedure for aluminated red phosphorus practically overcome interference from the citrate that is added to prevent precipitation of aluminum.

Lead, which may be present in red phosphorus, forms a precipitate. In aluminated samples to which the specified quantity of citrate has been added, up to 1500 p.p.m. of lead can be tolerated.

Neither nickel nor copper interferes in proportions less than 100 p.p.m. Larger proportions of copper cause high results.

Precision and Accuracy. The precision of the method was tested by analyzing in multiple a sample of pure red phosphorus, both alone and with known additions of iron. From 32 determinations in which the maximum deviation from the mean was 3 p.p.m., the standard deviation of a single value was shown to be 1.2 p.p.m. of iron.

To test the precision of the method on aluminated samples, 12 samples containing the equivalent of 30 mg. of aluminum hydroxide as the nitrate were analyzed. The maximum deviation from the mean was 2.7 p.p.m., and the standard deviation was 1.6 p.p.m. of iron. The accuracy is believed to be as good as the precision. Occasional discrepancies in the analysis of less pure samples were shown to be due to inhomogeneity of the samples.

DETERMINATION OF COPPER

Preparation of Calibration Curves. To a series of 100-ml. volumetric flasks add, in increments of 1 ml. from a microburet, from 0 to 12 ml. of standard copper solution A (1 ml. ≎ 0.025 mg. of copper) and from 0 to 10 ml. of standard copper solution B (1 ml. ≎ 0.005 mg. of copper). Then add to each flask 10 ml. of 3 N ammonium hydroxide and 10 ml. of the suspension of gum acacia. Dilute the mixture to about 70 ml., agitate it thoroughly, add 10 ml. of sodium diethyldithiocarbamate solution, and make the volume up to 100 ml. Allow 15 minutes for color development. Read the color intensity on a photometer fitted with a 425-mμ (blue) filter. For the solutions prepared from standard copper solution A, which represent 0 to 120 p.p.m. of copper on the basis of a 2.5-gram sample of red phosphorus, use 2-cm. cylindrical cells; for those prepared from standard copper solution B, which represent 0 to 20 p.p.m. of copper, use 5-cm. rectangular cells. Plot color intensity versus p.p.m. of copper.

Procedure. Weigh a 2.50-gram sample of red phosphorus into a 300-ml. tall-form beaker, and add 100 ml. of nitric acid (1 + 1). Heat the mixture gently to start the reaction, then allow the reaction to proceed in the cold. After the vigorous reaction subsides, evaporate the liquid until the evolution of brown fume ceases. Add 2 to 5 ml. of concentrated nitric acid to the cooled solution and reheat it until the evolution of brown fume ceases. Repeat the cycles of adding nitric acid and heating until a cycle fails to produce brown fume, then evaporate the liquid to a sirup. If the sirup is colored, heat it for a few minutes with about 0.2 gram of potassium chlorate. Add 10 to 20 ml. of water to the cooled solution and reheat it to boiling to remove chlorine and oxides of nitrogen. If the solution is not colorless after boiling for 10 minutes, re-evaporate it to a sirup and repeat the potasium chlorate treatment.

Transfer the degassed solution to a 100-ml. volumetric flask, and add 2.0 ml. of citric acid solution. Add ammonia until a drop of the solution turns Alkacid test paper a distinct green (pH > 8.5). Thoroughly mix 10 ml. of the suspension of gum acacia with the ammoniacal solution, and dilute the mixture to 70 ml. Add 10 ml. of sodium diethyldithiocarbamate and sufficient water to make 100 ml. Measure the color intensity with the photometer, using 5-cm. rectangular cells for 0 to 20 p.p.m. of copper and 2-cm. cylindrical cells for 20 to 120 p.p.m. of copper. Determine the p.p.m. of copper from the appropriate calibration curve.

Factors Affecting Color Development. The pH must be at least 8.5 for proper color development. A moderate excess of ammonium hydroxide does not interfere with color development, but a large excess precipitates diammonium phosphate. Phosphorus is without effect. The added citric acid eliminates interference from aluminum and decolorizes traces of iron which might otherwise cause a slight positive error.

Significant errors can be introduced by a few elements that form precipitates or colored complexes. Nickel forms a greenish-yellow complex with sodium diethyldithiocarbamate. The removal of nickel with dimethylglyoxime, as recommended by Haywood and Wood (*3*), introduces an error of about 0.015 mg. of copper (6 p.p.m. on basis of a 2.5-gram sample), probably because of the slight solubility of nickel dimethylglyoxime. It is recommended that nickel, if present, be removed with dimethylglyoxime and that a correction be made for the positive error introduced. Lead in amounts greater than 40 p.p.m. in the red phosphorus interferes by precipitation. None of the other known interfering elements has been detected in red phosphorus.

PRECISION AND ACCURACY. Since red phosphorus of known copper content was not available for analysis, the accuracy of the method could not be determined. The precision of the method was 2 p.p.m. of copper on a sample that analyzed 33 p.p.m. The precision was unaltered by the addition of sufficient standard copper solution to raise the copper content of the sample to 80 p.p.m. Results reproducible within 0.2 p.p.m. have been obtained on samples of red phosphorus that contained less than 10 p.p.m. of copper.

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Simplified Determination of Manganese in Caustic Soda

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A simple and rapid method for the determination of the traces of manganese in commercial caustic soda is described. By the use of visual comparison instead of photoelectric colorimetry the method is made more flexible for use in industrial control laboratories. The precision expressed as LU_2 was ±0.11 p.p.m. on a sample containing 0.30 p.p.m. of manganese.

IN A recent article (*2*) Williams and Andes described two methods for determining the small concentrations of manganese usually present in commercial caustic soda. The direct method developed the permanganate color by oxidizing with periodate the manganese in 20 grams of 50% sodium hydroxide, the color being measured in an Eimer and Amend photoelectric colorimeter on the 100 ml. of solution finally obtained. The extraction method involved the extraction of the manganese salt from 100 grams of 50% sodium hydroxide by a chloroform solution of 8-hydroxyquinoline, the reagent subsequently being destroyed and the manganese oxidized, after which the permanganate color was measured by the colorimeter also in 100 ml. of solution. The extraction method had an improved precision about in the ratio that would be expected from the use of a fivefold increase in sample size. Unfortunately this increase in precision, while necesssary for some exact analyses, was obtained at the expense of increased complexity and required time for the analyses. The direct procedure had an LU_1 (*1*) of ±0.18 p.p.m. which could be obtained only through very careful use of a sensitive photoelectric colorimeter because the developed pink colors were so weak.

It was necessary to devise a rapid and simple method for manganese which could be applied in laboratories that did not possess a sensitive colorimeter. Although the colors developed by the direct method were weak, they were visible to the eye, which led to the attempt to adapt the method to Nessler-tube comparison. After some experimentation such a method was developed.

SPECIAL APPARATUS AND REAGENTS

Phosphoric acid, 1 to 1. Equal volumes of C.P. 85% orthophosphoric acid and distilled water.

Treated phosphoric acid, 1 to 10. To 1 liter of distilled water add 100 ml. of 85% phosphoric acid. Place in a 2-liter beaker, add 0.8 gram of potassium periodate, and boil vigorously for 20 to 25 minutes. This boiling should reduce the volume to about 1 liter. Cool and preserve in a very clean glass-stoppered bottle which has been rinsed with the reagent. Do not add water after boiling.

Standard manganese solution. Dissolve 0.3077 gram of manganous sulfate monohydrate in water, add 10 ml. of 85% phosphoric acid, and dilute to 1 liter in a volumetric flask. Dilute 10 ml. of this solution to 1 liter. One milliliter of this second solution contains 1 microgram of manganese.

Nessler tubes. A set of matched 12-inch 100-ml. Nessler tubes should be used. These tubes should have optical glass flat bottoms and be held in a stand having an opaque white base.

PROCEDURE

Weigh 20 ± 1 grams of 50% sodium hydroxide (or the equivalent amount of other concentrations) into a 250-ml. wide-mouthed Erlenmeyer flask and dilute with 50 ml. of water. Add 50 ml. of 1 to 1 phosphoric acid and 0.8 gram of potassium periodate. Heat the solution to boiling and boil vigorously for 20 to 25 minutes, so that 50 to 70 ml. remain at the end of the boiling period. Cool to room temperature and dilute to 100 ml. with treated phosphoric acid in a 100-ml. graduated cylinder. For comparison with knowns, transfer to a Nessler tube that has been rinsed with about 10 ml. of the treated phosphoric acid.

Simultaneously with the samples, prepare a set of standards by adding 4, 6, 8, and 10 ml. of the 1 microgram per ml. standard manganese solution, equivalent to 0.2, 0.3, 0.4, and 0.5 p.p.m. of manganese, to a series of 250-ml. wide-mouthed Erlenmeyer flasks. Proceed as above, beginning with the dilution with 50 ml. of water. Compare colors and report samples to the nearest 0.05 p.p.m. These standards should cover the range of most samples of commercial liquid caustic soda but, if the sample color is lighter or darker, prepare additional standards.

DISCUSSION

It was found essential to use the treated phosphoric acid for all dilutions to avoid fading. The very small concentrations of permanganate present in the final solution, though easily perceptible to the eye, are very sensitive to destruction by slight traces of reducing matter. If the treated acid was boiled vigorously and all apparatus kept clean, no difficulty was encountered with fading. A few time studies indicated that it was preferable to use the standards for one day only, however.

This method was adaptable to the analysis of large groups of samples, the number being limited only by the size of the hot plate that was used. It was found simple enough to be placed in the hands of laboratory technicians having but minimum amounts of training. The use of a reagent blank was not necessary because standards and samples were prepared with the same reagents.

ACCURACY AND PRECISION

The method was tested for precision under routine conditions (*1*) by allowing seven routine analysts, previously unacquainted with the method, to make a total of 21 determinations on one sample of commercial 50% caustic soda. An average of 0.30 p.p.m. was obtained with an LU_2 of ±0.11 p.p.m. No single result differed from the average by more than 0.05 p.p.m. To test the accuracy, the same sample was carefully analyzed by the direct method (*2*) to obtain values of 0.30 and 0.33 p.p.m., and by the extraction method (*2*) to obtain results of 0.31 and 0.33 p.p.m. All results agreed with the average within the precision of the methods.

All precision criteria mentioned in this article were obtained by the techniques described by Moran (*1*). The LU_1 results, or limits of uncertainty under ideal conditions, were calculated from the results of ten replicate analyses made by one experienced chemist at one time on one sample, the LU_1 being expressed as three standard deviations. The LU_2 result, or limit of uncertainty under routine conditions, represents three standard deviations derived from a larger number of analyses made by routine technicians at various times on the same sample. Obviously the LU_2 test is open to more variations than the LU_1 test. When the LU_2 result on the currently described method was found satisfactory, no necessity for obtaining an LU_1 was seen.

A series of 17 consecutive tank-car shipments of 50% caustic soda was analyzed by both the authors' laboratory and the laboratory of the consignee of the shipments. The averages of the two series of tests were 0.33 and 0.32 p.p.m., with no result on any one shipment differing by more than 0.05 p.p.m.

It may seem somewhat surprising that by substituting visual comparison for instrument comparison an actual gain in precision was obtained. The limiting precision of the direct method (*2*) under the best conditions was ±0.18 p.p.m. while the present method had a precision of ±0.11 p.p.m. under routine conditions. While the modifications introduced into the current method may have improved precision somewhat, it is the authors' belief that the normal human eye may be superior for detecting slight changes in very light colors unless an exceptionally stable and sensitive photoelectric colorimeter is available.

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Determination of Total Beta-Carotene in Sweet Potatoes and Sweet Potato Products

An Improved Method

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A new method for the routine determination of carotene in sweet potatoes, sweet potato products, and by-products has been evolved from study of the various previously proposed methods. Consideration of the three essential steps of carotene analysis—i.e., extraction, purification, and spectrophotometric measurement—led to the selection of ethyl alcohol as a solvent for the extraction; of a dicalcium phosphate adsorption column for the purification; and of a synthetic hydrocarbon as a solvent for use in the spectrophotometric measurements.

DURING the course of analysis of a large number of samples incident to investigations on the methods of commercial extraction of carotene from sweet potatoes (*24*) and by-products of sweet potato starch manufacture (*1*), and on the stability of carotene in dehydrated sweet potatoes during storage (*2*), it became evident that no completely satisfactory method for the routine determination of carotene in sweet potatoes and sweet potato products and by-products is available in the literature. Consequently, detailed examinations have been made of the three essential steps in the procedure: (1) extraction of the carotene, (2) purification of the extracted carotene, and (3) spectrophotometric measurement of the finally purified carotene.

This communication presents the procedure finally adopted for the routine determination of total β-carotene in sweet potatoes and sweet potato products, evolved from studies and tests made of the various proposed changes in different steps in the procedure which have appeared in the literature. Though the procedure is especially adapted to sweet potatoes and sweet potato products, the section dealing with spectrophotometric measurement should be satisfactory for the evaluation of total β-carotene extracted and purified from other natural products. It is recognized that a variety of extraction and purification procedures are required for satisfactorily analyzing different products for β-carotene. However, the basic observations outlined regarding extraction and purification are equally applicable to the analysis of any material for carotene.

ANALYTICAL PROCEDURE

Weigh into 250-ml. ground-glass-stoppered Erlenmeyer flasks 0.5 to 5.0 grams of the finely divided sweet potato or sweet potato product. A food chopper provides a convenient method for grinding the sample. A portion of the ground sample from the chopper should be retained for moisture determination. The sample size will, of course, depend upon the expected carotene content. The final solution should contain approximately 2 mg. of carotene per liter for measurement through a 1-cm. cell. For fresh sweet potatoes a 5-gram sample, for dehydrated sweet potatoes a 2.5-gram sample, and for the high carotene-containing coagulum described elsewhere (*1*) a 0.5-gram sample will be satisfactory. If the sample is dehydrated, reconstitution by boiling in the Erlenmeyer flask for 30 minutes with about 40 ml. of water should precede the extraction.

Add 100 ml. of cold 95% ethyl alcohol to the Erlenmeyer flask and extract the carotene by shaking with a mechanical shaker for 30 minutes. Filter the extract through a sintered-glass funnel, using vacuum. Use 90% methyl alcohol followed by a small quantity of iso-octane to effect the transfer from the flask to the funnel. Wash the solid material on the sintered-glass funnel with small portions of the same two solvents. Transfer the filtrate quantitatively to a separatory funnel.

Grind in a mortar to a fine powder the solid material remaining on the sintered-glass funnel and re-extract as before with ethyl alcohol. Continue the extraction until a colorless extract is obtained and the residue is snow-white. Usually, a second extraction is sufficient for a fresh sweet potato. For a dehydrated sample a third extraction may be required, while a very high-carotene coagulum may require additional extractions.

Add 100 ml. of water and 2 to 3 grams of sodium chloride to the separatory funnel containing the combined extracts. Shake, and when the two phases have separated, transfer the alcohol-water layer to a second separatory funnel. Extract this solution with

Table I. Comparison of Alcoholic Potassium Hydroxide Refluxing and Cold Alcohol Shaking Methods for Extraction of Carotene

Sample No.	Carotene Content, Alcoholic Potassium Hydroxide Refluxing	Carotene Content, Cold Alcohol Shaking
	Mg./kg.	*Mg./kg.*
1	110.0	125.0
2	116.5	127.5
3	32.8	36.0
4	142.1	164.7
5	159.0	198.0
6	91.5	115.0
7	98.8	112.5

a 25- to 30-ml. portion of iso-octane, adding the iso-octane layer to the first separatory funnel. Continue this partition with fresh portions of iso-octane until the iso-octane remains colorless, combining these extracts in the first separatory funnel.

Filter the iso-octane solution through anhydrous sodium sulfate and then pour the entire solution, or an aliquot thereof, through an adsorption column of dicalcium phosphate and Dyno, previously prepared by the methods described by Moore (*14*). Collect the filtrate from the column in a volumetric flask. Wash the column with iso-octane and dilute the filtrate to a volume containing approximately 2 mg. per liter for measurement through 1-cm. cells. Use correspondingly more dilute solutions if longer cells are used. Measure the optical density of this solution in a spectrophotometer at 450 and 476 mμ. Calculate the carotene content of the sample from the equations:

$$\text{Carotene, mg. per kg.} = \frac{\text{optical density at 450 m}\mu}{245} \times \frac{1{,}000{,}000}{cl}$$

$$\text{Carotene, mg. per kg.} = \frac{\text{optical density at 476 m}\mu}{219} \times \frac{1{,}000{,}000}{cl}$$

where c is the concentration of the sample in the final aliquot measured, expressed in grams per liter, and l is the length, in centimeters, of the absorption cell used for the measurements. Report the average of the two calculations, which should not vary by more than 0.2 to 0.3%, as the carotene content of the sample.

EXTRACTION OF CAROTENE

A complete extraction of the unchanged carotene must be effected for a satisfactory determination of carotene in the sweet potato. The hot alcoholic potash extraction procedure of Peterson, Hughes, and Freeman (*18*), based on the earlier work of Willstätter and Stoll (*26*) and of Guilbert (*8*), has probably been the basis for the most commonly used procedure. It has been shown by Lease and Mitchell (*11*) and confirmed by Fraps, Meinke, and Kemmerer (*5*) that in the saponification step the alcoholic potash reacts with the sweet potato substance, yielding a resinous material from which the carotene can be extracted only with difficulty, and then never completely. It is well known that carotene is isomerized by alkalies. Carter and Gillam (*3*) and Zechmeister and Tuzson (*29*) have shown clearly that heating solutions containing carotenes will also cause considerable isomerization. It is, therefore, essential for a satisfactory determination of carotene in the sweet potato that a complete extraction of the unchanged carotene be carried out without saponification and without heating. Of various solvents tested for their relative efficiency in the extraction of carotene in the cold, ethyl alcohol (95%) proved the most satisfactory. This is the solvent used by Lease and Mitchell (*11*) and recently recommended by the Association of Official Agricultural Chemists in proposed changes to make their method for crude carotene in dried hays applicable to sweet potatoes (*10*). To permit simultaneous extraction of from 6 to 12 samples, a mechanical shaker was preferable to Waring Blendors. In the procedure recommended the solution from the last extraction should be colorless and the residues should be snow-white. (In the extraction of carotene from sweet potato material by saponification methods a white residue cannot be obtained.) Any chlorophyll retained in the solution will be removed in the purification step. Values for carotene obtained from the same samples by the saponification and by the cold alcohol extractions are compared in Table I. The purification and method of final evaluation were identical.

PURIFICATION OF EXTRACTED CAROTENE

The two general methods by which the iso-octane solution may be purified by removal of other carotenes, carotenoid pigments, and chlorophyll are phasic and chromatographic separations. Independent experiments described by many workers have shown clearly that phasic separations are not quantitative (*4*, *13*). The use of chromatographic techniques has been studied by many and summarized by Zechmeister (*27*) and by Zechmeister and Cholnoky (*28*). Complete chromatographic analysis involving the separation of the various isomers is not practical for routine analytical procedures (*16*). It is preferable that the adsorbent retain noncarotene impurities and permit the carotene in solution to pass through the column, completely purified and ready for final spectrophotometric measurement. This requirement is met in the so-called liquid chromatographic column technique of Zechmeister (*27*). Study of many adsorbents led to the selection of dicalcium phosphate, recommended by Moore (*13*). For reasons given below, petroleum ether solvents or the so-called "pure" hexanes and heptanes obtained from them, were considered unsatisfactory for the spectrophotometric measurements, and purified 2,2,4-trimethylpentane, or iso-octane, was selected.

In purifying the carotene solution by use of the dicalcium phosphate column, the chlorophyll, if present, is adsorbed as a green band near the top of the column, the various noncarotene carotenoids appear as poorly defined bands throughout the middle of the column, and the purified carotene passes through the column. Table II compares values for β-carotene from the same samples when the purification was made by the phasic separation and when it was made by chromatographic adsorption. The methods of extraction and final measurement of the purified solutions were identical.

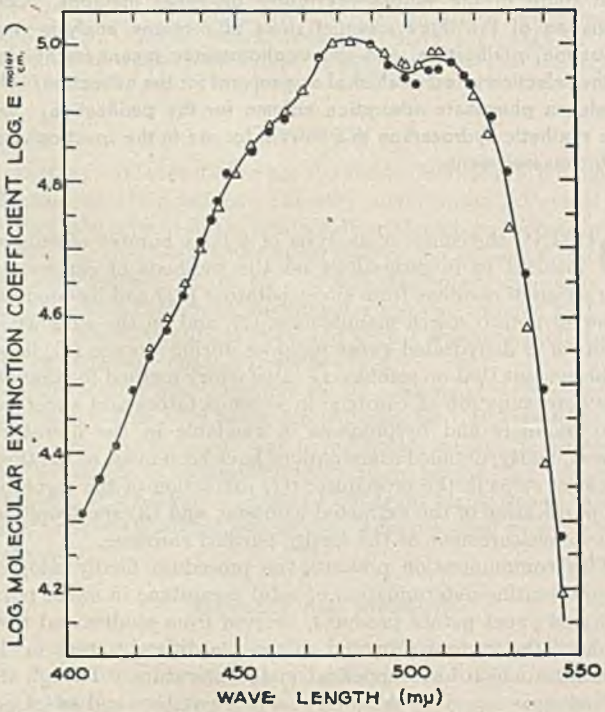

Figure 1. Molecular Extinction Curve of Pure β-Carotene in Carbon Disulfide

○ β-Carotene prepared and measured in the Southern Regional Research Laboratory
● β-Carotene prepared and measured by Smith (*23*)

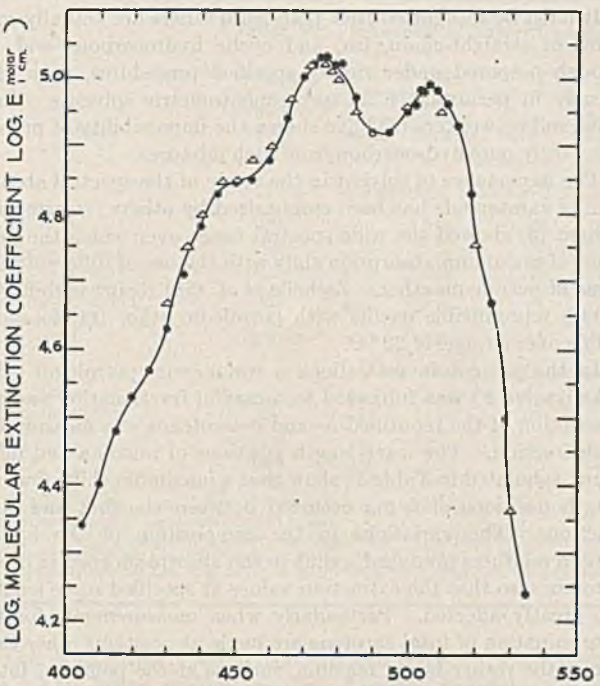

Figure 2. Molecular Extinction Curve of Pure α-Carotene in Carbon Disulfide

○ α-Carotene prepared and measured in the Southern Regional Research Laboratory
● α-Carotene prepared and measured by Smith (*23*)

Table II. Comparison of Phasic Separation and Chromatographic Column Methods of Purification of Extracted Carotene Samples

Sample No.	Carotene Content, Phasic Separation *Mg./kg.*	Carotene Content, Chromatographic Purification *Mg./kg.*
1	176.7	160.0
2	46.3	36.3
3	20.5	15.5
4	50.0	40.0
5	65.0	53.8
6	450.0	435.0
7	950.0	900.0

SPECTROPHOTOMETRIC MEASUREMENT OF PURIFIED CAROTENE

Spectrophotometric methods, when properly used for the quantitative evaluation of the concentration of a substance in solution, are more sensitive, more precise, and more accurate than visual or photoelectric methods. In using spectrophotometric methods, certain precautions must be observed rigidly. The spectrophotometer must provide adequate spectral isolation and be capable of permitting reproducible and accurate measurements of extinction coefficients. The solutions must be purified of substances having interfering absorption. The solvent selected and used must be reproducible in purity and composition. The extinction coefficients, at appropriately selected wave-length positions of characteristic adsorption, must be carefully determined from the most highly purified standards obtainable.

CALIBRATION OF SPECTROPHOTOMETER. The Cenco-Sheard spectrophotelometer used in these investigations was equipped with an aluminum replica grating to provide a smooth over-all response. The wave-length drum readings were calibrated by visual observation of the atomic lines from an A-H-4 mercury vapor lamp, and adjustments made in the positioning of the grating until agreement between the drum readings and true wave length of the mercury lines averaged within 0.3 to 0.4 mμ. Further checks which assured satisfactory performance of the instrument included a comparison of the absorption curve of an equimolecular mixture of potassium chromate and cupric sulfate pentahydrate, the solution proposed by Weigert (*25*) for calibration of spectrophotometers, with the curves obtained by Weigert (*25*) and by Smith (*23*) and a comparison of the transmission curve of a Corning didymium filter glass, CG No. 512, at a constant effective slit width of 5 mμ, with the transmission curve of the identical glass obtained from a General Electric recording spectrophotometer at the National Bureau of Standards.

Test of linearity of over-all response was made by plotting brightness measurements in foot-candles, as obtained by use of a small spot photometer, against intensities as read from the galvanometer of the spectrophotometer. Test for constancy of the intensity ratios was made by measuring the initial intensity and the transmitted intensity of a neutral glass filter over a series of varying original intensity levels. Both tests show that the response of the instrument is strictly linear and reliable only when galvanometer deflections are more than 2 cm. Consequently, in all studies reported in this paper the carotene samples were diluted until suitably large deflections for accurate measurement were obtained. A suitable concentration is about 2 mg. per liter, when 1-cm. absorption cells are used.

PURIFICATION OF SOLVENTS. The hydrocarbon and petroleum ether solvents were purified by adsorbent methods employing chromatographic columns of silica gel as described by Graff, O'Connor, and Skau (*6*). The carbon disulfide was purified by the methods described by Obach (*17*) and by Sameshima (*20*).

PURIFICATION OF CRYSTALLINE CAROTENE. The pure α- and β-carotenes obtained from the S.M.A. Corporation were repurified by repeatedly subjecting petroleum ether solutions to chromatographic purification through aluminum oxide columns, recrystallizing from 95% ethyl alcohol and dioxane, and carefully drying over phosphorus pentoxide. These procedures were continued until no increase in the magnitude of the absorption coefficients was observed and the measured values agreed with those reported in the literature. The finally purified carotenes gave single-banded adsorption on alumina columns and no adsorption on dicalcium phosphate columns.

In Figure 1 the logarithm of the molecular extinction coefficient (extinction coefficient times molecular weight, or logarithm $E^{molar}_{1\ cm.}$) is plotted against the wave length in millimicrons. This figure shows the excellent agreement between the data for the β-carotene purified in this manner and those obtained by Smith (*23*). Figure 2 shows similar agreement for α-carotene, which was purified in an identical manner.

SOLVENT EFFECTS. The widely used procedure of Peterson, Hughes, and Freeman (*18*) employs a spectrophotometer for the final measurement of the carotene solution. Optical density measurements are made at 450, 470, and 480 mμ. Through the use of recommended extinction coefficients given in Table III for a choice of three solvents, these absorption measurements are converted into concentration of carotene by use of the Beer-Lambert law. It has been observed by others (*10*, *15*) that this method does not yield reproducible results, particularly when studied in collaborative work. The same value for the carotene content is not obtained when measurements are made at the specified wave lengths, with the specified solvents. With carefully purified carotenes the extinction coefficients are considerably different from those recommended. Spectrophotometric curves of the purified carotene in any of the recommended solvents (Table III) show no apparent reason for the selection of the particular wave lengths for measurement of the concentration. It is reasonable to postulate, and will be proved by experiments, that these discrepancies are due primarily to a shift in characteristic absorption occasioned by differences in solvents actually used and not due to instrumentation errors nor to impurities.

Table III. Extinction Coefficients for β-Carotene (*18*)

Wave Length	80% Ethyl Ether 20% Ethyl Alcohol Miller (*12*)	Petroleum Ether (B.p. 40–60° C.), Seibert[a]	Skellysolve B (B.p. 60–70°C.), Authors[b]
4500	247	243	238
4550	243	231	227
4700	210	207	200
4800	221	212	212

[a] Coefficients obtained from H. F. Seibert, S.M.A. Corporation, Cleveland, Ohio, and checked by authors.

[b] Skellysolve B, a special commercial grade of petroleum ether, can be successfully substituted for petroleum ether (b.p. 40° to 60° C.) in the modified method described.

