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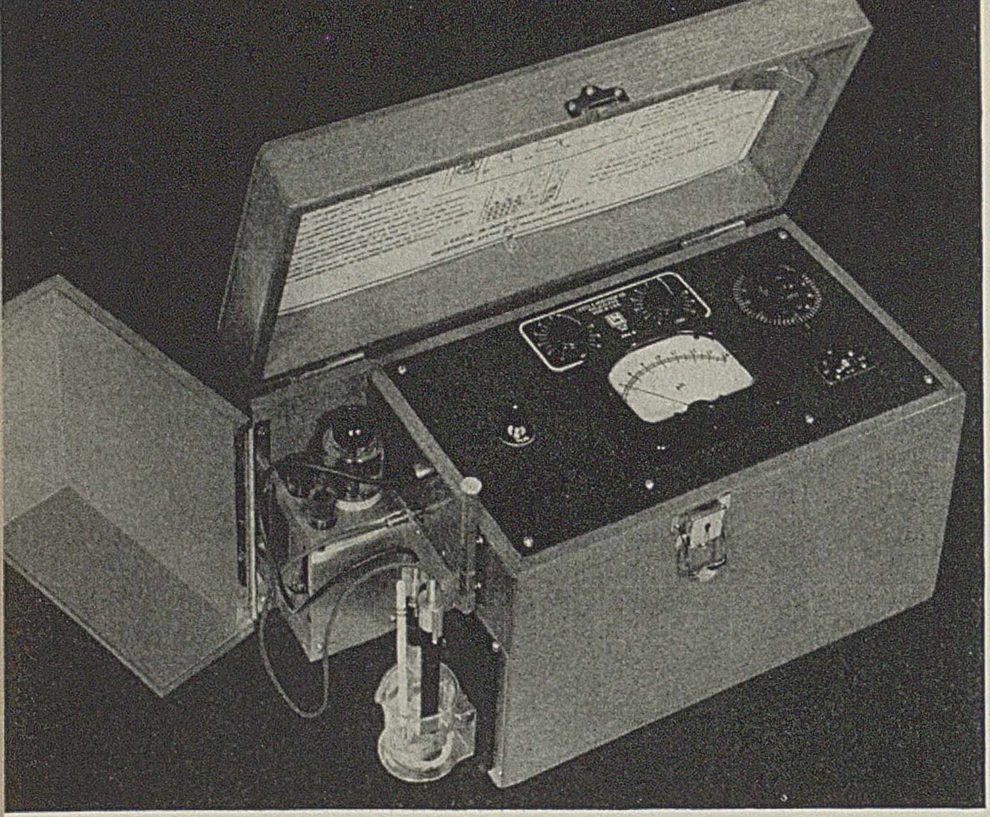

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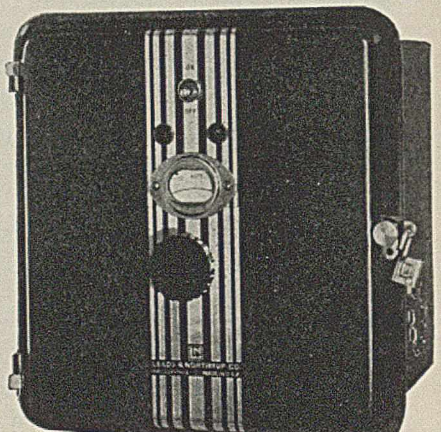

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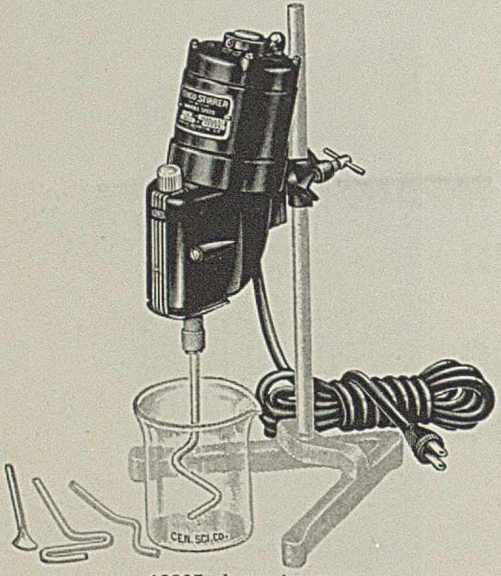

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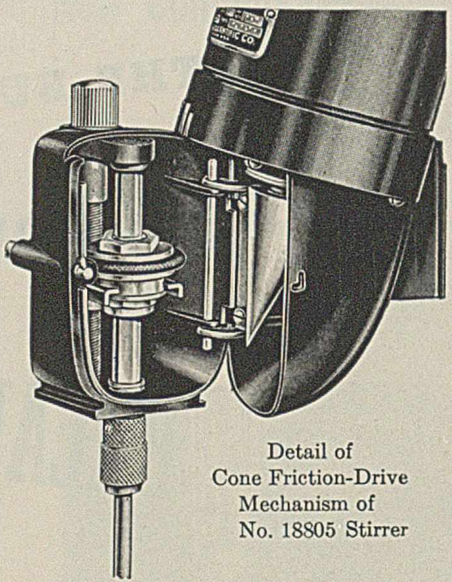

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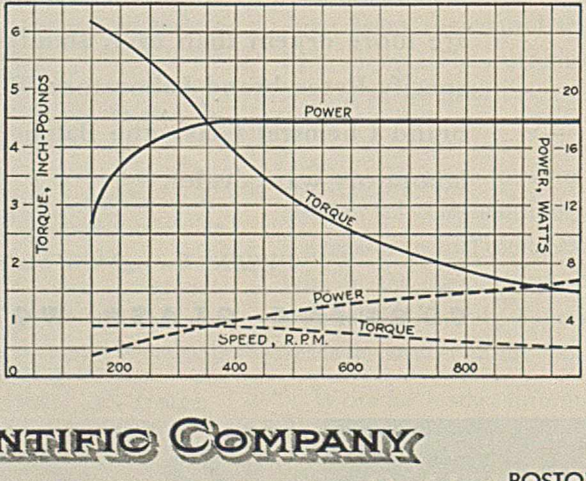

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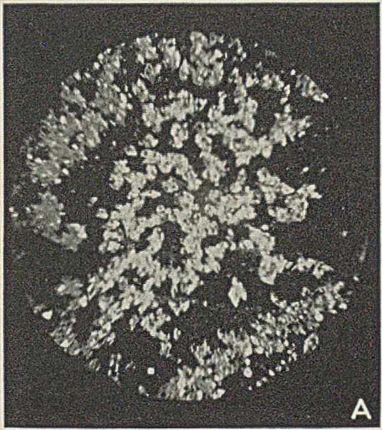
A

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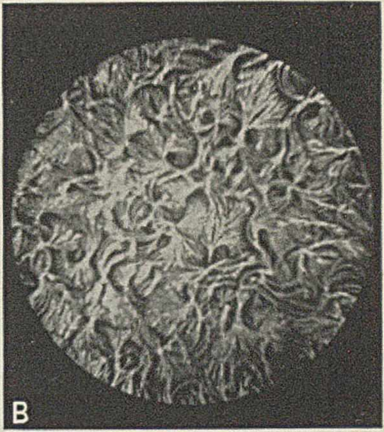
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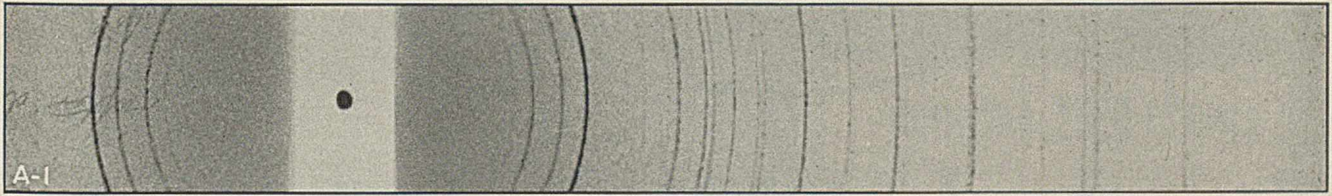
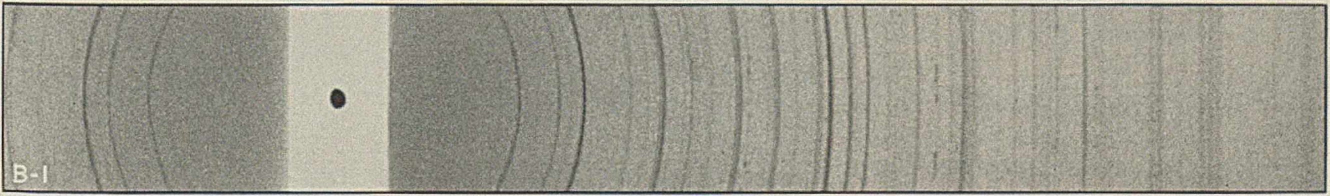

A-1


B-1

An x-ray diffraction pattern (A-1), registered by the dust sample, proved the presence of, and established the fact that it contained, sufficient silica compounds to be of toxic significance. ¶ From the x-ray diffraction pattern (B-1), registered by a specimen of the crystalline water-soluble extract of lung tissue, it was possible to identify the nature of the complex organic structure and establish the presence of silicates in the compound.

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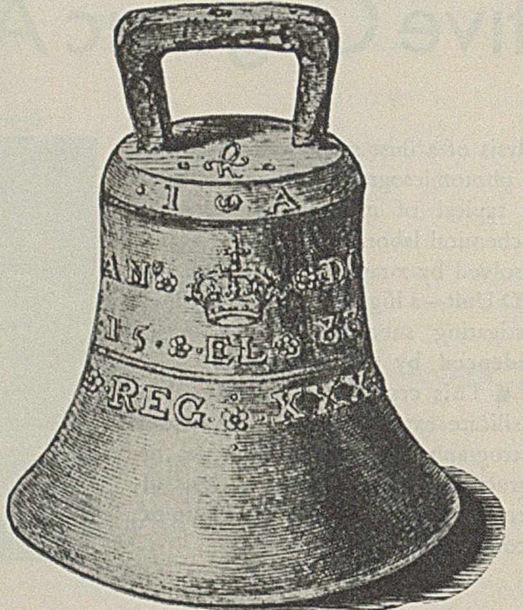
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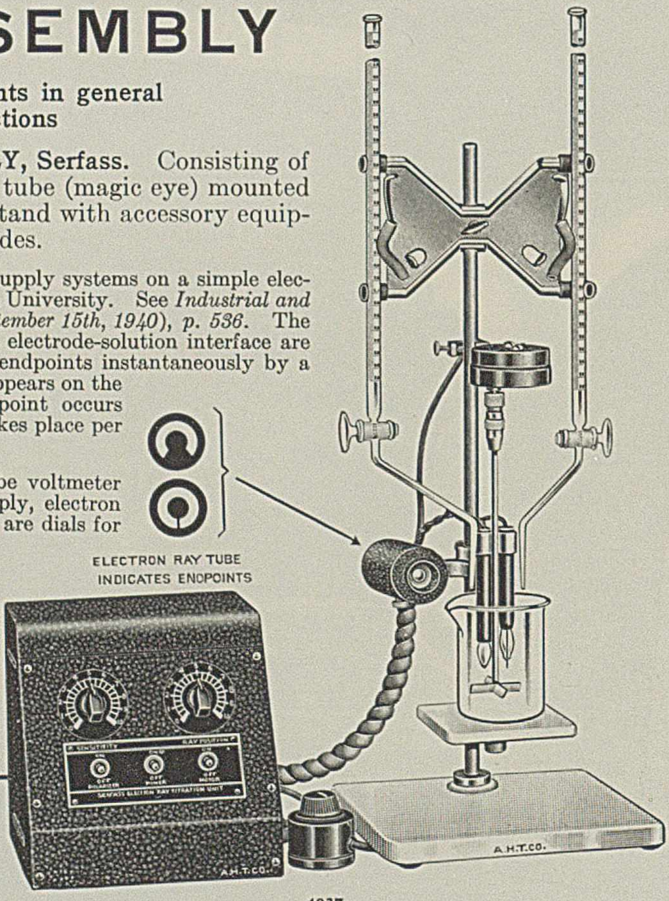

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INDUSTRIAL AND ENGINEERING CHEMISTRY

ANALYTICAL EDITION

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Symposium on Analytical Methods Used in the Petroleum Industry, pages 287 to 321.

Determination of the Heat of Combustion of Gasolines

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Esso Laboratories, Standard Oil Co. of Louisiana, Baton Rouge, La.

DETERMINATION of the heat of combustion of gasolines is becoming increasingly important and is included in certain aviation gasoline specifications. The application of this test to gasolines must be accompanied by a more closely controlled procedure than that ordinarily employed by petroleum testing laboratories for heavier fuels, in order to obviate losses of the more volatile components of the gasolines, such as butanes and pentanes, which have the highest heating values.

Considerable work has been published on the art of calorimetry since Andrews (*1*) first used the bomb calorimeter in 1848. A comprehensive bibliography on this subject is furnished by Kharasch (*14*). The apparatus, technique, and procedure of modern calorimetry have been described at considerable length by Dickinson (*4*), Jessup and Green (*10*), Richards and Gucker (*20*), Rossini (*23*), and White (*31*).

The work on the heat of combustion of hydrocarbons has been done mainly on pure compounds in order to study the relation between energy, structure, number of carbon atoms, and the influence of organic groups. For this purpose the apparatus and technique have been developed to such a high degree of precision and accuracy that, according to Rossini (*22*), measurements of quantities of energy can be made with uncertainties as low as 0.01 to 0.02 per cent. To attain this degree of accuracy considerable time, apparatus, and a precise technique are necessary. However, in the practical application of this test to gasolines, such precision is not warranted.

A procedure has been developed whereby six to eight determinations per day can be made on low-boiling (aviation) gasolines, with an accuracy of ±0.2 per cent.

Apparatus and Materials

A calorimeter of the adiabatic type was employed. This consisted of a double-valve oxygen bomb, a calorimeter bucket with stirrer, and a water-jacketed case equipped with a stirrer and connections to hot- and cold-water lines for maintaining adiabatic conditions.

A Beckmann thermometer calibrated by the National Bureau of Standards was used to measure the temperature rise. The jacket temperature was controlled with respect to the calorimeter bucket temperature by means of two 3-junction thermocouples and a galvanometer as shown in Figure 1. Slight differences in temperature between the bucket and the jacket are clearly shown by the galvanometer and thus a sensitive balance can be maintained.

The oxygen used should be at least 99.8 per cent pure and free from any combustible material. Commercial oxygen made by the liquid air process frequently contains as much as 0.3 per cent of hydrogen, possibly from contamination, and should be passed over copper oxide at 600° to 700° C. before being used for calorimetric work. Keffler (*11*, *12*) has shown that even electrolytic oxygen may contain considerable impurities. A number of cylinders of commercial oxygen made by the liquid air process were analyzed and found to contain from 0.01 to 0.3 per cent of hydrogen. Oxygen containing no carbonaceous material and an amount of hydrogen not exceeding 0.01 per cent was considered to be satisfactory without pretreatment.

Ordinary pharmaceutical capsules (No. 00) were employed. The ignition wire was pure iron and of No. 34 B. & S. gage. Combustion cups used were made both of platinum and illium. Benzoic acid used in calibrations was obtained from the National Bureau of Standards.

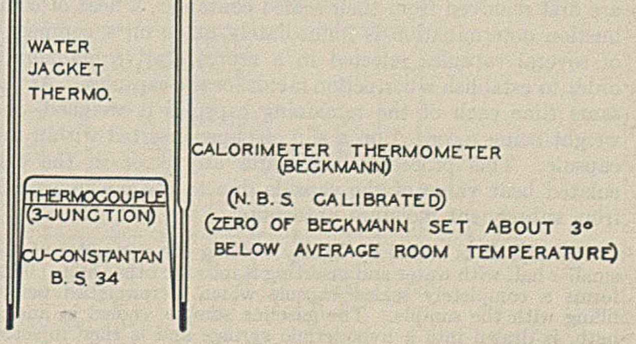

FIGURE 1. TEMPERATURE-CONTROL ARRANGEMENT

Procedure and Discussion

The procedure is standard in most respects, and is generally described in the literature. Calibrations were made using benzoic acid, the heating value of which was based on standards of e. m. f. and resistance maintained by the National Bureau of Standards. The heat units employed in the calculations were the same as those used by Rossini (*22*) which are:

1 calorie = 4.1833 international joules = 4.1850 absolute joules
1 absolute joule = 9.480 × 10^{-4} mean B. t. u.
1 calorie per gram = 1.7994 B. t. u. per pound

Sampling. A considerable saving in time is accomplished by basing calculations on a direct weighing of the sample rather than on a weight of sample burned as calculated from an analysis of the products of combustion. Jessup (*9*) has indicated that calculations on either basis are in close agreement when the sample is obviously completely burned.

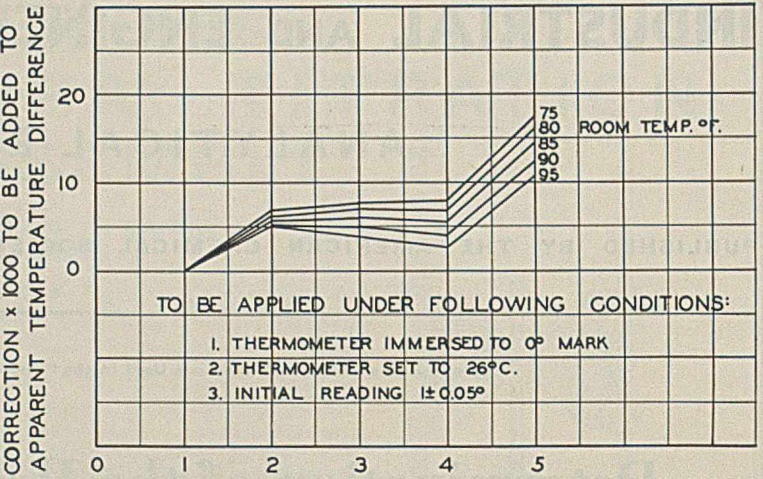

Figure 3. Example Correction Chart for Beckmann Thermometer

Thin-walled glass bulbs, flattened on two sides to withstand pressure changes, have been used by Richards and Barry (*19*), Jessup (*8*, *9*), and others. The advantages of the glass bulbs are that no corrections are necessary for the heat of combustion of the sample container, and that no absorption of moisture from the atmosphere is encountered. For complete combustion of liquid hydrocarbon samples enclosed in a container, such as a glass bulb or gelatin capsule, it is necessary that the container be completely filled with the liquid. This is done to prevent explosions within the oxygen bomb, upon ignition, with consequent scattering of the sample beyond the combustion zone, resulting in incomplete combustion. However, for gasoline samples containing considerable amounts of very volatile hydrocarbons, the use of glass bulbs is not recommended by the authors since, to fill these bulbs completely, it is necessary to heat and cool alternately.

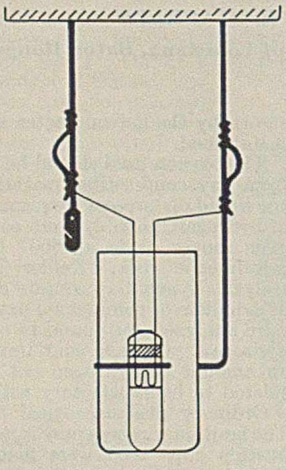

Figure 2. Ignition System

Accurate weights of representative samples of gasolines have been obtained by using gelatin capsules and employing a special technique for filling and sealing. When the capsules are first removed from their sealed container, a heat of combustion determination is immediately made on a composite of several capsules selected in a representative manner in order to establish a correction factor for the capsules. At the same time each of the remaining capsules is weighed, the weight being recorded on a slip of paper inserted within the capsule. This procedure eliminates any error in the calculated heat value of the capsule due to change in weight from subsequent moisture absorption.

The capsule is sealed by lightly wetting the perimeter of the smaller half with water and inserting it into the other half. This forms a completely sealed capsule which is reweighed before filling with the sample. The gasoline sample, cooled in an ice bath, is drawn into a hypodermic syringe and is then injected into the sealed capsule. The air is allowed to escape from the capsule through a small pinhole near the hole made by the hypodermic needle. When the capsule is completely filled the two holes are preferably sealed with a small drop of collodion or, when sealing samples of high volatility, by applying a small gelatin patch which has been previously weighed with the capsule and is wetted with water for sealing. The weight of this water (2 to 3 mg.) is estimated from a number of comparative weighings. If collodion is used, and is properly applied, its weight is negligible.

Where atmospheric conditions of high temperature and humidity are encountered, it is recommended that all sample handling be carried out in a room held at a constant low temperature and low humidity, so that when cold hydrocarbon samples are injected into the capsules no moisture condensation onto the capsules is encountered.

Sample Ignition. The capsule, completely filled with the sample, is suspended by means of the iron ignition wire near the bottom of an illium, stainless steel, or preferably a platinum cup, which is approximately 3.75 cm. (1.5 inches) deep, as shown in Figure 2. Although good combustion can be obtained in a shallow cup, the deep cup gives complete combustion more consistently for samples sealed in gelatin capsules. Various methods have been described by Richards and collaborators (*19*, *21*) to ensure complete combustion of a hydrocarbon sample. However, it has been shown by some investigators (*8*) that complete combustion can be obtained without using any foreign materials as combustion aids. In the work on gasolines it has been found that unburned hydrocarbons and carbon monoxide exist in negligible quantities whenever the sample burns with no visual carbon formation.

Jessup (*8*) has recommended using 30 atmospheres of oxygen pressure for complete combustion of hydrocarbons, while Richards and Jesse (*21*) claimed that with 35 atmospheres an explosion took place and with 20 atmospheres no carbonization occurred. In the experimental work on gasolines various oxygen pressures ranging from 15 to 40 atmospheres were used. It was found that the use of a pressure of 30 atmospheres resulted in the most consistent complete combustions.

Measurements. To attain the desired accuracy for gasoline work it is necessary to establish the following tolerances on the measurements involved:

Weights of sample and capsule	±0.1 mg.
Weight of calorimeter water	±0.1 gram
Thermometer (bucket) reading	±0.001° C.

Further, it is recommended that a sensitive galvanometer be used on the thermocouple circuit shown in Figure 1, so that the analyst can control the jacket temperature to within 0.1° C. of the bucket temperature during the temperature rise following ignition of the sample. When obtaining the water equivalent of the calorimeter, by burning standardized benzoic acid, the amount of sample should be such that the temperature rise obtained will closely approximate the temperature rise that results subsequently when analyzing the gasoline samples.

Banse and Parks (*2*) report satisfactory results with the use of a Beckmann thermometer, while other investigators (*8*) employ platinum resistance thermometers for more accurate measurements. In the case of a calibrated Beckmann thermometer much time can be saved by the use of a chart giving the total correction to be added to the nominal temperature difference observed. This total correction, as illustrated in Figure 3, includes the scale, emergent stem, and setting factor corrections as calculated on the basis of a Bureau of Standards certificate received with the thermometer. In the construction of the chart the total corrections to be applied to the apparent difference between the starting and final temperatures are calculated for final readings of 2°, 3°, 4°, and 5° at each of several room temperatures covering the range encountered. The points are joined with straight lines, since an appreciable part of the total correction will be due to errors in the scale graduations which are difficult to estimate at points not calibrated.

Calculations. Corrections to the total observed heat of combustion values are made for the fuse wire consumed and for acids formed by the oxidation of nitrogen and sulfur. The latter corrections are relatively small for gasoline work, amounting to only 3 to 5 B. t. u. per pound for samples meeting customary specifications for sulfur. The methods to be applied in precision calorimetry for correcting the data to standard states are described in publications of the National Bureau of Standards, particularly by Washburn (*29*).

The net, or lower, heat of combustion values are the ones usually written into gasoline specifications. These are obtained by correcting the gross values, as determined, for the heat of vaporization of water formed. This is most satisfactorily accomplished by actually determining the weight per cent of hydrogen in the gasoline by means of a combustion analysis.

Table I. Reproducibility of Results

No.	Values %	Maximum Deviation from Average %	Average Value *B. t. u./lb. gross*
25	100	0.26	20,664
24	96	0.25	20,666
23	92	0.22	20,669
22	88	0.19	20,670
21	84	0.17	20,673
16	64	0.10	20,671

Table II. Characteristics of Control Sample

	n-Heptane	Literature Values
Boiling point, ° C.	98.4	98.4
Freezing point, ° C.	−90.68	−90.6
Refractive index, n_D^{20}	1.38769	1.38777
Specific gravity, d_4^{20}	0.6836	0.6837

Results. Reproducibility of results is exemplified by 25 determinations made on a sample of *n*-heptane, as shown in Table I.

The *n*-heptane used had the characteristics shown in Table II.

The values obtained by this method may be compared with those of the National Bureau of Standards, which reported values of 20,731 B. t. u. per pound for a different sample of *n*-heptane from the same source and 20,714 B. t. u. per pound for pure *n*-heptane (*24*). These data indicate that the errors of the method used result in low values. The authors recommend, therefore, that the procedure be followed closely with the suggestions offered in order to keep the results within 0.2 to 0.3 per cent of the true values.

Estimation of Heats of Combustion

For laboratories that are not equipped to make this test, or for rapid estimations of heats of combustion, a correlation has been derived to yield reasonable values from other data which may be more readily obtainable. In Figure 4 a linear

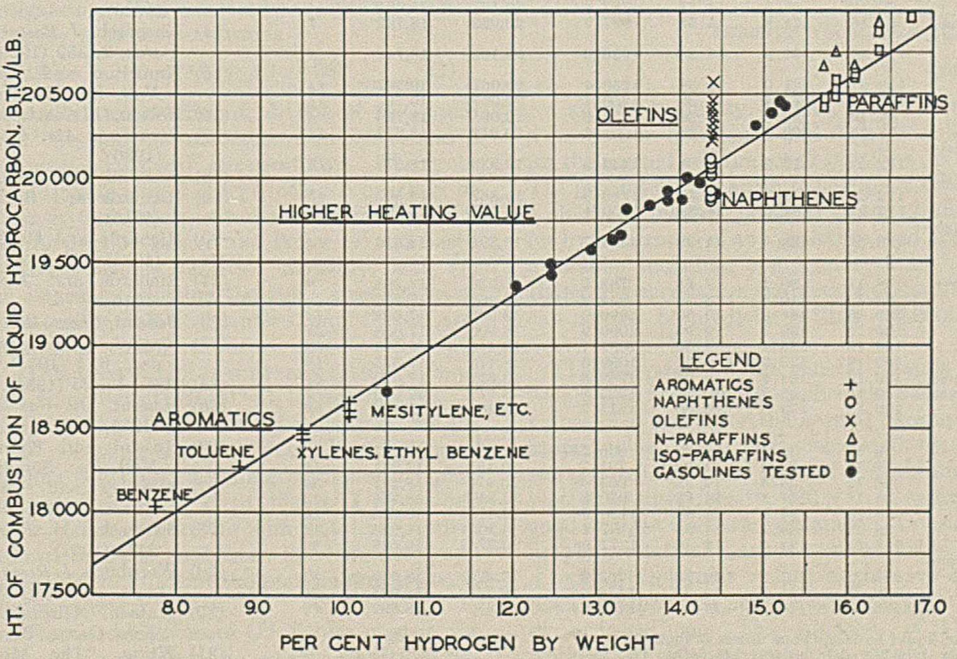

Figure 4. Correlation of Heats of Combustion with Per Cent Hydrogen

function is shown to relate the heats of combustion with hydrogen content. This correlation has been derived from the literature values for the heats of combustion of pure hydrocarbons boiling in the gasoline range, as given in Table III. The paraffin and aromatic hydrocarbons line up very well, but the naphthenes and olefins may diverge considerably. However, for gasolines of usual composition this curve may be applied. In Table IV there is tabulated a comparison of actual heats of combustion on gasolines with values estimated from the correlation in Figure 4.

The hydrogen content of gasolines is not generally determined by routine petroleum testing laboratories. Thus, in order to determine net heating values it is necessary to employ some means for obtaining reasonable approximations of the hydrogen content. Sweeney and Voorhies (*27*) present a correlation of hydrogen content with the average boiling point and gravity. The characterization factor, as given by Watson, Nelson, and Murphy (*30*), may also be employed to derive an approximate hydrogen content from readily obtainable inspections.

Table IV. Comparison of Estimated and Determined Heats of Combustion of Gasolines

Gasoline Sample	Weight % of Hydrogen	Heat of Combustion Determined	Heat of Combustion Estimated	Divergence
1	15.3	20,430	20,350	− 80
2	15.2	20,460	20,340	−120
3	15.1	20,400	20,300	−100
4	14.9	20,304	20,240	− 64
5	14.3	19,988	20,020	+ 32
6	14.1	20,003	19,980	− 23
7	14.0	19,885	19,950	+ 65
8	14.0	19,866	19,950	+ 84
9	13.9	19,930	19,900	− 30
10	13.8	19,867	19,880	+ 13
11	13.6	19,840	19,830	− 10
12	13.4	19,814	19,750	− 64
13	13.3	19,655	19,720	+ 65
14	13.2	19,640	19,690	+ 50
15	12.9	19,581	19,600	+ 19
16	12.5	19,499	19,450	− 49
17	12.5	19,420	19,450	+ 30
18	12.0	19,355	19,310	− 45
19	10.5	18,732	18,810	+ 78
			Av.	− 8

Table III. Heats of Combustion of Pure Hydrocarbons Boiling in the Gasoline Range

(Selected values from literature)

Hydrocarbon	Molecular Weight	Boiling Point	Hydrogen	Heat of Combustion^a Gross		Net	Reference
		° C.	*Weight %*	*° K., cal./mole*	*B. t. u./lb.*	*B. t. u./lb.*	
Paraffins							
n-Pentane	72.15	36.0	16.77	845.27	21,100	19,515	*24*
Isopentane	72.15	28.0	16.77	843.36	21,051	19,466	*15*
Neopentane	72.15	9.5	16.77	840.61	20,983	19,398	*15*
n-Hexane	86.18	68.8	16.37	1002.4	20,948	19,400	*24*
2-Methylpentane	86.18	60.2	16.37	998.54	20,867	19,319	*16*
2,3-Dimethylbutane	86.18	58.1	16.37	993.9	20,770	19,222	*14*
n-Heptane	100.20	98.4	16.10	1149.7	20,664	19,142	This paper
2-Methylhexane	100.20	90.0	16.10	1148.9	20,650	19,128	*14*
2,3-Dimethylpentane	100.20	89.7	16.10	1148.0	20,633	19,111	5
2,2,3-Trimethylbutane	100.20	80.9	16.10	1147.9	20,631	19,109	*14*
n-Octane	114.22	125.6	15.88	1316.4	20,754	19,252	*24*
2-Methylheptane	114.22	117.2	15.88	1306.1	20,591	19,089	*14*
2,4-Dimethylhexane	114.22	109.9	15.88	1298.4	20,470	18,968	*16*
2,2,4-Trimethylpentane	114.22	99.2	15.88	1303.40	20,549	19,047	*17*
n-Nonane	128.25	150.7	15.72	1473.4	20,688	19,201	*24*
2-Methyloctane	128.25	142.8	15.72	1454.1	20,417	18,930	*16*
2,3-Dimethylheptane	128 25	140.6	15.72	1458.8	20,483^b	18,996	*14*
2,2,5-Trimethylhexane	128.25	124.1	15.72	1458.8	20,483^b	18,996	*14*
2,2,4,4 - Tetramethylpentane	128.25	122.3	15.72	1458.8	20,483^b	18,996	*14*
Naphthenes							
Cyclopentane	70.13	49.5	14.38	783.6	20,121	18,761	*14*
Methylcyclopentane	84.16	71.8	14.38	937.5	20,062	18,702	*7*
1,2 - Dimethylcyclopentane	98.18	91.9	14.38	1096.0	20,102	18,742	*3*
1 - Methyl - 2 - ethylcyclopentane	112.21	121.0	14.38	1250.4	20,067^b	19,707	*14*
Propylcyclopentane	112.21	131.4	14.38	1250.4	20,067^b	19,707	*14*
Cyclohexane	84.16	80.8	14.38	939.0	20,095	18,735	*25*
Methylcyclohexane	98.18	100.3	14.38	1091.4	20,018	18,658	*18*
1,1 - Dimethylcyclohexane	112.21	119.9	14.38	1242.5	19,939	18,579	*13*
1,3 - Dimethylcyclohexane	112.21	122.7	14.38	1238.0	19,867	18,507	*13*
Ethylcyclohexane	112.21	131.6	14.38	1250.4	20,067^b	18,707	*14*
1,1,3 - Trimethylcyclohexane	126.23	138.7	14.38	1394.7	19,896	18,536	*14*
Aromatics							
Benzene	78.11	80.1	7.75	782.0	18,030	17,298	*6*
Toluene	92.13	110.8	8.76	934.2	18,261	17,433	*14*
o-Xylene	106.16	144.0	9.50	1090.9	18,506	17,608	*28*
m-Xylene	106.16	139.3	9.50	1090.9	18,506	17,608	*28*
p-Xylene	106.16	138.4	9.50	1087.1	18,441	17,543	*28*
Ethylbenzene	106.16	136.2	9.50	1089.0	18,473	17,575	*13*
1,3,5-Trimethylbenzene	120.19	164.6	10.06	1242.8	18,622	17,670	*28*
1,2,4-Trimethylbenzene	120.19	169.2	10.06	1239.8	18,577	17,625	*7*
Propylbenzene	120.19	159.5	10.06	1245.7	18,666	17,714	*28*
Olefins							
Pentene-1	70.13	30.2	14.38	806.78^g	20,581^c	19,221	*26*
2-Methylbutene-2	70.13	38.4	14.38	795.7	20,431	19,071	*18*
Hexene-1	84.16	63.6	14.38	963.9^g	20,477^c	19,117	*26*
2-Methylpentene-2	84.16	67.3	14.38	950.8	20,346^b	18,986	*14*
Heptene-1	98.18	94.9	14.38	1120.9^g	20,410^c	19,050	*26*
5-Methylhexene-1	98.18	84.7	14.38	1107.1	20,305^b	18,945	*14*
Octene-1	112.21	122.5	14.38	1277.9^g	20,378^c	19,018	*26*
2,4,4 - Trimethylpentene-1	112.21	101.2	14.38	1263.4	20,275^b	18,915	*14*
Nonene-1	126.23	145.3	14.38	1434.9^g	20,345^c	18,985	*26*
3-Methyloctene-1	126.23	136.3	14.38	1419.7	20,252^b	18,892	*14*

^{a} Heating values of liquid hydrocarbons unless designated by ^{g}.
^{b} Calculated values; considered to be accurate within 1%.
^{c} Values shown are calculated for liquid hydrocarbons.

Acknowledgments

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Temperature Coefficient of Density and Refractive Index for Hydrocarbons in the Liquid State

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Using the equation

$$dt/4 = d20/4 + \alpha(t - 20) + \beta(t - 20)^2$$

a single curve of α *vs.* molecular weight and a single curve of β *vs.* molecular weight have been found applicable to all types of hydrocarbons with very few exceptions. From these curves the temperature coefficient of density of a liquid hydrocarbon at atmospheric pressure can be predicted from the molecular weight within ±0.00002 gram per cc. per ° C. The only definite exceptions to this relation are benzene, pentaethylbenzene, and hexapropylbenzene which show coefficients 0.00010 gram per cc. per ° C. higher than the predicted values. The curves are also applicable to hydrocarbon mixtures.

This relation is more general than any previously published for predicting the temperature coefficient of density. The corresponding relationship between compressibility and molecular weight is being investigated.

Since Ward and Kurtz have shown that for hydrocarbons

$$\Delta n = 0.60\ \Delta d$$

an accurate method of calculating density change also provides a satisfactory method for calculating change in refractive index.

THE change of volume and density of hydrocarbons with change of temperature has been the subject of a number of careful investigations. The commonly accepted equation for change of density with temperature is

$$dt/4 = d20/4 + \alpha(t - 20) + \beta(t - 20)^2 \qquad (1)$$

where α is the temperature coefficient, $\Delta d/\Delta t$, of the liquid density, d, at 20° C., and one atmosphere pressure, and β covers the variation of $\Delta d/\Delta t$ with temperature t. The problem has been to correlate α and β with other properties, so that change of density with temperature can be predicted.

Early work in the field by Bearce and Peffer (*2*) was based on a plot of α and β against density. Recently Beale (*1*) proposed a new attack by plotting the cubical coefficient of expansion against boiling point. Paraffins, naphthenes, and aromatics form lines of similar curvature based on the data used by Beale. This type of plot is convenient, since cubical coefficient at 20° C. × density at 20° C. equals $\Delta d/\Delta t$.

Ward and Kurtz (*22*) derived a plot of density coefficient *vs.* density at 20° C. using a plot of cubical coefficient of expansion *vs.* boiling point, and a boiling point–density plot. The plot of density *vs.* density coefficient (Figure 11, *22*) reveals separate and very different lines for different hydrocarbon types. It is known that the naphthene lines on this graph will require some revision, but that the paraffin and aromatic lines are essentially correct.

The National Standard Petroleum Oil Tables used in the petroleum industry for correcting the specific gravity of oils for temperature change are based on a single curve of α *vs.* density, and a single curve of β *vs.* density. Since each hydrocarbon type has a curve of its own, the accuracy of a single curve for hydrocarbon mixtures is seriously dependent on composition. Jessup (*10*) confirmed this when he found that two oils of the same specific gravity but from different sources differed more than 30 per cent in their thermal expansion. Figure 11 of Ward and Kurtz (*22*) shows the aromatics, especially those of low molecular weight, to be widely divergent from the curve corresponding to the National Standard Petroleum Oil Tables.

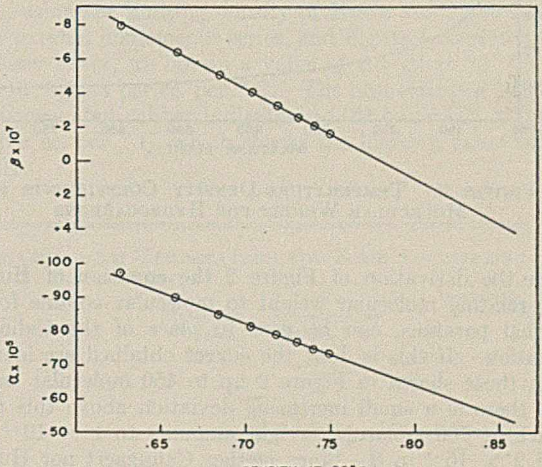


FIGURE 1. TEMPERATURE-DENSITY COEFFICIENTS *vs.* DENSITY FOR *n*-PARAFFINS

Calingaert, Beatty, Kuder, and Thomson (*3*) developed a correlation between α and β and number of carbon atoms for the normal and branched paraffins up to 20 carbon atoms. The present work is an amplification of their work and provides a single correlation between α and β and molecular weight for hydrocarbons of any structure, and applies to all data now available, including compounds of high molecular weight. Using this correlation the change of density with temperature can usually be predicted within ±0.00002 gram per cc. per ° C.

The derivation of the general relation between molecular weight and the α and β coefficients is simple. The smoothed values of α and β for the normal paraffins of 5 to 12 carbon atoms, which have been calculated by Calingaert and coworkers (*3*) from the data of Dornte and Smyth (*4*), were plotted against density, d20/4. As shown in Figure 1 very good straight lines were obtained. Consideration of physical property relations made it seem probable that a plot of α and β against molecular weight might give a single relation for both paraffins and naphthenes, and perhaps for other classes of hydrocarbons. The equation of Calingaert and coworkers (*3*) relating molecular weight to molecular volume and density was, therefore, used to convert the density coordinate in Figure 1 to molecular weight. In order to correct the resulting curve so that it would be representative of average paraffins rather than just normal paraffins, the data of Edgar and Calingaert (*5*) were used. These data indicate that the average $\Delta d/\Delta t$ for all nine isomeric heptanes is 1.5×10^{-5} unit higher than the value for the corresponding normal compound. The α coordinate of the graph of molecular weight *vs.* α was, therefore, shifted 1.5×10^{-5} unit. The graph thus obtained is shown as Figure 2 and numerical values for constructing such a graph are given in Table I.

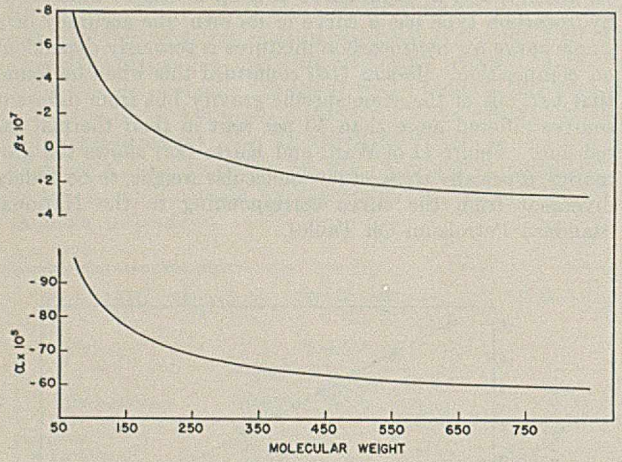


Figure 2. Temperature-Density Coefficients *vs.* Molecular Weight for Hydrocarbons

In the derivation of Figure 2 the equation of Huggins (*9*), relating molecular weight to molecular volume for the normal paraffins, can be used in place of the Calingaert equation. If this is done the curves obtained are identical with those shown in Figure 2 up to 450 molecular weight, but there is a small increasing deviation above this point, which at 700 molecular weight amounts to 1×10^{-5} in α and 2×10^{-8} in β. Since neither Calingaert nor Huggins claims accuracy for his density–molecular weight relations above 282 molecular weight (20 carbon atoms), and since the data for the higher molecular weight pure compounds are not sufficient to provide completely definite empirical evidence, we cannot yet be sure which relation is best. The authors have arbitrarily used the Calingaert relation in this work.

Having obtained a relation between the α and β coefficients and molecular weight for paraffins as shown in Figure 2 and Table I, it was necessary to determine the accuracy of this generalization for paraffins, and whether or not it could be used for other classes of hydrocarbons.

Examination of density data (*6*, *7*, *11*) at the two temperature extremes for all types of hydrocarbons on which densities are reported at two temperatures, at least 20° C. apart, provided the data which are presented in Table II. Inspection of Table II makes it clear that by using Equation 1 and Figure 2 the change of density with temperature can be calculated accurately for paraffins, naphthenes, aromatics, and a variety of unsaturated compounds. [Francis (*8A*) gives an equation for the density coefficient of paraffins which is essentially in agreement with this paper.] The average calculated density change for 98 compounds for an average temperature change of 74° C. is correct within ±0.0012 gram per cc., and the average calculated density coefficient agrees with the experimentally determined density coefficient within ±0.00002 gram per cc. per ° C. This is about ±3 per cent uncertainty on either the density change or the temperature coefficient. Furthermore, there is little systematic error since the deviation of the average (taking sign into consideration) is zero.

Table I. Data Necessary for Construction of Curves of α and β Coefficients Plotted against Molecular Weight

Molecular Weight	$\alpha \times 10^5$	$\beta \times 10^7$
72[a]	−97.4	−8.1
85	−91.5	−6.4
100	−86.7	−5.0
120	−82.0	−3.7
140	−78.5	−2.6
160	−75.8	−1.8
180	−73.7	−1.2
200	−71.9	−0.7
225	−70.3	−0.2
250	−69.0	+0.2
275	−67.9	+0.5
300	−66.8	+0.8
350	−65.2	+1.3
400	−63.8	+1.6
450	−62.8	+1.9
500	−62.0	+2.1
600	−60.8	+2.5
700	−60.1	+2.7
800	−59.5	+2.8

[a] Curve not recommended for less than 72 molecular weight.

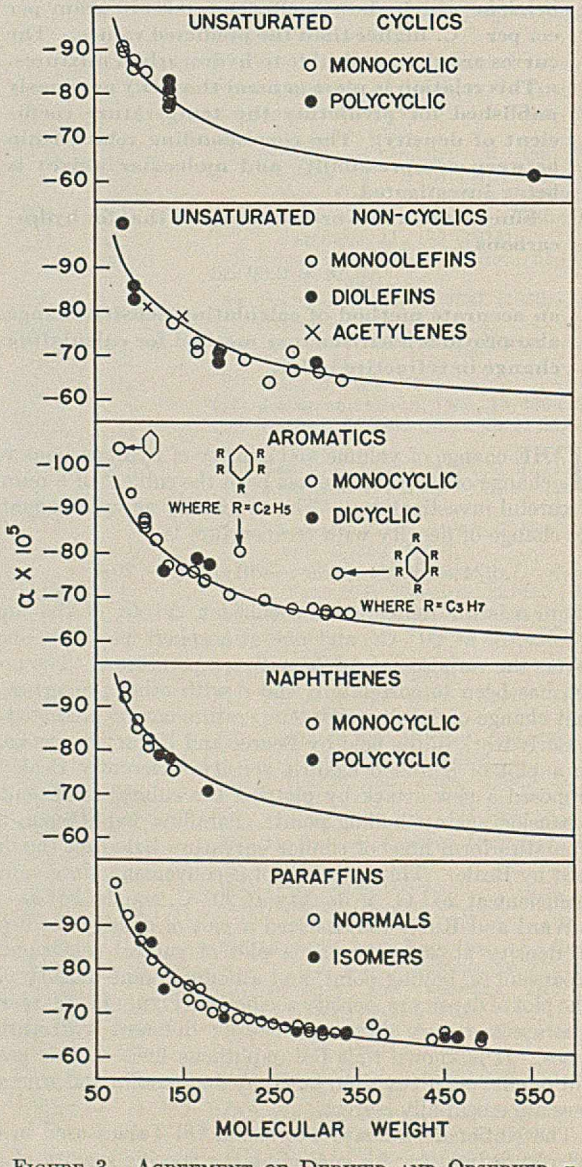


Figure 3. Agreement of Derived and Observed α for Hydrocarbons

TABLE II. COMPARISON OF CALCULATED AND EXPERIMENTAL CHANGE OF DENSITY

Hydrocarbon Type	No. of Compounds	Average Temperature Range, ° C.	Average Deviation Regardless of Sign		Deviation of Average Taking Sign into Account		Maximum Deviation of Any Single Compound	
			Δd^a	$\frac{\Delta d}{\Delta t} \times 10^5$	Δd^a	$\frac{\Delta d}{\Delta t} \times 10^5$	Δd^a	Corresponding Deviation of $\frac{\Delta d}{\Delta t} \times 10^5$
Paraffins	39	94	0.0015	2	+0.0004	0	+0.0065	+3
Naphthenes								
Mono	6	55	0.0010	2	−0.0008	−1	−0.0019	−3
Poly	3	59	0.0012	2	−0.0012	−2	−0.0021	−3
Aromatics								
Mono	18[b]	62	0.0005	1	+0.0002	0	+0.0011	+3
Di	3	67	0.0023	4	+0.0001	+1	−0.0033	−4
Olefins								
Mono	9	69	0.0012	2	−0.0008	−1	−0.0047	−5
Di	6	48	0.0017	4	−0.0001	−1	+0.0032	+7
Acetylenes	2	55	0.0013	3	−0.0001	0	−0.0014	−3
Unsaturated cyclics	12	62	0.0007	1	−0.0001	0	+0.0030	4
All hydrocarbons	98	74	0.0012	2	0	0	+0.0065	+3

[a] $\Delta d = (d_{t_1} - d_{t_2}$ observed$) - (d_{t_1} - d_{t_2}$ calculated$)$.

[b] Benzene, toluene, pentaethylbenzene, and hexapropylbenzene omitted from average.

Only a few compounds show poor agreement with the average data. Benzene, pentaethylbenzene, and hexapropylbenzene are badly out of line (+10 × 10^{-5} gram per cc. per ° C.). Toluene is slightly out of line (+ 4 × 10^{-5} gram per cc. per ° C.). Some of the large rings synthesized by Ruzicka are also out of line, while others check very well. Additional precise data on such compounds are needed. All the other data are in good agreement. The above-mentioned compounds were omitted from the average in Table II. All other reliable data, where the data cover an appreciable temperature range, have been included, and the worst deviations in each group have been indicated in the last two columns of Table II. The worst deviations in density change in the paraffin and naphthene groups correspond to ±0.00003 gram per cc. per ° C., or about ±5 per cent on the coefficient. The worst deviation in any group is about 10 per cent on the coefficient and probably represents poor data.

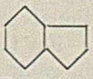
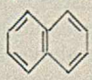
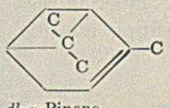
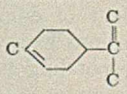
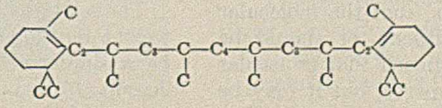
A further cross check on the accuracy of Equation 1 and Figure 2 was obtained by assuming that the β curve was correct, and taking all the difference between observed and calculated density change as error in the α coefficient. These observed α values (assuming β is correct) are plotted in Figure 3 for the same data as shown in Table II. Figure 3 makes it very clear that with the exception of the four aromatic compounds already mentioned, the agreement obtained is excellent and there are no systematic deviations.

One rather surprising thing about the data for paraffins which is shown by Figure 3 is that the normal paraffin data agree very exactly with the curve, although in its derivation a distinction between normal and average paraffins was made, and the curve was adjusted to agree with what the authors believe to be the best data for average paraffins. At any rate the final curve obtained (Figure 2) has excellent empirical justification, and is recommended for normal paraffins as well as for all other hydrocarbons.

The question may be raised, that compounds of unusual structure may not agree with this general system of correcting density. Table III was, therefore, prepared to show that for a specific group of varied compounds the agreement is good—that is, approximately ±0.001 gram per cc. or less for 50° C. change in temperature.

Also, using the limiting density of Kurtz and Lipkin (*15*) for the paraffin homologous series, and Figure 1 corrected for the isomer effect, we obtain a value of $\Delta d/\Delta t$ at 20° C. = 5.5 × 10^{-5} gram per cc. per ° C. The best estimate of data for hydrogenated rubber indicates $\Delta d/\Delta t$ to be 5.7 × 10^{-5} gram per cc. per ° C. which checks the limiting value satisfactorily.

TABLE III. DENSITY CHANGE WITH TEMPERATURE FOR SOME INTERESTING COMPOUNDS

	Molecular Weight	Temperature Range, ° C.	Deviation	
			Δd^a	$\frac{\Delta d}{\Delta t}$
$C—C_3—C$ *n*-Pentane	72	120	+0.0028	+0.00001
 Cyclooctane	112	58	−0.0005	−0.00001
 Hydrindane	124	58	−0.0009	−0.00002
 Naphthalene	128	97	−0.0033	−0.00003
 *dl*-α-Pinene	136	66	−0.0005	−0.00001
 *d*-Limonene	138	167	+0.0006	+0.00001
$C=C—C_{13}—C$ Hexadecene-1	224	65	−0.0003	−0.00001
$C—C_{18}—C$ *n*-Eicosane	281	98	0.0000	0.00000
 Octadecahydrocarotene	555	51	0.0001	0.00000

[a] $\Delta d = (d_{t_1} - d_{t_2}$ observed$) - (d_{t_1} - d_{t_2}$ calculated$)$.

TABLE IV. VALIDITY OF EQUATION 1 FOR CALCULATING DENSITIES AT TEMPERATURES RANGING FROM MELTING TO BOILING POINT

Temperature	*n*-Heptane Deviation		2,2-Dimethylpentane Deviation	
	Δd^a	$\frac{\Delta d}{\Delta t} \times 10^5$	Δd^a	$\frac{\Delta d}{\Delta t} \times 10^5$
° *C.*				
−120			+0.0072	+5
−110			+0.0060	+5
−90	+0.0004	0	+0.0039	+4
−70	−0.0001	0	+0.0024	+3
−50	−0.0003	0	+0.0013	+2
−30	−0.0006	−1	+0.0003	+1
−10	−0.0005	−2	−0.0001	0
+10	0	0	−0.0001	−1
+20	....	...	....	...
+30	−0.0001	−1	−0.0001	−1
+50	−0.0001	0	−0.0004	−1
+70	0	0	−0.0009	−2
+80			−0.0015	−2
+90	0	0		

[a] $\Delta d = (d20/4 - d_4^t \text{ observed}) - (d20/4 - d_4^t \text{ calculated})$ when *t* is 20° C. or higher.

$\Delta d = (d_4^t \text{ observed} - d20/4) - (d_4^t \text{ calculated} - d20/4)$ when *t* is less than 20° C.

One last point which deserves consideration is the ability of Equation 1 to fit the intermediate points in a density-temperature curve as well as the extreme points. In Table IV data are given for *n*-heptane and 2,2-dimethylpentane at temperatures ranging between the melting and boiling points, using the data for Dornte and Smyth (*4*) and Smyth and Stoops (*21*), respectively. The data for *n*-heptane between −90° and +90° C. agree within ±0.0005 gram per cc., but the observed deviations for 2,2-dimethylpentane are considerably larger than for *n*-heptane. Smyth and coworkers published data for eleven compounds between the melting point and boiling point, 2,2-dimethylpentane being the worst. The average deviation for all points of all 11 compounds is ±0.0009 gram per cc. These data and the data of Table II indicate that one should expect errors on the average of ±0.001 in density when correcting over a temperature range of 50° to 75° C.

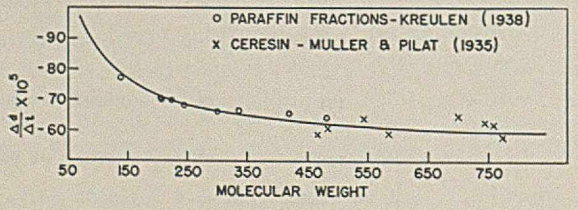


FIGURE 4. AGREEMENT OF DERIVED AND OBSERVED Δd/Δ*t* FOR PARAFFIN AND CERESIN FRACTIONS

The authors feel that the proposed method of correcting densities will be sufficiently accurate for practically all density corrections for pure compounds except in the case of the few aromatic compounds specifically mentioned, which are all highly symmetrical and mononuclear.

The question of hydrocarbon mixtures is under investigation. For the present it is recommended that Equation 1 and Figure 2 be used in the same manner as for pure hydrocarbons. However, the average molecular weight should be calculated on a mole per cent basis from the molecular weight and percentage of each constituent, or should be determined experimentally. It is recognized that molecular weight is not an easily determined property, but it may be estimated from correlations of molecular weight with other more easily determined physical properties such as density and viscosity (*19*). It is probable that the data of Jessup (*10*), which correlate thermal expansion factors with viscosity and specific gravity, are basically a correlation of coefficient of expansion with molecular weight.

Figures 4 and 5 show the agreement of thermal expansion data for hydrocarbon mixtures—(i. e., petroleum cuts). In Figure 4 are data on the paraffin fractions of Kreulen (*13*) and ceresin fractions of Muller and Pilat (*20*). The two investigators reported Δd/Δ*t* without giving any temperature range. Since Δd/Δ*t* can vary only a few per cent from α, depending on the temperature range and the sign and magnitude of β, the authors feel justified in plotting these Δd/Δ*t* values on the α *vs.* molecular weight curve. These data agree very well.

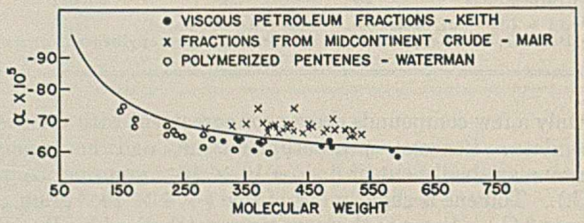


FIGURE 5. AGREEMENT OF DERIVED AND OBSERVED α FOR HYDROCARBON FRACTIONS

Figure 5 presents the data of three different laboratories on hydrocarbon fractions on which molecular weight and densities over a range of 40° C. or more are reported. Mair and Schicktanz (*17*) and Mair and Willingham (*18*) report data on mid-continent crude which has been separated into fractions in connection with their composition studies. Keith and Roess (*12*) report on viscous petroleum cuts which have also been separated according to boiling point and composition. Waterman, Leendertse, and Makkink (*23*) report on polymerized pentene fractions before and after hydrogenation. The data fall on both sides of the derived curve for α, assuming β is correct, and any one laboratory falls systematically on one side of the line or the other. Since the temperature coefficient of density is sensitive to small errors in either density or temperature, the deviations are probably caused by systematic experimental errors.

Additional precise data for temperature coefficients are needed. For the present, the authors feel that the curve of α *vs.* molecular weight is the best that can be drawn in view of the discrepancies between the data of various investigators. It is probable that it will be necessary to revise this curve slightly above 400 molecular weight when more precise data have become available.

Since it was shown by Ward and Kurtz (*22*) that a very simple relation

$$\Delta n = 0.60 \ \Delta d \qquad (2)$$

exists between the increment of refractive index and the increment of density, it is possible by using Figure 2 and Equations 1 and 2 to calculate the change in refractive index corresponding to a given change in density with sufficient accuracy for most purposes. More complete equations, such as the Sellmeier-Drude equation with the φ coefficient (*22*, Equation 4) or the Eykman equation (*8*, *14*, *16*), are recommended for more precise correlation of density change with refractive index change.

The relation between the α and β coefficients and molecular weight developed in this paper suggests that there should be a similar relation involving compressibility coefficients. Jessup (*10*) supports this with the evidence that oils of the same specific gravity and viscosity (which also means the same molecular weight) have the same compressibility. This will be investigated.

Acknowledgment

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Consistency Test for Lubricating Greases

Counterbalance Modification for Soft or Liquid Greases

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THE American Society for Testing Materials provides a method for determining the consistency of lubricating greases (*1*), by which consistency is expressed as a number indicative of the depth (mm./10) to which the standard double-pitched grease cone penetrates the sample in a free-falling period of 5 seconds, the total weight of the grease cone and the other moving parts attached to it being 150 grams. Numerous objections have been advanced to this method of test. Yet despite the fact that it is empirical and its results do not, and perhaps cannot, express fundamental properties of the grease in absolute units, the test has, nevertheless, been very useful as a manufacturing control and as a guide in purchase specifications.

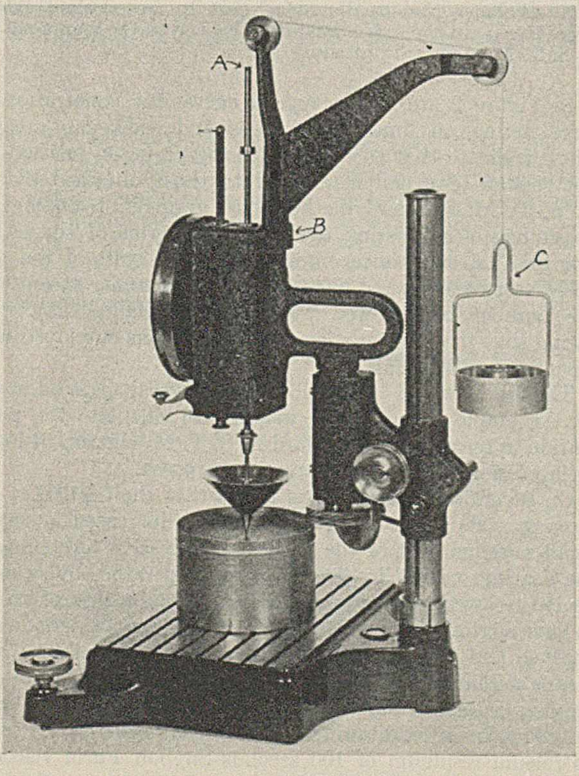

Figure 1. Penetrometer Assembled and Equipped with Counterbalancing Device

Greases generally are plastic substances; hence, their resistance to flow is of a twofold nature and, unlike viscosity, cannot be expressed by a single coefficient. When a stress, no matter how small, is applied to a viscous liquid, a permanent deformation results; with a plastic substance the stress must exceed a certain minimum. Other methods of test for more fundamentally expressing the plastic character of greases and similar substances are available. Among these should be mentioned the plastometer based on the work of Bingham and Green (*3*, *8*), the constant-sheer viscometer of Arveson (*2*), and more recently the consistometer of Blott and Samuel (*4*). The Stormer and MacMichael torsion type viscometers have also been proposed for this purpose.

The method of test which is the subject of this paper has been developed and used as an extension of the A. S. T. M. method to greases too soft for the standard A. S. T. M. procedure. The stated scope of the A. S. T. M. method—measuring the unworked or the worked consistency of lubricating greases which have a worked consistency less than 400—generally limits its use to greases no softer than No. 0 cup grease.

Greases much softer than this are regularly manufactured for lubricating washing machines, mine car journal bearings, rail curves, etc., and the consistencies or fluidities of such products have been customarily estimated in a number of ways, varying from appearance and feel through measurements by Saybolt, Stormer, and MacMichael viscometers, and by the use of special instruments such as the buret consistometer (*9*), the mobilometer (*6, 7*), and falling sphere-type instruments (*5, 10*).

It was considered desirable to work with the standard A. S. T. M. apparatus and method as far as possible. The proposed method of test involves the standard A. S. T. M. apparatus and procedure, with the addition of an easily removable attachment by means of which the force applied to the grease can be reduced to any desired quantity.

Table I. Results by A. S. T. M. and Proposed Methods Compared

	Consistency at 77° F.	
	A. S. T. M.	Proposed method
Force applied to sample, grams	150	25
Lime-soap cup grease		
Sample A	312	156
Sample B	235	95
Sample C	243	93
Sample D	196	72
Soda-soap sponge or fiber grease		
Sample A	383	225
Sample B	300	119
Sample C	208	67
Sample D	27	15
Fluid lime-soap grease	Too soft	366
Fluid soda-soap grease	Too soft	350
Cylinder stock	Too soft (viscosity Saybolt Universal at 210° F. 265 sec.)	355
Blown rapeseed oil	Too soft (viscosity Saybolt Universal at 210° F. 1638 sec.)	324
Crude residuum	Too soft (viscosity Saybolt Furol at 210° F. 100 sec.)	308

Figure 1 shows a penetrometer assembled and equipped with the counterbalancing device, which is fixed to the back of the penetrometer by means of two screws that enter the holes provided for securing the back plate of the original penetrometer. The modification is encompassed by *A*, a punctured screw to secure the thread; *B*, screws to secure the counterbalancing arm; and *C*, an aluminum cup to hold the counterbalancing weights. The two pulleys over which the thread passes are held between jeweled bearings. It can be installed or removed in a few minutes, although it does not interfere with regular A. S. T. M. penetrations when the thread is disconnected from the top of the shaft of the penetrometer.

In this manner the standard A. S. T. M. cone and attached moving parts are counterbalanced by means of a thread-arm-pulley-cup arrangement to reduce the force applied to the grease from the standard 150 grams to any desired lesser weight. It was found that 25 grams is a satisfactory minimum, less tending to give erratic results apparently due to unavoidable friction. Various types of fiber, horsehair, and catgut were tested in an effort to find a practical one with which friction will be low, and silk thread (Belding Heminway, pure silk A) was found most suitable.

To conduct a test, weights are put into the aluminum cup to counterbalance the usual moving part to any desired extent. From this point the test is conducted exactly in the manner of the A. S. T. M. standard procedure.

