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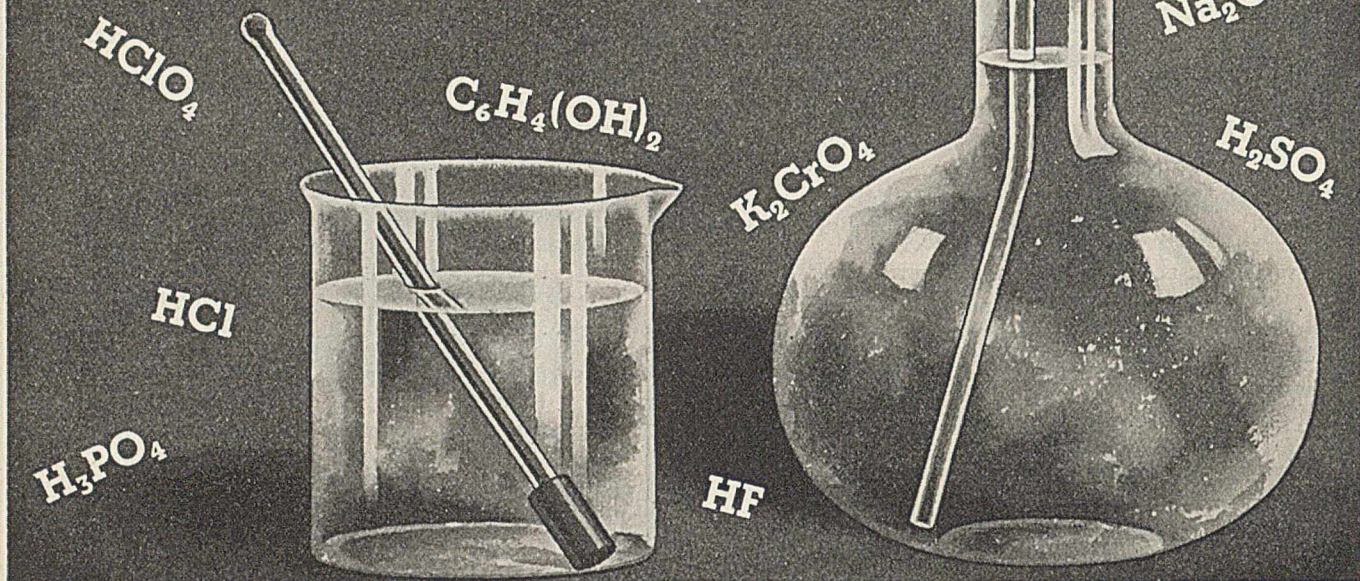
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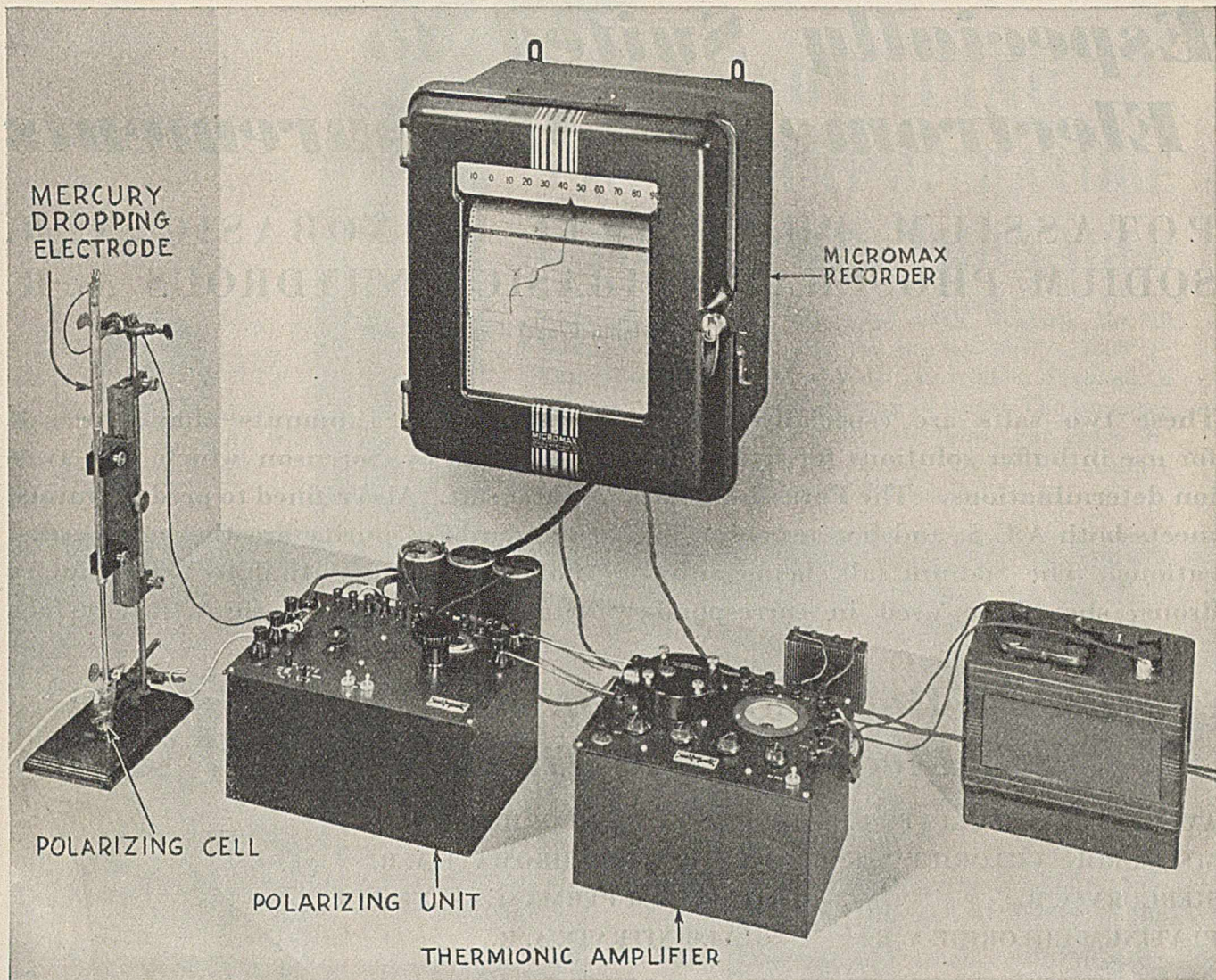
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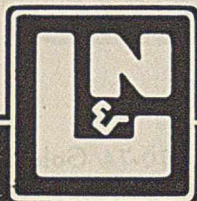
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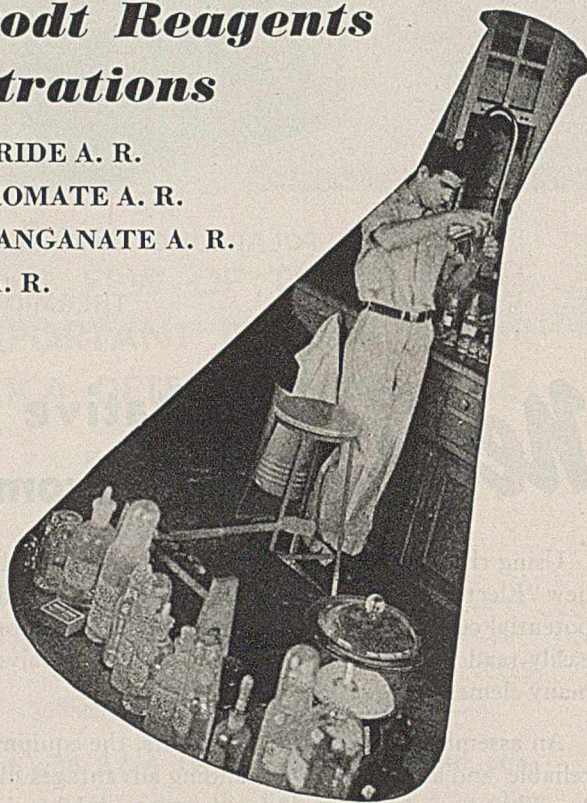
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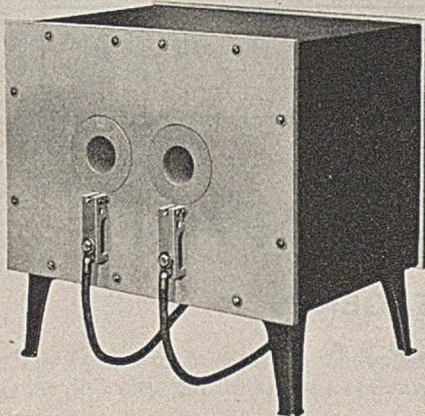
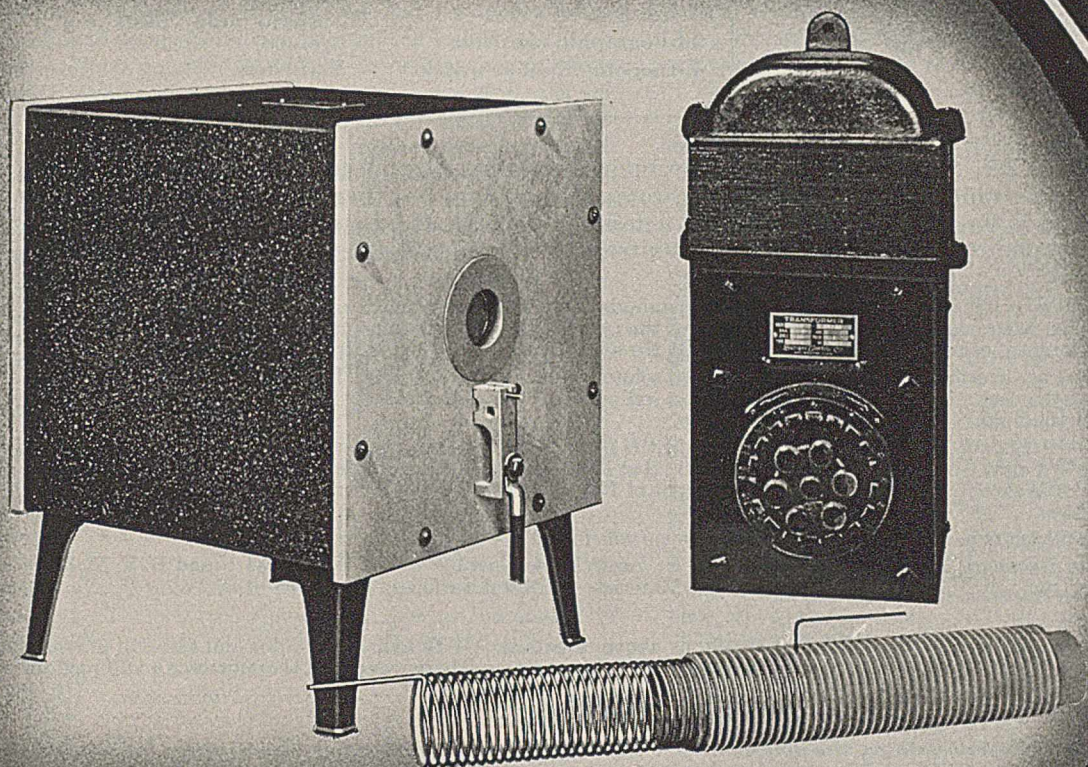
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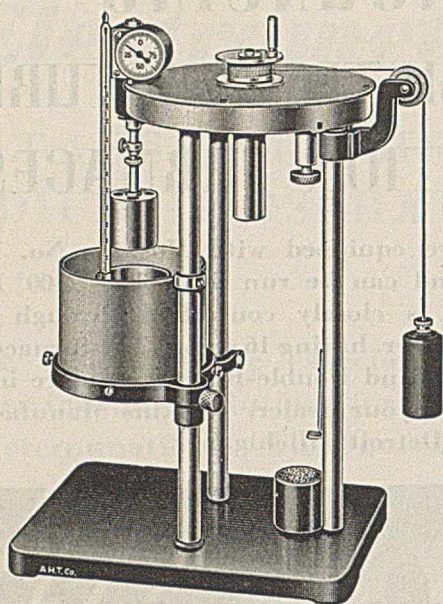
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See "Chemical Engineers' Handbook," p. 1273, John H. Perry, Editor-in-Chief (New York, 1934); and B. V. McBride and George Ehrnstrom, Jr., "Testing Organic Finishing Materials for Metal Surfaces," *The Iron Age*, Vol. 135, No. 23, 1935, p. 14.