These discrepancies are not due to instrument performance or calibration, as they are observed after tests described above have shown the performance of the spectrophotometer used to be satisfactory.

The influence of impurities in the extracted carotene in causing the shift of wave-length positions of characteristic absorption can be shown to be insignificantly small. The extracted carotene purified by the adsorption method described and by the phasic separation and the crystalline β-carotene repurified by the exhaustive process outlined, all contain varying amounts of impurities. The crystalline β-carotene is probably very pure (compare Figure 1). The extracted carotene purified by adsorption contains only isomers of β-carotene, while that purified by phasic separation undoubtedly contains other noncarotene carotenoids as well. When these three preparations are dissolved in either of the hyrocarbon solvents recommended by Peterson, Hughes, and Freeman (*18*) identical absorption curves, as regards the wave-length position of characteristic absorption, are obtained. When they are dissolved in the second hydrocarbon solvent again identical absorption curves are obtained, which differ, however, considerably from the first set of curves. The fact that the three preparations give identical curves in the same solvent shows that impurities are not responsible for the shift of characteristic absorption. The fact that different curves are obtained in the two hydrocarbon solvents is indicative of a solvent effect. Furthermore, the repurified carotene in the hydrocarbon solvent does not give a curve which agrees with that given by Peterson, Hughes, and Payne (*19*). However, the same carotene in carbon disulfide gives a curve which agrees exactly with the one observed by Smith (*23*). This is again an indication of solvent effect.

Moore (*13*) has shown that, by careful chromatographic separation on dicalcium phosphate columns, a number of unnamed noncarotene carotenoids can be removed from the β-carotene extracted by the phasic separation. These experiments have been confirmed here. As these impurities resemble α-carotene in absorption properties, the contamination of pure β-carotene with α-carotene should approximate, qualitatively at least, the effect produced by impurities. Hence, to samples of the purified β-carotene, various amounts of α-carotene were added. Table IV shows the effects of α-carotene upon the absorption of β-carotene. The maximum difference in the wave-length position of maxima and minima of the two pure pigments is about 5 mμ. The 50% alpha–50% beta mixture is found to have absorption maxima and minimum about midway between the corresponding points of the pure components, about 2 to 3 mμ from either, while 25% of alpha changed the absorption position of the pure β-carotene by only a little over 1 mμ. Consequently, the effect of less than 25% α-carotene or alpha-like absorbing impurities in β-carotene would be to produce a shift in the absorption spectra of the latter by an amount undetectable with the usual photoelectric spectrophotometer. But the difference in absorption positions between the petroleum ether solution of carotene prepared in this laboratory and that apparently used as a basis for obtaining the extinction coefficients in this solvent is about 5 mμ. The magnitude of the shift cannot be accounted for by contamination of the extracted β-carotene by small amounts of alpha-like absorbing carotenes and noncarotene carotenoid impurities.

Table IV. Effect of α-Carotene upon the Wave-Length Position of the Absorption of β-Carotene in Iso-octane Solution

Carotene Mixture % Beta	Carotene Mixture % Alpha	Maxima mμ	Maxima mμ	Minimum mμ
100	0	450	476	465
90	10	449	475	465
75	25	448	474	464
50	50	447	474	462
25	75	446	473	462
0	100	444	473	460

It must be recognized that petroleum ethers are actually mixtures of straight-chain, iso, and cyclic hydrocarbons and, although prepared under rigidly specified procedures, may vary greatly in performance as spectrophotometric solvents. Griswold and co-workers (*7*) have shown the impossibility of preparing a truly pure hydrocarbon from such mixtures.

The importance of solvent in the study of the spectral absorption of carotenoids has been emphasized by others. Carter and Gillam (*3*) showed the wide spectral range over which the positions of maximum absorption shift with the use of different fractions of petroleum ether. Zscheile *et al.* (*30*) report inability to obtain reproducible results with petroleum ether fractions distilling over a range of 20° C.

In the present investigations a commercial petroleum ether (Skellysolve F) was subjected to a careful fractionation and the absorption of the repurified α- and β-carotenes was measured in each fraction. The wave-length positions of maxima and minimum, tabulated in Table V, show that a maximum shift of wave-length positions of 6 mμ occurred between the first and fifth fractions. The variations in the composition of the hydrocarbon mixtures produced a shift in the absorption spectra of the carotenes, so that the extinction values at specified wave lengths are greatly affected. Particularly when measurements for the determination of total carotene are made at positions other than across the rather broad maxima, such as at the points of intersection of the alpha and beta absorption curves, which may occur on rather steep portions of the curves, a shift in the position of the absorption will produce a considerable error in the quantitative measurement. For example, from an absorption curve for β-carotene in a petroleum ether fraction, the extinction coefficient at 485 mμ is 160, at 480 mμ it is 204, while at 490 mμ it is only 120. Hence, any change in the character of the solvent, such as a use of a different petroleum ether fraction which will produce a shift in the bands as much as 5 mμ, can affect the value of the extinction coefficient at the predescribed wave-length position to the extent that quantitative measurement is meaningless. Fractions which introduce smaller wave-length changes still introduce serious error in any quantitative determination.

Table V. Wave-Length Positions of Maxima and Minimum of Absorption of Carotenes in Petroleum Ether and Petroleum Ether Fractions

Petroleum Ethers and Boiling Ranges	β-Carotene Maxima mμ	β-Carotene Minimum mμ	α-Carotene Maxima mμ	α-Carotene Minimum mμ
Skellysolve F, A.S.T.M., 30°–60° C.	448 474	464	444 470	458
Fraction 30°–35° C.	446 472	462	442 469	456
Fraction 35°–40° C.	447 474	464	444 470	458
Fraction 40°–55° C.	450 475	465	445 471	459
Fraction 55°–60° C.	452 476	466	446 472	460
Skellysolve B, A.S.T.M., 60°–70° C.	450 476	466	445 472	459

To illustrate the effect of the use of varying solvents upon the determined value of the carotene concentration, a sample of the very carefully purified and dried β-carotene was divided into numerous portions and dissolved in the petroleum ethers, Skellysolves, fractions from Skellysolve F, and other solvents for which extinction coefficients for β-carotene are available. For comparison, extinction coefficients in iso-octane (recommended later) were included. The concentration of the β-carotene in each solution was then determined. The results are tabulated in Table VI. Use of the petroleum ether solvents and the corresponding coefficients results in an error of approximately 5 to 6% of the carotene content. From the data obtained for the five fractions of Skellysolve F, with the use of the petroleum ether coefficients for Skellysolve F, it will be noted that the value for the 35° to 40° C

Table VI. Influence of Solvent on the Spectrophotometric Estimation of β-Carotene

Solvent	Source Extinction Coefficient $E^{g./l.}_{1\ cm.}$	Measured Carotene Content: A, Wave length, mμ	A, Extinction coefficient	A, Carotene, Mg./l.	B, Wave length, mμ	B, Extinction coefficient	B, Carotene, Mg./l.	C, Wave length, mμ	C, Extinction coefficient	C, Carotene, Mg./l.	Average carotene, Mg./l.	Weighed Carotene Content, Mg./l.	Discrepancy, %
Petroleum Ethers and Their Fractions with A.O.A.C. Coefficients													
Skellysolve F, A.S.T.M., 30–60° C.	(*18*)	450	243	1.38	470	207	1.43	480	212	1.29	1.37	1.43	4.2
Fraction 30–35° C.	(*18*)	450	243	1.54	470	207	1.65	480	212	1.45	1.55	1.61	3.7
Fraction 35–40° C.	(*18*)	450	243	1.34	470	207	1.40	480	212	1.27	1.34	1.36	1.5
Fraction 40–55° C.	(*18*)	450	243	1.39	470	207	1.40	480	212	1.37	1.39	1.51	8.0
Fraction 55–60° C.	(*18*)	450	243	1.48	470	207	1.51	480	212	1.43	1.47	1.60	8.2
Fraction 55–60° C.	(*18*)	450	238	1.53	470	200	1.56	480	212	1.43	1.51	1.60	5.6
Skellysolve B, A.S.T.M., 60–70° C.	(*18*)	450	238	1.61	470	200	1.64	480	212	1.56	1.60	1.70	5.9
Other Solvents with Extinction Coefficients from the Literature													
Iso-octane[a]	This paper	450	245	1.99	476	219	2.00	...	...	...	1.995	1.994	0.0
Carbon disulfide[b]	(*23*)	484	196	2.03	513	174	2.03	...	...	...	2.030	2.034	0.2
Petroleum ether, b.p. 40–55° C.[c]	(*21*)	447	245	1.85	465	200	1.92	475	211	1.96	1.910	1.898	0.6
Hexane[d]	(*30*)	450	258	1.40	466	206	1.46	478	228	1.41	1.423	1.462	2.7
Heptane[e]	(*92*)	455	240	1.34	480	210	1.36	...	...	...	1.350	1.380	2.2

[a] Rohm & Haas, b.p. 98–99° C. Purified by adsorbent method (*6*).
[b] Purified by chemical methods (*17*, *20*).
[c] Prepared by fractionation from Skellysolve F. Purified by adsorbent method (*6*).
[d] Eastman Kodak Co. synthetic, b.p. 68–69° C. Purified by adsorbent method (*6*).
[e] Eastman Kodak Co. synthetic, b.p. 98–98.5° C. Purified by adsorbent method (*6*).

fraction is in rather good agreement with the correct concentration. The lower boiling fraction shows a somewhat poorer agreement. With the higher boiling fractions agreement is very poor. Better values are obtained from the 55° to 60° C. fraction of Skellysolve F when the coefficients for Skellysolve B are used.

When the pure β-carotene is analyzed from solutions in iso-octane with the coefficients recommended in Table VII, in carbon disulfide with coefficients from Smith (*23*), and in a petroleum ether fraction from coefficients furnished by Seibert (*21*), very good agreement with the true concentrations is obtained. Use of Eastman Kodak Company synthetic hexane and heptane with coefficients from Zscheile (*30*) and Shrewsbury (*22*), respectively, yields carotene values somewhat too low. The hexane used by Zscheile (*30*) was obtained from petroleum ether and boils from 65° to 67° C. The maxima of β-carotene in this solvent were reported at 450 and 478 mμ. The hexane used in this laboratory is a synthetic product boiling from 68° to 69° C. and the β-carotene maxima were observed at 448 and 476 mμ. The heptane used here was also a synthetic product, boiling from 98° to 98.5° C., and the maxima for β-carotene were found at 453 and 478 mμ. Shrewsbury (*22*) does not describe his heptane but reports absorption maxima at 455 and 480 mμ. Consequently, the 2 to 3% discrepancies between the determined values of the β-carotene concentration and true values in these two solvents may be due to slight solvent effects.

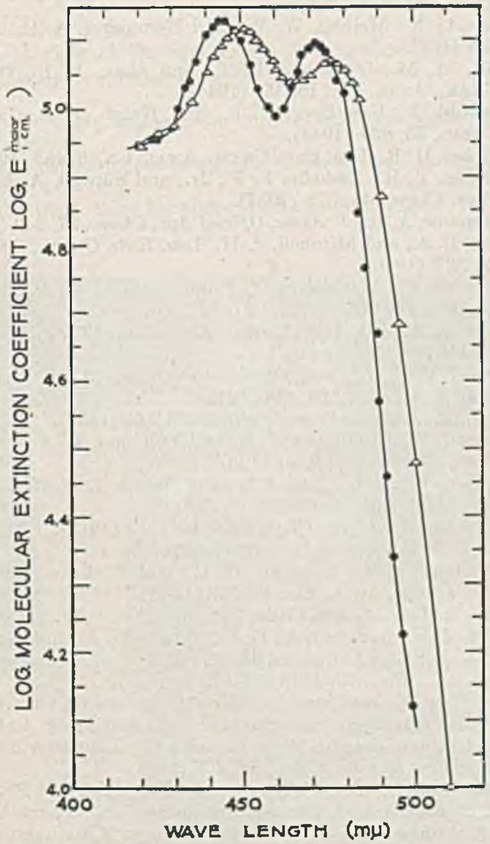

Figure 3. Molecular Extinction Curves of Pure α- and Pure β-Carotenes in 2,2,4-Trimethylpentane (Iso-octane)

● α-Carotene △ β-Carotene

The conclusion which can be obtained from the data given in Table VI is that very accurate determination of carotene by use of spectrophotometric measurements and published extinction coefficients can be obtained only if an exact description of the solvent in which they were measured is given and if that identical solvent is used.

Improved Procedure. To provide a method for the final determination of carotene by spectrophotometric measurement of the absorption of a prepared solution of the sample, and calculation of the concentration, by the use of Beer's law, from coefficients provided, a solvent which can be duplicated exactly in other laboratories must be selected. Petroleum ether fractions cannot be used with satisfaction. Griswold and his co-workers (*7*) have shown the presence of a large number of compounds in the petroleum ether fractions commonly used, and the impossibility of obtaining pure straight-chain hydrocarbons by fractionation. Commercially pure hexane and heptane have been suggested as solvents in the analysis for carotene (*22*, *30*), but these are recognized as mixtures.

Iso-octane (2,2,4-trimethylpentane), the synthetic hydrocarbon introduced as a solvent in spectrophotometry by Hogness and co-workers (*9*) because of its ease of purification, was selected. This solvent can be obtained in a very pure state, is readily available, and its cost is not excessive. In Figure 3 the spectral absorption curves of the pure α- and β-carotenes in iso-octane are compared. Table VII is a tabulation of data from the absorption curves of the two carotenes in iso-octane solution. For the determination of β-carotene in a solution free from all interfering carotenoids, as prepared by the methods described earlier, measurements at 450 and 476 mμ, peaks of the β-carotene bands, and use of the corresponding extinction coefficients, 245 and 219, respectively, permit a very accurate determination.

The method described has been used for the analyses of hundreds of samples of fresh and dehydrated sweet potatoes and of various sweet potato products. Table VIII shows representative results over the wide range of concentrations encountered in the analyses of these materials. The analysis of a carefully purified carotene by the complete method has been included in Table VI. After the spectrophotometric measurements have been completed, the carotene solutions are collected for recovery of the iso-octane by fractionation and chromatographic purification (*6*). In this manner the same supply of the solvent is used again and again and the final cost of the solvent is even less than when petroleum ether fractions, which cannot be recovered in this manner without considerable change in character, are used.

Table VII. Extinction Coefficients for Determining Carotenes in 2,2,4-Trimethylpentane (Iso-octane)

Carotene	Wave Length	Extinction Coefficient $E^{g./l.}_{1\ cm.}$	Absorption
	mμ		
I. Pure α-carotene	444	252	Maximum
	473	234	Maximum
II. Pure β-carotene	450	245	Maximum
	476	219	Maximum
III. Total (crude) carotene	449	242	Equality
	465	202	Equality
	477	218	Equality
IV. β-Carotene in the presence of alpha or alpha-like absorbing impurities	460	Alpha 182 Beta 214	Maximum Difference
	486	Alpha 110 Beta 176	Maximum Difference

Table VIII. Analyses of Sweet Potatoes and Various Sweet Potato Products by Proposed Method

Sample No. and Description	Carotene Content: Determination A	Determination B	Average
	Mg./kg.	*Mg./kg.*	*Mg./kg.*
Fresh sweet potato			
1	49.0	50.0	49.5
2	37.5	39.5	38.5
3	51.0	51.0	51.0
4	45.0	45.0	45.0
5	45.0	45.6	45.3
Sweet potato dried			
1	164.0	164.0	164.0
2	135.0	138.0	136.5
3	145.0	147.0	146.0
4	153.0	152.0	152.5
5	161.0	164.0	162.5
Dehydrated sweet potato (immediately after dehydration)			
1	123.0	121.0	122.0
2	110.0	112.0	111.0
3	113.0	113.0	113.0
4	85.0	87.5	86.2
5	118.0	118.0	118.0
Dehydrated sweet potato (after 30 days' storage under air)			
1	108.0	110.0	109.0
2	107.0	111.0	109.0
3	130.0	127.0	128.5
4	118.0	118.0	118.0
5	99.0	100.0	99.5
Dehydrated sweet potato (after 30 days' storage under CO_2)			
1	88.6	88.6	88.6
2	103.0	103.0	103.0
3	108.0	106.0	107.0
4	97.4	98.1	97.8
5	103.0	108.0	105.5
Sweet potato coagulum from starch plant waste water (*1*)			
1	730.0	730.0	730.0
2	1110.0	1110.0	1110.0
3	590.0	600.0	595.0
4	450.0	435.0	442.5
5	888.0	888.0	888.0
Sweet potato starch			
1	0.6	0.4	0.5
2	2.4	2.2	2.3
Sweet potato pulp dried (after removal of starch and pectin)			
1	32.0	30.2	31.1
2	22.5	22.5	22.5
3	36.7	43.3	40.0
4	50.8	50.8	50.8
5	26.2	30.0	28.1
Residue from sweet potato starch plant waste after removal of coagulum			
1	13.3	10.8	12.0
Sweet potato pulp residue			
1	49.0	50.0	49.5
2	87.5	87.5	87.5
3	85.0	85.0	85.0
4	50.8	50.8	50.8
5	90.0	100.0	95.0

SUMMARY

The three essential steps in the analysis for carotene—extraction, purification, and spectrophotometric measurement—have been studied in detail and from these studies a modified method has been proposed for the analysis of total β-carotene in sweet potatoes and sweet potato products.

It has been shown that the inconsistencies noted in the use of published extinction coefficients for carotene in petroleum ether fractions cannot be due solely to the presence of noncarotene impurities in the solutions and that they are due to the variable character of these mixed solvents. The easily purified solvent previously introduced into spectrophotometry, iso-octane (2,2,4-trimethylpentane), has been proposed for use in carotene analysis, and extinction coefficients in this solvent have been furnished.

Use of the proposed method has been illustrated by representative results in the analysis of various fresh and dehydrated sweet potatoes and sweet potato products.

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Study of Millin Technique for Determination of Carbon and Hydrogen in Coal

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The Millin technique for determination of carbon and hydrogen in coal has been studied. The procedures have been controlled by analysis of pure organic compounds and the technique has been found satisfactory for many other substances that are amenable to analysis by combustion.

THE purpose of the work described in this paper has been to verify a new rapid technique first described by Millin (*3*) for the macrodetermination of carbon and hydrogen in coal. The procedures used have been controlled by the analysis of pure organic compounds, and the technique developed has been found to give satisfactory results for many other substances which are amenable to analysis by combustion.

Analysis for carbon and hydrogen content of coal requires from 1 to 2 hours by the standard A.S.T.M. method (D-271–44). With the Millin procedure results for bituminous coal and anthracite are available in 25 and 45 minutes, respectively. The essential differences between the method described by Millin and that recommended by the A.S.T.M. are in the rate of oxygen flow, 100 ml. per minute in the former and 3 bubbles per second in the latter, and the substitution of silver turnings for a portion of the copper oxide in the combustion tube. The new procedure has been adapted for use with standard equipment and requires only the slight modification, noted above, from standard practice in charging the combustion tube.

APPARATUS

A general view of the apparatus used is shown in Figure 1; parts indicated by numbers are:

1. Needle valve and gage on supply tank of oxygen
2. Flowmeter
3. Preheating furnace filled with copper oxide wire, operating temperature 850° C.
4. Anhydrone tube for absorption of water vapor
5. Ascarite tube for absorption of carbon dioxide
6. Anhydrone–phosphorus pentoxide tube for final elimination of water vapor
7. Movable heating unit, about 13 cm. long, which serves to heat the inlet of the combustion tube and the boat containing the substance being analyzed, operating temperature 850° to 900° C.
8. Transparent section of combustion tube, 10 cm. in length
9. Movable heating unit, 33 cm. in length, used to heat the copper oxide wire and silver turnings, operating temperature 850° C.
10. Stationary furnace, 23 cm. in length, used for heating the lead chromate section, operating temperature 600° C.
11. Spun copper shield
12. Nesbitt bulb filled with Anhydrone
13. Nesbitt bulb filled with Ascarite

The fused quartz combustion tube used in this work (Figure 2) was made to specifications by the Amersil Company, Inc., Chestnut Avenue, Hillside, N. J. Its most convenient feature is the 10-cm. clear section 25 cm. from the charging end, which allows the operator to observe the combustion of the sample during the whole course of the determination. The reagents in the tube are separated in the usual manner by copper screen plugs. The movable copper oxide spiral at the entrance end is also fashioned from copper screening. The silver used is in the form of turnings tamped tightly together.

The spun copper shield over the exit end of the combustion tube serves to conduct heat from the furnace to the projecting end of the tube, thereby eliminating condensation of water vapor.

The Nesbitt bulbs used hold about 75 grams of 8 × 20 mesh Ascarite and are usable for at least 10 runs, thus allowing ample excess of reagents to ensure complete absorption of the carbon dioxide.

Figure 2 illustrates the positions and lengths of packing materials used.

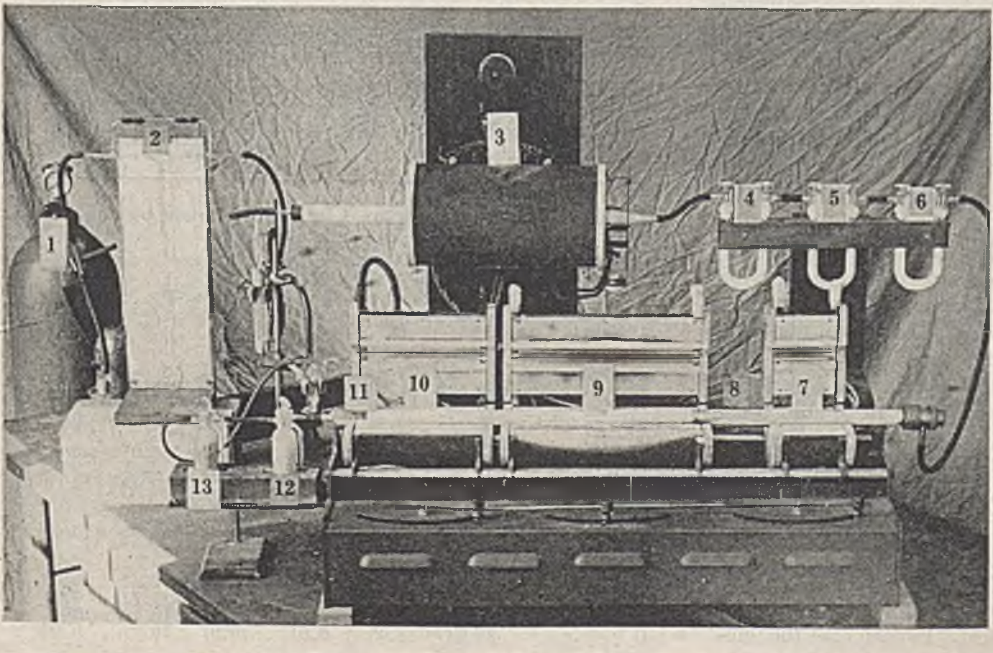

Figure 1. General View of Apparatus

PROCEDURE

With the furnaces at their operating temperatures the combustion train is tested in the usual manner until blanks indicate the apparatus is in a satisfactory condition. A gain of not more than 0.5 mg. in either absorption tube is considered satisfactory. Newly prepared tubes are conditioned by burning a small sample under normal operating procedure. After obtaining satisfactory conditions, absorption tubes 12 and 13 are attached and the boat containing the sample to be analyzed is inserted into the tube and moved to the clear section, followed by the copper oxide wire spiral. Furnace 7, which is at about 500° C., is at the extreme end of the stand. The oxygen needle valve, 1, is adjusted so that the flowmeter indicates a rate of 100 ml. per minute. The rheostat of furnace 7 is adjusted so that the unit will operate at 850° C., a temperature which it attains within a few minutes. Furnace 7 is slowly moved up to the boat and within 10 minutes will have completely covered it. After about 5 minutes both heaters 7 and 9 are pulled to the extreme end of the stand, so that furnace 7 is in its original position over the copper oxide spiral and a portion of heater 9 is over the clear section containing the charge. The rheostat on heater 7 is then adjusted to its original temperature setting, and after 5 more minutes, heater 9 is returned to its original position and the flow of oxygen is continued for another 5 minutes. At the end of this time (total of 25 minutes) the absorption tubes are shut off under pressure and then the flow of oxygen is cut off. A blowout tube, not indicated, which automatically controls the maximum pressure in the system makes this last step possible; it also prevents the manometer fluid from being forced into the train in event of misadjustment of the needle valve.

At the completion of the above steps the absorption tubes are placed near the balance and the train is ready for the next run. The tubes are allowed to cool to balance temperature, vented to the atmosphere for a few seconds while being wiped with a damp chamois skin, and then weighed, using a similar tube as counterpoise on the balance.

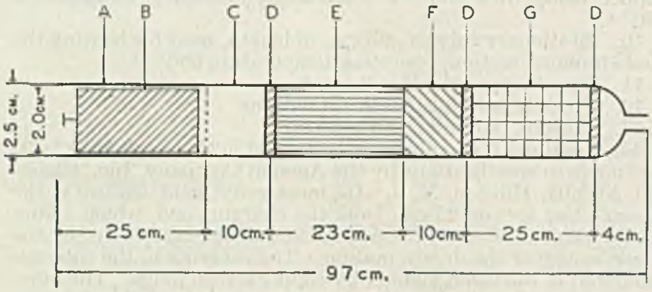

Figure 2. Fused Quartz Combustion Tube

A. Charging end
B. Removable, oxidized, copper screen spiral
C. Transparent section for combustion boat
D. Oxidized copper screen plugs
E. Cupric oxide (wire form)
F. Silver turnings
G. Lead chromate

All results for bituminous coals reported on in this paper were obtained by this procedure. In the paper by Millin (*3*) a time of 20 minutes is given for the analysis of coals; this lower rate may be due to the longer length of combustion tubing which was employed, thereby allowing the use of 35 cm. of copper oxide and 10 cm. of silver turnings in the center furnace, whereas the authors were limited, because of the standard design of the apparatus, to 23 cm. of copper oxide and 10 cm. of silver turnings. No indication was given that any of the samples analyzed were anthracites. In the case of anthracites more time was found necessary for complete combustion of the samples; hence the regular procedure was changed to allow heater 7 to be placed over the charge immediately and to remain there 10 to 15 minutes longer than usual.

The procedure was used for various other materials which, because of their greater volatility, required slight changes in technique. The increase in time required was used to volatilize the material slowly without allowing it to catch fire; the rate of oxygen flow was decreased slightly in some cases, although this was more of a conservative measure than a necessity.

In the preliminary tests to establish a minimum time for combustion, two Ascarite absorption tubes were placed in series on the train; the second in the series would show a gain if the first did not completely absorb all carbon dioxide formed during combustion. Through this procedure it was found that Fisher-type tubes, which have about one fourth the capacity for Ascarite as the Nesbitt tubes finally adopted, were too small to absorb the carbon dioxide quantitatively. To test for complete conversion of the carbon to carbon dioxide a bubbler tube containing a solution of palladous chloride (*4*) was attached to the end of the train.

RESULTS AND DISCUSSION

Table I shows typical results obtained using Bureau of Standards samples of sucrose and benzoic acid. In each case the ignition period was completed in 25 minutes and the sample tubes were removed and allowed to cool before weighings were made. In the case of benzoic acid the slightly low results for carbon may be attributed to the rapid rate at which the substance volatilized; no alteration in time of combustion was tried on this substance.

Table I. Tests on Bureau of Standards Samples

	1	2	3	4	Theoretical
Sucrose					
C, %	42.08	42.06	42.08	41.98	42.08
H, %	6.50	6.49	6.44	6.49	6.48
Benzoic acid					
C, %	68.67	68.75	...	...	68.83
H, %	4.94	4.99	...	...	4.96

Table II gives results of analysis of a bituminous coal sample by the standard A.S.T.M. and Millin procedures. Tables III and IV give results by the Millin procedure on anthracites, bituminous coals, carburetting oil, tar, abietic acid, and liquid hydrogenation products.