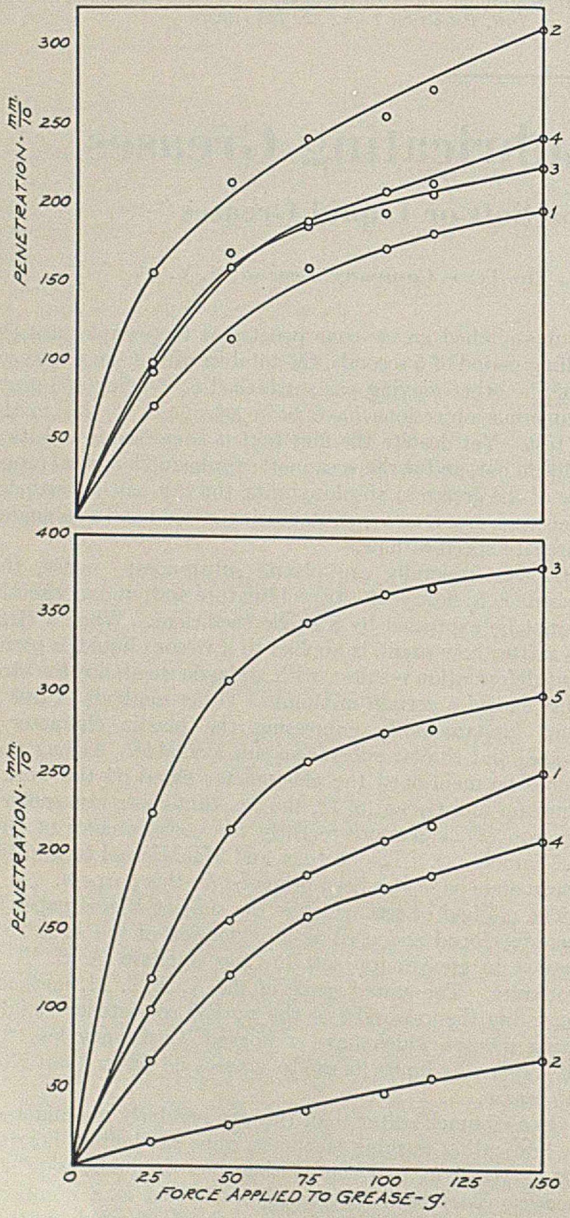

Figure 2. Effect of Weight on Extent of Penetration

Above. Lime-soap greases
Below. Soda-soap sponge or fiber greases

In Figure 2 are shown typical curves for penetration *vs.* force acting on lime-soap greases and soda-soap greases. These indicate that the results by the proposed method are not related in a simple manner to those obtained by the A. S. T. M. standard method (150 grams), precluding the possibility of expressing the former in terms of the latter. For this reason it is recommended that results of the proposed test be expressed in the customary manner except that the number be followed with (counterbalance, 25), indicating that the counterbalance procedure was employed with a net force of 25 grams.

Though it would be possible from several tests on a soft grease, employing different weights, to calculate the penetration in terms of the standard A. S. T. M. method, it is not believed necessary for the present purposes.

On several occasions it was found that the friction of the moving parts in the proposed apparatus increased, owing to small misalignment of the pulleys or excessive tightening of the bearings caused by jarring of the apparatus, and was reflected in lower penetrations. For this reason it is necessary to have a criterion by which the apparatus may be periodically checked and adjusted to give the highest penetration, which means minimum friction under the particular test condition. Having attained that adjustment, the apparatus is considered to be in condition to test a batch of samples. A crude petroleum residuum of 100 seconds Saybolt Furol viscosity at 210° F. (98.9° C.) has been found to be a particularly suitable reference material.

The precision of the proposed test meets the requirements of the standard A. S. T. M. method.

In Table I are given, for comparison, typical results obtained by the standard A. S. T. M. procedure and this proposed modification, both at the standard temperature of 77° F. (25° C.).

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Analytical Procedure for Mixtures of Organic Sulfur Compounds

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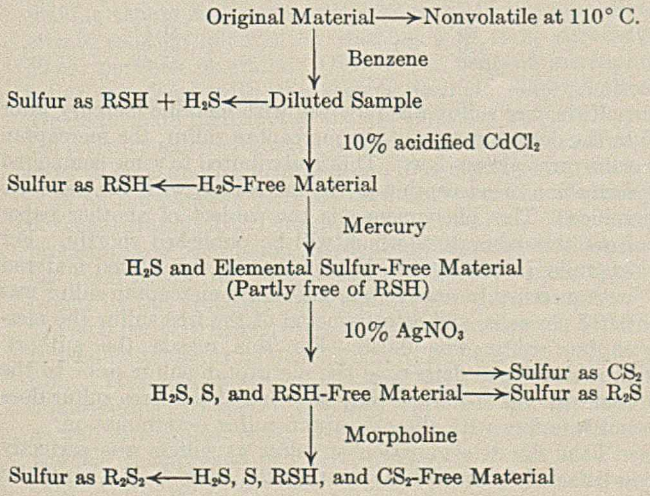
ANALYSES of mixtures of organic sulfur compounds were encountered requiring the development of reliable analytical methods which could be carried out in logical sequence. Preliminary qualitative analyses of these mixtures indicated hydrogen sulfide, mercaptans, free sulfur, carbon disulfide, and organic sulfides as the chief components. Tests on many mixtures showed no hydrocarbons present, and either no disulfides or only very small amounts.

While complete credit is not claimed for all the individual methods used, the procedure as a whole, including the use of benzene as the diluent, and the modifications of procedure and technique in the various methods employed are worthy of special note because of their value in making a rapid and accurate analysis of a mixture containing the above compounds.

Procedure

The undiluted liquid sample was tested qualitatively for the presence of hydrogen sulfide by shaking a small amount in a test tube with an excess of acidified cadmium chloride solution (*2*), a yellow precipitate indicating the presence of hydrogen sulfide. If a precipitate formed the material was filtered and the filtrate was shaken with a globule of clean mercury (*3*). Any darkening of the mercury indicated the presence of free sulfur.

Schematic Diagram of Procedure. Horizontal arrows indicate a determination. Vertical arrows indicate a separation or dilution.



Six to eight grams of the original liquid were accurately weighed from a ground-glass joint dropping bottle into a 500-cc. volumetric flask containing at least 300 cc. of c. p. benzene. The volumetric flask was stoppered immediately and tipped several times to ensure rapid solution. The dropping bottle was weighed again as rapidly as possible. Benzene was added to the flask up to the 500-cc. mark and the solution was thoroughly mixed.

If hydrogen sulfide was present, the diluted solution was transferred from the volumetric flask to a 1-liter separatory funnel and shaken for at least 5 minutes with 50 cc. of 10 per cent acidified cadmium chloride solution. The lower layer of cadmium chloride solution was discarded and the benzene solution was washed three successive times with 50 cc. of distilled water. The benzene solution was then filtered through a No. 42 Whatman filter paper into another separatory funnel, and 25-cc. portions of this hydrogen sulfide–free material were withdrawn by a pipet for the determination of sulfur as mercaptan according to Method I (*2*).

If no hydrogen sulfide was present the mercaptan sulfur was determined directly on the diluted sample. When hydrogen sulfide was desired quantitatively, the sum of sulfur as hydrogen sulfide and mercaptan was determined directly on the diluted sample using Method I; hydrogen sulfide was then removed with cadmium chloride solution as above and subsequently the sulfur as mercaptan was determined on the hydrogen sulfide–free material. The difference between these two determinations represented the per cent of sulfur as hydrogen sulfide.

If free sulfur was present, the remainder of the hydrogen sulfide–free material was shaken for at least 10 minutes with 50 cc. of clean mercury to precipitate free sulfur as mercuric sulfide. The mercury was drawn off with as much mercuric sulfide as possible.

If the mercaptan sulfur was over 1 per cent on the basis of the original material, the mercaptans were removed by shaking the unfiltered material in the separatory funnel with 25 cc. of 10 per cent silver nitrate solution. After washing with three successive 50-cc. portions of water, the material was filtered through a No. 42 Whatman filter paper into a glass-stoppered bottle. To a 150-cc. portion of this filtrate in a separatory funnel were added 50 cc. of a 1 to 1 solution of morpholine and absolute ethyl alcohol and the mixture was intimately mixed.

After centrifuging for 15 minutes, the supernatant liquid was decanted through a No. 41 Whatman filter paper into a 500-cc. separatory funnel where it was washed three successive times with 50-cc. portions of distilled water, or until the washings were no longer alkaline to litmus. The morpholine-alcohol-free solution was used for the determination of sulfur as disulfides by Method II (*3*) after its mercaptan sulfur content was determined by Method I.

Separate portions of the hydrogen sulfide–free and elementary sulfur–free material in the glass-stoppered bottle were taken for the determination of sulfur as carbon disulfide by Method III (*4*) and as sulfide by Method IV (*1*, *5*).

Method I

Determination of Per Cent of Sulfur as Mercaptans (also suitable for per cent of sulfur as hydrogen sulfide or combined per cent of sulfur as mercaptans and as hydrogen sulfide). Twenty-five cubic centimeters of sample were measured by a pipet into a 250-cc. glass-stoppered iodine flask containing 15 cc. of ferric alum indicator solution (6 grams of ferric ammonium sulfate dissolved in 100 cc. of a 1 to 1 nitric acid solution and diluted to 2 liters with alcohol) and an accurately measured excess quantity of 0.05 *N* silver nitrate solution. The mixture was shaken vigorously for at least 1 minute and the excess silver nitrate was titrated with 0.05 *N* ammonium thiocyanate to a salmon-pink end point. The per cent of sulfur as mercaptans was calculated on the basis of the original sample.

Method II

Determination of Per Cent Sulfur as Disulfides. Exactly 100 cc. of sample were mixed with 50 grams of glacial acetic acid and 25 grams of powdered zinc in a 250-cc. Erlenmeyer flask, which was immediately attached to a reflux condenser equipped at the top with a trap containing an accurately measured amount of 0.05 *N* silver nitrate solution, and diluted with a sufficient amount of distilled water (about 25 cc.) so that the tip of the outlet tube from the top of the condenser was just below the surface of the solution. The zinc–acetic acid mixture was refluxed slowly for 3 hours, after which it was cooled to room temperature before detaching the flask from the condenser. The mixture was decanted from the caked zinc into a 500-cc. separatory funnel and the flask and caked zinc were washed several times with distilled water, the washings (total of about 75 cc.) being added to the separatory funnel. The acetic acid–water solution was drawn off from the benzene solution and discarded.

The benzene was washed with successive portions of distilled water until the washings were no longer acid to litmus, after which it was filtered through No. 42 Whatman filter paper into a glass-stoppered bottle. Twenty-five cubic centimeters of the reduced and filtered benzene solution were taken for a mercaptan sulfur determination, following the procedure in Method I. The excess silver nitrate in the trap was titrated with 0.05 *N* ammonium thiocyanate solution as in Method I and the amount of silver nitrate which reacted with low-boiling mercaptans that escaped condensation was determined. The cubic centimeters of silver nitrate used by the trap were added to the cubic centimeters of silver nitrate used by the reduced benzene solution before calculating the amount of sulfur as disulfides in the original sample.

Method III

Determination of Per Cent Sulfur as Carbon Disulfide. Ten cubic centimeters of diluted sample were measured by pipet into a 250-cc. iodine flask containing 10 cc. of a fresh solution of potassium hydroxide in either absolute ethanol or methanol. The solution was gently swirled for at least 2 minutes and then neutralized with glacial acetic acid to the phenolphthalein end point. One cubic centimeter of fresh starch solution was added and the xanthic acid was titrated immediately with 0.1 *N* iodine solution. It was found that the xanthic acid solution could not be allowed to stand before titration with the iodine solution. During the titration with iodine the solution became milky white and the end point was observed when 1 drop of iodine solution turned the solution tan. As a further check on the end point, 100 cc. of water were added to the tan solution and the color was observed. Usually the purple color of starch in the presence of iodine became evident at once. If not, one more drop of iodine solution was always sufficient for a deep blue color. Duplicate titrations checked well within 0.05 cc. and were usually within 0.02 cc. or identical. The per cent of sulfur as carbon disulfide was calculated on the basis of the original sample.

Method IV

Determination of Sulfur as Sulfides. Fifty cubic centimeters of diluted sample were measured by a pipet into a 500-cc. separatory funnel containing 50 cc. of distilled water and an excess of bromine water; usually 10 cc. sufficed. The mixture was shaken violently for at least 10 minutes, after which 10 cc. of a 15 per cent potassium iodide solution were added and the mixture was shaken for 10 to 15 seconds; the liberated iodine was destroyed by adding a sufficient quantity of 0.1 *N* solution of sodium thiosulfate and again shaken for 10 to 15 seconds. The mixture was allowed to stand for 10 minutes to allow the two layers to separate and the lower water layer was drawn off into a 500-cc. Erlenmeyer flask. The tip of the separatory funnel was washed out carefully with water. The benzene solution was washed three successive times with 50-cc. portions of distilled water, the tip of the separatory funnel being washed out each time, and all washings were added to the solution in the Erlenmeyer flask. The water solution in the Erlenmeyer flask was titrated with 0.1 *N* potassium hydroxide solution, using methyl red indicator. The sulfur as sulfides was calculated to the basis of the original sample.

Method V

Per Cent of Nonvolatile Material at 110° C. Six to eight grams of the original liquid material were weighed from a dropping bottle into a porcelain crucible that had previously been dried at 110° C. and weighed. Evaporation was carried out slowly on top of a steam bath and when complete the crucible was placed in an oven at 110° C. for 30 minutes. The crucible was allowed to cool in a desiccator and then weighed. The difference in weight represented the nonvolatile material at 110° C and consisted almost entirely of elementary sulfur.

Discussion

The results of many analyses made by the above procedure and methods show that approximately 5 per cent of material is lost or otherwise unaccounted for at room temperature. Calculating the mercaptan and sulfide sulfur to the methyl derivatives and the sulfur as carbon disulfide to carbon disulfide, the total per cent varied from 95 to 100 per cent.

During the early part of this investigation it was found that secondary low-octane reference fuel was unsuitable for dilution purposes because the presence of a small amount of unsaturates appreciably interfered with the determination of sulfur as sulfides and as carbon disulfide.

When determining sulfur as carbon disulfide (Table I) it was found that the procedure of refluxing the alcoholic potassium hydroxide with the sample to form the xanthate was not only unnecessary but undesirable because it gave erroneous results, and that if free sulfur was not removed before forming the xanthate the results were far too high. In addition, if mercaptans are present in an amount more than 1 per cent of mercaptan sulfur, the xanthate procedure gives erroneous results.

Identical results were obtained with potassium hydroxide in either absolute ethanol or methanol, when freshly prepared. Samples of c. p. carbon disulfide weighed out, diluted, and determined according to the above procedure gave results of 84.21 per cent sulfur as carbon disulfide, the exact theoretical value for pure carbon disulfide. In this case, however, there were no filtrations necessary after removal of other constituents and hence no loss.

Table I. Effect of Time of Xanthate Formation on Carbon Disulfide Determination

Time of Contact *Seconds*	Sulfur as CS_2 %
30	78.07
60	81.13
120	81.64
240	81.64

If the free sulfur was removed with metallic mercury prior to the determination of the mercaptan sulfur, the mercaptan sulfur was always low. This is attributed to some compound formation or adsorption of the mercaptan with the mercuric sulfide. This phenomenon is the subject of another paper from this laboratory which will be published shortly. For example, in one sample, before treating the diluted material with mercury to remove free sulfur, the mercaptan sulfur was 0.077 per cent, and after removal of the free sulfur the mercaptan sulfur was 0.036. For this reason the authors' procedure is to determine the mercaptan sulfur prior to the removal of free sulfur; they have found that free sulfur does not interfere with the mercaptan sulfur determination.

That the determination of sulfur as sulfide was perfectly satisfactory was made evident by the analysis of a synthetic sample (Table II), the composition of which was unknown to the operator. It was found essential to shake the material with bromine water at least 10 minutes; otherwise the per cent sulfide sulfur would be low.

It has been found that if the disulfide sulfur of the original material is over 1 per cent, it interferes appreciably with the determination of the sulfide. In such cases, the H_2S—, S—, RSH—, and CS_2—free material is reduced with zinc and acetic acid as described above. The mercaptan formed is removed with silver nitrate before determining the sulfides on the residue.

TABLE II. ANALYSIS OF UNKNOWN SYNTHETIC SAMPLE

Sulfur as:	S Found	S Present	Compound	Found	Present
	%	%		%	%
RSH	0.00	0.00	CH_3SH	0.00	0.00
CS_2	70.18	72.42	CS_2	83.34	86.00
R_2S	6.70	6.71	$(CH_3)_2S$	12.98	13.00
Elementary	0.98	0.99	S	0.98	0.99
			Total	97.30	99.99

Since the quantity of hydrogen sulfide present is dependent on the efficiency of stabilization and is not of primary importance, it was not determined quantitatively in the majority of cases. The percentages of sulfur as carbon disulfide, sulfide, nonvolatile material at 110° C. (nearly all elementary sulfur), and mercaptan included 98 to 100 per cent of the total material present and were of primary importance. No difficulty was experienced with black silver sulfide in observing the end point of Method I for determining hydrogen sulfide. All that was necessary was to allow the benzene and aqueous layers to separate well before observing the color in the aqueous layer.

TABLE III. RESULTS OBTAINED ON VARIOUS SAMPLES

Sulfur as H_2S	Sulfur as RSH	Sulfur as CS_2	Sulfur as R_2S	Sulfur as R_2S_2	Nonvolatile at 110° C.	Total ($R=CH_3$)
%	%	%	%	%	%	%
..	0.16	79.40	1.52	..	..	97.47
..	0.02	79.33	0.06	..	..	94.33
..	0.00	80.54	0.12	..	..	95.76
..	0.08	66.23	10.10	0.09	..	98.46
..	..	80.24	...	..	..	95.29
..	..	80.59	...	..	..	95.70
..	0.15	79.88	0.20	..	..	95.48
..	0.05	80.30	0.14	..	..	95.73
..	0.00	72.42	6.70	..	..	96.32
..	0.18	79.02	0.70	..	..	95.47
..	0.26	79.13	0.72	..	..	95.76
..	0.41	76.98	1.03	..	0.33	94.36
..	0.35	77.78	1.80	..	0.30	96.68
..	0.04	74.12	0.42	..	5.27	94.16
..	0.23	79.42	0.82	..	0.89	97.14
0.04	0.02	78.51	1.02	..	0.04	95.37

If the mercaptan sulfur was over 1 per cent on the basis of the original material, the mercaptans were removed by shaking the diluted sample with 25 cc. of 10 per cent silver nitrate solution followed by washing with three successive 50-cc. portions of water. Over 1 per cent of mercaptan sulfur interfered with the carbon disulfide determination. The removal of mercaptans was accomplished before filtering the mercury sulfide from the removal of elementary sulfur in order to avoid another filtration, and thus a loss by evaporation.

In all the titration methods used there was the advantage of back-titration if the end point were overrun. The whole procedure has been found rapid, accurate, and practical, and has been in use for over a year. Table III gives typical results by this procedure on a number of routine samples.

The 5 per cent discrepancy in the total analysis is believed to be due to loss by evaporation through handling and filtration. This was shown by checking the composition of the liquid samples by specific gravities and fractional distillations as well as chemical tests. If as much as 5 per cent of other possible constituents had been present it would have been evident through these tests. Furthermore, when using synthetic samples of pure carbon disulfide and following this procedure, but without the filtrations and shaking required when other constituents are present, the values obtained were within 0.1 per cent of the theoretical for sulfur as carbon disulfide.

The method described is not limited to the low-boiling materials for which it was developed. When handling higher boiling materials no evaporation losses should be experienced during the several filtrations. Furthermore, if there is dilution with paraffinic material this method is still applicable. The two limitations involved are the complete absence of unsaturates, and dilution with a suitable solvent to a nonviscous state.

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Viscosity Measurement

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IN A PREVIOUS paper (*3*) simple and accurate viscometers were described for the measurement of the viscosities of liquids ranging from one third to more than one thousand times the viscosity of water. These instruments are now in extensive use throughout the world in the petroleum and chemical industries. It is the purpose of this paper to describe a further modification of the Ostwald viscometer which is particularly suited for measuring the viscosities of opaque liquids. It is also valuable in obtaining rate of shear–shearing stress data that are useful in studies relating to asphalts, wax crystallization, and oil-flow properties at low temperatures. In addition, the transition region between viscous flow and plastic flow may be investigated with the viscometer described here. Hence it should find application in studying plastic liquids in general.

A sketch of the viscometer, very similar to that previously described (*3*), is shown as Figure 1. Since it is designed for opaque liquids the efflux bulbs are on the bottom. When testing, the liquid flows from reservoir *A* into the pear-shaped 3-cc. efflux bulbs on the bottom; hence the meniscus is always in contact with clean unwetted glass and can be seen.

Operation of Viscometer

The viscometer is loaded by holding it in an inverted vertical position with the capillary side submerged in the test liquid. Suction is then applied to the other arm of the viscometer by a piece of rubber tubing to the mouth of the operator or to a water aspirator. The main reservoir, *A*, is filled and the liquid is brought into the capillary to the etched line just below *A*. The excess liquid is wiped off the end of the capillary arm and the instrument is inclined slightly to cause the oil to flow by gravity from the upper capillary into *A*; this small amount of liquid will be discharged into the main capillary leading to bulb *B*. A short piece of rubber tubing with a pinch clamp closing one end is then slipped over the open end of the upper capillary, which can then be turned to a vertical position and placed in the constant temperature bath. When the test temperature is reached the pinch clamp is removed and the liquid will flow by gravity into the three bulbs at the lower end of the instrument.

The first bulb which the liquid enters at the base of the capillary is for the purpose of allowing some liquid to discharge from the upper reservoir, *A*, and thus the diameter of the meniscus in this bulb is large throughout the test. This reduces both the effect of loading errors and surface tension corrections. As the liquid passes the etched line between bulbs *B* and *C* a stop watch is started and the time for the meniscus to reach the etched line between bulbs *C* and *D* is noted. At this point a second stop watch is started and the time for the meniscus to reach the etched line above bulb *D* is recorded. From each efflux time the viscosity is obtained by multiplying the respective viscometer constants by the respective efflux time. The viscosities so computed should agree. The constants for *C* and *D* are accurately established by calibration with liquids whose viscosities are accurately known. Equipment and procedure for calibration are explained in detail elsewhere (*1*, *4*, *5*).

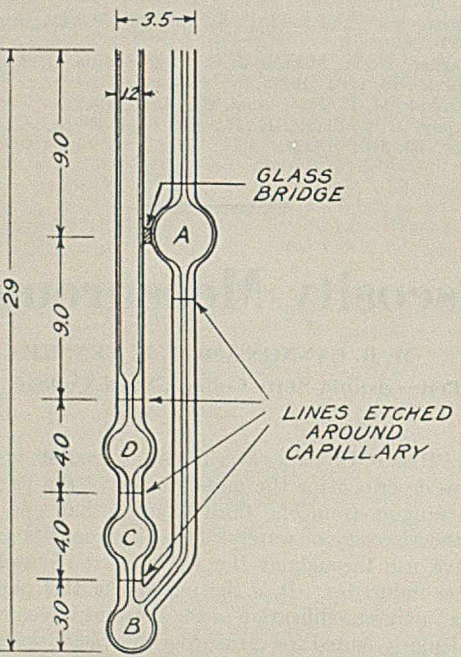

Figure 1. Viscometer for Opaque Liquids and Shearing Rate Studies

Dimensions in cm.

Shearing Rate Studies

As is well known, the viscosity of a true liquid or Newtonian fluid is independent of shearing rate. The presence or absence of plastic or semiplastic flow is conveniently obtained from shearing rate studies in which rate of shear in reciprocal seconds is plotted against shearing stress as dynes per square centimeter. In a Newtonian liquid such data yield a straight line passing through the origin using ordinary coordinates. The slope of such a line is inversely proportional to the viscosity of the fluid. In semiplastic flow a correlation of rate of shear–shearing stress data usually does not give a straight line. Such a line or curve may or may not go through the origin.

The definition of such shearing rate–shearing stress curves is conveniently obtained with this viscometer. Thus the character of the fluid under investigation is capable of better definition. Various externally applied pressures are easily applied, so that the fluid flows through the capillaries at different rates of shear. Depending upon the fluid and the viscometer dimensions, any suitable driving head may be applied to the viscometer arm by inert gas pressure, which is readily measurable on a manometer.

Such shearing rate studies are important in defining the flow characteristics of lubricating oils in the vicinity of their cloud and pour points. The A. S. T M. cloud and pour points of an oil afford only limited knowledge of the actual flow behavior of an oil at low temperatures. The use of pour-point depressors or wax-crystallization inhibitors has further complicated the significance and reliability of the routine pour-point tests of oils. A reasonable amount of work carried out at this college on the flow behavior of oils at low temperatures shows clearly the utility of a viscometer of this sort in studies relating to dewaxing, wax crystallization, pour-point depressors, low-temperature flow characteristics, and low-temperature storage of oil. Viscometers of the type described here have proved very useful in such investigations. They naturally yield much more significant and useful conclusions than are obtained simply from the cloud and pour-point data alone.

Magnitude and Source of Errors

This instrument is very similar to those previously described (*3*) and is superior to them only for measurements of the viscosity of opaque liquids and for measuring the effect of shearing stress on viscosity. The method of calculating the various corrections is identical to the methods given in the previous publication and need not be repeated here. The summation of the various errors is below 0.3 per cent.

The precision of measurements with this instrument when measuring viscosities of opaque liquids is ±0.2 per cent. The accuracy depends upon the accuracy to which the absolute viscosity of water is known at 20° C., since water at this temperature is used as the ultimate reference basis for calibration work. This error in the viscosity of water at 20° C. is probably in the neighborhood of 0.5 per cent. However, relative viscosities are very accurate and through the efforts of the American Society of Testing Materials the petroleum industry uses 1.007 centistokes as the kinematic viscosity of water at 20° C. This means that all relative viscosity measurements have the same reference basis.

The instruments described here can be constructed to cover any desired viscosity range by calculating the diameter of the capillary from Poiseuille's law. A charge of approximately 13 cc. is required. If desired, the dimensions of the instrument can be changed to require a charge of 5 cc., by reducing the size of the various bulbs and the capillary diameter. It is also possible to include a small bulb between the various measuring bulbs on the bottom, so that the operator does not have to stop one clock and start another at the same time.

Comparison with Other Viscometers

Anderson, Wright, and Griffin (*2*) have described an instrument designed for viscosity measurements on opaque liquids. Their instrument appears to be well designed and will undoubtedly yield accurate results. The instrument presented as Figure 1, however, is considerably simpler in design and therefore less expensive.

The Saybolt viscometer is used to determine viscosities of opaque liquids. However, the results are empirical and a large quantity of test liquid (90 cc.) is necessary. It does not lend itself to the application of external pressures for shearing rate studies without introducing serious errors.

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Quality Tests for Petroleum Solvent Naphthas

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PETROLEUM solvent naphthas were first supplied, as such, to replace turpentine in varnishes and paints. Called "mineral spirits", then as now, they were cut to conform with the evaporation rate and flash point of turpentine. As their use increased, they were followed by a faster evaporating fraction, called V. M. & P. naphtha, which provided a new tool for paint formulation. Later, shortly after the turn of the century, other light fractions were found useful in dry cleaning, rubber cements, and vegetable oil extraction, so that prior to the World War a half dozen more or less standardized naphthas were regularly available.

Not until comparatively recently, however, have petroleum solvent naphthas achieved a general acceptance by the protective coatings industry. This hesitance was due largely to a notorious lack of uniformity among naphthas, both in shipments of a single product and between items offered as strictly competitive. Efforts to correct this situation came from purchaser and supplier alike, and have resulted in a number of adequate quality tests.

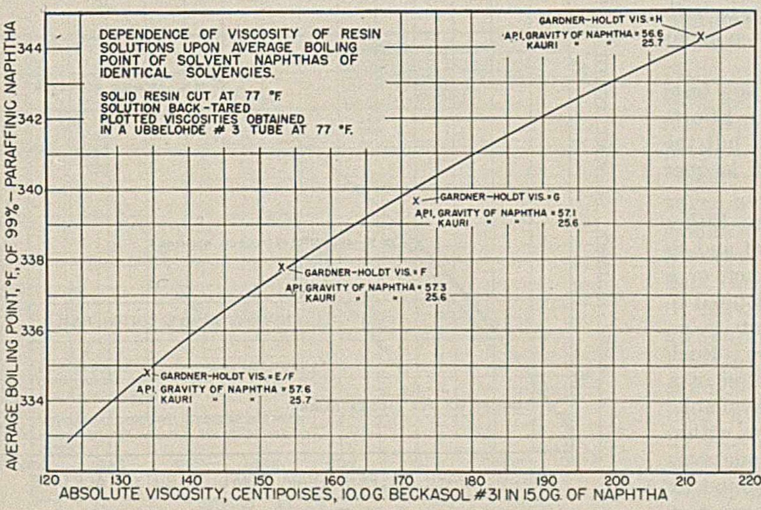


FIGURE 1

"Quality", in connection with petroleum products, usually connotes the degree of useful composition, or the ability to pass tests which guarantee performance—e. g., octane rating. Tests for purity, such as noncorrosiveness, are assumed as being met by such highly refined fractions as modern solvent naphthas, and thus the quality of a solvent naphtha is normally determined from inspections of its gravity, volatility, and solvency properties.

Use of the term "solvency" has recently been questioned (*23*). It has been pointed out that the behavior of otherwise similar naphthas may vary somewhat between different types of solutes, and that therefore such a term as "resin solvency" is more rigorously correct. Similarly, a naphtha's aromatic content, long accepted as a good measure of solvency, has now been interpreted in terms of resin solution viscosity, and a formidable equation derived for "aromatic coefficient" (*10*). Solvency, however, is commonly used to rate one quality of a naphtha, and is employed in this paper.

Volatility

The rate at which a naphtha leaves a film of a protective coating, or the pores of a solid, depends upon the evaporation rate of the naphtha and upon its rate of diffusion through the film or solid. "Solvent retention" varies widely, particularly among the several types of protective coating vehicles, and is best determined by drying-time measurements (*5*, *13*, *15*). Evaporation rate of the naphtha alone may be relatively determined by a number of existing methods (*4*, *6*, *12*, *13*, *14*, *16*, *17*, *24*, *26*, *29*, *35*, *36*, *38*, *40*, *43*, *44*), most of which are still confined to their parent laboratories. Some simple, inexpensive, precise, and accurate method for evaporation rate has long been sought by both manufacturers and consumers of naphthas, and would doubtless be adopted by a majority of their laboratories immediately after its final development. Meanwhile, volatility is controlled by the A. S. T. M. distillation, which not only involves temperatures at variance with those encountered in the actual use of solvent naphthas, but also fails to recognize the divergence in latent heats of vaporization between naphthas of similar boiling ranges and intermediate fill—e. g., between paraffinic and aromatic thinners.

Development of Solvency Tests

The first measure of solvency to be adopted by the petroleum industry was aniline

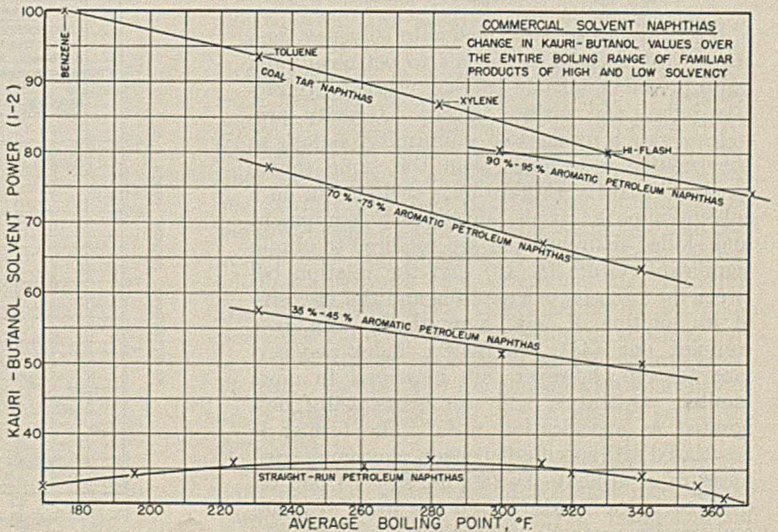


FIGURE 2

point (*41*). It remains as the only method which does not require any temperature control. Originally inapplicable to highly aromatic naphthas, because of the comparatively high freezing point of aniline, it has fortunately been supplemented by "mixed aniline point", wherein the aromatic naphtha is diluted with an equal volume of a paraffinic naphtha whose aniline point is 60° C. (*9*, *25*).

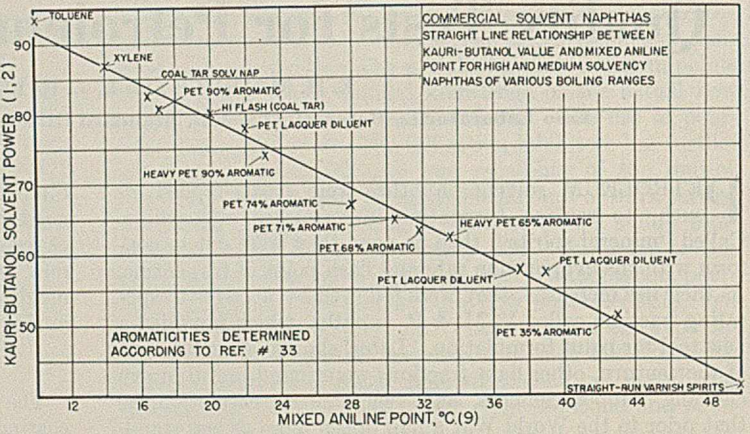


FIGURE 3

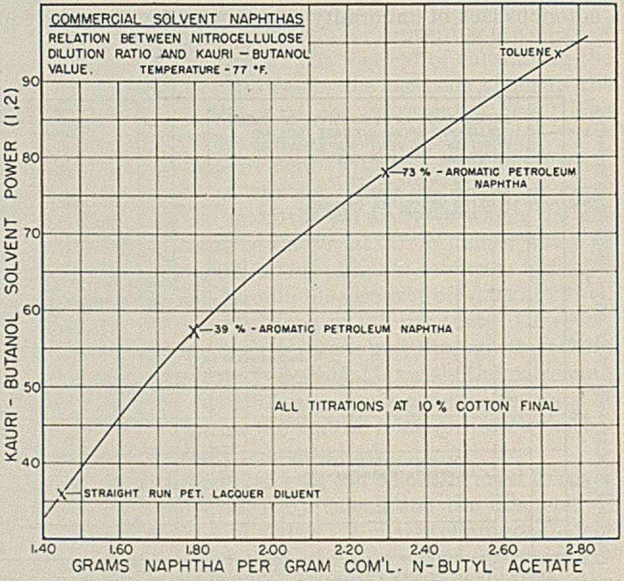


FIGURE 4

Earliest solvency test to be widely accepted by the paint and varnish industry was kauri-butanol value (*22*). It has proved so valuable that a number of refinements have been contributed by both the supplier (*1*, *2*, *3*) and consumer (*31*, *32*, *34*) industries, and standardized kauri solutions may be purchased ready for use. As might be expected, it has inevitably run afoul of an occasional supplier who felt it rated his product comparatively lower in solvency than did his favorite method, so that for a time—particularly among those who failed to appreciate its breadth of coverage or understand its correct interpretation—the fashion was to preface a discussion of solvency with a round condemnation of kauri-butanol value. The test survives, however, in both its original and modified forms, as by far the most popular quick appraisal of solvency.

Second in rank among the so-called "dilution ratio" tests is nitrocellulose dilution ratio, or "diluting power". Efforts have been made toward standardization (*7*, *11*, *18*), but the test is commonly restricted to the evaluation of lacquer diluents.

Other dilution ratio tests employ synthetic resins. Either the resin is dissolved in an oxygen-containing solvent and titrated to a cloud point with the hydrocarbon thinner, or a solution of the resin in a high-solvency naphtha is titrated to cloud with a reference naphtha of high aniline point—e. g., the 60° C. aniline point naphtha mentioned above. Such tests may be uniquely appropriate to the formulation of a given resin or naphtha, but the host of synthetics available, together with the constant improvements and changes within each type, render difficult any attempt to select one synthetic and hope for the adoption of a test built around it. General acceptance of any particular viscosity-solvency test is similarly hindered by the same circumstance.

Physical Property Tests

Physical properties which rate solvency, and which are deemed important to petroleum and paint products, include gravity, viscosity, refractive index, and surface tension. Gravity provides a rough measure of uniformity, as long as the product is derived from the same source stock. Viscosity (Figure 9) is seldom run on a solvent naphtha itself, since costly equipment and skilled manipulation are required to obtain significant results (*8*, *42*) and the relation between the viscosity of a naphtha and the viscosity of its solution of, say, a synthetic resin, is a complex one (*45*). Refractive index and surface tension, however, are measured in more familiar apparatus, and are occasionally designated as specification tests. The former is associated with specific dispersion, a recommended measure of aromaticity (*20*, *21*, *28*). Upon refractive index is also based the most accurate and precise method of proximate analysis yet developed (*27*, *30*, *33*).

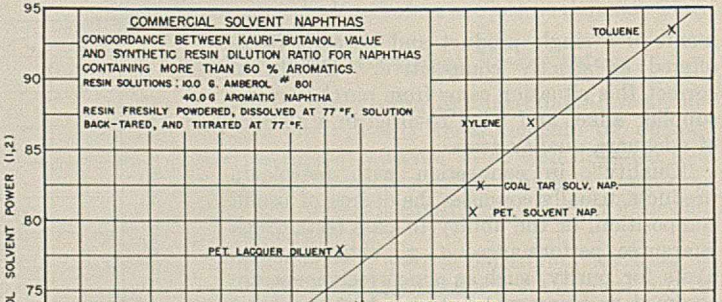
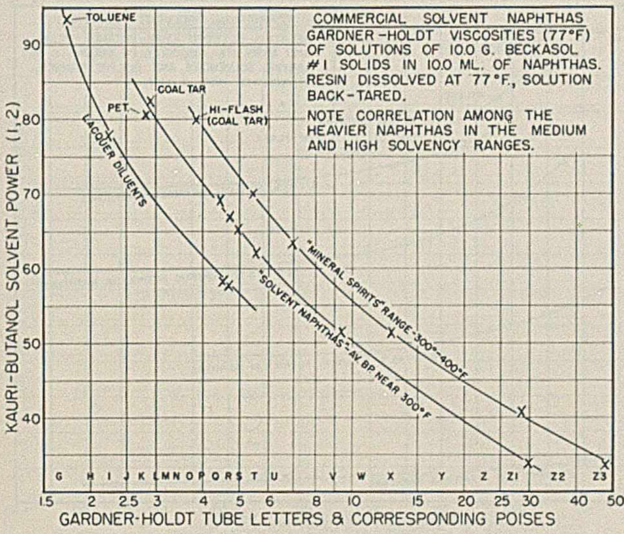


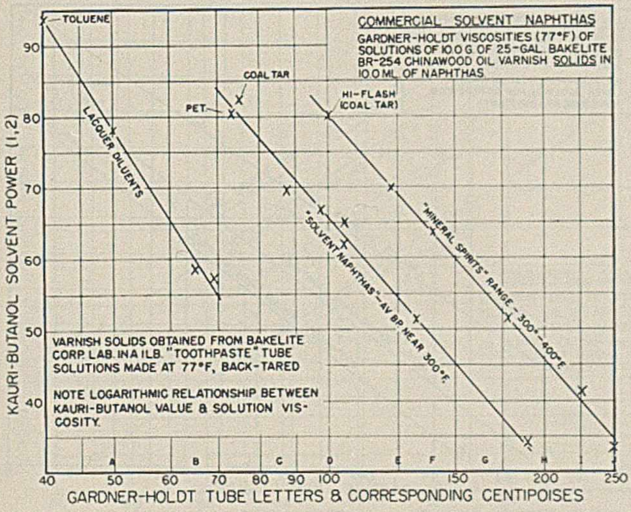
FIGURE 5


COMMERCIAL SOLVENT NAPHTHAS

GARDNER-HOLDT VISCOSITIES (77°F) OF SOLUTIONS OF 10.0 G. BECKASOL #1 SOLIDS IN 10.0 ML. OF NAPHTHAS. RESIN DISSOLVED AT 77°F., SOLUTION BACK-TARED.

NOTE CORRELATION AMONG THE HEAVIER NAPHTHAS IN THE MEDIUM AND HIGH SOLVENCY RANGES.

FIGURE 6

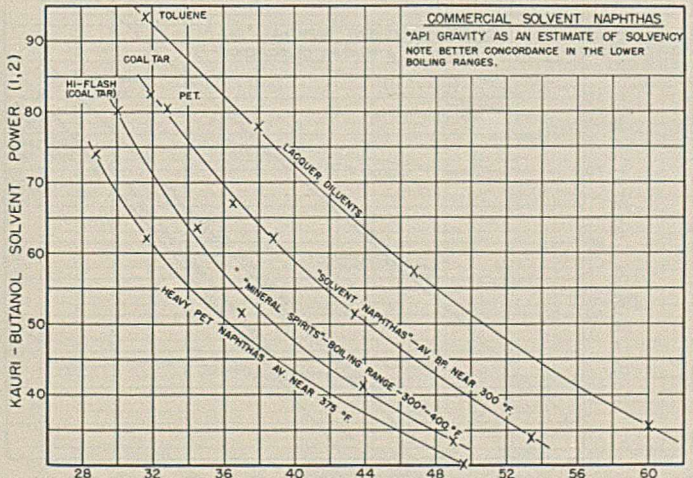

COMMERCIAL SOLVENT NAPHTHAS

GARDNER-HOLDT VISCOSITIES (77°F) OF SOLUTIONS OF 10.0 G OF 25-GAL. BAKELITE BR-254 CHINAWOOD OIL VARNISH SOLIDS IN 10.0 ML OF NAPHTHAS

VARNISH SOLIDS OBTAINED FROM BAKELITE CORP. LAB. IN A 1 LB. "TOOTHPASTE" TUBE SOLUTIONS MADE AT 77°F, BACK-TARED

NOTE LOGARITHMIC RELATIONSHIP BETWEEN KAURI-BUTANOL VALUE & SOLUTION VISCOSITY.

FIGURE 7


COMMERCIAL SOLVENT NAPHTHAS

°API GRAVITY AS AN ESTIMATE OF SOLVENCY NOTE BETTER CONCORDANCE IN THE LOWER BOILING RANGES.

FIGURE 8

Composition

Marketers of petroleum solvent naphthas customarily offer a line wherein each member is designed to perform satisfactorily wherever a need exists for a product of its volatility or solvency, or both. Thus, in order to meet the most difficult requirements which may be encountered, most present-day petroleum solvent naphthas are more highly refined than is ordinarily necessary, and consequently contain less than a total of 1 per cent of unsaturated hydrocarbons and objectionable sulfur compounds. Solvency, therefore, can be readily estimated in terms of a naphtha's content of paraffin, naphthene, and aromatic hydrocarbons. Since the solvency characteristics of each group have been recorded (*1*, *2*, *27*, *30*), proximate analysis not only provides a convenient control check, but also facilitates the correct replacement of a naphtha—or pair of naphthas—for the one or pair already in use.

Volatility *vs.* Solvency

In the foregoing list, no mention has been made of the critical importance of volatility to the correct interpretation of any solvency test. Unfortunately, all too many discussions of solvency neglect this vital point. Purchasers interested in making replacements, or testing new offerings, are ordinarily concerned with products of similar volatilities, and are likely to overlook slight differences in boiling range, average boiling point, evaporation rate, or average molecular weight. Many such apparently slight differences, however, can well make one naphtha and break a substitute, if disregarded in connection with otherwise impartial evaluations of solvency (Figure 1). Particularly mystifying are the discrepancies between solvency test results and actual performance among commercial "mineral spirits"—300°/400° fractions, with average boiling points lying between 330° and 355° F. In both their higher and lower solvency classifications no rhyme or reason seems to exist, unless the appraiser studies his distillation points and realizes that no two have identical average boiling points or average molecular weights. (Average boiling point is frequently taken, as herein, as the arithmetic average of the 10, 20, 30, 70, 80, and 90 per cent A. S. T. M. distillation points, and is obviously a measure of average molecular weight for any given hydrocarbon series. The 99 per cent–paraffinic naphthas shown in Figure 1 are, respectively, the 25%/45%, 25%/50%, 25%/55%, and 25%/60% heart cuts of a wide-cut alkylate containing 0.7 per cent olefins.)

It is contended, and herein not originally (*19*, *37*, *39*), that any two accurate and precise methods of measuring solvency, or performance, can be used interchangeably in so far as they apply to petroleum naphthas of the same volatility or average molecular weight. Figures 3 to 13, inclusive, correlate only a few among the large number of possible combinations, but should prove convincing to one familiar with the experimental limitations of the several test methods. Kauri-butanol value has been chosen for comparisons in an effort to find whether this most popular quality test will serve (1) as a substitute for other laboratory solvency tests, and (2) as a safe prediction of the performance of a solvent naphtha of any given volatility. Figures 2 and 14 show the change with volatility of kauri-butanol value and mixed aniline point, respectively.

Attention is called to the excellent concordance between kauri-butanol solvency and actual performance in terms of synthetic resin solution tolerance for low solvency thinners (Figure 5), and viscosity of a popular synthetic resin–tung oil spar varnish (Figure 7). The latter example illustrates the logarithmic relationship between solvency and solution viscosity for dispersions of the same character. Solutions of certain synthetics, however, do not follow this relationship throughout the entire solvency range of commercial solvent naphthas. Figure 6, dealing with a phenol-modified and oil-extended alkyd, indicates a change in the character of the dispersion with an increase in naphtha aromaticity. However, this not strictly logarithmic relationship with kauri-butanol solvency is nevertheless a smooth curve, and curvature is so gradual over any applicable solvency range that the function therein is essentially logarithmic. (Plotted viscosities range from 165 to 4600 centipoises.)

As a replacement for other laboratory solvency tests, kauri-butanol value is seen (Figures 3, 4, 8, 10–13) to provide a linear, or nearly linear, correlation of solvency for products of similar evaporation rates. Particularly replaceable, as straight-line functions, are such specification tests as mixed aniline point, specific dispersion, and per cent aromatics. Thus, bearing in mind that the laboratory requirements of kauri-butanol value comprise only 20 grams of a purchasable or easily made standard solution, one rough weighing, a simple titration, and no calculations—15 minutes of an inspector's time—whenever a need arises for a single solvency or performance test which covers the entire commercial naphtha solvency range and is applicable to products of any established volatility, kauri-butanol value seems to supply a ready answer.

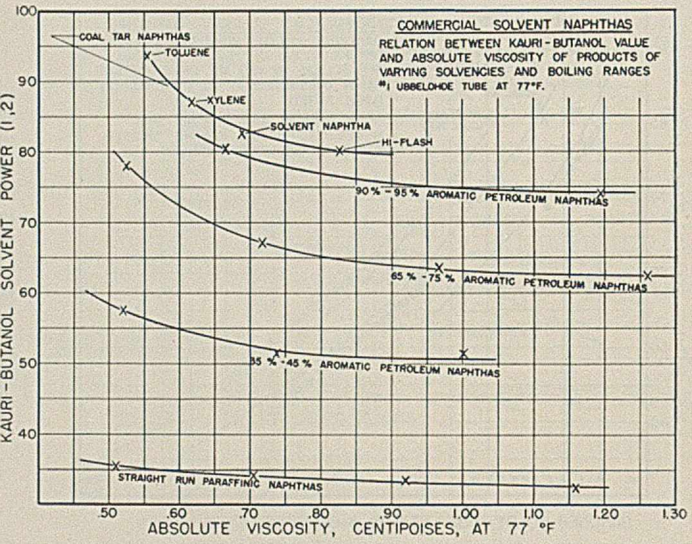


FIGURE 9

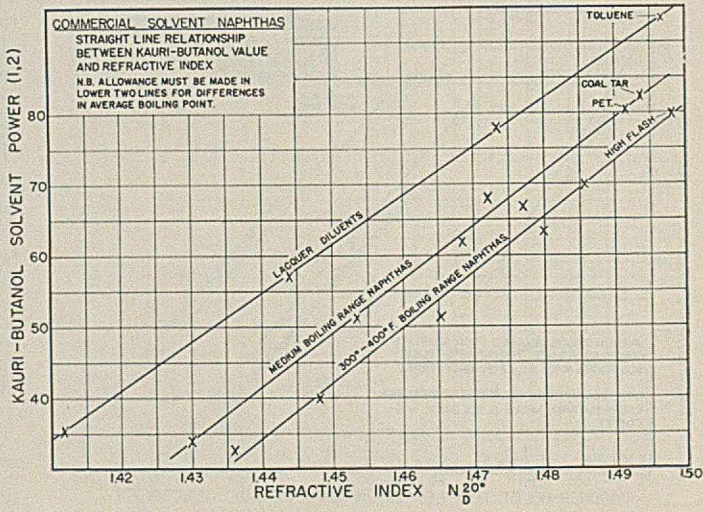


FIGURE 10

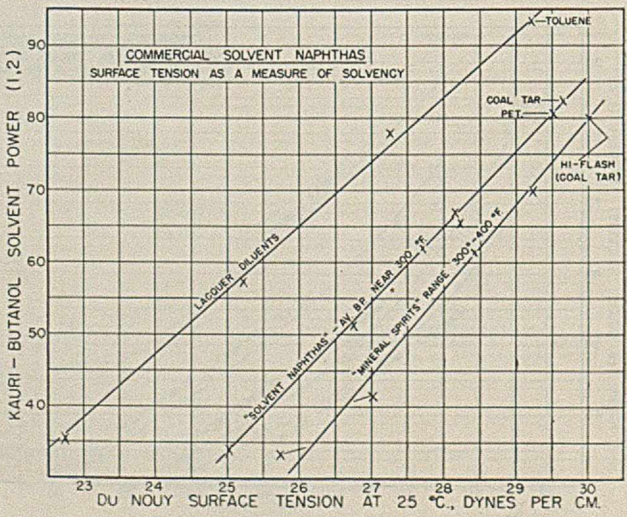


FIGURE 11

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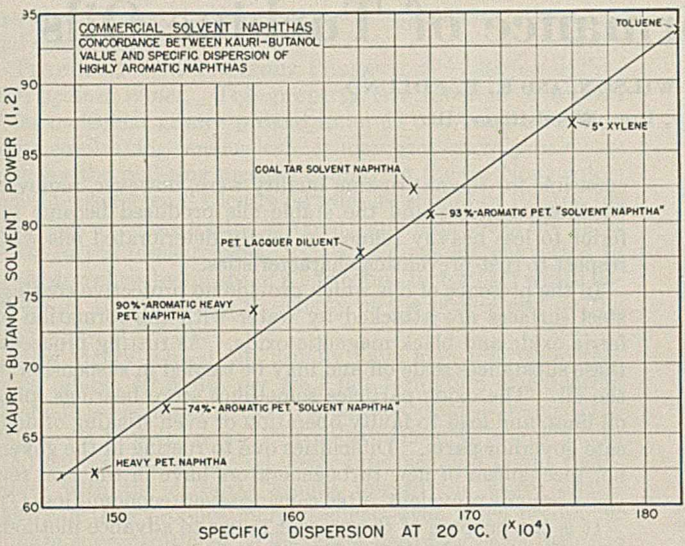


Figure 12

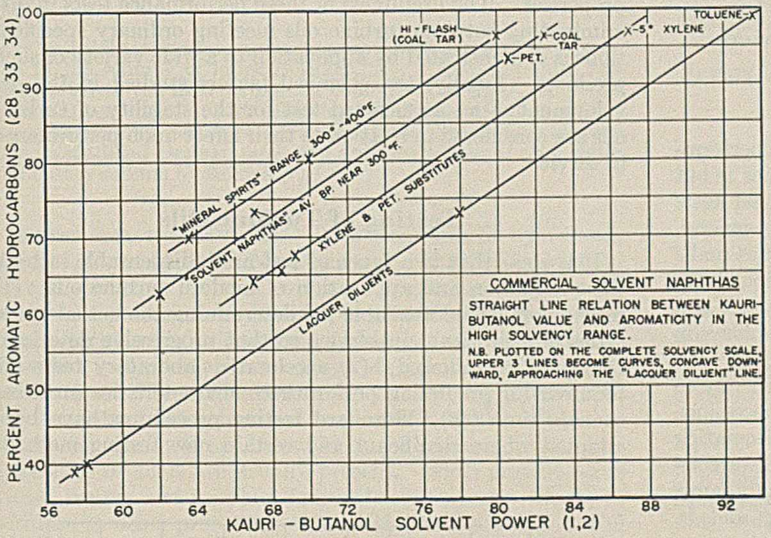
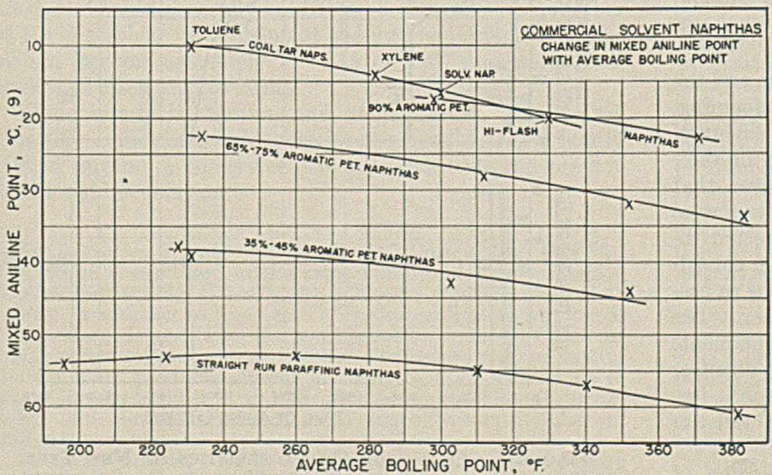


Figure 13



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Instrumental Methods of Chemical Analysis

Following the precedent set by the October, 1940, Analytical Edition, which dealt with American apparatus, instruments, and instrumentation, the October, 1941, issue will contain a systematized classification of instrumental methods of chemical analysis, covering the fundamental theory, description of equipment, and applications. Key references and the more important literature sources for each method will be included.

Readers of this journal can render invaluable aid to this undertaking and to their fellow chemists by supplying illustrations of actual installations with brief description or reference to any pertinent publications. Such examples will be of interest if they present results of high precision, ways of time-saving, handling large volume of work, or operation by relatively unskilled help, or are completely automatic.

Universities, research institutes, industrial laboratories, instrument companies, and governmental services, as well as individuals are earnestly requested to cooperate, so that the general treatment may be enhanced by illustrations of actual installations.

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Evaluation and Performance of Turbine Oils

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Progress in the design and construction of steam turbines has introduced new problems in lubrication and aggravated old ones. The importance of predicting the behavior in service of turbine oils has led to the development of suitable accelerated laboratory tests. Two essential requisites of a good turbine lubricant are the ability to protect steel surfaces against rusting and high stability toward oxidation. These tests are capable of revealing wide differences among turbine oils which meet conventional specifications. A discussion is presented of the chemical factors which influence the performance of oils in relation to the various methods employed by turbine operators to maintain an oil in serviceable condition.

IT IS becoming increasingly recognized that the performance of lubricating oils in modern steam turbines is but slightly if at all predictable from the conventional tests upon which specifications are commonly based. In general, these tests are able to exclude carelessly refined oils but make no distinctions as to the ultimate suitability of various well-refined products. Furthermore, progress in the design and construction of steam turbines has raised new problems in lubrication and aggravated old ones.

Since oils were employed in early steam turbines merely to provide lubrication, no special processing was necessary. With the advent of larger turbine installations, oil-circulating systems were introduced and several other functions were assigned to the oil. In addition to conventional hydrodynamic lubrication of the turbine shaft and thrust bearings and, in large units, also of couplings, the oil was required to act as a coolant. More recently, the same oil has been employed as a transfer medium to actuate the governor, and in geared units it lubricates high-speed gears. Development of larger and more efficient turbines operating at higher steam pressures and temperatures has further increased the demands on the lubricant.

Early turbine oils lacked stability toward oxidation and the products formed caused emulsification with water, foaming, and deposition of sludge (*5*). At first the improvement of turbine oils was chiefly directed toward reduction of their sludging tendency. It soon became apparent, however, that oil-soluble deterioration products (organic acids, etc.) were also harmful. Attention therefore began to be directed toward oxidation characteristics, to the neglect of other considerations such as ability to wet metal surfaces and thus to prevent rusting of turbine parts in the presence of water. The earlier-type turbine oils either contained certain components which promoted the formation of an adherent film of oil or soon produced similar compounds through oxidation. Improvement in sludging and emulsification characteristics necessitated by the more exacting requirements of the newer turbines was brought about largely by the application of modern refining methods. The desirable wetting agents responsible for the antirusting quality were, however, removed by these methods and the stable oils produced became inferior to less heavily refined or partly deteriorated oils with respect to rust-preventing characteristics.

In the presence of oils which provide no protective coating, steel surfaces are attacked by water with the formation of ferric oxide and black magnetic oxide. As rusting proceeds, these substances scale off and may be carried in suspension in the oil. The oxide particles sometimes score bearings, plug oil lines, and lead to faulty operation or even sticking of delicate governor parts. Difficulties due to rusting in the governor mechanism of new turbogenerators have in the past few years become prevalent, often causing severe economic loss (*1*).

It is the purpose of the present paper to advance methods for evaluating turbine oils, particularly in reference to stability and rust-prevention. This work has involved the development of laboratory tests for predicting these important characteristics, as well as a critical review of the older tests for properties. The usefulness of these performance tests in discriminating between turbine oils meeting ordinary specifications is demonstrated by application to a wide variety of such products. Finally, the chemical factors studied in the development of an accelerated test for the stability of turbine oils are considered in relation to their effect upon performance in service.

Testing of Turbine Oils

It is clear that two types of test are indispensable in both the production and application of modern turbine oils: (1) methods must be available for determining the actual properties of a lubricant in service so that progressive deterioration may be followed; (2) accelerated laboratory tests are required for predicting performance characteristics in a reasonable time (*36*). Standard testing procedures have been adopted where significant and certain new testing methods

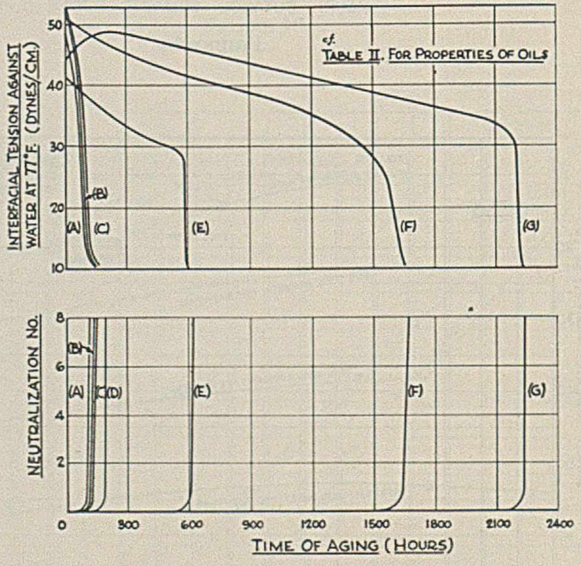

Figure 1. Oxidation Characteristics of New-Type Highly Refined Turbine Oils (Turbine Oil Stability Test)

have been devised in cooperation with turbine manufacturers and operators.

Tests for Instantaneous Properties. *Interfacial Tension against Water.* This property is a function of certain polar molecular groups present in an oil and bears a relation to its emulsifying tendencies. It may conveniently be measured by the pull-ring method employing the du Nöuy interfacial tensiometer. Cloudy oil samples should be filtered (or centrifuged) before testing to avoid contamination of the water phase in the measurement. Scale readings are converted to absolute values by means of a correction factor (*37*) which depends on the difference in density of the phases and on the dimensions of the ring.

New highly refined oils usually have high interfacial tensions (above 40 dynes per cm.) but formation of oxidation products (or contamination with used oil) sharply reduces the value. It is well known that polar molecules (soaps, acids, etc.) concentrate at the oil-water interface and orient themselves with the carboxyl groups toward the water phase; they can thus produce marked effects even when present in minute concentrations. This fact is used to great advantage because, in early stages of oxidation while mere traces of impurities are formed (values down to 30 dynes per cm.), interfacial tension is the most practical means for detecting them (Figure 1).

Interfacial tension measurements have been employed as a control in the refining of lubricating oil (*30*). They were also recommended to the first turbine oil committee of the A. S. T. M. about 20 years ago (*13*) for following the deterioration of turbine oils. Determinations were carried out by a drop-volume method using a modified Donnan pipet and aqueous phases of pure water and 0.01 *N* sodium hydroxide (*7*).

Neutralization Number. This is determined by a standard procedure (A. S. T. M. Designation D188-27T, Method A) and measures the acid content expressed in milligrams of equivalent potassium hydroxide per gram of oil. Since well-refined turbine oils have no measurable neutralization number (less than 0.05), free acids are a sign of oil deterioration or contamination. These substances are emulsifying agents and seriously affect the interfacial tension of the oil. When the interfacial tension drops below 30 dynes per cm., measurable quantities of acids are usually present. Some organic acids attack copper and iron and form oil-soluble soaps which, in addition to being promoters of emulsification, act as powerful oxidation catalysts.

Since various types of acids are formed on oxidation, depending on operating conditions and oil composition, a strict limit on neutralization number cannot be set. Highly refined oils should generally not exceed a neutralization number of 1.0 in service. At this point the interfacial tension of the oil has become extremely low (15 or less) and permanent emulsions often tend to form.

While interfacial tension and neutralization number are normally sufficient to characterize the condition of a highly refined turbine oil in service, the following tests can provide additional information:

Saponification Number (A. S. T. M. Designation D94-36). This value is expressed in the same units as the neutralization number but includes esters, soaps, and some potential acids (peroxides) in addition to free acids. The saponification number is thus always larger than the neutralization number (often as much as five to ten times as high) and embraces a large part of the oxidation products present in the oil. A sharp increase in saponification number is an indication of approaching oil breakdown and sludge formation. The saponification number of sludge is very high.

Viscosity Increase. An increase of the oil viscosity in service is due to an accumulation of oil-soluble oxidation products and is a forerunner of sludge formation.

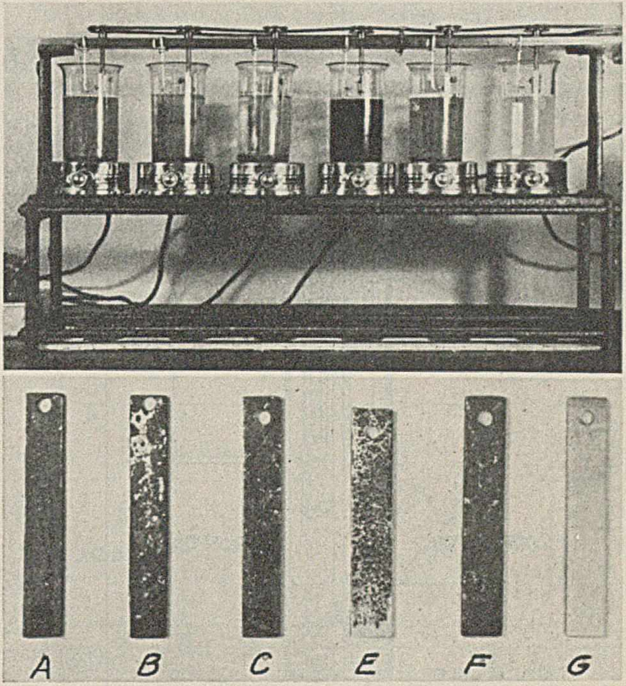

Figure 2. Rusting Tests on Six New-Type Highly Refined Oils after 48 Hours

Above. Assembly
Below. Specimens

Sludge. This determination has lost much of its significance with the advent of modern nonsludging turbine oils. The oxidation products in such oils remain in solution long after the oil has become unfit for service. However, permanent water-oil emulsions, which usually contain some metal soaps as stabilizers, often clog filters and appear as sludge. Sludge deposits in neglected turbine installations present a serious problem because they not only interfere with lubrication but also drastically reduce the life of subsequent charges of oil. The ash content of sludge consists mainly of iron oxide, often with a trace of copper (*3*, *27*).