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Multiple Tests on Catalysts for Coal Hydrogenation

T. E. WARREN, K. W. BOWLES, AND R. E. GILMORE

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IN THIS paper a simple method of experimental liquid-phase hydrogenation is described, and its application to the testing of catalysts for coal liquefaction is illustrated.

The method consists essentially in heating a number of separate samples of coal or other material in a stream of hydrogen under pressure. The loss in weight during this treatment is a measure of the amount of distillable products, which increases as the conditions of hydrogenation are improved. The principal advantage of the method over those now in use is that it is a relatively quick and inexpensive means of studying the effects of variations in the material charged. However, it has the disadvantage that the properties of the volatile products cannot be determined. Its proper use, therefore, is for the preliminary investigation of such subjects as catalysis, which require extensive experimentation.

Apparatus

The apparatus, as used at the Fuel Research Laboratories of the Canadian Bureau of Mines, is illustrated in Figures 1 and 2.

The dishes containing the samples are of Pyrex glass, and can be easily made from tubing of about 2.5-cm. diameter. Under the conditions of the tests reported herein, there is no significant change in the shape or weight of the glass—for example, the weights of two dishes exposed during a test at 445° C. and 204 atmospheres (3000 pounds per square inch) for 5 hours were as follows:

	No. 6	No. 20
Weight of dish, grams:		
Before hydrogenation	2.5315	2.5576
After hydrogenation	2.5316	2.5579

In the reaction chamber, the dishes are spaced at intervals of 1.8 cm. in a vertical column. Variation of the distance between them does not affect the results, as is shown by the following pairs of comparable tests:

Test No.	Space above Dish, Cm.	Loss in Weight, Per Cent of Ash- and Moisture-Free Coal
1-3	2.7	52.1
1-4	5.4	51.7
1-9	2.7	57.5
1-10	5.4	58.0
2-10	1.8	56.2
2-12	3.5	55.1
2-30	1.8	55.7
2-32	3.5	56.5

The number of dishes in the column is limited to about fifty by the difficulty of maintaining a constant temperature over a

long section of the reaction chamber. The temperatures are measured at the top, center, and bottom of the column by three thermocouples, located inside the tube to which the dishes are attached, and recorded automatically.

The reaction chamber, and also the auxiliary equipment used for heating it and for compressing and recirculating hydrogen, have been described previously (5).

Procedure

When a catalyst is to be used, it is weighed into a bottle in the form of a powder, and the corresponding quantity of pulverized coal is added. The bottle is shaken for 5 minutes to mix the coal and catalyst. The degree of mixing is not an important factor, for the results after shaking for 5 seconds and for 1 minute were practically identical. When a concentration of catalyst of the order of 0.01 per cent is to be made up, it is more convenient to add coal to a mixture having a concentration about ten times higher than to handle the minute amount of catalyst required. With this exception, it is best to make up the samples in order of increasing concentration in order to minimize the possibility of contaminating a dilute mixture with a concentrated one.

The rank of the coal has a major influence on the yield of volatile products and on the efficiency of catalysts. The particle size of the coal also has an effect. However, throughout the present work, only one batch of pulverized coal has been used, so that allowance need not be made for these factors.

The quantity of coal in the sample has a minor influence on the yield of volatile products. As might be expected, the smaller quantities give higher yields. In a series of tests on this variable, the loss in weight increased progressively from 57 to 62 per cent, when the weight of coal per sample was decreased between 1.0 and 0.2 gram. Throughout the catalyst tests, the samples have weighed between 0.6 and 0.9 gram.

When a vehicle is used, it is added after the sample of coal and catalyst has been weighed into the glass dish. The vehicle is measured from a 1-ml. pipet and is not weighed. Since the vehicle used in the present tests is a distillate product, practically all of it evaporates at the temperature of the reaction. Its influence, therefore, may not be the same as that of vehicles employed in a comparatively small closed system, where a considerable volume of vehicle remains in the liquid phase throughout the test.

After the samples have been weighed into the dishes and the vehicle, if any, has been added, the dishes are placed in the holders and the column is lowered into the reaction chamber. The head of the reaction chamber is tightened, and hydrogen is admitted slowly to avoid disturbing the pulverized coal. The heaters are then turned on, and the temperature is brought to about 445° C. in 2 hours. During the latter part of the heating period, the temperature rises at the rate of 3° C. per minute. During the heating period, the pressure in the system is brought up to 204 atmospheres (3000 pounds per square inch). When the temperature has reached 445° C., a flow of hydrogen at the rate of about 110 liters per hour at the conditions of the reaction, or 0.8 linear cm. per second in the unobstructed part of the reaction chamber, is begun. These conditions—445° C., 204 atmospheres,

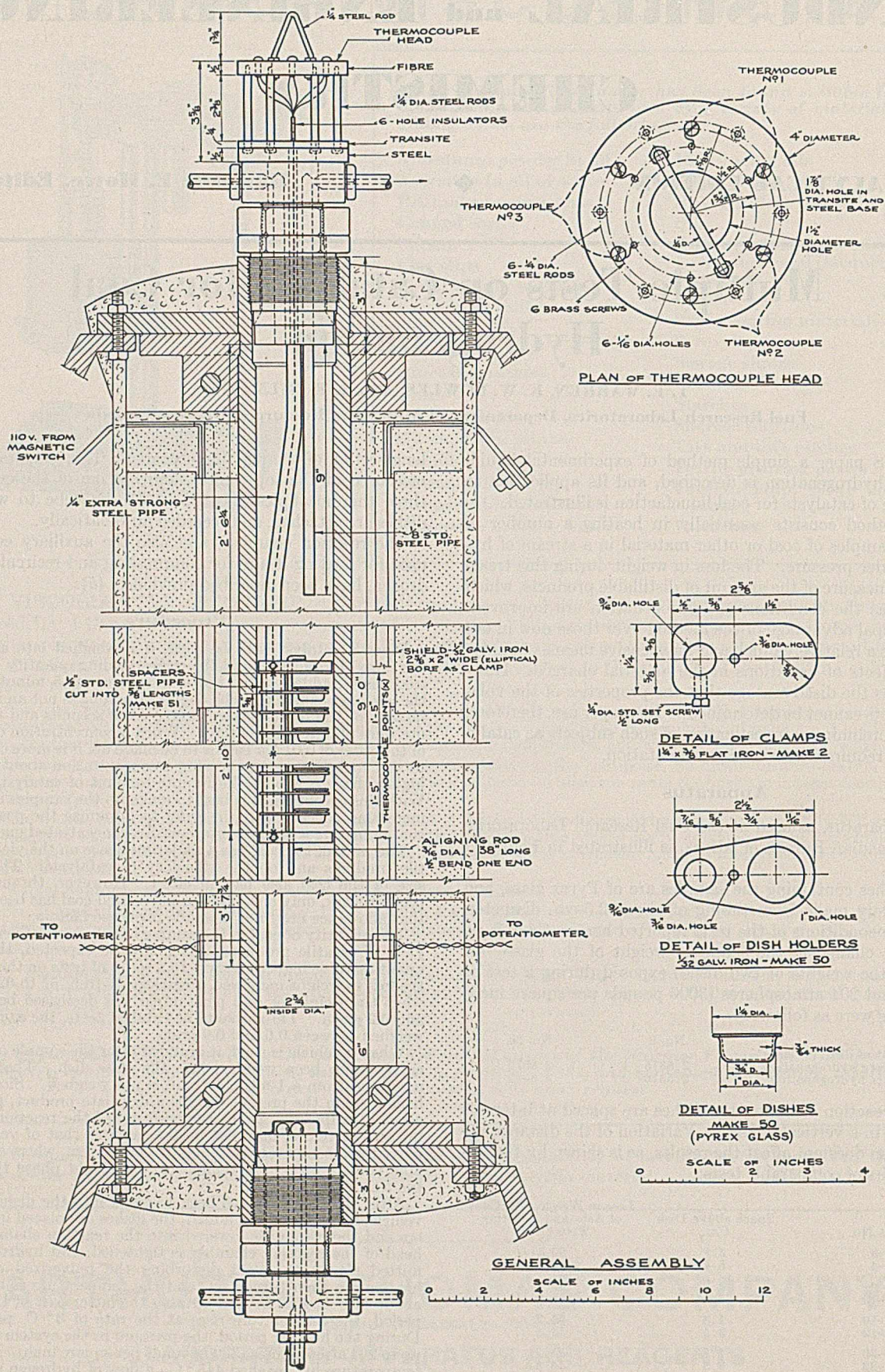


FIGURE 1. APPARATUS FOR MULTIPLE HYDROGENATION TESTS

TABLE I. PROXIMATE AND ULTIMATE ANALYSES

	As Used in Tests	Ash- and Moisture- Free Basis
Proximate analysis, %:		
Moisture	2.1	..
Ash	3.3	..
Volatile matter	37.2	39.3
Fixed carbon	57.4	60.7
Ultimate analysis, %:		
Carbon	79.7	84.2
Hydrogen	5.7	5.8
Ash	3.3	..
Sulfur	1.0	1.1
Nitrogen	1.7	1.8
Oxygen	8.6	7.1
Calorific value, calories per gram, gross	7960	8420

TABLE II. ANALYSIS OF ASH

	Per Cent of Ash	Per Cent of Coal
Ignition loss at 700° C.	2.29	0.076
SiO ₂	25.76	0.850
Al ₂ O ₃	17.72	0.585
Fe ₂ O ₃	35.44	1.170
TiO ₂	0.86	0.028
CaO	6.65	0.219
MgO	0.94	0.031
Na ₂ O	4.09	0.135
K ₂ O	0.49	0.016
SO ₃	4.77	0.157
MnO	0.20	0.007
P ₂ O ₅	0.44	0.015
Total	99.65	3.289

TABLE III. SIEVE ANALYSIS
(U. S. standard sieve)

	%
On 50-mesh	6.0
Through 50-, on 100-mesh	14.2
Through 100-, on 140-mesh	14.7
Through 140-, on 200-mesh	17.9
Through 200-, on 300-mesh	11.2
Through 300-mesh	36.0

and a rate of flow of about 0.8 cm. per second—are maintained for a period of 5 hours, after which the heating current is shut off and the chamber allowed to cool.