Sucrose is generally used as a control standard in combustion analysis. The data in Table I show that the Millin procedure is satisfactory in the analysis of sucrose. Table II shows the results obtained with the two methods on a sample of bituminous coal which was air-dried and ground to pass a 250-micron (No. 60) sieve. All other samples of coal used were prepared in like manner. The specified permissible difference for duplicate analysis,

Table II. Comparative Results by A.S.T.M. and Millin Procedures on a Bituminous Coal

Method	1	2	3	Time, Min.
A.S.T.M.				
C, %	84.00	83.91	84.19	120
H, %	4.13	4.10	4.12	
Millin				
C, %	84.20	84.20	84.30	25
H, %	4.13	4.10	4.10	

Table III. Typical Results on Coals by Millin Procedure

Sample Designation	Time of Combustion	Carbon			Hydrogen		
		Run 1	Run 2	Difference	Run 1	Run 2	Difference
	Min.	%	%	%	%	%	%
Bituminous coal							
A	25	79.19	79.14	0.05	4.62	4.66	0.04
B	25	75.27	75.27	0.00	5.18	5.21	0.03
C	25	82.91	82.65	0.25	4.32	4.30	0.02
D	25	72.66	72.38	0.28	4.89	4.87	0.02
E	25	79.21	79.15	0.06	5.06	5.01	0.05
Anthracite							
F	40	81.65	81.60	0.05	2.01	2.06	0.05
G	40	79.08	79.09	0.01	2.39	2.43	0.04
H	40	80.87	81.04	0.17	2.47	2.44	0.03
I	40	84.36	84.32	0.04	2.15	2.12	0.03
J	40	85.14	85.12	0.02	2.09	2.10	0.01

Table IV. Typical Results on Organic Materials by the Millin Procedure

(Time of combustion, 75 minutes)

Sample Designation	Carbon Run 1	Carbon Run 2	Difference or Theoretical	Hydrogen Run 1	Hydrogen Run 2	Difference or Theoretical
	%	%	%	%	%	%
Carburetting oil						
K	84.92	84.70	0.22	13.82	13.80	0.02
L	85.49	85.57	0.08	13.89	13.86	0.03
M	85.44	85.24	0.20	13.71	13.76	0.05
Tar						
N	92.58	92.40	0.18	6.39	6.37	0.02
O	92.63	92.71	0.08	6.51	6.51	0.00
P	92.50	92.49	0.01	6.39	6.42	0.03
Abietic acid (recrystallized)						
Q	79.35	79.30	79.40	9.87	9.90	10.00
Liquid hydrogenation products						
R	87.68	87.73	0.05	12.14	12.12	0.02
S	88.13	88.19	0.06	11 78	11.73	0.05
T	88.68	88.67	0.01	10.95	10.99	0.04
U	88.92	88.93	0.01	10.91	10.91	0.00

Table V. Statistical Analysis for Carbon and Hydrogen

Min. %	Max. %	Σn	m	s	$\Sigma n'$	m'	s'	B'	γ'
Carbon, A.S.T.M. permissible difference = 0.3%									
Anthracites									
55.74	91.73	208	100	0.181	207	100	0.172	0.4	<100
Bituminous coals									
34.10	91.10	124	50	0.420	118	48	0.317	0.4	<500
Hydrogen, A.S.T.M. permissible difference = 0.07%									
Anthracites									
0.34	3.30	211	100	0.049	211	100	0.049	0.2	<200
Bituminous coals									
0.34	5.78	127	50	0.143	121	48	0.088	0.8	<500

Min. Minimum value for single determination.
Max. Maximum value for single determination.
Σn. Total number of analyses reported.
m. Number of samples.
s. Standard error of difference between duplicates analyses.
$\Sigma n'$, m', s'. Values of Σn, m, and s after eliminating samples for which analyses showed evidence of gross error.
B': Approximate measure of normality of distribution of errors after elimination of gross errors.
γ'.- Calculated frequency of exceeding A.S.T.M. "permissible" difference between duplicate determinations per thousand.
<10 = 0 to 9.9, <20 = 10 to 19.9, <100 = 50 to 9.99, <200 = 100 to 199, etc.

according to A.S.T.M. standards on coal and coke (*1*), is 0.30% for carbon and 0.07% for hydrogen. That the duplicates obtained by this new procedure fall well within these limits is shown by the data of Table III, where a maximum difference of 0.28% is given for carbon and of 0.05% for hydrogen. Duplicate results that fall within the specified tolerances are generally obtained from two analyses, a third analysis being necessary only occasionally. In this respect it is usually the carbon value that is outside the tolerance and seldom the hydrogen.

Several other types of materials were analyzed (Table IV). It was found necessary, owing to the greater volatility of these substances, to lengthen the time of combustion to 75 minutes. Aside from this increase in time, which is considerably shorter than that used in the older method, the method works consistently well. The abietic acid analyzed was allowed to stand for some time before an analysis was made on it and may have been of questionable purity. The liquid hydrogenation products may have contained traces of water. They were separated by distillation and dried over phosphorus pentoxide and were expected to be pure hydrocarbons.

Table V summarizes the results obtained from a statistical analysis of 100 sets of values for percentages of carbon and hydrogen in 100 different samples of anthracite coals. These data were calculated in a manner identical to that used by Lowry and Junge (*2*). For comparison purposes data submitted by this laboratory and reported by Lowry and Junge (*2*) for 50 sets of values on 50 different samples of bituminous coals are included. An examination of Table V shows that values of B' in every case are less than unity; the data themselves do not give an indication of departure from normality.

The values of the frequency, γ', show a decided improvement in the case of both carbon and hydrogen, as do the values of s and s'. Analytical procedures are frequently controlled by the use of statistical methods, to give the equivalent of a "reasonable" permissible difference, which may be defined as that difference between duplicate determinations which would not require a third determination more than 50 times in 1000. A "reasonable" permissible difference equal to 1.96 s' would yield a value of $\gamma' = 50$.

In comparing the two methods it appears that a "reasonable" permissible difference for carbon by the Millin procedure would be calculated from the data on anthracites to be 0.34% and by the A.S.T.M. method on bituminous coals to be 0.62%, and similarly for hydrogen 0.10 and 0.17%.

Inasmuch as the data reported were obtained in small groups (never more than ten samples were run consecutively) and the whole group was collected over a period of 3 years, with four different operators during that period, it seems reasonable that for routine operation the limits should not be expanded. The following quotation from Selvig's comment (*5*) on the paper of Lowry and Junge (*2*) seems appropriate:

> It is not surprising that difficulties were experienced in the ultimate analysis in determining carbon and hydrogen, as this analysis requires a higher degree of manipulative skill and good condition of the combustion train, both of which are difficult to attain if determinations are made at irregular intervals. Here possibly it would be better not to raise the permissible difference between duplicate determinations but to make multiplicate rather than duplicate determinations to obtain the required precision.

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Estimation of Oxygen in Inert "Oxygen-Free" Atmospheres

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A GROWING number of industrial processes require atmospheres in which the oxygen content is far below 0.01% by volume. An analytical method capable of dealing with these minute concentrations of oxygen in atmospheres inert to the reagents employed is described below.

Oxygen at concentrations near 0.0001% in 1 liter of gas at room temperature and atmospheric pressure exerts a pressure below 1 micron and weighs about 1 microgram. The successful analysis of such a sample could be accomplished, but only by taking extreme precautions to eliminate measurable contamination before liberation of iodine and by determining this iodine in a solution that could be exposed almost with impunity to the atmosphere.

CHOICE OF METHOD

Of the chemical methods for estimating oxygen, the two most promising for further refinement seemed those involving the oxidation of ferrous or of manganous compounds in alkaline media.

The use of ferrous salts for the determination of oxygen was originated by Mohr (*2*, *8*) and developed further by Shaw (*11*), who determined the ferric ion colorimetrically with thiocyanate in acid solution, the blank being near 0.008% oxygen. The portion of this blank traceable to the ferrous ammonium sulfate was practically eliminated in this laboratory by leaving acid ferrous ammonium sulfate solutions overnight on the steam bath in contact with pure aluminum. Unfortunately, the oxidation, by the laboratory air, of ferrous ion in acid solutions could not be sufficiently reduced.

The use of manganous hydroxide and an iodide to determine oxygen dissolved in water was developed by Winkler (*12*) in a classic investigation. In this sensitive method, the oxidized manganous hydroxide liberates upon acidification an amount of iodine equivalent to the dissolved oxygen initially present. Various investigators (*1*, *3*, *4*, *6*, *9*, *10*) have adapted this scheme to the determination of oxygen in gases. Hand (*4*) demonstrated

A practical, sensitive, and reasonably reliable method, based upon the liberation of iodine by oxidized manganous hydroxide, has been developed for the determination of oxygen at concentrations above 0.0001% by volume in a liter of gas at atmospheric pressure; 0.01% is perhaps the concentration most convenient for the method. The decreasing reactivity of manganous hydroxide as its surface becomes oxidized sets the useful upper limit for the method near 0.1% oxygen. The final iodine determination, whether spectrophotometric (0.001% oxygen or less) or by titration with thiosulfate, must be carried out in solutions stable toward air.

that great sensitivity could be achieved in this way. His method suffers from the drawback that the sample must be introduced into a complicated apparatus that has been previously evacuated, and his preparation of standards is open to objection.

STABILITY OF STANDARD IODINE SOLUTIONS

Standard solutions containing iodine in microgram amounts, with and without added starch, were investigated on the G.E. recording spectrophotometer (*7*) in order to find conditions under which handling in contact with air would not cause appreciable oxidation of iodide.

The first standards were prepared according to Hand (*4*) by adding known amounts of permanganate ion to acid iodide solutions. After the permanganate had reacted, these standards continued to deepen rapidly in color. This instability ("afterbluing" or "oxygen error"), which is well known in iodometry, showed these solutions to be useless for the authors' purposes.

Satisfactory standards were finally made from known permanganate solutions.

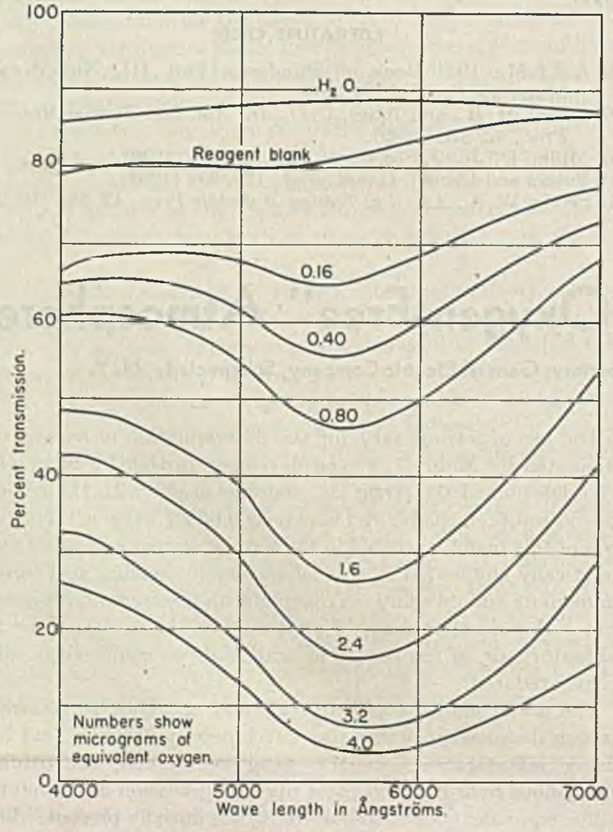

Figure 1. Transmittance Curves for Iodine Standards with 1 Cc. of Starch

The various reagents were added to glass-stoppered graduates in the order: 2 cc. of 1 N sodium hydroxide–0.1 M potassium iodide solution; 1 cc. of 3 N sulfuric acid; 0.5 cc. of 0.5 M manganous chloride; 0.001 N or 0.0001 N permanganate solution, freshly prepared by dilution; 2 cc. of 0.6 M sodium bicarbonate; 1% starch, 0.1 or 1.0 cc.; finally, boiled distilled water to a volume of 27 cc. The bicarbonate neutralizes acid and provides an inert atmosphere. It was blown in to ensure rapid action and to prevent the undesired precipitation of manganous carbonate. This addition of bicarbonate leaves the solution weakly acid; more was subsequently added dropwise to raise the pH to about 5.

In preparing standards from iodine solutions by the foregoing procedure, the permanganate was omitted, and the known iodine solution was added after the bicarbonate.

A representative family of absorption curves for the starch-iodine complex thus prepared is shown in Figure 1. Even with scrupulous cleanliness, a little color, representing usually a few tenths microgram of oxygen, developed when neither permanganate nor iodine was added; the "reagent blank" curve of Figure 1 is an example. The wave length for maximum absorption shifts toward the red as the concentration of the starch-iodine complex increases. In making the Beer's law calculations, I_0 for the reagent blank and I for the standard were taken at the wave length of maximum absorption.

The stability of standard solutions made according to the foregoing method was tested on the spectrophotometer. The curve in Figure 2, for example, was obtained by having the instrument record continuously for 26 minutes the transmittance of a standard containing the blue starch-iodine complex at a concentration equivalent to about 0.4 microgram of oxygen. (The instrument draws one complete curve every 3 minutes.) Standards containing starch cannot be kept for more than a few hours before blue particles begin to separate; this separation may have begun in the test of Figure 2, for the transmittance actually increased a little during the test. In any case, there was no indication of appreciable "oxygen error" in this or similar experiments.

Beer's law plots are shown in Figure 3 for three sets of standards. An insufficiency of starch appears to be responsible for the relatively low light absorption at the higher concentrations (compare curves A and B). In the most dilute range, the permanganate standards (curve C) absorbed less light than corresponding ones prepared with iodine (curve B), possibly because the reaction was quenched too soon in the attempt to reduce the risk of oxidation of iodide by air.

The spectrophotometric work thus proved that unwanted iodine formation could be made negligible. It also proved that the estimation of oxygen at concentrations below about 0.001% in 1 liter of gas can be carried out spectrophotometrically on the equivalent amount of iodine.

METHOD FOR OXYGEN

Reagents. A solution 1 N in sodium hydroxide and 0.1 M in potassium iodide; 3 N sulfuric acid; 0.5 M manganous chloride, slightly acid; 0.6 M sodium bicarbonate; 0.002 N (or another suitable concentration) sodium thiosulfate stabilized with sodium carbonate, freshly prepared by dilution; an inert gas containing no oxygen detectable by the present method.

The "oxygen-free" gas in this work was hydrogen that had been passed slowly (110 cc. per minute) in an all-glass system over copper at 600° C. and then over sodium hydroxide pellets to remove hydrogen sulfide. A 6-liter bulb inserted after the sodium hydroxide served as a reservoir, so that 1 liter of hydrogen could be withdrawn rather suddenly without diminishing the effectiveness of the purifier.

All solutions used for oxygen determinations were kept in gas washing bottles through which "oxygen-free" hydrogen was bubbled continuously. Rubber tubing used in connecting these and other vessels to the purification system was kept at a minimum.

The purity of the manganous chloride, which must be low in iron, is especially important; but all chemicals should be of high quality. The fact that repeated analyses of the purified hydrogen showed no detectable iodine proved that the reagents and the

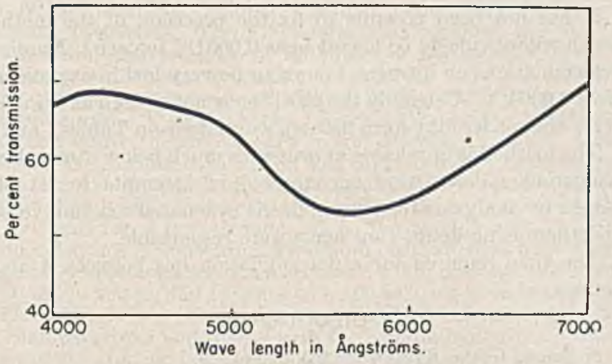

Figure 2. Stability Test on Permanganate Standard

Curve retraced continuously over 26-minute period in spectrophotometer

manipulation were good enough to keep oxygen or oxygenlike impurities below 1 microgram of equivalent oxygen.

Apparatus and Manipulation. The 1-liter reaction vessel (Figure 4) must be dry and clean; drops of a liquid that has been in contact with air must be avoided. Whenever glass apparatus (pipet included) has been in contact with manganous solutions and with oxygen, films of oxidized manganous compounds may be present; such films can usually be removed with strong hydrochloric acid. After a determination in which the oxygen content exceeded 0.1%, however, sodium sulfite was added along with the acid in the cleaning process. Boiled water and acetone were used for rinsing. Stopcocks were carefully greased and cleaned between determinations. Only vacuum-tested stopcocks were used, and these had occasionally to be changed, probably because of attack by the alkaline solutions.

The gas sample was usually obtained by streaming the gas to be analyzed for several hours through the reaction vessel. After the two stopcocks nearest the spherical bulb had been closed, the section below the lower stopcock was filled with water and tightly corked.

The solutions were introduced in the following order from the cylindrical reservoir into the spherical bulb: 10 cc. of sodium hydroxide–potassium iodide solution; 5 cc. of manganous chloride; 8.5 cc. of sulfuric acid. No matter what the solution, it was transferred by means of a pipet from the gas washing bottle into the clean, dry cylindrical reservoir through the female ground joint. The apparatus was then connected by means of the upper male ground joint (Figure 4) to the 6-liter bulb in the oxygen-free hydrogen train. The outlet from the cylindrical reservoir was connected to a bubbling bottle filled with sulfuric acid. The "oxygen-free" hydrogen was bubbled for 10 minutes through the solution in the reservoir; then the outlet was connected to the rough vacuum, whereupon the gas space in the reservoir was twice evacuated and refilled with the hydrogen. With all four stopcocks closed, the reaction vessel was disconnected, and the solution was transferred to the bulb by cooling the latter under the tap, by opening the necessary stopcock, and by careful shaking. The cylindrical reservoir was next cleaned with strong hydrochloric acid, and rinsed with boiled water. The stopcock and joints affected were regreased, and the reaction vessel was reconnected to the hydrogen train to receive the next solution.

Table I. Time of Shaking at Different Concentrations of Residual Oxygen

No.	Time of Shaking *Hours*	Residual Oxygen *% by volume*	Oxygen Found *% by volume*
1	1	0.0013	0.0015
2	1	0.028	0.020
3	1	0.028	0.019
4	2.5	0.028	0.028

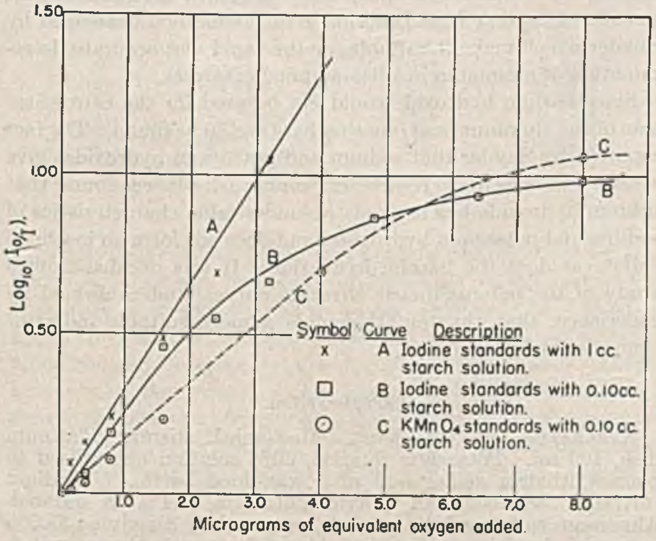

Figure 3. Beer's Law Curves for Iodine and Permanganate Standards

After the first two solutions had been introduced into the bulb, the reservoir and the attached tubes were filled with boiled distilled water, and the two upper stopcocks were closed. The vessel was then rotated by hand to form manganous hydroxide and to distribute it uniformly. It was next wrapped in a towel and strapped centrally to the table of a rotary shaker and shaken (usually for 2 hours) at a rate near 165 cycles per minute. Finally the sulfuric acid was transferred into the bulb in the manner described above.

The acid iodine solution was then drained out of the reaction vessel, and the pH raised rapidly to a value between 4 and 6 by adding sodium bicarbonate solution. Such solutions in glass-stoppered flasks could be kept in the dark without gaining appreciably in iodine content, which is not surprising since their compositions approximated those of the stable standards discussed above. Usually the iodine was titrated on an aliquot portion of the solution with thiosulfate, 0.002 *N* or stronger, 1 cc. of starch having been added.

Sensitivity and Reliability. The work of Winkler (*12*) and subsequent experience with his method leave no doubt that the oxidation of manganous hydroxide and the subsequent liberation of iodine affords the best chemical method for estimating oxygen dissolved in water. On this basis, the present method may be considered reliable, provided that (1) the blank is negligible, (2) the time of shaking is long enough to reduce all the oxygen, and (3) there is negligible "oxygen error" when the final solutions are handled in contact with air. Proof of the last point was given above.

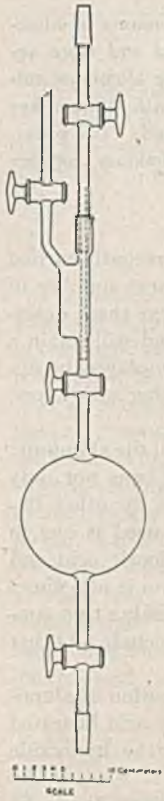

Figure 4. Reaction Bulb for Oxygen Determinations

When "oxygen-free" hydrogen was analyzed, no oxygen could be detected by the present method, the blank being considerably less than 1 microgram of oxygen. A similar result was obtained on the evacuated reaction vessel when no leaks occurred. This proves a negligible blank and also shows that oxygen adsorbed on the walls may be neglected. The last conclusion is in accord with the literature (*5*).

What constitutes a sufficiently long time of shaking is more difficult to establish, owing to the decrease in the reactivity of manganous hydroxide as its surface becomes oxidized. This decrease in reactivity was demonstrated in two series of experiments (Tables I and II).

In the experiments of Table I, the reaction vessel was exhausted to the pressure corresponding to the per cent residual oxygen, and immediately filled to atmospheric pressure with "oxygen-free" hydrogen. Oxygen determinations gave the results in the last

Table II. Results on Nitrogen at Various Partial Pressures

No.	Time of Shaking *Hours*	Oxygen in Reaction Vessel *% by volume*	Oxygen in Nitrogen *% by volume*
1	2.5	0.45	0.22
2	2	0.012	0.50
3	2	0.030	0.52

column. It is obvious that the requisite time of shaking increases with the initial oxygen concentration.

In the experiments of Table II, varying pressures of nitrogen that contained 0.45 ± 0.05% oxygen according to a careful Orsat analysis were left in the reaction vessel and supplemented with "oxygen-free" hydrogen as above. The percentages in the last column are to be compared with 0.45%; the others are the initial concentrations in the reaction vessel.

The results cited set the upper limit of usefulness for the method near 0.1%; more concentrated samples should be diluted if they must be analyzed in this way. The useful lower limit is near 0.0001%; 0.01% is perhaps the most favorable concentration. The color change in the manganous hydroxide during the analysis is a rough guide to the oxygen content of the sample.

It has not been possible to fix the precision of the method, which will obviously be lowest near 0.0001% oxygen. Duplicate determinations on nitrogen known to be very low in oxygen each gave 0.0004%. Certainly the precision is not so high as Winkler's (*12*); the reader may form his own estimate from Tables I and II.

The method is unreliable at pressures much below atmospheric. Numerous failures were encountered in attempts to establish blanks by analyzing for oxygen in the evacuated reaction vessels, and there is no doubt that leaks were responsible.

The time required for a determination lies between 4 and 8 hours.

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Volumetric Determination of Aluminum

Applied to Analyses of Silica-Alumina Catalysts

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A volumetric method for the determination of aluminum in silica-alumina catalysts is described, which is more rapid and more accurate than conventional gravimetric methods. The aluminum sulfate solution, containing tartrate, is neutralized with lithium hydroxide, and an excess of potassium fluoride is added. The potassium hydroxide released by the formation of the aluminum complex is titrated with hydrochloric acid.

ACTIVITY studies of silica-alumina catalysts recently carried out at these laboratories necessitated a large number of aluminum determinations. It was important that these determinations be carried out as rapidly as possible and still retain a high degree of accuracy, and that the method employed be applicable in the presence of moderate amounts of other substances, such as iron, magnesium, and alkalies.

The conventional method involving hydrolysis of the aluminum with ammonia, filtering, igniting, and weighing, was not only time-consuming but also subject to interference by other hydrolyzable materials present. A method often used is one in which the residue, after treatment with hydrofluoric acid and ignition, is calculated as alumina. This procedure is also time-consuming because of difficulty in igniting the residue to a constant weight, and alumina values thus obtained include all other metals present in the sample.

Several volumetric procedures for the determination of aluminum (*1–6*) are based on the titration of either the acid liberated on addition of sodium tartrate (or citrate) or the hydroxide liberated on addition of potassium fluoride.

The most generally applicable of the volumetric methods for aluminum appears to be the one recently described by Snyder (*4*). In this procedure the aluminum salt is neutralized to a phenolphthalein end point with barium hydroxide in the presence of sodium potassium tartrate. An excess of potassium fluoride is then added to release potassium hydroxide, which is titrated with standard acid.

$$\mathrm{Al(OH)_3 + 6KF \rightarrow AlF_3.3KF + 3KOH}$$

As stated by Snyder, this method cannot be applied in the presence of sulfate because of the precipitation of barium sulfate. In the analysis of silica-alumina catalysts large amounts of sulfate are necessarily present because of the methods required for dissolving the samples. The purpose of this paper is to describe the modifications that have been made in the method developed by Snyder which make it suitable for the rapid and accurate determination of aluminum in silica-alumina catalysts.

Since barium hydroxide could not be used for the neutralization of the aluminum salt, another base had to be found. The fact reported by Snyder that sodium and potassium hydroxides give erratic and inaccurate results was confirmed. It was found that lithium hydroxide has none of the undesirable characteristics of sodium and potassium hydroxides and does not form an insoluble sulfate as does the barium hydroxide. It was decided from a study of the potentiometric titration curves, and confirmed by experience, that thymolphthalein is a more suitable indicator than phenolphthalein.

EXPERIMENTAL

Apparatus and Reagents. Mechanical stirrer. Platinum dish, 100 ml. Potassium fluoride, 30% solution neutralized to phenolphthalein and stored in a wax-lined bottle. Sodium tartrate, 25% solution. Thymolphthalein, 0.1% in ethanol. Aluminum sulfate solution, 0.5 *N*, prepared by dissolving 55.535 grams of aluminum sulfate octadecahydrate in 1 liter of water. The alumina content of the aluminum sulfate was found by igniting samples at 2000° F. and weighing. Hydrochloric acid

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0.5 *N*, standardized against the aluminum sulfate solution. Lithium hydroxide, 0.5 *N*, standardized against the 0.5 *N* hydrochloric acid. (Ratio of milliliters of hydrochloric acid to milliliters of lithium hydroxide is equal to *R*.) All reagents were C.P. grade and were used without further purification.

PROCEDURE. Weigh a 1.0 to 1.5-gram sample into a platinum dish and ignite to remove carbon and ammonium salts. Cool, moisten the sample with water, and add 10 ml. of hydrochloric acid. Cautiously add hydrofluoric acid until the sample is completely dissolved. Evaporate the solution to dryness and ignite at red heat for a few seconds. Fuse the residue with approximately 3 grams of anhydrous potassium bisulfate over a low flame until no undissolved particles remain. Cool, dissolve the fusion in 80 ml. of water, and transfer to a 400-ml. tall-form beaker.

Place the beaker containing the dissolved sample under the mechanical stirrer and titrate with the lithium hydroxide. When most of the free acid is neutralized, as evidenced by the appearance of traces of precipitate in the solution, add 6 to 8 drops of thymolphthalein indicator and 25 ml. of 25% sodium tartrate. If the solution contains considerable magnesium or lead or more than 0.3 gram of aluminum oxide, add 50 ml. of the sodium tartrate. Continue the titration until appearance of a blue color, permanent for 30 seconds, and add 0.1 to 0.2-ml. excess of lithium hydroxide. Back-titrate with the 0.5 *N* hydrochloric acid until the blue color just disappears. Record the readings of the hydrochloric acid and lithium hydroxide burets as A_1 and B_1, respectively. Add 25 ml. of 30% potassium fluoride. The solution becomes blue immediately because of the liberation of hydroxyl ions. Titrate with the hydrochloric acid until the blue color disappears and add 1-ml. excess. Back-titrate with the lithium hydroxide until the blue color reappears. Record the readings of the hydrochloric acid and lithium hydroxide burets as A_2 and B_2, respectively. The back-titrations are necessary to ensure sharp, permanent end points.