Appearance. Badly deteriorated oils are usually very dark colored. Occasionally, however, an oil shows a persistent haze or a dark-brown opaque appearance without having a low interfacial tension, high neutralization number, or pungent odor. This is due to traces of iron soaps and colloidal hydrated iron oxide from rust and sludge deposits in the oil system. Such contamination usually reduces the life of the oil. Rust may also form in new turbines at an early period of operation if the oil used has no antirusting properties. In each case a trace analysis will show the presence of iron.

Dithizone Test. Most oil coolers are constructed of copper or bronze tubes, and copper lines are often present elsewhere in the oiling systems. Some organic acids formed on deterioration of an oil attack copper, forming oil-soluble soaps which are powerful catalysts for oxidation. Since the presence of these soaps is always an indication of actual or impending breakdown of an oil, their detection is of interest. This may be accomplished by the dithizone test as follows: A solution of diphenylthiocarbazone (dithizone) in carbon tetrachloride (5 mg. per 100 ml.) is added to the oil under investigation. Peroxides, which interfere, may be removed by a preliminary reduction with sulfur dioxide. If dissolved copper is present, the green dye turns red. Concentrations of the order of one part per million can be detected. This reagent was first applied by Fischer (*11*, *12*) and the procedure was later adapted to the determination directly in oil solution by Waring (*32*).

Steam Emulsion Number (A. S. T. M. Designation D157-36). This is generally recognized as the best method now available for determining the tendency of oil to separate water. However, interpretation is difficult, since no account is taken of the water remaining in the oil phase at the completion of the test. Furthermore, the relation between steam emulsion number and state of deterioration differs markedly for oils of large and small molecular size. The "demulsibility test" is of less value because it involves the wrong type of emulsion (oil-in-water).

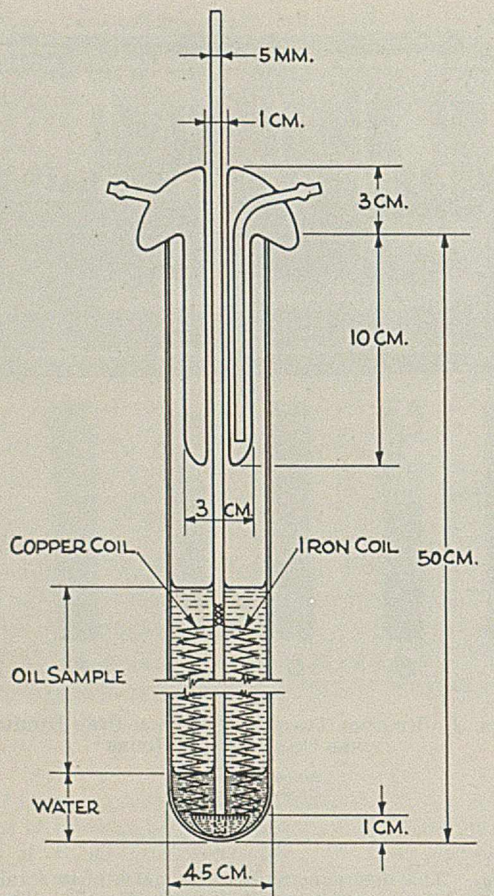

FIGURE 3. OXIDATION CELL FOR TURBINE OIL STABILITY TEST

ACCELERATED TESTS FOR PREDICTING PERFORMANCE CHARACTERISTICS. *Turbine Oil Rusting Test.* A clear distinction should be made between several kinds of corrosion which may occur in turbines. One type, which has been experienced for many years in the upper parts of oil reservoirs, etc., is caused by the action of water vapor and volatile acids from oxidized oil. Since the metal surfaces involved are not normally covered by oil, this is not essentially a problem in lubrication but can probably best be solved by application of a protective coating.

A second type of corrosion is the attack of metal surfaces, which come in contact with the oil, by organic acids formed through oxidation. This problem can be eliminated by using an oil of high stability.

In the present paper primary consideration is given to a type of attack which often occurs after only a short period of operation with new oils free of acid. This is purely a rusting phenomenon caused by droplets of liquid water coming in contact with steel surfaces which have presumably been covered by the lubricant and displacing it. An oil will protect against this more serious action only if it wets steel surfaces preferentially as compared with water.

The importance of the antirusting quality in turbine oil has become recognized. A test devised three years ago by Kuebler (*21*) in the laboratories of one of the major turbine builders employs a highly polished steel specimen suspended in the oil to be tested which is then stirred for a time to ensure wetting of the specimen. One per cent by volume of distilled water is added and stirring continued 8 hours a day for 5 days at room temperature.

In modifying the test in these laboratories to comply more nearly with conditions met in operation, the testing temperature is raised to 75° C., 10 per cent of water is added instead of 1 per cent, and stirring is carried on continuously for 48 hours. Under these more severe conditions rusting naturally proceeds rapidly in any oil which allows rust formation at room temperature. However, the converse is not true, for an oil which is effective at room temperature does not necessarily protect steel surfaces at 75° C. The more discriminating test has given results in better agreement with service data.

The general arrangement of the test apparatus is shown in Figure 2. The oil samples are contained in 600-ml. heavy-walled Pyrex beakers which are mounted on thermostatically controlled hot plates. Vigorous stirring is provided by all-glass stirrers. The test specimens are low-carbon cold-rolled steel with a hole at one end to allow suspension by means of an enameled or lacquered wire. They are ground, polished, and cleaned before use and must not be touched with the fingers; great care must be exercised in preparing the strips to ensure reproducible results. The specimen should not touch the sides of the beaker because a dead space will form in which water remains stationary, causing erratic results. Water is added during the test to replace that lost by evaporation. At the conclusion of the test the specimens are washed with naphtha and acetone and examined visually. Extent of rusting is expressed in per cent of surface rusted. Photographs of specimens from tests (Figure 2) show the wide variation in antirusting characteristics of several modern-type turbine oils.

Turbine Oil Stability Test. Turbine oils are expected to withstand continuous operation at moderately elevated temperatures in the presence of air, water, and metals without forming sludge or emulsions. Their service conditions are essentially different from those of automotive lubricants and, hence, efforts to evaluate turbine oils by commonly accepted oil-testing methods carried out at excessive temperatures were singularly unsuccessful. One of the first tests adapted specifically for turbine oils was that of Funk (*14, 15*). This test was later modified and other tests were devised (*6, 10, 23*).

The turbine oil stability test, developed in these laboratories for predicting the useful life expectancy of turbine oils, combines several features of earlier tests (*10, 20, 23, 26, 29*). Samples of oil are aged under accelerated conditions which do not deviate qualitatively from those met in practice and with the provision that all factors influencing rate of deterioration are maintained constant.

A 300-ml. sample of the oil under investigation is placed in a large test tube, 60 ml. (20 per cent by volume) of distilled water are added, and metal catalysts are introduced (a coil of iron and a coil of copper wire joined together). Pure iron wire (analytical grade) is employed, whereas copper wire ordinarily manufactured for electrical purposes is satisfactory. Both metal surfaces are carefully cleaned before using. Enough wire is taken to give 0.5 sq. cm. of copper surface and 0.5 sq. cm. of iron surface exposed per ml. of oil. Pure oxygen is supplied to the oil at a rate of 3 liters per hour through a glass tube terminating in a fritted-glass plate which disperses the gas into fine bubbles, ensuring intimate contact with the liquid and vigorous agitation. The oxygen escapes through a reflux condenser which retains water and volatile oxidation products to a considerable extent.

The oxidation cell (Figure 3) is immersed in a thermostated bath maintained at 100° ± 1° C. and the temperature of the sample comes to equilibrium at some value a few degrees lower because heat is continually lost through evaporation of water. In the tests carried out in these laboratories, the temperature was 95° ± 1° C.; it may deviate somewhat from this figure in other apparatus if the rate of heat transfer is different. The water which is lost slowly throughout the test is replaced occasionally, so as to maintain its level at least 3 cm. above the sintered plate. Test tubes, thermostat, and oxygen-flowmeters are, for convenience, similar to those employed in the Indiana oxidation test (*2*).

Small portions of the oil are withdrawn for interfacial tension and neutralization number measurements at intervals, as determined by appearance or the emanation of acidic odors, and the results are plotted as a function of time (Figures 1 and 4). Parts of the copper and iron coils are also removed, to maintain a constant ratio of metal surface to oil volume; the frequency of sam-

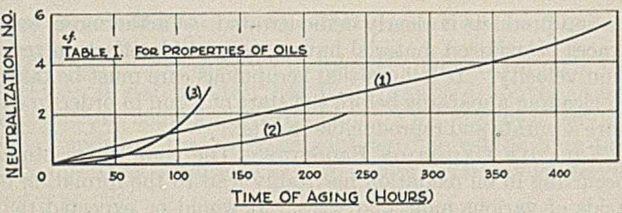

Figure 4. Oxidation Characteristics of Early-Type Lightly Refined Turbine Oils (Turbine Oil Stability Test)

pling then has no appreciable effect on the results. It can be seen that interfacial tension is more significant during early stages of oxidation, whereas neutralization number is more indicative when appreciable deterioration has occurred. Appearance and other tests previously described may yield significant information.

With careful manipulation the life of an oil, taken as the time to reach a neutralization number of 1.0, is reproducible within a ±5 per cent range. The test correlates well with practice, inasmuch as oils are rated in the same relative order as by their known service records. Because of the wide variation in operating conditions to which oils are subjected, a hard and fast prediction of their life expectancy in a given turbine cannot be made on the basis of any laboratory test. For example, it has been found that the ratio of the useful life of a certain oil in service to its life in the turbine oil stability test has ranged from 200:1 to 5:1.

Factors Influencing Oil Deterioration in Laboratory Tests

Several important variables have been investigated in the laboratory in establishing the above conditions for accelerated aging.

Oxygen Flow Rate. It is obviously desirable to maintain the flow rate at so high a value that the oil is kept saturated with oxygen at all times; the reaction velocity will then be insensitive to variations in flow above that rate. Data obtained at several rates (all other variables being held constant) are given in Figure 5, *A*. It was found that 3 liters per hour are sufficient for saturation but 1 liter per hour seemed to be somewhat inadequate. Excessively high flow rates should not be employed, so as to avoid the rapid elimination of volatile oxidation products (see Volatile Oxidation Products, below).

Temperature. Although no study of temperature coefficients has been made, reaction velocity is doubtless strongly dependent on this variable and precise control is therefore essential. The lower the temperature, the more time is required for testing. The temperature adopted is as high as is compatible with the presence of liquid water at atmospheric pressure.

Metal Catalysis. The general catalytic effect of metals on oil oxidation has been known for some time (*33*), but there has been confusion as to the difference in action of the various metals (*8, 9, 20, 28, 33, 34, 35*). Recently copper and iron have received special attention (*10, 23, 29*). Since both these metals are present in turbine lubricating systems, they were included in the laboratory stability test. The rate curves given in Figure 5, *C*1, demonstrate clearly the accelerating action of both metals, singly and in combination, in the presence of water. Although the activity of iron is less than that of copper per unit area, catalysis by iron may be the more important because of its greater extent of surface in a turbine. Since the reaction velocity varies with surface area exposed per unit quantity of oil (Figure 5, *C*2), the importance of keeping this ratio constant is evident.

The two metals together are less active than copper alone (Figure 5, *C*1) probably because iron, which stands higher in the electromotive series, hinders the solution of copper, which is the more active catalytically. Different results were obtained when copper and iron coils were connected together and when they were separated (Figure 5, *C*3). The former arrangement was adopted for the test so as to parallel turbine construction; good electrical contact must be maintained at all times in order to avoid variable galvanic effects which may lead to erratic results.

Since the use of tin-plated copper tubes has been proposed for turbine oil coolers, a single experiment was performed with

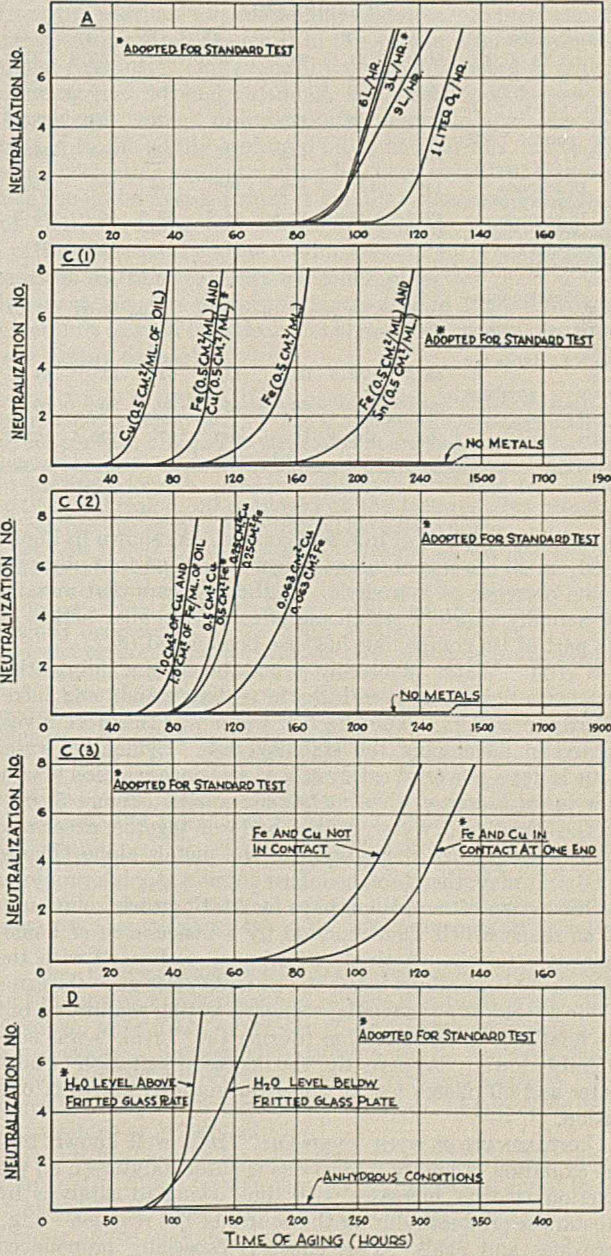

Figure 5. Factors Influencing Oil Deterioration in Turbine Oil Stability Test

A. Oxygen flow rate
C. Metal catalysis: (1) kind of metal, (2) ratio of metal surfaces to oil volume, (3) galvanic effects
D. Effect of water

Table I. Properties of Early-Type Lightly Refined Turbine Oils

Oil designation	1	2	3
Gravity, °A. P. I.	26.6	28.6	24.9
Color, N. P. A.	3+	5+	6+
Pour point, ° F.	+15	+25	+30
Flash point, ° F. (O. C.)	390	395	415
Fire point, ° F. (O. C.)	450	455	475
Viscosity at 100° F., S. U. seconds	177	281	480
Viscosity at 210° F., S. U. seconds	40	52	59.5
Viscosity index, Dean and Davis	62	104	82
Neutralization number	0.05	0.05	<0.05
Saponification number	1.6	0.5	0.4
Interfacial tension against water at 77° F., dynes per cm.	37	34	41.5
Steam emulsion number	180	560	330
Specific dispersion (*31*)	125.5	123	132

Table II. Properties of New-Type Highly Refined Turbine Oils

Oil designation	A	B	C	D	E	F	G
Gravity, °A. P. I.	30.4	31.6	29.6	33.6	31.1	32.8	32.1
Color, N. P. A.	−1	−1	−1	1+	−1	1½	−1
Pour point, ° F.	+20	0	+5	+5	+5	−5	+5
Flash point, ° F. (O. C.)	375	390	385	410	370	395	385
Fire point, ° F. (O. C.)	435	450	445	470	420	460	445
Viscosity at 100° F., S. U. seconds	146	156	156	156	157	153	156
Viscosity at 210° F., S. U. seconds	42.7	44.0	42.8	44.7	43.3	44.0	43.5
Viscosity index, Dean and Davis	95	107	81	118	91	111	97
Neutralization number	<0.03	<0.05	<0.03	<0.05	0.03	<0.03	<0.05
Saponification number	0.08	0.20	0.16	0.06	0.23	0.08	0.10
Interfacial tension against water at 77° F., dynes per cm.	48.5	52.5	52.5	43	41.5	51	44.5
Steam emulsion number	30	30	30	45	60	30	60
Specific dispersion (*31*)	108	105.5	110	100	97	106.5	102.5

tin and iron in place of iron and copper. As shown in Figure 5, *C*1, an oil life was obtained longer even than that observed in the presence of iron alone. It thus appears that metallic tin actually exerts a stabilizing effect. A similar action on the part of tin compounds has also been noted (*24*).

Water. Water is usually found in turbine lubrication systems, originating from leaks in sealing glands and infrequently in coolers. The effect of water was therefore investigated in developing the stability test. Evidently, water alone is not a powerful catalyst, if at all, since reaction is very slow in its presence when metals are absent (Figure 5, *C*1). On the other hand, water, copper, and iron together accelerate oil oxidation much more than do the metals alone (Figure 5, *D*). It may, therefore, be inferred that water is a promoter for the action of metals, perhaps facilitating their solution in oil as soaps which then function by a mechanism of homogeneous catalysis. A single experiment performed with the water level maintained below the sintered plate gave the same oil life as that observed under standard testing conditions, but the final rate of deterioration (during the "break") was considerably lower. Apparently, the degree of agitation of both water and oil phases has an effect during later stages of oxidation.

Contamination with Used Oil. It is well known that the oxidation of highly refined oils is autocatalytic—i. e., the reaction velocity increases with time owing to catalysis by substances produced during the course of the reaction—e. g., peroxides and acids. This effect is especially pronounced when metals are present, since the acids then form copper and iron soaps which are extremely powerful pro-oxidants. In Figure 6 are presented data for the oxidation of blends of turbine oil with used oil from a turbine. Since the addition of only 10 per cent of a mildly deteriorated oil reduced the oil life by as much as 75 per cent, the accelerating action of oxidation products is clearly demonstrated. Furthermore, even traces of oxidized material have a perceptible effect on reaction velocity. It follows that scrupulous care must be taken in cleaning apparatus before the start of a run in order to ensure accurate and reproducible results.

Volatile Oxidation Products. The complex reactions occurring in oil oxidation inevitably lead to the formation of acids of various molecular sizes. It would be expected that those of low molecular weight would be the most powerful pro-oxidants, since they are generally the strongest acids and attack metals most readily to form catalytically active soaps. The loss of these low-boiling acids by volatilization during the turbine oil stability test thus becomes a significant rate-determining factor. A few experiments performed in apparatus which provides for complete recirculation in a closed system have actually given considerably higher reaction velocities than other measurements in which the lightest acids were continuously swept out of the oil by the stream of oxygen. Accordingly, reflux condensers have been adopted for the test to retain as much of the volatile acids (and water) as is practicable without unduly complicated equipment.

Evaluation of Turbine Oils

Properties of three early-type and several modern turbine oils are presented in Tables I and II. The former are probably distillate cuts from unextracted lubricating oil stock; the latter appear to be well-treated neutrals.

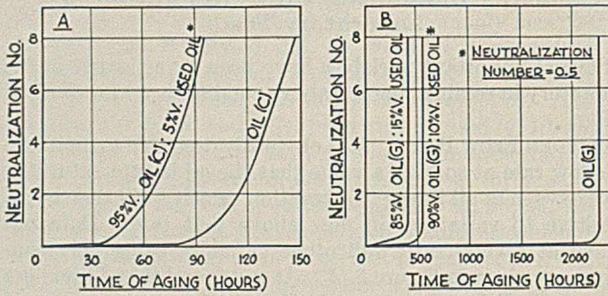

Figure 6. Deleterious Effect of Used Oil on Stability of Turbine Oils (Turbine Oil Stability Test)

A. Oil of ordinary inherent stability
B. Oil of high inherent stability

As shown in Figures 1 and 4, the difference in composition of the two types of oil results in widely different oxidation characteristics. The modern oils remain in serviceable condition throughout an initial induction period during which deterioration is very slow, whereas the lightly refined ones react at moderate velocity from the start of the run, with early foaming, emulsification, and sludge formation. It is nevertheless significant that the various highly refined oils show a twentyfold variation in resistance toward oxidation in spite of their similarity in other properties. Apparently the less stable oils contain only those naturally occurring antioxidants which are not removed in the course of refining; the more stable ones doubtless contain added inhibitors.

In contrast to the superiority of highly refined products with respect to oxidation stability, lightly refined oils are often more satisfactory in regard to rust-preventing characteristics. A picture of the turbine oil rusting test is given in Figure 2; the specimen for oil D is not shown but resembles that for C. It is evident that modern-type oils may vary from zero to complete protection against rusting.

Factors Influencing Oil Deterioration in Service

The influence of several variables on oil deterioration in the turbine oil stability test has been discussed above. Since these factors control the performance of a lubricant in service, it is important that they be considered in establishing turbine-operating conditions so as to ensure the maximum useful life of an oil.

Aeration and Venting. During rotation of the turbine shaft a partial vacuum is created within the upper part of the bearing by an action like that of a rotary vacuum pump (*22*). Since the oxygen which is dissolved in the oil may become involved in oxidation reactions, provision should be made to eliminate it as quickly as possible. This is usually accomplished by venting the oil reservoir directly to the atmosphere or by applying gentle suction.

The vented air is often saturated with water vapor and, in cases where the turbine oil has deteriorated, also with volatile acidic oxidation products. These vapors, unless quickly released, not only accelerate the deterioration of the oil but also cause corrosion and promote rusting by water particularly in the vapor space of oil tanks, bearing housings, and gear cases. The oil vapors escaping through the vents, if condensed, should not be returned to the system under any circumstances. Dantsizen (*6*) has shown that aliphatic acids ranging from formic to butyric are active in promoting rusting.

Temperature. Like most chemical reactions, oil oxidation is sharply accelerated by a rise in temperature. The best turbine oil maintained at approximately 95° C. (as in the turbine oil stability test) lasts several months, but if held at 150° C. (under oxygen pressure in the presence of water and catalytic metals) the life becomes a matter of hours. Lowering the operating temperature is therefore an effective way to increase the life of an oil in service. Since in modern turbines steam temperatures are high and the units are being built more and more compact, proper cooling is important.

Settling tanks which are inserted in turbine-lubricating systems to permit the separation of water, etc., function best when the oil is kept warm; these tanks are therefore usually located ahead of the oil coolers. It is, however, advisable not to exceed a temperature of 55° C. in the oil settlers, so as to avoid unnecessary oil deterioration. The practice of heating the oil in the settlers with built-in electric heaters or high-pressure steam coils to break an emulsion is decidedly harmful in view of the high local temperatures.

Metal Catalysis. Since catalysis by copper and iron is a function of the ratio of metal surface to oil volume, the rate of deterioration can be materially reduced by increasing the oil capacity of the lubricating system.

The replacement of catalytic metals (especially copper) by aluminum has been suggested (*20*). While some progress in this line is possible, there are several limitations to be considered, such as the cost, tensile properties, and the susceptibility of aluminum to attack by water (particularly, sea water) in the coolers. The use of tin-plated oil lines has been proposed and might prove to be advantageous (*18, 19*). Certain alloys might also be applicable. In any case the problem of catalysis by iron and copper remains serious, owing to the large number of existing installations containing both these metals.

Water. Water is a promoter for the catalytic action of metals on oil deterioration and may cause emulsification and rust formation. It is thus highly desirable that turbine installations have effective sealing glands which prevent the entrance of steam or water into the oil system. Furthermore, if water suddenly gains access to a highly deteriorated dry oil containing large amounts of oil-soluble oxidation products, emulsification and a sudden precipitation of sludge may occur.

In cases where the exclusion of water is impractical, it may be removed continuously by such methods as filtering, gravity-settling, or centrifuging. Filtration through clay has an adverse effect on modern turbine oils of high stability but cotton bags give excellent results. The use of a large oil volume permits a reduction in the rate of oil circulation and affords a better opportunity for the water to settle out. Centrifuging greatly accelerates the separation of suspended water, sludge, and solid particles—that is, all those impurities which if given a chance would settle out spontaneously—even in lubricating systems of relatively low capacity. However, caution should be exerted that the oil capacity is not reduced to extreme, as this may indirectly contribute to oil breakdown (see Metal Catalysis, above).

Used turbine oil is sometimes washed continuously with hot water to remove extractable oxidation products (acids); the water is then separated by centrifuging or filtration (*16, 17, 25*). This process can best be employed if water has already entered a system containing an appreciably deteriorated oil.

Contamination with Used Oil. Most cases of rusting known to the authors have occurred in new installations. Older units normally gave no trouble because some used oil from the previous fill, containing oxidation products capable of protecting steel, remained in the system after the conventional cleaning. This procedure usually consisted of manual scraping and wiping, steaming, and flushing with new oil. Accordingly, some turbine manufacturers and operators have turned to the addition of used oil to new oil fills. Although some protection against rusting has been obtained, this practice should be avoided since it greatly reduces oil life (Figure 6). Furthermore, very thorough cleaning of contaminated systems is necessary if the full life expectancy of an oil is to be realized. In three cases which exemplify this point a fresh highly stable oil of modern type was used in a new unit, in an older unit cleaned by conventional methods, and in one which was simply drained.

1. A new 35,000-kw. turbogenerator was charged with 15,140 liters (4000 gallons) of oil. The interfacial tension, originally 51 dynes per cm., dropped to 42 in 2000 hours and the unit has subsequently operated for 13,000 hours without measurable change in interfacial tension. The initial drop is attributed to contamination by break-in oil employed at the factory. No operating difficulties due to the lubricating oil have been noted.
2. An 8000-kw. turbogenerator cleaned in the conventional manner was charged with 1892.5 liters (500 gallons) of oil. The interfacial tension, originally 52 dynes per cm., fell to 37 within 24 hours and to 32 in 2000 hours. Although the unit has subsequently operated for 12,000 hours without further change in interfacial tension, emulsions tend to form, owing to contamination by oxidation products from the previous fill.
3. Two 785-horsepower turboblowers possessing a common oil system were charged with 3028 liters (800 gallons) of fresh turbine oil. No effort was made to clean the system after the old oil was drained. In only 1920 hours of operation the interfacial tension of the new oil had dropped from 48 to 23 dynes per cm., a measurable neutralization number and a hazy appearance had developed, and there were all the indications of an impending breakdown. In the turbine oil stability test the same oil had a lifetime of 2700 hours. Although these units operate under rather adverse conditions (bearing outlet temperature, 82.2° C., 180° F.), a much longer useful life would doubtless have been obtained were it not for the sludge left in the system from earlier operation.

It has been a custom in the past to remove periodically some of the used oil in a turbine and replace it with fresh oil. This practice, known as "sweetening", originated as a step to remove sludge. Since modern turbine oils do not form sludge during their useful life, this precaution is unnecessary. Any benefit is only temporary and the rate of oil deterioration is not reduced proportionally (*4*).

It is recommended for most efficient and economical operation that turbines be thoroughly cleaned with a suitable solvent before new lubricant is charged; modern-type oils containing added inhibitors should then function for years without appreciable deterioration. However, since the cleaning procedure removes contaminants which protect steel surfaces, rusting may be expected unless the lubricant employed affords protection.

Among numerous examples of the successful cleaning of neglected industrial and marine turbines, one in particular may be noted. A small geared turbogenerator caused the breakdown of former oil fills in a few hundred hours of operation. After thorough application of a special cleaner, the interfacial tension of the new oil charge decreased by only 0.5 dyne per cm. in 24 hours and has remained practically unchanged during several thousand hours of subsequent operation.

Acknowledgment

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Ring Method for the Determination of Interfacial Tension

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THE ring method for the determination of surface and interfacial tension has come into common use during the past decade or so. Interfacial tension may be used in studying small changes in concentration of impurities during the refining of petroleum (*5, 7, 8*) that are difficult to detect by other means. It is likewise useful in following the deterioration of hydrocarbon oil, either in accelerated stability tests or in actual service (*5, 6, 9, 10*). In applications of this nature the ring method is usually chosen on account of its simplicity.

Harkins and Jordan (*4*) have pointed out that values obtained by the ring method according to the simple equation $S = \frac{P'}{4\pi R}$ may be in error by as much as 30 per cent, or even more. In this equation S is the surface or interfacial tension in dynes per centimeter, P' is the maximum pull on the ring in dynes, and R is the radius of the ring in centimeters. These investigators have worked out, upon an empirical basis, factors which can be used to correct such values. These correction factors depend upon the density of the liquid or liquids, the maximum pull on the ring, and the dimensions of the ring. Freud and Freud (*2*) have substantiated this work from a fundamental standpoint.

Harkins and Jordan have prepared tables of their factors which are conveniently used for surface tension work. However, for interfacial tension measurements, the tables are inadequate except for the cases of very low scale readings and/or very great differences between the densities of the two phases. To handle the cases most generally met in the measurement of interfacial tension at hydrocarbon-water interfaces, it has been necessary to extend the data of Harkins and Jordan considerably.

The method employed consisted of a mathematical analysis of the tabulated data to ascertain whether they obeyed any "natural" mathematical relation which might constitute a reliable basis for extrapolation. It has been found that, for a given ring, the correction factor is determined by the relation:

$$(F - a)^2 = \frac{(4b}{(\pi^2} \cdot \frac{1)}{R^2)} \times \frac{P}{D - d} + C \tag{1}$$

Table I. Agreement between Data of Harkins and Jordan and Calculated from Equation 1

R/r	$P/(D-d)$	F (H and J)	F (Equation 1)
30	105.36	1.012	1.016
	79.017	0.967	0.972
	52.678	0.921	0.918
40	105.36	1.038	1.040
	79.017	0.996	0.999
	52.678	0.950	0.951
50	105.36	1.054	1.053
	79.017	1.013	1.014
	52.678	0.970	0.969
60	79.017	1.022	1.023
	63.213	0.998	0.998
	52.678	0.981	0.980

where $F = \frac{S}{P}$ = correction factor

S = interfacial or surface tension, dynes per cm.

P = maximum pull on ring, dynes per cm.

D and d = densities of the lower and upper phases, respectively (liquid-air, water-oil), etc.

and for the case of a given ring the following quantities are constant:

R = the radius of the ring

C = a constant, which depends upon the ratio r/R, where r = radius of the wire of the ring, in the following manner:

$$C = 0.04534 - 1.679 \frac{r}{R} \qquad (2)$$

and $a = 0.7250$ and $b = 0.0009075$ are universal constants for all rings.

It is apparent from Equation 1 that the dependence of F upon the quantity $P/(D-d)$ obeys a parabolic law for any given ring. The ability of Equations 1 and 2 to evaluate the data of Harkins and Jordan is illustrated in Table I. This satisfactory agreement in conjunction with the simple and standard mathematical form of Equation 1 provides reasonable certainty for extrapolating the data of Harkins and Jordan to the considerable degree required for application of the ring method to interfacial tension measurements.

Figure 1 presents the correction factor, F, as a function of the quantity $P/(D-d)$. Two sets of curves are given, the upper set applicable to a ring of circumference equal to 4 cm. and the lower set to one of 6 cm. Individual curves in each set apply to cases of definite values of R/r in the following manner:

For the lowest curves in each set, $R/r = 30$
For the second lowest curves in each set, $R/r = 40$
For the third curves from bottom in each set, $R/r = 50$
For the top curves in each set, $R/r = 60$

The curves were calculated from Equations 1 and 2.

It is indicated by the curves of Figure 1 that the correction values for a 6-cm. ring are much smaller than those for the 4-cm. ring. Upon this basis it follows that, in the interests of greater precision, the larger ring should be used, since the required degree of extrapolation for the correction factor is considerably less than for the smaller ring and the actual magnitudes of F are also smaller.

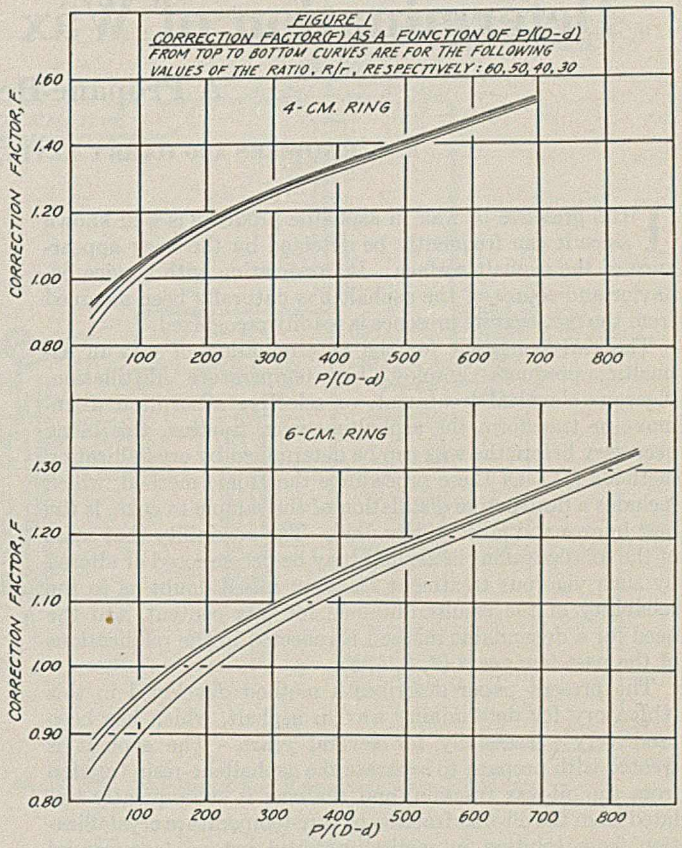
Table II. Oils Used for Correlation of Interfacial Tension by Ring and Capillary Methods

Oil	Description	Density at 25° C.
A	Specially treated kerosene cut	0.7825
B	Solvent-extracted transformer oil	0 8501
C	50-50 blend of A and B	0.8171
D	Untreated medium distillate cut from recycled stock taken from cracking unit	0.8469
E	Untreated heavy distillate cut from recycled stock taken from cracking unit	0.9765
F	67-33 blend of D and E	0.8907
G	33-67 blend of D and E	0.9334
H	Solvent-extracted 150 viscosity turbine oil	0.8843
I	Benzene	0.8735

Table III. Comparison of Ring and Capillary Methods for Determining Interfacial Tension of Oil against Water

(Temperature, 25° C.)

	S(Uncorrected)				F		S (Corrected)		
	4-Cm. Ring		6-Cm. Ring						
Oil	$R/r=$ 41.7	$R/r=$ 38.8	$R/r=$ 54.0	$R/r=$ 53.4	4-cm. ring	6-cm. ring	4-cm. ring	6-cm. ring	Capillary method
A	42.0	..	45.5	..	1.153	1.041	48.4	47.4	47.4
B	41.0	..	45.4	..	1.233	1.097	50.6	49.8	49.2
C	40.4	..	44.9	..	1.182	1.064	47.8	47.8	47.8
D	30.7	..	34.2	..	1.161	1.050	35.6	35.9	35.8
E	19.0	..	23.5	..	1.642	1.414	31.2	33.2	30.7
F	25.1	..	27.0	..	1.193	1.067	29.9	28.8	29.4
G	22.4	..	25.1	..	1.295	1.141	29.0	28.6	29.2
H	..	42.4	..	48.8	1.311	1.159	55.6	56.6	56.0
I	..	29.1	..	32.6	1.189	1.072	34.6	34.9	34.6



The validity of Equations 1 and 2 has been checked by means of measurements with two du Nöuy tensiometers (using 4- and 6-cm. rings) as well as by an independent method—namely, the capillary method as described by Bartell and Miller (*1*). Nine oils have been studied. A brief description of these oils is given in Table II, and interfacial tension data are shown in Table III.

These data show good agreement between the results of the capillary method and corrected results obtained by the ring method for 8 of the 9 oils shown above; and in the case of sample E, which has such a high density that $P/(D-d)$ is 922 and 1141, respectively, for the 4- and 6-cm. rings used, so that the correction factors are extremely high, the agreement is fair. The value for benzene is in good agreement with the value of 34.68 at 25° C. reported in the literature (*3*). For samples whose density approaches that of water, $P/(D-d)$ becomes very large and the ring method loses precision. Oils ordinarily encountered usually have a density of less than 0.90 and are nearly always under 0.95, however, and in this range the ring method, modified by the above outlined correction, is capable of reasonably good precision and accuracy.

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Determination of Wax in Asphaltic Products

A Propane-Hexone Method

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THE presence of wax in asphaltic products is well known since it can frequently be detected by the hazy appearance of the asphalt surface. Its association with service behavior and source of the asphalt has naturally been assumed from the fact that its presence is readily recognized.

The early methods for the determination of wax in asphaltic products employ high-temperature distillation, vigorous chemical treatment, or selective adsorption to remove or transform the asphaltene-resin fraction, this being necessary before the wax can be determined by crystallization methods (*1*). Of these procedures the Holde method, which includes a destructive distillation of the sample to coke, is the best known and most widely used. The possibility that some of the solid paraffins in asphalt may be decomposed or altered by such vigorous treatment has long raised doubt as to the reliability of the results obtained for wax content, and the need for a dependable method is reflected in the publications of the past few years (*2*, *3*, *5*, *6*).

The present paper describes a method developed in this laboratory for determining wax in asphalt, which has been used very successfully for several years. The asphalt is treated with propane to separate the asphaltene-resin fraction from the oil-wax fraction, and the wax is subsequently isolated from the oil-wax fraction by low-temperature crystallization from solution in methyl isobutyl ketone (commercial "Hexone").

In this method, advantage is taken of the well-known ability of propane to effect a rapid clean separation of the asphaltic and resinous materials which interfere with the crystallization of the wax in the dewaxing step. The mild conditions of the propane treatment offer little possibility of chemically or physically altering the wax; hence, it is determined in the form in which it actually occurs in the asphalt.

The use of methyl isobutyl ketone for the separation of the wax from the oil fraction has been found very satisfactory, since it possesses the requisite properties of a good wax-crystallizing solvent—namely, high oil solvency, low wax solvency, and good filter rates. These properties of Hexone were shown by Gross and Overbaugh (*4*) in their work on dewaxing lubricating oils.

Equipment

The propane-treating equipment is shown in Figure 1, and the complete assembly for this operation is shown in Figure 2. This apparatus has been constructed so that it can be operated rapidly with complete safety. *A*, the precipitation vessel, is surrounded by a jacket through which hot water or steam is circulated to obtain the desired precipitation temperature of 68.3–71.1° C. (155–160° F.). The copper tube which extends nearly to the bottom of *A* has a removable filter at the end which is made up of a 40-mesh copper screen, canvas cloth, filter paper, canvas cloth, and 40-mesh copper screen. Also attached at the bottom end of the filter tube and fitting inside the cylinder are two 40-mesh screen disks 1.27 cm. (0.5 inch) apart. The function of these disks is to collect the bulk of the precipitate and thereby prevent it from settling on the bottom of *A*, where it would tend to plug the filter. *B* is used as a transfer vessel and consists of a special high-pressure Pyrex glass tube fitted in a brass container with observation slots; it operates under a pressure of 123,000 kg. per sq. meter (175 pounds per square inch) and serves to collect the propane-soluble matter (oil and wax).

The equipment for the dewaxing step is substantially the same as that employed by other investigators (*1*). Two methods of chilling have been used—namely, (1) a refrigerated brine-cooled bath which contained sheathed openings 44 by 140 mm., suitable for standard 120-ml. (4-ounce) bottles and a conical opening for the filtering funnel, and (2) a kerosene bath chilled with solid carbon dioxide. In either method the temperature was readily maintained at −17.8° or −26° C. (0° or −15° F.), as desired.

Materials

Methyl isobutyl ketone (Hexone), and commercial propane.

Deasphalting and Deresining

PREPARATION OF SAMPLE. Weigh a 50-cc. beaker and stirring rod approximately, add 5.20 to 5.50 grams of asphalt sample, and record the gross weight of beaker, stirring rod, and sample to the second decimal. Add 11.0 ml. of benzene and weigh to nearest 0.1 gram; cover and warm on a steam bath until solution is complete. Reweigh, and if the heating procedure has reduced the amount of benzene to less than 8.8 grams, add benzene to bring the weight of benzene to this figure, which is equivalent to 10 ml.

Then pour the benzene solution into *A* (Figure 1), avoiding splashing the walls. Place the beaker and stirring rod with adhering solution on the steam bath during the course of the remaining operations and finally weigh (±0.01 gram) after the benzene has been completely evaporated.

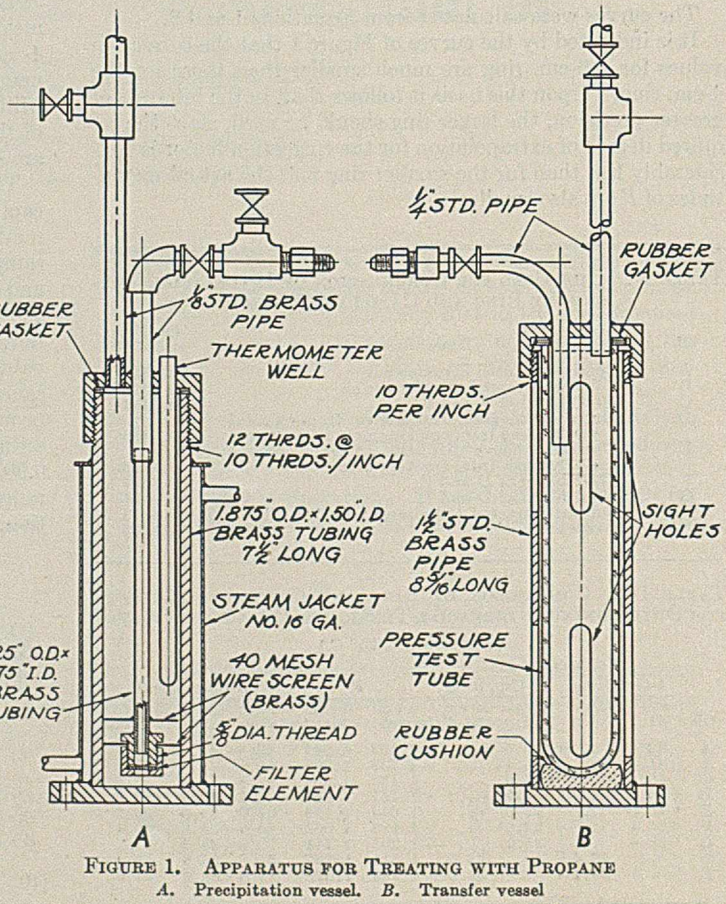

FIGURE 1. APPARATUS FOR TREATING WITH PROPANE
A. Precipitation vessel. *B.* Transfer vessel

Propane Treatment (Figure 2). The benzene solution of the sample having been transferred to *A*, screw the cover tightly into place and introduce 100 ml. of propane from the graduated propane reservoir, *XY*, compressed nitrogen gas serving to assist in the transfer. Nos. 1 through 14 of Figure 2 designate the various valves used in this assembly.

After closing the valves on *A*, detach it and thoroughly mix its contents by inverting and shaking for 30 seconds. Again attach to the propane line, open valve 8, and place a thermometer in the well. Connect a steam line to the jacket inlet (top) and pass steam through until the temperature in the vessel reaches 68.3° to 71.1° C. (155° to 160° F.). The pressure in *A* will be at approximately 246,000 kg. per sq. meter (350 pounds per square inch) at this temperature. With these conditions maintained, allow the precipitated asphaltenes and resins to settle for 5 minutes or longer, after which transfer the propane solution of oil and wax, while still being heated, to *B* in the manner of a pressure decantation. Completion of the transfer will be indicated by the approximate volume in *B*, but primarily by the rapid drop of pressure in *A*. When the pressure in *A* drops to 211,000 kg. per sq. meter (300 pounds per square inch), 35,000 kg. (50 pounds per square inch) pressure of nitrogen is superimposed on the contents of *A* through the connections leading to valve 13. Wash the contents of *A* once with 100 ml. of propane and during this washing operation allow the contents of *B* to evaporate slowly. When the contents of *A* have settled, pressure-decant the propane washings which it contains to *B*, from which the propane is permitted to escape as before. Remove test tube and wash contents into dish, using benzene as solvent, evaporate on steam bath, and record weight. This residue (oil plus wax) is then ready for the wax analysis.

Dewaxing

Warm 2 to 3 grams of this residue on a steam bath to approximately 65.5° C. (150° F.). At the same time, warm 75 ml. of Hexone to approximately the same temperature, then add enough of it to dissolve the sample. Transfer the dissolved sample to a 120-ml. (4-ounce) bottle and wash the dish into it with the remaining warm Hexone. Cork and shake thoroughly to mix the sample. Warm the solution to 65.5° C. (150° F.) on a steam bath, then allow to cool to room temperature, before placing in an ice bath for 20 to 30 minutes. After precooling in this manner, bring the mixture to a temperature of −17.8° C. (0° F.) by immersing in a suitable bath; an hour in a bath a few degrees below −17° C. (0° F.) has been found satisfactory.

Suction-filter the precipitated wax through Whatman's No. 42 (12.5-cm.) filter paper, wetted with cold Hexone, on a funnel at −17.8° C. (0° F.). Shake the stoppered bottle containing the wax-solvent mixture gently to break the solid structure and carefully pour into the filter, avoiding suction to dryness before washing. When the bulk of the mixture has been transferred to the funnel, discontinue the suction before "cracks" are formed in the wax cake. Wash the sample bottle immediately and thoroughly with approximately 20 ml. of cold Hexone at −17.8° C. (0° F.) and transfer the washings to the filter with the bulk of the wax, saving the bottle with any adhering wax. Again apply suction and continue until the wax is free of solvent. Remove the paper and wax and dissolve this wax, as well as that which was left adhering to the bottle, through the paper with hot benzene. Evaporate the benzene solution on a steam bath, dry the residue at 105° C. (221° F.) for 30 minutes to remove traces of benzene and Hexone, cool in a desiccator, weigh, and calculate the wax back in terms of the original asphalt sample.

Results

The potential utility of methyl isobutyl ketone as a solvent in the quantitative determination of wax was suggested by experiences with its use in dewaxing lubricating oils, which showed that it has excellent oil-solvent properties and low wax-solvent properties, and gives good filter rates (*4*).

Its suitability as a solvent for the analytical determination of wax in asphalt products was investigated by testing synthetic oil-wax samples.

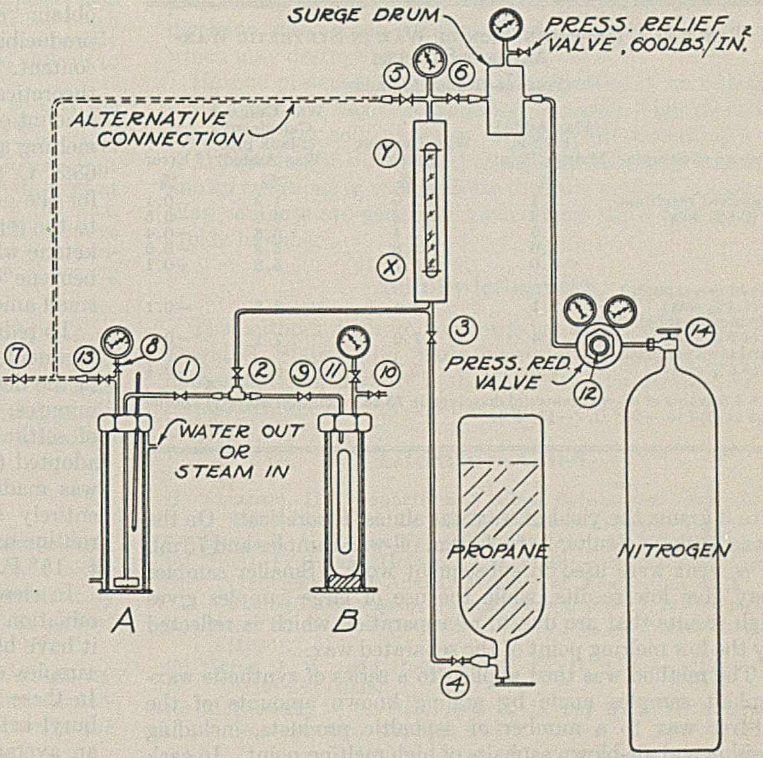

Figure 2. Assembly for Treating with Propane

The oil-free wax component of these samples was prepared from a coastal residuum by deasphalting it with propane, dewaxing the deasphalted oil with a solvent consisting of 40 per cent methyl ethyl ketone and 60 per cent benzene at −26.1° C. (−15° F.), and twice deoiling the wax at 10 to 1 dilution in the same mixed solvent. This wax was considered to be substantially oil-free and had a melting point of 69.4° C. (157° F.).

Preliminary tests were carried out to determine the most suitable solvent-oil ratio. For this purpose, 5 per cent of the oil-free wax was added to a high-viscosity propane deasphalted, dewaxed, and solvent-refined residual oil. Dewaxing tests were made in which the size of the sample was varied, but the volume (75 ml.) of methyl isobutyl ketone kept constant.

These results are shown in Table I, the first four tests of which were made on the blank oil and show that oil separation will occur if the solvent-oil ratio is too low. Similar tests made on the 5 per cent wax-oil sample (correction being made for the blank oil) indicate that the best accuracy is obtained with 2- to 3-gram samples. With dewaxing sample weights in this range, the melting point of the recovered wax was 65.6° C. (150° F.), as compared with 69.4° C. (157° F.) on the original wax, illustrating the good separation of wax and oil obtained with this solvent. The results show that with samples of

Table I. Effect of Sample Size on Accuracy of Wax Separation Step

	Methyl Isobutyl Ketone (75 Ml.)					
Charge Material	Weight of sample	Wax found[a]	Wax found less blank	Error	Melting point of "found" wax	
	Grams	%	%	%	° *C.*	° *F.*
Refined residual oil (no added wax)	0.3	0.4	..	..	....	
	1.0	0.5	..	..	....	
	3.0	0.8	..	..	....	
	5.0	2.3	..	..	Oil separation	
Refined residual oil (plus 5% of 157° F. melting point wax)	0.3	2.5	2.1	−2.9	....	
	1.0	4.9	4.4	−0.6	....	
	2.0	5.7	5.0	0.0	65.6	150
	3.0	5.6	4.8	−0.2	....	
	5.0	9.4	7.1	2.1	54.4 (*circa*)	130

[a] Wax determination made at −26.1° C. (−15° F.).

TABLE II. DETERMINATION OF WAX IN SYNTHETIC WAX-ASPHALT SAMPLES

(Propane-Hexone Method)

Nature of Sample	Wax Added (157° F. Melting Point)	Wax Content Found[a]	Wax Content Calculated (Blank plus Wax Added)	Error
	%	%	%	%
Dewaxed residuum (0.8% wax)	1.1	2.0	1.9	0.1
	2.9	3.2	3.7	−0.5
	5.0	5.4	5.8	−0.4
	5.0	5.8	5.8	−0.0
	5.0	5.7	5.8	−0.1
Air-blown asphalt 1 (1.4% wax)	2.1	3.4	3.5	−0.1
Air-blown asphalt 2 (4.7% wax)	2.4	7.0	7.1	−0.1
Air-blown asphalt 3 (5.8% wax)	2.3	7.7	8.1	−0.4

[a] 2.5 grams of oil-wax material dissolved in 75 cc. of methyl isobutyl ketone and chilled to −26° C. (−15° F.).

2 to 3 grams the yield of wax was almost theoretical. On the basis of these results, 2- to 3-gram oil-wax samples and 75 ml. of solvent were used in subsequent work. Smaller samples may give low results, while the use of large samples gives high results that are due to oil separation which is reflected by the low melting point of the separated wax.

The method was then applied to a series of synthetic wax-asphalt samples made by adding known amounts of the oil-free wax to a number of asphaltic products, including residua and air-blown asphalts of high melting point. In each case, the synthetic sample was fractionated with propane in the manner described and the wax determined on the oil-wax fraction. The asphaltene-resin fraction which is removed in the first step by the propane is a black brittle solid, while the oil-wax fraction is usually a dark green oil. The data on these synthetic samples are given in Table II. The "wax content calculated" is the per cent wax in the asphalt plus the wax added, and is compared with the "wax content found" to obtain "error". The results illustrate the accuracy and reproducibility of this method on asphalts of low and high wax content. It gives results which are slightly lower than the theoretical wax content based on the blank test and the amount of added wax. In the case of dewaxed residuum, the melting point of the recovered wax ranged from 63.9° to 68.3° C. (147° to 155° F.), as compared to 69.4° C. (157° F.) for the original added wax. The difference is probably due to the separation of low-melting wax by the methyl isobutyl ketone which was not separated in the methyl ethyl ketone-benzene dewaxing of the residuum or to the occlusion of small amounts of oil.

TABLE III. EFFECT OF DEASPHALTING SETTLING TIME ON WAX DETERMINATIONS

(Propane-Hexone Method)

Settling Time	Wax Found[a]	Melting Point of Wax	
Min.	%	° *C.*	° *F.*
	Sample 1		
5	2.33	61.1	142
10	2.02	61.7	143
20	2.22	61.1	142
30	2.42	58.3	137
	Sample 2		
5	6.67	61.7	143
10	5.98	61.1	142
20	6.50	61.7	143
30	6.61	59.4	139

[a] Dewaxing test made at −17.8° C. (0° F.).

To reduce the time of analyses by this method, several experiments were made to determine the effect of settling time in the deasphalting step. The time was varied from 5 to 30 minutes; the results (Table III) show that a short period of settling is entirely satisfactory and 5 minutes has been adopted for routine use. This series of wax determinations was made at −17.8° C. (0° F.). This temperature gave entirely satisfactory results and was adopted for general routine use, since it was more easily attained than −26.1° C. (−15° F.).

In view of the wide use of the Holde method for the determination of wax in asphaltic products, results (Table IV) by it have been compared with those by the present method on samples of asphalt to which were added amounts of wax. In these tests the average error of the propane–methyl isobutyl ketone method was −0.1 per cent, as compared with an average error of −4.1 per cent by the Holde method. Despite the higher wax content by the present method, its melting point is also higher, which is proof that the increased wax content is not due to oil separation but rather to the separation of existing solid paraffins which are pyrolytically decomposed and lost in the distillation step of the Holde method. These results indicate the present method to be more suitable for the determination of the naturally occurring wax in asphalt.

Consideration was given to substituting methyl isobutyl ketone for alcohol-ether in the Holde method. However, preliminary tests gave results for wax content which were even lower than when alcohol-ether was used. These results indicated that the so-called wax by the Holde method may contain oil.

The use of alcohol-ether for determination of wax in the propane-treated oil-wax fraction was also considered. In preliminary tests, excessive oil separation was obtained and further experiments were discontinued. The results illustrated well the superiority of methyl isobutyl ketone over alcohol-ether as solvent in the determination of wax.

TABLE IV. COMPARISON OF WAX[a] CONTENT BY PROPANE-HEXONE AND HOLDE METHODS

Nature of Sample	Wax Added (157° F. Melting Point)	Wax Content Calculated (Blank plus Wax Added)	Propane-Hexone				Holde[b]			
			Wax content found	Error	Melting point		Wax content found	Error	Melting point	
	%	%	%	%	° *C.*	° *F.*	%	%	° *C.*	° *F.*
Dewaxed residue	None	0.8	0.8	..	..	..	0.6	..	..	..
	5.0	5.8	5.6	−0.2	61.7	143	2.2	−3.6	58.3	137
Air-blown asphalt 1	None	1.4	1.4	..	58.9	138	1.6	..	..	..
	2.1	3.5	3.4	−0.1	65.6	150	..	..	..	..
	5.0	6.4	..	..	..	..	2.5	−3.9	57.8	136
Air-blown asphalt 2	None	4.7	4.7	..	66.1	151	1.0	..	..	..
	2.4	7.1	7.0	−0.1	..	..	..	..	..	..
	5.0	9.7	..	..	..	..	4.9	−4.8	57.8	136

[a] Wax determinations made at −26.1° C. (−15° F.).

[b] Blank corrections applied to results by Holde method are based on blanks obtained by proposed method, because the latter gave higher yields of wax of higher melting points, pointing to probable true wax content.

Method of Test for Melting Point of Wax

The following procedure has been found satisfactory for determining the melting point of the small samples of wax that are obtained in its determination. It is a refinement of a method long used in wax plants.

APPARATUS. Pour test jar (A. S. T. M.), test tube, 15 × 1.88 cm. (6 × 0.75 inches), thermometer, and 600-ml. beaker.

PROCEDURE. Melt the wax on a steam bath and wet the cold thermometer bulb with the molten wax to a depth of about 3 mm. Remove promptly, so that the layer of wax which adheres to the bulb weighs between 8 and 12 mg. A little experience soon teaches when the correct weight has been applied. If too much sample is taken, it will drop from the bulb when subsequently melted; if too little, the subsequent congealing will be difficult to observe.

With a cork fix the thermometer in the test tube, so that the bottom of the bulb is 12 mm. above the bottom of the tube. With a cork fix the test tube in the pour test bottle which is full of cold water (15° C.); the cork should have a small slit in it to permit gas to escape. Place the pour test bottle in a water bath kept at 75° C., or at least 5° C. above the melting point of the wax. After the wax has melted to a clear liquid, carefully remove the assembly from the bath and tilt from the vertical to a horizontal position once every 0.3° C. drop in temperature, observing the drop of wax on the bulb of the thermometer.

The temperature at which this drop of wax solidifies, as indicated by the absence of movement on tilting, is the end of the determination. The last temperature at which movement was observed on tilting the assembly is recorded as the melting point of the sample. Experience has shown that results can be reproduced to within 0.3° C.

Summary

This method comprises separating the asphaltene-resin fraction from the oil-wax fraction by hot liquid propane under pressure and determining the wax in the oil-wax fraction by crystallization at low temperatures from solution in methyl isobutyl ketone (Hexone).

The propane treatment effects a clean removal of the asphaltene-resin fraction, the presence of which interferes generally with crystallization methods for wax, and avoids the detrimental effects of more drastic pretreatments, such as digestion with strong sulfuric acid or destructive distillation, which may destroy some of the wax.

Hexone possesses the necessary properties of an outstanding reagent for wax determination—namely, high oil-solvent power, low wax-solvent power, and good filtration rates.

Application of the method to asphaltic samples containing known additions of wax indicate that the method is accurate. Wax contents are generally higher than those found by the Holde method.

Acknowledgment

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Indiana Stirring Oxidation Test for Lubricating Oils

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ATTEMPTS to develop laboratory tests suitable for predicting the oxidation stability of lubricating oils have been numerous since the first widely used test was published by Sligh (*7*) in 1924. Since that time some eighty papers have appeared either describing new laboratory tests or criticizing the old ones. The Indiana oxidation test (*1*, *5*), published in 1934, was extensively used for evaluating the stability of conventional oils. However, Maverick (*3*) and Rogers (*6*) subsequently pointed out that the test is not suitable for the more recently developed compounded oils, such as those containing inhibitors and detergents. Another well-known test, first appearing several years ago, is the Underwood oxidation test (*8*), which was first developed to evaluate bearing corrosion and was later modified to be applicable to the study of oxidation stability (*4*).

The general trend of opinion in the last several years has been to minimize the value of laboratory oxidation tests and to place more and more emphasis on the full-scale engine test. Notwithstanding the essential correctness of such a point of view, it remains so extremely important to have some simple and rapid method of predicting oil stability, especially in the development of improved oils, that the laboratory test has continued to receive a generous share of attention. This paper discusses a new laboratory testing technique which has been found valuable for predicting the oxidation stability of both inhibited and uninhibited crankcase lubricating oils.

A specific example of a compounded oil that was not correctly evaluated by the Indiana oxidation test was one of the first proposed heavy-duty lubricating oils—namely, one containing calcium naphthenate as detergent and a sulfurized saponifiable compound as inhibitor. Numerous engine tests had shown that the addition of either the inhibitor alone or the inhibitor plus the detergent was highly effective in improving the cleanliness of engines operated under severe test conditions. The Indiana oxidation test indicated that the compounded oils were far less stable than the control oil. Furthermore, compared to the extent of deterioration occurring in accelerated engine tests, the Indiana oxidation test could scarcely be called an accelerated test. These results are clearly shown in Table I.

TABLE I. EFFECT OF SULFURIZED SAPONIFIABLE ADDITIVE AND CALCIUM NAPHTHENATE

[Indiana oxidation tests. Summarized test conditions: 10 liters of air per hour blown through 300 cc. of oil at 171.7° C. (341° F.)]

	Sludge			Acidity		
	24 hours	48 hours	72 hours	24 hours	48 hours	72 hours
	Mg./10 g. oil			*Mg. KOH/g. oil*		
Oil A	0	0	0	0.8	1.6	...
Oil A + 3.0% sulfurized saponifiable additive	0	11	376	1.5	3.7	...
Oil A + 3.0% sulfurized saponifiable additive + 0.25% calcium naphthenate	19	161	400	1.7	2.8	3.3
Oil B	0	45	...	...	...	...
Oil B + 3.0% sulfurized saponifiable additive + 0.25% calcium naphthenate	10	300	...	1.7	3.7	...

Table II. Effect of Sulfurized Saponifiable Additive and Calcium Naphthenate

[Underwood oxidation tests[a]. Summarized test conditions: 1500 cc. of oil at 163° C. (325° F.) are recirculated through an apparatus primarily of iron construction. The oil is sprayed through several nozzles at a pressure of 700 grams (10 pounds) per sq. inch against a 5 × 25 cm. (2 × 10 inch) copper baffle, one stream of oil impinging on a hard metal bearing.]

	Sludge		Acidity	
	5 hours	10 hours	5 hours	10 hours
	Mg./10 g. oil		*Mg. KOH/g. oil*	
No Added Catalyst				
Oil B	73	600	5.2	10.1
Oil B + 3.0% sulfurized saponifiable additive + 0.25% calcium naphthenate	18	25	0.4	0.4
0.016% Fe_2O_3 as Iron Naphthenate				
Oil A	78	564	8.9	12.8
Oil A + 3.0% sulfurized saponifiable additive	41	60	0.94	1.0
0.010% Fe_2O_3 as Iron Naphthenate				
Oil B	204	1380	10.1	16.8
Oil B + 3.0% sulfurized saponifiable additive + 0.25% calcium naphthenate	56	81	0.8	0.9

[a] By courtesy of General Motors Research Laboratory.

On the other hand, the Underwood stability test agreed with the engine in showing that the compounded oils were more desirable and showed a remarkably accelerated rate of deterioration as compared to the Indiana oxidation test. Results of these tests are shown in Table II.

The results of the Indiana oxidation test are so far out of line with actual engine and Underwood test results that it seems apparent that it must neglect some important factor contributing to oil deterioration, present in actual engine operation and, at least to some extent, in the Underwood test. The latter test is a workable and useful laboratory tool for predicting engine performance. However, it was desired to develop a simpler test in which all the conditions contributing to oxidation could be more closely controlled.