After the chamber has cooled, the dishes containing the residues are removed and weighed. The loss in weight is corrected for the loss from the catalyst and for the moisture in the original coal. The yield of volatile material is taken as the corrected loss in weight calculated as per cent of the ash- and moisture-free coal. The loss from the catalyst is determined by treating a sample of the catalyst alone under the conditions of the test. This, of course, implies the assumption that the catalysts react in the same way in the presence and absence of coal, which, in some instances, is probably incorrect. However, this correction is usually so small that no large error is involved.

The reaction is sensitive to small changes in temperature. Thus, the average yield of twelve samples, treated at an average temperature of 443° C. was 58.3 per cent, and that of twelve samples, similarly treated at 445° C., was 56.1 per cent. Since there are unavoidable variations in temperature over the length of the column, inaccuracies as great as 3 per cent are possible in comparing samples located at different positions. As a correction, duplicate samples of coal containing no catalyst are located at six equidistant points on the column in each multiple test, and a graph is constructed of their loss in weight *vs.* their position. Each experimental sample is compared with the value on the graph corresponding to its position in the column. The measure of the efficiency of a catalyst is taken as the difference between the yield obtained with it and that which would have been obtained in the same position in its absence as read from the graph. The yield of volatile products from the coal used for the present tests was about 57 per cent in the absence of any catalyst, and more than 80 per cent in the presence of the more efficient catalysts.

Tests on Catalysts

The coal used throughout the tests on catalysts was produced in the Sydney area in Nova Scotia. Its rank was high-volatile A bituminous in the classification of the American Society for Testing Materials. The characteristics of the coal and its ash are given in Tables I, II, and III.

The vehicle added to some of the samples was representative of those which had been employed in the continuous tests at these laboratories. It was a part of the product of hydrogenation of a high-volatile A bituminous coal, produced by distilling the product to coke with open steam and discarding a low-boiling fraction. The distillation range, determined in the Hempel apparatus, was as follows:

Fraction	Per Cent by Weight
Water	0.2
Up to 170° C.	0.4
170 to 230° C.	12.8
230 to 300° C.	37.6
Above 300° C.	48.9
Distillation loss	0.1

Although this vehicle was entirely a distillate, it contained 0.003 per cent of tin. The increase in the yield of volatile products due to its use is as follows:

Test No.	Increased Yield, Per Cent of Ash- and Moisture-Free Coal
3-3	8.6
3-4	9.5
	Av. 9.1

Before beginning a survey for the purpose of testing the catalytic activity of a large number of materials, it was thought advisable to study a few known catalysts in different concentrations, and in the presence and absence of a vehicle. This was done partly to establish standard conditions for the tests, and partly to observe and compare the behavior of the known catalysts over a wide range of concentration. The catalytic materials were not specially prepared, but were used as received from the chemical supply houses.

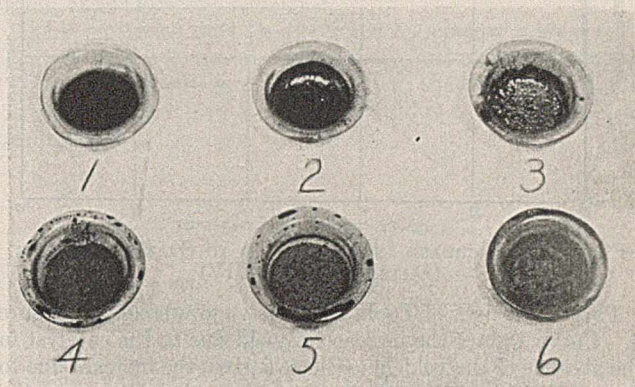


FIGURE 2. SAMPLE DISHES

1. Coal as charged
2. Residue from coal only
3. Residue from coal plus vehicle
4. Residue from coal plus vehicle plus 5 per cent stannous oxalate
5. Residue from coal plus vehicle plus 5 per cent stannous oxide
6. Residue from coal plus vehicle plus 9 per cent ammonium molybdate

STANNOUS OXIDE. Stannous oxide has been used in nearly all the continuous tests at these laboratories, and has also been used extensively as stannous hydroxide by the (British) Fuel Research Board (2). Its efficiency, under a variety of experimental conditions, was therefore known and it was well suited for the present work. The sample used for these tests had been prepared by slowly adding a solution of stannous chloride in dilute hydrochloric acid to a heated solution of sodium carbonate, filtering the precipitate, washing with distilled water, and drying.

TABLE IV. RESULTS OF TESTS WITH STANNOUS OXIDE
Yield of Volatile Products, Per Cent of Ash- and
Moisture-Free Coal

Stannous Oxide, Per Cent of Charge	Without Vehicle		With Vehicle	
	Total	Increase due to catalyst	Total	Increase due to catalyst + vehicle
0.0096	63.8	9.0	72.7	14.2
	63.6	8.9	74.1	15.1
0.0951	68.9	14.6	79.4	20.2
	69.7	15.4	79.5	20.1
0.899	75.7	21.5	82.1	22.5
	75.7	21.4	82.4	22.6
4.56	80.6	26.2	83.3	23.3
	80.5	26.0	83.7	23.5
9.51	80.5	25.7	84.4	24.1
	80.4	25.2	83.6	23.1

When the stannous oxide was treated alone under the conditions of the test, the loss in weight was as follows:

Test No.	Loss in Weight, Per Cent of Charge
2-47	12.23
2-48	12.25

The proportion of tin in stannous oxide (SnO) is 88.12 per cent, and in stannous hydroxide [$\text{Sn}(\text{OH})_2$] is 77.73 per cent. The residual tin was 87.76 per cent of the charge. It was in the form of small spheres.

The results of the test with varying proportions of stannous oxide, in the presence and absence of the vehicle, are given in Table IV.

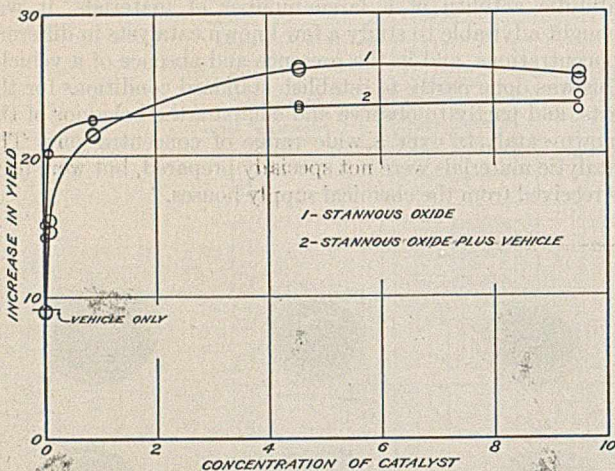


FIGURE 3. INCREASE IN YIELD DUE TO STANNOUS OXIDE
(DATA FROM TABLE IV)

Part of the data of Table IV is shown graphically in Figure 3. Curve 1 gives the increase in yield due to the catalyst in the absence of the vehicle. Curve 2 gives the increase due to the combined catalyst and vehicle; it therefore cuts the line of zero catalyst at 9.1 per cent, which is the average increase in yield due to the use of the vehicle.

STANNOUS OXALATE. Stannous oxalate is one of a number of organic compounds of tin claimed as catalysts for coal hydrogenation in British Patent 363,445 (1). It has been stated that this type of compound is used in the commercial hydrogenation plant of Imperial Chemical Industries at Billingham, England (3). The sample used for these tests had been prepared by precipitation from stannous chloride solution by potassium oxalate solution.

When it was treated alone under the conditions of the test, the loss in weight was as follows:

Test No.	Loss in Weight, Per Cent of Charge
2-51	43.13
2-52	43.19
Av.	43.16

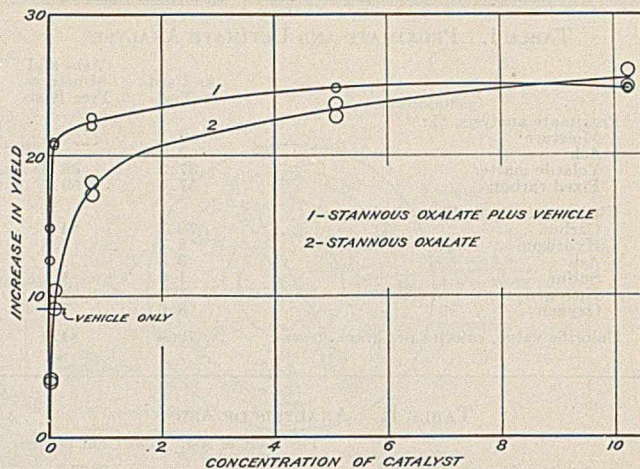


FIGURE 4. INCREASE IN YIELD DUE TO STANNOUS OXALATE
(DATA FROM TABLE V)

TABLE V. RESULTS OF TESTS WITH STANNOUS OXALATE
Yield of Volatile Products, Per Cent of Ash- and
Moisture-Free Coal

Stannous Oxalate, Per Cent of Charge	Without Vehicle		With Vehicle	
	Total	Increase due to catalyst	Total	Increase due to catalyst + vehicle
0.0104	60.0	3.9	72.0	14.8
	60.2	4.1	69.8	12.5
0.0955	66.4	10.4	78.0	20.7
	65.0	9.1	78.5	20.9
0.773	73.0	17.2	80.4	22.7
	73.5	18.1	79.9	22.1
5.09	78.1	22.8	82.7	24.8
	78.9	23.7	82.9	24.8
10.24	79.9	24.9	82.7	24.5
	80.9	26.0	83.0	24.7

The residue is, therefore, $100 - 43.16 = 56.84$ per cent of the charge. The proportion of tin in stannous oxalate is 57.43 per cent. The residual tin was in the form of spheres, much the same as those produced from the stannous oxide, but having a larger average size.