CALCULATIONS.

$$\text{Weight \% of } Al_2O_3 = \frac{[A - (B \times R)] \times N \times 0.017 \times 100}{\text{weight of sample}}$$

where $A = A_2 - A_1$ (volume of HCl)

$B = B_2 - B_1$ (volume of LiOH)

N = normality of HCl

$R = \text{ratio} \dfrac{\text{ml. of HCl}}{\text{ml. of LiOH}}$

TITRATION OF KNOWN SOLUTIONS. The reliability of the method was tested by titrating a number of solutions of known aluminum content. The solutions were prepared by dissolving aluminum wire in sulfuric acid or sodium hydroxide and by dissolving aluminum sulfate in water. The composition of the solution prepared from aluminum sulfate was found by evaporating aliquots to dryness, igniting to Al_2O_3 at 2000° F., and weighing. The results of these analyses are listed in Table I.

Table I. Analysis of Known Aluminum Solutions

Solution	Prepared from	Al_2O_3 Added *Gram*	Al_2O_3 Found *Gram*
1	Al wire	0.0638	0.0639
2	Al wire	0.0638	0.0642
3	Al wire	0.0830	0.0832
4	$Al_2(SO_4)_3$	0.1532	0.1532
5	$Al_2(SO_4)_3$	0.1532	0.1530
6	$Al_2(SO_4)_3$	0.1532	0.1534

INTERFERENCES. A study was made of the effects of the ions that may sometimes be present in silica-alumina catalysts. The impurities were added so as to be approximately equivalent to 5% of the material in a sample. Of the ions tested, only ammonium, tin, and manganese caused significant interference. Larger amounts of the colored ions, such as copper, chromium, and nickel, obscure the end points. The results of the interference studies are shown in Table II. It was found that a fivefold excess of iron and magnesia does not interfere if sufficient tartrate is added.

ANALYSIS OF SAMPLES. Several synthetic samples were prepared by adding 15.32% aluminum oxide to pure silica. Repeated analyses of these samples are shown in Table III.

Table II. Effect of Interfering Substances

Impurity	Al Added *Gram*	Al Found *Gram*	Difference *Gram*
Iron	0.0638	0.0638	0.0000
	0.0859	0.0856	−0.0003
Nickel	0.0859	0.0856	−0.0003
	0.1429	0.1420	−0.0009
Copper	0.0859	0.0861	+0.0002
Magnesium	0.0859	0.0862	+0.0003
	0.1429	0.1432	+0.0003
Calcium	0.0859	0.0864	+0.0005
	0.1429	0.1431	+0.0002
Sodium	0.0859	0.0850	−0.0009
	0.1429	0.1426	−0.0003
Potassium	0.0638	0.0638	0.0000
	0.1429	0.1421	−0.0008
Lead	0.0859	0.0846	−0.0013
Chromium	0.0859	0.0852	−0.0007
Manganese	0.1429	Color obscures end point	
Ammonium	0.1429	No end point	
Tin	0.1429	0.1321	−0.0108
Phosphate	0.1429	0.1438	+0.0009

Table III. Analysis of Synthetic Samples

Sample	Al_2O_3 Added, %	Al_2O_3 Found, %
1	15.32	15.30
2	15.32	15.39
3	15.32	15.34
4	15.32	15.32
5	15.32	15.31

Table IV. Analysis of Routine Laboratory Samples

Sample	Type of Catalyst	Al_2O_3, Wt. %
1	SiO_2–Al_2O_3	4.54 4.56
2	SiO_2–Al_2O_3	7.73 7.69
3	SiO_2–Al_2O_3	9.20 9.22
4	SiO_2–Al_2O_3	14.73 14.77
5	SiO_2–Al_2O_3	17.70 17.65
6	SiO_2–Al_2O_3	26.60 26.64
7	SiO_2–Al_2O_3	30.60 30.50

The precision that is obtained when the procedure is applied on a routine basis is illustrated by the results in Table IV. These analyses were made on a few typical catalyst samples that were submitted to the analytical laboratory for aluminum determinations.

DISCUSSION

The volumetric method reduces the time required for a determination of aluminum in catalysts from about 8 hours by the gravimetric method to about 2 hours. This means a saving not only in time but also in expensive platinum apparatus.

It is necessary that the hydrochloric acid be standardized against standard aluminum sulfate solutions. The normality of the solution used in the work reported here was about 3% higher when determined by the titration of aluminum than when standardized against sodium carbonate. Since this work was completed, it has been found that aluminum potassium sulfate can be used as a primary standard for the hydrochloric acid solution.

When fairly large amounts of other ions that form complexes with tartrate are present, more of the sodium tartrate solution must be added or low results will be obtained. Examples of such ions are lead, iron, and magnesium.

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Activated Glycerol Dichlorohydrin

A New Colorimetric Reagent for Vitamin A

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Activated glycerol dichlorohydrin is suggested as a new reagent to replace glycerol dichlorohydrin as obtained from various manufacturers, which has been found unreliable as a colorimetric reagent for vitamin A. The activated reagent is prepared by vacuum distillation of glycerol dichlorohydrin with antimony trichloride. A spectrophotometric study was made of the violet color produced by the addition of activated glycerol dichlorohydrin to a solution of vitamin A in chloroform. The color has been found to be stable from 2 to 10 minutes after addition of the reagent at the wave length of maximum absorption, 555 mμ. The color obeys Beer's law over a wide range. Free and esterified vitamin A give the same extinction coefficient with the reagent. The interference of vitamin D_2 and related sterols is negligible. Vitamin A and carotene can be determined simultaneously by reading at 555 and 800 mμ on the Beckman spectrophotometer or carotene interference can be evaluated by the method of Dann and Evelyn. The activated reagent is unaffected by traces of moisture found in the atmosphere on the most humid days, and leaves no deposit of antimony oxychloride on the cuvettes.

RECENTLY (*4*) the authors proposed the use of practical glycerol dichlorohydrin as a new reagent for the quantitative estimation of vitamin A. Later it was found that glycerol dichlorohydrin from other firms, and most of that from Eastman Kodak, did not give color when added to vitamin A.

By distilling glycerol dichlorohydrin with 1 to 5% antimony trichloride at 4- to 40-mm. pressure, a reagent was obtained which reacted with vitamin A as did the practical material. Activation could also be obtained by the addition of concentrated hydrochloric acid, acetyl chloride, phosphorus pentachloride, anhydrous aluminum chloride, and benzoyl chloride. Concentrated sulfuric acid, zinc chloride, and stannic chloride gave blue colors which did not change to violet. Glycerol 2,3-dichlorohydrin, glycerol 1,3-dibromohydrin, and glycerol 2,3-dichlorohydrin when activated gave blue colors changing to violet. Acetylated glycerol dichlorohydrin does not react with vitamin A even when activated.

The concentration of antimony calculated as the trichloride in the activated reagent varied from a trace to 0.67%. The activation of the reagent, however, is not due to antimony trichloride per se, since glycerol dichlorohydrin to which 0.1 to 1.0% of antimony trichloride is added is inactive toward vitamin A.

Although activated and practical glycerol dichlorohydrin react in an apparently similar manner with vitamin A, several differences were observed which indicates that they are not identical. (1) The absorption spectrum produced on the addition of carotene to the two reagents is different (see Figure 1). Between 400 and 550 mμ the color given with activated glycerol dichlorohydrin has a much lower absorption curve than the color produced with the practical reagent. (2) With the practical reagent at 550 mμ at the end of 15 minutes the *L* values of vitamin D_2, ergosterol, and 7-dehydrocholesterol are 11.28, 1.13, and 0.08 (*3*), respectively, while with the activated reagent the *L* values are 6.90, 0.25, and 0.29, respectively. [The term $L^{1\%}_{1\,\text{cm.}}$ was introduced by Dann and Evelyn (*1*) for use with photoelectric colorimeters which employ a band width of light 30 to 40 mμ wide. The authors have used the term with a Coleman universal spectrophotometer model 11 because it employs a band of light 35 mμ wide (*4*). Throughout this paper $L^{1\%}_{1\,\text{cm.}}$ is used for work done on the Coleman model 11 spectrophotometer, and $E^{1\%}_{1\,\text{cm.}}$ for work done on the Beckman quartz spectrophotometer.] (3) The *L* value with vitamin A of the practical glycerol dichlorohydrin varied between 1010 and 1100, that of the activated reagent varied between 1100 and 1270.

A study was made of the reproducibility of the activated reagent under constant use and kept at room temperature. From Table I it can be seen that three different batches of glycerol dichlorohydrin vacuum-distilled with 2% antimony trichloride gave average $L^{1\%}_{1\,\text{cm.}}$, 550 mμ, at 2 minutes, using concentrations of vitamin A between 2 and 5 micrograms, of 1210,

Table I. Stability of Reagent Glycreol Dichlorohydrin Distilled with 2% Antimony Trichloride

Batch No.	Date Tested	$L^{1\%}_{1\,\text{cm.}}$, λ 550 mμ	
		Average value for 2 to 5 γ of vitamin A	Single determination on 2 to 5 γ of vitamin A
1	June 6	1210 ± 33	...
	June 14	....	1210
	June 20	....	1270
	June 27	....	1240
	July 9	....	1200
	July 16	....	1260
2	Aug. 7	1230 ± 42	...
	Aug. 29	....	1230
	Sept. 7	....	1190
3	Sept. 24	1170 ± 17	...
	Oct. 2	....	1165
	Oct. 8	1140 ± 4	...
	Oct. 15	1160 ± 14	...
	Oct. 22	....	1180
	Oct. 26	....	1160
	Nov. 2	....	1140
	Dec. 17	....	1115

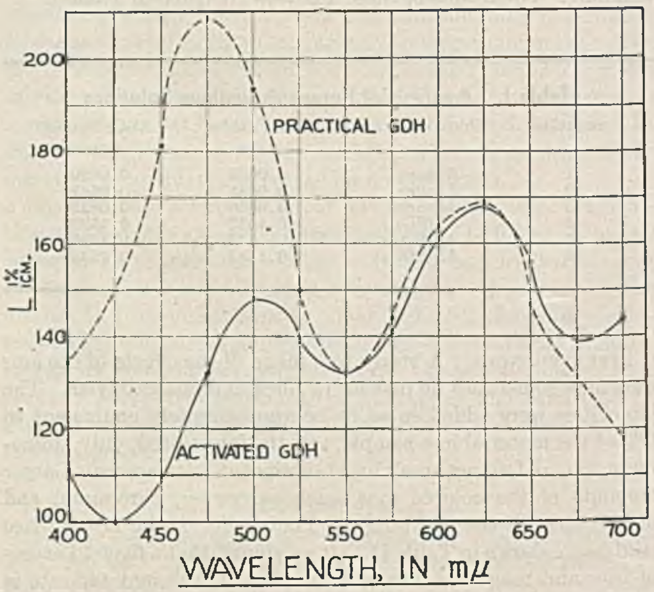

Figure 1. Absorption Curves of Green Colors Produced by Activated and Practical Glycerol Dichlorohydrin on Carotene

90% of β, 10% of α. 5.0 ml. of reaction mixture contained 108.8 micrograms o carotene. Readings taken on Coleman spectrophotometer

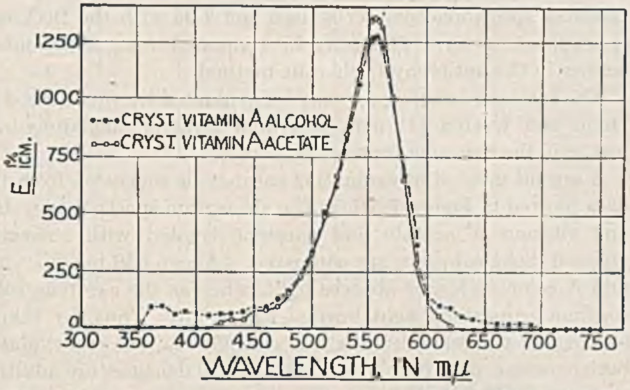

Figure 2. Absorption Curves of Violet Colors Produced by 4.89 Micrograms of Alcohol and 4.90 Micrograms of Acetate with Activated Glycerol Dichlorohydrin

Total volume of reaction mixture in each case, 5.0 ml. Readings taken on Beckman spectrophotometer

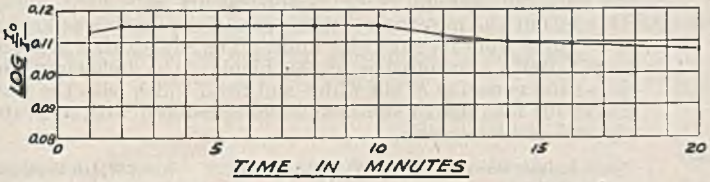

Figure 3. Stability of Violet Color Produced by Action of 4.07 Micrograms of Vitamin A with Activated Glycerol Dichlorohydrin

As shown by density readings on Beckman spectrophotometer at 555 mμ. Total volume of reaction mixture, 5.0 ml.

1235, and 1170. Although there is a 10% difference in the $L^{1\%}_{1\text{ cm.}}$ values between batches 1 and 3, it has been the authors' experience that when reagents are prepared from the same batch under constant conditions of pressure and antimony trichloride concentration, reproducible reagents result. (By reproducible reagents are meant those that give the same $L^{1\%}_{1\text{ cm.}}$ with vitamin A.) One batch of activated glycerol dichlorohydrin kept in a Pyrex bottle in the absence of light lost only 5% of its activity in 14 months.

From Table I can be had a measure of the stability of the reagent. The third column gives the average $L^{1\%}_{1\text{ cm.}}$ value and the average deviation from this value for three batches of activated glycerol dichlorohydrin, for concentrations of vitamin A between 2 and 5 micrograms. In the last column are presented $L^{1\%}_{1\text{ cm.}}$ values for single determinations for one particular concentration of vitamin A between 2 and 5 micrograms. It can be seen from the table that the reagent possesses good stability for about 2 months. After that time there is a slow decrease in the $L^{1\%}_{1\text{ cm.}}$ value given by the reagent.

In Figure 2 is presented the absorption spectrum taken on the Beckman spectrophotometer from 320 to 750 mμ of the violet color produced by the reaction of activated glycerol dichlorohydrin with crystalline vitamin A alcohol and crystalline vitamin A acetate. In order to be within the period of stability for the maxima, the readings were taken from 2 to 10 minutes after mixing the reagents because the violet color was found to be stable from 2 to 10 minutes, as seen in Figure 3.

The $E^{1\%}_{1\text{ cm.}}$ of the color produced by the action of activated glycerol dichlorohydrin on the crystalline alcohol was 1270 at its maximum wave lengths of 553 to 556 mμ, while the $E^{1\%}_{1\text{ cm.}}$ of the color produced with the crystalline acetate at its maximum wave lengths of 553 to 556 mμ was 1350 calculated for vitamin A content.

The shapes of the two curves are very similar. The smaller extinction of the alcohol compared to that of the acetate may have been due to either of two reasons: deterioration of the alcohol or an inherent difference in the reaction of the alcohol and acetate with activated glycerol dichlorohydrin.

In order to determine which of these conclusions was the correct one, the extinctions of the colors produced by the action of activated glycerol dichlorohydrin on a distilled natural ester concentrate and upon the unsaponifiable fraction of the same concentrate were calculated from the observed density readings at the maxima. Figure 4 shows the absorption curves of these colors. For the whole oil, the $E^{1\%}_{1\text{ cm.}}$ at the maxima of 553 to 556 mμ was 1420, while that for the unsaponifiable extract was 1410. Obviously, there is no appreciable difference in the behavior of the alcohol and ester toward glycerol dichlorohydrin, between 400 to 750 mμ, and the lower extinction observed above is probably due to some deterioration of the crystalline alcohol. (The $E^{1\%}_{1\text{ cm.}}$ 325 mμ, in absolute ethanol of the crystalline vitamin A alcohol was 1740, and its extinction ratios of 300/328 and 350/328 mμ were 0.69 and 0.49, respectively.) The upward trend of the curve from 400 to 320 mμ was due to something in the particular batch of concentrate used which reacted with the activated reagent, because using the same batch of reagent and other batches of concentrate, the upward sweep was not observed, nor was it observed with crystalline vitamin A alcohol and acetate (see Figure 2).

Since most of the authors' work on vitamin A determinations is done on the less expensive Coleman model 11 spectrophotometer, the absorption spectrum of the violet color produced with the whole oil of the above concentrate and activated glycerol dichlorohydrin was read from 400 to 700 mμ on this instrument. It is plotted in Figure 5 along with the absorption spectrum of the same color taken on the Beckman spectrophotometer. On the Coleman, the $L^{1\%}_{1\text{ cm.}}$ was 1140 at the maximum of 550 mμ, while on the Beckman the $E^{1\%}_{1\text{ cm.}}$ was 1420 at the maximum wave lengths of 553 to 556 mμ. Not only has the wave length of the maximum shifted in using the Coleman, but the height of the maximum has decreased and is more flat. This is to be expected, since the Coleman employs a band width of about 35 mμ as compared to the band width of 5 mμ or less which the authors used with the Beckman instrument. Similar results were obtained by Mellon (*2*) using two spectrophotometers, one with a band width of 5 mμ, the other with a band width of 35 mμ. Upon plotting the per cent transmittancy of a Corning glass 512, he found that with

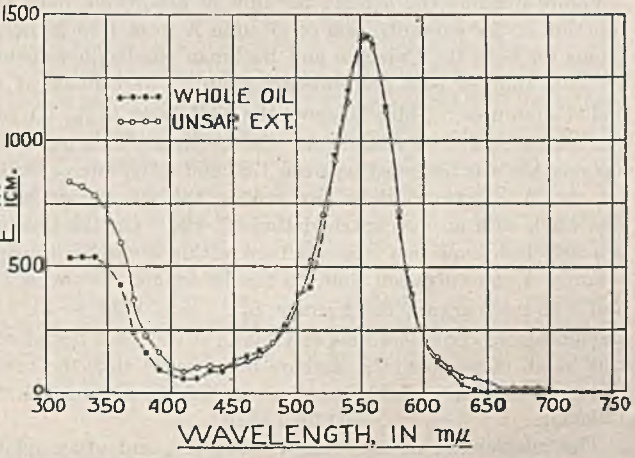

Figure 4. Absorption Curves of Colors Produced by Activated Glycerol Dichlorohydrin on a Natural Vitamin A Ester Concentrate (3.71 Micrograms of Vitamin A) and on Unsaponifiable Fraction of Same Batch of Concentrate (4.47 Micrograms of Vitamin A)

Total volume of reaction mixture in each case, 5.0 ml. Readings taken on Beckman spectrophotometer

Table II. Relation between Concentration and Extinction Coefficient of Color Produced on Addition of Activated Glycerol Dichlorohydrin to Vitamin A

Concentration of Vitamin A, γ/5 Ml.	$E^{1\%}_{1\,cm.}$ 555 mμ[a]	$L^{1\%}_{1\,cm.}$ 550 mμ[b]
0.94	1020	1060
1.36	1250	1130
1.87	1290	1140
2.73	1340	1140
2.81	1300	1110
3.74	1330	1110
4.68	1330	1100
6.82	1310	1060
8.18	1290	1050
9.36	1290	1010
13.63	1250	970
18.71	1180	900
28.07	1090	800

[a] Beckman spectrophotometer.
[b] Coleman.

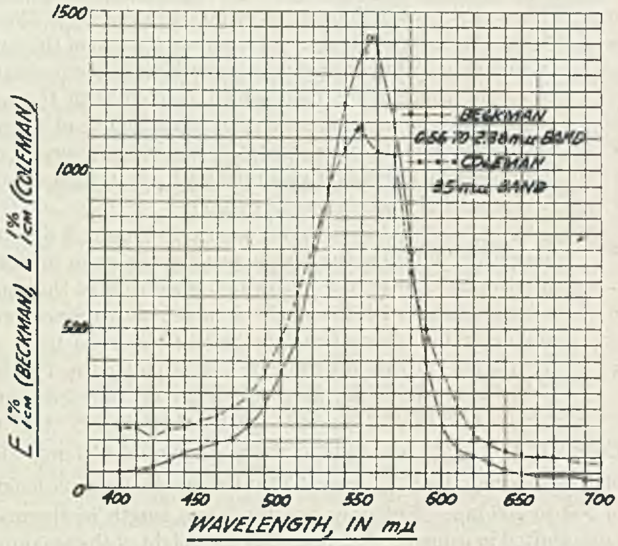

Figure 5. Absorption Spectrum on Beckman and Coleman Spectrophotometers of Violet Color Produced by Activated Glycerol Dichlorohydrin with 4.82 Micrograms of Vitamin A of a Whole Vitamin A Natural Ester Concentrate

Total volume of reaction mixture in each case, 5.0 ml.

the latter type of instrument some maxima not only were decreased (had lower extinction values) and shifted, but might even be eliminated altogether.

Figure 6 shows the density per unit of absorption path as a function of the concentration of vitamin A from 1 to 28 micrograms for both the Coleman and Beckman spectrophotometers. Density and per cent transmission readings were made at the end of 2 minutes. Table II shows the $E^{1\%}_{1\,cm.}$ and $L^{1\%}_{1\,cm.}$ for various concentrations of vitamin A. On the Beckman, a nearly linear relation was observed between 1.36 and 13.63 micrograms of vitamin A. Between these two values, the average extinction was 1300, with an average deviation of ±24. On the Coleman a nearly linear relation was observed within a smaller range of vitamin A concentration than on the Beckman. Between 1.36 and 4.68 micrograms, the average $L^{1\%}_{1\,cm.}$ was 1120 ± 15. Although higher concentrations of vitamin A were not tested with this batch of reagent, the authors have found that the nearly linear relation does hold up to about 5.5 micrograms on the Coleman.

The interference of carotene, vitamin D_2, and other related sterols in the estimation of vitamin A with activated glycerol dichlorohydrin was studied by measuring the absorption of the colored solutions produced under the same conditions as were employed for vitamin A measurements. As seen in Table III, the interferences with the exception of carotene are negligible. The error due to an equal weight of carotene is 11.0% when the Coleman spectrophotometer is used and 7.35 with the Beckman spectrophotometer. This may be compared with a 5% interference in the antimony trichloride method.

The carotene interference may be evaluated by the method of Dann and Evelyn (*1*) with activated glycerol dichlorohydrin, just as in the case of antimony trichloride.

A second method of evaluating carotene is suggested from the data plotted in Figure 7, where the absorption spectra of crystalline vitamin A acetate and carotene treated with activated glycerol dichlorohydrin are compared. Above 630 mμ the vitamin A color no longer absorbs light, whereas the carotene color continues absorbing light beyond this point. Thus, by taking readings at two wave lengths, 555 and 800 mμ, one can evaluate both carotene and vitamin A, as the optical densities are additive as shown in Table IV.

APPARATUS

A BECKMAN MODEL DU QUARTZ SPECTROPHOTOMETER with a tungsten light source and Corex cells of 1.00-cm. absorption path was employed for the region of 320 to 750 mμ. The wavelength setting of the instrument was calibrated with 405 and 546 mμ lines obtained by using a mercury arc as a light source. Throughout the measurements the sensitivity knob was kept at three turns from its clockwise limit. The slit width was varied to get 100% transmission of the blank. The following table shows the variation of slit width and band width with the wave length for readings of the violet color produced with activated glycerol dichlorohydrin.

Wave Length Range, mμ	Slit Width Variation, Mm.	Band Width Variation, mμ
320-390	1.8-0.15	8.16-1.41
400-500	0.075-0.028	0.75-0.56
500-600	0.028-0.042	0.56-1.43
600-630	0.042-0.064	1.43-2.38
630-700	0.064-0.040	2.38-1.90

Readings were taken at 1 mμ intervals near the maxima, otherwise at 10 mμ intervals.

COLEMAN UNIVERSAL SPECTROPHOTOMETER, model 11, was used for measurements with a PC-4 filter in the region of 400 to 700 mμ. The instrument was calibrated according to the directions given by the manufacturer. This instrument employs a band of light 35 mμ wide (which can be located with a precision of less than 2 mμ). For this reason $L^{1\%}_{1\,cm.}$ values are reported instead of $E^{1\%}_{1\,cm.}$ values, which are used for monochromatic light. Direct readings of per cent transmission were made on the galvanometer scale by setting the blank at 100. The absorption path was 1.3 cm. Readings were taken at 10 mμ intervals.

REAGENTS

GLYCEROL DICHLOROHYDRIN, practical grade of Eastman Kodak. 1,3-dichloro-2-hydroxypropane from Ohio Chemical Mfg. Co. A mixture of the 1,3- and 2,3-dichlorohydrins from the Shell Chemical Co.

ACTIVATED GLYCEROL DICHLOROHYDRIN. To 1000 ml. of any of the above glycerol dichlorohydrins were added 100 ml. of chloroform containing 10 to 50 grams of dissolved antimony

Table III. Interference of Carotene, Vitamin D_2, and Related Sterols on Reaction of Glycerol Dichlorohydrin with Vitamin A

			Concentration	Time after Adding Reagent			Interference at 2 Minutes
				2 Min.	5 Min.	10 Min.	
			Mg./100 ml.				%
$E^{1\%}_{1\,cm.}$	λ 555	Vitamin A	0.06	1390	1390	1390	
$E^{1\%}_{1\,cm.}$	λ 555	Carotene	1.31	102	114	122	7.35
$L^{1\%}_{1\,cm.}$	λ 550	Vitamin A	0.06	1150	1150	1150	
$L^{1\%}_{1\,cm.}$	λ 550	Carotene	2.18	126	132	132	11.00
$L^{1\%}_{1\,cm.}$	λ 550	Calciferol	62.6	1.79	4.03	6.25	0.16
$L^{1\%}_{1\,cm.}$	λ 550	Ergosterol	52.2	0.14	0.14	0.19	0.01
$L^{1\%}_{1\,cm.}$	λ 550	7-Dehydrocholesterol	33.4	0.21	0.21	0.21	0.02
$L^{1\%}_{1\,cm.}$	λ 550	Cholesterol	160.0	0.00	0.00	0.00	0.00

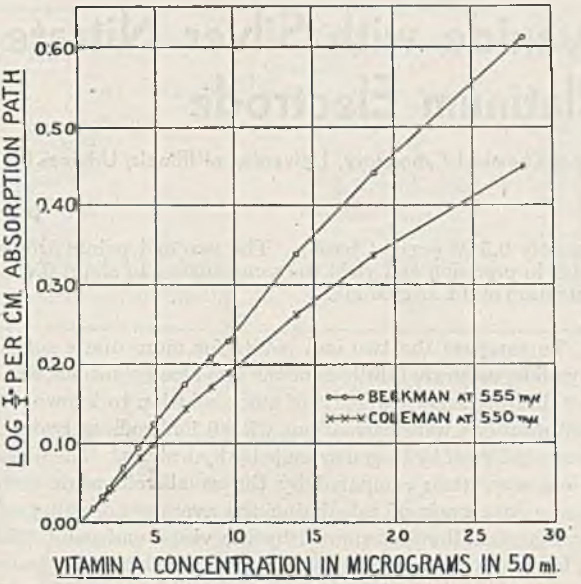

Figure 6. Relation between Absorption at Maximum, and Vitamin Concentration

Total volume of reaction mixture, 5.0 ml.

trichloride (prepared without anhydrous precautions). Later, it was found that the solid can be added directly. The solutions were mixed and distilled under a reduced pressure of 4 to 40 mm. of mercury in an all-glass apparatus. The chloroform fraction was discarded and the product collected and stored in a dry glass-stoppered bottle at room temperature. The dichlorohydrins from the Shell Chemical Co. were somewhat less satisfactory in the preparation of activated glycerol dichlorohydrin because they required two distillations with antimony trichloride before a colorless reagent was obtained. The product thus obtained became colored in 3 to 4 weeks.

CHLOROFORM, analytical reagent grade, dried over anhydrous sodium sulfate, distilled, and kept over the same drying agent.

ANTIMONY TRICHLORIDE, reagent grade, Merck.

CRYSTALLINE VITAMIN A ALCOHOL and crystalline vitamin A acetate from Distillation Products, Inc.

DISTILLED VITAMIN A NATURAL ESTER CONCENTRATE, Control No. PC-3, from Distillation Products, Inc., which comes in sealed gelatin capsules. The $E^{1\%}_{1\text{ cm.}}$ of the concentrate in absolute ethanol was 100.75. Taking the $E^{1\%}_{1\text{ cm.}}$ from crystalline vitamin A as 1780, the concentrate was found to contain 5.65% vitamin A. The concentrate from each capsule was used for one day only. The above data for the oil were supplied by Distillation Products, Inc., and were confirmed by the authors' measurements.

COLOR DEVELOPMENT

All dilutions were made, and all colors were developed in a constant-temperature bath at 25° C.

To 4.0 ml. of activated glycerol dichlorohydrin in a 10-ml. glass-stoppered cylinder, was added 1 ml. of chloroform containing the desired concentration of vitamin A, carotene, or both. The mixture was shaken several times to ensure homogeneity and placed in the water bath until ready to be read in the spectrophotometer.