It was thought preferable to examine one by one some of the more outstanding conditions involved in engine tests that would be expected to contribute to oil deterioration. If one or more test conditions could be isolated as being responsible for the rapid oil deterioration and for correlation with the engine in the case of the oils previously mentioned, it would be possible to devise a simple test incorporating these particular conditions.

Development of Stirring Test Technique

Two specific objectives were sought in this study: (1) to line up the control oil and the oil containing sulfurized additive so as to show the latter more stable towards deterioration, and (2) to obtain a much more accelerated rate of deterioration of the control oil than is observed in the Indiana oxidation test. The most striking of the conditions present in engine tests are shown below, with a description of the results obtained when this test condition was emphasized.

A large amount of metallic catalyst is present in engine tests. An enormous amount of metallic iron is exposed to the oil in addition to the smaller amounts of copper present in bearings, bushings, and tubing. However, simply adding iron and copper catalysts to the Indiana oxidation test caused little improvement in test results. Data from these tests are shown in Table III for the control and inhibited oils.

In engine tests, a small part of the oil is continuously exposed in thin films on the various parts of the piston and on other parts of the engine above the oil level in the crankcase. To examine this effect, an apparatus was constructed whereby oil at a bulk temperature of 171.7° C. (341° F.) was recirculated by spraying over a copper plate at 179.4° C. (355° F.). The rate of oil circulation was such that only a thin film of oil covered the copper plate at all times. This procedure did not cause appreciably accelerated deterioration of the oil, and did not show the compounded oil as superior to the control oil.

Table III. Effect of Sulfurized Saponifiable Additive

[Indiana oxidation tests in presence of metallic catalysts. Summarized test conditions: 10 liters of air per hour blown through 300 cc. of oil at 171.7° C. (341° F.)]

	Sludge		Acidity	
	24 hours	48 hours	24 hours	48 hours
	Mg./10 g. oil		*Mg. KOH/g. oil*	
0.112% Iron Naphthenate (0.016% Fe_2O_3) as Catalyst[a,b]				
Oil A	0	0	3.3	6.1
Oil A + 3.0% sulfurized saponifiable additive	0	10	3.6	6.5
0.112% Copper Naphthenate as Catalyst[c,b]				
Oil A	0	0	3.6	2.1
Oil A + 3.0% sulfurized saponifiable additive	124	181	5.9	3.9
10 Sq. Inches of Metallic Copper per 300 Grams of Oil as Catalyst[d,b]				
Oil A	0	13	3.7	6.2
Oil A + 3.0% sulfurized saponifiable additive	0	190	3.5	4.3

[a] Tests repeated with 10 times the amount of iron naphthenate.
[b] Deterioration only slightly accelerated. Same relative stabilities of the oils.
[c] Tests repeated with 10 times the amount of copper naphthenate.
[d] Tests repeated with 10 times the amount of copper.

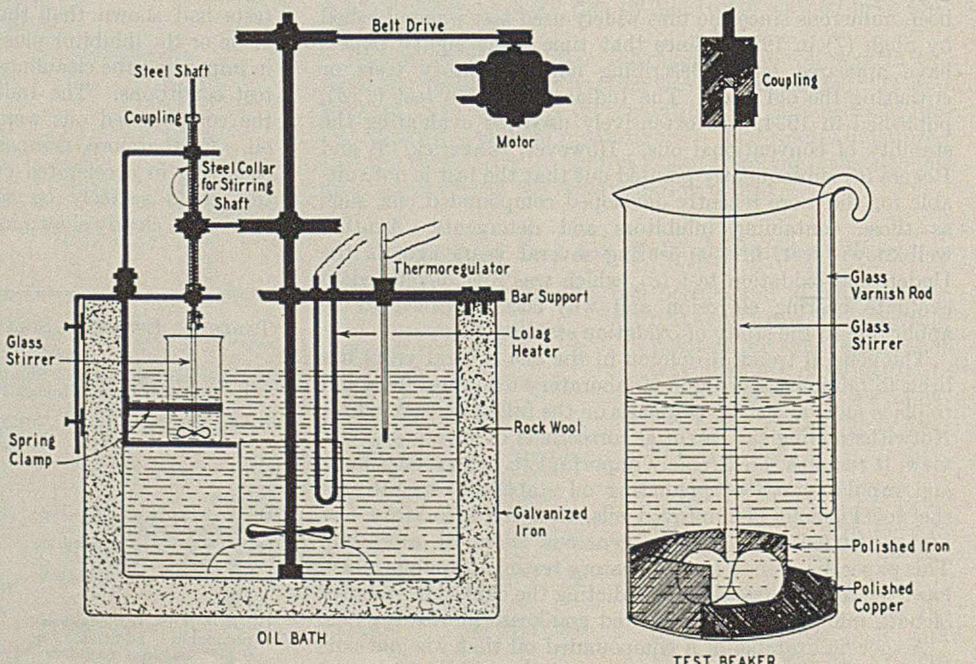

Figure 1. Diagram of Indiana Stirring Oxidation Test Apparatus

Table IV. Effect of Sulfurized Saponifiable Additive and Calcium Naphthenate

[Indiana stirring oxidation tests. Summarized test conditions: 500-cc. beaker, 250 cc. of oil, 5 sq. inches of Cu, 10 sq. inches of Fe, 1300 r. p. m., 165.5° C. (330° F.)]

	Increase in Saybolt Viscosity at 100° F. in 48 Hours	Sludge		Acidity		Varnish Equivalent to Standard Rods	
		24 hours	48 hours	24 hours	48 hours	24 hours	48 hours
	Sec.	*Mg./10 g.*		*Mg. KOH/g.*			
Oil A	1210	356	958	6.8	10.2	5	2
Oil A + 3.0% sulfurized saponifiable additive	253	29	150	2.2	2.8	9–10	8
Oil A + 3.0% sulfurized saponifiable additive + 0.25% calcium naphthenate	354	20	160	2.8	7.0	10	10

Table V. Effect of Various Concentrations of Phosphorus Inhibitor

[Indiana oxidation tests. Summarized test conditions: 10 liters of air per hour blown through 300 cc. of oil at 171.7° C. (341° F.)]

	Sludge			
	24 hours	48 hours	72 hours	96 hours
	Mg./10 g. oil			
Oil A	0	0	3	42
Oil A + 0.25% phosphorus inhibitor	14	20	29	55
Oil A + 0.50% phosphorus inhibitor	23	40	51	74
Oil A + 1.0% phosphorus inhibitor	27	41	53	72

In engine tests, oil is subjected to very high temperatures on the piston walls and in the ring grooves. It is generally thought that a large part of oil deterioration in the engine takes place in the region of these local high temperatures, rather than in the crankcase. The Indiana test was modified so that a small part of the oil was continuously subjected to a metal surface at a considerably higher temperature than the bulk of the oil. However, no favorable change in test results was noted.

Aeration is obtained in the engine not by blowing a stream of air through the oil, as in the Indiana oxidation test, but by beating the air into the oil through the action of the rapidly turning crankshaft and by further contact of air with the oil in the splash or forced-feed lubrication system. The conditions are such in the engine that the volatile oxidation products are to a large extent retained in the oil. The importance of this factor was first emphasized in relation to bearing corrosion by Davis (*2*). As a first means of evaluating the importance of this factor, Indiana oxidation tests were run on the control oil and on the compounded oils, in which the volatile products were returned to the bulk of the oil by means of a condenser. Test results were unsatisfactory and similar to those obtained from the regular Indiana oxidation test. However, an interesting observation was made when this type of test was run with copper wire in the condenser. The volatile products from the control oil rapidly attacked the copper, even at the relatively low temperatures prevalent in the condenser, causing the formation of green copper soaps; whereas the oil containing the sulfurized inhibitor gave off an appreciable amount of hydrogen sulfide, coating the copper and preventing the attack of the copper by the volatile oxidation products. This would explain the failure of the addition of metallic catalysts to the regular Indiana oxidation test to accelerate deterioration significantly and to show the inhibited oil in a favorable light. Blowing with air removes the volatile oxidation products before they have a chance to exert their effect on the metallic catalysts and thus the full harmful effect of the metal catalysts is never experienced.

As an alternative method of keeping the volatile oxidation products in the oil, tests were devised wherein the oil was aerated by rapid stirring, rather than by blowing with air.

In the test conditions hereinafter referred to as the Indiana stirring oxidation test, the following test conditions have been used:

Sample, 250 cc. of oil in a 500-cc. tall-form beaker
Temperature, 165.5° C. (330° F.)
Catalyst, 32.26 sq. cm. (5 sq. inches) of copper surface, 64.52 sq. cm. (10 sq. inches) of iron surface
Aeration, stirring at 1300 r. p. m. with a glass stirrer (two blades, rounded, 2 × 2 cm., at a 40° pitch)

Figure 1 is a diagrammatic sketch of the apparatus used. Actually the oil bath is arranged so that fan tests can be run simultaneously. It is necessary to keep the oil bath at 341° F. to maintain the oil in the test beaker at 330° F.

This test shows that the compounded oil is appreciably better than the control oil and that greatly accelerated deterioration of the control oil has occurred. Results of the Indiana stirring oxidation test on these oils are shown in Table IV.

In the Indiana stirring oxidation test, four deterioration products of the oil are measured. The viscosity, sludge, and acidity values are self-explanatory, as shown in Table IV. The varnish values are obtained by suspending glass rods in the oils under test. One rod is removed every 24 hours, rinsed with naphtha, carefully wiped free of any loosely adhering sludge with cotton, and visually compared to a set of ten standard varnish rods. A rating of 10 signifies a perfectly clean, varnish-free rod; a rating of 1 signifies a rod heavily coated with varnish. Intermediate ratings signify varnish to an extent represented by the proximity of the rating to 10 or 1.

In Table IV it may be noted that the addition of the inhibitor alone causes greatly improved over-all stability. A further addition of the detergent causes still greater improvement in varnish, but has a slight detrimental effect on acidity and viscosity development. However, some detergents, in addition to improving varnish characteristics, actually cause an improvement in the over-all stability of the oil.

It was realized that a laboratory test correlation with engine performance, based on one short series of oils, was of little importance if not supported by further data. Numerous accelerated engine stability tests had shown that a particular phosphorus-type inhibitor caused improved performance as regards engine cleanliness and oil stability in proportion to the concentration of the inhibitor used. This improved performance was certainly not predicted by Indiana oxidation tests as shown in Table V. However, when this series of oils was run in the Indiana stirring oxidation test, the oils showed improved stability in all respects in proportion to the amount of inhibitor used (Table VI).

Table VI. Effect of Various Concentrations of Phosphorus Inhibitor

[Indiana stirring oxidation tests. Summarized test conditions: 500-cc. beaker, 250 cc. of oil, 5 sq. inches of Cu, 10 sq. inches of Fe, 1300 r. p. m., 165.5° C. (330° F.)]

	Increase in Saybolt Viscosity at 100° F. in 48 Hours	Sludge			Acidity			Varnish Equivalent to Standard Rods		
		24 hours	48 hours	72 hours	24 hours	48 hours	72 hours	24 hours	48 hours	72 hours
	Sec.	*Mg./10 g.*			*Mg. KOH/g.*					
Oil A	1210	356	958	...	6.8	10.2	...	5	2	...
Oil A + 0.25% phosphorus inhibitor	833	56	420	730	4.5	5.6	...	6	2–3	...
Oil A + 0.50% phosphorus inhibitor	758	26	320	600	2.3	4.0	...	8	3	...
Oil A + 1.0% phosphorus inhibitor	116	8	12	20	0.8	1.5	2.1	10	9	9

Table VII. Comparison of Tests on the Control and Inhibited Oils with and without Metal Catalysts

[Indiana stirring oxidation tests. Summarized test conditions: 500-cc. beaker, 250 cc. of oil (5 sq. inches of Cu, 10 sq. inches of Fe)[a], 1300 r. p. m., 165.5° C (330° F.)]

		Saybolt Viscosity, 100° F., Increase		Sludge				Acidity				Varnish Equivalent to Standard Rods			
	Catalyst	48 hours	96 hours	24 hours	48 hours	72 hours	96 hours	24 hours	48 hours	72 hours	96 hours	24 hours	48 hours	72 hours	96 hours
		Sec.	*Sec.*		*Mg./10 g.*				*Mg .KOH/g.*						
Oil A	No metals	160	221	0	0	0	0	0.8	1.0	1.1	1.1	10	10	10	9
Oil A	With metals	1210	...	356	958	...	...	6.8	10.2	...	...	5	2	...	...
Oil A + 3.0% sulfurized saponifiable additive	No metals	220	...	...	285	399	...	...	1.7	5.6	...	...	9	7-8	...
Oil A + 3.0% sulfurized saponifiable additive	With metals	253	...	29	150	310	...	2.2	2.8	7.5	...	9-10	8	6	...

[a] Used only in tests specified as containing metals.

Theoretical

Because of the need for the use of this test as a practical tool, it has been impossible to investigate the test variables as completely as would be desirable from a scientific viewpoint. However, sufficient background has been obtained to make possible some generalizations regarding what factors are important in the test.

It is not immediately apparent why the stirring test in the presence of metals causes more rapid deterioration than a blowing test at approximately the same temperature, and why it reverses the rate of deterioration observed in blowing tests on uninhibited and sulfur-inhibited oils.

The first natural assumption would be that the rate of deterioration is tied in very closely with the rate of oxygen absorption. This is true only in part in the tests under consideration. Addition of either copper or iron catalysts does cause an increased rate of oxygen absorption, using either the blowing or stirring methods of aeration. The increase is much less where the sulfur inhibitor is present. However, the more rapid rate of deterioration in stirring tests in the presence of metals, compared to that observed in blowing tests in the presence of metals, is not explained by increased oxygen absorption. Oxygen absorption tests were run on the uninhibited oil at 171.7° C. (341° F.) in the presence of the same ratios of metals as used in the Indiana stirring oxidation test with (*a*) aeration by blowing as in the Indiana oxidation test, and (*b*) aeration by rapid stirring as in the Indiana stirring oxidation test. These tests showed essentially the same rate of oxygen absorption in both cases and, in fact, even a slightly lower rate when the stirring technique was used. It seems indicated from somewhat limited data that the more rapid deterioration in the stirring test must be explained by secondary reactions rather than by the primary reaction involving the rate of oxygen absorption.

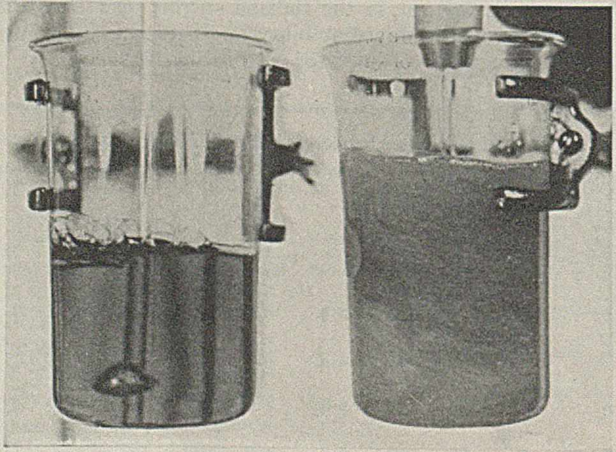

Figure 2. Bubbles in Air-Blowing and Stirring Tests

A logical possibility is that the stirring causes the volatile oxidation products to be retained in the oil for a relatively longer period of time than in blowing tests and that this allows secondary reactions to occur. An examination of the actual mechanics of aeration by stirring compared to aeration by blowing is of interest in this respect. Figure 2 gives an indication of the size of the bubbles involved in an air-blowing test compared with the bubbles in the stirring test.

Since the volatile oxidation products are removed by the bubbles rising through the oil and escaping to the air, the extent of the contact of these gaseous products with the oil and metal catalysts is determined by the surface of the bubbles and by their rate of escape. A rough calculation shows that in stirring tests the gaseous products are in contact with the oil at least several thousand times as long as in blowing tests.

Assuming that this effective retention of volatile products is significant, it still remains to be explained in what way volatile products accelerate deterioration. The first possibility is that, neglecting the presence of the metals, the volatile products react with themselves or with the nonvolatile fraction of the oxidized oil to form the measurable deterioration products. The other possibility is that the volatile products in contact with the metal catalysts undergo secondary reactions, possibly through actual chemical combination with the metal, to give deterioration products. The data in Table VII show that the presence of the metal is necessary for accelerated deterioration of the uninhibited oil to occur and for rating uninhibited *vs.* inhibited oils in accordance with engine performance.

The above facts lead to the generalization that accelerated deterioration of an uninhibited oil in the Indiana stirring oxidation test is due mainly to the effective retention of volatile oxidation products which undergo secondary reactions in the presence of metallic catalysts to cause the formation of the conventionally measured deterioration products, such as sludge, varnish, etc. The relatively good performance of the sulfur-inhibited oil in the same test is apparently due to the deactivation of the metal catalyst by the inhibitor, or to the effects of the inhibitor upon the secondary reactions.

The same generalizations, concerning the relative performance of an uninhibited and a sulfur-inhibited oil in engine tests, are probably applicable. In the engine, the volatile oxidation products are to a large extent retained in the oil and freely contact the extensive metal surface exposed.

Effect of Variables in Test Conditions

Some of the variables in the test conditions have been examined briefly from the standpoint of obtaining orientation as to their effect on rate of deterioration. Stirring speed, amount and type of metallic catalyst, stirring blade pitch and size, and temperature would all be expected to affect the

Table VIII. Effect of Change in Test Conditions on Deterioration of Control Oil

[Indiana stirring oxidation tests. Test conditions: (unless otherwise specified) 500-cc. beaker, 250 cc. of oil A, 5 sq. inches of Cu., 10 sq. inches of Fe, 1300 r. p. m., 165.5° C. (330° F.)]

Change in Test Conditions	Increase in Saybolt Viscosity at 100° F., in 48 Hours	Sludge			Acidity			Varnish Equivalent to Standard Rods		
		24 hours	48 hours	72 hours	24 hours	48 hours	72 hours	24 hours	48 hours	72 hours
	Sec.		*Mg./10 g.*			*Mg. KOH/g.*				
No change	1210	356	958	...	6.8	10.2	...	5	2	...
Both metal catalysts omitted	160	0	0	0	0.8	1.0	1.1	10	10	10
Copper omitted	135	0	34	40	0.8	1.7	2.8	10	7	4–5
Iron omitted	1212	705	951	...	6.7	9.5	...	1	1	...
Propeller pitch lowered from 40° to 20°	670	147	820	1140	2.8	6.7	10.4	5	2	...
Stirring rate lowered to 760 r. p. m.	241	118	176	...	1.1	2.8	3.8	9–10	6–7	3
Stirring rate raised to 1740 r. p. m.	2630	327	963	...	8.8	19.0	...	1	1	...

rate of deterioration. Table VIII shows the effect of changes in test conditions. As indicated previously, in the absence of any metallic catalyst, the test is not an accelerated test. In the presence of metallic iron alone as catalyst, the test is somewhat accelerated over that in which no metallic catalyst at all is used, but does not compare with the rate of deterioration noted when copper is present. Stirring with either a low-pitch propeller or at decreased r. p. m. markedly lowers rate of deterioration, and, conversely, increasing the r. p. m. of the stirring rate markedly accelerates deterioration. Since the test results do depend closely on all the test variables, extreme care must be taken to ensure reproducibility of results. However, even in crude form, the test is valuable for showing the marked improvement caused by adding suitable additives to oils.

Application of Stirring Technique to Study of Bearing Corrosion

The stirring test technique has also been found suitable for the investigation of bearing corrosion. Owing in all probability to the more effective retention of the corrosive volatile oxidation products, stirring corrosion tests show much more rapid corrosion than corrosion tests involving aeration by blowing. For example, a section of a cadmium-silver bearing suspended in oil A, under the Indiana oxidation test conditions, shows corrosion only after 80 to 90 hours. Under Indiana stirring oxidation test conditions, appreciable corrosion occurs in less than 20 hours.

The corrosion of copper-lead bearings, even under Indiana stirring oxidation test conditions, did not proceed rapidly. In most cases, after a small amount of initial corrosion, the corrosion stopped entirely. It was assumed that in the case of the more stable oils only the lead was attacked, and that continued corrosion did not occur because only a very small amount of lead could easily contact the oil. In the low stability oils, sufficient corrosive products are formed to corrode the copper, in which case corrosion of the copper-lead bearings proceeds as is expected.

Therefore, in most cases, the corrosion loss of a lead strip has been measured rather than that of a copper-lead bearing.

Table IX. Application of Indiana Stirring Oxidation Test to Study of Bearing Corrosion

[Test conditions: lead strip (7 sq. cm. surface) and section of Cu-Pb bearing (5 sq. cm. surface) suspended in oil oxidizing under Indiana stirring oxidation test conditions (additional Cu and Fe catalysts omitted)]

Oil	Lead Strip Corrosion Loss				
	0–1 hour	1–2 hours	2–3 hours	3–4 hours	4–20 hours
			Mg./10 sq. cm. surface		
A	2.3	3.4	9.6	25	530
C	0.4	1.7	11.0	38	554
D	0.6	2.4	12.1	43	1340
E	0.7	0.6	1.0	1.0	67
F	0.4	0.3	0.3	0.4	3.1
G	13.7	7.6	7.7	6.0	15.2
H	30.0	7.3	2.1	1.4	21
I	12.6	9.0	5.7	3.1	42
J	0.9	1.0	1.0	3.1	13
K	11.4	50	46	44	935

Typical lead strip corrosion data are shown for a few oils in Table IX.

Samples A, C, and D represent oils which are not particularly stable toward corrosion caused by oxidation of the oil, although they are probably sufficiently stable for ordinary automotive use. Oils E, F, and J are highly stable toward corrosion and are probably suitable in this respect for heavy-duty service. Oils G, H, and I represent products which are inhibited toward corrosion due to oxidation, but which cause corrosion in the early stages of the test. This is thought to be caused by the acidic nature of the inhibitor itself. It is possible that these oils in long contact with hard metal bearings would cause a harmful amount of corrosion. Oil K contains an additive which is not only corrosive itself but accelerates oxidation of the oil and the corrosion caused thereby.

Thus the stirring corrosion test is not only useful in showing corrosion tendencies due to oxidation of the oil, but also measures the slower corrosion caused by the corrosive nature of the additives themselves.

Value of Stirring Test Technique

This paper is not meant to bring forward a standardized or uniformly applicable laboratory test technique for the evaluation of the oxidation stability of lubricating oils. Rather it means to emphasize the importance of a combination of several oxidation conditions which exist in engine operation, and which are believed to contribute largely toward the extent and nature of oil deterioration in the engine. It is believed that any successful laboratory test should provide for effective retention of volatile oxidation products and contact of these products with metallic catalyst, and that the stirring technique provides the most convenient method for obtaining this effect. Admittedly, in the test described above, some of the conditions are arbitrarily chosen. However, retaining the essential features of the test, it should be possible to select other test variables so that the test is applicable for predicting performance under a wide variety of engine conditions, although it is agreed that the only final evaluation of a crankcase oil is its performance in engines in actual service. It is also believed that the essential features of the test not only may be applicable to the evaluation of crankcase oils, but also may be suitable for predicting performance of industrial oils, turbine oils, and other circulating oils.

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Viscosity Determination of Cellulose

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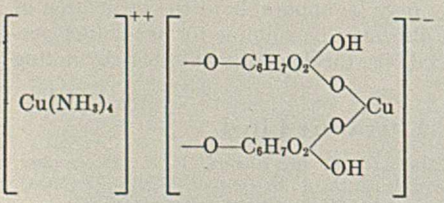
The constitution of cuprammonium cellulose and the ammonia partial pressure of different copper-ammonia compounds with and without the addition of salts have been investigated, as has the influence of oxygen on cuprammonium cellulose solutions. These solutions absorb oxygen, especially quickly in the presence of mercury, and the consequent strong reduction of the viscosity of the cuprammonium cellulose solution makes this method uncertain.

In the viscosity determination of cellulose by its conversion into nitrates the nitration is carried out with phosphoric or glacial acetic acid containing mixed acids. A quick process for nitration and stabilization is described, which produces very little degradation of cellulose and gives easily reproducible results.

THE relationship between the micelle (molecular) weight of cellulose and the viscosity of derivatives has been studied for more than 30 years (*2, 4, 8, 13, 15, 17–22*) with more or less success. To determine the viscosity of cellulose the Ost method (*19*), based on its transformation into cuprammonium cellulose, with different modifications, such as that of the Hercules Powder Company (*14*), is used. The author in 1909 (*2*) and in many publications thereafter used conversion into cellulose nitrates for determining the viscosity of cellulose compounds.

The following study has been made to show that the cuprammonium method described by Ost (*19*) has many disadvantages and should be replaced by improved methods. It is known, especially through the research work of Traube (*23*) and Hess (*15, 16*), that cuprammonium cellulose solutions or swellings contain an alcoholate in which the copper is bound partly as a cation and partly as an anion according to the formula:



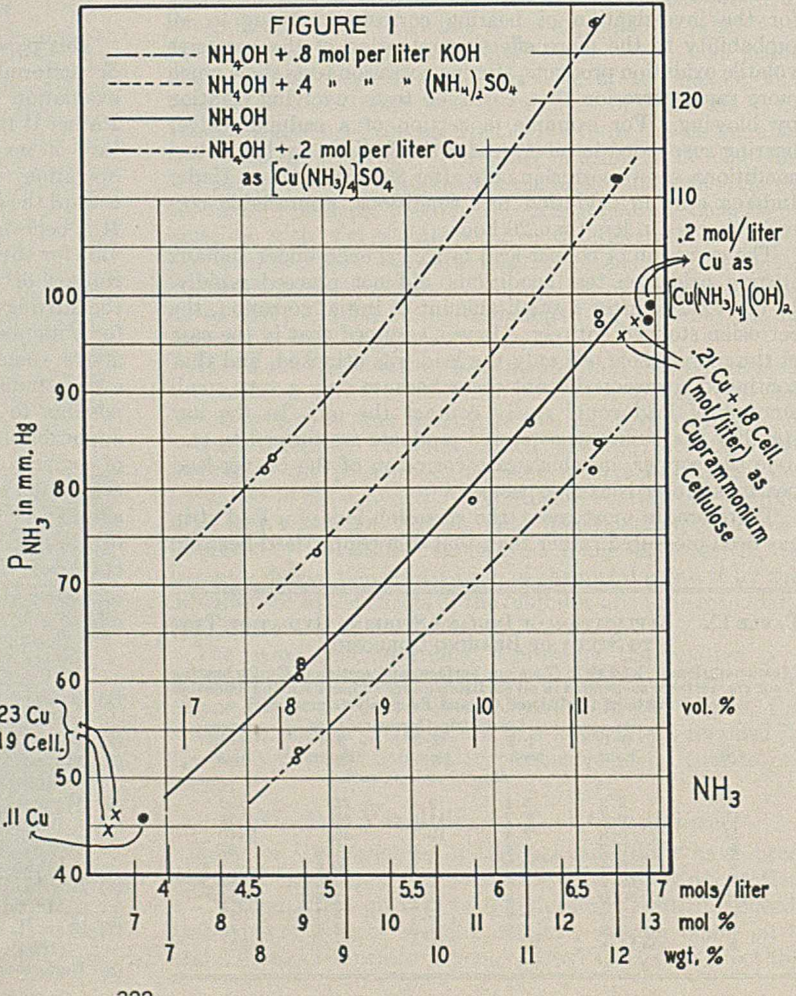
With his collaborator Innes (*7*), the author tried to get some insight into the composition of these copper cellulose solutions by determining the ammonia vapor pressure over cuprammonium and cuprammonium cellulose solutions. The results are reproduced in Figure 1.

Unfortunately on account of compensation phenomena—salting-out effects and stronger absorption of ammonia—it is impossible to determine in this way whether an increase in ammonia concentration really takes place when cellulose forms this alcoholate. It would necessarily occur if, according to Traube (*23*), 4 moles of ammonia are set free from the cuprammonium compound which furnishes the aniogen-bound copper atom. Observations in industry seem to show that by the dissolution of cellulose in cuprammonium a certain amount of ammonia is set free, so that the addition of more copper hydroxide and, therefore, of cellulose is made possible.

Figure 2 shows the different light absorption of solutions of copper tetrammino sulfate, cuprammonium, and the copper cellulose compound. The complex sulfate which does not dissolve cellulose has a different composition from the cuprammonium solution and the copper cellulose compound.

With Innes (*7*) and A. B. Cramer experiments were carried out which show how quickly cuprammonium cellulose solutions change their viscosity if they come in contact with oxygen. Oxygen is absorbed quickly, especially in the presence of mercury.

Figure 3 shows the apparatus which has been used.



Two Erlenmeyer flasks, wrapped in black paper to avoid the influence of light, were fixed on a noiseless shaking machine constructed by the author and his collaborators (*11*). The flasks contained the copper cellulose solution with 2.62 per cent of cellulose. In one flask some mercury was added. These flasks were connected with burets which allowed the measurement of quantity and speed of absorption of oxygen. Samples were taken from the flask and their viscosity was measured in an Ostwald viscometer.

Figure 4 shows the rate of absorption of oxygen by copper cellulose solutions and their change in viscosity with time. The solutions of cuprammonium cellulose absorb oxygen rather quickly. A quick reduction of the viscosity of the copper cellulose solution takes place. Combined with this oxygen absorption is a very strong degradation of the dissolved cellulose. Part of the oxygen is used to degrade and oxidize cellulose and its degradation products. Part of the oxygen transforms the ammonia into ammonium nitrite which is partly decomposed in alkaline medium with formation of free nitrogen, and partly oxidized with formation of ammonium nitrate.

In one experiment during the treatment of cuprammonium free of cellulose with oxygen 13.8 per cent of the ammonia was oxidized to ammonium nitrite according to the reaction: $2NH_3 + 1^1/_2O_2 = NH_4NO_2 + H_2O$. In this experiment 1137 ml. of oxygen were absorbed. The nitrogen present in the oxygen (about 4 per cent nitrogen) was taken into account. By the decomposition of ammonium nitrite 94.5 ml. of nitrogen were formed according to the reaction: $NH_4NO_2 = N_2 + 2H_2O$.

It can be seen from Figure 4 that the viscosity of cuprammonium cellulose solution is reduced to one half in the absence of mercury after 3.33 hours, and in the presence of

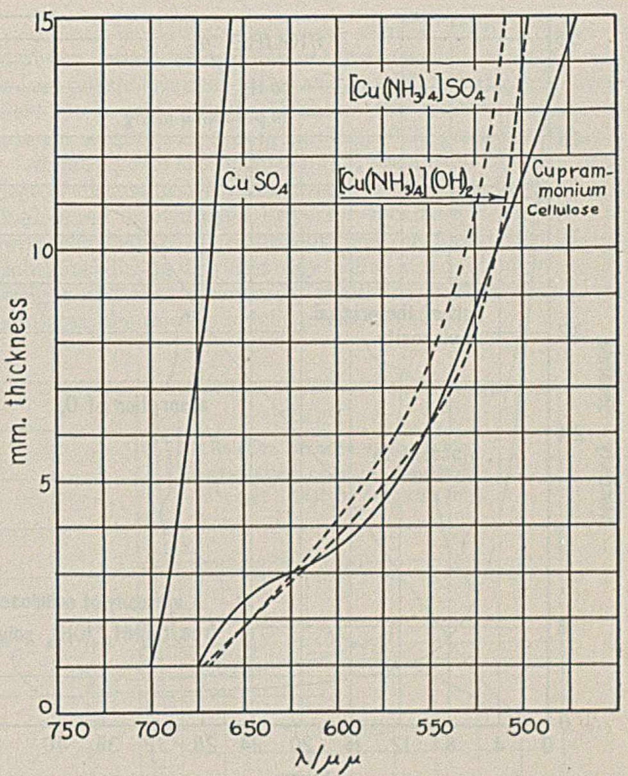


Figure 2. Light Absorption of Solutions of Copper Tetrammino Sulfate, Cuprammonium, and Copper Cellulose Compound

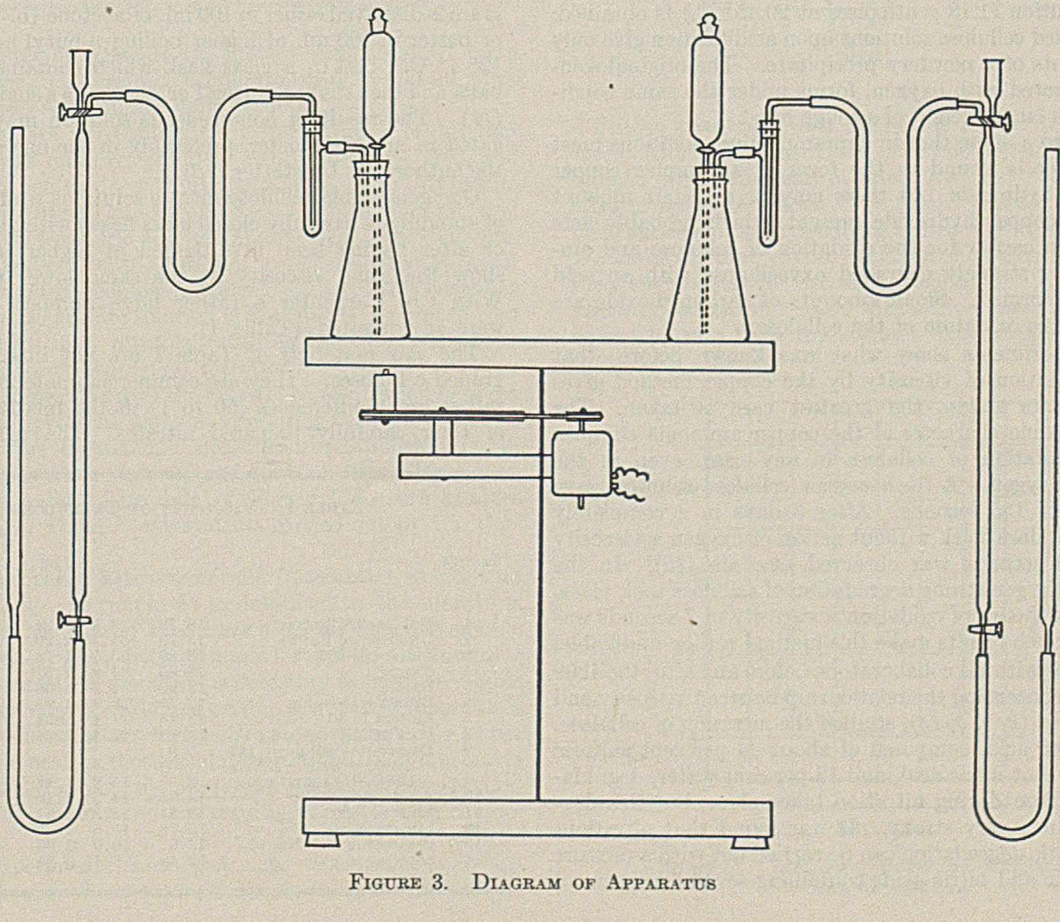
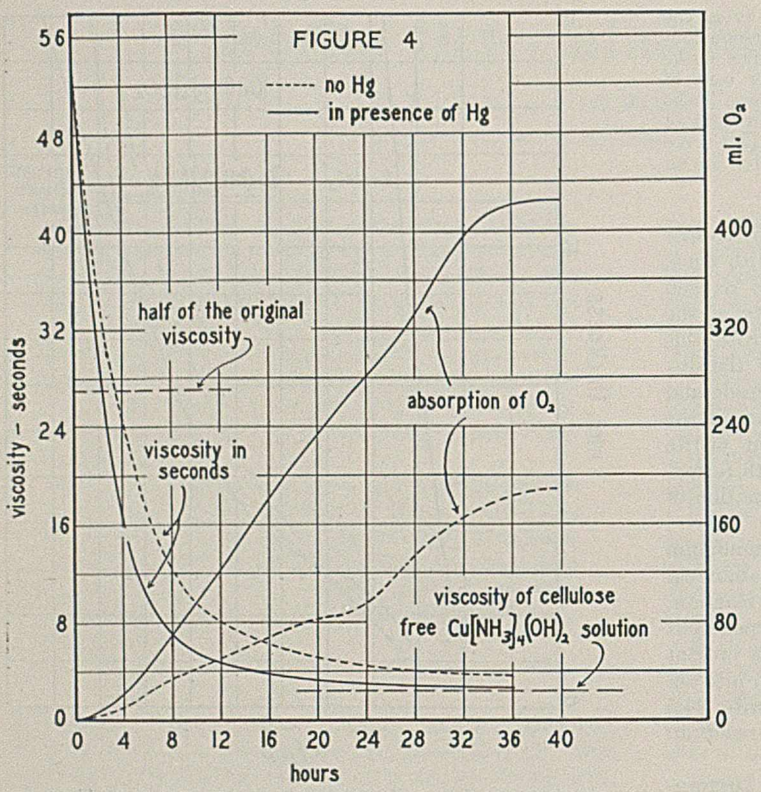


Figure 3. Diagram of Apparatus



mercury after 2.5 hours. After 24 to 36 hours the degradation of cellulose and the decrease in viscosity are so advanced that practically the viscosity of the cellulose-free cuprammonium solution (1.18 centipoises at 20.45° C.) is obtained. Those oxidized cellulose solutions upon acidification give only small amounts of a powdery precipitate. The original solution, not treated with oxygen, forms under the same conditions a much larger weight of a tough film.

We have to assume that in cuprammonium solutions most of the copper is bound in the form of a complex copper tetrammino hydroxide, but there may be a certain amount of colloidal copper hydroxide present, which probably acts as an oxygen carrier for the oxidation of cellulose and ammonia. Very strongly degraded oxycellulose with an acid character is formed. Small amounts of carbon dioxide are formed by this oxidation of the cellulose.

These experiments show what was known before—that the determination of viscosity by the copper method gives unreliable data unless the greatest care is taken. The strongly alkaline character of the copper ammonia complex causes degradation of cellulose in any case, even in the absence of oxygen. A fresh copper cellulose solution gave a viscosity of 155 seconds. After 3 days in a completely filled, closed, dark flask without action of oxygen a viscosity of only 130 seconds was observed (see also *19*). In the presence of oxygen strong degradation of cellulose took place. After several hours of oxidation a viscosity of 7 seconds was observed. Such results make this method rather unreliable.

The author with his collaborators, before and after the 1909 publication concerning the relationship between viscosity and micelle weight (*2*, *3*, *6*, *13*), studied the nitration of cellulose. With a mixed acid, composed of about 44 per cent sulfuric acid, 44 per cent nitric acid, and 12 per cent water, degradation of cellulose during nitration takes place, but this degradation is not very strong. It was found that nitrations with very little degradation can be carried out with a mixture of phosphoric and nitric acids containing several per cent of free phosphorus pentoxide—for instance, with mixtures containing 50 to 60 per cent of nitric acid, 25 to 35 per cent of phosphoric acid, and 5 to 15 per cent of phosphorus pentoxide. With Rueff (*10*) and W. L. C. Hui, the author has shown that such mixtures nitrate cellulose in less than 5 minutes to very high nitrogen contents, up to 13.8 to 13.9 per cent of nitrogen. Similar results can be obtained by a quick nitration of cellulose (lasting less than 5 minutes) with mixtures of water-free nitric acid and water-free glacial acetic acid containing 80 per cent nitric acid and 20 per cent acetic acid. Those experiments were carried out with Smith (*12*) and Ch. Carpenter. Nitrates with about 13.80 per cent nitrogen are obtained. Both mixed acids can be used at room temperature. After as much as possible of the adhering spent acid has been pressed from the nitrated material, this material is introduced into an excess of cooled (−10° to −30° C.), diluted alcohol (1 to 1), washed several times with this 45 to 50 per cent alcohol, boiled 3 times with 96 per cent alcohol for 5 minutes, and squeezed out after each boiling.

The whole operation—nitration and stabilization—takes about 45 minutes and forms highly nitrated, clear soluble cellulose nitrates of high stability. After stabilization the alcohol may be replaced by ether (free of acid and peroxides), which is removed in an evacuated apparatus at room or somewhat elevated temperature. This drying operation also is finished in a very short time, giving a somewhat hygroscopic dry material. Of this, 0.25 gram is dissolved either in 100 ml. of acetone (b. p. 56.5° C.), or better in 100 ml. of higher boiling *n*-butyl acetate (b. p. 125.1° C.), best in a glass flask which contains some glass balls, and then shaken during 1 or 2 hours on a shaking machine (*11*). The resulting homogeneous solution may be investigated in any viscometer, preferably in the one described by the author and Umstätter (*13*).

One gets stable cellulose nitrate solutions which after days of standing in carefully closed glass flasks with glass stoppers, or after having been investigated at higher temperatures, show the same viscosity at the same lower temperature. With Ch. Carpenter a rather large number of materials were investigated (Table I).

The raw materials of Table I are not intentionally degraded celluloses. They are commercial materials, but show rather great differences (50 to 1) in the relative viscosities of their carefully prepared nitrates. The values for un-

Table I. Viscosity of Cellulose

Sample No.	Material	N %	η rel.	Log η rel.	Viscosity of 0.25% Nitrate Solution in *n*-Butyl Acetate *Centipoises*
1	Unbleached linters	13.76	173.8	2.24	134.4
2	Unbleached linters	13.79	158.5	2.20	122.5
3	Linters N-500	13.80	60.3	1.78	46.6
4	Ramie	13.86	37.2	1.57	28.75
5	Ramie	13.92	36.3	1.56	28.1
6	Brown wood pulp	13.70	26.9	1.43	20.8
7	Linters N-30	13.86	17.4	1.24	13.44
8	Pure cellulose wood pulp	13.72	17.4	1.24	13.44
9	Dynamite cellulose (nitrated with HNO_3-H_2SO_4-H_2O mixture)	12.3	15.2	1.18	11.75
10	Sulfite wood pulp	13.65	14.5	1.16	11.2
11	Linters 1000	13.84	12.8	1.11	9.9
12	Linters N-10	13.78	11.5	1.06	8.7
13	Guncotton (see No. 9)	13.6	10.0	1.00	7.73
14	Soda wood pulp	13.43	3.47	0.54	2.65

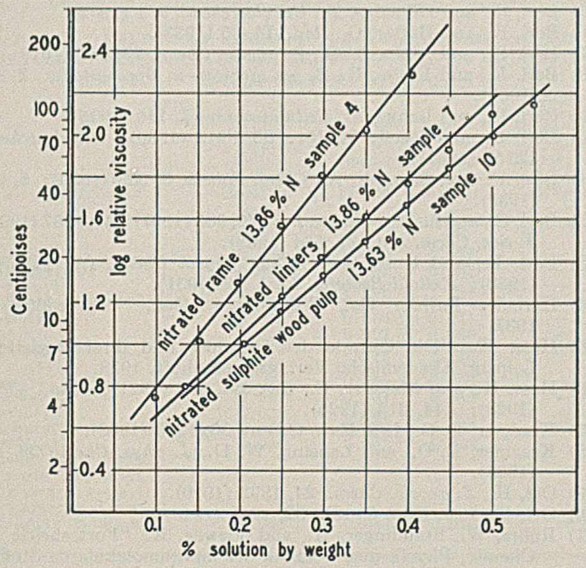


Figure 5. Relationship between Concentration and Relative Viscosity of Cellulose Nitrates Produced by Phosphoric-Nitric Acid Nitration

t, 25° C.
Solvent, n-butyl acetate (0.773 centipoise)

Table II. Viscosity of Nitrate Solutions

	Ramie N %	Ramie η rel.	Linters N %	Linters η rel.
H_3PO_4, P_2O_5, HNO_3	13.9	37	13.8	13
CH_3COOH, HNO_3	13.6	34	13.6	13
H_2SO_4, H_2O, HNO_3	13.6	20	13.6	10

bleached linter nitrates are the highest ever obtained for a 0.25 per cent (0.25 gram of cellulose nitrate in 100 ml. of n-butyl acetate) solution in n-butyl acetate.

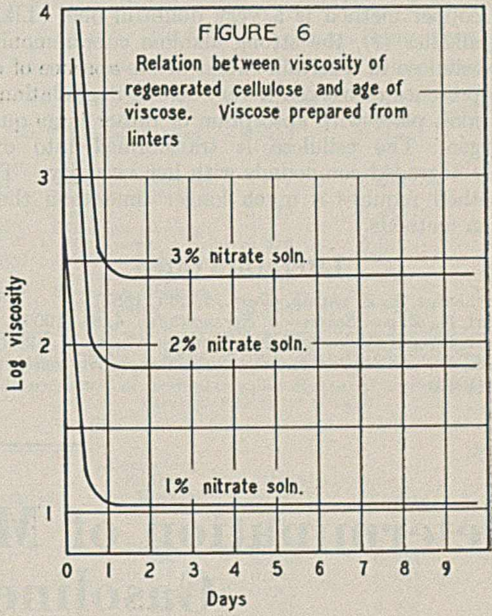
All these data were obtained by the nitration of different celluloses with mixtures of nitric acid, phosphoric acid, and phosphorus pentoxide with the exception of the dynamite cellulose (No. 9) and guncotton (No. 13) which were nitrated with nitric acid–sulfuric acid–water mixtures. The dynamite cellulose nitrates (No. 9) until now were considered as rather slightly degraded cellulose nitrates. The relative viscosity of their n-butyl acetate solution is less than 9 per cent of that of unbleached linter nitrates, resulting from the phosphoric acid (phosphorus pentoxide) nitration.

Figure 5 shows that over the range of concentration between 0.2 and 0.45 per cent and for viscosities between 8 and 80 centipoises the logarithmic Berl-Bütler relationship (*1*, *4*, *13*) between relative viscosity and concentration—log $\eta_{rel.} = k \times C$—is valid. The data of Figure 5 concern samples 5, 7, and 9 of Table I (experiments carried out by Ch. Carpenter).

The relationship between micelle (molecular) weight and viscosity is not so simple as is described in the literature. The author has reason to believe that all derivatives of a nondegraded or very little degraded cellulose are insoluble and that a certain degradation is necessary to produce soluble cellulose derivatives. He has produced at low temperatures insoluble cellulose nitrates with nitrogen contents up to 13 per cent. Upon heating those insoluble esters with water in sealed glass tubes at 135° C., the nitrogen content decreases several tenths of a per cent and the resulting nitrates are acetone-soluble.

These experiments show that a small degradation (compared with one which occurs during nitration with sulfuric acid–nitric acid–water mixtures) results when cellulose of different origin and different treatment is nitrated with mixed phosphoric acid–nitric acid or with mixed glacial acetic acid–nitric acid. Table II shows the relative viscosity of nitrate solutions in n-butyl acetate (0.25 gram per 100 ml.).

About 3 years ago in Pittsburgh, the author had the privilege of discussing with The Svedberg of Upsala his important high-speed centrifuge. Professor Svedberg told him that with the help of his ultracentrifuge he found that viscose solutions during the first day show a reduction in micelle weight and that afterwards, until this viscose solution coagulates, the micelle weight remains constant.



Fifteen years ago with Lange the author (*9*) studied viscose. After different time intervals carefully coagulated samples were dried and nitrated, and the viscosity of those nitrates was determined. The results (Figure 6) are in complete agreement with Svedberg's ultracentrifuge observations. We know (*5*) that viscose solutions show first a decrease and then an increase in viscosity (Figure 7). This increase in viscosity has nothing to do with an increased micelle weight, as can be seen from the author's experiment, but is due to

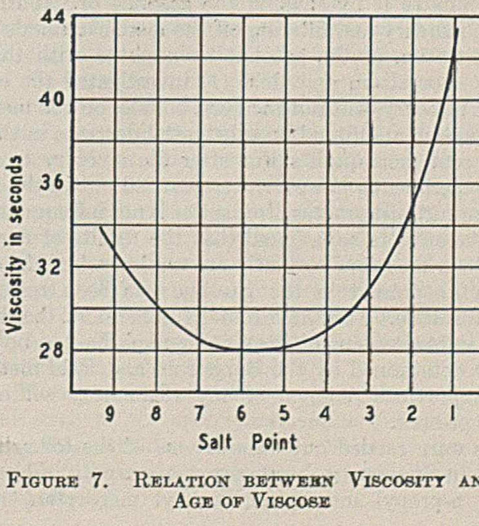


Figure 7. Relation between Viscosity and Age of Viscose

the formation of a gel structure. The decrease in viscosity is a function of degradation and desolvation.

These newer nitration methods have the great advantage that they can be carried out very quickly. They give nitrates which in repeated experiments show the same viscosities of their solutions if the same cellulosic material and the same conditions of nitration are used.

Nitration, washing, drying, and dissolution of nitrates are rather harmless operations which can be carried out in every laboratory by the trained chemist and workman. The stabilized nitrates do not change their properties if kept wet in carefully closed containers. When no longer needed the nitrated material may be burned in small quantities, or decomposed by putting it into warm, strong alkali.

The copper method is a very doubtful one. Like other strong alkalies (*2*), the strong alkaline cuprammonium degrades cellulose to a certain extent in the absence of oxygen. In the presence of oxygen a very strong degradation of cellulose takes place with absorption of rather large quantities of oxygen. The cellulose is transformed into oxidized, strongly degraded compounds with low viscosity. The copper method requires a much longer time than the newer nitration methods.

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Determination of Mercaptan Sulfur Content of Gasolines and Naphthas

Effect of Mercuric Sulfide and Elementary Sulfur

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THE mercaptan sulfur content of gasoline or naphtha is usually determined by titration using silver nitrate (*3*), ammonium thiocyanate, and ferric alum indicator. When elementary sulfur is present in the sample it is common practice to remove it by shaking the gasoline or naphtha with metallic mercury and filtering off the mercuric sulfide formed before titration of the gasoline or naphtha with the silver nitrate. Borgstrom and Reid (*1*) investigated the effect of metallic mercury, but not mercuric sulfide, on the mercaptan determination and found no substantial decrease in the value for per cent mercaptan sulfur after the mercury treatment. These experiments, however, were carried out in the absence of free sulfur. In practice, free sulfur is not infrequently present. The authors have found that the results of mercaptan sulfur determinations regularly are too low when the elementary sulfur present in the gasoline has been removed as mercuric sulfide. They have found, furthermore, that the mercaptan sulfur content of gasoline or naphtha can be quantitatively determined by the Borgstrom and Reid method (*1*) without previous removal of any elementary sulfur which may be present.

Tests were carried out on solutions of the following mercaptans in Stoddard solvent: ethyl mercaptan, *n*-butyl mercaptan, *n*-propyl mercaptan, *n*-amyl mercaptan, *n*-heptyl mercaptan, benzyl mercaptan, isobutyl mercaptan, and *tert*-butyl mercaptan. A blend of equal parts of the solutions of ethyl mercaptan, *n*-propyl mercaptan, *n*-amyl mercaptan, and isoamyl mercaptan was also used in the tests. The solutions thus prepared contained 0.04 to 0.07 per cent of mercaptan sulfur. When it was desired to have elementary sulfur present in the test solution, Stoddard solvent containing 0.158 per cent of elementary sulfur was blended with the mercaptan solution.

The effect of the removal of elementary sulfur, as mercuric sulfide, on the mercaptan sulfur content of the Stoddard solvent is shown in Table I. The elementary sulfur was removed by shaking 50 cc. of the test solution with 2 cc. of metallic mercury in a 120-ml. (4-ounce) bottle for 15 minutes. The mercuric sulfide formed was removed by filtration through Whatman No. 40 filter paper.

Table I illustrates the decrease in mercaptan sulfur found in the Stoddard solvent after removal of the elementary sulfur as mercuric sulfide. It also indicates that the decrease in mercaptan sulfur content is dependent upon the particular mercaptan present and decreases with increase in the length of the hydrocarbon chain attached to the mercaptan group. Tertiary butyl mercaptan is not influenced by the mercuric sulfide.

TABLE I. EFFECT OF REMOVAL OF ELEMENTARY SULFUR BY METALLIC MERCURY ON MERCAPTAN SULFUR CONTENT OF STODDARD SOLVENT

Mercaptan	Elementary Sulfur in Test Solution	Mercaptan Sulfur Found	Mercaptan Sulfur Initially present	Change in Mercaptan Sulfur Content Due to Shaking with Metallic Mercury
	% by weight	%	%	%
Ethyl	0.006	0.060	0.075	−20
n-Propyl	0.026	0.051	0.055	− 7
n-Propyl	0.059	0.036	0.041	−12
n-Butyl	0.026	0.046	0.054	−15
n-Butyl	0.059	0.036	0.041	−12
n-Amyl	0.026	0.057	0.056	+ 2
n-Amyl	0.059	0.042	0.041	+ 2
n-Heptyl	0.059	0.039	0.039	0
Benzyl	0.026	0.054	0.053	+ 2
Benzyl	0.059	0.037	0.040	− 8
Isobutyl	0.026	0.052	0.058	−10
Isobutyl	0.059	0.039	0.043	− 9
tert-Butyl	0.059	0.043	0.043	0
Blend of equal parts of ethyl, *n*-propyl, *n*-amyl, and isoamyl mercaptan solutions	0.008	0.037	0.040	− 8

The decrease in the mercaptan sulfur content of the Stoddard solvent appears to be due to adsorption of mercaptans by the mercuric sulfide formed from the interaction of free sulfur and metallic mercury. This postulate of adsorption was tested in the following manner:

> Mercuric sulfide, which had been precipitated from aqueous mercuric chloride solution by hydrogen sulfide and was therefore free from mercaptans, was collected on a Büchner funnel, washed twice with water, with 95 per cent alcohol, and then with naphtha, after which it was shaken with naphtha containing 0.05 per cent mercaptan sulfur (present as *n*-propyl mercaptan). The mercuric sulfide was collected on a Büchner funnel, then shaken with mercaptan-free naphtha, which acquired sufficient mercaptan to give a positive mercaptan test. The presence of mercaptan was found even in a third treatment of this mercuric sulfide with fresh mercaptan-free naphtha.

These results show that some of the mercaptan which had been taken up by the mercuric sulfide was extracted by the fresh naphtha and indicates that *n*-propyl mercaptan is adsorbed by mercuric sulfide. That metallic mercury in the absence of elementary sulfur does not react with mercaptans is well known and has been confirmed by the results shown in Table II.

Any factor which favors rapid formation of mercuric sulfide, such as increasing the amount of mercury used in treatment of the gasoline or increasing the amount of sulfur in the gasoline, increases the removal of mercaptan sulfur from the Stoddard solvent. Furthermore, the authors have found that the addition of mercuric sulfide to a mercaptan solution decreased the percentage of mercaptan sulfur as found by silver nitrate titration. This is illustrated in Tables I, III, and IV.

TABLE II. EFFECT OF METALLIC MERCURY

(On determination of mercaptan sulfur content of Stoddard solvent where no elementary sulfur is present)

Mercaptan	Mercaptan Sulfur Found (after shaking with metallic mercury)	Mercaptan Sulfur Initially present	Deviation
	%	%	%
Ethyl	0.078	0.078	0
Mercaptan blend (see Table I)	0.040	0.040	0

TABLE III. EFFECT OF AMOUNT OF MERCURY AND ELEMENTARY SULFUR

(On determination of mercaptan sulfur content of Stoddard solvent)

Metallic Mercury Added to Mercaptan Blend (See Table I)	Elementary Sulfur in Solution	Mercaptan Sulfur Found	Mercaptan Sulfur Initially present	Change from Mercaptan Sulfur Initially Present
Cc.	%	%	%	%
0	...	0.040	0.040	0
1	0.008	0.038	0.040	− 5
3	0.008	0.037	0.040	− 8
6	0.008	0.035	0.040	−13
3	0.014	0.030	0.034	−12

TABLE IV. TREATMENT OF MERCAPTAN–STODDARD SOLVENT BLEND WITH 1 PER CENT OF MERCURIC SULFIDE

Mercaptan Sulfur Found	Mercaptan Sulfur Initially present	Change from Mercaptan Sulfur Initially Present
%	%	%
0.042	0.049	−14

TABLE V. EFFECTS OF VARIOUS CONDITIONS

(On determination of mercaptan sulfur content of Stoddard solvent)

Mercaptan	Condition Used	Mercaptan Sulfur Found	Mercaptan Sulfur Initially present	Change from Mercaptan Sulfur Initially Present
		%	%	%
Ethyl	Agitation with air	0.077	0.078	−1
Ethyl	Agitation with filter paper	0.079	0.078	+1
Ethyl	Filtration through filter paper	0.076	0.078	−3
n-Butyl	Agitation with filter paper	0.064	0.065	−2
n-Butyl	Filtration through filter paper	0.065	0.065	0

TABLE VI. EFFECT OF ELEMENTARY SULFUR

(On determination of mercaptan sulfur content of Stoddard solvent by titration with silver nitrate)

Mercaptan	Elementary Sulfur by Weight	Mercaptan Sulfur Found	Mercaptan Sulfur Present	Error on Basis of Mercaptan Sulfur Actually Present
	%	%	%	%
Ethyl	0.060	0.075	0.075	0
n-Butyl	0.026	0.055	0.054	+2
n-Propyl	0.059	0.042	0.041	+2
n-Amyl	0.059	0.042	0.041	+2
n-Heptyl	0.059	0.039	0.039	0
Benzyl	0.059	0.041	0.041	0
Isobutyl	0.026	0.059	0.058	+2
Isobutyl	0.059	0.045	0.043	+5
tert-Butyl	0.059	0.044	0.043	+2
Mixture of ethyl, *n*-propyl, *n*-amyl, and isoamyl mercaptans	0.008	0.040	0.040	0

That adsorption of mercaptans on metal sulfides takes place to a considerable extent has been found by Greer (*2*), who used cupric sulfide to remove mercaptans from gasoline and thus to sweeten it. Lead, stannic, cadmium, and arsenious sulfides were also found to be effective, but to a lesser degree than cupric sulfide; mercuric sulfide was not tested by Greer.

In order to be certain that adsorption on mercuric sulfide caused the decrease in the percentage of mercaptan sulfur as determined by silver nitrate titration after the removal of free sulfur, the authors investigated other factors that might be responsible for this lowering effect, such as the loss of mercaptans by evaporation during filtration of the mercuric sulfide from the Stoddard solvent, the possibility of adsorption of mercaptans by the filter paper used [tested by shaking 50 cc. of the mercaptan solution in a 120-ml. (4-ounce) bottle with strips of Whatman No. 40 filter paper], and possible oxidation by the oxygen of the air [tested by shaking the solution in a 120-ml. (4-ounce) bottle for 15 minutes]. The results obtained are shown in Table V.

All the results in Table V are within the limits of experimental error of the mercaptan sulfur determination, thus showing that agitation with air or filtration through Whatman No. 40 filter paper is without appreciable effect on the determination.

Since the authors' results indicated that there was a noticeable difference between the amount of mercaptan sulfur found after treatment of the Stoddard solvent containing elementary sulfur with metallic mercury and that amount which is actually present in the material, it is advisable not to remove the free sulfur prior to the mercaptan sulfur determination but to titrate the mercaptan sulfur present in the Stoddard solvent directly with silver nitrate. That the elementary sulfur has no effect on the determination of mercaptan sulfur in the Stoddard solvent is shown by Table VI.

The deviations from the amounts of mercaptan sulfur actually present as shown in Table VI are all within the limits of experimental error, showing that it is justifiable to determine the mercaptan sulfur content of Stoddard solvent (or other hydrocarbon material) by titration with silver nitrate without removal of elementary sulfur present in the material under test.

Where a considerable quantity of elementary sulfur is present, the color of the precipitate obtained during titration of the mercaptans with silver nitrate solution may pass through various shades of orange, red, or brown and persistent emulsions may be formed. The addition of quantities of 95 per cent alcohol as high as 100 cc. may be necessary to break these emulsions and bring the precipitate into the interface so that the color of the solution may be noted.

Summary and Conclusions

Contrary to the current practice of removing elementary sulfur by means of metallic mercury before determination of the mercaptan sulfur content of gasolines or naphthas, the determination of the mercaptan sulfur content should be made on the initial gasoline or naphtha, ignoring any elementary sulfur which may be present. Certain mercaptans are adsorbed by mercuric sulfide, resulting in such cases in low values for the mercaptan sulfur content of the naphtha which has been agitated with mercuric sulfide. Any loss of mercaptans which might take place on filtration of Stoddard solvent solutions through Whatman No. 40 filter paper or on normal agitation of such solutions with air is within the limits of experimental error of the mercaptan sulfur determination.

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Determination of Water in Benzene

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A solution of sodium triphenylmethyl in ethyl ether has been investigated as a reagent for the analysis of water in solution in benzene. The analyses have been made on samples containing a relatively small concentration of water. The color change of the reagent is used as the indicator, and relatively high precision is obtainable on low water concentrations. The reagent is suitable for the analysis of other substances.

A NUMBER of ingenious methods have been devised for the analysis of water dissolved in benzene and other organic liquids—for example, the use of calcium carbide (*3*) with the determination of the acetylene produced; the use of calcium hydride (*8*) with the determination of the evolved hydrogen; the use of alpha-naphthoxydichlorophosphine (*1, 7*) with titration of the hydrogen chloride; the use of a reagent consisting of liquid sulfur dioxide and iodine dissolved in anhydrous methyl alcohol (*4*), where the reagent reacts with water forming sulfuric and hydroiodic acids, which are caused to combine with pyridine, and the excess iodine is determined; and the determination of the solubility of silver perchlorate (*6*) which varies with the water content of benzene.

The authors have used a solution of sodium triphenylmethyl dissolved in ethyl ether for the determination of water in solution in benzene. Bent and Lesnick (*2*), who used this reagent to determine the amount of water adsorbed on glass surfaces, indicate that the partial pressure of water in equilibrium with this substance is very low and that equilibrium is reached rapidly. In order to obtain samples of benzene containing reproducible concentrations of water, a stream of nitrogen containing a known partial pressure of water was passed through dry benzene. The titration with the standardized reagent was accomplished without removing the sample from the apparatus. The standardization was also done within the apparatus by means of a sample of moist nitrogen.

Apparatus

The apparatus used is shown in Figure 1.

Tube 46 is the entry tube for dry oxygen-free nitrogen, for which three paths of travel are provided. For use in operating valves, siphons, etc., it passes through three phosphorus pentoxide drying tubes, 13, 14, and 15, each 60 cm. long and about 2.5 cm. in diameter, and then enters manifold 41. For use as a carrier gas for water vapor at its saturation pressure at 25° C. it passes through drying tube 12 and then through bubblers 1, 2, and 3 (only one shown); at other temperatures, it passes through drying tube 16 and then bubblers 4, 5, 6, 7, 8, and 9 (only one shown).

Vessels 10 and 11 are bubblers for observing the rate of gas flow. Vessels 17, 20, 21, 24, and 28 are valves containing mercury which are opened by suction or closed by nitrogen pressure from auxiliary manifold 43, vessel 38 being the mercury storage for 28. Tube 18 is the inner tube of valve 17. Tube 35 is for equalizing pressure. Vessels 47, 34, 36, 49, and 27 are mercury bubblers designed to protect stopcocks from ether and benzene vapors. Vessel 48 is a mercury bubbler to prevent water vapor from vessels 4 to 9 coming in contact with the benzene solution. In vessel 19, which has a volume of about 200 cc., water is dissolved in benzene by passing moist nitrogen through it. Mercury valve 21 serves to remove a sample from 19 and place it in the titrating vessel, 22. Storage vessel 30 with a volume of 350 cc. is for supplying the ether solution of sodium triphenylmethyl the discharge of which is through tube 31.