The results of the tests with varying proportions of stannous oxalate are given in Table V, and shown graphically in Figure 4.

AMMONIUM MOLYBDATE. Compounds of molybdenum are good catalysts for the hydrogenation of coal tars, but have been considered inferior to tin compounds for the liquefaction of coal. Ammonium molybdate was included in these tests, because it had previously been studied in comparison with other catalytic materials (4), and because it was a compound of a multivalent element which could be partly reduced under the conditions of the test.

When treated alone under the conditions of the test, the loss in weight was as follows:

Test No.	Loss in Weight, Per Cent of Charge
2-45	25.29
2-46	25.12
Av.	25.21

The residue was, therefore, 74.79 per cent of the original ammonium molybdate. If only molybdenum trioxide had been formed, the residue would have been 81.53 per cent of the charge, and if only the dioxide it would have been 72.47 per cent. The residue was also used as a catalyst.

The results of the tests with ammonium molybdate and with the residue are given in Tables VI and VII, and shown graphically in Figure 5. In Figure 5, curve 3, the dotted line is made by plotting the concentration of ammonium molyb-

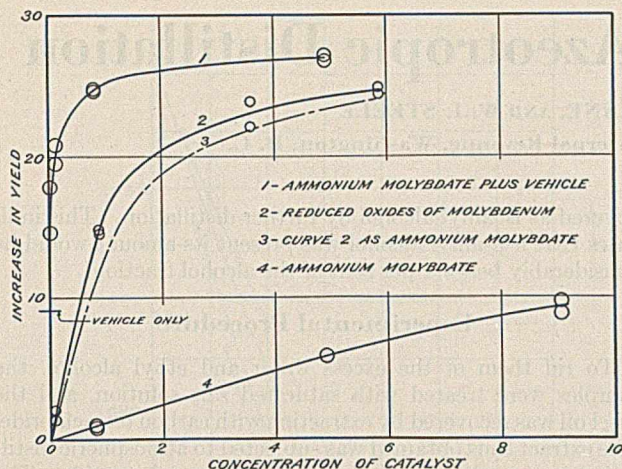


FIGURE 5. INCREASE IN YIELD DUE TO AMMONIUM MOLYBDATE AND REDUCED AMMONIUM MOLYBDATE (DATA FROM TABLES VI AND VII)

TABLE VI. RESULTS OF TESTS WITH AMMONIUM MOLYBDATE

Ammonium Molybdate, Per Cent of Charge	Yield of Volatile Products, Per Cent of Ash- and Moisture-Free Coal		With Vehicle	
	Without Vehicle Total	Increase due to catalyst	Total	Increase due to catalyst + vehicle
0.0145	57.6	0.6	75.1	14.6
	55.7	-1.5	78.1	17.8
0.121	58.2	0.9	80.9	20.8
	56.2	-1.2	79.3	19.5
0.817	58.4	1.0	84.2	24.8
	58.2	0.8	83.6	24.6
4.91	63.2	5.8	85.7	27.2
	63.1	5.8	83.0	26.8
9.06	66.0	8.8	84.7	..
	66.8	9.7	83.6	..

TABLE VII. RESULTS OF TESTS WITH REDUCED AMMONIUM MOLYBDATE

Reduced Molybdate, Per Cent of Charge	Yield of Volatile Products, Per Cent of Ash- and Moisture-Free Coal, without Vehicle	
	Total	Increase due to catalyst
0.0070	57.5	-0.4
	58.0	0.3
0.0825	59.0	1.4
	59.6	2.1
0.889	71.9	14.5
	72.0	14.8
3.59	81.1	23.9
	79.3	22.1
5.86	81.6	24.4
	82.1	24.9

date required to produce the corresponding concentration of residue shown in curve 2.

Discussion

The effect of catalysts in small concentrations is pronounced. For instance, 0.01 per cent of stannous oxide brings about the production of nine hundred times its own weight of volatile material. However, in high concentrations the catalysts are much less efficient, and there is practically no increase in yield when the catalyst concentration is increased beyond 5 per cent. Suitable concentrations for test purposes, therefore, would be 1 per cent in the absence and 0.1 per cent in the presence of a vehicle.

The vehicle renders the catalysts more effective in small concentrations, but slightly decreases their efficiency at high concentrations. It tends to eliminate differences in their efficiency, and for this reason comparative tests of catalytic

materials would probably be more informative in the absence of a vehicle.

The effect of preliminary reduction in the absence of coal increases the efficiency of ammonium molybdate. It is advisable, therefore, to make comparative tests on both reduced and nonreduced materials. The preliminary reduction, when carried out quantitatively, also serves to indicate the state of combination in which the catalyst exists under the conditions of the test.

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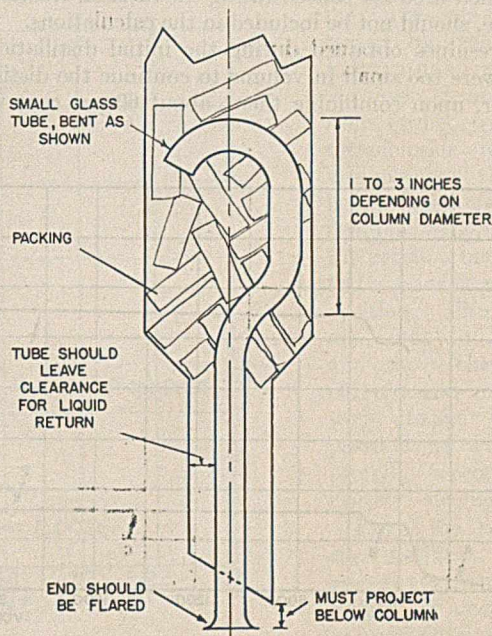
Laboratory Fractionating Column

GEORGE F. REYLING

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SMALL packed laboratory fractionating columns with constricted bases often tend to become filled with condensed liquid which cannot return to the flask because of pressure of the rising vapors. Consequently the column becomes filled with liquid and fails to operate properly when near its maximum capacity.

This condition may be alleviated by placing a glass tube, bent as shown in the diagram, in the bottom of the column. This arrangement permits return of the condensed liquid to the flask, and at the same time allows the vapors to pass unhindered to the top of the column.



Analysis of Fusel Oil by Azeotropic Distillation

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DURING the process of fermentation as normally applied in the production of ethyl alcohol, the starting raw materials contain proteins and amino acids which by the action of enzymes and yeast (*S*) produce a product known as fusel oil. The major portion consists of alcohols boiling between ethyl and hexyl and small amounts of ethyl alcohol, water, acids, esters, furfuraldehydes, and higher boiling alcohols. In Table I are shown results of the analysis of fusel oil by previous investigators.

TABLE I. ANALYSIS OF FUSEL OIL

	Type of Mash			
	Mandya molasses (<i>6</i>)	Kaoling (<i>5</i>)	Molasses (<i>5</i>)	Sweet potatoes (<i>5</i>)
Water	18
Acid	0.1
Ethyl alcohol	8
Isopropyl alcohol	0.5
<i>n</i> -Propyl alcohol	18	6.3	1.8	..
Isobutyl alcohol	5.5	0.6
<i>n</i> -Butyl alcohol	6
Active amyl alcohol	41	17.5	12.4	77.4
Isoamyl alcohol		66.7	50.7	12.9
<i>n</i> -Amyl alcohol	3	0.5

These indicate that the qualitative and quantitative aspects of fusel oil depend on many factors and are not controlled alone by the type of mash used. The other factors may be (*a*) type of yeast or enzyme used for fermentation, (*b*) condition and environment under which fermentation proceeds, and (*c*) method of recovery of fusel oil from the rectifying column (*3*). These facts were corroborated by the results of the present investigation in which the fusel oil fractions used were produced from almost identical "mash bills" in two different distilleries.

In Table II are given the weight percentage amounts of the alcohols found in the two samples of fusel oil, produced from mash containing more than 90 per cent corn. The results, as given, are calculated on the total weight of alcohols present, and are not representative of the fusel oil fractions as received. The amounts of water and ethyl alcohol present depend on the method used for concentrating the fusel oil fraction and, therefore, should not be included in the calculations.

The residues obtained during the initial distillation procedure were too small in volume to continue the distillation. However, upon combining them, about 60 per cent was re-

covered as isoamyl alcohol by further distillation. This indicates that if *n*-amyl alcohol was present its amount would be considerably below 1 per cent of the alcohol fraction.

Experimental Procedure

To rid them of the excess water and ethyl alcohol, the samples were treated with saturated salt solution, and the fusel oil was recovered by extraction with carbon tetrachloride. The extract thus obtained was subjected to atmospheric distillation in a modified 120-plate bubble cap column (*2*). The presence of the carbon tetrachloride facilitated the removal of the small amounts of water and ethyl alcohol still present in the mixture, by virtue of the low-boiling ternary azeotrope formed by water, ethyl alcohol, and carbon tetrachloride (*4*). By continued azeotropic distillation all the *n*-propyl alcohol and isobutyl alcohol were removed, leaving in the pot the alcohols boiling above *n*-butyl alcohol. However, because of an insufficient amount of carbon tetrachloride some isobutyl alcohol remained behind and was distilled along with the active amyl and isoamyl alcohols.

TABLE II. ALCOHOLS IN FUSEL OIL

Alcohol	Distillery A	Distillery B
	Wt. %	Wt. %
<i>n</i> -Propyl	20.4	1.7
Isobutyl	23.9	12.2
Active amyl	14.6	23.4
Isoamyl	36.3	59.7
Residue	4.8	2.96

In Figure 1 is shown the separation occurring during the distillation according to boiling point (curve 2), refractive index (curve 1), and specific rotation (curve 3). On curve 2, *A* indicates the ternary azeotrope water-ethyl alcohol-carbon tetrachloride, *B* the binary azeotrope *n*-propyl alcohol-carbon tetrachloride, and *C* the binary azeotrope isobutyl alcohol-carbon tetrachloride.

There was no indication of the presence of isopropyl alcohol. However, to be sure, plateau *A* was subjected to further extraction and subsequent distillation procedure, the results of which indicated the absence of isopropyl alcohol.