All density readings reported in this paper are the averages of duplicate determinations.

SUMMARY

Glycerol dichlorohydrin from various sources does not always produce color with vitamin A. By distilling glycerol dichlorohydrin with 1 to 5% of antimony trichloride under reduced pressure, a reagent results which behaves similarly to practical glycerol dichlorohydrin in giving a transient blue, then violet, color with vitamin A which is stable for 8 minutes, is not affected by traces of moisture present in the atmosphere on the most humid days, and does not leave a white deposit of antimony oxychloride on the cuvettes. The activated reagent differs from the practical in its behavior toward carotene and various sterols.

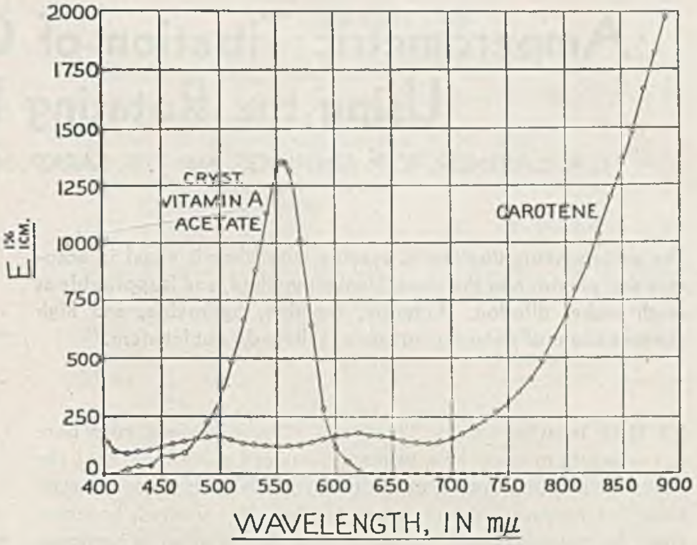

Figure 7. Absorption Curves of the Colors Produced by Activated Glycerol Dichlorohydrin on 4.90 Micrograms of Vitamin A Acetate and 65.44 Micrograms of Carotene

90% of β, 10% of α. Total volume of the reaction mixture in each case, 5.0 ml. Readings taken on Beckman spectrophotometer

Table IV. Mixed Color Method for Estimation of Vitamin A and Carotene Mixtures by Activated Glycerol Dichlorohydrin

Vitamin A	Carotene	Observed Density 555 mμ	Observed Density 800 mμ	Calculated Density 555 mμ	Calculated Density 800 mμ
γ/ml.	γ/ml.				
3.98	...	0.115	0.00	...	...
...	10.88	0.027	0.136	...	...
...	21.76	0.056	0.291	...	...
...	32.64	0.085	0.439	...	...
...	43.52	0.113	0.580	...	...
3.98	10.88	0.146	0.131	0.142	0.136
3.98	21.76	0.173	0.284	0.171	0.291
3.98	32.64	0.198	0.442	0.200	0.439
3.98	43.52	0.224	0.580	0.228	0.580

The absorption spectrum was taken on the Beckman spectrophotometer between 320 and 750 mμ of the violet color produced by the action of activated glycerol dichlorohydrin with crystalline vitamin A alcohol, crystalline vitamin A acetate, a natural ester concentrate, and its unsaponifiable fraction. In each case the observed maxima were between 553 and 556 mμ. The $E^{1\%}_{1\text{ cm.}}$ of the vitamin A in the natural ester concentrate and its unsaponifiable fraction were almost identical, 1420 and 1410, respectively. A nearly linear relationship was observed at 555 mμ between 1.26 and 13.63 micrograms of vitamin A and optical density.

On the Coleman model 11 spectrophotometer, the maximum has shifted to 550 mμ. The $L^{1\%}_{1\text{ cm.}}$ value is about 20% lower than the $E^{1\%}_{1\text{ cm.}}$ value on the Beckman. On the Coleman, a nearly linear relationship between vitamin concentration and optical density existed between 2 and 5.5 micrograms of vitamin A.

Under the conditions employed for vitamin A determinations using activated glycerol dichlorohydrin, the interference of vitamin D and related sterols is negligible.

The carotene interference can be evaluated by the method of Dann and Evelyn or by reading at 555 and 800 mμ on the Beckman spectrophotometer, since the violet vitamin A color does not absorb at 800 mμ.

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Amperometric Titration of Cyanide with Silver Nitrate, Using the Rotating Platinum Electrode

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The amperometric titration of cyanide with silver is equal in accuracy and precision to the visual Denigès method, and is applicable at much higher dilution. Chloride, bromide, hydroxide, and high concentrations of potassium nitrate or sulfate do not interfere.

IT HAS been shown by Thompson (*19*), who used very pure potassium cyanide as a primary standard substance, that the silver nitrate titration of cyanide to $Ag(CN)_2^-$ is more accurate than the mercuric chloride titration Wick (*21*) showed, however, that the potentiometric mercuric chloride titration is accurate. The original method of Liebig (*12*), based on the formation of a turbidity due to silver cyanide, is subject to error in alkaline (*3*, *18*) and ammoniacal (*8*, *21*) solution. The Denigès (*4*) titration, based on a turbidity due to silver iodide in the presence of ammonia, gives high results in the presence of a large excess of ammonia (*8*, *9*, *20*, *21*), but yields accurate results if the concentration of ammonia is carefully regulated (*8*, *9*, *19*, *21*).

The potentiometric titration of cyanide with silver has been described by Treadwell (*20*), Müller and Lauterbach (*16*), and Clark (*2*). Wick (*21*) concluded that the potentiometric titration gives accurate results. Read and Read (*17*) suggested a bimetallic electrode titration, and Gregory and Hughan (*6*), using the null-point equivalence potential method of Cavanagh (*1*), report that the potentiometric method is superior to the Liebig method (*5*) for the determination of cyanide in plating solutions. The potentiometric method has also been used for the indirect determination of nickel (*14*), cobalt (*15*), and zinc (*7*, *13*).

The successful amperometric titrations of halides with silver nitrate using the rotating platinum electrode (*10*, *11*) suggested a similar method for cyanide. The present paper describes an accurate comparison of the amperometric end point with the Denigès titration, which has been proved to be accurate to within 0.2% and probably 0.1% by reference to pure potassium cyanide (*19*) and to the potentiometric end point (*19*, *21*).

EXPERIMENTAL

A 0.500 *N* solution of reagent quality silver nitrate and a 1.0 *M* solution of c.p. potassium cyanide in 0.1 *N* sodium hydroxide were compared accurately, using weight burets, finishing each titration with 0.01 *N* silver nitrate prepared by diluting a known weight of stock solution to a known volume, and using a volume buret for the final titration. The end point was observed by both the visual (Denigès) and amperometric methods. No blank correction was applied to the visual end point.

For the amperometric titration, the apparatus and technique previously described (*10*) were used, with the mercury–mercuric iodide–potassium iodide reference electrode and a galvanometer sensitivity of about 0.02 microampere per mm. The residual current before the end point was extremely small, and very sharp end points were observed. Between titrations, the silver was removed from the platinum electrode by anodic polarization or by using nitric acid to prevent an anodic residual current due to dissolution of silver in the cyanide solution. If nitric acid was used to remove the silver, the electrode was allowed to stand in ammonium hydroxide solution for a few minutes before rinsing with water and using it again.

In Table I, experimental data are presented for the titration of 20-gram samples of 1.0 *M* potassium cyanide, diluted to about 100 ml. with 0.1 *N* sodium hydroxide to give a final cyanide concentration of 0.2 *M* (0.1 *N* with respect to silver). For purposes of calculation, the silver nitrate solution was assumed to be exactly 0.5 *N* (weight basis). The two end points are comparable in precision and yield the same answer to about 0.1% in the titration of 0.1 *M* cyanide.

To compare the two end points for more dilute solutions of cyanide, accurate dilutions of the two stock solutions were made by diluting known weights of stock solution to known volumes. All dilutions were carried out with 0.1 *N* sodium hydroxide, to prevent loss of hydrogen cyanide by hydrolysis. The dilute solutions were then compared by the usual volumetric technique, using as a basis of calculation the average normality of stock cyanide solution determined by the visual end point (Table I). The results of the comparison are given in Table II.

The two end points were comparable in precision and accuracy at cyanide concentrations as low as 0.002 *N*.

The visual end point became indistinct at 2×10^{-4} *N* cyanide and failed at higher dilutions, whereas a distinct amperometric end point was still observed in titrating 4×10^{-6} *N* cyanide (8×10^{-6} *M*) with 5×10^{-4} *N* silver nitrate. In general, it is recommended that for the amperometric titration a fivefold more concentrated silver solution than cyanide be used to avoid the necessity of correcting the current for dilution effect. For the titration of very dilute cyanide, the lowest practical limit for silver nitrate concentration is of the order of 5×10^{-4} *N* to obtain a distinct end point.

Table I. Comparison of Visual and Amperometric End Points in Titration of 0.1 *M* Cyanide

V = visual, A = amperometric end point

KCN Solution *Grams*	$AgNO_3$ Solution *Grams*		Normality of Stock KCN, Calcd.	Deviation from Mean %	End Point
19.737	20.068		0.50839	−0.07	V
19.806	20.168		0.50914	+0.08	V
19.142	19.479		0.50880	+0.01	V
20.470	20.828		0.50874	0.00	V
20.185	20.532		0.50864	−0.03	V
		Av.	0.50873	±0.04	
19.853	20.173		0.50808	+0.02	A
18.763	19.058		0.50786	−0.06	A
20.920	21.278		0.50856	+0.08	A
19.967	20.302		0.50839	+0.05	A
19.911	20.225		0.50791	−0.05	A
		Av.	0.50816	±0.05	

Table II. Comparison of Visual and Amperometric Titration of 100 Ml. of Dilute Potassium Cyanide in 0.1 *N* Sodium Hydroxide with Silver Nitrate

Approximate Normality of Cyanide	End Point	% Error	Average Error, %
0.02	Visual	+0.3, +0.2, +0.3, +0.5, +0.1	+0.3
	Amperometric	−0.3, −0.3, −0.4, −0.4, −0.4	0.4
$\times 10^{-3}$	Visual	+1.0, +0.8, +0.8, +0.7, +0.7	+0.8
	Amperometric	−0.4, −0.1, −0.1, −0.1, −0.1	−0.2
2×10^{-4}	Visual	−0.3, −3.1, −3.3, −3.3, −3.6	−2.7
	Amperometric	−2.7, −2.7, −2.6, −2.4	−2.6
2×10^{-5}	Visual	No end point	
	Amperometric	+6.5, −1.6, +1.1, +0.7, +4.9	+2.3
4×10^{-6}	Visual	No end point	
	Amperometric	+9.2, +12.8, +2.3, +2.3, −2.3	+4.9

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Table III. Effect of Salts and Hydroxide in Titration of 0.002 *N* Cyanide

(In 0.1 *N* sodium hydroxide unless otherwise stated)

Salt Added	% Error	Average Error, %
0.001 *N* KCl	+0.6, +0.6, +0.4	+0.5
0.004 *N* KCl	+0.4, +0.3, +0.1	+0.3
0.1 *N* KCl	+0.4, −0.2, +0.2	+0.1
0.001 *N* KBr	−0.1, +0.6, +0.5	+0.3
0.004 *N* KBr	+0.3, 0.0, +0.7	+0.3
0.1 *N* KBr	+0.4, +0.4, +0.4	+0.4
1.0 *N* KNO_3 + 0.02 *N* NaOH	−0.2, +0.1, −0.4	−0.2
1.0 *N* KNO_3 + 1.0 *N* NaOH	−0.8, −0.8, −0.6	−0.7
0.5 *M* K_2SO_4 + 0.02 *N* NaOH	−0.2, +0.1, −0.1	−0.1
Satd. K_2SO_4 + 1.0 *N* NaOH	−0.8, −0.6, −0.2	−0.5

EFFECT OF CHLORIDE, BROMIDE, HYDROXIDE, AND HIGH CONCENTRATIONS OF SALTS

A series of titrations of 0.002 *N* cyanide in the presence of various concentrations of chloride, bromide, hydroxide, nitrate, and sulfate was carried out (Table III). The errors again were computed with reference to the visual end point titration of 0.1 *N* cyanide. In general the results are accurate to within 0.5% in the presence of 50-fold excess of chloride or bromide or in 1 *N* salt solutions. High concentrations of alkali tend to give low results.

INTERFERENCES

Iodide, sulfide, sulfhydryl compounds, etc., which form extremely insoluble silver salts, or materials which form more stable complexes with silver than cyanide does, will, in general, interfere.

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Vapor-Liquid Equilibrium Still for Miscible Liquids

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A new apparatus is described for the determination of vapor-liquid equilibrium data; it consists of an electrically heated still fitted with a Cottrell pump, a vapor-liquid disengagement chamber, and a condensate trap. Both the boiling liquid and the vapor circulate within the apparatus, and boiling points may be determined with accuracy, as the system ensures complete equilibrium between the two phases. A simple test for the entrainment of liquid in the vapor is described, and it is shown that in the new apparatus less than 0.05% entrainment occurs with negligible effect upon equilibrium data.

VAPOR-liquid equilibrium determinations reported by different investigators frequently show wide inconsistencies, and it is only rarely that a new examination of a system confirms previous results. Very few systems are known to form ideal solutions, whereby the vapor-liquid relationships may be calculated by Raoult's law from vapor pressures, and the engineer must usually depend upon experimental data for the design of distillation and other contacting equipment. It is, therefore, not surprising to find that such equipment frequently does not operate to the predicted specifications, and the need for greater reliability in equilibrium determinations is very evident. There is also a need for the accurate measurement of other physical properties of systems, such as boiling points and vapor pressure-temperature relationships, which enable the calculation of activity coefficients for the mathematical correlation and extension of results.

Many different forms of apparatus have been proposed for the examination of the vapor-liquid relationships of miscible liquids. Some of the more recent are those of Jones, Schoenborn, and Colburn (*5*), Langdon and Keyes (*6*), Othmer (*7*), and the modifications by York and Holmes (*10*). From a careful analysis of these and other forms, it would appear that no one type of apparatus so far described is entirely free from possible sources of error, and a still operating on a new principle is described in this paper in the hope that it may assist in progress towards the elimination of these faults, and at the same time make it possible to determine accurately the true boiling points of the mixtures being investigated.

Various methods have been adopted to prevent partial condensation and refluxing of the vapors. These methods fall generally into one or other of two main classes, in which either the vapor line is jacketed with the same vapors, or some form of external heating is applied to the exposed vapor-conveying sections, respectively. Combinations of the two methods are also described. Vapor-jacketing when used alone does not appear to be a fully effective means of reflux-prevention. This is particularly evident with liquids of high boiling point, with which refluxing from the jacketed vapor line may become visibly quite pronounced. Further, in considerations of apparatus of this type (*7*), the enrichment of the vapors with respect to the more volatile component before they reach the vapor line does not appear always to have been recognized. It is obvious that this enrichment can occur by partial condensation on the outer body of the still at all points above the level of the boiling liquid.

In several forms of apparatus, external heating is adopted to compensate for heat losses from the upper parts of the still (*1*, *5*, *6*, *8*, *10*) and so prevent refluxing of the vapors, although the danger of evaporation of thin films and spray droplets on such heated surfaces has been pointed out (*7*). Despite this possibility of error, the method appears to have been used successfully. Carey and Lewis (*1*) have surrounded the entire vaporization chamber with an accurately heated jacket, and the careful technique of these investigators has led Jones *et al.* (*5*) to concede that the possible sources of error in this type of apparatus may not be important when special precautions are taken. Nevertheless, it must be considered a disadvantage that the accuracy of results should depend upon strict operating conditions which cannot always be defined clearly.

Very little attention has been given to the difficulties which are undoubtedly associated with ensuring equilibrium between a boiling liquid mixture and its vapor, and it has usually been assumed that the vapor attains this equilibrium during a relatively short passage through the liquid in the boiling vessel, or in a separate equilibrium chamber. This assumption has not been confirmed in ebullioscopic investigations, where, until the development of the Cottrell device (*4*), elaborate precautions and a skillful technique were necessary to obtain complete equilibrium, and hence a steady boiling point. It is difficult to assess the significance of this in vapor-liquid equilibrium determinations, but it is unlikely that the vapors produced by normal boiling in a flask are in true equilibrium with the main bulk of the liquid.

Of more obvious importance is the possibility of local heterogeneity within the boiling liquid, due to the returning condensed vapor. It has been assumed that the agitation induced by the boiling liquid is sufficient to ensure prompt and thorough mixing of the still contents (*7*). The validity of this assumption has been questioned by Langdon and Keyes (*6*), who found it necessary to provide mechanical agitation in their equilibrium still. Jones, Schoenborn, and Colburn (*5*) also point out that the returning liquid may tend to flash-vaporize because of its lower boiling point, but it is doubtful whether these authors achieve any improvement in this regard by returning the condensate as a somewhat superheated vapor. The heterogeneity of the still contents may be further aggravated by the fluctuations in the condensate level in the wide-bore return line usually adopted.

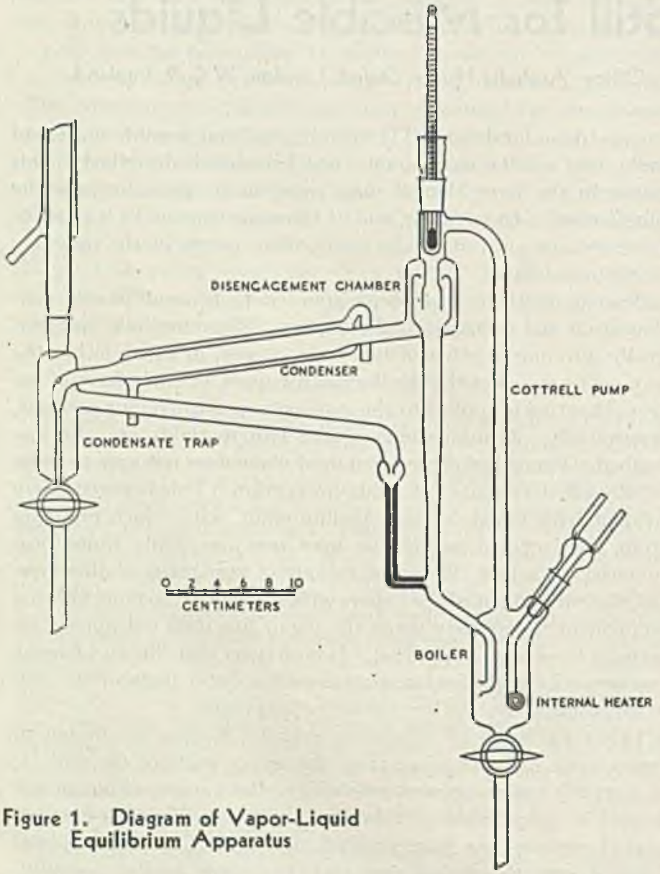

Figure 1. Diagram of Vapor-Liquid Equilibrium Apparatus

In work previously reported in the literature, it is usual for the steady operation of the equilibrium still to be interrupted in some way before taking samples of the boiling liquid and condensate. Errors may then be introduced into equilibrium data by changes in the composition of the still contents prior to and during sampling (*6*, *7*), either by loss of vapor from the still, or by the return of excess condensate during the period usually allowed for boiling to cease. Langdon and Keyes (*6*) were able to prevent the drainage of the condensate line in their apparatus, but found it necessary to analyze successive samples of the boiling liquid and extrapolate the data to obtain a value for the composition of the liquid at the commencement of the sampling period. More reliable results should be obtained if both liquid and condensed vapor samples are taken simultaneously, under such conditions that the equilibrium established within the apparatus is not disturbed.

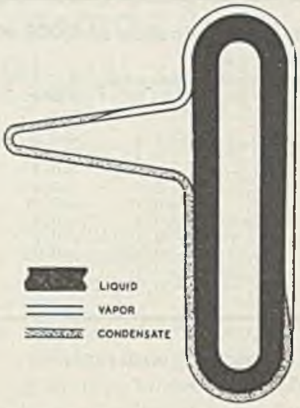

Figure 2

The need for accurate temperature data as well as vapor-liquid equilibrium compositions has been emphasized recently (*2*), but hitherto had received little attention. Precise temperature measurements may be ensured by the use of the Cottrell pump, which is incorporated in the equilibrium still due to Colburn, and described by Chilton (*3*) and Scatchard, Raymond, and Gilmann (*8*). Most forms of apparatus, however, provide for measurement of temperature in the vapor phase only, or in the boiling liquid in close proximity to the source of heat. If it could be assumed that under these conditions both the liquid and the vapor in contact with the thermometer represent the desired equilibrium conditions, either of these methods would be accurate, but it is usual for such data to show obvious inconsistencies in temperature measurements.

THE APPARATUS

In the design of the new apparatus, an attempt has been made to contribute further towards the elimination of the defects discussed above. The apparatus is illustrated in Figure 1. It is based on the well-established vapor-recirculation principle, but differs essentially from others of this type in that the boiling liquid is also circulated rapidly, as represented schematically in Figure 2, and in this regard the apparatus resembles that described by Swietoslawski (*9*) for the determination of boiling points. The liquid and vapor are not permitted to separate within the boiler, but are maintained in intimate contact as they pass up the modified Cottrell pump to the thermometer, and thence to the vapor-liquid disengagement chamber (see Figure 1). The conditions prevailing within the Cottrell tube during the operation of the apparatus are ideally designed to achieve the desired equilibrium between liquid and vapor and enable the boiling points of the mixtures under examination to be determined with complete accuracy. In the disengagement chamber the vapors are separated from the boiling liquid, and pass to the condensate system in such a manner that refluxing is virtually impossible. The stream of hot liquid disengaged from the vapor within the chamber is combined with the recycling condensate before it returns to the boiler, and it is clear that, at equilibrium, the liquid-vapor mixture leaving the boiler is identical in quantity and composition with the combined liquid streams returning to it. This procedure is very convenient, as it ensures steadiness of composition within the boiler, and leaves no possibility of uneven flash-vaporization due to local points of heterogeneity.

The apparatus is sturdy, and may be readily constructed in Pyrex by glass-blowers of average ability. Variations in the dimensions may be made to suit the conditions of an investigation, but those indicated by Figure 1 will be found convenient for most systems, with possibly the exception of the wide Cottrell tube (10 mm. in outside diameter), which is designed primarily for the low vapor density of systems under reduced pressure, and a somewhat smaller tube (8 mm. in outside diameter) may be found better for pressures around atmospheric.

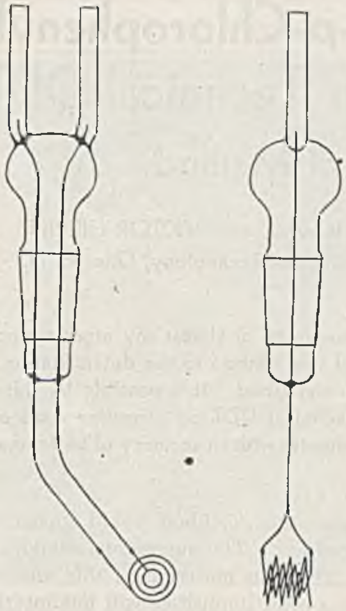

Figure 3. Internal Heating Element

The relatively small boiler (capacity approximately 100 cc.) is provided with both external and internal heating elements. The bulk of the heat requirements should be applied externally, but the internal element will usually be found essential in order to maintain the steady boiling rate required for the successful operation of the apparatus.

The external heater is made by winding a suitable length of Nichrome wire on a thin layer of asbestos paper, or micanite, around the boiler, and subsequently covering with asbestos cord or tape. The internal element may conveniently be made from 37.5 cm. (15 inches) of 28-gage platinum wire, compactly wound in three concentric coils, and attached to tungsten leads fused in a standard cone joint, as shown in Figure 3. This forms a simple, easily removable heating unit, which will ensure a steady vigorous ebullition of vapors even in liquids which are very prone to bumping. An e.m.f. of approximately 6 volts will provide sufficient current for this heater.

The vapors generated within the boiler carry a stream of liquid into the Cottrell tube, and thus a liquid-vapor mixture is pumped up to the thermometer. This mixture is then directed downwards into the disengagement chamber, which consists of three concentric tubes, through the inner of which the mixture enters. Probably because of its downward momentum, the liquid is separated cleanly from the vapor at the bottom of this tube, and it flows away to return to the boiler. The disengaged vapors pass upwards a short distance within the space between the inner and intermediate tubes of the chamber and then escape to the outer jacket, through which they pass downwards to the condenser. The disengagement chamber is thus jacketed with the issuing vapors.

In systems of high boiling point, where radiation losses may permit some condensation of the vapor during the short travel upwards in the chamber, heat losses may be balanced by suitable external heating. Since both liquid and vapor which may be in the outer jacket pass to the condensate system, neither slight heating nor cooling of the outer walls can introduce any errors in the condensate composition.

The condenser and condensate trap present no new features. The condensate trap is essentially the same as that described by Othmer (*7*); it has been provided with a standard-taper joint, to which a further condenser may be fitted if desired, and this in turn is connected to a suitable system for precise pressure regulation.

Overflow from the condensate trap is returned to rejoin the circulating hot liquid through a small drip counter and capillary tube. There is very little liquid holdup within the capillary, which also serves to damp out fluctuations of the liquid level during boiling. The combined liquid and condensed vapor streams re-enter the boiler through a small tube which passes to near the bottom of the vessel, and the mouth is so placed and shaped that there is no tendency for vapor bubbles to pass out through it.

In operation, the apparatus should be filled and the boiling rate adjusted so as to maintain the steady pumping of a mixture of liquid and vapor through the Cottrell tube, and the liquid level is best kept fluctuating gently just above the capillary, in the drip counter. These conditions will be found satisfied by a wide range of boiling rates, but the volume of liquid within the boiler will require adjustment to within a few milliliters. A very rapid boiling rate will cause visible entrainment in the disengagement chamber; uneven or slow boiling allows vapor to pass up the Cottrell pump without entraining a stream of liquid, thus making this device ineffective. Strictly self-consistent data may be obtained over a wide range of operating conditions within these clearly defined conditions.

After allowing sufficient time of operation to ensure steady conditions within the apparatus, samples of the boiling liquid and condensed vapor are best taken simultaneously, without interrupting the heating in any way. The sample of boiling liquid should be collected in a small flask immersed in an ice bath, or it may be necessary in some cases to attach a small cooler to the sampling outlet (*6*).

It is hoped that data obtained using the apparatus will become available for publication at a later date.

ENTRAINMENT

With so short a distance within the disengagement chamber between the point of separation of liquid and vapor, the possibilities of entrainment are obvious, although none could be observed during trials of the apparatus over a wide range of boiling rates. The fine droplets which are characteristically found above the surface of some boiling liquids, due to collapsing vapor bubbles, appear to be entirely absent.

A simple test has been used to detect and quantitatively measure the entrainment. This test may be applied to any form of vapor-liquid equilibrium apparatus so far described, and may also be useful for the indication of evaporation of spray droplets from superheated surfaces. The boiler of the apparatus is charged with a 20% solution of potassium chloride, the condensate trap filled with distilled water, and the system allowed to boil at a constant rate for several hours, at the end of which the contents of the trap are tested for chloride by the standard opalescence method with silver nitrate. The results for a number of different boiling rates are given in Table I, and it is evident that the maximum entrainment obtained would not have any significant effect upon vapor-liquid equilibrium data.

Table I. Entrainment of Liquid in Vapor

Voltage Applied to Heater	Distillation Rate	Potassium Chloride in		Entrainment
		Liquid	Condensate	
Volts	*Ml./min.*	%	%	%
100	3.2	20	0.001	0.005
125	5.5	20	0.005	0.025
150	7.5	20	0.01	0.05

ACKNOWLEDGMENT

The author wishes to acknowledge the helpful criticism and assistance of John E. Cornish and R. F. Pickering during the development of this apparatus; also the provision of facilities for making and testing the apparatus by Beckers Pty., Ltd., of Adelaide, South Australia.

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Determination of 2,2-bis-*p*-Chlorophenyl-1,1,1-trichloroethane in Technical DDT

A Microscopical Method

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A microscopical method for analysis of mixtures of organic compounds is proposed, which depends on the influence of impurities on the rate of crystallization of the major component from the melt. The method is applicable to a large number of industrially important systems such as TNT or other explosives, pharmaceuticals, dye intermediates, or almost any organic reaction product. The application of this method to the determination of *p,p'*-DDT in technical DDT is described. It is possible by this method to analyze samples of technical DDT on a routine basis of one sample every 10 to 15 minutes with an accuracy of better than ±0.5% *p,p'*-DDT.