Buret 29, which has a volume of 22 cc., and is calibrated in 0.25 cc. divisions, contains a glass plunger, 39, which is ground to fit the lower opening of the buret. A pure gum rubber tubing gives a flexible connection at the top for operation of the plunger. The reagent flows through tube 45 and its capillary tip. Vessel 22, the titrating vessel, has the same dimensions as the buret and is calibrated in 1-cc. divisions. Tip 40 is used in the cleaning operations. Vessel 23 is a gas buret of 250-cc. volume calibrated in 5-cc. divisions, and connected to mercury storage vessel 42. Capillary tubes 26, 25, and 37 provide outlets to the atmosphere while preventing back-diffusion into the apparatus. Additional protection against back-diffusion of the atmosphere into the apparatus is provided by the connections which enable a stream of dry nitrogen to pass from manifold 41 through these outlets.

Vessels 1, 2, 3, 17, 19, 20, 21, 22, 23, and 24 with their connecting tubes were kept in a water thermostat at 25° C. It was found necessary to have two small sections of connecting tubing above the water level of the thermostat, and these were wound with resistance wire and heated to prevent the condensation of water in them.

Preparation of Materials

Nitrogen was taken from a commercial cylinder and was passed through both a tube containing copper turnings heated to 420° C. and sulfuric acid bubblers.

Thiophene-free benzene was dried differently for the different experiments (Table I). For experiments A_1 and A_2 it was allowed to stand over freshly cut sodium for 2 weeks. For experiments C_1, C_2, C_3, and C_4 it stood over a large quantity of phosphorus pentoxide for 2 weeks and was shaken frequently. For experiments E_1 to E_5, in which it was considered anhydrous, it was dried by passing the vapor slowly through phosphorus pentoxide. The apparatus for this consisted of two vertical cylindrical vessels connected by a horizontal tube wound externally with a heating coil. Both vessels and tube contained phosphorus pentoxide and each vessel could be heated. Eleven passages of the material were performed before the benzene was considered anhydrous and was transferred to the analysis apparatus. In experiments D_1 to D_4 the residual benzene from experiments E_1 to E_5 was used, and in experiments B_1 to B_4 the residual benzene from experiments D_1 to D_4 was used. In all cases the benzene was boiled to remove dissolved oxygen before drying and also before introduction into the apparatus.

Sodium triphenylmethyl solution in ethyl ether was prepared in a 200-cc. cylindrical vessel, the top of which terminated in a small-bore tube. To the side another tube was connected which terminated in a long capillary sealed at the lower end. With the vessel dry and containing oxygen-free nitrogen 175 cc. of anhydrous ether were added, followed by 35 to 45 grams of 28 per cent by weight sodium amalgam and 9 grams of triphenylchloromethane. The top tube was sealed and the vessel vigorously shaken for 5 minutes about every hour for 2 days.

Procedures

The sodium triphenylmethyl solution was introduced into storage vessel 30 through tip 32. The vessel was dried by passing purified nitrogen through it for 12 hours, tip 32 was then broken, a slow stream of nitrogen was allowed to exhaust through it, and the capillary tip of the vessel containing the reagent was opened and inserted in 32. One of the other connecting tubes of the reagent vessel was connected to a source of dry nitrogen by means of rubber tubing, and the reagent was slowly forced into 30. Tip 32 was then sealed.

The benzene was introduced in a similar manner into vessel 19 through a side tube on its top (not shown in Figure 1). The entire apparatus was evacuated before operations were started. After all vessels, connecting tubes, etc., had been dried they were filled with dry nitrogen.

The technique of operation consists of passing purified nitrogen from the manifold first through saturators and then through benzene in vessel 19. A sample is withdrawn from 19 and placed in vessel 21 by operating the appropriate mercury valves through the use of both nitrogen pressure and vacuum, and enough is forced into titrating vessel 22 for analysis. The reagent is forced into 29 in a similar manner and the titration is conducted by plunger 39. Stirring is accomplished during a titration by means of occasional passage of nitrogen from 44 through 22. The end point is judged from the first appearance of a permanent faint pink tint in the benzene.

In order to make sure that the titrating vessel is completely dry before a titration is begun, a quantity of reagent is dropped into it, allowed to stand for a few hours, and then forced out through tip 33. After a sample is titrated it is forced out through 33, and a new sample is taken from 21 for a check analysis. To establish the attainment of equilibrium this operation is repeated with further passages of wet nitrogen through the benzene. It was found that the rate of passage of the nitrogen below 5 cc. per minute had no effect on the results.

In order to standardize the reagent a known volume was placed in the titrating vessel, and nitrogen from vessel 23 containing a known partial pressure of water was slowly bubbled through it, until it just became discolored.

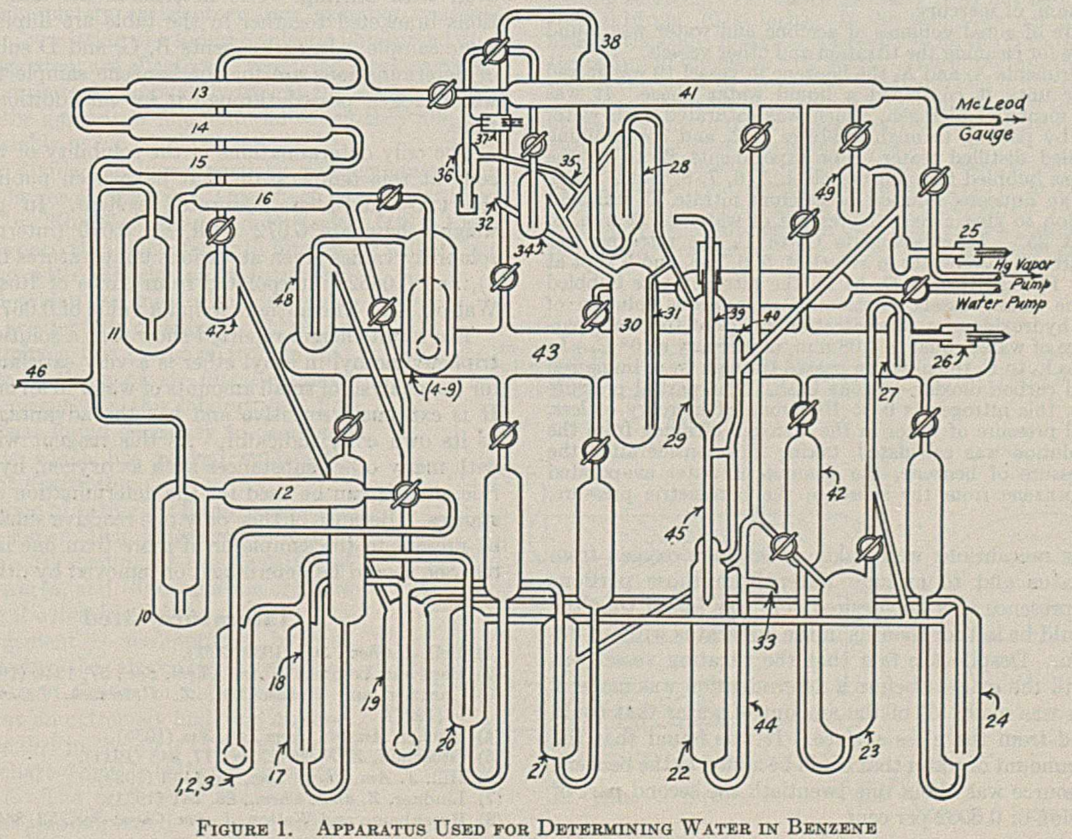

Figure 1. Apparatus Used for Determining Water in Benzene

Table I. Analysis of Water in Benzene at 25°

Experiment No.	Rate of Flow of Nitrogen	Time of Flow	Analysis		Standardization			Water in Benzene		Partial Pressures of Water	
			Volume of benzene	Volume of reagent	Volume of wet nitrogen	Volume of reagent	Water equivalent of reagent	Titration	Corrected average	Entering nitrogen	Leaving nitrogen
	Cc./min.	*Hours*	*Cc.*	*Cc.*	*Cc.*	*Cc.*	*G./cc. × 10⁻⁴*	*% by weight*		*Mm. of Hg*	
A_1	...	..	7.80	17.20	75	6.00	2.845	0.0709	...	23.517	25.51
A_2	...	...	7.80	17.27	90	7.15	2.868	0.0711	...	....	...
					93	7.23	2.822	....	0.067	....	...
B_1	2.1	48	12.04	4.27	400	10.0	9.114	0.0362	...	12.00	10.48
B_2	...	..	12.04	4.31	405	10.0	9.233	0.0365	...	....	...
B_3	...	..	12.04	4.26	...	...	....	0.0360	...	....	...
B_4	1.7	24	13.10	4.58	...	...	....	0.0357	0.032	....	...
C_1	2.3	52	12.04	1.63	347.5	7.23	10.12	0.0165	...	4.57	3.99
C_2	1.8	32	15.13	3.96	183	7.25	5.760	0.0168	...	....	...
C_3	...	..	15.50	4.05	181	7.25	5.712	0.0168	...	....	...
C_4	1.7	48	15.13	3.94	...	...	....	0.0167	...	....	...
C_5	...	..	15.20	3.99	...	...	....	0.0169	0.013	....	...
D_1	1.8	48	14.68	0.93	468	10.00	10.67	0.0076	...	1.08	0.94
D_2	...	..	15.28	1.00	473	10.00	10.73	0.0078	...	....	...
D_3	1.7	24	15.28	0.97	...	...	....	0.0078	...	....	...
D_4	...	..	15.28	1.00	...	...	....	0.0079	0.004	....	...
E_1	0	0	11.51	0.40	450	9.50	10.80	0.0042	...	....	...
E_2	...	..	23.00	0.70	473	10.00	10.82	0.0037	...	....	...
E_3	1.8	52	11.51	0.38	...	...	....	0.0039	...	6×10^{-4}	...
E_4	...	..	15.63	0.40	...	...	....	0.0031	...	....	...
E_5	...	..	15.63	0.45	...	...	....	0.0035	0.000	....	...
F	0	0	8.33	1.60	...	...	....	0.0233	0.019	....	...

Corrections, determined in two parts, were applied in the benzene titrations for the amount of reagent that would just cause the faint pink color used as the end point. First, to a sample of benzene in the titrating vessel enough reagent was added to cause a faint pink color. The sample was observed until the color had just disappeared. The amount of reagent needed to bring the color back to the shade used in the determinations was the correction applied to every titration. Because the visual observation of the disappearance of the pink color may be in error or a trace of reactive impurity other than water may be present in the benzene, a second correction was applied that is equal to the minimum value of the titration using the best drying technique. Its value was 0.004 per cent by weight.

The pure nitrogen or the exhaust from the saturators could be analyzed at any time by taking a sample in vessel 23. The purified nitrogen, when passed through a dilute sample of the reagent in the titrating vessel, completely evaporated the ether without decolorizing it. From this result it may be calculated that the partial pressures of oxygen, water, or other reactive impurities are less than an effective partial pressure of water of 1×10^{-4} mm. of mercury.

A mixture of equal volumes of acetone and water was found satisfactory for cleaning the titration and other vessels.

For experiments A_1 and A_2 the benzene in vessel 19 was mixed with water until it contained a liquid water phase. It was stirred by means of nitrogen, which was saturated with water at 25° C. by passing through bubblers 1, 2, and 3 containing freshly boiled distilled water. For experiments B_1 to B_4 the nitrogen was bubbled through vessels 4, 5, 6, 7, 8, and 9 which contained an aqueous solution of calcium nitrate of sufficient concentration to give a partial pressure of water of 12 mm. of mercury at 25°. In experiments C_1 to C_5 the nitrogen was bubbled through pure water in vessels 4, 5, 6, 7, 8, and 9 kept at 0° in ice. In experiments D_1 to D_4 the nitrogen was bubbled through the same vessels, containing an aqueous solution of potassium hydroxide of a concentration sufficient to give a partial pressure of water equal to 1.08 mm. of mercury at 0° C. In experiments E_1 to E_5 the nitrogen passed through traps immersed in a stirred carbon dioxide–acetone bath. The partial pressure of water in this nitrogen is 6×10^{-4} mm. of mercury or less. The partial pressure of water in the nitrogen escaping from the benzene solution was calculated, taking into consideration the partial pressure of benzene, the amount of water evaporated with the benzene from the solution, the barometric pressure, etc.

Rigorous precautions were taken to exclude oxygen from the apparatus and to exclude water from those portions where its presence was not desired. It was found that the reagent could be left for months in the apparatus without decolorization. Despite the fact that the titrating vessel was washed with the reagent before a determination was made, a calculation was made (*5*) of the amount of water that could be obtained from the glass surface. It was found that the maximum amount of water that could be added to the benzene from this source was about one twentieth the second part of the correction or 0.0002 per cent.

Results

In Table I are shown the results of the determination of the water content of benzene using a solution of sodium triphenylmethyl as the reagent. Experiments A_1 and A_2 give the values for benzene in contact with liquid water and saturated with it at 25° C. Experiments E_1 to E_5 give the second correction term. E_1 and E_2 were determined on benzene that had been thoroughly dried in the vapor phase, and E_3, E_4, and E_5 were checks made after nitrogen, which had been dried by passage through traps at −80° C., had been bubbled through the benzene. Experiment F was a single determination on a sample of benzene dried by standing 2 weeks over sodium and 2 weeks over phosphorus pentoxide with intermittent stirring. This shows that the liquid in contact with a drying agent is dried very slowly even with stirring. The determinations and standardizations bracketed together in the table are duplicates on the same sample. In experiments B, C, and D subsequent sets of determinations are for the benzene sample that has had wet nitrogen passed through it for an additional period of time.

The only determinations of the solubility of water in benzene at this temperature that have been published are for the two-liquid-phase saturated system. In per cent by weight these are 0.072 (Hill, *6*), 0.070 (interpolated from solubility values given at various temperatures by Groschuff, *5*), and 0.0652 (interpolated from curve of Rosenbaum and Walton, *8*). The authors found a value of 0.067.

The results herein reported show that a solution of sodium triphenylmethyl in ethyl ether is a very satisfactory reagent for the analysis of small amounts of water in an organic liquid. It is extremely sensitive and has the advantage of serving as its own color indicator. As this reagent will also react with many other substances such as oxygen, hydrogen chloride, etc., it can be used for the determination of these substances. Because of this, only one reactive substance should be present in the sample or, if more than one is present, all but one should be determined or removed by other means.

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Measuring Smokes and Rating Efficiencies of Industrial Air Filters

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To attain the extremely clean air required by some industrial processes, the ultimate in air filtration is necessary. A technique is described whereby it is possible to classify air filters critically by continuous measurement of concentrations of smokelike materials in filtered and unfiltered air. By determining density differences of impingement traces, it is possible to calculate percentage efficiencies of air filters. The apparatus consists of an impingement recorder and a photoelectric densitometer. The recorder operates continuously by impingement of air from a self-metering orifice on moving paper. The unit is readily portable.

MANY modern industrial processes must be conducted in an extremely clean atmosphere, so that the product being manufactured will remain uncontaminated or the equipment being used will continue to function well. Examples of such requirements are to be found in the photographic, optical, and communication industries. For these purposes, the air cleaned by the ordinary methods of filtration is not completely satisfactory—for example, viscous-type air filters, consisting of a liquid or plastic film spread on a surface of large area, are effective in removing large particles. In terms of percentage removal by weight the efficiency may be high, yet the amount of fine material which they allow to pass is appreciable.

Very finely divided air-borne particles will agglomerate in time to form larger aggregates. This effect has been studied scientifically by Whytelaw-Gray and Patterson (*12*). Practically, it is noticed that ducts fed with filtered air will in time become coated with particles of agglomerated finer material, which become a source of much trouble when accidentally dislodged. It is in an attempt to diminish this source of trouble that more effective methods of air filtration have been studied recently in this laboratory. For this study it was found necessary to develop a new technique which has proved sufficiently useful to merit description.

This technique of rating air filters consists of three general steps: (1) impingement of dirt on moving paper, (2) reading of the densities of the recorded traces, and (3) evaluation of filters by comparing the densities of the traces.

The impingement is accomplished by continuously drawing the air being investigated through a jet, and thence to the surface of a paper chart, at an extremely high and uniform velocity. The dirt in the air is thus transferred to the paper chart which is being moved slowly below the jet. The reading of the recorded traces can be accomplished by comparison with known standards or by means of a densitometer. Filter efficiencies are determined by operating impinging equipment simultaneously in filtered and in unfiltered air and then making calculations based upon the density differences shown by the two recorder traces.

Impingement Apparatus

The vital point of the design of the Kodak smoke recorder is in the manner in which the jet is utilized. As long as the pressure drop across the jet exceeds 0.53 atmosphere the flow of air is constant (*11*). By the use of this principle, one avoids in a simple manner the question of metering of air, which has proved an almost unsurmountable obstacle in the design of similar recorders by other workers in the past.

The orifice of the jet used for quantitative studies is rectangular in shape and about 0.178 × 1.07 mm. (0.007 × 0.042 inch) in size. It permits 2.15 liters (0.076 cubic foot) per minute of air to impinge upon a disk of 11.0-cm. Whatman No. 50 filter paper held and driven by a 24-hour clock of the kind used for recorders of the usual industrial type. The jet is held rigidly in such a manner that the long dimension of the rectangular opening lies on a radius of the chart and the end of the jet is about 0.63 mm. (0.025 inch) above the paper. At distances greater or less than this, the traces have indefinite edges, while at about 0.63 mm. (0.025 inch) traces with sharp edges are obtained.

Figures 1 and 2 show a favored jet construction. The tapered portion of the body next to the cut that receives the "slab" is relieved eccentrically, so that the sleeve, when it is driven into position, will be unhampered in squeezing the slab against its seating surfaces. The sleeve generally need not be driven more than 0.15 cm. (0.06 inch). If the slab does not fit perfectly against the body, it may be necessary to fill the open ring between the body and the sleeve with solder. It is important that the bell-mouth entrances to the orifices be smooth and of the same shape, since the coefficient of discharge is dependent upon the condition of the entrance to the orifice and variations in shape influence the output of jets otherwise closely similar.

The jet dimensions mentioned above were chosen to pass a volume of air of such order of magnitude as to be handled by laboratory-size air pumps at the vacuum required. A Nelson pump or a water aspirator has been found sufficient to handle the continuous air flow through 2 or 3 jets, while industrial-size vacuum

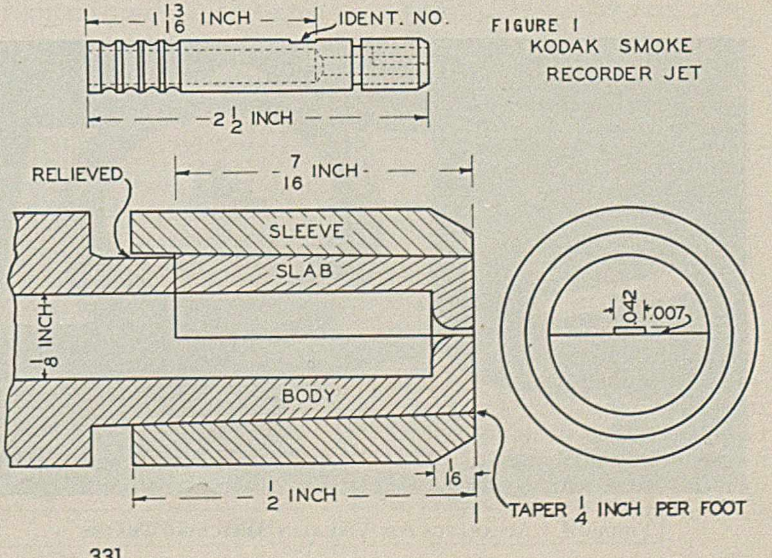

FIGURE 1 KODAK SMOKE RECORDER JET

pumps of high capacity operating at 0.53 atmosphere can accommodate many jets. A wider jet gives records which are easier to read but the vacuum pump capacity then required is difficult to meet. As a precaution against accidental plugging, an orifice flowmeter is used regularly to verify the amount of air passed by the jets. Occasional cleaning of the jets is necessary. In this laboratory a chart less than 15 cm. (6 inches) in diameter is usually employed. Where the air is unduly dirty a larger chart can be used and the diameter of the trace enlarged to diminish the densities. Use of an 8- rather than a 24-hour clock will have the same effect.

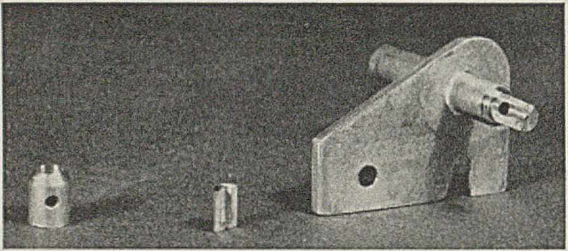

Figure 2. Construction of Jet

To prevent lint and other relatively large air-borne particles from plugging the jet, a bolting silk screen (120-mesh, 0.63-cm., 0.25-inch, diameter) is held in the body of the jet between two lengths of 0.63-cm. (0.25-inch) outside diameter brass tubing. In this laboratory it was found necessary to change the screens no oftener than once daily when using outdoor air. The dirt removed by the bolting silk screen is of sufficiently large size to be filtered out in practice by any reasonably efficient filter. Such large particles can be separated by sedimentation, a technique often used in reporting the results of surveys concerning atmospheric pollution (*1*, *8*).

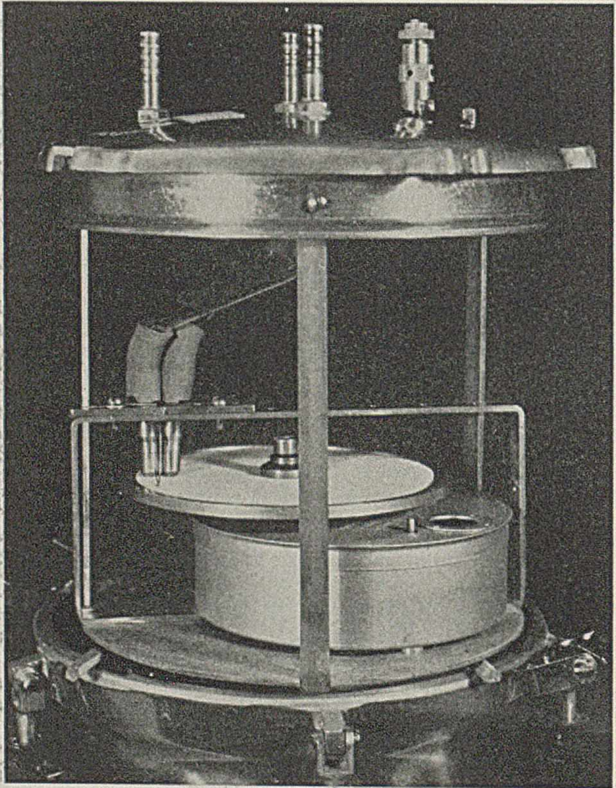

Figure 3. Impinging and Recording Mechanism

It was found that a 9.5-liter (10-quart) aluminum pressure cooker met the requirements as a container for the impinging and recording mechanism. The clock and jet assembly are suspended from the cover, making the recorder easy to service by removal of the top. The air inlets and outlet are tapped through the cover as shown in Figure 3.

Evaluation of Records

Qualitative and semiquantitative results can be obtained in air-filter studies by matching traces with a standard gray scale by reflected light. This suffices for qualitative work. In Figure 4 is shown a rough apparatus for this purpose and a typical chart. Standard gray scales can be prepared by exposing and developing matte-surface photographic paper to various degrees of blackness and then determining reflected densities by means of a densitometer. These reflection densitometer readings were converted into reflection "dirt units", which are defined as the products of the densities and a constant. This constant is a factor which converts the density reading to a 0–100 scale for ease of mathematical manipulations. Its value depends upon the upper limit of density chosen for the investigation. Each laboratory must determine this constant; its absolute value is not a matter of great importance, however, since the purpose of the test is almost always measurement of the "smudging power" of dirt present in air.

Quantitative results can be obtained by the use of a modified Capstaff-Purdy densitometer (*4*) equipped with a slitlike aperture. A photoelectric transmission densitometer (Figure 5), which was developed in conjunction with an extensive survey of the efficiencies of different types of air filters, has made possible rapid and accurate reading of charts without the eye fatigue which accompanies the use of a comparator or a visual densitometer, such as the Capstaff-Purdy.

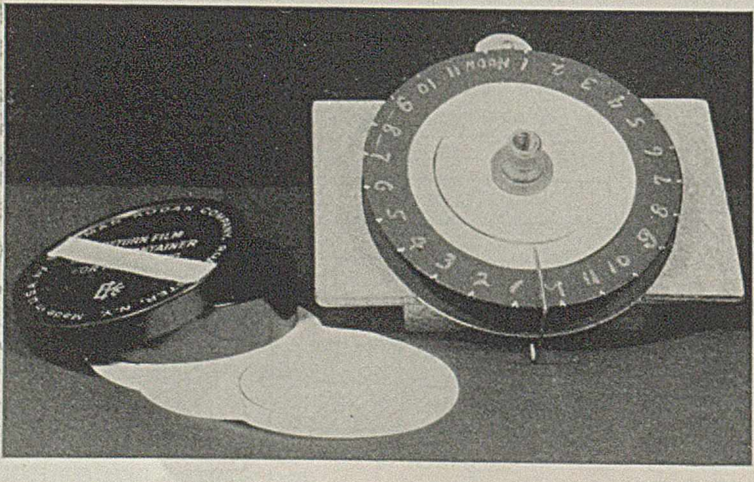

Figure 4. Apparatus for Visually Matching Traces

The optical system of the photoelectric densitometer is shown in Figure 6. In order to read the densities of the traces, the charts are placed between the box and the hinged head, so that the trace covers the 9-mm. slit. This slit is of such curvature that the reading represents an integration of a 1-hour record. The current produced in the phototube as a result of the light transmitted by the record is conducted to the circuit shown in Figure 7. The use of two photocells, one in each arm of the Wheatstone bridge, minimizes errors due to fluctuations in energy from the light source. The diaphragm covering the photocell contained in the box is necessary to equalize more nearly the amount of light falling on each tube.

Calibration of the instrument was accomplished by photographic step tablets with a wide range of densities. During calibration a piece of Whatman No. 50 filter paper was placed between the step tablet and the slit aperture to simulate

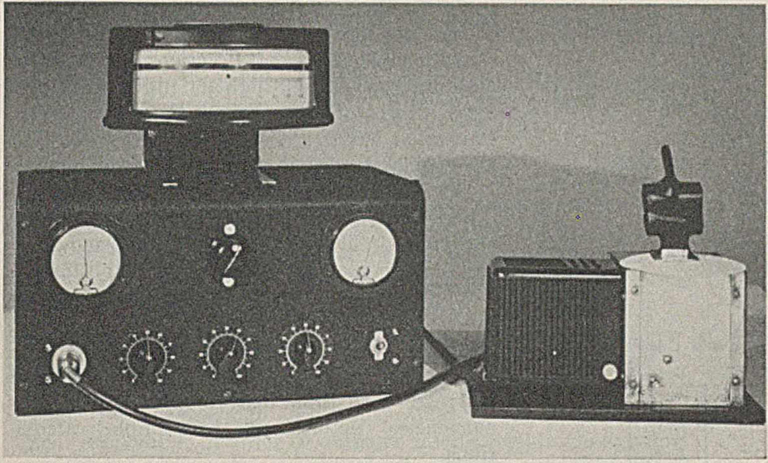

Figure 5. Photoelectric Transmission Densitometer

more nearly the actual conditions encountered while reading recorder charts. It has been found recently that matte Eastman acetate sheeting is more uniform in texture than paper and is more satisfactory than paper for recording light traces, where the zero correction is a matter of importance. These transmission densitometer readings, known as dirt units, when subtracted from 100 give the transmission value for the corresponding dirt trace.

It is customary in this laboratory to calculate air filter efficiencies by totaling separately the hourly dirt units for filtered and unfiltered air over a 24-hour period. The efficiency is calculated by the equation:

$$\text{Percentage efficiency of air filter} = 100 \times \frac{\text{daily total dirt units for unfiltered air} - \text{daily total dirt units for filtered air}}{\text{daily total dirt units for unfiltered air}}$$

Use of Kodak Smoke Recorder

From the previous discussion, it is obvious that the recorder is well suited to the study of air filtration and determination of the times of occurrence of heavy smoke loads; however, it has been found useful for other studies involving the purity of air. Spot tests have been used to determine by chemical means whether suspected contaminants, other than soot, were present. In this case simple circular jets of brass or glass can be used instead of the rectangular jets, which are more difficult to construct. When the particulate matter is of low concentration and when the time of occurrence is not important, a stationary paper can be used, and thus the air-borne material can be impinged upon a small area in order to concentrate the contaminant for chemical analysis. Transparent dusts are collected readily for microscopic examination on glass plates, cellulose acetate sheeting, or microscope slides set in special holders. This instrument is not designed for public health studies, since counts of siliceous dust are of value only when made with instruments previously used and for which there is an established body of experience.

Advantages

The efficiency of the deposition process in the Kodak smoke recorder has been shown by several methods to be very high, and the simplicity of the apparatus permits 24-hour unsupervised operation. The instrument is easily portable and can be put into operation rapidly to take readings at widely separated locations. In this respect it surpasses the Dill–Bureau of Standards (*5*) method, which requires a laboratory setup and the almost constant attention of an operator during the test.

The cost of constructing the recorder is comparatively low and it is far cheaper and more compact than the equipment of Hazard (*7*), which is designed especially to preserve traces for microscopic examination. With reasonably careful handling the charts from the Kodak smoke recorder can be evaluated and preserved as permanent records. The Owens automatic air filter (*10*) is designed primarily for studies of atmospheric pollution. It operates by filtration through paper and is less sensitive, producing discontinuous records estimated to be $^1/_{35}$ as dark as those obtained by the recorder described herein. From 4 to 6 spots are produced per hour by the Owens apparatus. Drinker and Hatch (*6*) describe a number of techniques which apply more to industrial dusts than to smokes and smoke removal, as do Bloomfield and Dallavalle (*2*, *3*).

Since the Kodak technique measures the smokelike particles in air, or in effect the smudging power of the air-borne dirt, the filter efficiencies obtained will not agree with those determined by the American Society of Heating and Ventilating Engineers (*9*) and other methods. This, however, is not a serious matter—the A. S. H. V. E. method uses a synthetic mixture of lampblack and coal ash as a test material and is designed to measure efficiencies of viscous-type air filters under conditions where relatively coarse dirt must be removed, while the Kodak technique is designed to measure the efficiency of removing the finest smoke particles as well. The usefulness of this technique is demonstrated by the consistent data obtained in studying the efficiencies of air filters having ratings of about 90 per cent on the Kodak scale, and in measuring the effect of improvements made upon such filters. This is true since the record obtained from efficiently filtered city air by the use of most recorders is so faint that small differences cannot be perceived.

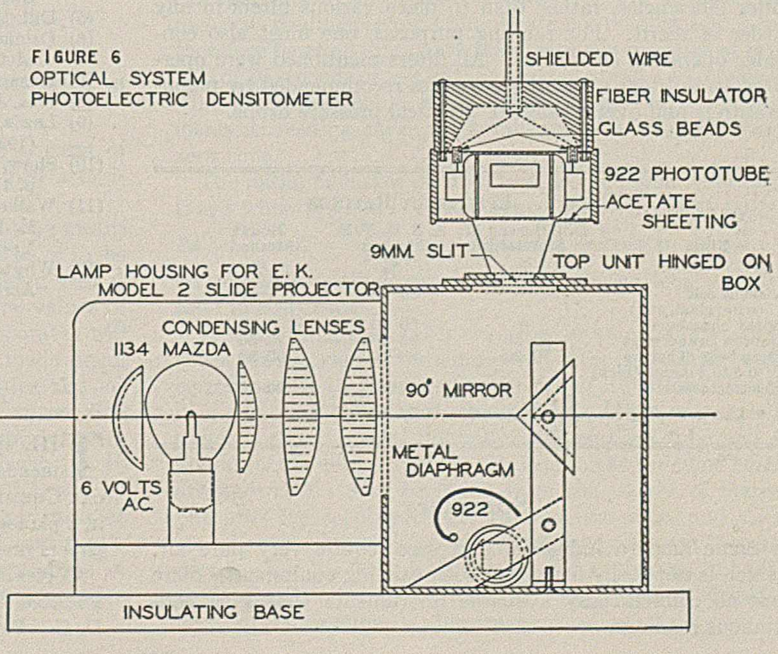

FIGURE 6
OPTICAL SYSTEM
PHOTOELECTRIC DENSITOMETER

ELECTRICAL CIRCUIT - PHOTOELECTRIC DENSITOMETER

FIGURE 7

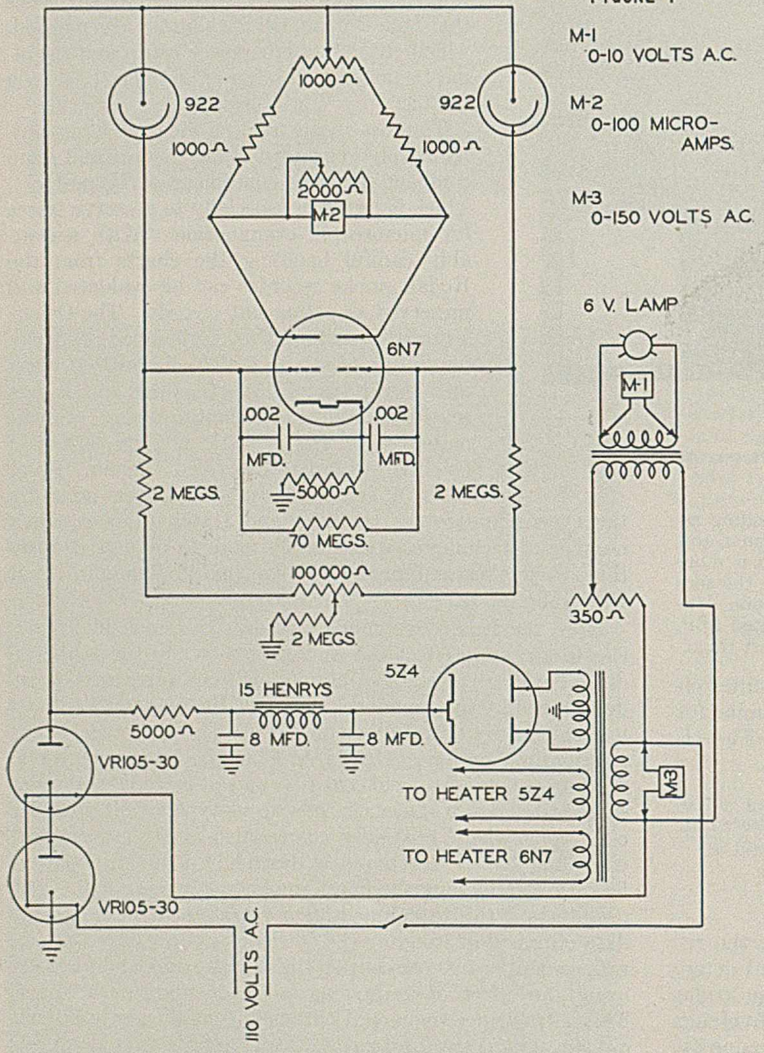

Table I is presented to describe the Kodak smoke scale of filter efficiencies, rather than to place various filters in any order of merit. For ranking purposes, one must also consider operating conditions. All filters mentioned were operated on outdoor air at the velocities recommended by manufacturers and over a range of practical pressure drops.

Table I. Efficiency Ratings

Filter	Dill–Bureau of Standards	A. S. H. V. E. Method	Kodak Method
	%	%	%
Viscous cell (wire, glass, etc.)	[a]	80–90	5–10
Spray chambers	[a]	80–90	5–10
Canton flannel bags	20–30	95–100	20–30
Deep beds of cotton (0.5 to 2 inches thick)	70–90	98–100	60–80
Electrostatic	90–100	100	90–100

[a] This method gives poor results below 20%.

Summary

Some modern industrial processes require very pure air, which is not easily measured with existing equipment; there are no commercially available instruments that give continuous readings.

The smoke-recording instrument described is easily portable and will give 24-hour records without supervision. It functions by impinging air from a jet at very high and uniform velocity upon a piece of paper driven by a clock in an evacuated vessel. At a pressure drop of 0.53 atmosphere the jet is self-metering, thus avoiding air-measurement difficulties.

The instrument is designed primarily for studying air filters of very high efficiency, but can also be used for chemical tests and for collecting specimens for microscopic examination.

A photoelectric densitometer is described. The impingement charts from the recorder can be read with this instrument and air-filter efficiencies determined by simple calculations.

The Kodak smoke scale is not absolute. Its character is shown by comparisons with the A. S. H. V. E. and Dill–Bureau of Standards methods for different filter types.

Acknowledgments

Thanks are due E. K. Carver, superintendent of the Department of Manufacturing Experiments, and C. K. Flint, manager of Kodak Park, for permission to publish this description of the Kodak smoke recorder and the technique of air-filter evaluation. A. F. Pundt and J. R. Peer are to be thanked for conscientious evaluation of many thousands of recorder charts. J. R. Peer and E. J. Klodinski constructed the photoelectric densitometer. The novel features of the Kodak smoke recorder have been covered by a patent application.

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A. C. S. Analytical Reagents

THE specifications for analytical reagent chemicals, recommended by the Committee on Analytical Reagents, American Chemical Society, from 1924 to 1941, have been reproduced in a planographed volume in the general style of the abstracts of papers presented at American Chemical Society meetings.

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Particle Size Determination by Sedimentation

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J. L. BINDER, The Pure Oil Company, Chicago, Ill.

THERE are many occasions when the ordinary screen analysis of granular material does not permit sufficiently fine differentiation between particle sizes. In such circumstances, sedimentation methods offer a means of obtaining as high a degree of differentiation as is desired.

Several different experimental methods of measuring particle size by sedimentation have been used but probably the simplest is that used by Kelly and others (*2*, *5*), which consists essentially of measuring the change in pressure exerted by the suspension as the suspended material separates out. Generally, in order to measure small pressure changes, an inclined manometer attached to the settling tube is used.

Evaluation of Experimental Data

The relationship between the pressure changes and the weight of material separated out may lead to serious errors in the particle size determination if the physical dimensions of the apparatus are not considered. When the pressures are indicated by the positions of the meniscus in the inclined arm of the manometer, which is filled with the suspending medium, the relationship as given by Kraemer and Stamm (*4*) is:

$$W_P = \frac{ds\,(S + A \sin b)}{s - d}\,(l_0 - l_t) = k_1 \Delta l \qquad (1)$$

where W_P = weight of material that has settled out at time t
d = density of suspending medium
s = density of suspended solid
S = cross-sectional area of bore of inclined arm of manometer
A = cross-sectional area of settling tube
l_0 = meniscus reading at $t = 0$
l_t = meniscus reading at time t

When S is so small compared to A that it can be neglected, Equation 1 reduces to that given by Kelly (*2*), except that Kelly's equation gives the amount in suspension at any time.

$$W_I = \frac{dVs \sin b}{h\,(s - d)}\,(l_0 - l_t) = W_0 - W_P = k_2 \Delta l \qquad (2)$$

where W_I = weight of material in suspension at time t
V = volume of suspension above side tube
h = height of suspension above side tube
W_0 = total weight of solid initially in suspension of volume V

Physically, this omission of S means that the amount of liquid entering the settling tube from the inclined arm is neglected.

If it is desired to evaluate the sedimentation data by means of Equation 2, the dimensions of the apparatus have to be adjusted accordingly. This can be done by making area A very large compared to area S. But for ordinary values of S (diameter 1 to 5 mm.) this means that the apparatus will be unduly large. On the other hand, if S is made small compared to a convenient value for A, difficulties and erroneous results may be encountered because the suspending medium will move too slowly in the inclined arm, owing to capillary attraction. Therefore, the safest procedure is to use Equation 1 in evaluating the data. Values of k_1 and k_2, obtained with an inclined manometer type of apparatus at the Drexel Institute of Technology, were 0.531 and 0.417, respectively, when operating with aqueous suspensions of calcium carbonate and with such a difference it is imperative to use Equation 1.

Another relation for the weight of material separated out and the pressure changes is that given by Duncombe and Withrow (*1*):

$$\%\,W_P = \frac{l_0 - l_t}{l_0 - l_f} \times 100 \qquad (3)$$

where l_f = final meniscus reading.

Despite its simplicity, the difficulties involved in the determination of l_f limit the general usefulness of this relationship.

Operating Variables

An examination of Equation 1 shows that the factors which are constant for any one experiment and apparatus are the densities of liquid and solid and the areas, while l_0 and l_t are the only variables that have to be measured. The various W_P's are calculated from the l readings and the sum of these values for the total settling time should equal the weight of solid initially in the suspension.

The determination of l_0 may offer some difficulties. In the determination of the total meniscus change the relationship between the initial level of the suspension and the level of the meniscus exerts considerable influence at the start of the experiment. Although the relative position of these two levels is usually approximated prior to a settling experiment, it is almost impossible to have them in their exact positions in the actual determination. Therefore, the meniscus level is either somewhat above the actual level corresponding to the level of the suspension in the settling tube, or it is somewhat below the actual level. In the first case the meniscus level will drop at a rate faster than that corresponding to the settling out of particles and in the second case it will drop at a rate lower than the actual rate. In extreme instances of the second case the meniscus may actually be observed to stand still or even move upward for a short time. It is, therefore, necessary that the actual meniscus level be determined graphically by plotting meniscus readings *vs.* time and extrapolating to zero time. Generally, it will be found that meniscus readings below 1 minute are not reliable, and it may therefore be of advantage to take meniscus readings at intervals of 30 seconds or less in the period of about 1 to 5 minutes. This procedure should give sufficient points of the time *vs.* meniscus reading curve to permit accurate extrapolation to zero time.

The initial meniscus position can also be found from Equation 1 when W_P and k_1 can be determined accurately because $\Delta l = l_0 - l_t = \frac{W_P}{k_1}$. In this case it is best to measure Δl for complete settling because then W_P is the total weight of solid in suspension.

In using Equation 1 it is desirable to know W_0 in order to check the accuracy of the summation of the individual weights corresponding to the l readings. When Equation 2 is used, it is necessary to know W_0 accurately. If the suspension is uniform and the total volume of the settling tube and the volume of the tube above the side arm (all to the same height) are known, W_0 may be found from the weight of material put into the settling tube. In some cases, k_1 and Δl for complete settling may be found accurately enough to permit determining W_0 from Equation 1. Of course, an aliquot of the suspension could be analyzed, but again it would be necessary to assume a uniform suspension.

Viscosity of Suspending Medium

The viscosity of the suspending medium is primarily determined by the largest particle size which is to be measured. If the viscosity of the medium is too low, particles above a certain size will settle so rapidly that differentiation will not be possible and if it is necessary to obtain closer differentiation a medium of higher viscosity must be used. The viscosity which is required can be approximated from Stokes' law if an estimate of the largest particle size is available. According to Knapp (*3*), the minimum allowable viscosity is given by:

$$\mu_{\text{min.}} = \sqrt{0.37\, r^3_{\text{max.}}\, gd\,(s - d)} \tag{4}$$

where $r_{\text{max.}}$ is the maximum particle radius, g is the gravitational constant, and the other terms are as previously defined.

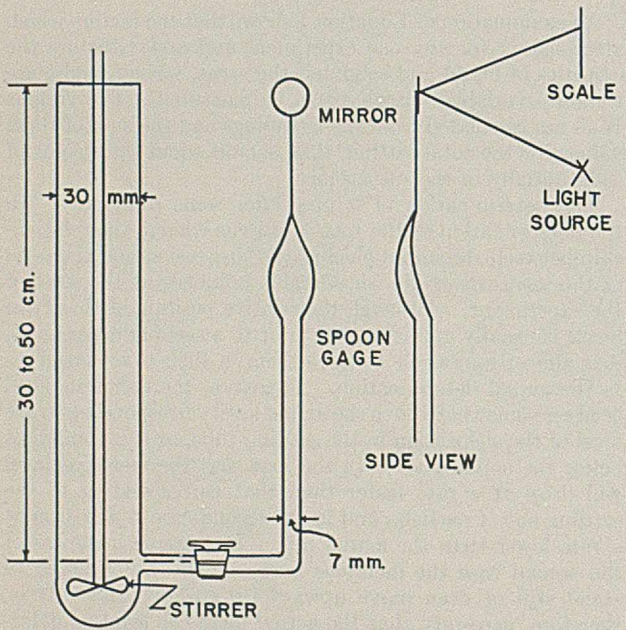

Figure 1. Apparatus for Particle Size Determination

Occasionally it was observed that the curve of weight settled *vs.* time showed a curvature which was slightly concave upward in the early part of the settling period. An analysis of a number of such curves indicated that the occurrence of this inverted section of the curves was found with solids of a wide particle size range which contained a considerable percentage of large particles. The slope of this part of a curve, of course, indicated that the reverse of sedimentation was taking place. Close observation of the settling process revealed that during the period of rapid settling—that is, in the part represented by the steep portion of the settling curve—the liquid which returned from the semicapillary tube entered the settling tube with sufficient velocity to set up an upward current. As a consequence some particles which had settled past the level of the side arm were lifted above this level and immediately exerted an increased pressure which resulted in a slowing up of the rate of meniscus fall. Translated into the weight *vs.* time curve this means a decrease in the slope dW/dt and when normal settling is resumed a discontinuity is introduced in the settling process. The remedy for such a condition is the use of a suspending medium of higher viscosity which will retard the rate of fall of the meniscus to a point where the liquid draining from the semicapillary tube will not set up eddy currents.

Smallest and Largest Particle Sizes

When, in a particular experiment, a suspending medium is used which has a viscosity high enough to permit accurate measurement of the fall of the majority of the particles, it will usually be found that for this medium the smallest particles settle too slowly and the largest too quickly. The size of the smallest particles can generally be found accurately enough by extrapolating the accumulation curve of weight settled out *vs.* time to complete settling and using this value of the time in the Stokes' equation. This curve becomes asymptotic to a line parallel to the time axis but the error introduced by extrapolating to 100 per cent settled out is small since the radii of the particles are small.

It is more difficult to arrive at the size of the largest particles. In the usual case they will generally settle so rapidly that accurate measurements cannot be made at less than one minute. As an approximation it is possible to extrapolate the curve to the origin with a straight line and in some cases this is accurate enough. Of course, a screen analysis will also indicate the upper limit of particle size. The other, more accurate, procedure is to use a medium of higher viscosity for these particles, so that the time of fall is increased sufficiently to permit accurate measurement.

Improved Apparatus

The discussion of the above factors shows that the methods which are based on a moving meniscus level involve experimental difficulties which may result in appreciable inaccuracies. Furthermore, with large particle sizes these methods are of little use because suspending media of high viscosity must be used to permit accurate measurement of the time of fall of the particles. On account of the high viscosity, the liquid moves so slowly in the capillary side arm that the measurements are practically worthless.

The apparatus shown in Figure 1 was developed in the laboratories of the Pure Oil Company. It permits the use of a suspending medium of high viscosity and with it particle sizes corresponding to 32-mesh (about 500 microns in diameter) have been measured employing an S. A. E. 40 oil as suspending medium.

The settling tube is large enough to permit the introduction of a motor-driven stirrer arranged to give an upward motion to the suspension. The spoon gage, made by elongating a thin-walled bulb and then flattening on one side, is thin enough so that a pressure difference of a few millimeters of mercury will impart a noticeable displacement to the pointer. The optical arrangement amplifies the pointer movement.

In use, the whole apparatus is filled with the suspending medium to a fixed point on the settling tube. After closing the stopcock, a weighed amount of the material under investigation is stirred in until the suspension is uniform. Upon cessation of stirring, the stopcock is opened and readings of the pointer position are taken at various times. The apparatus must be protected from thermal and mechanical changes.

The deflections of the pointer are converted to pressure changes by calibrating the gage. This can be done, as described by Knapp (*3*), by immersing cylinders of known volumes in the suspending liquid in the settling tube. The increases in height of the liquid are converted to pressure increases and these are plotted against the corresponding pointer displacements. The resulting curve is a calibration curve of the gage.

From the pressure changes the weight of material separated out is found by Equation 5.

$$\Delta P = \frac{W_P}{A}\left(1 - \frac{d}{s}\right) \tag{5}$$

in which the symbols have the same meaning as before. Obviously, the percentages settled out can be obtained also by means of Equation 3. After constructing the accumulation curve, the particle size distribution curve is obtained in the usual manner.

There are many advantages of this apparatus in actual use. Since a given height, h, of the liquid always corresponds to a definite position, l, of the pointer it is apparent that, knowing the bulk density of the material (determined with the liquid which is used as the suspending medium), the final position of the pointer, l_f, can be calculated. This corresponds to complete settling. Since there is no flow of liquid from the side arm, disturbances which can be caused in this way in the manometer type of apparatus are eliminated. Because of the amplification of the pointer displacement, closer differentiation of particle sizes is possible.

Experience has shown that this apparatus is more convenient in use than the usual type, and particle sizes of materials can be measured with it that are impossible to measure with the manometer type.

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Presented before the Division of Industrial and Engineering Chemistry at the 100th Meeting of the American Chemical Society, Detroit, Mich.

Recovery of Mercuric Iodide and Iodine from Nesslerized Solutions

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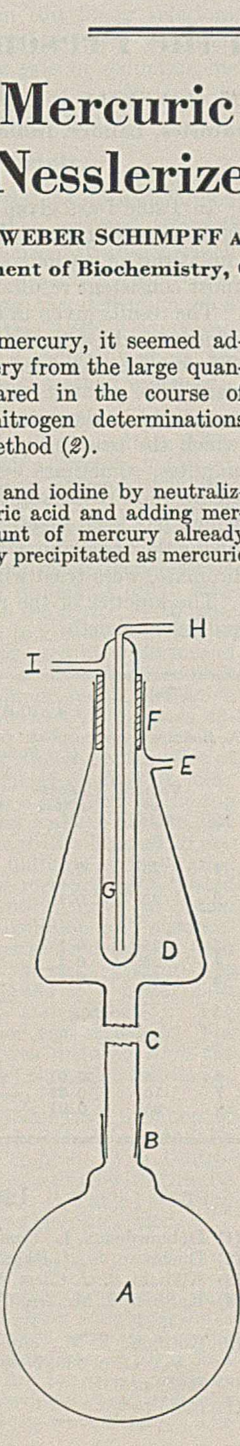
BECAUSE of the rising cost of mercury, it seemed advisable to investigate its recovery from the large quantities of nesslerized solutions prepared in the course of running hundreds of nonprotein nitrogen determinations according to the Koch-McMeekin method (*2*).

Pullman (*4*) recovered the mercury and iodine by neutralizing the nesslerized solution with sulfuric acid and adding mercuric nitrate equivalent to the amount of mercury already present. He stated that all the mercury precipitated as mercuric iodide. However, this method involved the use of a second mercury compound which required a rather large additional expenditure in order to recover the original mercuric iodide. Clifford (*1*) recovered mercuric iodide by neutralizing the nesslerized solution with sulfuric acid. Only a part of the mercuric iodide precipitated from the solution on standing.

In this investigation mercuric iodide and free iodine were precipitated by adding sulfuric acid and sodium dichromate to the nesslerized solution. The free iodine was then separated from the mercuric iodide by a distillation procedure. The method is simple and inexpensive, and results in the almost quantitative recovery of iodine and of mercury as mercuric iodide.



Apparatus

The apparatus consists of a 3-liter round-bottomed short-necked flask, A, with standard-taper ground-glass joint 25/40, B, connected by a 50-cm. (20-inch) length of 20-mm. (outside diameter) Pyrex tubing, C, to an opening in the bottom of a 1-liter Erlenmeyer flask, D, which has a side arm, E, attached near the top. Through the mouth of the Erlenmeyer flask, F, there extends a cooling finger, G, which contains a running water inlet, H, and outlet, I. G is fitted into F by means of a rubber washer which must be renewed occasionally—a glass connection would be preferable.

Procedure

To 10 liters of the nesslerized solution contained in an earthenware crock are added, in the order given, 150 cc. of concentrated sulfuric acid and 75 cc. of 1.3 molar sodium dichromate solution. Upon addition of the sulfuric acid the mixture first becomes milky, then develops a pink color. Upon addition of the sodium dichromate solution, the color darkens considerably and a small amount of iodine vapor becomes noticeable. The mixture is covered and allowed to stand at room temperature in the hood for 12 hours, during which time the mercuric iodide and iodine are completely precipitated. The supernatant liquid is decanted and the residual mass transferred to flask A. (In case the nesslerized solution has been prepared in the course of urea determinations in which a direct nesslerization procedure has been used, it is advisable to free the precipitate from the supernatant liquid by suction filtration and to wash the residue with water prior to its transfer to the round-bottomed flask. This procedure removes the organic material which causes foaming during the heating process.) Enough water is introduced in transferring the precipitate to fill the flask one-fourth to one-half full. (The water facilitates the rapid removal of free iodine from the mixture of mercuric iodide and iodine during the subsequent procedure.)

The apparatus is assembled as shown. The mixture is boiled gently until A is free of iodine vapors. The apparatus is then disconnected and the free iodine, which has condensed on the cold finger, is scraped or washed into a beaker, collected in a Büchner funnel, and allowed to dry in the air. The mercuric iodide remaining in A is separated by suction filtration and washed well with distilled water and then with three 25-cc. portions of 95 per cent ethyl alcohol. It is heated in an oven at 105° C. for 30 minutes in order to remove any moisture or free iodine that may still be present. The mercuric iodide is then ready for use in the preparation of Nessler-Folin reagent.

Results

From 54 batches of nesslerized solution, 10 liters each, an average of 45 grams of iodine and 84 grams of mercuric iodide was recovered. The calculated amounts present in the 10 liters were 48.8 grams of iodine and 87.7 grams of mercuric iodide. Percentage yield: mercuric iodide, 95.7; iodine, 92.2.

Preparation of Nessler-Folin Reagent. The Nessler-Folin reagent is prepared according to the method of Koch (*3*) except that 40.3 grams of the recovered mercuric iodide (instead of 30 grams of mercury and 22.5 grams of iodine) are added to 30 grams of potassium iodide in 30 cc. of water. The resulting solution is filtered, adjusted with a solution of iodine in potassium iodide, and diluted to 200 cc. This stock solution is then added to 975 cc. of 2.5 molar sodium hydroxide to give the Nessler-Folin reagent. No difference has been observed in the behavior of the solutions prepared by the two methods.

The recovered iodine has been used successfully in the preparation of Nessler-Folin reagent according to the method of Koch (*3*).

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Determination of Iodate Ion in the Presence of Cupric Ion

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FOR a number of routine determinations a method for estimating iodate ion in the presence of copper salts was required. Of the methods suggested for the estimation of iodates of alkali metals or iodic acid alone, the most important are: reducing iodates with oxalic acid and back-titrating the excess of oxalic acid (*1*), reducing iodates with titanous chloride (*3*), and allowing the iodate and potassium iodide to react in the presence of a mineral acid and titrating the liberated iodine against standard sodium thiosulfate solution (*5*). The last reaction is sufficiently rapid and accurate for all purposes. The velocity of the reaction

$$6H^+ + IO_3^- + 5I^- \longrightarrow 3I_2 + 3H_2O$$

in acetic acid solution has been shown to be proportional to the square of the concentration of hydrogen and iodide ions and directly proportional to the concentration of iodate ion (*2*). This reaction has also been utilized for estimation of iodate ion in the presence of bromate and chlorate ions. If, however, estimation of iodate ion be attempted in the presence of copper ions, a complication is likely to arise on account of the liberation of iodine through the simultaneous reaction of cupric ions with potassium iodide according to the equation

$$2Cu^{++} + 2I^- \longrightarrow 2Cu + I_2$$

Kolthoff and Cremer (*4, 7*) showed that trivalent arsenic can be estimated volumetrically in the presence of copper ions by adding sodium pyrophosphate to a neutral solution of the mixture, when copper ions form a blue complex and no longer react with potassium iodide. It was found, however, that the complex of copper does not decompose in acidic solution up to pH 5.0, but decomposes at greater acidity to react with potassium iodide. The authors made use of this fact for the estimation of iodate ion in the presence of copper salts.

Mixtures containing known amounts of potassium iodate and copper sulfate were prepared. An excess of sodium pyrophosphate (free from reducing agent), acetic acid, and potassium iodide solution were added, in this order, to each of the solutions to be titrated. The iodine was liberated slowly and was titrated against standard sodium thiosulfate solution, using starch as indicator. After iodine had ceased to separate, the solution was set aside and kept for 24 hours in the dark. Under these conditions no more iodine was evolved, showing that the blue copper complex did not decompose to react with iodide.

In Table I are given typical results obtained in the course of this investigation. In the fifth column are given the exact quantities of various solutions that were found to give the most consistent results.

The results given in the last column show that the amount of iodate added to the solution in terms of its equivalent iodine can be estimated with accuracy even in the presence of very large amounts of copper salts. The only difficulty encountered in the present case was the extreme slowness with which the reaction proceeded, each titration taking several minutes, sometimes even half an hour, for completion. A number of catalysts, including ammonium molybdate (*6*), which has been mentioned by Kolthoff as suitable for catalyzing the liberation of bromine from a mixture of bromide and bromate, were tried without success.

The kinetics of the reaction are being studied and will be published shortly.

Table I. Typical Results

A. Sodium pyrophosphate solution, 10%. B. Acetic acid solution, 10%. C. Potassium iodide solution, 10%.

No.	Volume of KIO_3	Concentration N	Volume of 0.2 N $CuSO_4$	Conditions	Volume of 0.1 N $Na_2S_2O_3$ Theoretical	Found
	Cc.		*Cc.*	*Cc.*	*Cc.*	*Cc.*
1	25	0.1	..	5 B 10 C	25.0	25.0
2	25	0.1	..	75 A 12 B 10 C	25.0	25.0
3	25	0.1	10	10 C	25.0	25.0
4	25	0.1	25	10 C	25.0	25.0
5	50	0.1	50	150 A 25 B 20 C	50.0	50.05
					Volume of 0.01 N $Na_2S_2O_3$	
6	5	0.01	25	Same as in 4	5.0	5.0
7	10	0.01	25	Same as in 4	10.0	10.0
8	25	0.01	25	Same as in 4	25.0	25.05

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A Polarographic Study of Aliphatic Nitro Compounds

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A POLAROGRAPHIC study was made of six aliphatic nitro compounds with the expectation of developing a method for the quantitative determination of these compounds. The investigation also included a determination of the half-wave potentials. The current due to the reduction of the compounds in acid solution was found to be proportional to their concentration, but in neutral solution there was a slight but reproducible deviation from this linear relationship. The compounds were reduced at a lower potential in acid than in neutral solution. The ease of reduction increases slightly with increase of molecular weight, and is greater for primary than for secondary compounds.

Apparatus and Materials

The polarographic method of analysis has been described by different investigators (*3*, *4*). The current-potential curves may be obtained with an automatic instrument which makes a photographic record, or by changing the voltage manually in certain steps and reading the deflection of a galvanometer at each voltage. The latter method is less convenient but is also less expensive and generally more accurate. In this investigation the manual method was used.

The apparatus was assembled from available parts. A Kohlrausch slide-wire bridge was used to vary the voltage across the cell. The voltage was measured with a Weston, model 45, voltmeter with a 3-volt range, which could be read accurately to 0.01 volt and approximately to 0.002 volt. A Leeds & Northrup galvanometer, HS type, was available with a coil with a 7-second period. Calibrated shunts were used in order that one fiftieth of the current should flow through the galvanometer—i. e., 0.13 microampere through the cell containing dilute solutions would cause a deflection of 1 mm. on the scale. With more concentrated solutions a shunt was used to give a sensitivity of one five-hundredth. A straight scale was used at a distance of about 2 meters from the galvanometer. Scale deflections were proportional to the current, since the maximum angular deflection was about 5 degrees. Current of the desired voltage was obtained from a lead storage battery.

The capillary cathode was prepared by drawing out a piece of thermometer tubing to an external diameter of about 1 mm., and was sealed to a piece of tubing with a reservoir at the top for the mercury. The end of the capillary was cut back to give a drop of mercury about every 5 seconds with a head of 25 cm. of mercury. Since the magnitude of the diffusion current varied with the drop time, the pressure upon the mercury was adjusted at the start of each series of experiments in order to obtain comparable results by using a 0.005 *M* solution of 1-nitropropane in 0.05 *M* sulfuric acid to give the same deflection each time at an applied voltage of 1.60 across the cell. Pressure was applied by using an aspirator bulb attached to a 1-liter flask and was measured with a mercury-filled manometer (*5*). The cell was a 50-ml. conical flask with a side arm sealed in. For some of the experiments dissolved air was removed from the solutions with nitrogen which had bubbled through a solution of chromous sulfate to remove traces of oxygen (*6*).

Five of the nitro compounds were available from members of the division of organic chemistry and had been purified by rectification in a modified Podbielniak column. The 1-nitrobutane was a good commercial grade. It was dried with Drierite and had a boiling point range of 152–154° C. In Table I are listed the boiling point ranges of the compounds which were used.

Experimental and Results

Solutions of each of the aliphatic nitro compounds were electrolyzed in 0.05 *M* sulfuric acid or sodium sulfate as indifferent electrolytes. Sodium sulfate solutions were used at the beginning of the investigation, but it soon became evident that a change of the compounds to the aci-nitro form was probably responsible for the lack of a linear proportionality between the concentration of the nitro compound and the wave height. The investigation was therefore continued with sulfuric acid solutions, in which case the wave height was found to be proportional to the concentration within a few per cent error. The stock solutions were 0.05 and 0.005 *M* solutions of the nitro compound in either 0.05 *M* sulfuric or sodium sulfate. The concentrations were varied from 0.0005 to 0.0167 *M* by mixing at the time of the experiment measured amounts of the stock solution with 10 ml. of the indifferent electrolyte.

The influence of pressure on the drop time and galvanometer deflection was investigated with a solution of 0.0046 *M* 1-nitropropane in 0.05 *M* sulfuric acid, with 1.60 volts across the cell.

The results tabulated in Table II indicate that it is important to have a reproducible pressure to obtain precision in the results, and this was accomplished as mentioned above. An analysis error of 1 per cent can be caused by a 1-mm. variation of pressure on the mercury of the capillary electrode.

The influence of temperature was determined by electrolyzing a 0.0167 *M* 2-nitropropane solution in 0.05 *M* sulfuric acid. The results tabulated in Table III indicate that a 2° variation in temperature will change the diffusion current by 3 per cent. All results reported in this paper were obtained with the cell immersed in a water bath at 25° ± 0.5° C.

The average of the oscillations caused by the growth and dropping of the mercury drops has generally been taken as the current when polarograms are obtained with a recording polarograph. In the manual method twice as many readings would be required. The use of the lower values of the oscillations was tried, and in plotting the wave height against the concentration of the compound, straight-line graphs were obtained which differed only in magnitude of deflection from those which were obtained when the average deflection was used. Since the minima of the oscillations were more reproducible, they were used to calculate the diffusion current from the galvanometer deflections.