Curves 1 and 2 respond alike to change. The low dip of curve 1 located near 2900 ml. is due to the presence of some

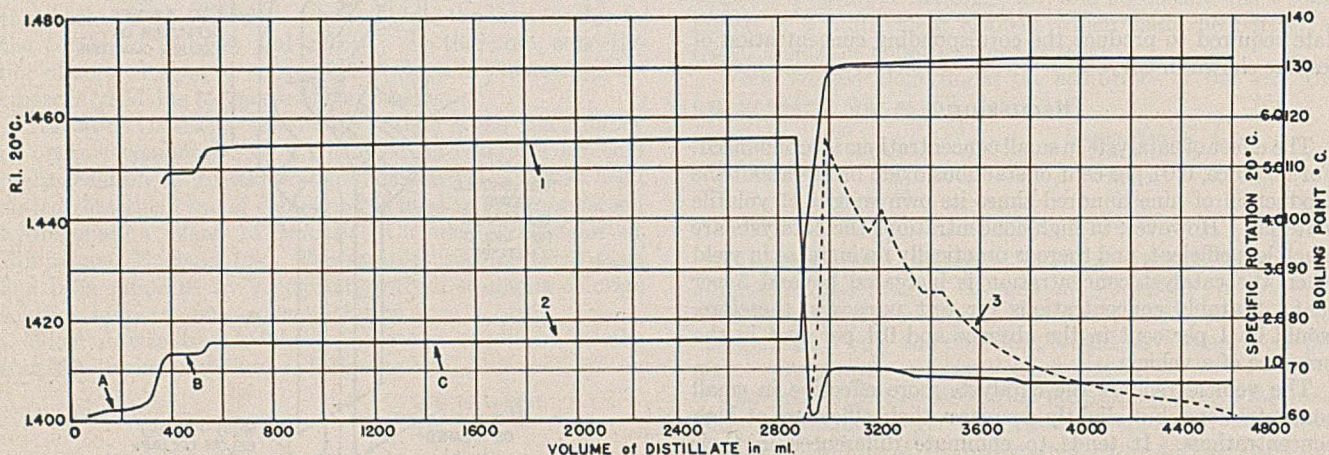


FIGURE 1. SEPARATION DURING DISTILLATION

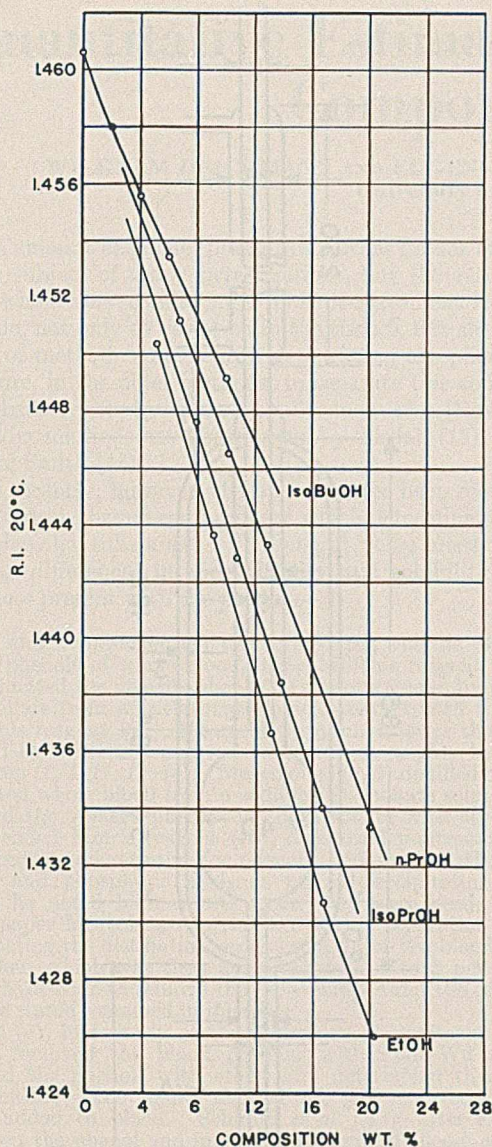


FIGURE 2

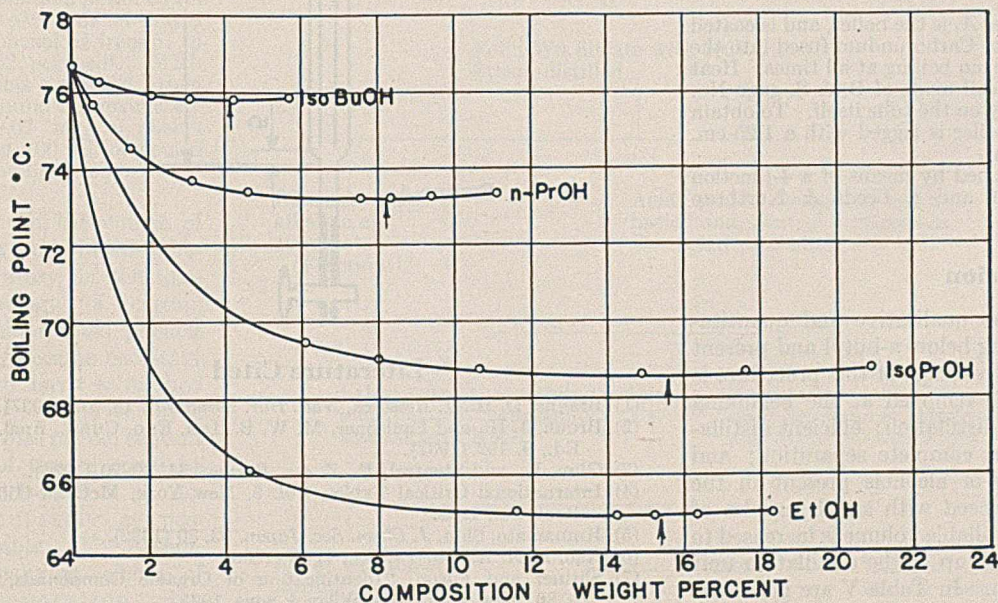


FIGURE 3. AZEOTROPIC CURVES OF ALCOHOLS WITH CARBON TETRACHLORIDE

isobutyl alcohol, which remained in the residue in the pot because of insufficient quantities of carbon tetrachloride to form the azeotrope.

The irregularities noted in curve 3 are due to the intermittent distillation procedure used. The still was not run continuously, and consequently on starting each day there were produced abnormal conditions which were most evident in the specific rotation determinations. It is interesting to note that one fraction was obtained which had the value $[\alpha]_D^{20} - 5.57$. Accordingly, using the value for pure *l*-amyl alcohol of $[\alpha]_D^{20} - 5.78$ the purity was calculated as 96.3 per cent (1).

The alcohols—*n*-propyl, isobutyl, and isoamyl—were identified as the phenyl urethane derivatives. The urethanes were prepared directly from the azeotropic mixtures by refluxing approximately 10 ml. of azeotrope with 1 ml. of phenyl isocyanate for 20 minutes. A small amount of sodium bicarbonate was added to aid the reaction. After refluxing, the carbon tetrachloride was removed by evaporating on the steam bath and the urethane taken up in hot petroleum ether from which it precipitated upon cooling.

The melting point of some of the derivatives thus formed did not agree with the values given in the literature. However, the same melting points were obtained independent of either the method of preparation or the source of the alcohol.

TABLE III. MELTING POINTS

Alcohol	Phenyl Urethane	
	Found ° C.	Literature ° C.
Ethyl	51-51.5	52
Isopropyl	87	90
<i>n</i> -Propyl	51.5	58
Isobutyl	85.5-86	80
<i>n</i> -Butyl	59.5	57
Isoamyl	55	55

In Table III are given the melting points as found by experiment and those given in the literature (7). Although the melting points of the urethanes obtained from ethyl and *n*-propyl alcohols are the same, mixed melting points are definite proof that the derivatives are not the same. It is to be noted also that the melting points of the urethanes of isobutyl and *n*-butyl alcohols are higher than the values given in the literature.

The amount of alcohol in the azeotropic mixtures was determined by refractive index measurements. However, since the solutions formed by carbon tetrachloride with the alcohols are abnormal, it was necessary to determine experimentally the relation between refractive index and composition. The curves are given in Figure 2 and show the change of refractive index n_D^{20} with change in composition for ethyl, isopropyl, *n*-propyl, and isobutyl alcohols.

From the weight of the distillate and its refractive index the weight of alcohol present was obtained.

Azeotropes

It was noted during the investigation that in certain mixtures, the molal composition and boiling point of the azeotrope did not check with the values as given in International Critical Tables. Consequently the composition and boiling points of the azeotropes of ethyl, isopropyl, *n*-propyl, and isobutyl alcohol with carbon tetrachloride were determined.

TABLE IV. AZEOTROPE VALUES

Alcohol	Experimental Values			International Critical Tables		
	B. P. ° C.	Alcohol Mole %	Pressure Mm. Hg	B. P. ° C.	Alcohol Mole %	Pressure Mm. Hg
Ethyl	64.92	38.0	760.4	64.95	39	760
Isopropyl	68.6	32.1	762.5	67.0	36.0	760
<i>n</i> -Propyl	73.2	18.7	763.5	72.8	25	760
Isobutyl	75.75	8.2	762.5	75.8	11	760

In Table IV is given a comparison of the values obtained with those given in International Critical Tables (4). The discrepancies between the observed and reference values may be assumed as real, and not totally dependent on the slight variation in pressures existing during the determinations.

TABLE V. ALCOHOL VOLUME

Alcohol	Alcohol to Produce 100 Ml. of Azeotrope Ml.
Ethyl	26.9
Isopropyl	27.3
<i>n</i> -Propyl	15.1
Isobutyl	7.86

In Figure 3 are shown the azeotropic curves of the alcohols with carbon tetrachloride. Because of the flatness of the curves, it was impossible to obtain the correct value for the composition of the azeotrope by visual inspection. Accordingly, the true values were obtained by subjecting the mixtures of the various alcohols and carbon tetrachloride to a distillation in a 90-cm. (3-foot) column packed with small glass helices. The molal composition of the azeotrope was then determined by measuring the refractive index of the distillate, and referring to the curves in Figure 2.

Apparatus

In Figure 4 is shown the Cottrell boiling point apparatus used in the determination of the azeotropes.

The lower tube on the apparatus, *A*, is the boiler, and is coated on the inner surface with a layer of Carborundum fused into the glass. This ensures uniform and even boiling at all times. Heat is applied by means of a heating coil made of B. & S. gage No. 22 Nichrome wire wrapped directly on the tube itself. To obtain uniform heating conditions, the boiler is lagged with a 1.25-cm. (0.5-inch) layer of magnesia cement.

The boiling points were determined by means of a 4-junction copper-constantan thermoelement and a Leeds & Northrup potentiometer No. 248,801.