TECHNICAL DDT usually contains about 75% of the compound 2,2-bis-*p*-chlorophenyl-1,1,1-trichloroethane (*p,p'*-DDT), about 15% of the isomer 2-*o*-chlorophenyl-2-*p'*-chlorophenyl-1,1,1-trichloroethane (*o,p'*-DDT), and about 10% of other by-products of the reaction (*3*). Since the activity of DDT as an insecticide depends to a large extent on the amount of *p,p'*-DDT, it is important to be able to analyze quantitatively for this isomer. For this purpose, probably the most accurate of several methods of analyzing the technical material has been proposed by Cristol, Hayes, and Haller (*2*). This method is based on the insolubility of *p,p'*-DDT in 75% aqueous ethanol. The method is accurate (within 1%) and the technique is simple; it does, however, require temperature control and at least 8 hours for an analysis.

A microscopical method based on the rate of crystal growth of *p,p'*-DDT from the melt is described below. The basis for this analysis is the observation that rate of crystallization from the melt is a function of its purity (Figure 1). A pure compound will crystallize much more rapidly than the same compound in a less pure state. The nature of the impurity is not so important in most cases, since the mechanism of the decrease in rate of growth is almost entirely due to the interference of impurity molecules on crystal formation. If an adsorption effect were encountered where molecules of one impurity were adsorbed on the growing crystal faces, it would then be necessary to prepare the known rate curves on mixtures containing the same compounds that would be encountered in practice.

The technique of analyzing mixtures by determining the rate of crystallization of the principal component is applicable to a number of systems. It is limited, in general, to those mixtures that (1) do not decompose or sublime on melting; (2) can be supercooled to a constant known temperature before complete solidification; and (3) grow at a measurable rate at a convenient temperature. The method has the particular advantages of speed and the application to systems of isomers where no good absolute procedure for analysis exists. The method is applicable to a large number of industrially important systems such as TNT or other explosives, pharmaceuticals, dye intermediates, or almost any organic reaction product.

The basic assumption, made at the start of the present work, is that a technical sample of DDT containing 75% *p,p'*-DDT would behave in the same way as a mixture of 75% *p,p'*-DDT and 25% *o,p'*-DDT—in other words, that crystals of *p,p'*-DDT would grow at the same rate whether the melt contained only *p,p'*-DDT and *o,p'*-DDT or all the usual impurities and by-products were present. The final results have indicated the validity of this assumption.

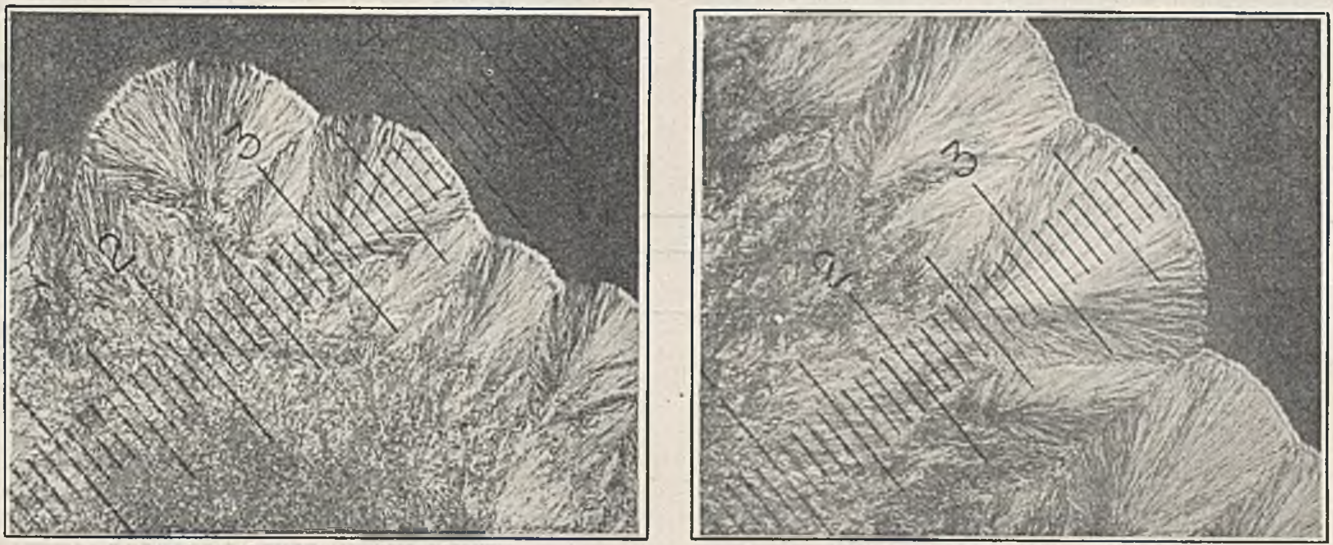
A possible limitation of the method is the fact that compounds insoluble in the melt do not affect the rate of growth. A 50:50 mixture of *p,p'*-DDT and an insoluble component such as water, glass, dirt, or fibers would appear to be 100% *p,p'*-DDT by this method. The microscope would, however, show the presence of extraneous materials of this sort. On the other hand, extraneous solid impurities will not interfere with the analysis by this method except in so far as they interfere with the observation of the crystal front. This would occur only if the per cent solids was very high; in any case, the method of sampling suggested below would eliminate the possibility.

Since the rate of growth of crystals from the melt is also a function of the temperature, it is necessary to control, or be able to measure, the temperature. It is sufficient in an actual analysis to determine the temperature by supporting a thermometer with the bulb on the microscope stage near the preparation. It was necessary during the standardization work on this analysis to use a simple hot stage (Figure 2) to allow rapid changes in temperature and accurate control of any temperature desired. Although the dimensions of this hot stage are flexible, the difficulty of construction increases with the size of the chamber. The stage is heated with circulating liquid, usually water, whose temperature is controlled by a constant-temperature bath. Care must be exercised that the thermometer in the system records the temperature of the water as near the hot stage chamber as possible.

The rate of growth is determined using a microscope equipped with an eyepiece having a micrometer scale. The eyepiece micrometer scale must be calibrated in the usual way (*1*) with a stage micrometer scale before use. An eyepiece scale such that each division corresponds to about 5 microns or less is best. To increase the visibility of the crystal front of the *p,p'*-DDT, crossed Nicols may be used (Figure 1). (In this case the eyepiece micrometer scale must be calibrated with the analyzer Nicol in place.)

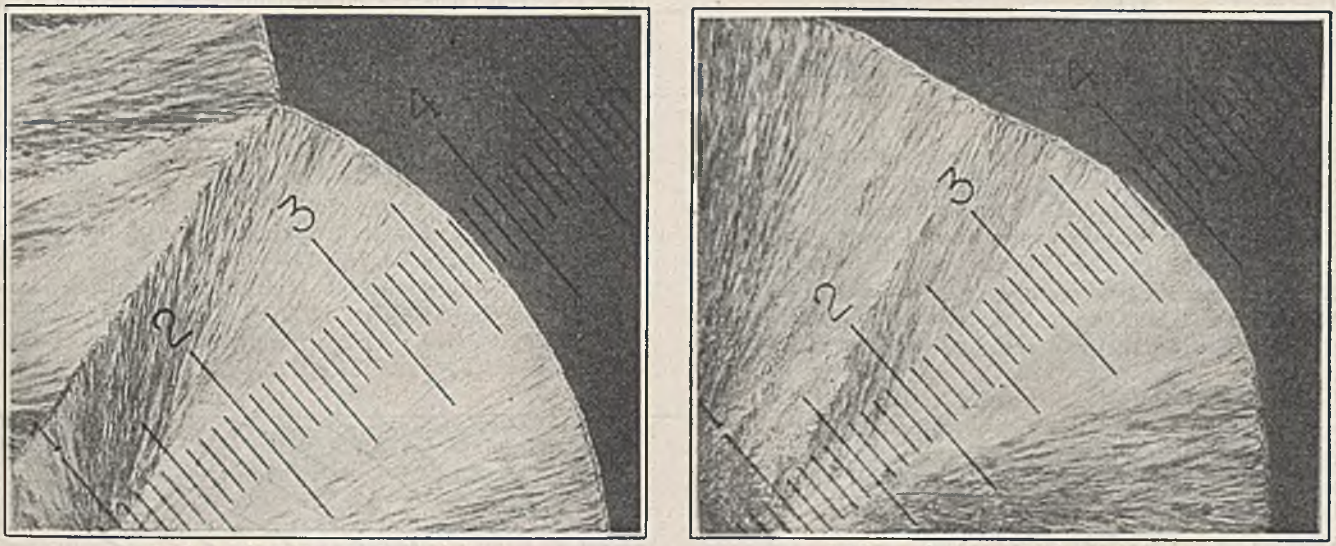
Certain precautions must be observed in order to obtain accurate results. The most important of these is sampling. Most industrial mixtures are not thoroughly mixed when considered microscopically. It is possible to obtain 50-mg. samples of technical DDT from a single container that vary as much as 6% in amount of *p,p'*-DDT. To eliminate this problem, which is common to all methods of microanalysis, a quick and efficient method of sampling must be used. This is provided for technical DDT by melting (avoid superheating above 120° C.) a 3- to 4-gram sample in an evaporating dish on a hot plate, stirring the liquid for a minute with a glass rod before removing the microsample of one drop with the rod and placing it on a clean microscope slide. Other precautions almost as important as sampling are discussed below.

The hot preparation must be allowed to come to temperature equilibrium with the surroundings before being placed on the microscope stage (about 2 minutes) and must be allowed to come to complete equilibrium on the microscope stage (2 minutes) before a measurement is made.



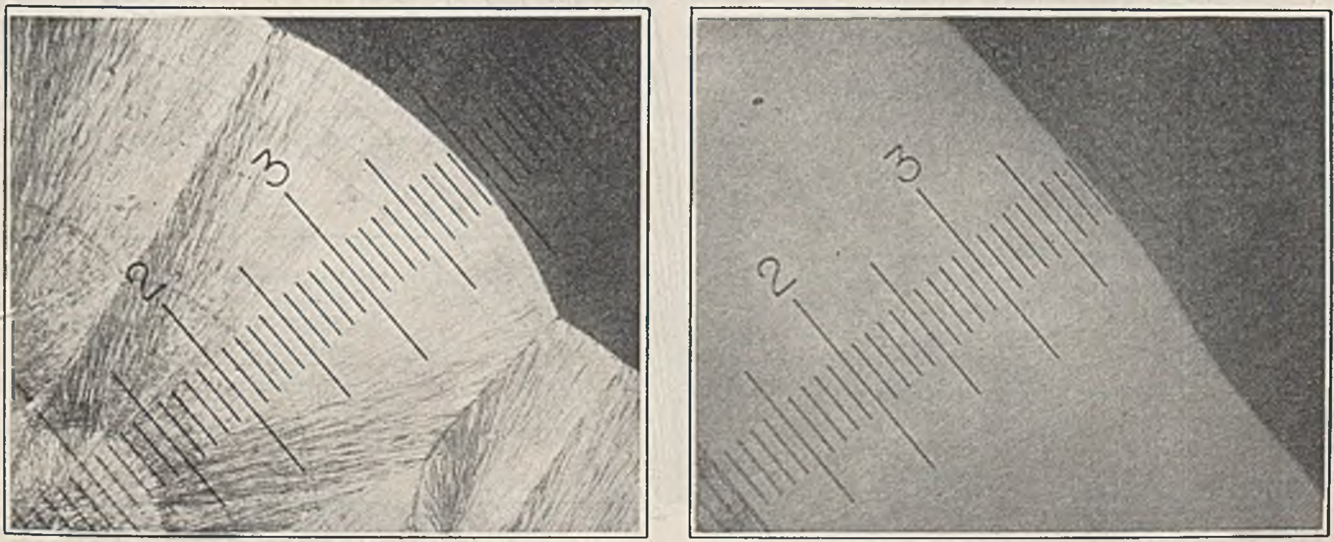
65% p,p'-DDT; 35% o,p'-DDT

72% p,p'-DDT; 28% o,p'-DDT



81% p,p'-DDT; 19% o,p'-DDT

82% p,p'-DDT; 18% o,p'-DDT



93% p,p'-DDT; 7% o,p'-DDT

100% p,p'-DDT; 0% o,p'-DDT

Figure 1. Growing Crystal Fronts of *p,p'*-DDT in Mixtures of *p,p'*-DDT and *o,p'*-DDT. × 200

To prevent heating of the preparation the light source must be as low in intensity as possible and still furnish easy observation of the crystal front. Normal illumination is probably satisfactory, especially if crossed Nicols are used. For best results a heat-absorbing filter—e.g., Aklo filter made by Corning—should be used. It is also possible to determine a temperature correction by placing the thermometer bulb in place of the preparation for 1 to 2 minutes to obtain the temperature difference between the recorded value and the preparation. In general, a temperature difference of 0.1° C. is equivalent to a percentage difference of 0.3%; hence the temperature must be as accurate as possible. With normal diffuse illumination, crossed Nicols, and a heat-absorbing filter the heat gain in the preparation will be less than 0.1° C.

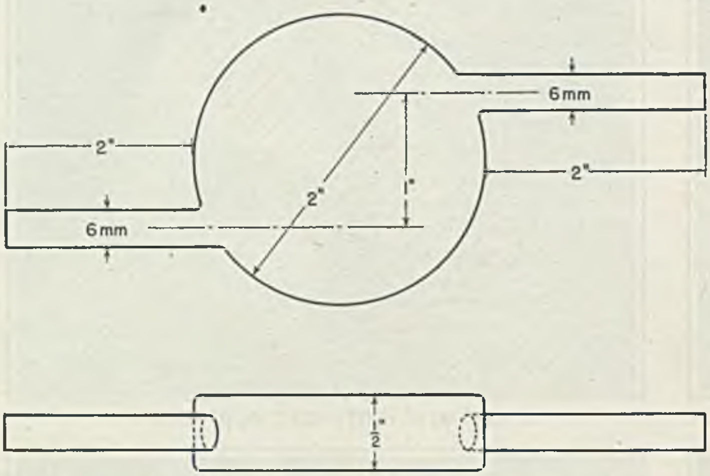


Figure 2. Diagram of a Simple Circulating Liquid Hot Stage

The measurement should be made for a time sufficiently long to give a reading of at least 10 eyepiece micrometer divisions. This will require as long as 15 minutes for very impure DDT (at low temperatures) but nearly pure DDT will require only 2 to 3 minutes.

The method would be more accurate and require less time if a permanent temperature control were available. This would be practical if a large number of routine analyses were necessary. For an occasional analysis or for a small number of analyses it is neither desirable nor necessary to go to the trouble to obtain temperature control. The results will be only slightly less accurate when no control is used (±0.5% compared with ±0.3%). Because of the heating effect of the illumination, the results without temperature control will tend to be high by perhaps 0.2 to 0.3%.

For the most accurate analysis of a number of samples of DDT the hot stage shown in Figure 2 should be used with a constant temperature of about 30° C. With this arrangement results having a precision of ±0.3% at the rate of one analysis every 10 minutes are easily possible.

PROCEDURE FOR ANALYSIS OF DDT MIXTURES FOR *p,p'*-DDT

A small sample (3 to 4 grams) is melted with as little superheating as possible on a hot plate (to avoid slight decomposition or volatilizing one or more components, the temperature should not exceed 120° C.). The melt is mixed by stirring for about one minute with a glass rod. One drop is then placed on a clean microscope slide and covered with a clean cover glass. The cover glass is pressed down firmly to give a thin film of DDT. If necessary, the preparation is seeded at the edge of the cover glass with a crystal of *p,p'*-DDT to initiate growth. The preparation is then allowed to cool for 2 minutes before placing on the microscope stage. At this same time a thermometer is placed on the stage with the bulb near the preparation. After 2 more minutes on the microscope stage the temperature is recorded and the crystal front focused with the eyepiece micrometer scale. The rate of growth of the *p,p'*-DDT is determined over a period of 5 to 10 minutes. The temperature is noted several times during the determination, so that the average may be used in determining the per cent *p,p'*-DDT. The rate of growth expressed in microns in 5 minutes and the average temperature are used in the graph (Figure 3) to determine the per cent *p,p'*-DDT.

If a temperature-controlled hot stage is used, less time is required to reach equilibrium. If the slide, usually a microscope slide cut in half 2.5 × 3.75 cm. (1 × 1.5 inches), is placed on the hot stage with a drop of water between the slide and stage to increase the rate of heat flow, the rate of crystal growth can be measured as soon as the crystal front becomes well formed.

ANALYTICAL RESULTS WITH KNOWN MIXTURES OF *p,p'*-DDT AND *o,p'*-DDT

Mixtures of pure *p,p'*-DDT, melting point 108.5–109° C., with *o,p'*-DDT, melting point 74.0–74.5° C., have been studied by the procedure outlined above. These mixtures, ranging in composition from 65 to 100% *p,p'*-DDT, were melted and thoroughly mixed with a fine glass rod before being covered with a cover glass.

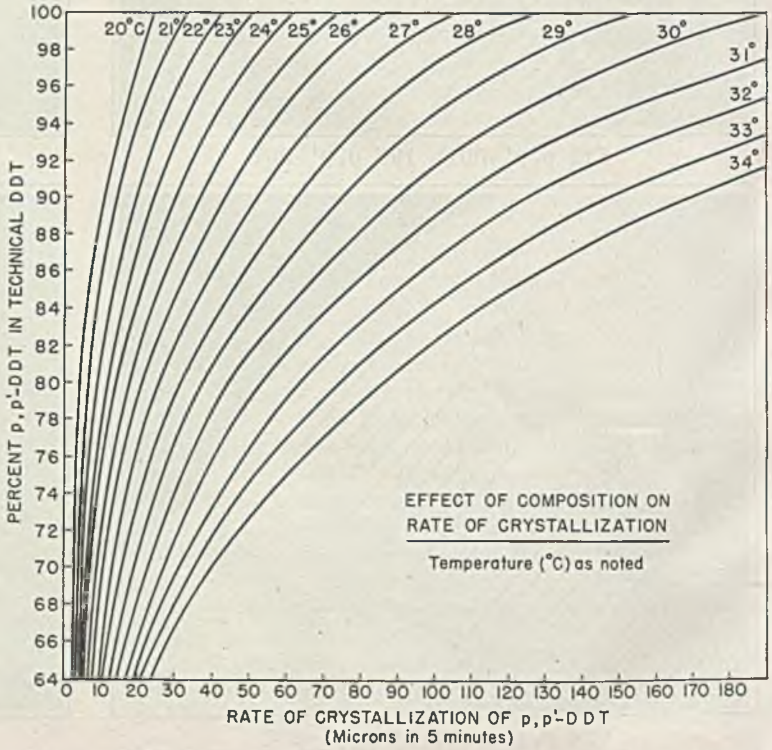


Figure 3. Rate of Growth of Crystal Front of *p,p'*-DDT as a Function of Purity of Mixture

The authors will be glad to furnish large reproductions of this graph to anyone requesting a copy

Six of these preparations having compositions of 65, 72, 81, 82, 93, and 100% p,p'-DDT were used to determine the relation between rate of growth of p,p'-DDT and composition. These data were plotted, smoothed by graphical means, and replotted as shown in Figure 3. All the data taken on known mixtures gave rates which checked to ±0.6 micron. This corresponds to about ±0.3% p,p'-DDT at 30° C. and a mixture of 80% p,p'-DDT. The error would be higher for lower temperatures and smaller percentages of p,p'-DDT and less at higher temperatures and concentrations of p,p'-DDT.

The results of the application of the method of analysis to three commercially available samples of technical DDT are shown in Table I. A comparison of the rate of crystallization method of analysis with the recrystallization from 75% ethanol procedure of Cristol, Hayes, and Haller (*2*) is given by comparison of the analytical data by the two methods. The same samples were analyzed by both procedures and the data are presented in Tables I and II. The two methods check very well with each other. The data in Table II were obtained by as careful work as possible by an experienced analytical chemist. The data in Table I were obtained with no temperature control and no particular precautions or care not described completely above.

Table I. Analysis of Samples of Technical DDT by Rate of Crystallization of p,p'-DDT from the Melt

	Sample I		Sample II	Sample III
	75.7	75.2	73.1	71.8
	74.8	75.2	74.7	72.1
	76.0	74.6	73.4	71.5
	75.3	75.6	73.1	72.8
	75.2	74.7	74.1	71.8
	74.9	75.4	73.8	72.4
	75.3	75.1	...	...
	75.9	...	...	...
Average		75.3	73.5	71.9
Maximum deviation		0.7	1.2	0.9
Average deviation		0.3	0.5	0.4

It is possible with care to double the precision of the method, but this may not be advisable because the accuracy of the method is not known. The accuracy is based on the analysis of known mixtures of p,p'-DDT and o,p'-DDT and the effect of the other by-products and impurities on the rate of crystallization of p,p'-DDT is assumed to be equivalent to an equal quantity of o,p'-DDT. There is no way to check this hypothesis accurately. The fact that the results agree within 1% with results obtained by the method of Cristol, Hayes, and Haller is significant only within the limits of error in that agreement—namely, 1%. Claims of accuracy beyond that limit of less than 1% are unfortunately not justified.

Table II. Analysis of Samples of Technical DDT by Recrystallization from Saturated 75% Ethanol

	Sample I	Sample II	Sample III
	75.7	72.9	69.9
	76.4	74.5	72.1
Av.	76.0	73.7	71.0

Further study of the rate data leads to an interesting and significant observation. The Arrhenius relation between the reaction velocity and temperature, in gaseous and liquid systems, is given by the equation

$$\log k = \frac{-E}{2.303R} \times \frac{1}{T} + B$$

where the symbols have their usual significance. This equation is found to represent the data of the present work (see Figure 4) if k is considered to be the linear rate of crystallization. The Arrhenius constants, determined in the usual way, are presented in Table III.

Table III. Slope and Intercepts for Curves of Log Rate against Reciprocal Temperature

Per Cent Purity	$\frac{-E}{2.3R} \times 10^3$	$E \times 10^3$	Log B
100	7.27	33.2	26.3
93	6.87	31.5	24.7
82	6.56	30.0	23.5
72	6.24	28.6	22.1
65	5.78	26.5	20.3

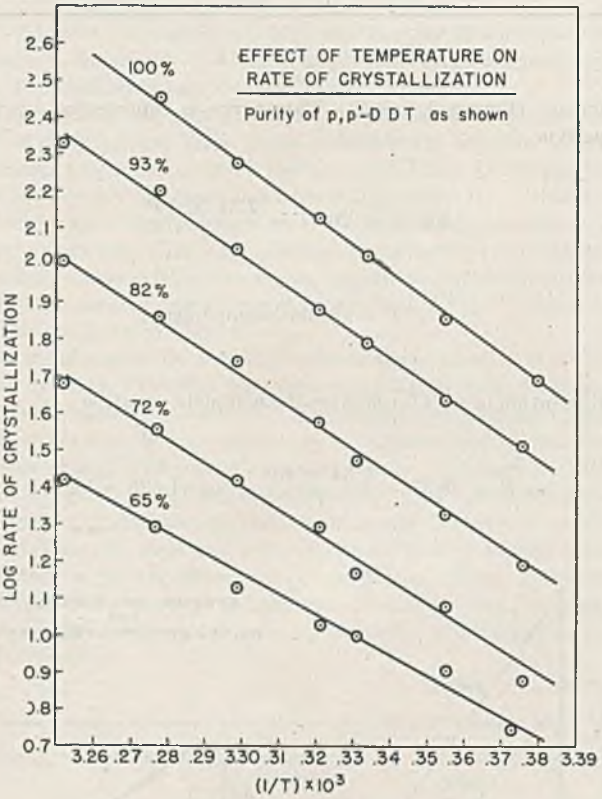


Figure 4. Result of Application of Arrhenius Rate Equation to Rate of Crystallization of p,p'-DDT

The significance of the constant E (which is analogous to the activation energy in a chemical reaction) is probably based on the energy required for a molecule to assume a position relative to the crystal front convenient for crystallization. It would be interesting to study the effect of molecular symmetry on this energy constant. Presumably a symmetrical molecule would have less difficulty orienting itself on the crystal front than an unsymmetrical molecule and consequently should have a lower value for E.

If the rate of crystallization is plotted against the log of per cent impurity a series of curves of the linear type $y = m(x - a)$ is obtained (Figure 5). The common abscissa of these lines, estimated from the figure, is 1.625 (ca. 42% impurity). Calculated values of the slopes for the various temperatures are presented in Table IV.

A linear relation is found to exist between the log of the absolute value of the slope, m, and the reciprocal of the absolute tem-

Table IV. Variation of Curve Slopes (Figure 5) with Temperature

Temperature, °C.	Slope ($x - 1$)	Log Slope	$(1/T) \times 10^3$, °K.
34	270	2.431	3.257
33	236	2.373	3.268
32	202	2.304	3.279
31	168	2.225	3.289
30	139	2.143	3.300
29	114	2.053	3.311
28	95.9	1.982	3.322
27	80.6	1.906	3.333
26	67.8	1.831	3.344
25	56.9	1.755	3.356
24	46.5	1.667	3.367
23	38.8	1.589	3.378
22	30.8	1.489	3.390
21	24.8	1.394	3.401

Table V. Comparison of Observed and Calculated Values

Impurity %	Temperature °C.	Rate (Observed)	Rate (Calculated)	Deviation from Observed Value %
2	27	90	60	33
3	27	83	69	17
4	27	72	78	8.3
5	27	72	74	2.8
5	33	218	224	2.8
6	27	67	68	1.5
6	33	200	204	2.0
7	30	109	107	1.8
7	33	184	187	1.6
18	24	17	17	0
18	31	61	62	1.6
19	26	23	23	0
28	22	5.5	5.4	1.8
28	25	10	9.8	2.0
30	27	13	12	7.7
30	33	36	36	0
32	27	12	12	0
32	33	30	29	3.3
34	27	10	7.4	26
36	27	9.	5.5	39

perature (Figure 5, inset). This curve is represented by the equation

$$\log m = 26.37 - \frac{7.34 \times 10^3}{T}$$

T = absolute temperature

Substitution of $f(T)$ for m gives the complete equation

$$\log R = 26.37 - \frac{7.34 \times 10^3}{T} + \log (1.625 - \log c)$$

R = rate of crystallization, microns in 5 minutes
T = absolute temperature
c = per cent impurity in mixture

Table V indicates the range of validity of this equation.

The portions of Table V above 28 and below 7% impurity are extrapolations of the equation beyond the region covered by the lines of Figure 5. In the range between 5 and 32% impurity, where the equation fits the data well, the calculated values for low rates are probably the more trustworthy, since it is difficult to interpolate low rate readings on Figure 3 within 10 to 20%.

It is interesting to note that the experimental rate of crystallization does not fall to zero with approximately equal amounts of pure and impure material, as the curves in Figure 5 indicate. Dotted lines for two of the curves show the true trend, which may be directed toward zero rate at 100% impurity. Although this region is theoretically interesting, it would be difficult and time-consuming to investigate experimentally.

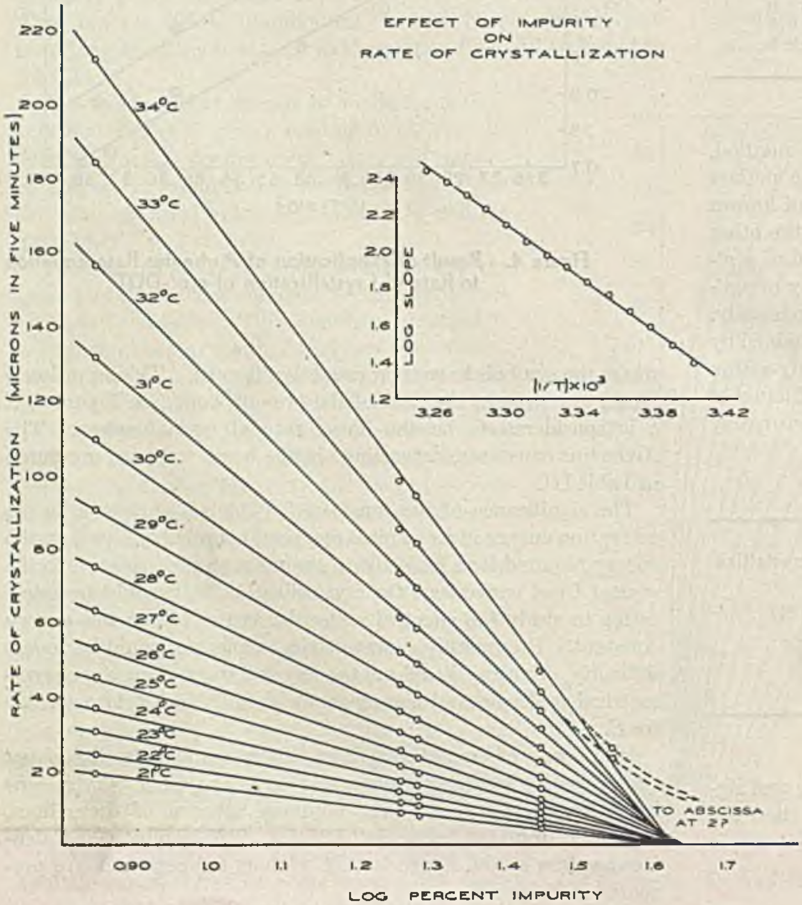


Figure 5. Rate of Crystallization *vs.* Log Per Cent Impurity

ACKNOWLEDGMENT

The authors wish to acknowledge the generous donation of a sample of pure *o,p'*-DDT by H. L. Haller of the Bureau of Entomology and Plant Quarantine.