In some preliminary experiments, current-potential curves were obtained for the electrolysis of 0.05 *M* sulfuric acid through which nitrogen had been bubbled to remove air. In those cases when the air had not been removed from the solution oxygen maxima were not observed, for which the authors cannot offer an explanation. A small but definite

TABLE I. BOILING POINT RANGES

	° *C.*		° *C.*
Nitromethane	100.5	2-Nitropropane	117–118
Nitroethane	115	1-Nitrobutane	152–154
1-Nitropropane	130.8–131.6	2-Nitrobutane	139

TABLE II. INFLUENCE OF PRESSURE ON DROP TIME

Pressure *Mm. Hg*	Drop Time *Seconds*	Current *Microamperes*	Change in Current for 1 Mm. %
240	6.5	3.45	...
250	5.6	3.79	1.0
260	5.0	4.09	0.93
270	4.5	4.35	0.90

TABLE III. INFLUENCE OF TEMPERATURE ON CURRENT

Temperature ° *C.*	Current *Microamperes*	Change per Degree %
15	14.5	−1.4
20	15.7	−1.4
25	16.9	...
30	18.1	+1.4

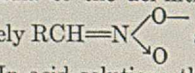
Table IV. Diffusion Current in 0.05 *M* Sulfuric Acid

	Molar Concentration of Nitro Compound							
	0.000455	0.000833	0.00115	0.00167	0.00455	0.00833	0.0115	0.0167
	Microamperes							
Nitromethane	0.49	0.89	1.11	1.74	5.7	10.6	14.4	21.1
	0.51	0.89	1.25	1.79	5.4	10.3	14.2	20.7
Nitroethane	0.36	0.66	0.89	1.31	3.9	7.4	10.2	15.3
	0.40	0.67	0.89	1.29	4.2	7.6	10.5	15.0
1-Nitropropane	0.33	0.65	0.89	1.28	3.6	6.9	9.6	14.3
	0.35	0.64	0.88	1.29	3.8	6.9	9.7	14.2
1-Nitrobutane	0.34	0.65	0.93	1.34	..	..	..	..
	0.33	0.67	0.91	1.35	..	..	..	..
2-Nitropropane	0.39	0.70	0.98	1.39	4.4	8.1	11.3	16.4
	0.39	0.72	0.95	1.38	4.3	8.0	11.3	16.4
2-Nitrobutane	0.40	0.74	1.01	1.44	4.5	8.2	11.6	16.7
	0.40	0.74	0.99	1.48	4.5	7.8	11.4	16.9

Table V. Diffusion Current in 0.05 *M* Sodium Sulfate

	Molar Concentration of Nitro Compound				
	0.00455	0.00833	0.0115	0.0143	0.0167
	Microamperes				
Nitromethane	5.2	8.7	11.6	13.2	14.9
	5.2	8.4	11.1	13.3	15.0
Nitroethane	5.8	9.1	13.0	16.0	18.6
	5.2	9.5	12.7	15.4	17.5
1-Nitropropane	4.9	8.7	11.8	15.0	16.9
	4.7	8.5	11.9	14.5	16.8
2-Nitropropane	4.4	7.8	10.7	13.2	15.6
	4.4	7.9	10.8	13.3	15.5
2-Nitrobutane	4.3	7.6	10.3	12.7	14.7
	4.2	8.1	10.9	12.7	14.7

polarization current of increasing magnitude was obtained at increasing voltages. Hence, in most of the later experiments air was not removed from the solution but the curve was established for the electrolyte, then a desired amount of the compound was added, and the curve was again determined. The difference between the two curves was ascribed to the effect of the compound and gave the desired wave height. Deflections thus calculated were constant until a potential of 0.9 volt was reached, and attained another almost constant value at 1.4 volts. In sodium sulfate solutions the deflections were observed at 0.8 and 1.6 volts.

Two representative results from numerous data are tabulated in Tables IV and V for each concentration. These were obtained with a capillary electrode delivering 0.00162 gram of mercury per drop and with a drop time of about 5 seconds. The results show that the wave heights were proportional to the concentration of the nitro compounds in all the cases when sulfuric acid was used as the indifferent electrolyte. Straight-line relationships were not obtained when the compounds were dissolved in sodium sulfate solutions. Nitromethane showed the largest deviation, while 1-nitrobutane showed the least. The partial conversion of the nitro compound to an aci-nitro form in neutral solution and its complete conversion in an alkaline solution can explain the trend of the results. The half-wave potentials show that the nitro compounds were reduced more easily in acid than in neutral solution; in fact, they could not be reduced in 0.1 *N* sodium hydroxide. With tetramethylammonium hydroxide as the indifferent electrolyte a lower cathode potential could be reached, but even in this case no reduction was apparent. The formula of the aci-nitro ion which cannot be reduced is very likely  $RCH{=}N\langle^{O-}_{\rightarrow O}$ according to Hantzch and others (*1*, *2*). In acid solutions the nitro compound is probably reduced to the oxime and not all the way to the amine, in view of the fact that only one wave height was observed in the voltage range which it was possible to use with sulfuric acid as supporting electrolyte. Further support to this idea is given by the fact that nitromethane is reduced to methyl hydroxylamine in acid solutions with zinc dust and can only be reduced further to methylamine with hydroiodic acid.

The half-wave or apparent reduction potential for a particular compound is defined as the potential of the cathode which will cause half the rise in current due to the substance in the solution and is usually considered to be independent of changes in the concentration of the compound as long as the hydrogen-ion concentration remains constant.

The half-wave potentials were measured with a Leeds & Northrup Type K potentiometer, using a mercury–mercurous sulfate electrode, 0.05 *M* in sodium sulfate, as reference electrode. Its potential was determined by comparing it with a normal calomel electrode through a salt bridge. Since oxidation-reduction potentials are often given with respect to other electrodes, primarily the normal calomel and hydrogen electrodes, the potentials listed in the last two columns of Table VI are with respect to these two electrodes. The results are tabulated for the dilute solutions. For the concentrated solutions the potential is approximately 0.01 volt more negative in the case of the sodium sulfate solutions and 0.04 volt in the case of the sulfuric acid solutions—i. e., the value 1.066 for 0.00046 *M* nitromethane became 1.106 for 0.0167 *M* solution.

The results show that there was not enough difference between the values of the half-wave potentials of the nitro compounds to determine them separately in the presence of each other.

Table VI. Half-Wave Potentials

	Applied Potential at Half-Wave	Cathode Potential		
		Against reference electrode	Against *N* calomel electrode	Against hydrogen electrode
	In 0.05 *M* sulfuric acid			
Nitromethane	1.066	1.137	0.721	0.440
Nitroethane	1.048	1.115	0.699	0.418
1-Nitropropane	1.008	1.069	0.653	0.372
1-Nitrobutane	0.943	1.017	0.601	0.320
2-Nitropropane	1.052	1.129	0.713	0.432
2-Nitrobutane	1.022	1.097	0.681	0.400
	In 0.05 *M* sodium sulfate			
Nitromethane	1.23	1.35	0.93	0.65
Nitroethane	1.24	1.36	0.94	0.66
1-Nitropropane	1.23	1.35	0.93	0.65
1-Nitrobutane	1.21	1.30	0.88	0.60
2-Nitropropane	1.29	1.40	0.98	0.70
2-Nitrobutane	1.30	1.39	0.97	0.69

Summary

The reduction of six aliphatic nitro compounds at a dropping mercury cathode was studied with a manually operated polarograph in the concentration range 0.0005 to 0.017 molar. The deflections of the galvanometer were proportional to the concentration of the compound within a few per cent error. A 0.05 *M* sulfuric acid solution was used as the indifferent electrolyte. In neutral 0.05 *M* sodium sulfate solution a partial conversion to an aci-nitro form was probably the cause of the deviation from a linear relationship. The half-wave potentials were also determined, but it was not possible to determine the compounds separately in the presence of each other.

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Tracer Isotopes in Analytical Chemistry

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IN THE past, applications of physics and physical chemistry to analytical chemistry have afforded valuable new means for investigating and solving many problems of analysis. The use of isotopic atoms as tracers is the latest development to be added to an already impressive list, which includes many physical methods involving various optical, electrical, and thermal measurements. These tracer atoms are in general identical with the ordinary atoms of the elements except that they are "labeled" or "tagged" by virtue of possessing either a different atomic weight (or mass number) or the ability to undergo a spontaneous transformation to a different atom. This latter change, radioactivity, is accompanied by the emission of particles or radiation which can be readily detected or measured. Investigations employing tracer atoms thus fall naturally into two classes, those involving stable isotopes, which depend for analysis on a difference in mass, and those using unstable isotopes, the determination of which depends on the measurement of radioactivity.

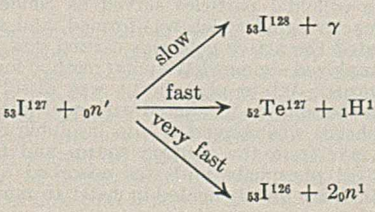
Radioactive Tracers

Previous to 1934 investigations of analytical processes by radioactive means were confined to cases involving the naturally occurring radioactive isotopes (*23*). With the discovery of artificial radioactivity by Curie and Joliot (*6*) this new property of the common elements became available for studies of the various phases of analytical chemistry. At the present time radioactive isotopes of 87 elements have been artificially produced, making application to their analytical chemistry possible.

Preparation and Separation of Radioactive Elements

Some 330 artificial radioactive isotopes have been prepared by six kinds of bombardment of the naturally occurring atoms. These involve the bombardment of the target material by a stream of (1) neutrons (n), (2) protons (p), (3) deuterons (d), (4) alpha particles or He^{++} (α), (5) electrons, and (6) gamma rays produced in a suitable manner. The last two are unimportant for the production of useful quantities of the radioelements and will not be considered. With each of the first four kinds of projectiles, four or five different types of nuclear reaction are possible. Only one or two types of reaction for each kind of bombarding particle will be indicated [for a more complete discussion of this subject consult (*37*, *53*)].

Bombarding the same natural isotope of a given element with neutrons frequently results in more than one nuclear reaction, as, for example,



(The subscript indicates the atomic number and the superscript the mass number of the isotope.) Here we see that I^{128}, Te^{127}, or I^{126}, all of which are radioactive, is produced, depending on whether slow, fast, or very fast neutrons are used. These transformations today are more commonly represented as (n,γ), (n,p), and ($n,2n$) reactions, indicating the projectile and the emitted particle, respectively, rather than by the more cumbersome equations above. Other neutron reactions that have been observed include (n,α) and (n,n) types. An example of the last one is In^{115} (n,n) In^{115*} where the asterisk indicates a radioactive isomer of the stable In^{115}.

Proton reactions are usually of the (p,n) type, though (p,γ), (p,α), and (p,p) are also known. The preparation of radiobromine is an excellent example of the (p,n) reaction:

$${}_{34}Se^{80} + {}_1H^1 \longrightarrow {}_{35}Br^{80} + {}_0n^1$$

In the case of deuterons (d,p) and (d,n) reactions are most commonly obtained, with (d,α) and ($d,2n$) less frequent. Typical of the first two are:

$${}_{15}P^{31} + {}_1H^2 \longrightarrow {}_{15}P^{32} + {}_1H^1$$
$${}_{16}S^{32} + {}_1H^2 \longrightarrow {}_{17}Cl^{33} + {}_0n^1$$

Five alpha-particle reactions have been observed: (α,n), (α,p), (α,d), ($\alpha,2n$), and (α,α), the first of which is the most common. While the above bombardment of S^{32} with deuterons yields radio-Cl^{33}, bombardment with He^{++} gives radio-Cl^{34}:

$${}_{16}S^{32} + {}_2He^4 \longrightarrow {}_{17}Cl^{34} + {}_1H^2$$

The half-lives of Cl^{33} and Cl^{34} are 2.8 seconds and 33 minutes, respectively. Thus, a given element may frequently be made radioactive in more than one way.

The best source of beams of protons, deuterons, and alpha particles for the above reactions is the "cyclotron" of Lawrence and Livingston (*33*, *34*). These same three particles may also be accelerated to high energies in the electrostatic generator (*22*). Neutrons are obtained by bombardment of beryllium with alpha particles from naturally occurring radioactive substances, such as radium, radon, and polonium, or as a by-product of a bombardment in the cyclotron or the electrostatic generator. Usually the projectile in the cyclotron is the deuteron and the target is beryllium, deuterium, or boron. The energy of the emitted neutrons depends on the nature of the target material and the energy of the deuterons.

Although the number of artificial radioelements known is large, the choice of a particular radioelement to use in an investigation is subject to a number of restrictions. Since these radioelements decay in accordance with the well-known exponential or first-order law, the time of half-life must be sufficiently long so that a conveniently measurable amount of radioactivity remains after completion of an experiment. Sometimes an element with a somewhat too short half-life (such as C^{11}, half-life = 21 minutes) may be used (*50*), provided a very high initial intensity can be obtained or a very sensitive instrument is available for quantitatively determining the radioactivity. Having tentatively selected an apparently suitable isotope, the means of preparation at one's disposal must be considered. Even though the various projectiles needed can be readily had, there still remains the question of the relative abundance of the natural isotope which must be bombarded to prepare the desired element. Thus, C^{14} is very readily prepared from C^{13} by the (d,p) reaction but C^{13} is present in ordinary carbon to the extent of only 1.1 per cent. The various restrictions indicated above seriously limit the number of radioactive isotopes actually remaining for use in chemical investigations, but the number available is still large.

Except when elements are transformed into radioactive isotopes of the same element, the elements produced in the transmutation process must be removed from the parent substance. In separations involving the radioactive elements, ordinary chemical and physical methods are generally applicable. No new chemical properties are conferred on an atom by virtue of its radioactivity, and the mass difference between stable and unstable isotopes is small enough to preclude appreciable variations in reactivity due to isotope effects.

Relatively few radioactive atoms are produced in the transmutation process. At such extremely low concentrations (of the order of 10^{-10} to 10^{-15} mole) many chemical procedures become uncertain. Some metallic sulfides, for example, have molar solubilities of the order of 10^{-12}. This corresponds to about 10^{11} atoms needed for precipitation, as contrasted with perhaps 10^{7} atoms produced in the transmutation process. Accordingly, the radioactive atoms could not be isolated by precipitation as the sulfide. Likewise, at such small concentrations, adsorption effects are more pronounced than at higher concentrations, as seen from the shape of the adsorption isotherm. Loss of active material could thus occur through adsorption on other precipitates formed during the separation process.

To ensure the efficient separation of the active isotope, a small amount of the corresponding inactive isotope is added after activation, and before making the separation. The active atoms are "carried" through the reactions necessary for their separation with a minimum loss. (Obviously, the active atoms cannot later be separated from the bulk of the inactive atoms added as carrier.) Occasionally, an active form can be isolated without using a carrier. In this case, the so-called specific activity (active atoms/total number of isotopic atoms) is at a maximum. Such separations frequently require no special methods other than those commonly used.

Chemical separation of active isotopes can be made with or without the use of a carrier.

In the preparation of radiosulfur, Voge (*64*) bombarded carbon tetrachloride with fast neutrons, obtaining radiosulfur in the form of elementary sulfur and various volatile, hydrolyzable compounds. The mixture was oxidized with alkaline hypobromite, a trace of sodium sulfate added as carrier, and barium sulfate precipitated from the acidified solution. Radiosulfur may also be prepared by bombarding sulfur with deuterons; no carrier sulfur is needed, as there is ample inactive sulfur left unaffected by the bombardment. Oxidation and precipitation as barium sulfate leave the active sulfur in a form readily converted into radioactive hydrogen sulfide.

Numerous methods are available for separating the radioactive halogens. The early method of Szilard and Chalmers (*61*) has recently been studied in detail by Lu and Sugden (*38*). The Szilard and Chalmers method consisted in irradiating liquid ethyl iodide containing a trace of free iodine with neutrons. A reducing agent was then added, and the iodine was converted to iodide and precipitated with silver nitrate. The precipitated silver iodide contained the bulk of the activity. In studying the method quantitatively, Lu and Sugden found that if free halogen was added to ethylene dibromide or butyl iodide before irradiation, the yield of extractable active isotope was better than when the free halogen is omitted. However, if phenyl bromide or phenyl iodide was irradiated, free halogen was without effect in increasing the yield. The halogen was extracted with aqueous solutions of acids, with sodium hydroxide or thiosulfate, or by metals (finely divided copper, silver, aluminum, and zinc). The addition of 4 per cent aniline before irradiation increased the percentage of radioactive material extractable by acids. Phenol likewise produced an increased, though smaller, extractability from water solutions. Presumably these compounds react preferentially with the radioactive bromine atoms liberated by gamma-ray recoil, enabling the active atoms to be extracted in highly concentrated form.

A method of interest in the preparation of radioactive hydrogen bromide, which depends on the complete and rapid exchange of bromine atoms with gaseous hydrogen bromide, has been given by Liberatore and Wiig (*35*). Radiobromine is produced by proton bombardment of selenium. When gaseous hydrogen bromide is heated with the powdered selenium, the radioactive bromine atoms exchange with the bromine atoms in the hydrogen bromide, giving radioactive hydrogen bromide. The radioactive bromine is recovered almost completely in this form.

A large number of separations are made most conveniently by conventional chemical methods. In any such process, however, the danger of loss or contamination through coprecipitation should be considered. Impurities in the material bombarded may become radioactive, and accompany the desired active species during the separation. Much remains to be known regarding the behavior of matter at such small concentrations in passing through a series of reactions.

As an example, during the separation of radioactive zinc from copper, the precipitation of copper sulfide will result in some loss of zinc through adsorption on the precipitate. If no carrier is used for the zinc, such losses may account for an appreciable fraction of the activity. A satisfactory alternative method for this separation is either precipitation of the copper with salicylaldoxime (*16*) at a pH of about 3, or electrodeposition of the copper from sulfuric-nitric acid solution. The zinc remains in solution, and if no carrier is added, a high specific activity is obtained.

Electrochemical methods have been used in separations involving the radioelements. Electrodeposition from the gas phase or from solution has been attempted in the separation of radioiodine. Thus, when alkyl iodides are bombarded with neutrons, the corresponding radioactive isotope of iodine is formed. These active atoms are ejected from the molecule, as the result of gamma ray recoil, in charged form. Fermi (*15*) was unsuccessful in depositing radioiodine thus produced from gaseous ethyl iodide and methyl iodide. However, Paneth and Fay (*44*) succeeded in depositing iodine on copper and silver electrodes in good yield from neutron-irradiated liquid organic iodides. Govaerts (*19*) concentrated P^{32} after neutron bombardment of carbon disulfide by depositing the phosphorus directly from the carbon disulfide on a copper anode. Fay and Paneth (*13*) were able to deposit on copper and platinum electrodes no more than 35 per cent of the active arsenic produced by neutron bombardment of gaseous arsine.

Electrodeposition from aqueous solution is an effective means of separation. Radiocopper has been isolated by internal electrolysis on zinc, and also on a rotating lead plate (*24*). Steigman (*58*) used high-speed rotating disks and currents of 10 milliamperes for the same separation. Livingood and Seaborg (*36*) separated radioactive antimony by internal electrolysis on tin. Electrodepositions should prove of great value in making separations. Electrolysis with a mercury cathode (*25*) should be of use in many cases, although it does not appear to have been used as yet.

Extraction and adsorption methods for separating the radioelements have been successful. Grahame and Seaborg (*21*) have studied the partition of small amounts of radioelements between ether and hydrochloric acid, and conclude that extraction processes have certain unique advantages over other methods. The extracted element has a high specific activity, and the danger of contamination of the sample by some unsuspected radioelement is avoided. Data are given for the extraction of iron, gallium, and cobalt. Erbacher and Philipp (*11*) extracted radioactive halogens from neutron-irradiated alkyl halides with water.

These investigators also isolated radioactive halogens by adsorption on charcoal (*10*). The neutron-irradiated alkyl halides were shaken with charcoal, and the active halogen was later desorbed by boiling with water. Roginskiĭ and Gopstein (*49*) recommend the use of aluminum oxide as adsorbent. The chromatographic method thus may come to play an important part in making difficult separations. In separating radioactive gold Majer (*40*) irradiated with neutrons an alkaline gold chloride solution to which a small amount of colloidal gold had been added. The colloidal particles served as condensation nuclei for the radioactive gold which was formed, and as the colloidal gold flocculated the active gold was carried down with it. Erbacher (*8*) employed a somewhat similar method for concentrating radiophosphorus. White phosphorus was dissolved in carbon disulfide and the solution irradiated with neutrons. Some of the white phosphorus was converted into insoluble red phosphorus by gamma rays from the neutron source and the radioactive phosphorus (as phosphate ion) was adsorbed on the surface. The precipitate was merely heated in water to remove the radioactive phosphate.

By extraction with water Maier-Leibnitz (*39*) recovered radiophosphorus from neutron-irradiated triphenylphosphate dissolved in benzene. The yields were small. Better results were secured by bombarding carbon disulfide with neutrons and filtering off the resulting small amount of precipitate which contained most of the active phosphorus.

Radioelements have also been separated by volatilization. Thus, Alvarez, Helmholz, and Nelson (*1*) volatilized radioactive cadmium from deuteron-bombarded silver. Ruben and Kamen (*52*) separated radioactive carbon from neutron-irradiated ammonium nitrate solution by pumping off the vapors, which contained the radiocarbon mainly as carbon dioxide.

From the foregoing survey, it appears that no fixed rules exist for separating radioelements in form suitable for use as indicators. In choosing a method, consideration must be given to the sharpness of the separation, the time required, and the form in which the active element is finally to be used. Many separations have been made merely for the purpose of establishing the chemical identity of some newly created radioelement, with no thought of indicator work. The splendid table of Seaborg (*53*) gives literature references which should lead to at least one method for separating any of the known radioelements. All the good methods of separation have not yet been discovered, however, and those interested in this field have ample opportunity to draw upon past experience and to exercise their ingenuity in developing new procedures.

Measurement of the Radiations

As the artificial radioelements are detected and determined by means of the ionizing radiations which they emit, the proper choice of apparatus for this purpose is of utmost importance. Three general types of detecting apparatus are in use at present. One simple and widely used type of detecting device is the quartz fiber (or Lauritsen) electroscope (*32*). This instrument is adapted to the measurement of all kinds of radiations emitted by the radioelements but has the disadvantage of being less sensitive than the other instruments.

A second somewhat more sensitive type is the combined ionization chamber–electrometer, which is also suitable for the detection of all kinds of radioactive radiations. A number of these instruments have been described (*3*, *7*).

The most sensitive detecting device obtainable, and at the same time probably the most useful for the chemist, is the Geiger-Müller counter, which may be adapted to the measurement of the activity of solids, liquids, or gases. Special types of counters for use with solutions have been constructed by Olson (*42*) and Bale (*2*), and for use with gases by Ruben (*51*) and Seaborg (*54*). A description of various counter circuits as well as the construction of several types of counters is given by Neher (*60*). For tracer studies the authors feel that the Geiger-Müller counter has wide applicability. In many cases the activity is diluted by the carrier, and again in the reaction itself. In adsorption experiments, for example, only small amounts of the radioelement are adsorbed, and the most sensitive means for measuring these quantities must be used. The type of counter used by Bale (*2*) for measuring the activity of liquids has proved extremely satisfactory in both chemical and biological studies.

If the radioactive element is merely to be detected in some phase of the reaction, the material has only to be placed somewhere near the counter tube or window of the ionization chamber, but this is insufficient for making quantitative measurements. When the radiation is used as a quantitative measure of an element, certain precautions are essential. The rate of decay of the material should be known. This can be found from published data, or better, from frequent measurements of the activity of the sample over a period of time. All measurements must be made in as nearly identical fashion as possible. The radioactive material should always be placed the same distance from the counter tube and the counter should always operate at the same voltage. A "background" count (count due to stray radiation) should always be taken and subtracted from the principal count. It is also desirable to check the counter for fluctuations by frequent counts on some long-lived natural radioactive material such as a potassium salt. Extremely strong sources should not be counted, for the counter generally is inaccurate above one thousand counts per minute. It is preferable to dilute the sample to give somewhat weaker activities. Strong samples are more conveniently measured on ionization chambers, where variation of the sensitivity is possible.

Occasionally the vessels used in making measurements on solutions become slightly radioactive.

Applications

DETERMINATION OF SOLUBILITY. As it is possible to measure accurately extremely small amounts of a radioelement, radioactive indicators are helpful in making solubility measurements.

A definite amount of the insoluble compound is prepared containing a known amount of radioactivity. After equilibrium in the solvent has been reached, a portion of the solvent is removed and the activity measured. The fraction of the original activity recovered indicates the fraction of the material which dissolved. This method has been recently used in determining the solubility of ammonium phosphomolybdate (using radioactive phosphorus, *14*), cobaltic hydroxide (*5*), cobalt α-nitroso-β-naphthol and cobalt β-nitroso-α-naphthol (*4*). In the case of cobaltic hydroxide, the value found for the solubility was 5.6×10^{-3} mg. per liter, as contrasted with an earlier value of 3.18 mg. per liter obtained by another method. Presumably the higher value was the result of colloidal cobaltic hydroxide remaining in the solution. The solubility of cobalt α-nitroso-β-naphthol was found to be 1.5 mg. per liter, while the β-nitroso-α-naphthol derivative dissolved to the extent of only 0.17 mg. per liter. Ishibashi and Kishi (*27*) determined the solubility of lead salicylaldoxime using thorium B (an isotope of lead) as indicator and obtained the value 4.0×10^{-6} mole per liter.

EFFICIENCY OF SEPARATION. One of the earliest studies of this type was made by Erbacher and Philipp (*9*). Using radioactive gold, they studied the completeness with which gold can be separated from platinum and iridium in mixtures containing the three elements.

When a hot alkaline solution of the elements was treated with sodium formate, the metals were precipitated. After washing and igniting, they were digested with aqua regia, whereupon the gold and platinum dissolved, leaving the iridium behind. The results obtained for iridium by this procedure were always high, presumably indicating incomplete removal of gold and platinum. Examination of the iridium fraction indicated that the gold (radioactive) was incompletely removed.

The solution containing gold and platinum, after separation from iridium, was treated with hydrogen peroxide, which precipitated the gold. When precipitation was thought complete, the gold was filtered off and platinum precipitated from the filtrate with sodium formate. In the case of the gold fraction, high results again were obtained, presumably the result of contamination by platinum. Measurement of the activity revealed, however, that contamination by platinum was greater even than had been expected. Actually, only 97 per cent of the gold was recovered in the so-called gold fraction. The remaining 3 per cent appeared in the platinum fraction. In another series of experiments, it was found that even after half of the platinum had been precipitated along with the gold by the peroxide, recovery of the gold was incomplete. The unsatisfactory nature of the peroxide separation was thus demonstrated.

In connection with other studies, Wiig and Flagg (*65*) found the precipitation of stannous tin by potassium ferricyanide to be complete in solutions 1 molar in hydrochloric acid. Radioactive tin was produced by deuteron bombardment of metallic tin. This was dissolved in hydrochloric acid, and aliquot parts of the solution were precipitated with excess ferricyanide. Examination of the filtrate with a counter of the type described by Bale (*2*) indicated complete removal of the tin.

The work of Grahame and Seaborg (*21*) indicates another aspect of analytical chemistry which is served by radioactive indicators. The extraction of iron and gallium chlorides by ether was shown to be extremely efficient as a means of separating these elements from cadmium and manganese. A method was also suggested for the identification of radioelements, using the extraction procedure. The distribution coefficient for a known stable element between two phases may be determined. Then, if an unknown radioelement is found, its distribution coefficient may be determined, which in turn serves for its identification.

Coprecipitation. Studies of a somewhat different nature are being carried out by Flewelling and Flagg (*17*). Using radioactive beryllium, the behavior of this element in separations made with 8-hydroxyquinoline is being studied. Thus, for example, it has been found that in the separation of aluminum and beryllium by the method of Kolthoff and Sandell (*30*), the pH must be kept below a value of 6. At higher pH values the appearance of radioactivity in the precipitate of aluminum hydroxyquinolate indicates that beryllium is also being precipitated.

Properties of Analytical Precipitates. An extension of the method of Paneth (*43*) for studying the properties of surfaces, hitherto confined to elements having natural radioactive isotopes, has become possible by use of artificial radioactive indicators. Thus, the specific surface of silver chloride has been determined (*31*) by shaking the precipitate in a solution containing radioactive chloride ions and measuring the rate of uptake of the radioactive ions.

Kolthoff and O'Brien (*29*) have measured the specific surface of silver bromide by the method of Paneth, using radioactive bromine. They found that exchange between bromide ion and silver bromide was not confined to the surface layer. Only in the presence of a dye such as wool violet, which prevented the recrystallization process from taking place, could exchange be confined to the surface layer of the precipitate. On surfaces containing wool violet, however, it was possible to measure the specific surface of both fresh and aged precipitates. They found that freshly precipitated silver bromide had a large surface, and that the air-dried product underwent thermal aging. Such an aging process requires that silver bromide on an active (fresh) surface have marked thermal mobility, and that ions or molecules can move around to more normal positions. When fresh surface is continuously exposed as a result of such a process, there should be an opportunity for the exchange $AgBr + BrBr^* \leftrightarrows AgBr^* + BrBr$ to take place. It was found that upon shaking the solid with radioactive bromine either dissolved in ethyl bromide or in the gas phase, the speed of incorporation of radioactive bromine into the solid decreased as the surface decreased and that the radioactive bromine actually penetrated the solid below the surface. Thus the mechanism of the thermal aging process was shown.

Somewhat similar experiments have been performed by Polesitskiĭ (*46*), who attributed a decreasing rate of exchange between bromide ion and solid silver bromide to the aging process. Preaged precipitates gave slower rates than did fresh precipitates, and silver bromide which had been previously fused showed no exchange.

Analytical Methods for Rare Elements. Artificial radioactivity promises to be extremely useful in extending our knowledge of the analytical chemistry of the rarer elements. At the time of the discovery of the artificial radioelements, numbers 43, 61, 85, and 87 were still unknown or in doubt. Elements 43, 85, and probably 61 (*47*) have been prepared artificially and the behavior of 43 and 85 has been investigated with the aid of related stable elements as carriers. Element 85 has been made by bombarding bismuth with 32 M. e. v. alpha particles and its properties have been studied by Segré, MacKenzie, and Corson (*57*). Using iodine as a carrier, 85 was found to be much more metallic that iodine and to bear little resemblance to the halogens. It is precipitated by hydrogen sulfide but not by silver nitrate; it is extracted by carbon tetrachloride to a much smaller extent than is iodine, etc. Past attempts to isolate 85, based on a strict similarity with iodine, probably failed because of such differences in behavior.

Similarly, radioelement 43 has been found (*45, 56*) to resemble rhenium in not being precipitated along with manganese sulfide and to differ from rhenium in not being volatilized from a hot sulfuric acid solution in a current of hydrogen chloride. The discovery of such differences in behavior, together with the use of the artificial radioelement as a tracer, should lead to methods of concentration and analysis of stable isotopes of elements 43, 85, 93, etc., should they exist in detectable quantities.

Analysis by "Radioactivation". One very interesting application of radioelements is the determination of traces of impurity in a substance by conversion of the impurity into a radioactive substance by bombardment in the cyclotron.

In order to test for gallium in pure iron, Seaborg and Livingood (*55*) bombarded a sample with deuterons. When pure iron is bombarded with deuterons the reaction Fe^{58} (d,p) Fe^{59} is the only one giving rise to radioactivity. If present, Ga^{69} and Ga^{71} would yield radioactive Ga^{70} and Ga^{72}. For the sake of simplicity, let us consider only Ga^{72}, though both must be taken into account. Thus, when iron containing gallium is bombarded with deuterons, radio-Fe^{59} and radio-Ga^{72} result. These two radioelements have half-lives of 47 days and 14 hours, respectively, and so the radioactive intensities in the bombarded sample were readily determined to be in the ratio of 2000 to 1. If the quantities of Fe^{58} and of Ga^{71} in the iron sample are the same, and if the efficiencies of conversion (or the yield) are the same, then the radioactive intensities should be the same for the same bombardments. For two elements as close in atomic number as iron and gallium, the efficiencies may be assumed to be the same, so that the activities depend only on the relative amounts of Fe^{58} and Ga^{71} present. Ordinary iron contains only 0.28 per cent Fe^{58} and since the activity of Ga^{72} is $^1/_{2000}$ that of Fe^{59}, the amount of Ga^{71} must be $^1/_{2000}$ that of Fe^{58}. It was found that the sample of iron contained about 6 p. p. m. of gallium, and one tenth of this quantity could readily have been detected. Similar experiments have been carried out on copper in silver (*28*), copper in nickel (*55*), iron in cobalt oxide (*55*), sulfur in a sheet of paper (*55*), and dysprosium in fractions of yttrium earths (*18*).

In using activation as a method of analysis great care must be taken to avoid introduction of traces of impurities during the bombardment. While this procedure will probably be used only infrequently, it illustrates the power of this new tool.

Stable Isotopes

Since this review deals primarily with the radioelements as tracers, only brief mention will be made of the use of stable isotopes. For a discussion of deuterium the reader is referred to the book by Farkas (*12*). Through the efforts of Urey and his colleagues (*26, 59, 62*) limited quantities of enriched samples of other stable isotopes, notably C^{13}, N^{15}, and S^{34} are available at present with commercial production soon to be realized.

A sample containing more than the natural or normal percentage of the desired isotope (C^{13}, etc.) is in general obtained by (1) diffusion through porous membranes or a gaseous substance, (2) the thermal diffusion method of Clusius and Dickel, or (3) exchange reactions and distillations which produce differences in composition by taking advantage of differences in physical and chemical properties. Except for deuterium, the most convenient method of quantitatively determining the amount of the heavy isotope present is by the mass spectrometer. The construction, operation, and cost of a suitable instrument have been discussed in detail by Nier (*41*).

Having a sample enriched in the isotope of an element, the sort of use to which it can be put is well illustrated by the excellent work of Rittenberg and Foster (*48*, *63*) on the analysis of mixtures of amino acids.

From such a mixture of acids one can in general isolate either all of a particular amino acid in impure form or some of it in a pure state, but not all of the pure acid. The per cent of the pure acid can be determined, however, by the "isotope dilution method". The procedure is to add *a* grams of pure amino acid A containing C_0 atom per cent excess of N^{15} (or C^{13}) to a known weight, *W*, of a mixture of amino acids and then to isolate from this mixture a pure sample of amino acid A. (Obviously the *a* grams added become uniformly mixed with that already present in the unknown mixture.) The pure sample of amino acid A just isolated is now analyzed for N^{15}, by the mass spectrometer.

If it is found to contain *C* atom per cent excess of N^{15}, then the fraction of the amino acid A present in the original unknown mixture is given by $(C_0/C - 1)\frac{a}{W}$. Since only very small samples are needed for an isotope analysis, large losses in purification are permissible. According to Rittenberg, the error of the method may be reduced to 1 per cent by the proper choice of conditions.

Obviously, this method may be applied to the analysis of other mixtures, provided there is no loss of the heavy isotope through exchange reactions and provided a pure sample of the substance, for which analysis is being made, can be isolated. It is claimed that the method can be modified so that the isolated sample need not be quite pure (*20*).

Conclusion

The methods outlined have, of course, a number of advantages and disadvantages as compared with the usual analytical procedures. Tracer isotopes can be used to solve many problems with which ordinary methods cannot possibly cope. The analysis can often be performed more rapidly and more conveniently, particularly with radioactive isotopes, than by ordinary qualitative and quantitative analysis. Furthermore, there is no doubt about the identity of the substance being measured—that is, only one species can be radioactive or exhibit the proper half-life period. Finally, the accuracy of a determination can be varied by counting much or little, as desired (for a discussion of errors in counting, see Neher, *60*).

One disadvantage inherent in the use of either stable or radioactive isotopes is the lack of general availability of the isotopes themselves and of the necessary instruments for their quantitative determination. These substances are, however, becoming increasingly available and the detection devices are not expensive to build and operate. As compared with the counter the mass spectrometer is somewhat more expensive both in construction and operation. The reproducibility of results is perhaps not so great as with standardized analytical procedures but with exercise of reasonable care satisfactory accuracy can be attained.

In making use of tracer analysis, a choice may have to be made between the use of a stable or radioactive isotope, as with carbon, nitrogen, or sulfur. Here a number of facts will have to be considered, such as availability of the isotope and the measuring device, the relative costs of the two procedures, the time available for an experiment (the only radionitrogens known are N^{13} and N^{16} with half-lives of 10 minutes and 8 seconds, respectively), and the extent to which the tracer atom can be diluted and still be determined quantitatively. Like any other method, the isotope method cannot be used indiscriminately in attacking chemical problems. Its success in the hands of any investigator will be determined by the care and thoughtfulness with which it is used.

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The S. I. L. Viscometer

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A kinematic viscometer has been developed and proved practical in actual routine testing operations. It is almost, if not fully, as satisfactory as a more expensive patented instrument of foreign origin which has been extensively used.

DURING the past few years there has been an increasing tendency in laboratories of the petroleum industry to determine viscosity by means of long-capillary glass instruments, commonly designated as "kinematic" viscometers. These instruments are fundamentally more accurate than short-outlet "commercial" viscometers such as the Saybolt, Redwood, and Engler, and have been used for many years in research or investigative work. They are now being adopted for routine testing and considerable progress has been made in minimizing certain inherent deficiencies, such as fragility and the need for fussy manipulation.

The two kinematic viscometers which are most familiar to the petroleum industry in the United States are probably the Ubbelohde (*5*) and the Fenske (*2*). The first is so costly that its use has been restricted and the second lacks several characteristics which the authors consider desirable. The Zeitfuchs (*6*) viscometer possesses fundamental characteristics which seem to place it almost on a par with the Ubbelohde, but it is also patented and the original negotiations for its use by the companies with which the authors are associated were unsuccessful. The work of developing the S. I. L. viscometer, described in this paper, had reached an advanced stage before the dedication of the Zeitfuchs' patent to the public was announced. The S. I. L. instrument, as finally evolved, differs from the Zeitfuchs sufficiently to justify a published description.

Characteristics of Viscometers

The U-tube type of viscometer was described by Ostwald (*4*) about 1893 and has been used in numerous forms and modifications. The B. S. I. (*3*) U-tube viscometers are standards of the Institute of Petroleum of Great Britain. They are of the conventional Ostwald type and do not seem to involve any original features.

The Fenske (*1*, *2*) modification of the Ostwald viscometer is characterized by a bent form which minimizes errors due to deviations from a strictly vertical position while in use. This advantage is attained by some sacrifice of precision in filling, and it is necessary to use calibration constants that vary with the temperature of test. The Fenske viscometer is, however, widely used in the United States and is a practical instrument in spite of its obvious defects.

The Ubbelohde (*5*) or suspended level viscometer represents an important advance over the conventional Ostwald or U-tube type. Its characteristic feature from the point of view of routine use is freedom from the necessity of accurate filling. There are numerous other theoretical and practical advantages, including the possibility of construction with multiple capillaries as proposed by FitzSimons (*1*).

The Zeitfuchs (*6*) viscometer is an ingenious development and the details adapting the instrument to routine use have been worked out in a thoroughgoing manner. The characteristic feature is an overflow gallery and auxiliary withdrawal tube on the capillary arm, which facilitates precise nonautomatic adjustment of the volume of oil.

The S. I. L. viscometer, described in this paper, embodies the feature of an overflow gallery which is on the open arm instead of the capillary arm and which permits precise automatic establishment of the correct volume after the oil under test has reached the desired temperature. This overflow gallery has a definite similarity to that of the familiar Saybolt viscometer.

Description

Figure 1 and Table I indicate the form and dimensions of the series of S. I. L. viscometers at present in use. The dimensional tolerances have been accepted as practical manufacturing specifications by the commercial organization from which instruments now in use have been purchased.

CALIBRATION. Instruments, as purchased, are uncalibrated and lack the upper circular mark (4, Figure 1). Test runs are made in comparison with previously standardized viscometers and the position of the mark is established so that constant *C* (Equation 1 or 2) is within ±0.2 per cent of the standard value for the size of instrument under test. The mark is then engraved on the glass by the conventional acid etching method.

OPERATION. With the upper end of tube 2 (Figure 1) closed by the operator's fingertip, the liquid to be tested is poured into tube 1 and allowed to flow through opening *J* until this is submerged at least 0.62 cm. (0.25 inch), but not more than 1.9 cm. (0.75 inch), with bulb *A* completely filled. The liquid should be free from extraneous matter and preliminary filtration or straining is frequently desirable. It can be poured directly into the viscometer from a lipped beaker but if spillage is likely to cause inconvenience, a small funnel may be used. If the liquid does not flow readily through *J*, it may be warmed moderately. This is rarely necessary except when extremely viscous products are to be tested at temperatures appreciably above 38° C. (100° F.).

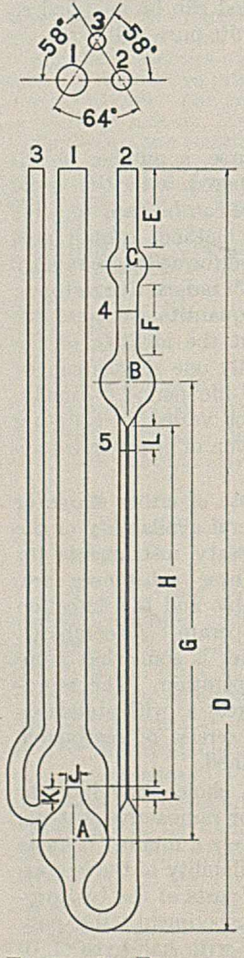

FIGURE 1. FORM AND ARRANGEMENT OF S. I. L. VISCOMETER

After introducing the liquid the upper end of tube 2 is opened, and the filled viscometer is placed in the thermostatic bath. Sufficient time is allowed to bring the liquid to the temperature of test and the excess is then withdrawn through tube 3 by suction (preferably mechanical suction with a trap in the line to retain the fluid). Suction is then applied to tube 2 and the liquid is drawn up until its upper level is just below the middle of bulb *C*. Particular care must be taken at the beginning of this operation to avoid even the slightest positive pressure in tube 2, as it will cause some of the liquid to pass through orifice *J* into gallery *K* and destroy the accuracy of the volume adjustment previously made.

The suction is then released and the time required for the meniscus to pass from mark 4 down to mark 5 is determined. The liquid is then brought up into *C* again and the timing operation repeated. It is usually desirable to make at least three determinations and a larger number is necessary if the difference between any two values is in excess of 0.1 per cent. It is desirable to have a series of determinations with the average difference from the mean not in excess of 0.05 per cent. The instrument is then emptied, cleaned, and dried, preliminary to use with another sample. Except for referee testing, check determinations involving a refilling with the same sample are rarely necessary unless there is uncertainty regarding the homogeneity of the liquid or the cleanliness of the apparatus.

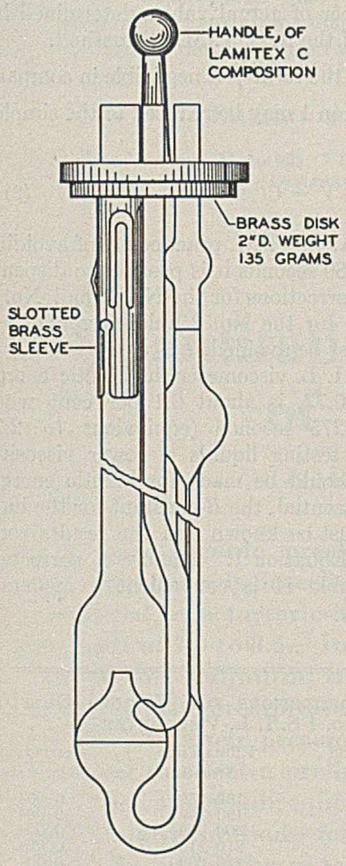

Figure 2. General Features of Tube Holder

Accessories

There are a number of major and minor accessories that are essential for accurate and efficient viscosity measurement. These range from thermometers and thermostatic baths to assemblies of tubing and cocks for applying suction and pressure. The authors and their associates have developed a number of these accessories which have been found satisfactory. Most of them, however, are of general rather than specific usefulness and it is not proposed to include a detailed description in the present paper.

Table I. Dimensions of S. I. L. Viscometers

(Refer to Figure 1)

		Mm.
Outside diameter		
Bulb *A*	Approx.	26
Bulb *B*	Approx.	21
Bulb *C*	Approx.	13
Tube 1		11 ± 0.2
Tube 2	Approx.	7
Tube 3	Approx.	6
Center distance		
From 1 to 3		17 ± 0.3
From 1 to 2		18 ± 0.3
From 2 to 3		17 ± 0.3
D		295 ± 3.0
E		40 minimum
F		25 minimum
G		178 ± 2.0
H		145 ± 0.5
I		5 ± 1.0
K		7 minimum
L		20 ± 2.0
		Ml.
Volume of *A*		7 minimum
Volume of *B*		4.8 ± 0.1

S. I. L. Viscometer Size No.	Calibration Constant, *C*	Capillary Diameter, Mm.	Inside Diameter of Opening *J*, Mm.
1	0.01	0.62 ± 0.01	4.5 ± 0.1
2	0.10	1.10 ± 0.01	5.5 ± 0.1
3	1.00	1.96 ± 0.02	6.5 ± 0.1
4	10.00	3.50 ± 0.02	7.5 ± 0.1

Wall thicknesses of tubes 1, 2, and 3, approximately 1.0 mm.
Capillary, trumpet-shaped ends
Marking, size number and manufacturer's or purchaser's serial number etched or otherwise permanently marked, preferably on flare at lower end of tube 1

Two accessories, however, were developed to take care of specific requirements of the Ubbelohde and S. I. L. viscometers.

Tube Holder. The tube holder shown in Figure 2 was developed to accomplish accurate alignment of the viscometer in a vertical position, easy removal from the thermostatic bath and easy separation of the holder and the viscometer, and protection of the viscometer from breakage.

The tube holder is usable only with thermostatic baths having rigid top plates and accurately machined recess surfaces on which the holders rest. The circular form shown in Figure 2 is desirable because it is both easy to fabricate and convenient for the operator, who can rotate the holder to the position which suits him best without changing its alignment from the vertical. A square or rectangular form is, however, entirely usable. It is desirable to have holders interchangeable and this necessitates standard sizes and spacing for the holes and accurate adherence to the dimensional limits specified for the viscometers.

Other types of holders accomplishing the same results can undoubtedly be made and the present description is offered simply as a report on a mechanical development that has proved highly satisfactory and has taken care of the varying preferences concerning such details as filling, operating, and cleaning viscometers with or without intermittent removal from thermostatic baths. The holder, when in place, provides a degree of protection against breakage equivalent to that of the metal supporting member of Zeitfuchs or a glass bridge such as is usually found on Fenske viscometers. The construction of the holder is such that glass bridges could be used on S. I. L. or Ubbelohde viscometers, if desired, to reduce the possibility of breakage when instruments are not in the holders. In addition, it would be entirely feasible to attach a shielding cage which would cover the entire length of the viscometer. Operators associated with the authors have indicated a preference for instruments without bridges and the breakage has been so infrequent that cages have not seemed necessary.

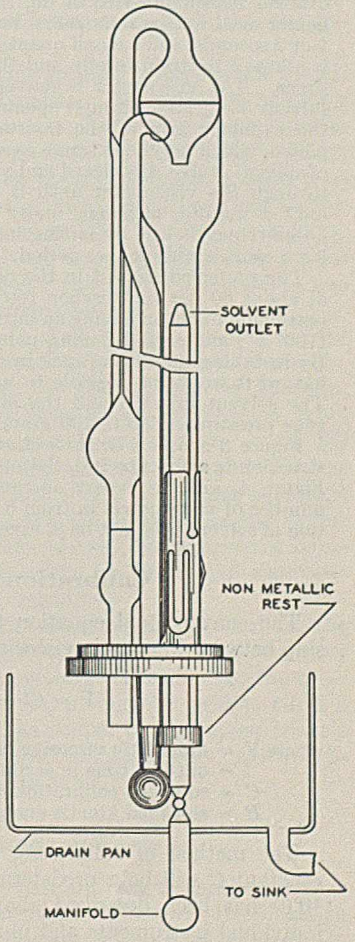

Figure 3. Details of Cleaning Rack

Cleaning Rack. The S. I. L. viscometer is slightly inferior to most if not all of the other types of kinematic instruments with respect to ease of cleaning between tests. This is due to the gallery. The Zeitfuchs viscometer also has a gallery but if it is not cleaned perfectly no harm results, whereas any unremoved liquid in the gallery of the S. I. L. instrument may contaminate the oil under test.

The cleaning rack shown in Figures 3 and 4 was actually developed to facilitate operations with Ubbelohde viscometers but is particularly valuable with the S. I. L. instrument. It is so convenient and efficient that operators using it do not notice any important difference between the two instruments with respect to cleaning.

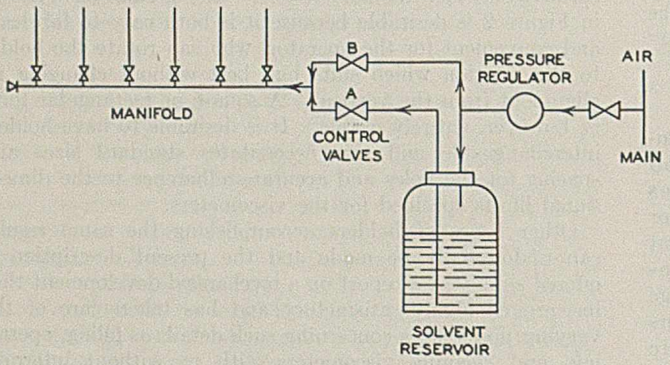

FIGURE 4. GENERAL ARRANGEMENT OF CLEANING RACK

The actual cleaning procedure involves placing a viscometer, drained reasonably free of oil, in the position indicated. The holder need not be removed. Valve *A* (Figure 4) is opened for 1 or 2 seconds, and a small quantity of solvent is blown in. This is allowed to drain briefly and the operation is repeated several times. The viscometer is moved around so that some of the solvent is injected through opening *J* (Figure 1) and washes out the capillary arm of the instrument. After washing is completed, which may in extreme cases require eight or ten "squirts" of solvent, valve *A* is closed and valve *B* is opened. Air is blown through the viscometer until it is dry, which usually requires only a minute, although under ordinary operating condition, no efficiency is lost by letting instruments remain "on the air" for a considerably longer period.

The preferred solvent in the authors' laboratory is a mixture of about 60 per cent carbon tetrachloride and 40 per cent of a petroleum naphtha having an initial boiling point of about 38° C. (100° F.) and a final boiling point of about 150° C. (300° F.). By installing the drying rack in a location where there is no fire hazard it would be possible to use straight petroleum naphtha. The solvent injected and the air used for drying are under a gage pressure of 350 to 700 grams per sq. cm. (5 to 10 pounds).

Figure 3 shows a single section of the rack. The usual construction is a six-tube installation, as shown diagrammatically in Figure 4, and an expert operator can clean and dry the full number of viscometers in from 5 to 10 minutes. The consumption of solvent need not be in excess of 400 cc. per tube cleaned.

Calibration Constants

The conventional equation for representing the relationship between kinematic viscosity and efflux time is:

$$V = Ct - \frac{B}{t} \qquad (1)$$

where V = kinematic viscosity in centistokes
t = outflow time in seconds
C = so-called calibration constant of the instrument
B = so-called kinetic energy constant of the instrument

The method of calibrating S. I. L. viscometers so that constant C will be a predetermined value (0.01, 0.1, 1.0, or 10.0) has been described above. Constant B varies with individual instruments and must be actually determined by suitable methods if the highest degree of precision is required.

An adequate degree of precision is possible for all oils having viscosities in excess of 3 or 4 centistokes by assuming that the average B-constant for S. I. L. viscometers is 0.77. This figure was obtained by Zeitfuchs (*6*) for instruments of the same essential dimensions, and although questionable from a theoretical point of view has proved reasonably close to the limited number of actual values determined by the authors through use of the A. S. T. M. (*1*) method.

When the magnitude of the term $\frac{B}{t}$ is negligible in comparison to the term Ct, Equation 1 may be reduced to the simpler form

$$V = Ct \qquad (2)$$

By following the A. S. T. M. practice (*1*) of avoiding efflux times less than 80 seconds it is possible to dispense with kinetic energy corrections for the No. 3 and No. 4 instruments and also for the No. 2 unless errors of less than 0.1 per cent must be avoided.

With the No. 1 S. I. L. viscometer the kinetic energy correction, if $B = 0.77$, is about 0.1 per cent when the efflux time is 275 seconds (equivalent to 2.75 centistokes). When testing liquids of lower viscosity, suitable allowances should be made for kinetic energy. If high accuracy is essential, the B-constant for the individual instrument must be known and the results computed by the use of Equation 1. The use of correction values shown in Table II is convenient if moderate accuracy is adequate.

TABLE II. NEGATIVE CORRECTIONS FOR VARIOUS OUTFLOW TIMES WITH NO. 1 S. I. L. VISCOMETER

Efflux Time *Seconds*	Correction *Centistoke*	Efflux Time *Seconds*	Correction *Centistoke*
80–89	0.010	180–189	0.004
90–99	0.009	190–199	0.004
100–109	0.008	200–209	0.004
110–119	0.007	210–219	0.004
120–129	0.006	220–229	0.004
130–139	0.006	230–239	0.003
140–149	0.006	240–249	0.003
150–159	0.005	250–259	0.003
160–169	0.005	260–269	0.003
170–179	0.005	270–279[a]	0.003

[a] Above 280 no correction unless an accuracy in hundredths of a per cent is expected.

S. I. L. Viscometers of Other Dimensions

The possible usefulness of viscometers having C constants intermediate between those of the series described above has been recognized. Experimental instruments are being obtained and it is planned to give them a trial in actual testing service.

Commercial Availability

The authors have been able to purchase uncalibrated S. I. L. viscometers made to the specifications listed in Table I at less than two thirds of the price they pay currently for uncalibrated Ubbelohde instruments supplied by the same manufacturer. The amount of laboratory work involved in adjusting S. I. L. viscometers to predetermined calibration constants is only slightly more than the work of evaluating constants for tubes already marked.

No commercial supply of reliably adjusted or calibrated viscometers has as yet been developed, nor is any known to exist for the other types of "kinematic" instruments. It is believed that this deficiency may be corrected when kinematic viscometers are used by a larger number of laboratories that are not equipped to do their own calibration work.

The cleaning rack described is commercially available.

Acknowledgments

W. H. Schaer, instrument maker of the Standard Inspection Laboratory, deserves credit for the development of the tube holder described in this paper. The cooperation of the commercial organizations manufacturing the viscometers and the cleaning racks has been very helpful.

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Quantitative Determination and Separation of Copper with Benzotriazole

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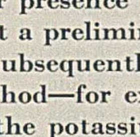
A new organic precipitant for copper, benzotriazole, is described. Copper is precipitated in a tartaric-acetic acid solution at a pH of 7.0 to 8.5. In the absence of silver, nickel, cadmium, zinc, cobalt, and ferrous iron the precipitate can be weighed directly. In their presence the reagent can be used to effect a preliminary separation, and the copper subsequently determined by a standard method—for example, electrolytically or by the potassium iodide–thiosulfate method.

Benzotriazole is an excellent precipitant for copper in iron and steel preparatory to the analysis by the standard iodide method. It possesses the advantage over the sulfide precipitation that arsenic, antimony, and molybdenum are not precipitated.

The paper presents data on the proper conditions of acidity, temperature, pH, etc., for precipitation. A detailed procedure for determining copper in iron and steel is given.

ALTHOUGH benzo-1,2,3-triazole



has been known for many years, little work on its application to the quantitative analysis for copper has been published. Remington and Moyer (*4*) made a qualitative study of the reagent and also reported a gravimetric procedure for the quantitative determination of cuprous copper, silver, and zinc.

The compound itself is light, white, needle-crystalline, and soluble in alcohol, benzene, and water, a 2 per cent aqueous solution at room temperature being nearly saturated. It reacts with copper in ammoniacal solution to give a blue-green precipitate of the composition $(C_6H_4N_3)_2Cu$. Experimental work was undertaken in the chemical laboratory of the Battelle Memorial Institute to determine the conditions under which the precipitation of copper is complete, particularly in the analysis of copper in cast irons, steels, and other copper-bearing materials.

The advantages of a specific reagent to precipitate metals are known to all analytical chemists. Benzotriazole, as shown in this paper, is specific for copper, but certain other ions are also precipitated. In the presence of Fe^{++}, Ag^{+}, Ni^{++}, Cd^{++}, Zn^{++}, and Co^{++} the copper precipitate cannot be weighed directly. On the other hand, the copper can be precipitated from a solution containing arsenic, antimony, molybdenum, and tin which are coprecipitated with copper by hydrogen sulfide and which interfere in subsequent potassium iodide–thiosulfate determinations.

While some investigators (*1, 2, 3*) have shown that copper can be titrated in the presence of moderate amounts of arsenic, trivalent iron, and antimony by the addition of fluorides, phthalates, and acetates as buffers, the presence of large amounts of these elements is still undesirable. Park (*3*) states that the presence of large amounts of fluoride reduces the accuracy of the titration and that if manganese is present with iron and arsenic the solution is buffered. In any event, where speed and accuracy are required, the absence of interfering elements is highly beneficial, as no special time-consuming treatments are then necessary.

The benzotriazole method, therefore, can be used for the direct precipitation and gravimetric determination of copper in the absence of certain interfering elements. In the presence of interfering ions the reagent may be used to effect a preliminary separation and the copper in the copper triazole precipitate can be determined iodometrically, electrolytically, or by other standard procedures.

Experimental Work

The experimental results on establishing the best conditions to precipitate the copper are reported below. Precipitation is done in a solution containing tartaric and acetic acid. In most of the experimental work the copper in the copper triazole precipitate was determined by the potassium iodide–

Table I. Effect of Amount of Benzotriazole on Precipitation of Copper

Benzotriazole Added[a]	Copper Present	Copper Found	Difference
Ml.	Gram	Gram	Gram
15	0.0101	0.0015	−0.0086
25	0.0101	0.0035	−0.0066
35	0.0101	0.0090	−0.0011
45	0.0101	0.0100	−0.0001
55	0.0101	0.0102	+0.0001
65	0.0101	0.0101	0.0000
50	0.0101	0.0102	+0.0001
50	0.0101	0.0101	0.0000
50	0.0180	0.0180	0.0000
50	0.0172	0.0173	+0.0001

[a] 2 per cent aqueous solution.

Table II. Effect of Temperature and Time of Digestion on Precipitation of Copper with Benzotriazole

Temperature	Time of Digestion	Copper Present	Copper Found	Difference
° C.	Min.	Gram	Gram	Gram
100	30	0.0101	0.0101	0.0000
100	15	0.0101	0.0100	−0.0001
100	5	0.0101	0.0101	0.0000
25	30	0.0101	0.0101	0.0000
25	15	0.0101	0.0101	0.0000
25	5	0.0101	0.0100	−0.0001

thiosulfate method. In this connection it was found that the precipitate must be ignited to cupric oxide. If it is merely dissolved in nitric acid, the copper triazole will again precipitate when the solution is neutralized and made acid with acetic acid prior to the addition of potassium iodide.

Hydrogen-Ion Concentration Required for Complete Precipitation of Copper. Copper was precipitated by benzotriazole from a series of synthetic copper solutions containing known amounts of copper, and also containing tartaric acid and acetic acid to approximate the conditions under which the copper would ordinarily be precipitated in an analysis. The solutions were adjusted to the desired pH by adding ammonia, using a glass-electrode type of pH meter, and the copper was precipitated with benzotriazole. The precipitate was then filtered, ignited to copper oxide, and titrated by the potassium iodide–thiosulfate method. The precipitation was complete between pH 7.0 and 8.5. Below pH 5.0 no precipitation occurred, while at pH 8.8 the precipitate began to dissolve.

Amount of Benzotriazole Necessary for Complete Precipitation of Copper. The amount of reagent necessary for the complete precipitation of copper from ammoniacal tartrate solution was determined by adding increasing amounts of a 2 per cent aqueous solution of benzotriazole to synthetic solutions of copper that had been adjusted to the proper hydrogen-ion concentration. The results in Table I indicate that at least 45 ml. of the reagent solution are required to precipitate completely 0.0100 gram of copper, and that 50 ml. of the reagent solution effect the complete separation of 0.0180 gram of copper. This latter amount represents the upper limit of copper permissible for rapid and convenient handling of the voluminous precipitate.

Effect of Temperature and Time of Digestion. Results shown in Table II indicate that a temperature of 25° to 100° C. and a digestion time of 5 to 30 minutes were equally effective in quantitatively precipitating the copper. As an aid to filtration, however, it is recommended that the solution be kept hot (70° to 80° C.) and that it be digested until the precipitate fully coagulates.

Effect of Volume. Table III shows that the volume of the solution, within comparatively wide limits, is without effect on the completeness of precipitation of the copper.

Sensitivity of Precipitation of Copper by Benzotriazole. The sensitivity of the copper-benzotriazole reaction was determined by adding benzotriazole to solutions containing known amounts of copper. The copper solutions were 200 ml. in volume, containing 7 grams of tartaric acid and 10 ml. of acetic acid, and were adjusted with ammonium hydroxide to the litmus color change. The results, shown in Table IV, indicate that as little as 0.0002 gram of copper is determinable in 200 ml. of solution.

Percentage of Copper in Copper Triazole Precipitate. In order to determine the percentage of copper in the copper triazole precipitate, synthetic copper solutions were precipitated by benzotriazole and the precipitate was filtered on weighed sintered-glass filtering crucibles. The crucible and precipitate were dried for 2 to 3 hours at 135° to 140° C., cooled in a desiccator, and weighed. Temperatures of 105° to 110° C. were found to be too low for satisfactory drying.

Table III. Effect of Volume of Solution on Precipitation of Copper with Benzotriazole

Volume of Solution	Copper Present	Copper Found	Difference
Ml.	Gram	Gram	Gram
125	0.0101	0.0101	0.0000
200	0.0101	0.0101	0.0000
300	0.0101	0.0101	0.0000
500	0.0101	0.0101	0.0000

Table IV. Analyses of Standard Copper Solutions by Benzotriazole in a Volume of 200 Ml.

Copper Present	Copper Found	Difference
Gram	Gram	Gram
0.0002	0.0002	0.0000
0.0005	0.0005	0.0000
0.0007	0.0007	0.0000
0.0010	0.0010	0.0000
0.0020	0.0020	0.0000
0.0038	0.0038	0.0000
0.0051	0.0051	0.0000
0.0089	0.0089	0.0000
0.0100	0.0100	0.0000

The results in Table V indicate that the copper triazole precipitate is of the formula $(C_6H_4N_3)_2Cu$ and the copper found in the precipitate is in close agreement with the theoretical 21.216 per cent. Except in the presence of interfering elements, such as those discussed in the following paragraph, the direct gravimetric determination of copper as $(C_6H_4N_3)_2Cu$ is possible.

Elements Precipitated by Benzotriazole in Ammoniacal Tartrate Solution. Qualitative tests showed that benzotriazole precipitates the following metals, either completely or partially, from ammoniacal tartrate-acetate solution: Fe^{++}, Ag^{+}, Ni^{++}, Cd^{++}, Zn^{++}, and Co^{++}. The following are not precipitated: Fe^{+++}, Se^{++++}, Te^{++++}, Sb^{+++}, Sb^{+++++}, As^{+++++}, Sn^{++}, Cr^{+++}, Cr^{++++++}, Al^{+++}, and Mo^{++++++}.