Discussion

By azeotropic distillation, the qualitative and quantitative estimation of alcohols boiling below *n*-butyl and present in fusel oil is simplified. The advantage of this procedure is threefold: The water present is removed at the beginning and does not interfere with the distillation; efficient distillation units are not necessary for complete separation; and because of the low percentage of alcohols present in the azeotropes, it is possible to proceed with small samples of fusel oil. In other words, the distillable volume is increased to the point where the factor of holdup of the distillation unit need not enter into the problem. In Table V are given the volumes of alcohols necessary to produce 100 ml. of azeotrope.

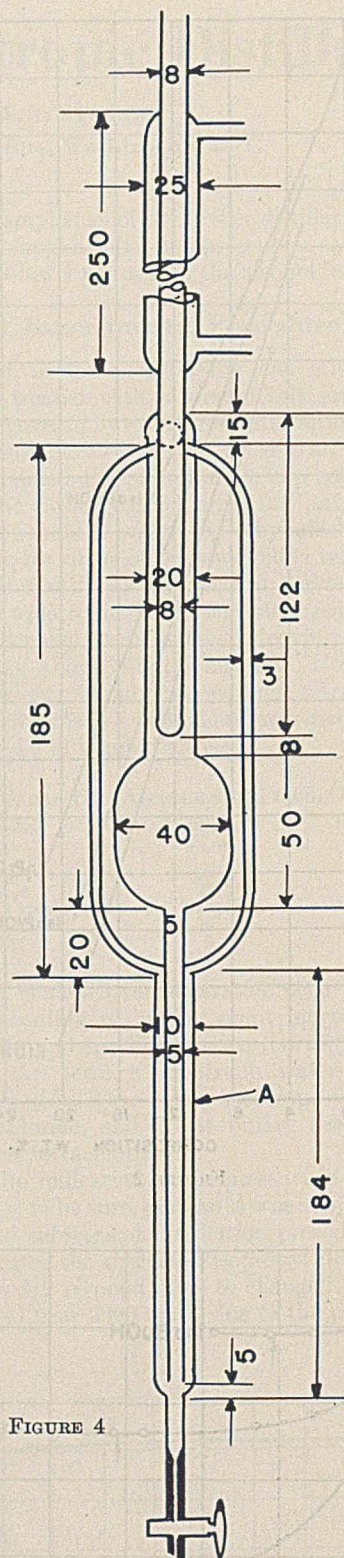


FIGURE 4

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Quantitative Estimation of Phenol and Related Compounds in Tissues

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THE amount of phenol present in normal tissues has been the subject of many investigations, but the results are on the whole very conflicting. This disagreement is apparently due, not only to variation in the tissues, but also to the variety of methods employed in determining the phenol and the failure, in the older methods, to separate this compound from substances that react in a similar manner. [Reviews of these older methods have been given by Tisdall (16), Pelkan (11), and Smith (14)].

More recently, however, these errors have been recognized and procedures have been proposed which determine only the truly phenolic substances. In general these methods are based on differences in the volatility and solubility of the substances present with the phenols.

Haas and Schlesinger (7) determined the volatile and non-volatile phenols of whole blood, using Millon's reagent. Smith (14) estimated the volatile phenols of various tissues by treating the distillate from a trichloroacetic acid extract with the Folin and Denis reagent (5). His results are much lower than those obtained by other investigators who did not employ the distillation step (1, 4, 11, 12, 15). Marcolongo (8, 9) distilled oxalated or citrated whole blood from a sodium bicarbonate solution and extracted the volatile phenols in the distillate with ether. He recommended Moir's reagent (10), diazotized *p*-nitroaniline, as being specific and sensitive for phenols, and avoided the use of sulfuric and phosphoric acids as protein-precipitating agents because he noted high results when they were used. In his second paper Marcolongo carried the phenol separation further by extracting the distillation residue of a Folin-Wu blood filtrate with ether, which was then extracted with 4 to 5 per cent of sodium hydroxide to remove the "oxy-acids" from the diphenols which he stated remained in the ether.

Barac (2), in a study of the hydrolysis of potassium phenol sulfate, removed the blood proteins with Folin-Wu reagent, extracted the phenols with ether, and determined them spectrographically. His results showed 100 per cent recoveries of phenol added to blood. Schmidt *et al.* (13), after extensive studies on the phenol and imidazole content of blood, conclude that "practically the entire 'diazo value' of the blood, generally reported in the literature as phenol, is actually made up of ether-insoluble compounds." They used a continuous ether extraction and obtained recoveries of added phenol of from 51 to 82 per cent. With this method they found approximately 0.02 mg. of phenol in 100 ml. of pooled human blood.

In the course of a study in this laboratory on the toxicology of certain chlorinated phenols it became necessary to have a method by which the true total phenol content of tissues could be determined as accurately as possible. The accompanying scheme of separation was adopted.

Preliminary results seem to offer some explanation for discrepancies reported in the past.

Initial studies with trichloroacetic acid filtrates gave high results when phenol was added to the tissue. The source of error appeared to be a neutral volatile substance which was formed during the distillation. This substance could be removed by distilling the phenols into an alkaline solution, which was then evaporated to a small volume. When this procedure was followed, control experiments without tissue gave almost perfect recoveries, but the recovery of phenol added to blood was poor, indicating a loss before or during the distillation. Results obtained by this method in the past are therefore open to question.

Precipitation of the tissue proteins with the Folin-Wu reagent from an aqueous extract of the ground tissue proved to be more satisfactory. Steam-distillation of the filtrate into alkali and evaporation of the distillate gave recoveries of phenol ranging from 68 to 90 per cent of the amount added to blood. Apparently some phenol was carried down with the protein precipitate (3, 7).

In order to determine the effect of interfering compounds on the colorimetric determination of phenol with the Moir reagent, a number of compounds that might theoretically be present in tissue were treated with this reagent and their approximate phenol equivalents were estimated.

Reagents Required

A standard solution of phenol containing 0.1 mg. of phenol in 1 ml. of 0.1 *N* hydrochloric acid (6). The working standard containing 0.003 mg. of phenol in 1 ml. of 0.1 *N* hydrochloric acid was prepared weekly from this solution.

Sulfuric acid, 0.67 *N*
Sodium tungstate, 10 per cent
Sodium hydroxide, 0.5 and 4 per cent
Sodium acetate solution, 25 per cent, in aqueous gum acacia, 0.5 per cent

A solution containing 1.5 grams of *p*-nitroaniline dissolved in 40 ml. of hydrochloric acid (sp. gr. 1.19) was diluted to 500 ml.

The Moir reagent was prepared daily by treating 25 ml. of this solution with 0.75 ml. of sodium nitrite, 10 per cent (10).

Sodium carbonate, 20 per cent
Hydrochloric acid, 10 per cent
Sand, Ottawa
Ether, U. S. P.

Procedure

The organ was ground, mixed with 10 ml. of water, and pulped with dry sand in a mortar. It was then washed into a flask with 30 ml. of water and treated with 20 ml. of sodium tungstate solution, followed by 20 ml. of sulfuric acid added dropwise from a buret. In the case of blood, 20 ml. of oxalated blood were

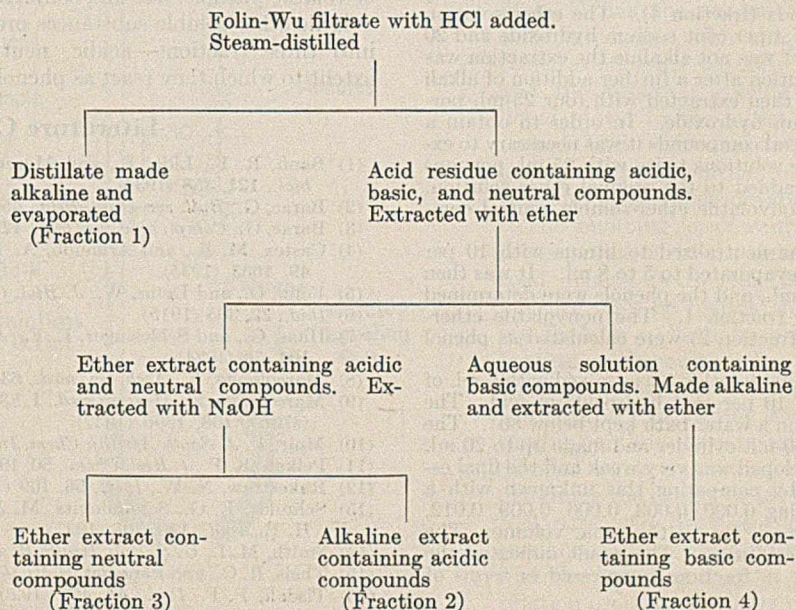


TABLE I. RECOVERY OF PHENOL ADDED TO RABBIT BLOOD AND MUSCLE

Tissue	(Determined by steam-distillation)			
	Phenol Originally Present Mg. %	Phenol Added Mg. %	Total Phenol Found Mg. %	Added Phenol Recovered %
Blood	0.318	0.996	1.046	73.0
	0.247	2.000	2.042	89.7
	0.255	2.000	1.760	75.3
	0.150	2.000	1.880	86.5
	0.171	2.000	1.524	67.7
	0.185	3.000	2.850	88.8
	0.195	3.000	2.400	73.5
	0.250	3.000	2.500	75.0
	Muscle	0.250	2.000	1.880
0.200		2.000	1.853	82.7

TABLE II. DISTRIBUTION IN NORMAL RABBIT TISSUES OF SUBSTANCES WHICH REACT AS PHENOL

Tissue	(Expressed in milligrams per 100 grams of tissue)			
	Fraction 1 (Volatile Acidic)	Fraction 2 (Nonvolatile Acidic)	Fraction 3 (Nonvolatile Neutral)	Fraction 4 (Basic)
Blood	0.16-0.24	0.15-0.33	0.03-0.07	0.06-0.08
Brain	0.19-0.25	0.34-0.55	0.05-0.06	0.02-0.07
Heart	0.14-0.24	0.21-0.54	0.00-0.07	0.04-0.09
Kidney	0.19-0.51	0.42-0.78	0.12-0.16	0.14-0.18
Lungs	0.18-0.24	0.32-0.53	0.05-0.10	0.08-0.13
Stomach	0.11-0.24	0.23-0.43	0.03-0.04	0.08-0.10
Fat	0.09-0.23	0.12-0.27	0.04-0.07	0.04-0.07
Liver	0.12-0.22	0.15-0.54	0.04-0.09	0.05-0.09
Muscle	0.13-0.22	0.12-0.33	0.05-0.07	0.06-0.07

diluted with 40 ml. of water and after 10 minutes the proteins were precipitated as above. After standing for at least 15 minutes the mixtures were filtered. When the customary 20-gram sample was used, 1 ml. of the filtrate represented 0.2 gram of tissue. Samples of 20 grams or more should be used, although 10-gram samples gave reproducible results.