The analyses of technical DDT by the ethanol solubility method of Cristol, Hayes, and Haller were carried out by Maurice Kayner of the Armour Research Foundation.

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Presented before the Division of Analytical and Micro Chemistry at the 109th Meeting of the American Chemical Society, Atlantic City, N. J.

NOTES ON ANALYTICAL PROCEDURES

Iodometric Method of Analysis for Organic Peroxides

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BECAUSE of its accuracy, reliability, and general applicability, the iodometric method of analysis for organic peroxides has been utilized more often than any other. In spite of this wide usage, rarely have two groups of workers carried out the analysis in the same solvent. This is due primarily to the fact that the solvents used heretofore have not been completely satisfactory. Acetic acid has been used often, but, because of the rapid oxidation of iodide ions by atmospheric oxygen, the analyses must be carried out in an inert atmosphere of nitrogen (*1*) or carbon dioxide (*4*). Acetone is not very satisfactory because it reacts with iodine in the presence of water (*2*, *3*). Alcohols require no precautions against oxygen, but the liberation of iodine is slow and the solutions must be heated to incipient boiling (*3*). Most other solvents have been eliminated because of unfavorable side reactions or the low solubility of the reactants in the medium.

Table I. Iodometric Peroxide Analyses with Acetic Anhydride

Peroxide	% Active Oxygen after Standing		
	5 min.	15 min.	20 min.
Benzoyl peroxide (50-mg. sample)	6.60 6.59	6.60 6.61	6.60 6.60
Peroxide in isopropyl ether	0.0493	0.0601	0.0601 0.0601
Peroxide in *n*-butyl ether	0.0247	0.0325	0.0335 0.0335
Peroxide in glyceryl trioleate	0.0335	0.0407 0.0407	0.406
Peroxide in diallyl phthalate	0.0401	0.0488	0.0488

The author has found that acetic anhydride is an excellent solvent for iodometric peroxide analyses. It is a good solvent for both peroxides and sodium iodide, it does not react with iodine, no precautions against oxygen are necessary, and the iodide-peroxide reactions are rapid when it is used as the solvent. In addition, the use of starch indicator (after dilution with water) makes possible the carrying out of accurate analyses on colored solutions.

ANALYTICAL PROCEDURE

The peroxide sample is placed in a glass-stoppered Erlenmeyer flask and 5 to 10 ml. of reagent acetic anhydride and 1 gram of powdered sodium iodide are added. After swirling to dissolve the iodide, the solution is allowed to stand for 5 to 20 minutes. Water (50 to 75 ml.) is added, the mixture is shaken vigorously for about a half minute, and the iodine is titrated with standard thiosulfate, using starch indicator. With very dilute solutions a slight positive correction of the starch end point may be necessary.

When polymers or other water-insoluble substances are present in the peroxide sample, it is advantageous to add a small amount of chloroform to the initial reaction mixture. After the subsequent addition of water, a two-phase system results which may be titrated in the usual manner to a starch end point or by observing the disappearance of the iodine color in the chloroform layer.

The acetic anhydride should not contain much acetic acid, since the rate of the atmospheric oxygen–iodide reaction is accelerated by acetic acid. Mallinckrodt reagent-grade acetic anhydride from a freshly opened bottle gave a blank of less than 0.01 ml. of 0.1 *N* thiosulfate after standing for 20 minutes with sodium iodide in air. Technical acetic anhydride has been used but it sometimes requires a small correction factor.

The method has been used most often with benzoyl peroxide (purified by adding three times a chloroform solution to cold methanol with stirring) and it has been found that 50-mg. samples can be correctly analyzed to within 0.2% (Table I). Other acyl peroxides gave results which were as reproducible as those with benzoyl peroxide. In the application of the method to peroxygen in ethers and ethylene derivatives, slightly longer reaction times were necessary to ensure complete reaction. A few typical examples are given in Table I.

Most substances do not interfere with the method, as is evident from Table II. Pyridine interferes when starch indicator is used but is harmless in its absence. The addition of phenols appears to result in slightly low results. Some ethylene derivatives react rapidly enough with iodine to cause trouble. Although the addition of acrylonitrile, methacrylonitrile, vinyl acetate, methyl acrylate, and allyl acetate resulted in nearly quantitative analyses, styrene and oleic acid reacted slightly and cyclohexene considerably under the experimental conditions. Thus, peroxygen analyses in the presence of ethylene derivatives—e.g., vegetable oils—require preliminary tests to determine the importance of iodine addition.

Table II. Effect of Added Substances on Analysis of Benzoyl Peroxide

(1 ml. of added substance, 50 mg. of peroxide, and 10 ml. of solvent)

Added Substances	% Peroxide by Analysis
None	99.8
Benzene, toluene	99.8
Carbon tetrachloride, chloroform	99.8
Ethyl acetate, ethanol	99.8
Cyclohexane, acetone	99.8
Nitrobenzene	99.7
Pyridine (without starch)	99.7
Acrylonitrile, methacrylonitrile	99.8
Vinyl acetate, methyl acrylate	99.7
Allyl acetate	99.4
Styrene	98.0
Oleic acid	97.0
Cyclohexene	80.0
Phenol	98.5
p-Cresol	98.5

ACKNOWLEDGMENT

The author wishes to express his appreciation to P. D. Bartlett for advice during the course of this investigation, and to the Pittsburgh Plate Glass Company for support of this research.

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Small All-Glass Ground-Joint Filters

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NOT long ago Craig and Post (*2*) described several small all-glass centrifugal filters in which the filtration takes place between the ground surfaces of a filter body and the filter stick. This paper describes an extension of this principle of filtering between ground surfaces, in which use is made of short standard-taper rough-ground joints. A preliminary description of one of these filters has been given (*1*). This development not only makes possible a much greater variety of filter designs, but at the same time confers several advantages on this type of filter in addition to those pointed out by Craig and Post. The filters can be used in the centrifuge in essentially the same manner as described by these authors, or they can be used in conventional setups for suction or positive pressure, but are not well suited for gravity filtration.

The ₸ ($^1/_{10}$) filter-grindings have at least three distinct advantages over the very short, irregular-taper and low-angle grindings described by Craig and Post: The parts are interchangeable; the sticks always seat properly; and the sticks can be seated firmly so that they remain in place—no spring is required. An additional development consists of the variation of the "porosity" of the filters by controlling the fineness of the grinding—e.g., various porosities can be made by grinding with Carborundum powder of various sizes.

Several ground filters are illustrated in Figure 1. Various designs of filter bodies are represented by *H*, *E*, *A*, *C*, *I*, and *G*; of filter sticks by 1, 2, 3, 4, 5, and 6. *D* is a simple test-tube receiver with a heavy inside rim. *B* and *B'* are supporting tubes, the latter having a tiny vent. *F* and *F'* are funnels, the latter of light wall. Rubber supports (about 1 mm. thick) are used where indicated. Most glass parts were fabricated from standard-wall Pyrex tubing. The ground joints were made on the tubes with the aid of ₸ graphite and cast iron tapers for shaping and grinding, or commercial ₸ full-length joints were sealed to the larger tubing. Either before or after sealing, the joint was ground on a cast iron $^1/_{10}$ taper with 150-mesh Carborundum-water mixture. The sealing operation destroys the top 10 to 20 mm. of the grinding on the full-length joints, leaving a ground surface of 10- to 15-mm. length. While finishing the lower end of this joint in the blow torch the bottom 5 mm. of grinding may or may not be destroyed. In any case control of the diameter and length of ground zone on both the body of the filter and the filter stick is simple when commercial ₸ ground joints are used. [If commercial ₸ "blank" (unground) joints could be used, the cost of these filters should be reduced.]

No doubt tapers other than $^1/_{10}$ would also be suitable. Several porosities can be had for a given filter body by grinding each of several filter sticks with a different mesh of Carborundum. For general purposes 150-mesh Carborundum has been found satisfactory for all grindings. It is feasible to make these filter surfaces simply by grinding commercial joints against each other with Carborundum. This procedure is likely to destroy the interchangeability.

All the filters illustrated in Figure 1 are shown arranged for use in the 100-cc. brass cups of a No. 2 International centrifuge: *G*, *H*, and *I* can also be adapted for positive pressure, *H* and *I* for negative pressure. Other designs are readily constructed, such as heated or cooled, and larger or smaller capacity filters. Various styles of filter sticks can be used with various filter bodies.

The filter body, *I*, in conjunction with stick 3 (or 5, etc.) can be used in the same ways as a Corning 15 F fritted filter.

Combination *E4FE* is similar to one of Craig and Post. The weight of *E4* is supported at the glass-to-glass contact of filter stick 4 and funnel *F*, between which liquid readily passes because they are not blown perfectly symmetrical. Although the weight of *E4* has been as much as 30 to 40 grams, no breakages have occurred at 1580 r.p.m. The ground neck of *E*, sticks 4 and 4', and funnel *F* should, of course, be made of reasonably heavy wall (about 1.5 mm. thick). The vented stick, 4', is useful if it is desired to filter a hot solution. For handling hot solutions in volatile solvents bottle *A* with vented stick 1 is better, because there is less evaporation loss.

Setup *G5B'F'E* is arranged for positive pressure or centrifugal filtration of a solution preliminary to carrying out crystallization or precipitation in *E*. A short-stemmed version of *I* can be used in place of *G*, and *C* can be the receiver in place of *E*. (The supports *B* and *B'* are better made of aluminum than of glass.)

Combination *H6E* is designed as an internally heated extractor. Solvent can be distilled from *E* through 6 to a condenser and thence returned to *H*. Filtration can be hastened from time to time by centrifugation. Filter sticks such as 6 can be made shorter, and provided with a loose cap to prevent material from falling into *E* when *H* is charged with material to be extracted. Another arrangement similar to *H6E* has been described (*1*). To avoid breakage this design should not be centrifuged at speeds much higher than 1000 r.p.m.

Setup *A1BC2* is shown in position for centrifugally filtering a hot solution (to free it from debris) preliminary to crystallization. In dissolving the material the solvent can be refluxed while *A1* is hung from a hook through the eye of 1. The maximum volume which can be so handled is slightly less than half the total capacity of *A*. During the crystallization in *C*, this bottle is kept closed by the filter stick by hanging the bottle with a hook through the eye of 2. After equilibrium between crystals and solution is established, the filtration is accomplished by centrifuging arrangement *C2D*. This closed "filter-bottle" design, *C2*, is especially advantageous for small-scale solubility determinations, and quantitative handling of recrystallizations or precipitations by centrifugal filtration. Only the one tube must be handled on the balance. Before hanging in the balance the outside of *C* is wiped if necessary with a wet cloth, washed with tap water, then with redistilled acetone. With a similar glass tube as counterpoise the weight is thus easily obtained accurate to ±0.1 mg. or better. The weighings are made with the bottle closed for the determination of the weight of solution and (after filtration) of the wet crystals; and with the bottle open (the filter stick pushed in and the tube lying on the balance pan) for getting the weight of the dry (or drying) crystals. The rate of loss of methanol vapor through a dry filter grinding ₸ 10/8 is about 6 mg. in 24 hours at 25° C.

The rate of filtration in the centrifuge from such a closed bottle is only very slightly less than through an open filter if the bottle is not over half full, the temperature of the contents is at or below that of the centrifuge when the stick is pulled up, and the receiver

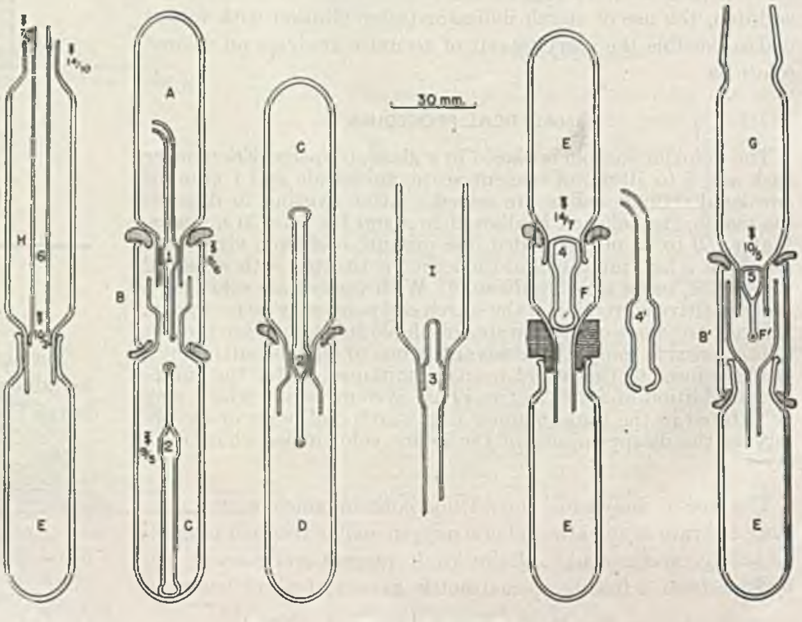

Figure 1. Ground-Joint Filters

has a vent—a tiny hole punched near the top of *D* suffices. (The vent is less helpful the smaller the volume to be filtered.) It is often possible to take advantage of nearly the full capacity of the bottle by removing some of the clear supernatant with a pipet before the filtration. Sometimes a few cubic millimeters of dry ice are added to a bottle three-fourths full just before pulling up the stick; the filtration is as rapid as through an open or vented filter.

The rate of filtration through the ₸ filters ground with 150-mesh Carborundum is very high, even though the length of the ground zone of contact is as much as 5 to 10 mm.

A filter such as *I* (Figure 1) having ₸ 10/8 was compared with a Corning 15 F fritted filter. Both were fitted with rubber collars and placed on receivers such as *D*, then charged with 10.0 of distilled water and centrifuged at 1580 r.p.m.; both filters let through 8.5 cc. in 2 minutes. If the receiver had no vent the ground filter was dry in a total of 3 minutes but the fritted filter held 1 cc. for at least 5 minutes; if the receiver had a vent both filters were dry in 3 minutes. The holdup of the ground filter was 0.05 cc., of the fritted filter 0.15 cc.

The retentiveness (in the centrifuge) of these two filters was comparable: both prevented the passage of any visible amount of barium sulfate when tested by the method of Scribner and Wilson (*3*); both readily allowed *Staphylococcus aureus* (1μ diameter) to pass through. (It is hoped that ground filters can be made which will retain the *Staphylococcus* and other bacteria. Experiments on this are being continued.)

There is room in the No. 2 International centrifuge (100-cc. brass cups) for a total length of filter plus receiver of 225 mm. when these have outside diameter of 25 mm. or less. Filters of type *C*2 weighing 30 to 50 grams have been repeatedly carried by receiver *D* without breakage at 1850 r.p.m. Still longer (larger capacity) filter bottles can be made for use with smaller capacity receivers in cases where much of the supernatant solution can be pipetted off before filtration. It would be wise to make them smaller and/or from lighter wall tubing if, for special purposes, speeds of 2000 r.p.m. or more are desired. The speed of 1580 r.p.m. has often given a holdup of only 20 mg. of mother liquor on 1 gram of moderate sized crystals.

SUMMARY

Small (up to 30 cc.) all-glass filters are described in which filtration occurs between standard-taper rough-ground surfaces. These filters are equal to or superior to small Corning F fritted filters in the following respects: they give equal rates of filtration, and have equal retentiveness; They have smaller holdup, are much easier to clean, and do not contaminate preparations with particles of glass. In adaptability of design they have distinct advantages over the filters described by Craig and Post. A new filter bottle is described which is particularly suitable for use in the centrifuge for determinations of solubility and for quantitative handling of recrystallizations and precipitations.

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Funds for carrying out this work were kindly supplied by the Mallinckrodt Chemical Works.

Solution Intake Unit for Improved Operation of the Flame Photometer

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IN USING a recent model of a commercial flame photometer, annoying drift and fatigue of the phototube were encountered (*1*). As a result one standard solution had to be run alternately with the sample solution tested. An improved solution intake unit has been added to the atomizing system which increases the speed and accuracy of operation.

Figure 1 shows the original solution intake and the improved unit. With this double capillary intake and the three-way stopcock, the standard solution can be left in the system continuously, changing only the beaker containing the sample solution, which is alternated with a beaker of distilled water for flushing the atomizing system. A sample reading can be made very quickly, after setting the instrument on the 100-mark with the standard solution. In other words, the time allowed for drifting of the phototube has been kept at a minimum. However, the most important improvement is the elimination of the extra operation of handling the standard solution which now stays continuously in the system.

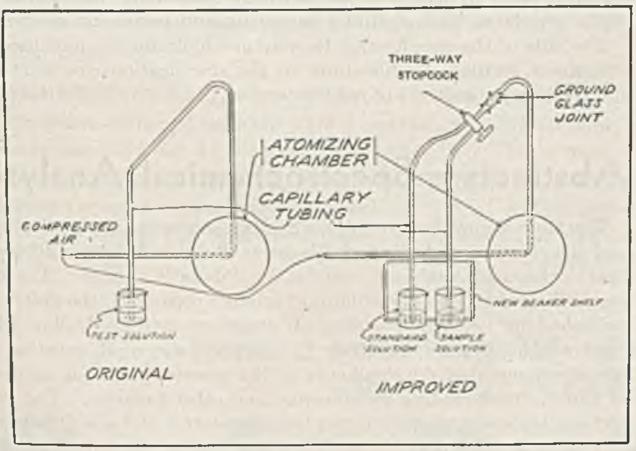

Figure 1. Original and Improved Solution Intake Unit for Flame Photometer

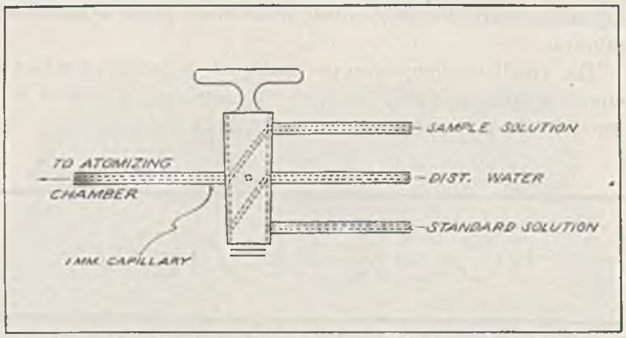

Figure 2. Four-way Stopcock for Solution Intake Unit

A further possible improvement is shown in Figure 2, where a four-way stopcock allows a beaker of distilled water to be added for flushing the atomizing system. This distilled water remains continuously in the system like the standard solution; thus the operator need handle only the beaker containing the sample solution.

ACKNOWLEDGMENT

The assistance of Jane L. Showacre in trying out the new unit is appreciated.

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Cleaning Laboratory Glassware

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School of Biological Sciences, Stanford University, Calif.

THE device illustrated in Figure 1 has proved particularly useful in cleaning laboratory glassware with corrosive fluids such as chromic acid or sulfuric-nitric acid mixtures. It is also useful for drying glassware with organic solvents such as acetone, or for making collodion membranes in test tubes. The unit is constructed of Pyrex and can be heated directly if hot cleaning solution is desired.

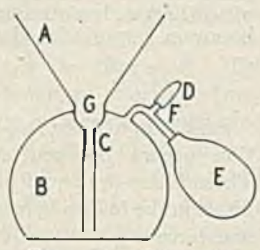

Figure 1. Apparatus

A, 4 to 5-inch funnel; *B*, 0.5 to 1.0-liter flask; *C*, constriction in 10-mm. tube, internal diameter, 2 to 3 mm.; *D*, medicine-dropper bulb; *E*, 60-ml. rubber bulb; *F*, 8-mm. tubing; *G*, throat, about 18-mm. internal diameter

In operation, a flask, beaker, etc., is inverted inside the funnel, *A*, directly over the throat, *G*. Abrupt pressure on the rubber bulb, *E*, produces a strong jet of fluid which floods the walls of the vessel and then drains back into the funnel. On release of the bulb, the excess fluid is sucked back into chamber *B*. Flasks, test tubes, beakers, bottles, and graduates are acid-cleaned in this manner very rapidly. Flasks, for example, have been acid-treated at a rate of over 750 per hour.

If the vessels being cleaned contain a large amount of reducing material which can wash back into the chamber, the cleaning solution will deteriorate. However, in normal use this does not occur. Most of the cleaning action probably occurs in the film of acid left in the flask. That this film of acid is sufficient to clean the glassware thoroughly, if the flasks are left standing for a short time, is indicated by the fact that after rinsing with distilled water, interference rings form within 1 or 2 minutes.

The small medicine-dropper bulb, *D*, is removed when the chamber is being filled. To prevent accidents, it is wise to remove *D* whenever the device is not actually in use.

BOOK REVIEWS

Qualitative Organic Microanalysis. *Frank Schneider.* iv + 218 pages. John Wiley & Sons, Inc., 440 Fourth Ave, New York 16, N. Y., 1946. Price, $3.50.

In this short book the author has attempted to create a "guide to the microtechniques required for the identification of organic compounds". The first half of the manual consists of a compilation of numerous published micromethods applicable to fundamental organic operations. The latter half is an abbreviated treatment of the problems of qualitative organic analysis along with laboratory directions for preparing about 30 derivatives.

Techniques of separation and the handling of mixtures are not adequately treated by the author, and consequently he had no reason to discuss some of the newer practical micromethods for this work. One thinks particularly of diffusion analysis and chromatography. The latter might have been mentioned under the heading "purification of the sample".

Since many difficult industrial problems in the field of organic identification are being solved every day by methods of chemical microscopy, it would seem that the author ought to have offered more encouragement to the reader in the use of the microscope as a tool in organic analysis. He mentions the scarcity of optical data for organic compounds; yet he does not list even the most valuable literature sources of such data now in existence. For instance, there is no mention of Winchell's recent book which lists optical data for over a thousand organic compounds, or of the Barker tables which are being published in England.

The first portion of the book dealing with organic operations is abundantly provided with diagrams of the microapparatus recommended. Such a collection should prove a useful reminder to even the experienced organic chemist who may have seen them before. Unfortunately some of the pieces drawn are too large to be practical for true microwork—i.e., 30 to 100 mg. of substance—being more suitable for "submacro" work, 0.5 to 1.5 ml. Yet this criticism does not detract from the usefulness of the manual.

The book is free from typographical errors and is attractively printed in a medium-sized type suitable for student use. On pages 121 and 122 the author uses "crystalline form" indiscriminately when he means "crystal habit" in some instances. Another slip is the frequent use of the word "microscopic" for the more appropriate "microscopical".

In spite of our criticism the book fills a useful purpose and is a pioneer in the field which it covers. J. A. KUCK

Standard Methods for Testing Petroleum and Its Products. 7th edition. 550 pages. Institute of Petroleum, 26 Portland Place, London, W.1, England; and American Society for Testing Materials, 1916 Race St., Philadelphia 3, Pa. Price, 15s. or $3.25.

An added feature is a list of new methods, revisions of methods and specifications, and withdrawals. Two new methods have been added, and 21 standards and two specifications have been effected by various changes. The conversion tables for petroleum oils have been withdrawn.

One of the new methods is a modification of a test for the determination of carbon disulfide in tar and its products to be applied to petroleum products. The other new method is intended to detect the coagulation of bitumen emulsions at low temperatures.

The method for knock rating of aviation fuel (weak mixture) has been rewritten to correspond to the A.S.T.M. format. Several changes have been made in the knock rating methods for experimental fuels over 100-octane number and for motor fuel.

Changes in procedure and interpretation of tests are few. A larger sample is permitted in the test for low acidity. Copper strip tests for corrosive sulfur are to be interpreted as one of six classifications of color change. Methods for the determination of tetraethyllead in motor fuel by bromination and hydrochloric acid are modified. The bromination method is not applicable directly to blends containing alcohol and is not recommended for fuels containing a high percentage of unsaturated hydrocarbons.

Modifications are indicated in apparatus for the following methods: distillation of liquid asphaltic bitumen, drop point of greases, flash point (closed) by means of the Pensky-Martens apparatus, penetration of bituminous materials, recovery of asphaltic bitumen from asphalts, residue on evaporation of kerosene and tractor fuel, sludging value of transformer oil, softening point of asphaltic bitumen (ring-and-ball method), viscosity by the Redwood apparatus, and water and sediment by means of centrifuge.

Editorial changes have been made in methods for ash of petroleum products, color by means of the Lovibond tintometer, distillation of crude petroleum, and sampling petroleum and petroleum products.

The title of the specification for wartime hydrometers now has an emergency status. Modifications in the specifications for wartime standard thermometers are more extensive. F. E. BUCHAN

Abstracts—Spectrochemical Analysis

The Ohio Valley Spectrographic Society announces the publication and distribution of Collected Abstracts Published during 1945 on Spectrochemical Analysis, compiled by Edwin S. Hodge. The 64-page lithographed booklet contains verbatim copy of all the abstracts published in 1945 by *Chemical Abstracts* on articles dealing with spectrochemical analysis. Over 80 references are cited, covering all the latest reported developments in the science, including analysis of alloys, direct-reading instruments, and other progress. The subject matter is arranged according to twelve topics and is well indexed.