Recommended Procedure for Copper in Cast Irons and Steels. Inasmuch as interfering elements are usually present, the direct gravimetric method is not applicable to irons and steels. The benzotriazole method, however, separates the copper from such elements as arsenic, antimony, molybdenum, and tin which interfere in the hydrogen sulfide–potassium iodide–thiosulfate method. Benzotriazole is used for the preliminary separation, and the copper can be determined in the precipitate by standard methods. The writer recommends the iodide-thiosulfate method because of its applicability, speed, and simplicity.

Table V. Percentage of Copper in Copper Triazole Precipitate

Copper Added	Copper Triazole Precipitate		Copper in Triazole Precipitate
Gram	*Gram*		%
0.0100	0.0468		21.37
0.0100	0.0474		21.10
0.0100	0.0472		21.19
0.0071	0.0334		21.26
0.0050	0.0236		21.19
0.0050	0.0234		21.37
0.0050	0.0236		21.19
0.0050	0.0235		21.28
		Av.	21.24
		Theoretical	21.22

Transfer an appropriate weight of sample, from 1 to 10 grams depending on the copper content and the accuracy desired, to a 400-ml., or larger, beaker. Add 25 ml. of nitric acid (sp. gr. 1.13) per gram of sample and heat until dissolution of the sample is complete and the oxides of nitrogen have been expelled. If more than 0.50 per cent of chromium is present the sample may be dissolved in hydrochloric acid and the iron subsequently oxidized by nitric acid. Add 7 grams of tartaric acid per gram of iron and 10 ml. of acetic acid, and adjust the volume to 200 to 300 ml. Make just alkaline to litmus with ammonium hydroxide and add 50 ml. of a 2 per cent aqueous solution of benzotriazole. Digest on a warm plate until the precipitate coagulates. Introduce paper pulp, stir, and filter through a Whatman No. 40, or equivalent, filter paper, washing the precipitate thoroughly with cold water. Transfer the paper and precipitate to a crucible and ignite at red heat, preferably in a muffle. Brush the ignited copper oxide into a 250-ml. beaker, add 10 ml. of nitric acid, and evaporate just to dryness on a hot plate. Add 20 ml. of water and, dropwise, sufficient 6 per cent sodium hydroxide solution to produce a permanent precipitate. Add 10 ml. of acetic acid and boil until the hydroxide dissolves. Cool to room temperature, add 6 ml. of 50 per cent potassium iodide solution, and titrate the liberated iodine with standard sodium thiosulfate solution, using starch as indicator.

Reagents. Nitric acid, specific gravity 1.13 and 1.42, glacial acetic acid, c. p. tartaric acid, and ammonium hydroxide, specific gravity 0.90.

Benzotriazole solution, 2.0 per cent by weight in water (may be purchased from the Eastman Kodak Company, Rochester, N. Y.).

Sodium hydroxide, 6 per cent by weight in water, potassium iodide, 50 per cent by weight in water, standard sodium thiosulfate solution, and starch indicator solution.

Application of Benzotriazole Separation of Copper to Analysis of Bureau of Standards Steels and Cast Irons. Table VI shows the results obtained on standard steels issued by the National Bureau of Standards, using the procedure described above.

Analysis of Copper Ores. The separation was used on copper ores. The copper contents of the ores were established by the electrolytic method which consisted of decomposing in nitric-sulfuric acid, diluting, filtering off the residue, and electrolyzing the filtrate using stationary electrodes. The benzotriazole-iodide method consisted of separating the copper as copper triazole and analyzing by the potassium iodide–thiosulfate method described for the iron and steel samples.

Table VII shows the results obtained on two copper ores by the two methods.

Discussion

The benzotriazole precipitation is specific for copper, and determinations may be made gravimetrically unless such ions as Ag$^+$, Ni^{++}, Fe^{++}, Cd^{++}, Zn^{++}, and Co^{++} are present. In the analysis of iron and steel interfering elements are likely to be present; so the separation is only preliminary and the final determination of copper is by a standard method. Because the potassium iodide–thiosulfate method is most widely used in industry this discussion relates largely to advantages and disadvantages of hydrogen sulfide (or hypo) versus benzotriazole precipitation of copper preparatory to the potassium iodide–thiosulfate determination. Other standard methods of determining copper besides the potassium iodide–thiosulfate can be employed.

Table VI. Analyses of Bureau of Standards Samples

Bureau of Standards Sample No.	Weight	Copper Present	Copper Found	Difference
	Grams	%	%	%
8e	10.0	0.008	0.008	0.000
9c	5.0	0.020	0.020	0.000
55a	5.0	0.046	0.045	−0.001
16c	5.0	0.060	0.062	+0.002
15b	3.0	0.145[a]	0.153	+0.008
34a	2.0	0.222	0.223	+0.001

[a] Ten laboratories reported on this sample. The results varied from 0.136 to 0.153 per cent of copper. J. I. Hofman of the Bureau of Standards reported 0.148, whereas the ferrous laboratory reported 0.153 per cent.

Table VII. Analysis of Copper Ores by Electrolysis and Benzotriazole

	Copper Found	
Weight	Electrolysis	Benzotriazole iodide
Gram	%	%
1.0	1.03	1.03
1.0	1.03	1.03
1.0	1.02	1.01
0.5	3.25	3.25
0.5	3.25	3.26
0.5	3.26	3.26

Advantages and Disadvantages

The benzotriazole separation in the determination of copper in cast irons and steels possesses the following advantages over the hydrogen sulfide–iodide–thiosulfate method:

It permits a more rapid dissolution of the sample than is possible in the other procedure, wherein a nonoxidizing acid attack is advisable.

It permits a more complete dissolution of the sample. This is most helpful in the analysis of certain cast irons which are not sufficiently decomposed by nonoxidizing acids to yield a sulfide precipitate free from iron.

It affords a clean separation from Mo^{++++++}, Se^{++++}, Te^{++++}, Sb^{+++++}, and As^{+++++}, which may interfere in the iodide titration.

The copper-triazole precipitate may be ignited more rapidly than the copper sulfide precipitate with less danger of fusion.

The disadvantages attending the benzotriazole separation are:

The reagent is expensive, 100 grams costing approximately $25, and about 1 gram is used per determination.

The conditions for precipitation are comparatively narrow (pH 7.0 to 8.5), whereas extreme latitude is permitted in the sulfide precipitation.

The separation by benzotriazole is not practical for materials containing large amounts of nickel, cobalt, silver, cadmium, and zinc because these metals also precipitate, and a large bulk of precipitate difficult to filter and ignite results.

Acknowledgments

The writer wishes to acknowledge the permission of the Battelle Memorial Institute, which financed the investigation, to publish the results, and his indebtedness to John D. Sullivan, James F. Shea, and Arnold E. Pavlish for valuable suggestions and assistance in the preparation of this paper.

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A Vacuum Tube Time-Delay Relay

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A NECESSARY auxiliary for many laboratory appliances and industrial devices is a time-delay relay or switch. The control of compressors, refrigerators, and other motor-driven devices which are likely to be injured by the "chattering" or the too frequent operation of a sensitive relay, is greatly facilitated by the use of a time-delay switch. The automatic application of plate voltage to thyratron rectifiers or x-ray tubes at a given interval after the filament current has been turned on is a convenience afforded only by an automatic time-delay relay. Although the device presented here was designed primarily for use in conjunction with a sensitive vacuum tube relay (*3*) for the operation of a thermostatically controlled refrigerator, many other uses may be suggested.

Very short time-delay action, from a small fraction of a second to a few seconds, may be obtained from a vacuum tube relay by placing a high-capacity condenser across the terminals of the magnetic relay (*1*, *3*). Although this procedure may limit chattering, the time-delay feature is a function of the rate of charge and discharge of the condenser and consequently its flexibility is limited to the comparatively narrow range afforded by condensers of practical size. Several commercial types of relays are available in which the time-delay action is obtained by a clockwork mechanism which trips a switch. Although a wide range of time-delay intervals is made available by this type of mechanism, the complexity of the clockwork trip unit makes its cost prohibitive in many instances. Other time-delay relays based upon the principle of the thermal inertia of an electrically heated bimetallic element are commercially available. These units offer difficulties of construction for the average laboratory technician.

Le Van (*2*) has utilized the cathode heating time of a vacuum tube as the basis of a time-delay switch. The unit described below likewise obtains time-delay action from the heating time necessary to allow electrons to flow from the cathode to plate of a vacuum tube rectifier. The circuit provides a simple, inexpensive, reliable, and easily constructed alternative time-delay device, which can be operated by a bimetallic thermoregulator of the type whose contacts open when the temperature setting is exceeded.

A schematic diagram of a single-tube relay unit is shown in Figure 1 *A*. When contact is made across contacts *XX* by means of a switch or relay, heater current begins to flow in the vacuum tube rectifier, *T*-1. When the cathodes of this tube reach a temperature sufficient to allow electrons to flow to the plates, the relay magnet becomes energized. The relay closes when *T*-1 has reached a temperature sufficiently high to allow the passage of the minimum amount of current which will offset the relay spring tension, and remains closed as long as the cathodes of *T*-1 exceed this minimum temperature.

If the circuit across the contacts *XX* is broken, the relay does not immediately release. Instead, the heater of *T*-1 slowly cools, causing a gradual decrease in the passage of current from the cathodes to the plates and through the relay coil. When the flow of current is no longer sufficient to offset the relay spring tension, the load circuit is opened.

Large variations in time interval may be obtained by increasing or decreasing the number of rectifier tubes used in cascade. Thus, one or more rectifier tubes connected as shown in Figure 1 *B* may be inserted in the relay unit shown in *A* at the lettered points.

When contact is made across contacts *XX* in a two-tube circuit of the type described above, heater current begins to flow in rectifier *T*-1. When the cathodes of this tube reach a temperature sufficient to allow electrons to flow, the heater of rectifier *T*-2 starts to heat, since the direct current load of the first rectifier is the heater of rectifier of *T*-2. As the second rectifier begins to pass current, the relay magnet becomes energized, since it is now directly connected across the output of the second rectifier.

Starting time delays up to 3.5 minutes have been obtained by using a series of five tubes connected in such a fashion that the output of each tube is used to supply the heater of the following rectifier. Changes in time interval may be accomplished by by-passing one or several tubes in the cascade. Rapid changeover may be facilitated by simply removing one or more tubes and replacing them with dummy plugs, certain terminals of which have been connected as shown in Figure 2.

Minor changes in the magnitude of the time-delay interval may be obtained by the adjustment of the spring tension on the relay contacts. An increase of spring tension will require a greater relay-actuating current, which will necessitate a longer heating period for the final rectifier tube. Although an increase in spring tension will cause an increase in the starting time interval, a corresponding decrease in the cooling or open contact delay will be produced. Since maximum reliability of operation is obtained at one definite adjustment of spring tension, only slight changes in time delay action may be made by this method.

A third method of producing variations in the time-delay interval is realized by changing the capacity of condenser *C*-1. Although the main purpose of this condenser is to prevent chattering of the relay when an alternating current power supply is used, slight time-delay variations may be

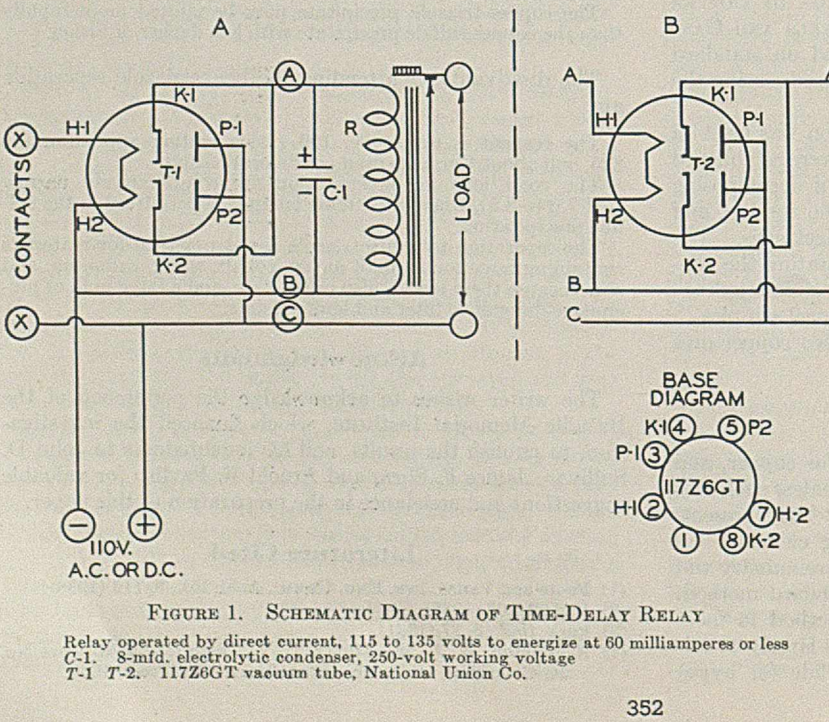

FIGURE 1. SCHEMATIC DIAGRAM OF TIME-DELAY RELAY

Relay operated by direct current, 115 to 135 volts to energize at 60 milliamperes or less
C-1. 8-mfd. electrolytic condenser, 250-volt working voltage
T-1 *T*-2. 117Z6GT vacuum tube, National Union Co.

gained by changing its capacity within practical limits (1 to 16 microfarads). If a high-capacity C-1 is used when 115-volt alternating current is applied, the direct current potential across the relay coil may reach as high as 160 volts. Danger of injury to the relay coil may result unless a current-limiting resistor is placed in series with the coil.

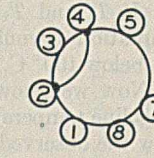

FIGURE 2

The time-delay relay described above offers a number of advantages over many of the commercially available devices, despite its simplicity of construction and low cost. Since standard radio replacement parts were used throughout the construction, the total cost of parts for the two-tube unit did not exceed \$6.50. The use of rectifier tubes which require 117 volts for heater operation eliminates the necessity for filament current-limiting resistors or transformers and consequently permits the use of several tubes in cascade. Furthermore, the design permits the operation of the relay unit from either alternating or direct current power supplies. When a direct current power supply is used, proper polarity must be observed, as shown in Figure 1.

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Calibration of Existing Gum-Stability Test Bombs

In Terms of the New A. S. T. M. Bomb

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A method is presented whereby induction period bombs of non-A. S. T. M. type may be so calibrated as to yield "A. S. T. M. induction periods". This permits comparable results without the large expense of replacing useful equipment now in existence.

IT IS now well known that the deterioration of gasoline in storage, leading to the formation of gum, is a manifestation of atmospheric oxidation. It is accordingly reasonable that some form of an accelerated oxidation test employing air or oxygen at elevated temperatures will be required as a measure of stability. In 1930, Hunn, Fischer, and Blackwood (*3*) introduced a bomb test for this purpose, employing a temperature of 100° C. and an oxygen pressure of 7 kg. per sq. cm. (100 pounds per sq. inch) gage. Since that time, the bomb test has been rather widely adopted and used in one form or another—i. e., the length of the induction period or the gum formed after a given oxidation time. It has been rather difficult, however, to compare the bomb results obtained in different laboratories because of important differences in both the equipment and the testing procedure employed (*5*). Recently the American Society for Testing Materials has met this need by standardizing the bomb equipment and the testing procedure.

In this laboratory, there are already available twenty bombs of a type different from that specified by the A. S. T. M., and it would be advantageous to be able to calibrate them so that they would yield induction periods equal to those obtained by the A. S. T. M. bomb and procedure. Such a calibration would obviate the necessity for replacing useful and expensive equipment in order to obtain results comparable to those from other laboratories. This situation undoubtedly holds also for many other laboratories. An investigation was accordingly undertaken with the above objective in mind. The A. S. T. M. bomb would, of course, be used for referee purposes.

Equipment

The A. S. T. M. bomb setup was purchased complete from one of the equipment manufacturers, and unless otherwise noted was operated according to A. S. T. M. specifications.

The bombs already available in this laboratory are of the Universal Oil Products type (*2*). They were operated "in place" starting with the bath at room temperature, and they used a 100-ml. gasoline sample contained in a 240-ml. (8-ounce) oil sample bottle. The induction periods obtained with the U. O. P. bombs were selected according to A. S. T. M. specifications.

Temperature Correction

The variation of the induction period with the temperature can be expressed by the equation (*1*):

$$\log \text{induction period} = A + B/T$$

where A and B are constants depending on the particular gasoline, and T is the absolute temperature. The value of the slope, B, of this equation, when the temperature is expressed in degrees Kelvin, falls between the limits of about 5000 to 6500, averaging close to 5500, on the basis of a very large number of tests made in this laboratory with different gasolines. Over a fairly narrow temperature range (± about 2° C.), a simplified correction factor can be introduced which deviates only slightly from the rigorous equation given above. Considering now induction period determinations made in the range of 98° to 102° C., we can correct these to 100° C. by use of the simple factor:

$$F = 1 + 0.1\ \Delta T \qquad (1)$$

Here, ΔT is the difference between the reference temperature, 100° C., and the operating temperature (in the range 98° to 102° C.), and is always positive, so that F is always larger than 1. The observed induction period is multiplied by this factor, F, when the operating temperature is about 100° C. and divided by it when below 100° C.

In Table I are given induction periods determined at 98° and 102°, corrected to 100° by the exact equation and by the simplified factor, choosing materials having an extreme difference in temperature susceptibility characteristics (B = 5000 and 6500). The deviations shown in the last column become smaller as the operating temperature more nearly approaches 100° C.

Calibration of U. O. P. Bombs to Give A. S. T. M. Induction Periods

Let us assume that induction periods are determined in the A. S. T. M. bomb at a bath temperature of T_1, and in the U. O. P. bomb at a bath temperature of T_2. These will then be designated as $IP_{\text{A. S. T. M.}, T_1}$, and $IP_{\text{U. O. P.}, T_2}$. The temperature correction factors (see Equation 1) corresponding to the A. S. T. M. and U. O. P. induction periods (at bath temperatures T_1 and T_2) will be denoted by F_1 and F_2, respectively. As a matter of simplicity, it will be assumed in this case that T_1 and T_2 are both above 100° C., whereupon

$$(IP_{\text{A. S. T. M.}, T_1})\, F_1 = IP_{100^\circ \text{ C.}} \tag{2}$$

$$(IP_{\text{U. O. P.}, T_2} - C)\, F_2 = IP_{100^\circ \text{ C.}} \tag{3}$$

Equation 2 is self-evident; in Equation 3 we have first subtracted a correction factor, C, from the observed induction period before applying the temperature correction factor, F_2. C corrects for the heating-up lag of the gasoline in the U. O. P. bomb, and also for any difference in the equilibrium gasoline temperature in the A. S. T. M. and U. O. P. bombs (when the respective bath temperatures are the same). Combining Equations 2 and 3, we obtain

$$C = (IP_{\text{U. O. P.}, T_2}) - \frac{F_1}{F_2}(IP_{\text{A. S. T. M.}, T_1}) \tag{4}$$

TABLE I. INDUCTION PERIODS CALCULATED BY SIMPLIFIED FACTOR METHOD

Operating Temperature, T	B Values Assumed	Induction Periods: Observed values	Corrected to 100° C.: Exact equation	Corrected to 100° C.: Simplified factor	Error by Use of Simplified Factor
° C.		Min.	Min.	Min.	Min.
102	5000	204	240	245	+5
102	6500	194	240	233	−7
98	5000	283	240	236	−4
98	6500	298	240	248	+8

(If T_1 and T_2 were both below 100° C., the F factor of Equation 4 would be F_2/F_1. If T_1 were above 100° C. and T_2 below 100° C., the F factor would be F_1F_2.)

Now we know from previous work that the equilibrium gasoline temperature in the U. O. P. bomb is some 0.6° C. below the observed bath temperature, but we would guess that the equilibrium gasoline temperature in the A. S. T. M. bomb is practically the same as its bath temperature. [Gasoline temperatures have been obtained during the heating-up period of the U. O. P. bombs by means of thermocouples fitted through a special bomb top. The time correction to be applied to an observed U. O. P. induction period in order to obtain an isothermal induction period is 30 minutes for this particular bath setup, as computed from the heating curves (*1, 4*).] Accordingly, the value of C will depend on the length of the induction period. In determining C for any type of bomb, it is not necessary to know the actual temperature lag or the equilibrium temperature level reached by the gasoline in the bomb. We merely run a number of induction periods in both the A. S. T. M. and unknown bombs and calculate C by means of Equation 4. C is then plotted against the length of the induction period observed for the unknown bomb—i. e., at a bath temperature of T_2—and a best straight line is drawn through the points, corresponding to the equation

$$C = m\,(IP_{\text{obs.}, T_2}) + b \tag{5}$$

If the value of m equals 0 (perfectly horizontal line), then the equilibrium gasoline temperature is the same in the unknown bomb as in the A. S. T. M. bomb, for the same bath temperature. If the value of b equals 0, then the heating-up lag of the gasoline in the unknown bomb is the same as that in the A. S. T. M. bomb.

Once we have established the characteristics of C, we may employ the unknown bomb and obtain induction periods equivalent to those in the A. S. T. M. bomb at 100° C. by means of Equation 3. Equation 3 as written assumes the bath temperature, T_2, of the unknown bomb (in this case, U. O. P.) to be above 100° C. If T_2 were below 100° C., Equation 3 would read

$$(IP_{\text{obs.}, T_2} - C)/F_2 = IP_{100^\circ \text{ C.}}$$

TABLE II. CORRELATION BETWEEN A. S. T. M. AND U. O. P. INDUCTION PERIODS

Gasoline Item No.	Bath Temperature: A. S. T. M. (T_1)	Bath Temperature: U. O. P. (T_2)	Observed Induction Period: A. S. T. M.	Observed Induction Period: U. O. P.	C for U. O. P. Bomb: Calcd. by Equation 4	C for U. O. P. Bomb: Smoothed value from Figure 1	Induction Periods, Corrected to 100° C.: A. S. T. M.	Induction Periods, Corrected to 100° C.: U. O. P.[a]	Deviation of Corrected U. O. P. from Corrected A. S. T. M. Induction Period	
	° C.	° C.	Min.	Min.	Min.	Min.	Min.	Min.	Min.	%
1	101.1	101.1	20	40	20	23	22	19	− 3	−14
2	101.0	101.0	20	45	25	23	22	24	+ 2	+ 9
3	100.9	101.0	20	45	25	23	22	24	+ 2	+ 9
4	101.0	101.0	30	55	25	24	33	34	+ 1	+ 3
5	101.0	101.0	45	70	25	25	50	50	0	0
6	101.0	101.0	95	120	25	28	105	101	− 4	− 4
7	101.0	101.1	150	175	26	32	165	159	− 6	− 4
8	101.1	101.2	160	175	16	32	178	160	−18	−10
9	100.8	100.8	195	215	20	35	211	194	−17	− 8
10	101.0	101.0	205	240	35	37	226	223	− 3	− 1
11	101.0	101.1	220	265	47	39	242	251	+ 9	+ 4
12	101.0	101.1	255	295	42	41	281	282	+ 1	0
13	100.8	101.1	270	295	32	41	292	282	−10	− 3
14	101.0	100.9	255	300	43	41	281	282	+ 1	0
15	100.8	100.8	250	305	55	41	270	285	+15	+ 6
16	100.8	101.1	290	320	38	42	313	309	− 4	− 1
17	100.9	101.0	285	340	58	44	311	326	+15	+ 5
18	101.1	101.2	295	345	53	44	327	337	+10	+ 3
19	100.6	100.8	350	410	66	49	371	390	+19	+ 5
20	101.1	101.2	395	435	44	50	438	431	− 7	− 2
21	100.9	101.0	400	470	74	53	436	459	+23	+ 5
22	101.0	101.0	430	495	65	55	473	484	+11	+ 2
23	101.0	101.0	460	510	50	56	506	499	− 7	− 1
24	101.0	101.1	470	515	49	56	517	509	− 8	− 2
25	100.8	100.9	465	530	69	57	502	516	+14	+ 3
26	101.0	101.1	530	635	110	64	583	634	+51	+ 9
27	101.0	101.1	595	645	55	65	655	644	−11	− 2
28	101.0	101.0	580	655	75	66	638	648	+10	+ 2
29	101.0	101.1	670	725	61	71	737	726	−11	− 1
30	100.9	101.0	870	920	58	84	948	920	−28	− 3

[a] Using smoothed value of C taken from Figure 1 (column 7).

In order to test the above relations, induction periods were determined for 30 different gasoline samples in both the A. S. T. M. and U. O. P. bombs. A. S. T. M. induction periods were obtained with 50 ml. of gasoline instead of 100 ml., but all other A. S. T. M. specifications were followed in carrying through the procedure. U. O. P. induction periods were obtained with 100 ml. of gasoline in a 240-ml. (8-ounce) oil sample bottle, and the U. O. P. bombs were operated "in place"; the induction periods were selected according to A. S. T. M. specifications. To obtain gasolines differing in type and in the length of the induction period, a number of base stock gasolines were treated to various extents with caustic solution to reduce the induction period; in order to lengthen the induction period, several different inhibitors were added to the variously treated base stock gasolines.

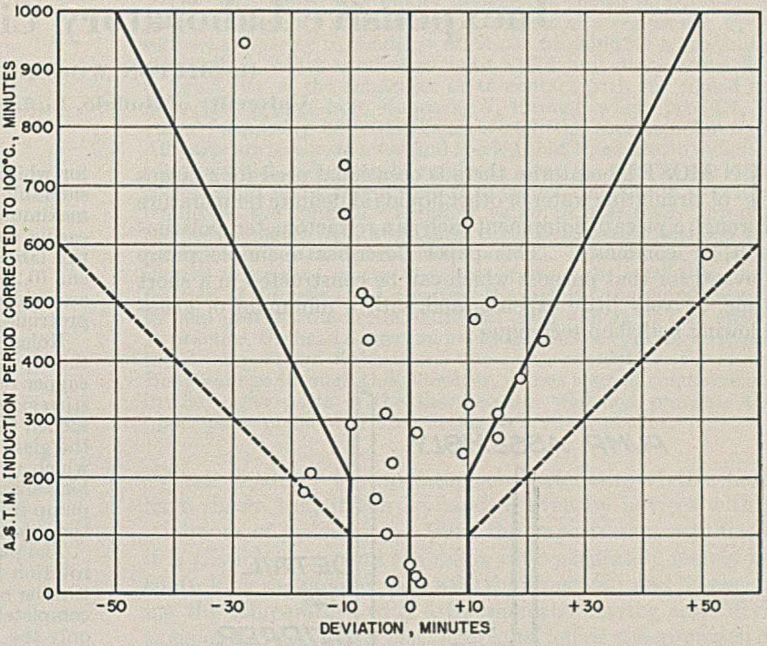

FIGURE 2. DEVIATION OF CORRECTED U. O. P. INDUCTION PERIOD FROM CORRECTED A. S. T. M. INDUCTION PERIOD

Solid "funnel" indicates 5 per cent deviation, broken line indicates 10 per cent deviation

The data and calculations are presented in Table II. Column 6 gives the values of C calculated by means of Equation 4. These are plotted against the observed U. O. P. induction period ($IP_{\text{U. O. P.}, T_2}$) in Figure 1. The line drawn through the points corresponds to the equation (see Equation 5)

$$C = 0.07\,(IP_{\text{U. O. P.}, T_2}) + 20 \qquad (6)$$

This would indicate a temperature lag of about 20 minutes and an equilibrium gasoline temperature about 0.7° C. below that of the bath temperature, in comparison with the A. S. T. M. bomb. These figures are in very good agreement with previous values obtained directly—i. e., 25 minutes and 0.6° C. (A temperature lag of about 5 minutes is assumed for the A. S. T. M. bomb. The difference in temperature lag for the two bombs is thus 25 minutes.) A small change in the position of the line of Figure 1 may appreciably change the indicated lag and temperature level figures noted above, but will have a negligible effect on the final corrected induction period. Indeed, in placing the line of Figure 1, a considerable amount of latitude may be allowed, since a displacement corresponding to a 5-minute change in C at any particular point will raise or lower the induction period by only this amount.

Column 7 of Table II lists the "smoothed" values of C taken from Figure 1 (actually calculated by means of Equation 6) and these were used to calculate U. O. P. induction periods corrected to 100° C. (by means of Equation 3) as given in column 9 of Table II. The A. S. T. M. induction periods were corrected to 100° C. in the usual way by means of Equation 2 and these are listed in column 8. The deviations of the completely corrected U. O. P. induction periods from the corrected A. S. T. M. induction periods are shown in columns 10 and 11, and are plotted in Figure 2. The solid lines forming the "funnel" of Figure 2 indicate a deviation of 10 minutes up to an induction period of 200 minutes, and 5 per cent thereafter. The dotted lines forming the larger funnel indicate a 10 per cent deviation beyond 100 minutes. The points fall well within the 5 per cent funnel on the whole. The actual distribution of points is as follows:

Deviation of Corrected U. O. P. Induction Period from Corrected A. S. T. M. Induction Period		Number of Points
I. 0 to 10 minutes		18
II. Greater than 10 minutes		
a. 0 to 5% deviation	8	
b. 6 to 10% deviation	4	12
Total		30

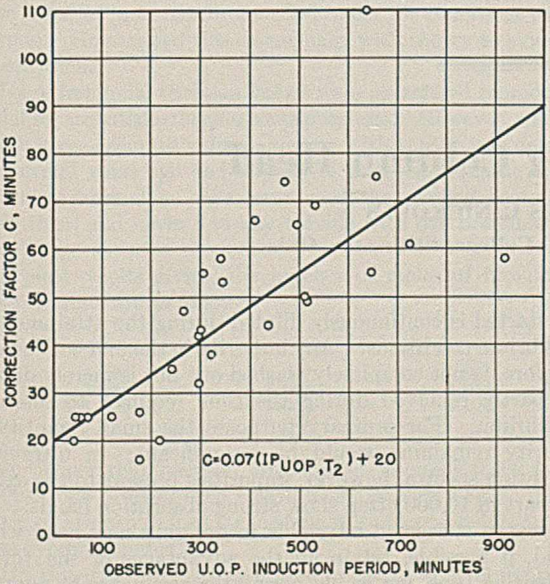

FIGURE 1. CORRECTION FACTOR C AS A FUNCTION OF LENGTH OF OBSERVED U. O. P. INDUCTION PERIOD

Of the 4 points that deviated by more than 10 minutes and 5 per cent (II, *b*, above) from the corrected A. S. T. M. induction period, a change of 2 minutes in the induction period would bring 1 of these points within the 5 per cent limit and a change of 10 minutes would bring 2 more within this limit.

Since the A. S. T. M. method allows a 15-minute deviation of duplicate A. S. T. M. induction periods by the same operator, or one of 20 per cent of the smaller value for different laboratories, the above results indicate that a calibration of existing bombs, in the manner described herein, is capable of yielding corrected induction periods equal to those obtained with the A. S. T. M. bomb, well within the limit of error of the A. S. T. M. method.

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Inexpensive Laboratory Circulating Pump

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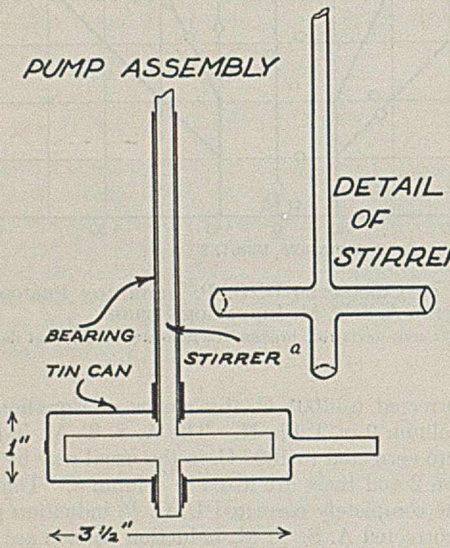
IN MOST laboratories there is occasional need for a means of circulating water or other liquids at definite temperature through a piece of equipment such as a refractometer, polarimeter, or condenser. This paper describes a simple pump devised for that purpose which can be constructed in a short time, at very little expense, and with a minimum of glassblowing and shop technique.



The essential parts of the pump are a long-shanked, glass, "centrifugal stirrer" (*1*) and a flat circular tin can with a tightly fitting cover. A large-sized shoe-polish can or ointment can is ideal.

A centrifugal stirrer by its rotation sucks liquid up through the center and throws it out through the hollow arms. For use in the pump, the stirrer is made in slightly modified form as shown in the diagram. Nine-millimeter or larger Pyrex tubing is suitable for the lower part of the stirrer, while the shank may be of smaller diameter. The length of the stirring arms will depend on the diameter of the can used and to a certain extent also on the purpose for which the pump is made. In general, short arms with considerable distance between their ends and the casing produce maximum flow and low lift, while long arms with ends close to the casing result in a higher lift and somewhat diminished flow. In this laboratory most of the pumps made have allowed about 0.63 cm. (0.25 inch) of space at the ends of the arms when the pump is assembled. Tube *a* of the stirrer need be only long enough to protrude 1.25 cm. (0.5 inch) through the bottom of the can.

Holes (1.25 cm., 0.5 inch) are drilled through the centers of the top and bottom of the can and a 0.63-cm. (0.25-inch) brass or copper outlet tube is soldered on at the side. Bearings for the stirrer are made from the proper size of glass tubing and are attached to the can by small sections of rubber tubing slipped over the glass and into the holes in the can. The parts of the stirrer which run in the bearings are greased before assembling. The long shank and bearing of the stirrer prevent pressure inside the pump from forcing liquid up through the bearing rather than out the side tube.

The pump is operated by any kind of variable-speed motor, its rotation being free enough so that even a small compressed air turbine or wind motor (*2*) supplies sufficient power. It may be completely immersed in the liquid to be circulated or may have only the protruding lower tube immersed. In the latter case, it may be necessary to prime the pump before it will work.

Several pumps of this kind have given surprisingly good performance in this laboratory. Tests made on one pump of the dimensions shown in the diagram, running at only a moderate speed, gave a pumping rate of 1300 ml. per minute through a horizontal line and 650 ml. per minute when water was lifted 60 cm. (2 feet). The maximum lift at this speed was about 90 cm. (3 feet), though, of course, higher speeds would increase both lift and pumping rate.

Changes in design, such as the use of better bearings, or the attachment of the discharge tube tangentially instead of radially, would undoubtedly increase efficiency. However, the desire has been to keep the device simple and easy to make, and the cost low. A coat of water-resistant varnish would make the can last longer in contact with water.

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A Convenient Distilling Column Head

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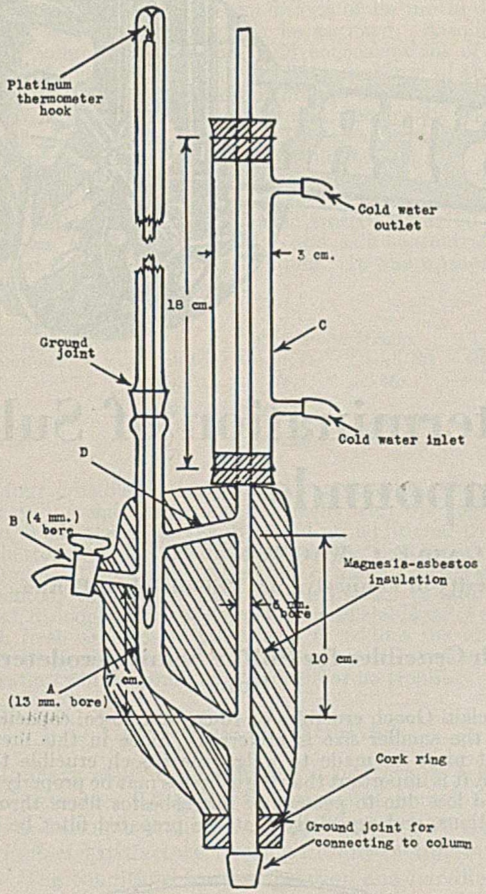
DURING the construction of a number of highly efficient fractionating columns needed in this laboratory for the preparation of spectroscopically pure samples of various organic compounds, the question of the type of column head best suited to the problem came to the fore. Most of the authorities consulted seemed to prefer the totally condensing head, because of the greater ease of control of product and reflux rates, the readiness with which the changing conditions at the head can be followed by temperature measurements, and the lack of necessity for the careful control of the condenser. Unfortunately, however, totally condensing heads are so constructed that the condensate formed when the column is first started is continuously diluted during the attainment of equilibrium conditions. Any impurity in the first condensate, therefore, is not completely washed out but is merely diluted and partly removed during the time required to establish equilibrium. For ordinary purposes the small quantity of impurity remaining would be insignificant; in ultraviolet absorption spectra, however, impurities present to the extent of 1 part in 10,000 often show strong absorption bands. For this reason it seemed advisable to design a new head which would, if possible, retain all the advantages of the totally condensing type, yet would permit the product to be removed in the vapor state and condensed in an external condenser.



The head which was finally designed is shown in the accompanying diagram. Essentially, it consists of a condenser, *C*, of sufficient capacity to condense all vapor reaching it; a thermometer well, *A*, which is offset so as to avoid any disturbance due to proximity of the condenser or to contact with the cooled reflux; and a large-bore stopcock, *B*, through which product, in vapor form, may be withdrawn through the thermometer well. All parts are so constructed and leveled that there are no indentations in which reflux can be retained; even the tube to the stopcock is short and slanted upward to permit condensate to return readily to the column. To allow vapor to pass freely through the thermometer well, a bridging tube, *D*, is sealed between the condenser tube and the thermometer well. The bridge, which is slanted downward in the direction of the well, catches a small fraction of the reflux and diverts it through the thermometer well to help prevent the accumulation of dead vapors in that space. In practice, the head is surrounded by a celluloid cylinder to lessen rapid temperature fluctuations due to air currents in the room. Heat leakage through this, however, causes a small condensation in the upper parts of the thermometer well and prevents the upper parts of the well from acting as a vapor pocket.

Tests made of the operating characteristics of this head have shown that it can be handled even by novices with a minimum of instruction. With the vaporization rate fixed, it is possible to control the reflux ratio accurately merely by controlling the product rate with the stopcock; and by checking the temperature with a thermometer having scale divisions of 0.1° C., it has been simple to follow the approach of the column to equilibrium under total reflux, to note with fair accuracy the time required for equilibrium to be attained, and to observe signs of flooding long before other signs than that given by the temperature change made their appearance.

Although the head has thus far been used only with columns of 1.2-cm. diameter and from 100- to 170-cm. height, packed with glass or Nichrome helices, its performance should be equally excellent with other laboratory columns.

Bromination of Phenols by Means of Bromide-Bromate Solution

SIR: A recent article (*4*) with the above title presented bromine titrations for a variety of substituted phenols, many of which show good agreement with theory. Others, however, including *o*- and *p*-cresols, four xylenols, and other alkyl phenols, were reported to be overbrominated under the conditions used by Sprung. He ascribed this discrepancy with theory to side-chain substitution.

These fractional titration values were considered reproducible, and if so, are satisfactory for some purposes. However, a method which gives accurate values agreeing with theory was described (*2*) several years ago and applied to phenols, aromatic amines, and nitro aromatics. We have used the method occasionally since then, and never had any trouble with overbromination of cresols.

Typical results giving the number of moles of bromine per mole of cresol are as follows:

o-Cresol	*m*-Cresol	*p*-Cresol
1.996	3.007	2.006
1.985	2.995	2.014
1.998	3.000	2.006
	3.007	

Also, 50 per cent *o*-cresol, 50 per cent *m*-cresol, 2.502 (theory 2.500); one third of each cresol, 2.337 (theory 2.333). Similar results (*1*) were obtained for the four xylenols which Sprung found were overbrominated.

The essential difference in procedure seems to be in the time of standing with excess bromine. The nuclear substitutions have velocity constants (*3*) of the order of at least 10^6, so that no delay is necessary after the appearance of free bromine, and the merest trace of excess is sufficient. Since the formation of bromine is a time reaction, however, an excess of bromide-bromate can be used; but by employing a lower concentration of acid (sulfuric or hydrochloric) the production of bromine can be controlled to any desired rate. As soon as a yellow color appears, bromination can be stopped by addition of potassium iodide. A sharp distinction between nuclear and side-chain substitution is thus possible. The iodine can be titrated immediately with sodium thiosulfate. To accelerate attainment of the end point more acid can be added before or during this titration.

Sprung used about eight moles of potassium bromide for one of potassium bromate. A much smaller proportion of bromide, a little over two moles, is sufficient, as explained in the original article (*2*). It may be that this lower concentration of salt facilitates accurate titration.

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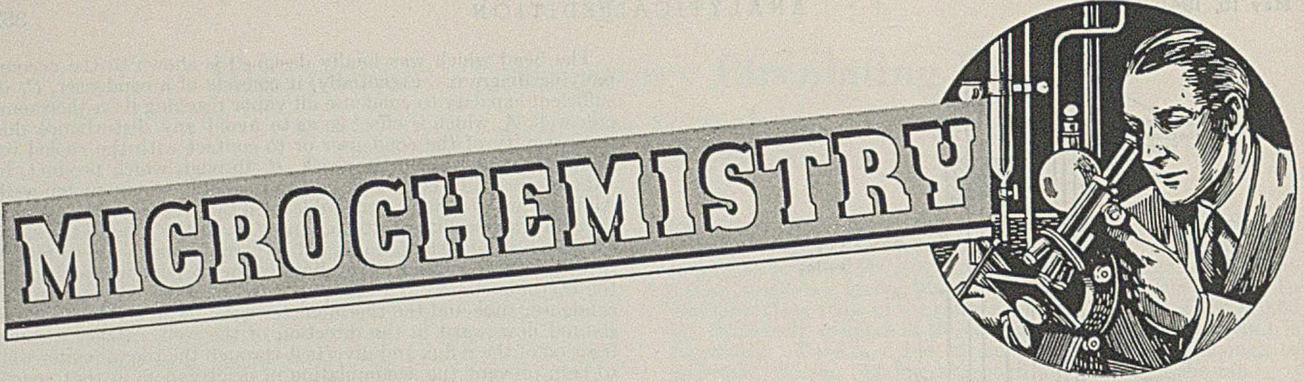

Procedure for Semimicrodetermination of Sulfur in Organic Compounds

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A SATISFACTORY procedure for the semimicrodetermination of sulfur in organic compounds by use of the sodium peroxide bomb has hitherto been lacking, and no bomb equipment suitable for the purpose has been described. The feasibility of using the sodium peroxide macro- or microbomb for decomposition of semimicrosamples has doubtless been tested by many analysts. The few opinions available here with respect to the use of the microbomb in this way are contradictory. Some preliminary test analyses made with semimicrosamples and a macrobomb gave acceptable results when the charge consisted of about 0.03 gram of sample (taurine), 0.2 gram of potassium perchlorate, 0.2 gram of sucrose, and 8 grams of sodium peroxide. As this procedure appears to involve a deliberate imposition of unfavorable conditions for precipitation of barium sulfate, it has not been examined further.

This paper presents descriptions of a bomb assembly and an analytical procedure which permit the determination of sulfur in solid or liquid organic substances by decomposition of semimicrosamples in admixture with sodium peroxide, potassium perchlorate, and sucrose in a metal bomb, the sulfur being weighed as barium sulfate. The magnitudes of sample, combustion charge, and apparatus are intermediate between those of the familiar macroprocedure (7) and the microprocedure of Elek and Hill (5).

Parr Sodium Peroxide Semimicrobomb

Inquiry disclosed the fact that the Parr Instrument Company, Moline, Ill., had previously designed a bomb assembly with a cup of about 8-cc. capacity, and presumably suitable for semimicroanalysis. One of these outfits was secured and was found satisfactory.

The form of the apparatus, and some of the principal dimensions, are shown in Figure 1. The dimensions indicated are taken from blueprints provided by the Parr Instrument Company, from which the apparatus may be obtained. The cup is made of either 98 per cent nickel or 30 per cent nickel steel, and the cover of either 98 per cent nickel or nickel-plated brass. Neither stainless steel nor any other alloy of chromium is suitable for parts which are to be exposed to the ignited sodium peroxide mixture. The screw collars are made of chromium-plated bronze. Lead gaskets were used; rubber gaskets are available and would doubtless serve about as well. In either case, since the charge is ignited by applying a flame to the bomb, care must be taken not to overheat the gasket.

Gooch Crucibles for Sulfur Semimicrodeterminations

Porcelain Gooch crucibles of 10-cc. and 15-cc. capacities were used; the smaller size is preferred. Since in this method an attempt must be made to weigh the Gooch crucible to about 0.02 mg. it is important that the asbestos mat be properly formed, to avoid loss due to passage of fine asbestos fibers through the perforations, and especially that the prepared filter be brought

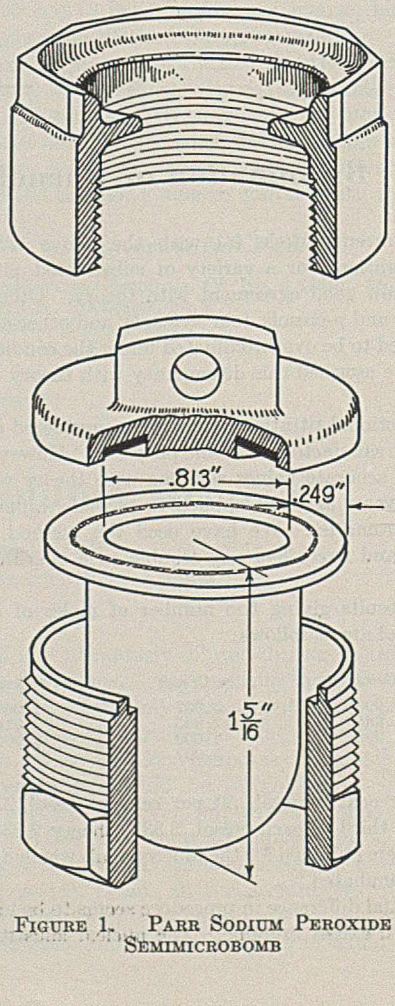

FIGURE 1. PARR SODIUM PEROXIDE SEMIMICROBOMB

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to constant weight under the conditions of its use in analysis. Constancy of weight should never be assumed. A solution, in which the volume, temperature, and concentrations of sodium chloride and hydrochloric acid approximate those of the liquid to be filtered in analysis, is passed through the filtering crucible, which is then washed, dried, ignited, and weighed by the procedures to be used in the analysis. This treatment should be repeated until the weight is constant within 0.05 mg.

The importance of these precautions is shown by the following data, obtained with four 10-cc. Gooch crucibles. Each crucible was prepared as usual, and was then treated with 150 cc. of a liquid whose temperature, acidity, and salt concentration approximated those of the analysis liquid. It was washed, dried, and weighed as described below.

Treatment with Conditioning Solution	Changes in Weight			
	Gooch I	Gooch II	Gooch III	Gooch IV
	Mg.	*Mg.*	*Mg.*	*Mg.*
1	Before first weighing			
2	+0.02	−0.28	−0.44	−0.02
3	....	−0.03	−0.01	....

The four crucibles did not behave uniformly; two attained constancy of weight after one treatment with the conditioning solution, while the other two required an additional treatment. The asbestos mat thus conditioned may be used for a considerable number of analyses. After five or more precipitates have accumulated, the greater part of the barium sulfate may be removed, dislodging not more than a superficial layer of asbestos. Enough fresh asbestos is introduced to restore the mat to its original thickness, and the crucible is brought to constant weight, an operation which should involve little or no trouble.

Conditions for Analysis

Preliminary experiments showed a mixture of 4 grams of sodium peroxide, 0.2 gram of potassium perchlorate, and sucrose and sample totaling 0.2 gram (0.02 to 0.05-gram sample) to effect satisfactory decompositions in the semimicrobomb. The conditions for precipitation and handling of the barium sulfate obtained from such charges are chosen with a view to controlling some of the errors which are unavoidable when the small precipitate of barium sulfate is formed in the presence of considerable sodium chloride, some barium chloride, hydrochloric acid, and sodium sulfate.

To avoid excessive contamination of barium sulfate by salts (*9*, *10*, *18*, *21*), precipitation is effected in a volume of about 150 cc. (a dilution greater than in the macromethod, *9*), and with a dilute precipitant added rapidly, as suggested by Hintz and Weber (*8*). This procedure has been found advantageous for macroprecipitations under like conditions (*8*, cf. *19*), though perhaps of reduced advantage in the present method because of the delay in the appearance and subsidence of the small precipitate of barium sulfate (*14*). The "reversed precipitation" appears to have some merits (*16*, *19*), but it has been reported to increase contamination by anions (*15*, *19*) and so was not tried. The acidity (1 cc. of concentrated hydrochloric acid in a volume of 150 cc.) is such that increase in the solubility of barium sulfate and occlusion of "free" sulfuric acid (sodium hydrogen sulfate, *2*) and of chlorides (*10*) are not favored. To minimize coprecipitation by adsorption on slowly growing crystals (*12*, *20*, *24*, *25*), and to render the precipitate more promptly filterable, granulation of the precipitate is hastened by addition of picric acid (*19*). Results which indicate the value of this procedure are given in Table IV.

No provision is made for avoiding interference of nitrate (*6*), which need be present only to the extent that it may be formed during decomposition of nitrogenous —e. g., nitro— compounds. No provision is made for avoiding interference by iron or chromium. The familiar devices for avoidance of contamination of barium sulfate precipitates by iron (*1*, *17*, *23*) are inconvenient or uncertain. Errors due to chromic ion are avoidable in part by addition of alkali acetate (*17*), but this increases the concentration of salts present. Chromate ion may cause serious contamination (*4*) because of coprecipitation of mixed crystals of isomorphous barium sulfate and barium chromate (*3*, *11*, *13*). It is therefore advisable to use a bomb which yields little or no iron or chromium, and to replace a cup or cover found to yield considerable of either. The nickel bomb and nickel-plated cover specified above are satisfactory; stainless steel and illium parts are not satisfactory.

Procedure

Transfer to the bomb cup 0.2 gram of powdered potassium perchlorate. Introduce the sample (finely powdered if a solid; for manipulation and analysis of liquids see below), which should be sufficient to yield from 20 to 100 mg. of barium sulfate, and should be weighed to 0.02 mg. Add sucrose in such amount that the sum of sample plus sucrose is 0.2 gram. Weigh out rapidly 4 grams (±0.1 gram) of granular sodium peroxide (the grade low in sulfur) and transfer to the cup. A satisfactory procedure, especially in humid weather, is to support the bomb cup on the left-hand pan of a trip scale, place a small beaker on the right-hand pan, and introduce water to counterpoise the bomb cup, into which the sodium peroxide is weighed directly and rapidly. A measuring cup of proper capacity would be a convenience.

Make certain that the gasket is in good condition, and then adjust the cover in place and secure it firmly by tightening the screw collars. To mix the charge shake the apparatus vigorously, and finally tap the cup against the table top to settle the charge. Support the apparatus in a vertical position by means of a clamp and ring stand, at such height that the cup can be heated by the flame of a blast lamp seated on the table top. It is advisable to wear goggles, and to place an iron plate or other protective device in front of or around the bomb while the charge is ignited. The explosion hazard which attends the use of this apparatus cannot yet be estimated. Sodium peroxide macrobombs sometimes explode with dangerous violence, but the factor of safety should be considerably greater with the smaller bomb because of its relatively heavier construction and the reduced charge which it contains. The first semimicrocup used developed a perforation in the bottom after about a hundred decompositions, and this presumably followed a gradual weakening of the wall which might have led to explosive rupture.

Adjust the blast lamp flame so that it is 7.5 cm. in length and 3 to 4 mm. in diameter. First bring the tip of the flame to a point about 1 cm. below the bomb for about 15 seconds, and then raise the flame so that it touches the bottom of the bomb. This gradual heating appears to prevent the projection of a portion of the charge against the inner surface of the cover, to which some of it may adhere and thus escape combustion. Heat the bomb in this way for 30 seconds; a heating period much longer than this may melt the gasket.

Cool the apparatus, finally, in tap water, and remove the cover. Wash the lower surface of the cover with hot distilled water, collecting the washings in a 250-cc. beaker. Wash the bomb externally (discard these washings) and then, with the aid of a thick glass rod, place the cup on its side in the beaker. Add water to a volume of about 50 cc., cover the beaker, and allow the contents of the cup to dissolve, if necessary warming gently at first to start the action. Using the glass rod lift out the bomb cup and wash it externally. Then grasp it between the fingers and wash the interior, collecting the washings with the main extract. Cover the beaker and allow the liquid to cool somewhat. Insert the glass rod obliquely, so that it projects through the lip of the beaker, push the watch glass slightly away from the rod, and then cautiously pour 8 cc. of concentrated hydrochloric acid along the sloping rod, so that the acid enters the liquid at a point well under the cover. This procedure minimizes loss due to spraying. Test a drop of the liquid on Congo red paper, and if necessary add more acid until the liquid is just acid in reaction.

To the solution add 1 cc. of concentrated hydrochloric acid in excess, and warm on the hot plate to expel most of the carbon dioxide. Filter the liquid through paper, receiving the filtrate in a 250-cc. beaker, and wash the first beaker, the watch glass, and finally the filter, with hot water. To the filtered solution add 15 cc. of a saturated aqueous solution of picric acid (about 1 per cent), and dilute the liquid to a volume of about 140 cc. Cover the beaker and heat the solution to boiling. Meanwhile measure out 7 to 10 cc. of 0.1 *N* barium chloride solution, heat to boiling, and then add it rapidly, with stirring, to the hot sulfate solution. Digest the liquid at or near 100° C. for an hour or more, when the precipitate may be removed by filtration. Alternatively allow the analysis to stand until the following day before filtering; in this case the picric acid is dispensable.

Decant the liquid through a weighed Gooch crucible (10-cc.),

Table I. Analysis of Potassium Sulfate

K_2SO_4	Sulfur	$BaSO_4$	Sulfur Found	Difference
Mg.	*Mg.*	*Mg.*	*Mg.*	*Mg.*
100.31	18.45(5)	133.90	18.39(1)	−0.06
100.31	18.45(5)	134.06	18.41(3)	−0.04
100.31	18.45(5)	134.10	18.41(9)	−0.04

wash the precipitate several times with hot water by decantation, and then transfer it to the filtering crucible with the aid of a fine stream of hot water. Dislodge any barium sulfate adhering to the beaker and stirring rod by thorough manipulation with a small policeman and transfer to the filter. Wash the precipitate in the Gooch crucible five times with hot water. Dry the crucible in an oven at 120° for 30 minutes, and then transfer to a large porcelain crucible supported on a triangle above a Bunsen burner. Cover the larger crucible with its lid, and heat for 30 minutes with the full flame of the burner. Allow the Gooch crucible to cool somewhat, transfer it to a desiccator, and when it has cooled to room temperature set it in the balance case. After 15 minutes weigh the crucible to 0.02 mg.

The procedure for precipitation and eventual weighing of barium sulfate, as described in the last two paragraphs, was tested in preliminary trials. Aliquot portions of a standard solution of potassium sulfate (recrystallized from hot water, dried at 120°, ground in a mortar, redried at 120°, and kept in a desiccator over calcium chloride) were analyzed, with addition of 5 grams of sodium chloride to simulate the conditions encountered in the analysis of organic compounds. The results of the final trials appear in Table I.

Blank Analysis. Blank analyses were conducted by the procedure described, using 0.2 gram of sucrose and omitting the sample. The blanks obtained in the experimental trials yielded precipitates not visible, but filtration showed presence of insoluble material. It seems advisable to conduct blanks in triplicate, and to use the averaged result, as individual results may show variations. Some results obtained by the entire procedure described above, applied to fifteen organic compounds, are collected in Table II.

Procedure for Analysis of Liquids. Liquid substances which are not volatile or sensitive to atmospheric moisture, and which are not attacked by sodium peroxide upon contact, may be weighed from a Lunge-Rey pipet or other similar device, directly into the bomb cup. Liquids which cannot safely be handled in this way must be weighed and introduced into the bomb in sealed thin-walled glass ampoules, which can be broken during the mixing of the charge after the bomb is closed. The decomposition in the bomb then effects a silica fusion of the thinner parts of the glass bulb, only the thicker glass of the stem ordinarily surviving the action. [Rapid silica fusions of minerals might be possible if samples were ground impalpably fine. A specimen of orthoclase, submitted to decomposition in a macrobomb, was rendered water-soluble except for a small residue of the less finely ground material (*22*).]

Acidification of the aqueous extract leads to separation of gelatinous silicic acid, which must be removed before the barium sulfate is precipitated. The interference of silicic acid following decomposition of samples contained in glass ampoules is not mentioned in familiar descriptions of the sodium peroxide bomb procedure. This consequence of the use of a glass container for an organic sample may affect analyses for any element determinable by use of the sodium peroxide bomb, especially if a gravimetric method is to be employed. Some comments on the obstruction offered by silicic acid in the determination of halogen in liquid substances will appear in a later paper.

The removal of silicic acid is effected by the dehydration procedure familiar in mineral analysis.

After extraction of the ignited charge acidify the liquid, evaporate to dryness on a steam bath, and moisten the dry residue with 5 cc. of concentrated hydrochloric acid. Again evaporate to dryness, and heat the residue for 1 to 2 hours on the steam bath. Extract soluble material in about 75 cc. of hot water, pass the extract through a paper filter, transfer the silica residue to the filter, and wash five times with hot water. Add 1 cc. of concentrated hydrochloric acid and 15 cc. of saturated picric acid solution. Dilute the liquid to 140 cc., and then proceed as described above.

Some results which indicate the usefulness of this procedure are given in Table III.

Effect of Picric Acid on Semimicroprecipitation of Barium Sulfate

Some trials of the procedure described were made in the presence and absence of picric acid to test its effectiveness

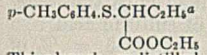
Table II. Semimicrodetermination of Sulfur in Organic Compounds

(By use of sodium peroxide bomb)

Compound	Sample	$BaSO_4$	Sulfur		
			Calcd.	Found	Difference
	Mg.	*Mg.*	%	%	%
Sulfanilic acid	41.61	55.84	18.52	18.43	−0.09
	28.55	38.31		18.43	−0.09
p-Toluenesulfonamide	32.19	44.48	18.71	18.98	+0.27
	38.30	53.20		19.08	+0.37
N-*p*-tolylbenzenesulfonamide (m. p. 122° corrected)	49.05	46.37	12.97	12.98	+0.01
	48.41	45.57		12.96	−0.01
	27.12	25.61		12.97	0.00
	35.79	33.73		12.95	−0.02
	34.57	32.27		12.82	−0.15
	30.46	28.14		12.69	−0.28
	46.17	43.70		13.00	+0.03
N-methyl-*N*-*p*-tolylbenzenesulfonamide	33.73	30.78	12.28	12.53	+0.25
	41.71	36.86		12.15	−0.13
N-methyl-*p*-aminophenol sulfate	30.38	21.10	9.64	9.54	−0.10
	30.24	21.70		9.85	+0.21
Sulfanilamide Analysis by macromethod (*7*) gave 18.68, 18.69, 18.72, and 18.73% sulfur, average 18.71%	33.92	45.26	18.73	18.32	−0.41
	30.33	40.69		18.43	−0.30
	30.35	40.92		18.52	−0.21
	33.60	45.52		18.61	−0.12
	31.14	42.90		18.92	+0.19
	30.89	41.37		18.40	−0.33
	36.54	49.71		18.69	−0.04
	34.21	45.76		18.37	−0.36
	20.57	28.02		18.71	−0.02
	30.60	40.96		18.39	−0.34
	34.73	46.77		18.50	−0.23
	36.09	49.11		18.69	−0.04
Thiocarbanilide (m. p. 152–3° observed)	31.85	32.39	14.03	13.97	−0.06
Thiourea	32.00	97.92	42.11	42.03	−0.08
	27.75	84.86		42.00	−0.11
$(CH_3)_2CH\underset{\substack{\mid \\ CONH_2}}{CH}.S.C_4H_9$	32.23	40.07	16.95	17.07	+0.12
$p\text{-}CH_3C_6H_4.S.\underset{\substack{\mid \\ COOC_2H_5}}{CH}C_2H_5$	25.35	24.59	13.46	13.63	+0.17
	19.79	19.82		13.72	+0.26
$C_2H_5SO_2CH_2CONH_2$	25.66	40.20	21.21	21.51	+0.30
	35.99	54.91		20.96	−0.25
	36.64	56.79		21.34	+0.13
	37.72	57.99		21.11	−0.10
Bis-[*p*,*p*′-(*N*-methyl-*N*-benzenesulfonyl)]-diphenylmethane	39.39	36.86	12.67	12.85	+0.18
	31.35	29.10		12.74	+0.07
Methyl-*p*-tolylsulfone	33.15	46.36	18.85	19.21	+0.36
	37.19	51.79		19.12	+0.27
Bis-(phenylsulfonyl)-methane	29.36	47.81	21.70	22.36	+0.66
	40.45	64.34		21.85	+0.15
Taurine Purity 98.8% based on Kjeldahl analysis for nitrogen (10 results averaged 11.07%)	35.15	64.53	(25.62)	25.22	Purity calcd. from sulfur 98.6%
	32.05	58.83		25.22	
	22.67	41.81		25.33	

TABLE III. SEMIMICRODETERMINATION OF SULFUR IN ORGANIC COMPOUNDS

(By use of sodium peroxide bomb, with procedure modified to provide for removal of silica introduced by decomposition in presence of glass ampoule)

Compound	Sample	BaSO$_4$	Sulfur		
			Calcd.	Found	Difference
	Mg.	*Mg.*	%	%	%
Solid Substances					
Sulfanilamide	39.96	53.62	18.73	18.43	−0.30
	40.30	54.83		18.54	−0.19
	31.09	41.67		18.41	−0.32
N-*p*-tolylbenzenesulfonamide	31.39	29.64	12.97	12.93	−0.04
	40.44	38.67		13.13	+0.16
	43.51	41.42		13.08	+0.11
Liquid Substances					
 $p\text{-}CH_3C_6H_4.S.\underset{\underset{COOC_2H_5}{|}}{CH}C_2H_5$[a]	18.32	18.11	13.46	13.57	+0.11
	15.59	15.34		13.52	+0.06
	31.78	31.23		13.50	+0.04
Thiophene[b], redistilled synthetic, b. p. 85° observed	37.59	102.52	38.13	37.48	−0.65
	27.05	74.21		37.68	−0.45
	24.42	67.09		37.74	−0.39
	16.52	45.23		37.61	−0.52
	15.54	42.35		37.43	−0.70

[a] This compound is a liquid but is not sensibly volatile, and need not be weighed in glass ampoule. Results in Table II were obtained with samples weighed directly into bomb cup from Lunge-Rey pipet.

[b] Results for thiophene average about 0.5% too low, owing presumably to volatilization of undecomposed thiophene into space above charge during ignition.

in hastening the granulation of precipitated barium sulfate in semimicroanalysis, and to determine whether or not the presence of picric acid adversely affects the accuracy of the method. The results of these tests are listed in Table IV.