A known volume of the filtrate was placed in a 250-ml. flask equipped with a ground-glass joint and 1 ml. of concentrated hydrochloric acid was added for each 25 ml. of the filtrate. The flask was connected to an all-glass distillation apparatus and the contents were distilled with steam, the volume being kept constant. Approximately 270 ml. of distillate were collected in a flask containing 2 ml. of 4 per cent sodium hydroxide, evaporated slowly on a hot plate to 8 to 10 ml., and then filtered into a 50-ml. graduated cylinder. The flask and filter were washed until the filtrate reached a volume of 20 ml. A standard containing 0.015 mg. of phenol in 20 ml. was prepared from the stock solution. Four milliliters of sodium acetate-gum acacia were added to each solution, followed by 2 ml. of the diazotized *p*-nitroaniline and, after 1 minute, by 4 ml. of sodium carbonate. The solutions were compared in a colorimeter after 3 minutes. The volatile phenols (fraction 1) were calculated from this result.

The distillation residue was concentrated to 100 ml., filtered into a separatory funnel, and then extracted with five 25-ml. portions of ether. The aqueous solution was saved for the determination of basic compounds (fraction 4). The ether solution was extracted with 5 ml. of 4 per cent sodium hydroxide and 20 ml. of water. If the extract was not alkaline the extraction was repeated with the same solution after a further addition of alkali (2 ml.), and the ether was then extracted with four 25-ml. portions of 0.5 per cent sodium hydroxide. In order to obtain a sharp separation of the neutral compounds it was necessary to extract the combined alkaline solutions twice with 25-ml. portions of ether, which were then added to the original ether solution. The latter contained the nonvolatile ether-soluble neutral compounds (fraction 3).

The alkaline solution was neutralized to litmus with 10 per cent hydrochloric acid and evaporated to 5 to 8 ml. It was then filtered and made up to 20 ml., and the phenols were determined by the procedure used for fraction 1. The nonvolatile ether-soluble acidic compounds (fraction 2) were calculated as phenol from this result.

The ether extract containing fraction 3 was mixed with 5 ml. of water containing a drop of 10 per cent hydrochloric acid. The ether was then evaporated on a water bath kept below 80°. The residue was filtered into a 50-ml. cylinder and made up to 20 ml. In most cases the color developed was very weak and the final estimation was carried out by comparing this unknown with a series of standards containing 0.000, 0.003, 0.006, 0.009, 0.012, and 0.015 mg. of phenol made up to the same volume. The comparison was made in test tubes. The result indicated the quantity of the compounds in fraction 3 expressed in terms of phenol.

The aqueous solution containing fraction 4 (from the first extraction) was made just alkaline to litmus with 4 per cent sodium hydroxide and extracted 5 times with 25-ml. portions of ether. The combined ether solution was treated in the same manner as that which contained fraction 3 and the color developed was determined in the same way. The total ether-soluble basic compounds were calculated as phenol from this result.

With careful work the results were reproducible. It is essential that sharp separations be obtained in the extraction steps, that the water used be free from phenols, and that the colorimetric readings be taken promptly 3 minutes after the addition of the alkali.

Results

Table I gives the results obtained when phenol was added to normal tissues and recovered by steam distillation as described.

Table II gives the results when the tissues of four normal rabbits were used to determine the normal tissue content of substances which react as phenol.

The substances which may theoretically be present in normal tissue extracts are given in Table III, classified according to the fraction in which they should occur.

TABLE III. CLASSIFICATION OF COMPOUNDS WHICH MAY BE PRESENT IN EXTRACTS OF NORMAL TISSUE

(Figures show approximate molar concentrations which give a color equivalent to 0.00001 molar phenol solution when Moir's reagent is used.)

Fraction 1 ^a	Fraction 3
Phenol	Lecithin
<i>p</i> -Cresol (0.00257)	β -Nicotinamide
Pyruvic acid (0.0005)	Indican
Formic acid (no color)	Urea (0.22)
Butyric acid (no color)	
Higher fatty acids	Fraction 4
	Choline (0.13)
Fraction 2	Taurine
β -Hydroxybutyric acid	Indole (0.027)
Acetoacetic acid	Histamine
Homogenistic acid	Aliphatic amines of low molecular weight
β -Nicotinic acid	
Hydroquinone (0.00005)	
Catechol (0.000025)	
Hippuric acid (0.04)	
Ethyl mercaptan (no color)	

^a The alkaline evaporation of the distillate removes acetone (0.07), ethyl alcohol (0.09), acetaldehyde (0.00028), and methyl glyoxal.

Summary

A method is reported for the separation and determination of volatile phenols, free and conjugated, in tissues. The non-volatile ether-soluble substances present have been separated into three fractions—acidic, neutral, and basic—and the extent to which they react as phenol has been determined.

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Apparatus for Determining Moisture by the Distillation Method

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THE continued interest in the distillation method for the determination of moisture (1, 2, 3) in materials containing no low-boiling liquids appreciably miscible with water lies in the fact that it measures only the actual water which is given off at the boiling temperature of the liquid used, whereas by the oven methods the total loss in weight is obtained. Total loss includes, besides the true moisture content, the weight of other volatile constituents of the material under examination, plus the weight of any water that may be formed from the oxidation of the nonvolatile constituents, minus any gain in weight due to the formation of nonvolatile oxidation products.

In the usual Bidwell-Sterling apparatus, as well as in any modification of which the authors are aware, it is necessary to bring the moisture clinging to the walls of the condenser into the measuring tube either by the use of a buret brush or by the introduction of some substance (1, 2, 3) to reduce its tendency to adhere to the glass. Using the apparatus described in this paper, it is unnecessary to resort to such practices. The entire determination may be completed in less than 2 hours.

The general procedure, which can readily be gathered from

the diagram, is as follows: The water and toluene, which are distilled from a flask immersed in an oil bath, pass through a slanted tube and down through a condenser whose outlet is beneath the toluene in the measuring vessel.

The advantages of locating the condenser on the downcoming tube are not immediately apparent but become so when compared with the operation of the condenser in other locations. In the Bidwell-Sterling apparatus the vapors of toluene and water travel up into the reflux condenser, condense, and flow back by gravity. Most of the water condenses above the toluene, and the droplets which cling to the glass can be dislodged only by additional manipulation.

In the early forms of the apparatus described in this paper and in an apparatus recently reported by Avellar de Loureiro (1) the condenser was placed around the receiver. Under these conditions the distillate tended to form a milky suspension of water in toluene from which the droplets of water were deposited on the cooled walls of the receiver to probably the same degree as with the original Bidwell-Sterling apparatus. It was not possible for the condensed toluene to flow over these droplets, and some method of bringing the droplets into the measuring tube was necessary. On the other

hand, with the condenser on the downcoming tube, all the droplets of water deposited on the cold walls of the condenser are washed by the condensing toluene or are dislodged by the surging toluene mentioned below in connection with the bumping. The milky suspension, which practically always forms except with samples having a very low moisture content, is not circulated past cold walls.

Strangely enough, no considerable amount of milky suspension or toluene distillate ever accumulates in the upper part of the receiver. This results from the automatic sucking-back caused by the building up of the column of distilled toluene in the cooled tube leading down from the flask, along with the vigorous surging caused by the bumping in the distillation flask. When the column of toluene builds up to a sufficient height, the surging causes some of the cooled condensate to drop into the distilling flask; and the resultant cooling effect causes the entire liquid, down to the outlet of the condenser, to be sucked back into the distillation flask. The frequency of this operation depends on the rate of distillation; usually it occurs about once every 10 minutes.

The bumping is, of course, an almost invariable accompaniment to the determination of moisture in solid foodstuffs by the distillation method. Its violence may be reduced by immersing the distilling flask in a bath to bring about more uniform heating. However, when bumping was entirely eliminated—for example, by placing the sample in a cloth bag and suspending it in the toluene—neither the surging nor the automatic suck-back took place. When distilled water was added to the toluene in order to determine the extent of its recovery, the surging and suck-back were likewise not observed. On adding a small quantity of dry sand to the toluene-water mixture the bumping once more occurred, and the distillation proceeded entirely unaided.

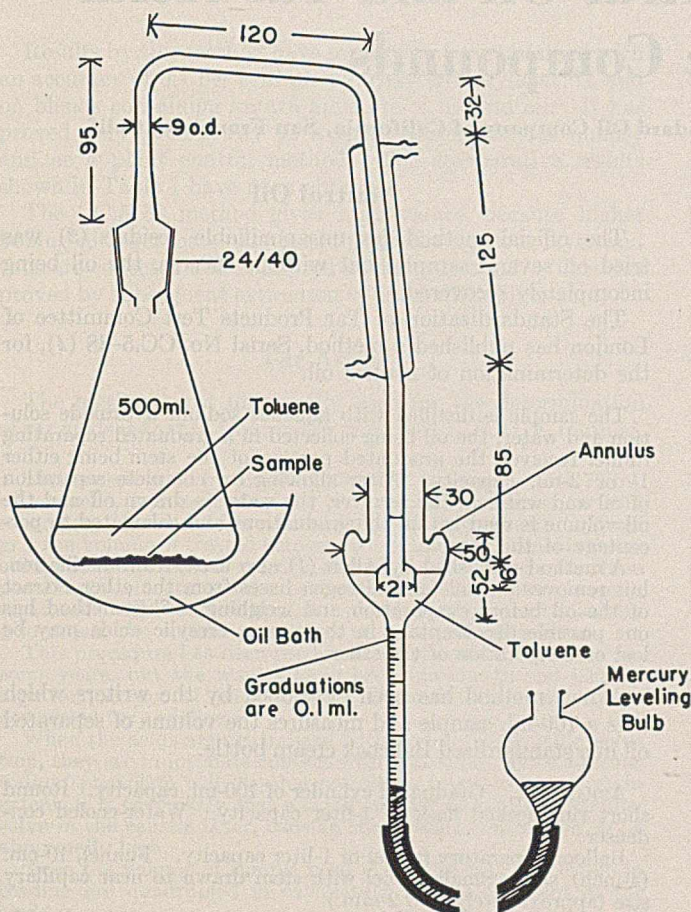


DIAGRAM OF APPARATUS
Dimensions in millimeters

The repeated automatic suck-back is important to the determination of the moisture by this method. Careful observation of the progress of the distillation of the water shows that the first portions which come over condense in large clear drops and quickly sink into the measuring vessel; later, the condensed droplets become very small and the milky suspension results. As a consequence of the repeated suck-back, the fine droplets are repeatedly distilled, and each time this occurs a considerable number of clear droplets sink into the measuring tube, with the final result that the determination is completed with no supernatant suspension. This condition is frequently reached in 1 hour, although in some cases it may require 2 hours or more.