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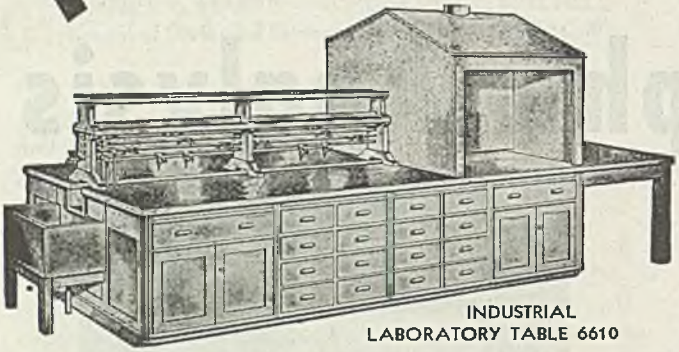

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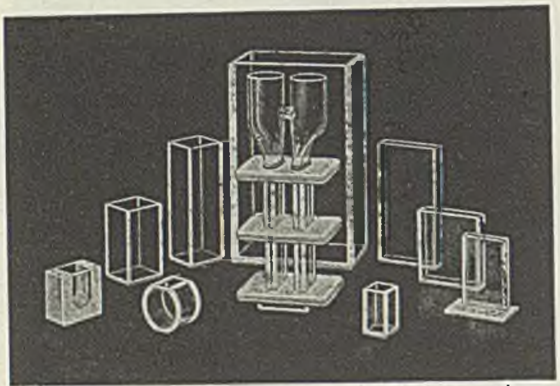

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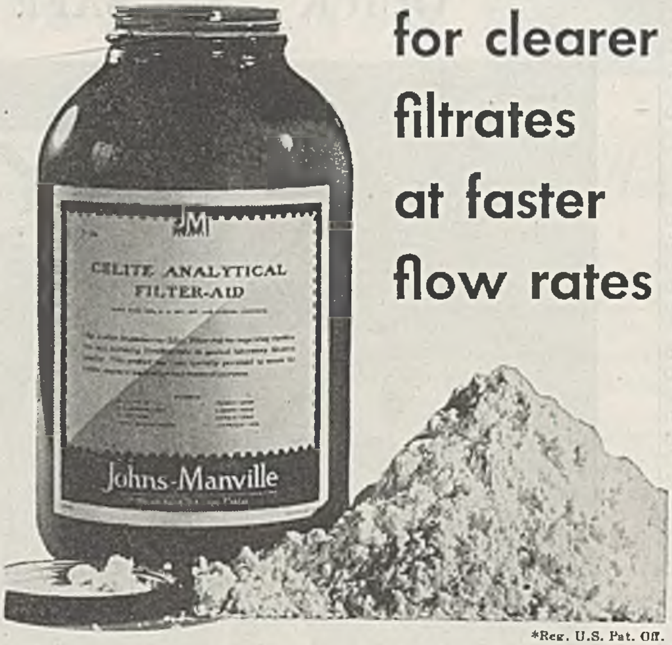
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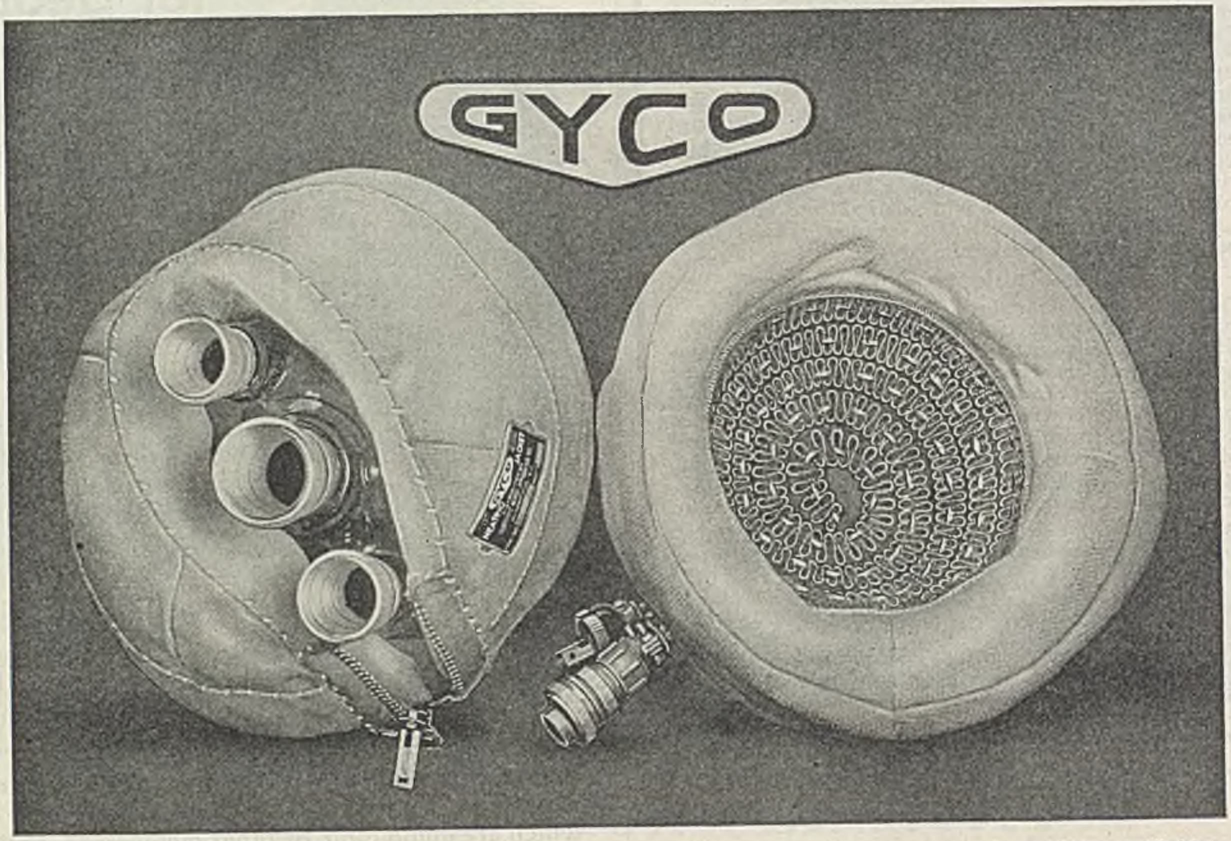
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Current Developments in

INSTRUMENTATION IN ANALYSIS

Discussed by Ralph H. Müller

On several occasions we have referred, in this column, to the recent developments in electronics and hinted that new and unexpected things might be done with "triggers and gates". Until a careful, definitive outline of these developments is written for the chemist, we wish to discuss them briefly, primarily to indicate why they should be of interest to the analyst. We do this partly in self-defense, because we have used these terms so freely.

Before the advent of television techniques, it was customary to regard the role of electronics primarily as one of amplification. Any phenomenon which could be converted to an equivalent electrical quantity would be amplified until it was measurable by relatively rugged meters. By means of compensation or null-method techniques it was often possible to use the amplifier solely as an indicator or criterion of balance. Under these circumstances even the cautious and suspicious investigator could be assured that the mysterious and uncertain vagaries of the amplifier did not affect the results of his measurements. The widely used principle of inverse feedback or degeneration has modified this state of affairs and for some time it has been possible to obtain high degrees of amplification relatively independent of tube characteristics and supply voltage.

The needs of television, radar, and related techniques have given rise to other approaches. They are concerned with the precise determination of time intervals and to the extent that various phenomena can be translated into terms of elapsed time, however short, they are of wide and general applicability.

Trigger Generators

The initiation of any timing mechanism and its subsequent stopping must be very rapid and definite, particularly if the time interval is short. It is best accomplished by a sharp impulse or transient potential. Pulse generators of great variety are available, and since it is often their function to set off or activate other circuits they are often called trigger circuits or generators. They belong to the general class of relaxation oscillators which are characterized by two stable states of equilibrium with a highly unstable intermediate state. A pair of vacuum tubes in an oscillator of this sort can be made to exhibit the following properties: One of the pair is normally in the nonconducting state while the other is passing its rated value of current. If a small disturbance occurs in the circuit (accidental or intentional) the conducting tube will rapidly energize the quiescent tube and its own output will drop to zero. This transition or switching is a cumulative process and can be made to occur in a microsecond or fraction thereof. In comparison with a conventional sinusoidal oscillator, this generator is very jerky and violent in its action and its output approximates a square wave—that is, the plate potentials abruptly rise and fall between certain limits. The violent and abrupt transitions thus provide the means for producing sharply defined pulses or triggers.

Oscillators of this class have many uses and can be modified to meet a variety of requirements. One of the oldest examples is the multivibrator which was invented in 1919. In its simplest form it consists of two triodes, each of which is capacitatively coupled to the other. In the free-running condition, each tube extinguishes the other in turn and the system oscillates violently at a period which is quite simply controlled by capacitance and resistance values. In a simple modification, one tube may be kept inoperative (biased) indefinitely or until a signal is applied to its grid. Upon receipt of the signal the multivibrator will execute an oscillation and return to the inoperative or standby condition.

A variation of this class is very aptly termed the "flip-flop". This circuit is normally quiescent but upon receipt of a signal it will "flip" to the new condition and remain there for a definite interval and then rapidly "flop" back to the original condition. To those who may be horrified by the "flippant" terminology, it might be well to point out that it was first used by our British cousins, and on most occasions we have been content to regard them as the custodians of our mutual heritage.

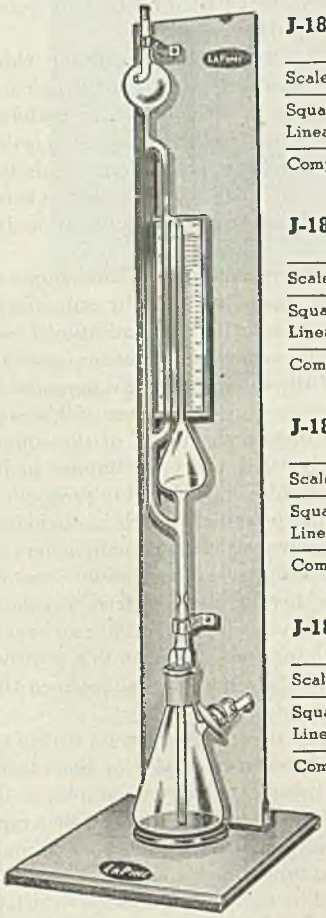
Another example is afforded by the blocking oscillator which normally executes sinusoidal oscillations at extremely high frequencies, but is arranged to block or throttle itself after performing a single cycle of operations. After this blocking action is dissipated, it undergoes another brief burst and so on. This has been referred to as a "suicide circuit", but when the action is occurring several thousand times a second, that designation becomes somewhat unconvincing.

The fact that the output of most relaxation oscillators approximates a square wave, or can be made to do so by subsequent limiting or clipping is one of the reasons for many additional uses of these devices. It furnishes the means of producung very accurate time delay functions. If the square wave is differentiated a positive and negative pulse are produced and these will be separated or spaced in time according to the width of the square wave. Differentiation is exactly what the term implies in its mathematical sense. A signal or pulse is produced in proportion to the time rate of change of the potential, which is obviously greatest at the sides of the square wave. It is actually achieved by coupling with a small series capacitor and large shunt resistor. It is now apparent perhaps why this succession of triggers can be so useful. The positive trigger may be used to initiate an event, and the negative trigger (as such, or upon inversion to a positive trigger) to terminate the event. The time interval between the triggers can be varied accurately and at will.

A single square wave has many uses aside from its utility in producing triggers. A common use is as a "gate" or short-term switch. If it is used as a negative gate it may be employed to switch off or inactivate a circuit for a definite period and then rapidly restore it to its sensitive condition. In the same sense it may be used as a "time vernier" for accurate interpolation.

A common example is afforded by the electronic switch which is a useful adjunct to the cathode ray oscillograph. Its function is to permit the simultaneous viewing of two distinct phenomena on a single cathode ray tube. The electronic switch accomplishes this by alternately "gating" or switching off the separate amplifiers which are receiving the two phenomena. The output of both amplifiers drives the oscillograph. The phenomena are then presented alternately at high speed and thus appear to be presented simultaneously. Other provisions enable one to superimpose the images or to separate them in the vertical direction.

Trigger generators and gates can be interconnected in an almost



Instrumentation

unlimited number of ways to provide complex sequences of operations, switching, coding of impulses, and delay operations. In many ways they can replace mechanical devices, particularly if high-speed operation is required.

The period of a relaxation oscillator is easily controlled by changing resistance, capacitance, or the control voltages. Therefore any phenomenon which can be converted to a change in one of these variables can be made to vary the rate of the oscillator. For example, a change in dielectric constant would change the value of a capacitor and therefore control the period of the oscillator. Similarly a change in light intensity could be used to change the resistance of a phototube, or the resultant photocurrent could produce a change in one of the control voltages.

Since the final measurement is in terms of elapsed time or a time delay, it might be expected that the conventional use of a meter is unnecessary or impractical. In most cases the cathode ray tube is the most convenient indicator. In some instances it is possible to make the final measurement with much simpler devices. For example, if a delayed trigger is produced, the delay of which is a function of light intensity, then one can provide another delay circuit which is precisely adjustable and proceed to find the time delay which is necessary to match the delay of the light measuring circuit. The correct value can be indicated by combining the two delayed triggers and using them to actuate an indicating tube. The latter is so arranged that only the simultaneous appearance of each trigger will cause it to function.

To the extent that trigger circuits can replace some of the conventional methods, one can expect more positive and definite behavior on the part of our measuring devices. It is not surprising that the extraordinarily critical requirements of television scanning and reproduction are best met by this class of devices. Conversely, their success in this field is the best indication of their reliability. A further measure of their precision may be inferred from range values which are attainable in radar which, in the best cases, is expressible in matters of yards. Fifty yards or so is traversed by light or radar echoes in a very short time interval!

It may be evident from the general properties of these circuits that the oscillograph is practically indispensable in any work involving their use; indeed the oscillograph is often the most convenient device as a final indicator. Conversely, trigger circuits have greatly improved oscillographic technique. Whenever transient phenomena are viewed it is often impossible to see those parts of the trace which are moving very rapidly. It is common practice to apply an intensifying pulse to the tube during these intervals to restore the pattern brilliance. Another useful practice consists in the periodic application of blanking pulses to the beam. In this way, a pattern can be punctuated by known time markers. Interpolating gates also have their uses. Very frequently a limited portion of a recurrent phenomenon is of interest and that portion may be selected by a suitable gate and the rest of the trace eliminated. At the instant at which this gate appears, a very fast sweep is generated in the oscillograph and the restricted portion of the phenomenon can be spread out over the entire screen. This is greatly superior to the older method of gross horizontal expansion.

The fundamentals of these techniques are available in several monographs and the more recent developments are appearing currently in *Electronics*. Among the more useful sources are: "Television", Zworykin, V. K., and Morton, G. A., John Wiley, New York, 1940; "Ultra-High Frequency Techniques", J. G. Brainerd, Ed., D. Van Nostrand, 1942; "Electrical Counting", W. B. Lewis, Macmillan, New York, 1943; "Time Bases", O. S. Puckle, John Wiley, New York, 1943; "Basic Radio", J. B. Hoag, D. Van Nostrand, New York, 1942. Most recent methods will appear in "M.I.T.—Radiation Laboratory Series", the first volumes of which are promised by McGraw-Hill for early 1947.

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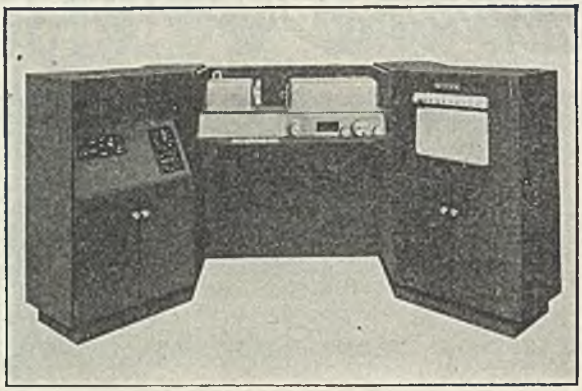

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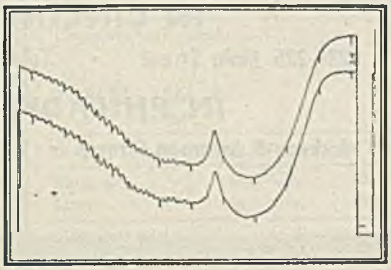

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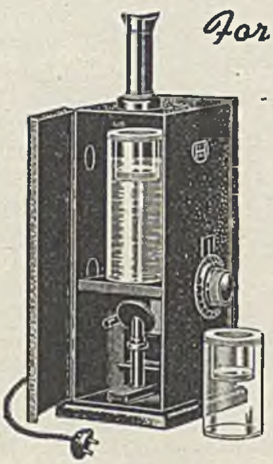

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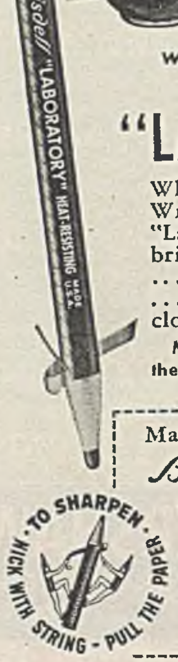

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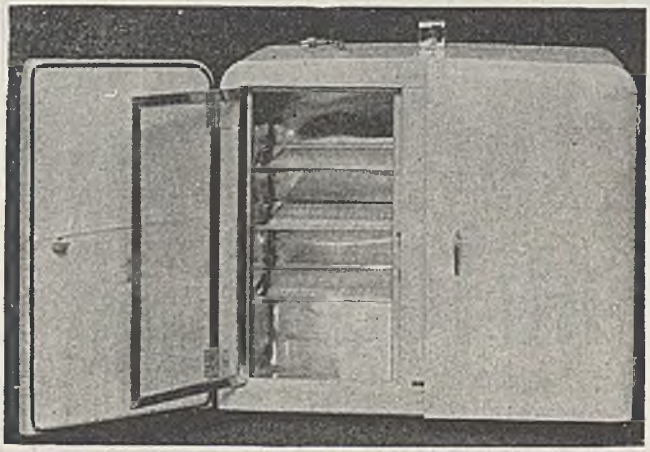

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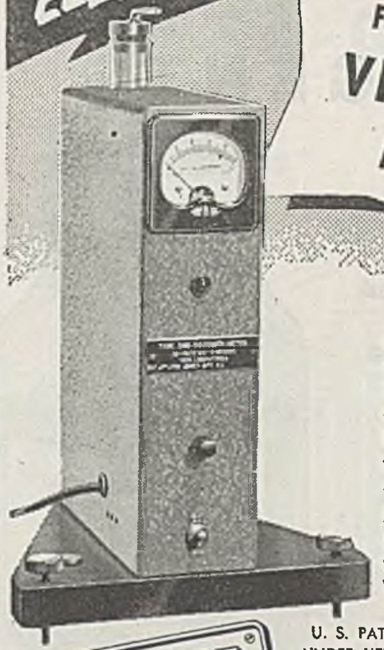

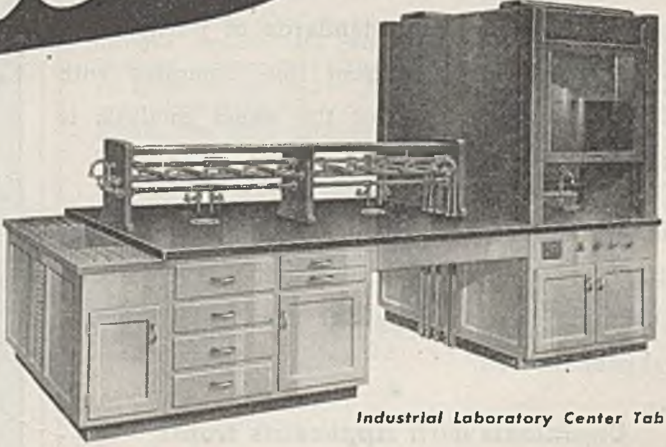

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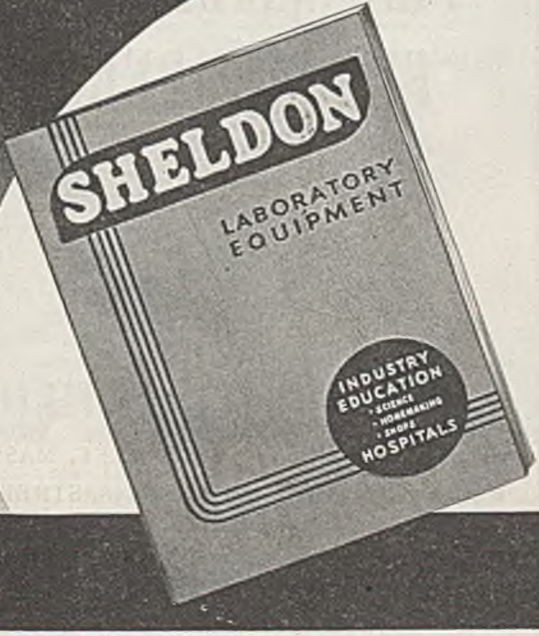

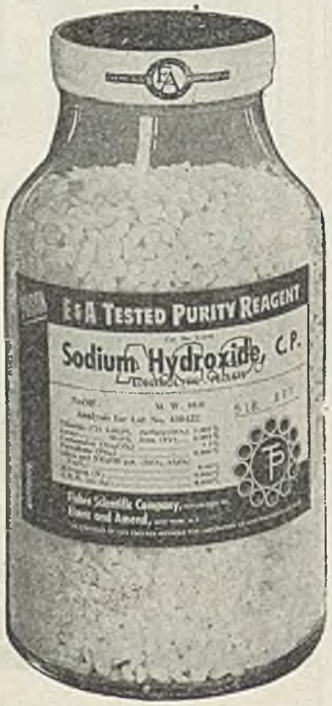
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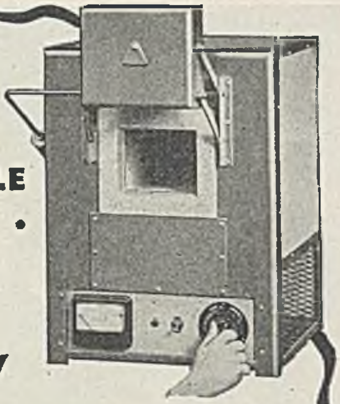

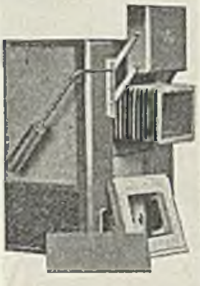

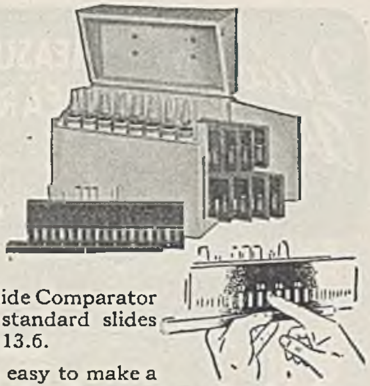


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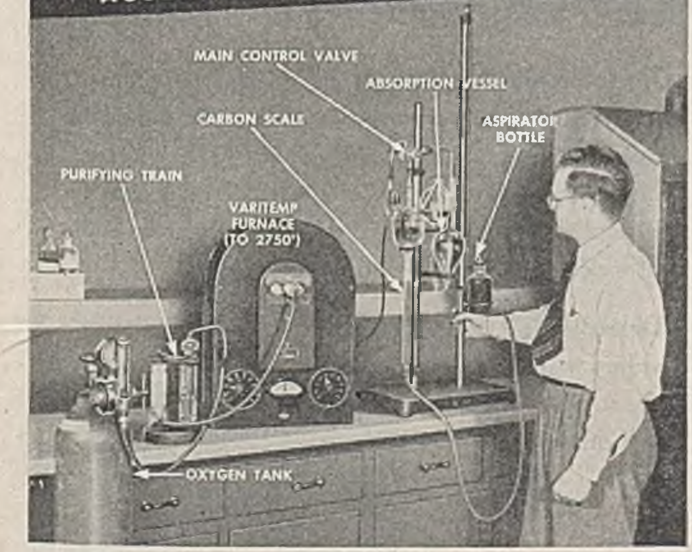
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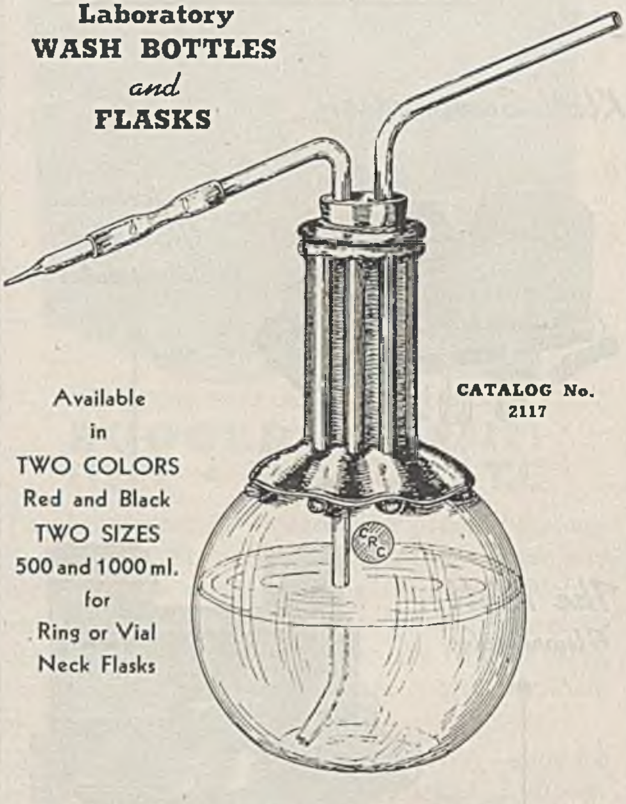

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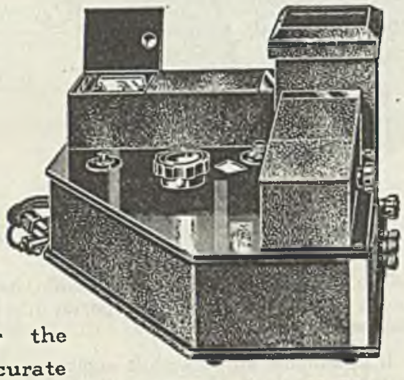

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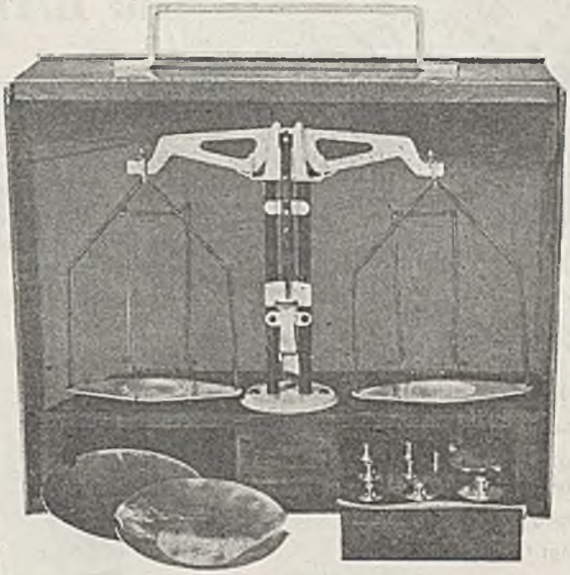

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RUGGED • COMPACT LIGHT • ACCURATE

This handy portable balance with patented features is ideally suited for field or laboratory where any kind of routine rough weighing is required. Weighing only 2$^1/_2$ pounds and equipped with an ingenious device which completely secures the moving parts, this new portable balance may be carried anywhere without damage.

Designed so that it is "set-up" and always ready for instant use, it is unnecessary to assemble any parts before using or to take parts down after using. The balance is constructed with precision and weighs accurately. It has an all aluminum cabinet, finished attractively, with sliding doors.

The ideal instrument for your personal laboratory!

It will be found useful in educational laboratories, industrial laboratories, dental laboratories, photographers, jewelers, etc.

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SENSITIVITY	10 milligrams
BEAM	Aluminum with protective construction
KNIVES AND BEARINGS	Finely ground tool steel
CABINET	Front and back doors removable 8″ high x 10″ wide x 3″ deep
BASE	Black wood with compartments for set of weights and balance pans
INDICATOR	Equipped with adjustment to zero

No. 11500 VOLAND PORTABLE BALANCE
Model 20, complete with set of weights and balance pans. Each $24.75

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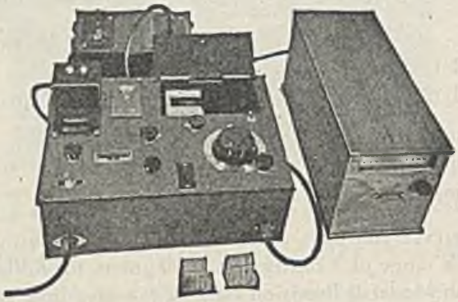

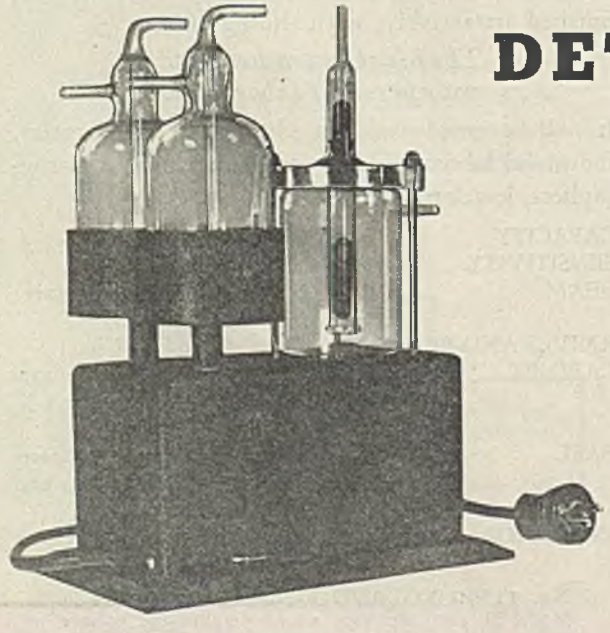

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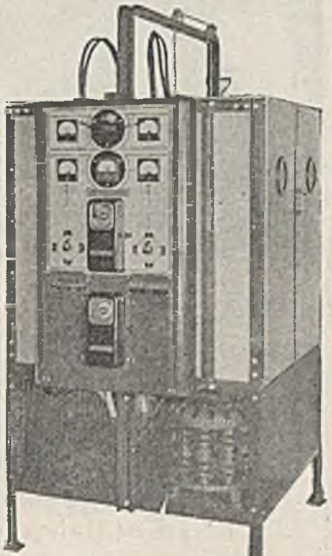

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