Table IV indicates that when picric acid is used the precipitate may safely be collected after digestion for an hour, but that in the absence of picric acid a digestion period of 1 hour, or even of 2 hours, is insufficient and leads to negative error. It is shown also that precipitates of semimicro size may not be ready for filtration in 10 to 15 minutes, as was shown by Lindsly (*19*) to be permissible in macroanalysis. The results (one good, two low but passable, one very low) obtained after such early filtration suggest that to ensure consistently satisfactory analyses a longer digestion period is advisable. When the precipitate is allowed to stand overnight before filtration, satisfactory results are obtained whether or not picric acid is present. There is no clear indication that by allowing the liquid and precipitate to stand overnight the chloride inclusion is decreased and the composition of the precipitate improved, as reported for the macromethod by Johnston and Adams (*10*), or that the presence of picric acid slightly increases coprecipitation of barium chloride (*19*). The procedure may not be sufficiently accurate to show a consistent noticeable response to these influences, which may also be compensatory. In most of the analyses reported in Tables II and III picric acid was used and the precipitate was allowed to stand with the liquid overnight before filtration.

In accuracy, precision, and range of applicability the procedure described may be considered satisfactory, and on the whole it compares well with the macro- and micromethods. Tables II and III list the unselected results of analyses made independently a year apart by the two junior authors. Table IV includes results which probably represent the method at its best. Accuracy is affected by relatively small manipulative irregularities, as the manipulations are those of the macromethod executed on a reduced scale.

Summary

This paper describes a Parr sodium peroxide bomb assembly suitable for the decomposition of semimicrosamples of organic compounds, a gravimetric semimicroprocedure for determination of sulfur in organic compounds by combustion in the semimicrobomb, and a procedure for removal of silicic acid introduced when liquid samples in glass ampoules are decomposed in the sodium peroxide bomb.

Tests indicate that in the semimicromethod the digestion period required to render the precipitate of barium sulfate filterable is shortened when precipitation is effected in the presence of picric acid.

TABLE IV. EFFECT OF PICRIC ACID IN SEMIMICROPRECIPITATION OF BARIUM SULFATE

(Substance analyzed: *N*-*p*-tolylbenzenesulfonamide. Sulfur, calculated, 12.97%)

Picric Acid	Time of Digestion	Sample	BaSO$_4$	Sulfur	
				Found	Error
	Min.	*Mg.*	*Mg.*	%	%
Yes	10–15	27.35	30.37	12.37	−0.60
		32.52	34.91	12.79	−0.18
		28.30	29.99	12.96	−0.01
		29.65	32.12	12.68	−0.29
	Hours				
Yes	1	41.04	38.75	12.97	0.00
No		35.97	33.00	12.60	−0.37
		30.41	27.87	12.58	−0.39
Yes	2	35.44	33.47	12.97	0.00
		30.24	28.47	12.93	−0.04
No		29.74	27.44	12.68	−0.29
		29.84	27.56	12.69	−0.28
Yes	Overnight	31.15	29.30	12.92	−0.05
		39.05	37.18	13.08	+0.11
No		33.09	31.17	12.94	−0.03
		35.61	33.52	12.93	−0.04

Acknowledgment

Grateful acknowledgment is made to the Faculty Research Committee of the University of Pennsylvania for a grant to aid this study, to the Parr Instrument Company for information and cooperation with respect to the bomb assembly, to J. P. Gibbons, who submitted the procedure to confirmatory trials, and to Harry Green, who performed the experiments on the use of the sodium peroxide macrobomb for analysis of semimicrosamples.

Experimental work has been started leading to the extension of the use of the semimicrobomb to the determination of halogens, phosphorus, and arsenic in organic compounds.

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Determination of Cleanliness of Feather and Down Bedding Materials

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FEATHERS and downs used in articles of bedding and furniture are obtained from geese, ducks, and chickens, the principal geographic sources being China, Eastern Europe, and the United States. When plucked from the fowl, such materials contain bits of skin, flesh, blood, and other extraneous decomposable organic matter.

Under the provisions of the New York State Bedding Law and Rules (*9*), feathers and downs must be properly cleaned before being sold by processors for use in pillows, comforters, cushions, and other articles of bedding and furniture. Rule 1 (e) (*9*) specifies that tests for cleanliness be made in accordance with the following procedure:

> Allow a one-half ounce sample of the material to stand in one quart of freshly boiled but cold water for at least two hours, and then thoroughly agitate the material. Strain off the water through clean muslin into a clean container. There shall be no visible sediment or cloudiness and no cloudiness or offensive odor shall develop in the wash water when allowed to stand for seventy-two (72) hours in an unsealed container at room temperature not below seventy (70) degrees Fahrenheit.

Cleanliness tests of the same type are used by some other states, and are enumerated in purchase specifications of the Federal Government (*3*) and the City of New York (*8*).

The long period of time needed to obtain results with the above test, together with difficulties encountered in interpreting the results in terms of cloudiness and odor, showed the need for chemical tests which could be made in a few hours and which would be more indicative of the cleanliness of such materials.

Free and Combined Ammonia

Since ammonia is formed in the natural decomposition of organic matter, it occurred to the authors that more ammonia and water-soluble ammonia compounds should be present in unwashed materials, and therefore serve as an indicator of the relative amounts of decomposing organic matter present in washed and unwashed feathers and downs.

To determine the ammonia content, the procedure was almost identical with that employed in the micromethod used by this laboratory for detecting second-hand cotton (*5*, *6*) and kapok (*7*) filling materials, the ammonia being finally liberated in a modified Parnas and Wagner micro-Kjeldahl distilling apparatus.

Five grams of feathers and down are boiled for 20 minutes in 200 ml. of water containing 1 ml. of 0.1 *N* hydrochloric acid, then filtered and washed with hot water. The combined filtrate and washings are evaporated on a hot plate to a volume of 4 to 6 ml. The residue is washed into a graduated Kramer-Gittelman tube, cooled, and diluted with water to 12.5 ml.

A 5-ml. aliquot is pipetted into a large culture tube, 250 × 25 mm. in diameter, 5 drops of caprylic alcohol are added to prevent foaming, and then 7 ml. of saturated borax solution. The culture tube is immediately inserted into the steam-distilling apparatus (Figure 1), and the liberated ammonia is distilled over through a water-cooled block-tin condenser into a 50-ml. Erlenmeyer flask containing 10 ml. of 2 per cent boric acid and 5 drops of methyl red indicator (0.05 per cent methyl red in 95 per cent ethyl alcohol). The culture tube is kept in the apparatus for 5 minutes after the top of the tin condenser has become too hot to touch. During the last 2 minutes the Erlenmeyer flask is lowered so that the end of the condenser is above the boric acid solution.

The solution is titrated with 0.01 *N* sulfuric acid, using a microburet, until the color is a deep pink. It is then heated to boiling, and the titration is continued until a full red color is reached. The number of milliliters of sulfuric acid used is noted.

A blank determination is made using water and the reagents alone. The milliliters of sulfuric acid obtained with the blank are subtracted to get the corrected volume of sulfuric acid.

Calculations: Ml. of H_2SO_4 (corrected) $\times\ 0.0085 = \%$ of NH_3 in sample

Oxygen Consumed

The second chemical test used was the Knight test (*4*), with certain modifications. This is a test for oxygen consumed and serves to indicate the relative amounts of oxidizable matter present in washed and unwashed materials.

Ten grams of feathers and down are transferred to a large Mason jar and 1 liter of water at room temperature is added. The material is thoroughly wetted by shaking and placed in an incubator at 25° C. for one hour. It is then filtered through 19-cm. coarse filter paper, and 100 ml. of filtrate are pipetted into a porcelain casserole. The liquid is made just acid to litmus with 6 *N* sulfuric acid and 1 ml. of acid is added in excess. The solution is titrated in the cold with 0.1 *N* potassium permanganate by adding 2-drop portions and then stirring until a pink color persists for 60 seconds.

The number of milliliters of potassium permanganate used is noted, and calculated to number of grams of oxygen per 100,000 grams of sample (oxygen number).

1 ml. of 0.1 *N* $KMnO_4$ = 0.8 mg. of oxygen = 80, oxygen number.

Chlorides

A study of the chloride test (*1*, *2*) as a cleanliness indicator had been planned. However, preliminary analyses of well waters used by some processors for washing feathers showed very high sodium chloride contents. This indicated that further work on the chloride test would be valueless and therefore the study was discontinued.

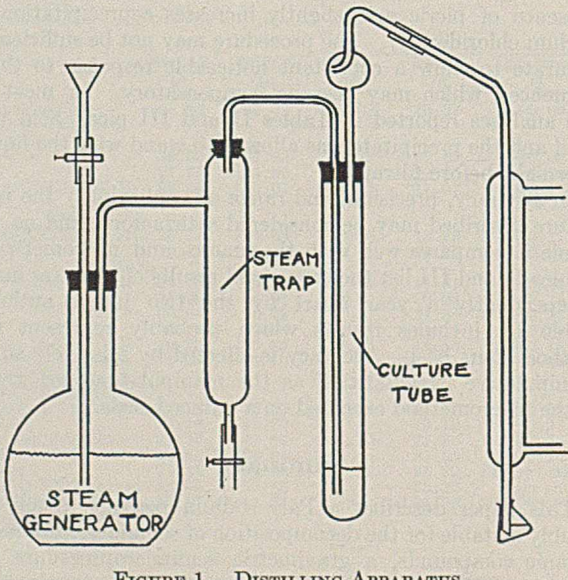

FIGURE 1. DISTILLING APPARATUS

Samples Used

In order to obtain materials for analysis, visits were made to factories of six of the largest feather processors in this country, where feathers and downs of various types were washed and dried in the presence of the authors.

The raw feathers (sometimes after a preliminary dusting) were agitated for approximately 20 minutes in a washing solution consisting of water and a small amount of detergents. The dirty wash solution was then drained off, and the feathers were given 2 or more rinsings by agitating them in plain water for periods of 10 to 20 minutes each, draining after each rinsing. The wet feathers were centrifuged for approximately 10 minutes to remove most of the remaining water, and then transferred to a steam-jacketed drying chamber, where they were agitated by rotating paddles while a current of warm air passed through them and carried off the residual moisture.

A total of 86 samples of feathers and downs was obtained; 43 were unwashed materials; 43 consisted of the same materials after washing and drying. These materials, sampled before washing and after washing and drying, were of the following types:

Type	No. of Samples
Chicken, butcher, domestic	12
Duck, China	13
Duck, Long Island	3
Goose, China	9
Goose, European	6
	43

Results of Analyses

Each sample was analyzed by the oxygen-consumed test, the ammonia test, and the present cleanliness test (Table I).

The results of the oxygen test are reported as "oxygen numbers", the oxygen number of a sample being the number of parts (by weight) of oxygen consumed during the test, calculated to 100,000 parts of sample. The results of the ammonia test are reported as the per cent of water-soluble ammonia found. The results of the present cleanliness test are reported in the routine terminology of this test.

The data contained in Table I are summarized in Table II, which lists the number of samples giving various analytical results. Six samples (Long Island duck feathers) were not included in this summary as it was found best to deal separately with them. Table II, then, summarizes the results obtained on analysis of 80 samples: 40 samples of unwashed materials, and 40 samples of the same materials after washing and drying.

Table I. Analytical Results

Description	Present Cleanliness Test: Before Washing: Solution	Before Washing: Odor	After Washing: Solution	After Washing: Odor	Oxygen Number: Before washing	Oxygen Number: After washing	Per Cent of Ammonia: Before washing	Per Cent of Ammonia: After washing
Chicken Feathers, Domestic, Butcher								
Brown and gray	Cloudy	Bad	Slightly cloudy	Slight	103	8	0.129	0.009
	Cloudy	Bad	Clear	O. K.	99	8	0.146	0.009
	Cloudy	Bad	Slightly cloudy	Slight	133	8	0.170	0.009
	Cloudy	Bad	Clear	O. K.	178	8	0.221	0.008
	Cloudy	Bad	Clear	O. K.	124	8	0.102	0.011
	Cloudy	Bad	Clear	O. K.	90	8	0.115	0.009
Brown quilled	Cloudy	Bad	Clear	Slight	120	27[a]	0.185	0.018[a]
	Cloudy	Bad	Clear	Slight	122	25[a]	0.191	0.018[a]
Gray	Cloudy	Bad	Clear	O. K.	92	8	0.149	0.018
White	Cloudy	Bad	Clear	O. K.	176	8	0.085	0.010
	Cloudy	Bad	Clear	O. K.	54	8	0.132	0.009
	Cloudy	Bad	Clear	O. K.	80	8	0.069	0.011
Duck Feathers and Down								
Gray China	Cloudy	Bad	Clear	O. K.	38	8	0.043	0.006[b]
	Cloudy	Slight	Clear	Slight	29	8	0.081	0.011[b]
	Cloudy	Bad	Slightly cloudy	Slight	72	8	0.120	0.014
	Slightly cloudy	Slight	Slightly cloudy	Slight	38	16	0.088	0.009
	Cloudy	Bad	Slightly cloudy	O. K.	40	8	0.062	0.008
	Cloudy	Bad	Clear	O. K.	36	8	0.072	0.010
	Cloudy	Slight	Clear	O. K.	32	8	0.076	0.008
	Cloudy	Slight	Clear	O. K.	28	8	0.064	0.003[c]
	Slightly cloudy	Slight	Clear	O. K.	36	8[d]	0.065	0.010
	Cloudy	Slight	Clear	O. K.	38	8	0.087	0.010
White L. I.	Clear[e]	O. K.	Clear	O. K.	8[e]	8	0.013	0.008[b,e]
	Slightly cloudy[e]	Slight	Clear	O. K.	10[e]	8	0.014[e]	0.006[b,e]
	Slightly cloudy[e]	Slight	Clear	O. K.	8[e]	8	0.017[e]	0.006[b,e]
Gray China	Slightly cloudy	Bad	Slightly cloudy	O. K.	28	8	0.089	0.010
	Cloudy	Slight	Slightly cloudy	O. K.	40	8	0.044	0.007
	Cloudy	Slight	Slightly cloudy	O. K.	32	8	0.049	0.004
Goose Feathers and Down								
Gray China	Cloudy	Bad	Clear	Slight	40	8	0.026	0.007[b]
	Cloudy	Slight	Clear	O. K.	68	8	0.068	0.010
	Cloudy	Slight	Clear	O. K.	28	8	0.086	0.009
	Cloudy	Slight	Clear	O. K.	30	8	0.065	0.009
	Cloudy	Slight	Clear	O. K.	28	8	0.103	0.009
	Slightly cloudy	Slight	Clear	Slight	28	8	0.085	0.008
White China	Slightly cloudy	Slight	Clear	O. K.	37	7	0.024	0.009[b]
	Slightly cloudy	O. K.	Clear	O. K.	34	8	0.059	0.011
	Cloudy	Slight	Clear	Slight	32	8[d]	0.064	0.012
White Hungarian	Cloudy	Bad	Clear	O. K.	101	8	0.067	0.005[b]
	Cloudy	Bad	Clear	Slight	103	8	0.064	0.006[b]
	Cloudy	Slight	Clear	O. K.	27	8	0.049	0.009
	Cloudy	Bad	Clear	Slight	92	12	0.058	0.012
	Cloudy	Bad	Slightly cloudy	O. K.	40	8	0.037	0.005
	Cloudy	Slight	Clear	O. K.	38	8	0.052	0.005

[a] These two samples washed by same concern.
[b] Ammonia-solution used as one of detergents in initial washing step.
[c] Final rinsing in ammonia-solution.
[d] Treated with ozone immediately after washing and drying.
[e] Long Island duck feathers are washed to some extent before being sold to processors.

Interpretation of Results

Present Cleanliness Test. Table II shows (column 4) that none of the unwashed material had a clear solution, regardless of odor. At first sight it might seem that material showing a clear solution could be classed as properly washed. However, 22.5 per cent of the washed materials had a slight cloudiness, and therefore would be classed by this standard as improperly washed.

If materials showing a cloudy solution were rated as "not properly clean", 15 per cent (column 5) of the unwashed materials would be passed as properly washed.

The presence of a cloudy solution is shown to be a much better indicator of improper washing than a bad odor; 85 per cent of the unwashed material had a cloudy solution, whereas only 55 per cent had a bad odor.

Oxygen-Consumed Test. All the unwashed materials had oxygen numbers above 20.

Of the washed materials 95 per cent had oxygen numbers below 20. The remaining 5 per cent consisted of two materials, both washed by the same concern. All the materials washed by the other five concerns had oxygen numbers below 20.

Two samples of washed materials had been treated with ozone immediately after washing and drying; their oxygen numbers were well below 20 in spite of this treatment.

On the basis of this test, feathers and downs having oxygen numbers above 20 could be classed as "not properly clean".

Ammonia Test. All the unwashed materials had water-soluble ammonia contents above 0.020 per cent, and all the washed materials had

Table II. Summary of Analyses of 80 Samples

Present Cleanliness Test, Rule 1(e) Solution	Odor	Before Washing					After Washing				
		Chicken feathers (butcher) (twelve samples)	Duck feathers and down (thirteen samples)	Goose feathers and down (fifteen samples)	Combined all types (forty samples)	Percentage of all types (100%)	Chicken feathers (butcher) (twelve samples)	Duck feathers and down (thirteen samples)	Goose feathers and down (fifteen samples)	Combined all types (forty samples)	Percentage of all types (100%)
Clear	O. K.	..	..	..	0	0	8	6	10	24	60
Clear	Slight	..	..	..	0	0	2	1	4	7	17.5
Clear	Bad	..	..	..	0	0	..	..	..	0	0
Slightly cloudy	O. K.	..	..	1	1	2.5	..	4	1	5	12.5
Slightly cloudy	Slight	..	2	2	4	10	..	2	..	2	5
Slightly cloudy	Bad	..	1	..	1	2.5	2	..	..	2	5
Cloudy	O. K.	..	..	..	0	0	..	..	..	0	0
Cloudy	Slight	..	6	7	13	32.5	..	..	..	0	0
Cloudy	Bad	12	4	5	21	52.5	..	..	..	0	0
Oxygen Number											
Under 20		..	..	..	0	0	10	13[a]	15[a]	38	95
20-49		..	12	11	23	57.5	2[b]	..	..	2	5
50-99		5	1	2	8	20	..	..	..	0	0
100 and over		7	..	2	9	22.5	..	..	..	0	0
Ammonia, %											
0.000-0.009		..	..	..	0	0	6	7[c,d]	11[d]	24	60
0.010-0.019		..	..	..	0	0	6	6[b]	4	16	40
0.020-0.049		..	2	4	6	15	..	..	..	0	0
0.050-0.099		2	10	10	22	55	..	..	..	0	0
0.100 and over		10	1	1	12	30	..	..	..	0	0

[a] One sample of goose feathers and one sample of duck feathers treated with ozone immediately after washing and drying.
[b] Two of these samples washed by same concern.
[c] One sample received final rinsing in ammonia solution.
[d] In 5 samples of duck feathers and 4 samples of goose feathers, ammonia solution used as one of detergents in initial washing step.

ammonia contents below 0.020 per cent. The ammonia contents of the washed materials were less than 0.020 per cent even in the 10 cases where ammonia solution was used in the processing as one of the washing or rinsing agents.

If this test were used as a standard, feathers and downs having water-soluble ammonia contents above 0.020 per cent could be classed as "not properly clean".

Relative Efficiencies of Three Tests. Table II shows a significant correlation between the results of the oxygen and ammonia tests. Each of the 40 unwashed materials had an oxygen number above 20 and an ammonia content above 0.020 per cent. Similarly, 95 per cent of the 40 washed materials had both an oxygen number below 20 and an ammonia content below 0.020 per cent. If both these tests were used as standards, feathers and downs having either ammonia contents above 0.020 per cent or oxygen numbers above 20 could be classed as "not properly clean".

As an aid in comparing the oxygen and ammonia tests with the present cleanliness test, Table III was prepared. It enumerates all the results possible with the present test, groups the number of samples which gave each result, and lists the maximum and minimum oxygen numbers and per cents of ammonia found in the materials which comprise each group.

Table III. Comparison of Ammonia and Oxygen Tests with Present Cleanliness Test[a]

Present Cleanliness Test	Unwashed Samples			Washed Samples		
	No. of samples	Oxygen number range	Per cent ammonia range	No. of samples	Oxygen number range	Per cent ammonia range
Clear solution						
Odor O. K.	None	..	..	23	6-8	0.003-0.018
Odor slight	None	..	..	8	8-26	0.006-0.018
Odor bad	None	..	..	None	..	..
Slightly cloudy solution						
Odor O. K.	1	34	0.059	5	8	0.004-0.009
Odor slight	4	28-38	0.065-0.087	4	8-16	0.008-0.014
Odor bad	1	28	0.088	None	..	..
Cloudy solution						
Odor O. K.	None	..	..	None	..	..
Odor slight	13	27-68	0.048-0.103	None	..	..
Odor bad	21	36-178	0.026-0.206	None	..	..

[a] Like Table II, does not include 6 samples of L. I. duck feathers.

The data presented in Table III show that the presence of a slight cloudiness has no significance in telling whether materials are washed or unwashed. Materials having a slight cloudiness had oxygen numbers varying widely from 8 to 38 and ammonia contents ranging from a low of 0.008 per cent to a high of 0.088 per cent.

The relative efficiencies of the three tests are compared in Table IV.

Table IV. Relative Efficiencies of Three Tests

Test Used	Best Standard Found for Designating Material as "Not Properly Clean"	On Basis of This Standard: Unwashed materials detected	On Basis of This Standard: Washed materials rated "not properly clean"
		%	%
Present cleanliness	Cloudy solution	85	None
Oxygen consumed	Oxygen number above 20	95	5
Ammonia	Ammonia content above 0.020 per cent	100	None

Long Island Duck Feathers

Long Island duck feathers are washed to some extent before being sold to the feather processors, and therefore do not properly fall into the category of completely unwashed feathers from a cleanliness viewpoint. Accordingly, they were not included in Tables II, III, and IV. This viewpoint was borne out by the results presented in Table V.

Table V shows that the three samples of duck feathers, as received by the feather processors, contained much less decomposing and oxidizable matter than most of the completely unwashed materials. In fact, these three materials before washing by the processors would be classed as "properly clean" by all three cleanliness tests, according to the standards used in Table IV. However, one sample had an ammonia content of 0.017 per cent, which is close to the ammonia standard of 0.020 per cent. Therefore, samples of this type of duck feather might easily show an ammonia content greater than 0.020 per cent when received by the processors.

TABLE V. LONG ISLAND DUCK FEATHERS

(Before and after washing by processors)

Present Cleanliness Test				Oxygen Number		Per Cent of Ammonia	
Before Washing		After Washing		Before washing	After washing	Before washing	After washing
Solution	Odor	Solution	Odor				
Clear	O. K.	Clear	O. K.	8	8	0.013	0.008
Slightly cloudy	Slight	Clear	O. K.	10	8	0.014	0.006
Slightly cloudy	Slight	Clear	O. K.	8	8	0.017	0.006

Summary

The ammonia test was found to be the best of the three cleanliness tests. Using 0.020 per cent water-soluble ammonia as a dividing line, it detected all the unwashed materials in the 40 cases of this type enumerated in Table II. The use of ammonia solution as washing or rinsing agent did not interfere with this test in any of the ten cases tried. The test showed good possibility of indicating in some cases that Long Island duck feathers are not sufficiently clean, when received by processors, to use without further washing.

The oxygen-consumed test was second-best for detecting unwashed material. Using an oxygen number of 20 as the dividing line, it detected 95 per cent of the unwashed materials in the 40 cases enumerated in Table II. Treating washed feathers with ozone did not interfere with the oxygen test, in the two cases so treated. The test showed little possibility for use with Long Island duck feathers.

The present cleanliness test rated last place. Using a "cloudy solution" as a dividing line, it detected only 85 per cent of the unwashed materials in the 40 cases enumerated in Table II, and showed little possibility for use with Long Island duck feathers.

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Microdetermination of Molecular Weights of Dark-Colored Organic Materials

Cryoscopic Method

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THE cryoscopic method for the microdetermination of molecular weights involves measuring the depression of the melting point (*4*), the freezing point (*1*), or both the melting and freezing points (*6*) of some pure solvent. Since the freezing points of many available solvents, and of the solutions of organic materials in these solvents, can be measured more accurately than can the corresponding melting points, the freezing point procedure is used exclusively in this laboratory.

This procedure, which also requires less time and manipulation than do any of the above-mentioned cryoscopic procedures, has been used successfully by the writer in determining the molecular weights of ester gums and dark-colored resins. Molecular weight determinations on ester gum are useful, along with other analytical data, in estimating the proportions of mono-, di-, or tri-esters present. In the case of resins, the molecular weight values give an indication of the degree of condensation. Some resinous materials, however, form solutions too dark to permit accurate observation of the freezing points by the regular freezing point procedure.

This difficulty has been overcome by placing a small glass capsule (Figure 1) in the molecular weight tube with the unknown and solvent. This capsule is made by placing a lead shot (BB) in the bottom of the molecular-weight tube and sealing off at a distance of 10 to 12 mm. from the bottom. The lead shot keeps the capsule submerged in the solution. The annular space thus formed between this capsule and the molecular-weight tube contains only a very thin layer (0.5 to 1 mm. in thickness) of the solution, in which the first appearance of crystals, upon cooling, can be readily detected.

A device, constructed of aluminum, which facilitates thorough mixing of the melted sample and solvent without their removal from the hot oil bath, is shown in Figure 2—above, the normal position for a determination; below, the tubes tilted through approximately 180° to permit thorough mixing of the contents. The molecular-weight tubes are held in place by spring steel sections s and s', which can be adjusted to hold tubes of different lengths. The entire device fits easily into a 300-cc. culture flask.

Procedure

In carrying out an actual determination, 8 to 11 mg. of the unknown and 80 to 130 mg. of a pure grade of camphor, or some other suitable solvent (*5*), are weighed directly in a very thin-walled molecular-weight tube, the capsule is inserted, and the tube is carefully sealed (Figure 1). Duplicate determinations can be carried out simultaneously. The oil bath, which is maintained 5° to 10° above the melting point of the pure solvent until a thoroughly mixed liquid solution of sample and solvent is obtained, is cooled 1° C. per minute and the freezing point of the solution in the molecular-weight tubes is observed. The point at which the crystals first appear can be more easily observed with the aid of a hand lens. This procedure is repeated using the same solutions, and the average of the values thus obtained is reported as the freezing point of the solutions. The molecular weight of the unknown is then calculated by the equation:

$$\text{Mol. wt.} = \frac{W \times K \times 1000}{S \times (t_1 - t_2)}$$

where W is the weight of solute (unknown); S is the weight of solvent; t_1 and t_2 are the freezing temperatures of the pure solvent

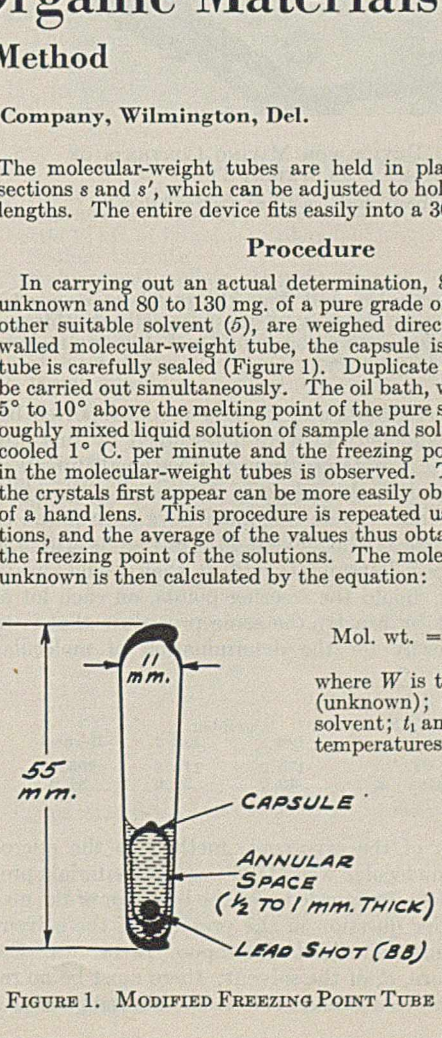

FIGURE 1. MODIFIED FREEZING POINT TUBE

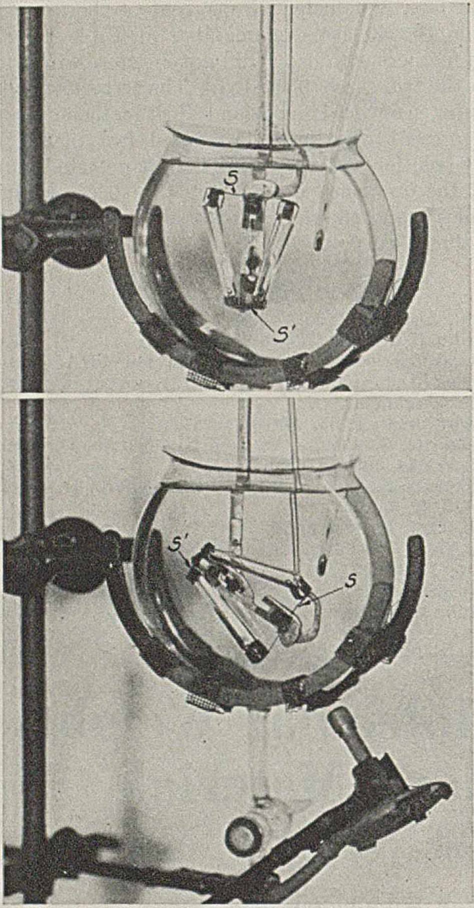

FIGURE 2. DEVICE FOR MIXING CONTENTS OF MOLECULAR WEIGHT TUBES

Normal position above, tilted position below

and solution, respectively; and K is the molal freezing point lowering, or cryoscopic constant, of the pure solvent, obtained by the above procedure with a pure compound of known molecular weight, such as benzoic acid.

The cryoscopic constants and freezing points reported below for camphor and borneol were determined by this procedure. Benzoic acid, obtained from the National Bureau of Standards, was used as the solute in determining the cryoscopic constants. Since these constants have been found to vary with the source of the solvent (*6*), as well as with the method used for their determination (*2*, *3*), they should always be determined, as should the freezing points, on each lot of cryoscopic solvent by exactly the same procedure that is to be used subsequently for the determination of molecular weights.

	Camphor Lot 1	Camphor Lot 2	Borneol
Freezing point, ° C.	176.0	176.8	205.1
Cryoscopic constant, K	40.0	39.6	34.9

The application of the cryoscopic method to the microdetermination of molecular weights of organic materials presupposes certain definite knowledge of the behavior of the material (solute) under question in the presence of the solvent selected: The solute must not decompose at or near the freezing temperature, t_1, of the solvent; there must be no reaction between the solute and solvent at this temperature; there must be no association of the molecules of the solute in the solvent; and the molal freezing point constant, K, must be independent of the concentration of the solute.

In Table I are reported molecular-weight values obtained by the freezing point procedure using the device described above for dark-colored organic materials. All weighings were made on a semimicrobalance, sensitive to 0.02 mg.

Summary

A device is described which permits the microdetermination of molecular weights of dark-colored organic materials by measuring the depression of the freezing point of a pure solvent. This procedure, which has been used in this laboratory for the past 2 years, ensures the same accuracy, about 5 per cent, as that obtained by measuring the depression of the melting point of the solvent. The freezing point procedure

TABLE I. MOLECULAR-WEIGHT MICRODETERMINATIONS BY THE CRYOSCOPIC METHOD

Wt. of Solute *Mg.*	Wt. of Solvent *Mg.*	Freezing Point Depression ° *C.*	Molecular Weight Found Camphor	Molecular Weight Found Borneol	Theoretical Molecular Weight	Error %
			Retene			
9.01	113.96	13.0	243	...	234.3	+3.7
8.17	102.94	12.9	246	...	..	+5.0
8.11	125.78	11.2	228[a]	...	..	−2.7
8.46	122.04	12.3	223[a]	...	..	−4.8
8.02	106.92	11.6	...	226	..	−3.5
7.79	89.43	14.0	...	217	..	−7.4
			Hydroquinone Dimyristyl Ether			
9.50	106.45	7.3	489	...	502.8	−2.7
9.88	105.34	7.8	481	...	..	−4.3
8.64	93.66	7.2	512	...	..	+1.8
8.36	93.97	7.0	508	...	..	+1.0
9.23	108.46	6.6	516	...	..	+2.6
11.15	108.42	8.1	508	...	..	+1.0
9.23	109.37	7.0	477[a]	...	..	−5.1
8.70	128.44	5.4	497[a]	...	..	−1.2
9.23	133.41	6.1	473[a]	...	..	−5.9
			Tetrabromophenolsulfonphthalein			
9.41	109.05	5.2	657[a]	...	670.0	−1.9
8.45	101.89	5.1	644[a]	...	..	−3.9
9.43	112.47	4.9	678[a]	...	..	+1.2
9.25	112.73	5.0	650[a]	...	..	−3.0
10.82	122.60	5.5	635[a]	...	..	−5.2
			1-Naphthol Benzein			
8.61	119.65	7.5	380[a]	...	392.4	−3.2
8.94	127.02	7.4	377[a]	...	..	−3.9
8.55	115.07	7.6	387[a]	...	..	−1.4
8.91	126.09	7.5	373[a]	...	..	−4.9
9.58	117.60	7.1	...	400	..	+1.9
8.44	116.06	6.2	...	409	..	+4.2
9.00	125.25	6.3	...	398	..	+1.5
8.40	108.32	6.6	...	410	..	+4.5
			Vinsol[b], Dark Resin			
10.89	109.88	10.0	396	...	..	...
9.19	101.66	9.1	397	...	..	...
12.45	109.37	9.7	...	410	..	...
11.03	102.49	9.0	...	417	..	...
			Vinsol[b]-Treated, Dark Resin			
10.15	100.54	6.6	612	...	..	...
10.18	102.12	6.8	586	...	..	...
			Vinsol[b] Fraction, Dark Resin			
9.90	105.06	4.6	819	...	..	...
9.76	100.76	4.9	791	...	..	...
			Ester Gums			
10.16	101.68	4.2	952	...	..	...
9.83	99.52	4.3	919	...	..	...
8.90	105.19	4.1	825	...	..	...
8.76	107.09	4.0	818	...	..	...
9.44	100.81	3.9	960	...	..	...
9.09	100.09	3.8	956	...	..	...
8.87	103.06	3.3	1043	...	..	...
9.11	104.10	3.4	1030	...	..	...
8.71	98.70	3.8	929	...	..	...
9.51	102.94	4.1	901	...	..	...

[a] Camphor from lot 2 used as solvent.

[b] Registered in U. S. Patent Office by Hercules Powder Co. Vinsol is essentially a gasoline-insoluble pine wood resin.

requires less time and manipulation than does the melting point procedure.

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Determination of Zinc by Precipitation as Zinc Anthranilate

A Gravimetric Semimicromethod

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THE need for a more rapid and accurate method for the determination of zinc in tin-lead solder led to the investigation of the application of anthranilic acid, in view of the high sensitivity of the reaction involved. A method formerly in use required at least 4 hours for a determination on solder, while the recovery of zinc was always less than the total zinc present.

Funk and Ditt (*2*) have shown that zinc can be quantitatively precipitated by the sodium salt of anthranilic acid when it is added to a neutral solution or one faintly acid with acetic acid. Precipitation takes place from a dilute solution at room temperature. Zinc anthranilate is crystalline and may be easily filtered. The sensitivity of the precipitation reaction is 1 in 1,000,000. Anthranilic acid, which may be used for analytical purposes, can be purchased from the Eastman Kodak Company, Rochester, N. Y.

The literature contains no method describing the use of anthranilic acid for determining zinc in white metal alloys.

Interfering Elements

Among the metals which may cause interference by coprecipitating to a marked extent are copper and iron. The concern is chiefly with copper, as iron causes no interference unless more than 10 mg. is present. The effect of iron upon the determination of zinc is shown in Table I. The data were obtained by taking various quantities of pure iron and pure zinc which were carried through as described below.

Copper, which reacts with sodium anthranilate like zinc (*2*), can cause interference even when present in minute amount. Funk and Ditt (*3*) describe its accurate precipitation and determination. The sensitivity in the precipitation reaction between the copper and anthranilate ions is the same as with zinc.

Of the splendid methods described in the literature for accurately separating copper from certain elements, including zinc, two are especially suitable. Copper can be completely separated from all the other elements present in all kinds of white metal alloys, in the form of a black, finely divided suspension of metallic copper from a sodium hydroxide solution, by addition of hydrazine hydrochloride (*4*). The copper is filtered off and the zinc determined in the filtrate.

Microquantities of copper, in the range from 0.05 to about 50 micrograms of copper, can be determined accurately by a colorimetric method, using the very sensitive organic reagent dithizon (*1*) and the Keil colorimeter.

The present method may be used for the determination of semimicroquantities of zinc, present as impurity in tin-lead solder in amount from 0.01 to 0.10 per cent, and for quantities of about 8 per cent in zinc-tin alloys.

The procedure, with certain modifications, can be used for determining zinc in other material of greater zinc content—for example, the familiar fluxing agent consisting of a large quantity of zinc chloride with a small amount of ammonium chloride. It may also be used for the determination of zinc oxide impregnated in a certain type of enamel, coating the inside surface of tin cans (Table II) in which various foods are packed, notably corn and meats.

The time necessary to carry out a zinc-tin analysis is 1 hour, about 2 hours for solder, 1.5 hours for zinc chloride soldering salts, and 1.5 to 2 hours for the zinc oxide content of enamel coating.

The accuracy of the method is shown in Table III, giving data obtained by analyses of a sample of flux, and in Table IV, in which several of the analyses were carried out consecutively, in duplicate.

Solutions and Materials Required

A saturated solution of pure bromine in concentrated hydrochloric acid is prepared by shaking vigorously in a glass-stoppered bottle 12 ml. of bromine in 100 ml. of acid.

Sodium tartrate.

Sodium anthranilate reagent, made by weighing 3 grams of anthranilic acid into a beaker and adding about 20 ml. of water and 22 ml. of *N* sodium hydroxide. Finally the solution is made neutral or faintly acid by adjustment with 2 per cent acetic acid, filtered, and made up to volume in a 100-ml. flask.

Gooch crucibles of about 10-ml. capacity.

Procedure

Solder and Zinc-Tin Alloys. Dissolve the sample in bromine-hydrochloric acid, 0.5 gram for solder and 0.05 gram for zinc-tin alloys. When solution of the sample is complete add 2

Table I. Effect of Iron upon Zinc Determinations

Zinc Added *Mg.*	Iron Added *Mg.*	Weight of Precipitate *Mg.*	Zinc Found *Mg.*
1.40	0.10	7.30	1.41
1.80	6.25	9.00	1.74
0.20	10.00	1.05	0.20
0.30	20.00	55.50	10.75
0.14	15.00	41.10	7.96
0.11	5.00	0.60	0.116
0.115	8.00	0.60	0.116

Table II. Zinc Determination in Enamel Coatings from Tin Cans

(Area of sample, 6.452 sq. cm., 1 square inch)

Film Weight of Sample *Mg.*	Weight of Precipitate *Mg.*	Zinc Added *Mg.*	Total Zinc Present *Mg.*	Zinc Found *Mg.*	Recovery %
5.5	5.60			1.08	
5.5	6.40	0.15	1.23	1.24	99.0

Table III. Determinations on a Sample of Zinc Chloride Soldering Salts

(Zinc added, 0.30 mg. Total zinc present, 18.26 mg.)

Aliquot Taken from 200-Ml. Volume	Weight of Sample	Weight of Precipitate	Zinc Found	Recovery
Ml.	*Gram*	*Mg.*	*Mg.*	%
20	0.08209	185.2	35.82	
10	0.041045	92.8	17.975	
10	0.041045	92.7	17.96	
10	0.041045	92.7	17.96	
10	0.041045	94.1	18.23	99.8

Table IV. Zinc Determination in White Metal Alloys

Sample	Weight of Sample	Zinc Added	Total Zinc Present	Weight of Precipitate	Zinc Found	Recovery
	Gram	*Mg.*	*Mg.*	*Mg.*	*Mg.*	%
Solder	0.50			1.45	0.28	
	0.50	0.08	0.36	1.85	0.36	
	0.50			0.90	0.17	
	0.50	0.35	0.52	2.70	0.52	
	0.50			1.30	0.25	
	0.50	0.15	0.40	2.10	0.41	102.5
	0.25			3.30	0.64	
	0.25			3.30	0.64	
	0.25	1.05	0.74	3.85	0.75	101.3
	0.50			10.80	2.09	
	0.50			10.90	2.11	
	0.50	0.175	2.29	11.90	2.30	100.4
Solder sample containing 5.23 per cent of iron	0.50			1.50	0.29	
	0.50	0.175	0.47	2.40	0.47	
Zinc-tin alloy	0.05			22.20	4.30	
	0.05			22.20	4.30	
	0.05	0.40	4.70	24.20	4.69	99.8
Synthetic mixtures of pure tin, lead, and zinc		0.30		1.55	0.30	
		0.50		2.60	0.504	100.7
		4.00		20.80	4.03	100.7
		0.675		3.40	0.669	98.6
		6.00		31.10	6.02	100.4
		5.55		29.00	5.62	101.2
		6.50		33.60	6.50	

to 3 ml. of concentrated sulfuric acid and evaporate to fumes. Lead, which usually is not present in zinc-tin alloys, is filtered after suitable dilution, and washed with 2 per cent sulfuric acid wash solution. Dissolve in the filtrate 0.3 gram of sodium tartrate to hold tin in solution. Neutralize the solution to litmus, first adding a saturated solution of sodium hydroxide drop by drop and concluding the neutralization with powdered sodium carbonate, adding a slight excess. Add 2 per cent acetic acid until the solution is neutral or faintly acid. Add to the cold solution 25 ml. of the reagent slowly with constant stirring. Allow the solution to stand for 30 minutes or longer for complete precipitation of zinc.

Filter through a weighed Gooch crucible, washing the precipitate with a solution containing one part of reagent to 15 parts of water by volume. Wash out the excess reagent by two or three washings with alcohol. Dry the crucible in the oven at 100° to 105° C. for 30 minutes, cool, weigh, and calculate the zinc content. Zinc anthranilate contains 19.37 per cent of zinc.

Semimicroquantities of Zinc in Presence of Large Amounts of Iron. In the presence of large amounts of iron semimicroquantities of zinc can be accurately determined by a procedure described in the literature (*5*), which is a modification of the basic acetate separation of iron. It can be used to separate very large quantiites of iron, as much as 0.5 gram and higher, quantitatively from elements present as impurities in alloy steels and minerals.

White Metal Alloys. Dissolve a 0.5-gram sample in bromine-hydrochloric acid. When solution is complete add 1 gram of potassium chloride to the acid solution of the metallic chlorides. Evaporate to apparent dryness, break up the residue, and heat at 100° C. until the odor of hydrochloric acid is very faint (5 to 7 minutes). In the presence of potassium chloride, it is possible to evaporate the solution to dryness without decomposition of ferric chloride. Enough hydrochloric acid remains to give a clear solution when the residue is treated with 20 ml. of water and boiled gently.

Dissolve 3 grams of sodium acetate in 100 ml. of water and make the solution neutral to litmus with the addition of 1 per cent acetic acid. Add the sodium acetate to the ferric chloride solution, dilute to 400 ml., heat just to boiling, and hold at this temperature for 1 minute. The basic acetate soon precipitates. Filter the solution while hot, and wash the precipitate with hot 1 per cent ammonium acetate solution. Continue the washing until the volume is 600 ml. Transfer the filtrate to an 800-ml. beaker, add 5 ml. of concentrated sulfuric acid, and evaporate the solution down to fumes. Just before fumes of sulfuric acid appear add 5 ml. of concentrated nitric acid to destroy interfering ammonium salts. Continue evaporation to dense fumes of sulfuric acid. Cool, wash into a 150-ml. beaker, and evaporate to a volume of 15 ml. Neutralize, first adding a saturated sodium hydroxide solution, then powdered sodium carbonate until alkaline, and finally make slightly acid by adding a few drops of 2 per cent acetic acid. Add 0.3 gram of sodium tartrate, following the regular procedure, and finally precipitate zinc by adding 25 ml. of reagent.

This is an excellent method for separating large quantities of iron from small amounts of zinc, as there is neither adsorption nor coprecipitation of zinc. The iron content of the solder sample shown in Table IV was found to be 5.23 per cent, a quantity much too large to enable determination of zinc according to the regular procedure without removal of iron. The zinc content of the sample is 0.058 per cent. The recoveries are proof of sufficient precision and accuracy.

Zinc Chloride Fluxes. Take any convenient weight of sample, dissolve in water containing a few drops of hydrochloric acid, and make up to volume in a volumetric flask. Measure off aliquots accurately in a 150-ml. beaker, using a buret of 10-ml. capacity, neutralize the solution to litmus with powdered sodium carbonate, add the anthranilic acid reagent, and continue as in the procedure for white metal alloys. Calculation of the amount of zinc chloride from the value obtained for zinc, carried out in duplicate, shown in Table III gives 91.20 per cent. These experiments also prove precision and accuracy to be entirely sufficient.

Enamel Coating of Tin Cans. Cut a disk with an area of 12.9 sq. cm. (2 sq. inches), and remove the enamel film from the whole piece, or cut the disk into two 6.452-sq. cm. (1-sq. inch) pieces, using one of them for the determination. The film weight is obtained by weighing the section before and after removal of the film. Immerse the sample in a few milliliters of chloroform in a 50-ml. beaker for rapid removal of the enamel coating. Evaporate the chloroform cautiously to avoid loss of small portions of the film. Add 1 to 2 ml. of concentrated sulfuric acid, heat over a small flame, and add a few drops of Superoxol to destroy organic matter. Cool and add 10 ml. of water and 0.10 to 0.20 gram of sodium tartrate. Allow to dissolve and continue as in the other procedures.

Synthetic Mixtures of Tin, Lead, and Zinc. Suitable standard samples of known zinc content were not available as a means for determining accuracy. Therefore pure tin and lead were taken in the same proportion as in the type of solder most widely used—i. e., 40 per cent of tin and 60 per cent lead—together with various added quantities of pure zinc, carefully measured from a solution of a zinc salt.

The data obtained by these analyses, shown in Table IV, give proof of the accuracy.

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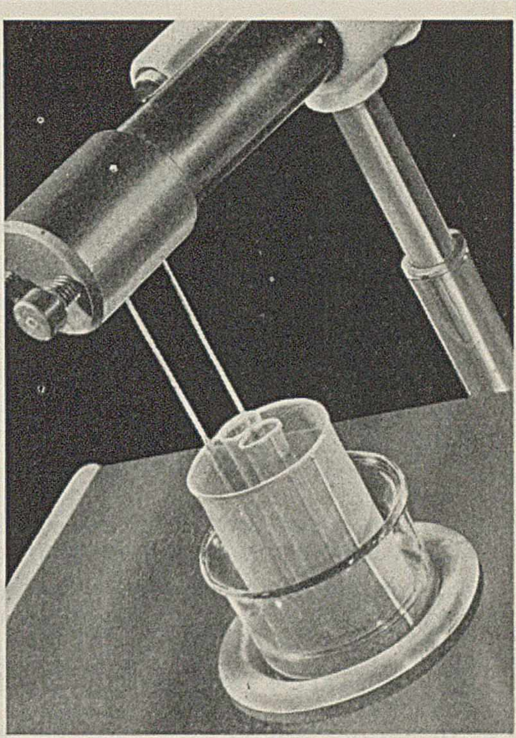

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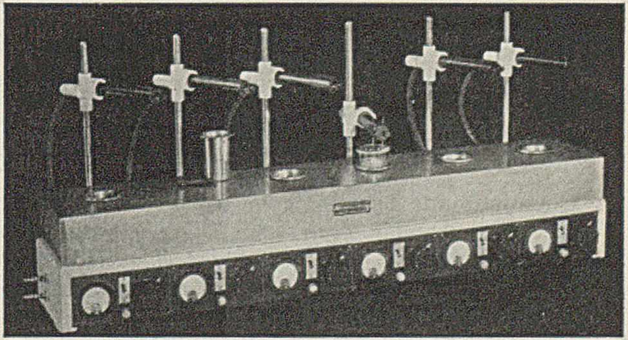

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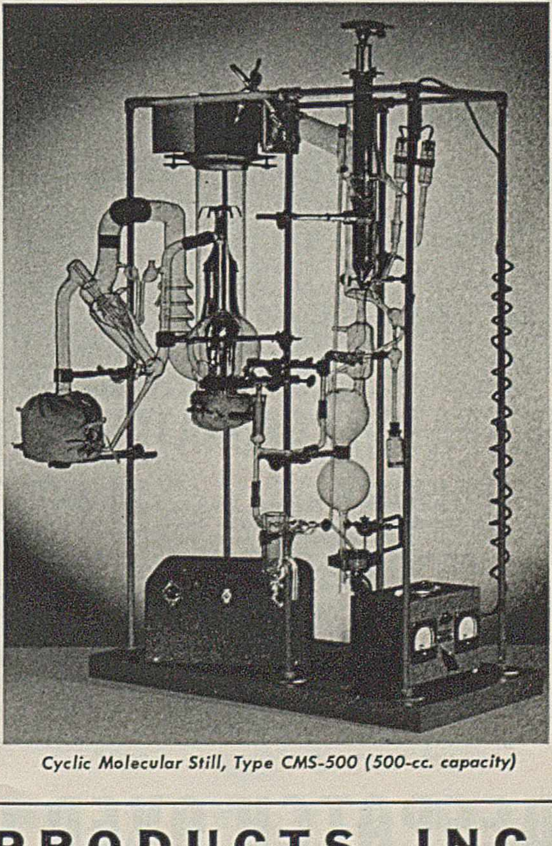

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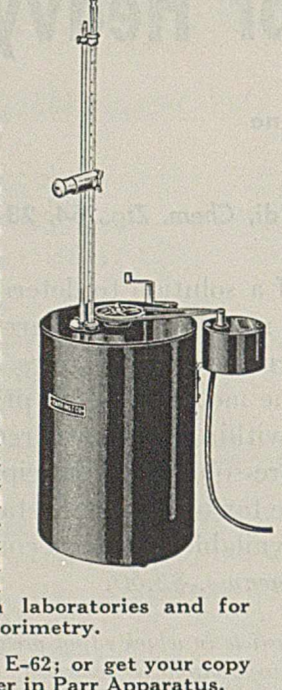

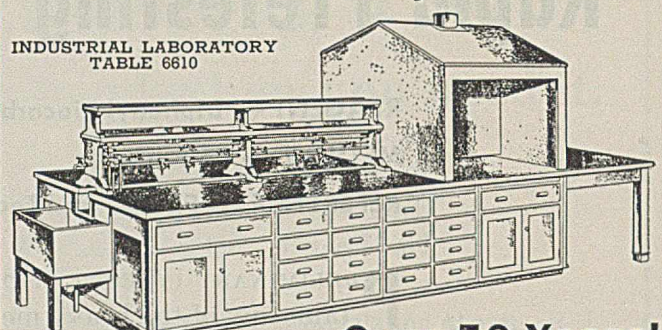
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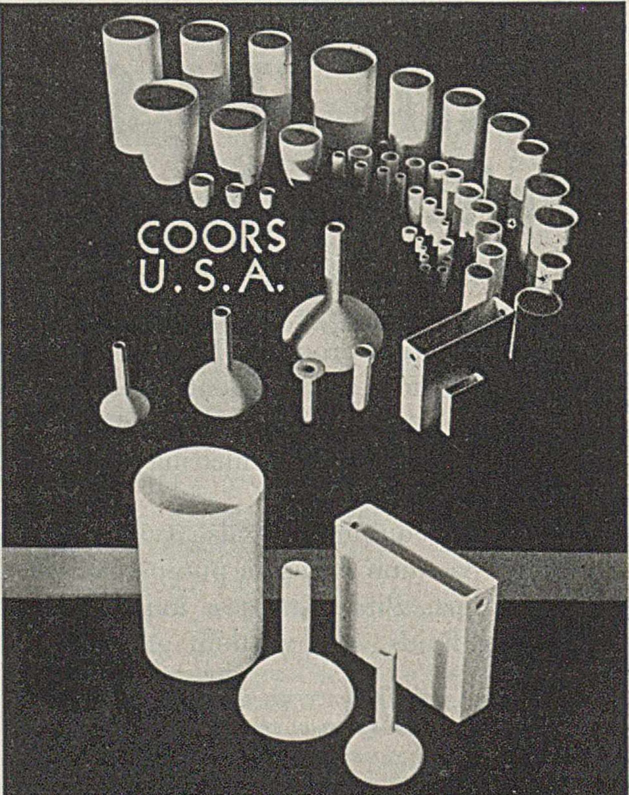
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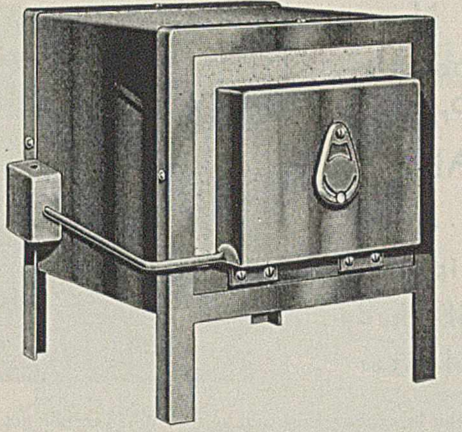

INTERMEDIATE MUFFLE FURNACE

With Multiple Replaceable Units

This furnace has been designated as "Intermediate" because it lies between the small auxiliary furnace and the standard laboratory muffle furnace.

It has been designed primarily for general laboratory requirements where the service will be light or intermittent. All materials are of the highest commercial grades, and are the same as those of larger and more expensive furnaces. Due to the small size and to the low cost, however, it is not as efficient at higher temperatures as the standard laboratory furnace.

It may be used at temperatures up to 1750°F. (955°C.) without noticeable shortening of element life, and may occasionally be used up to a maximum temperature of 1850°F. (1010°C.) for short periods of time.

The furnace input is 1150 watts maximum. The multiple replaceable heating units are of the construction as furnished with the furnaces described on page 429 of our Catalog 5.

Unless some means is used to control the temperature this furnace will overheat and burn out. The rheostat listed below will permit gradual control down to a minimum temperature of approximately 900°F. (482°C.)

The muffle measures $5^1/_4''$ wide by 8″ deep by $3^3/_4''$ high. Overall dimensions are $13^5/_8''$ wide by 14″ deep by $13^3/_4''$ high.

8720—MUFFLE FURNACE—"Intermediate" with multiple replaceable units. For operation on 110 volts A. C. or D. C. $35.00

8721—RHEOSTAT only for the above furnace. For operation on 110 volts A. C. or D. C. $12.50

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- Ammonia, anhydrous and aqua
- Ammonium persulphate
- Asplit Cement
- Bleaching powder
- Carbon bisulphide
- Carbon tetrachloride
- Causplit Cement
- Caustic Soda
- Chlorine, liquid
- Copperas
- Ferric chloride
- Hydrochloric acid
- Hydrofluoric acid
- Hydrogen peroxide
- Kryolith
- Kryocide
- Mixed acid
- Nitric acid
- Orthosil
- Penchlor Acid-proof Cement
- Pennpaint
- Pennsalt Cleaners
- Pensal
- Perchloron
- Sal ammoniac
- Salt
- Salt cake
- Soda ash
- Sodium aluminate
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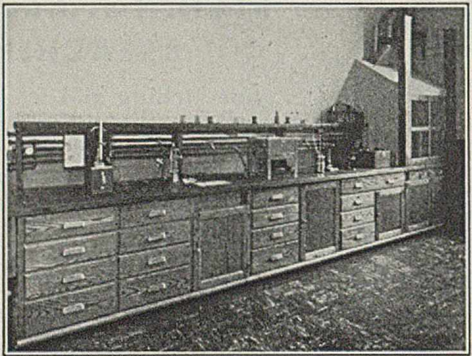

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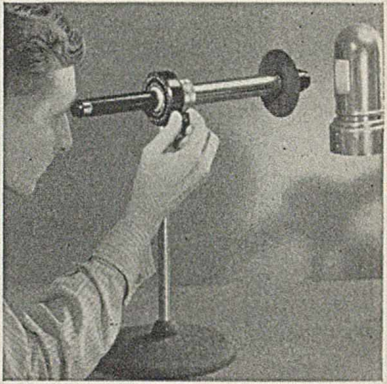

For routine laboratory work and for research in certain fields, Spencer has developed a new, moderately priced Polarimeter.

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For a folder describing the new Polarimeter, write Dept. S48.

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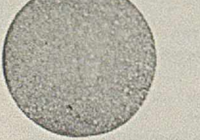
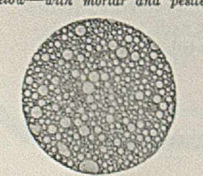


Above—with Hand Homogenizer
Below—with mortar and pestle



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International HAND HOMOGENIZER

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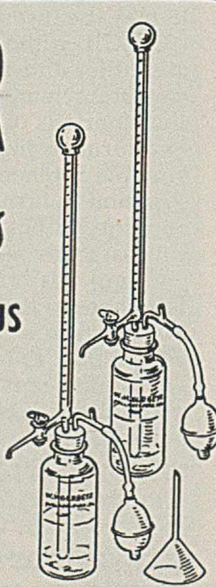

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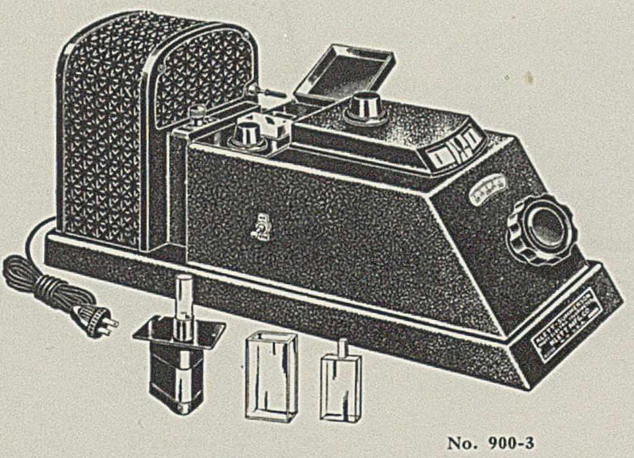
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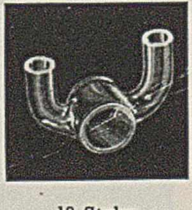
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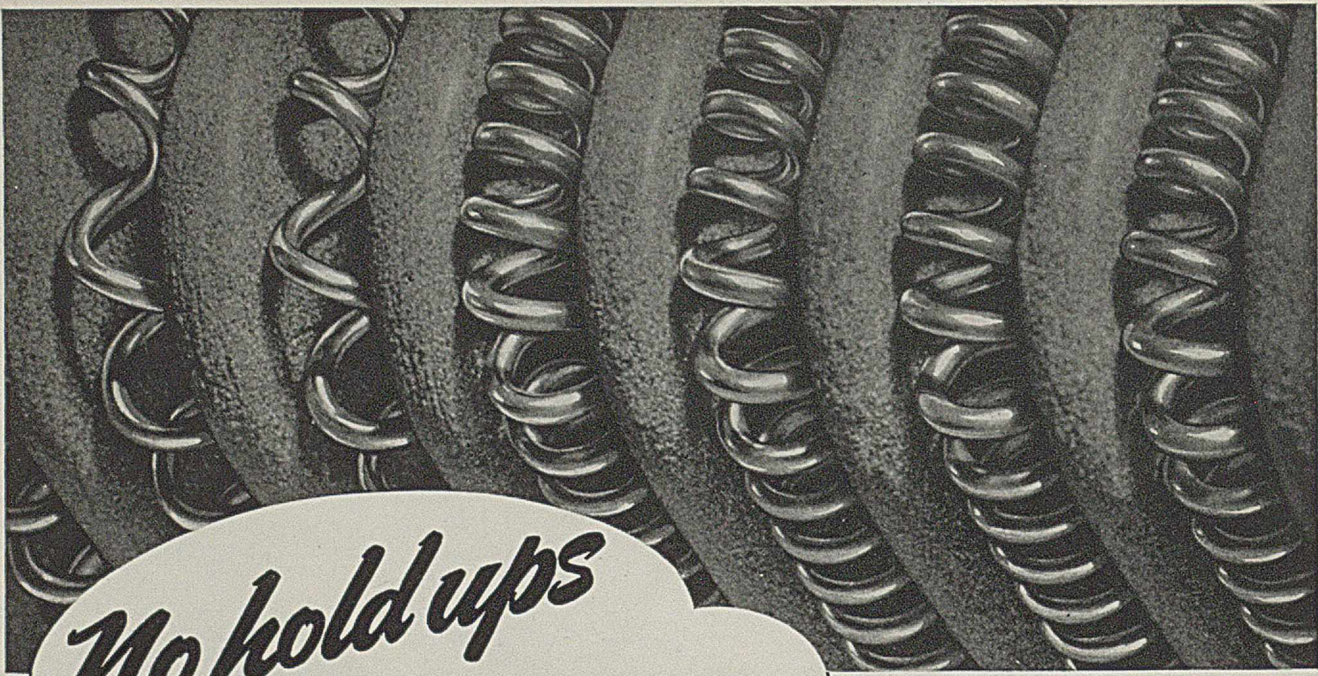

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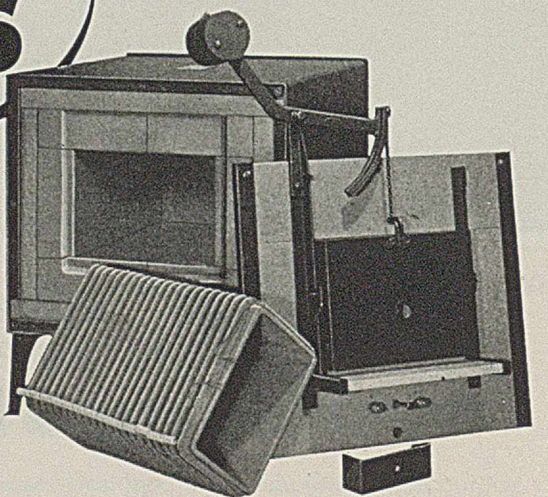

In an electric laboratory furnace, the vital part is obviously the heating element. As you may know, we are the originators of the nickel-chromium heating element alloys. The first use of these Chromel alloys was in Hoskins Electric Furnaces more than thirty years ago. Today, Chromel is found in appliances in millions of homes. Hence, we have a big stake in this alloy—which is your assurance that when you buy a Hoskins Furnace, its heating element will be right. . . . Above is an enlarged view of the wound muffle of our FD-204 furnace. A given furnace won't operate on both 110 and 220 volts. Voltage of 110 is by far the most popular for laboratory furnaces. And for that voltage the FD-204 unit is 13 gauge. For the same furnace to run on 220 also, the wire would be 17 gauge, which has a 60% less cross-section than 13 gauge. . . . This furnace has 4½″ of insulation. . . . To avoid "hold-ups", due to premature burn-outs, buy Hoskins Laboratory Furnaces. Write to your dealer or to us. . . . Hoskins Manufacturing Company, Detroit, Michigan.

1 The Chromel helical unit is wrapped around the one-piece grooved muffle, and is easy to apply.

2 The insulation is 3″ thick in the FD-202, and in the larger FD-204, it's 4½″.

3 The sliding door minimizes the heat loss, that results from opening the door. It seldom needs to be full open.

4 Heavier Chromel unit can be used, because one furnace operates on only one voltage.

5 The furnace operates on line voltage, with temperature control through a rheostat.

6 A small, inexpensive pyrometer, giving approximate temperature measurements, is available for mounting on this furnace.

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