Since it is impossible to control the bumping accurately, two other points should be emphasized—namely, the use of an enlarged or bell-shaped end on the condenser tube and an annular ring on the receiver. The function of the enlarged end is to reduce the violence with which the liquid is driven into the receiver. However, in spite of this provision an especially violent bump will occasionally drive the toluene up the sides of the receiving vessel with sufficient velocity to cause a drop or two of liquid to splash out. The insertion of the annular ring eliminated this loss by causing the liquid to be thrown back into the center of the receiver.

The mercury leveling bulb connected to the bottom of the graduated receiver proved advantageous at times in collecting droplets clinging to the sides of the measuring tube and in

leveling the top meniscus of the water layer in order to facilitate reading.

A series of moisture determinations was made on ground soybeans with the following results: 6.73, 6.64, 6.71, 6.59, 6.73, and 6.80 per cent. The maximum difference in this series is 0.21 per cent, whereas the maximum difference due to the error in reading the graduated measuring tube, assuming it can be read to ± 0.01 cc. would be 0.134 per cent, since the total volume of water obtained is about 1.00 cc. The samples used weighed 15 grams to the nearest milligram. The temperature of the oil bath surrounding the distillation flask varied from 110° to 155° C.

Summary

An apparatus for the determination of moisture has been devised and has been found to be superior to those of the Bidwell-Sterling type, because the removal of droplets of water forming on the walls of the condenser is accomplished automatically and the milky suspension forming in the receiver is eliminated by automatic redistillation.

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Determination of Neutral Oil and Tar Acids in Phenolic Compounds

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Improved methods of testing for neutral oil and tar acids in phenolic compounds have been worked out in the authors' laboratories on the basis of known blends and pure compounds. The adoption of these improved methods will result in more accurate analysis, the sum of the percentages of neutral oil, tar acids, and water not exceeding 100, as is frequently the case with existing methods. Specifications formulated on the basis of these analytical procedures will represent quality which is at once rigid and dependable.

PHENOLIC compounds or cresylic acids obtained from such sources as petroleum, coal tar, and low- and high-temperature carbonization processes are known to contain varying amounts of neutral oil and tar acids. The neutral oil has been found to be a hydrocarbon mixture of boiling range similar to the acids from which they were extracted, while the acids consist exclusively of phenol, cresols, xylenols, and higher phenolic homologs. Since the amount of neutral oil and tar acids present is a prime consideration in specifications for phenols covering a wide field of industrial usefulness, it is important to determine these constituents with a high degree of accuracy and reproducibility.

Neutral Oil

The official method for unsaponifiable residue (2) was tried on several samples but without success, the oil being incompletely recovered.

The Standardization of Tar Products Test Committee of London has published a method, Serial No. CC.5-38 (4), for the determination of neutral oil.

The sample is distilled with aqueous sodium hydroxide solution and water, the oil being collected in a graduated separating funnel receiver, the graduated portion of the stem being either 1- or 3-ml. capacity. After allowing for complete separation of oil and water in the receiver, the water is drawn off and the oil volume is read within the graduations and calculated to percentage of the sample.

A method published by Allen (1) also uses steam-distillation, but removes phenols and nitrogen bases from the ether extract of the oil before evaporation and weighing. This method has one possible disadvantage in that some cresylic acids may be lost on evaporation of the ether.

A new method has been developed by the writers which uses a 100-ml. sample and measures the volume of separated oil in a standardized Babcock cream bottle.

APPARATUS. Graduated cylinder of 100-ml. capacity. Round short ring-necked flask of 1-liter capacity. Water-cooled condenser.

Balloon separatory funnel of 1-liter capacity. Funnel, 10-cm. (4-inch) size. Small funnel with stem drawn to near capillary size (approximately 1 to 2 mm.).

Babcock bottle, 9-inch, 9-gram, 50 per cent $\times 1/2$. Beaker of 600-ml. capacity. Burner and shield. Boiling beads and Alundum chips.

REAGENT. Sodium hydroxide, 9 to 10 grams per 100 ml.

PROCEDURE. One hundred milliliters of sample and 400 ml. of sodium hydroxide are carefully transferred into a 1-liter round short ring-necked flask containing glass beads and Alundum chips. The flask is then fitted to the condenser and the contents are boiled under reflux for 15 minutes, with appropriate flame adjustment to prevent bumping; the flame is then removed and the cresylate solution quickly and cautiously transferred into a 1-liter balloon separatory funnel with the aid of the 10-cm. (4-inch) funnel. That portion of the insoluble material remaining in the flask is rinsed into the separatory funnel with several small portions of the cresylate solution, as drawn from the lower layer in the separatory funnel. (A convenient means of handling the refluxing flask in pouring the cresylate solution is to attach a buret clamp firmly to its neck.)

The solution is then allowed to settle for 30 minutes, permitting the insoluble material to rise to the top. The major portion of the caustic layer is drawn off into a 600-ml. beaker with the exception of a few milliliters, which, together with the insoluble material, are transferred into a 9-inch, 9-gram Babcock bottle. This transfer is made with the aid of a short-stemmed funnel drawn to capillary size for insertion in the neck. The material adhering to the inside walls of the separatory funnel, as well as in the transfer funnel, is washed into the Babcock bottle, using some of the cresylate solution contained in the beaker. The Babcock bottle is then filled, raising the insoluble material within the graduations on the neck.

The sample is then centrifuged at a speed of 1400 r. p. m. for 15 minutes, after which the per cent of insoluble material (neutral oil) is read and reported to the nearest 0.1 per cent.

TABLE I. DETERMINATION OF NEUTRAL OIL

	Method CC.5-38	New Method
	%	%
Sample 1	2.20	1.0, 1.0
Sample 2	3.04	1.1, 1.1
Sample 3	3.36	1.5, 1.4
Sample 4	0.09	0.1, 0.2
Blend containing 0.5 per cent of oil	..	0.5, 0.5
Blend containing 1.0 per cent of oil	..	0.9, 0.9

Results by this method have repeatedly been obtained with an accuracy of 0.1 per cent on a variety of cresylic acids, and on blends containing known amounts of neutral oil. It has proved very satisfactory as a specification test for quality and as a plant control method. The comparative results shown in Table I have been obtained.

The CC.5-38 method gives high values, because higher boiling nitrogen bases are insoluble in the aqueous layer and thus are collected and measured in the neutral oil. This was proved by subsequent extraction of bases with dilute acid.

Tar Acids

The method most universally used for the determination of tar acids is that of Chapin (3), called the U. S. D. A. method.

This is performed by distilling 25 ml. of the sample with 75 ml. of kerosene, and collecting the condensate in a Weiss tar-acid separatory funnel. After a treatment with sulfuric acid (1.50 sp. gr.) the volume of treated kerosene solution in the funnel is measured, the cresylic acids are neutralized and extracted with three portions of aqueous sodium hydroxide, and the volume is again measured. The contraction in volume is then multiplied by 4 to obtain the volume percentage of total phenols present.

This procedure has been used in the authors' laboratories for some years, but the results have been inaccurate and usually high for the type of acids tested. These inaccuracies may be accounted for as follows:

When the acids are neutralized with sodium hydroxide solution, they are in intimate contact with kerosene. Since aqueous sodium phenolate will dissolve petroleum fractions to a certain extent, it is very likely that a small amount of kerosene will dissolve in the caustic layer, causing the volume contraction to be abnormally high.

Since the volume of sample used is only 25 ml., any errors in reading are quadrupled in calculating volume per cent of tar acids.

There is a certain amount of mechanical entrainment of kerosene in the caustic solution, and liquid droplets adhere to the

sides of the Weiss funnel after the several extractions have been made, causing certain inaccuracies.

In an effort to remove these difficulties, the authors have worked out a liberation method which yields accurate results on pure acids and commercial phenolic products.

Liberation Method for Tar Acids

REAGENTS. Sodium hydroxide substantially free of carbonate, 200 grams per liter. Sulfuric acid, 25 ± 1 per cent by weight. Sulfuric acid, specific gravity at 25° C., 1.50 to 1.51. Petroleum ether.

APPARATUS. Pipet, 100-ml., standardized to deliver 100.0 ml. at 25° C. with full drainage; 100-ml. and 250-ml. graduated cylinders; one 500-ml. and two 1-liter pear-shaped separatory funnels. Weiss tar-acid separatory funnel, type 2; 150-ml. and 800-ml. beakers. Small funnel with stem drawn to near capillary size (approximately 1 to 2 mm.).

PROCEDURE. Into a 1-liter separatory funnel containing 215 ml. of sodium hydroxide reagent 100 ml. of cresylic acid at 25° C. are pipetted and 100 ml. of petroleum ether are added. (The 100-ml. sample at 25° C. must be transferred quantitatively. A convenient method is to use a portion of the first petroleum ether wash to rinse the pipet with the aid of a small funnel inserted in the pipet.) The funnel is shaken carefully for several minutes, releasing the pressure occasionally. (During the manipulations involved in this determination, care must be taken to make all transfers and extractions quantitatively, rinsing the separatory funnels wherever possible with the solution being used as the wash.) After separation, the cresylate solution is transferred to a second 1-liter separatory funnel and extracted with 50 ml. of petroleum ether. It is shaken for several minutes, separated, and the aqueous layer drained into an 800-ml. beaker.

The petroleum ether extracts are combined and washed twice, first with a 25-ml. portion of sodium hydroxide reagent and then with 25 ml. of water, adding the caustic and water washes to the cresylate solution contained in the beaker.

The beaker and contents are placed on a steam bath under a jet of air for 30 minutes, then placed in a shallow ice bath. After the solution has cooled, it is acidified with constant stirring, using 25 per cent sulfuric acid until a cloud just persists (approximately 125 to 135 ml. should be added). During acidification, the temperature must be kept below 37.78° C. (100° F.).

The cresylate solution is transferred to a 1-liter separatory funnel, using water to rinse the beaker, and 40 ml. of 25 per cent sulfuric acid are added. It is shaken and separation of the liberated tar acids allowed. Then the aqueous layer is drained into another 1-liter separatory funnel and 50 ml. of 25 per cent sulfuric acid are added. The solution is shaken and at least 30 minutes are allowed for the second separation of tar acids.

The tar acids in the first separatory funnel are transferred into a Weiss tar-acid funnel, the aqueous layer is drained back into the first separatory funnel, and the remaining tar acids are extracted with two 50-ml. portions of petroleum ether. In the meantime the tar acids liberated in the second separatory funnel are added to those contained in the Weiss funnel.

The liberated tar acids in the Weiss funnel are now treated with 55 ml. of sulfuric acid (sp. gr. 1.50 to 1.51). In treating the liberated tar acids with sulfuric acid, it is suggested that mixing be secured by inverting the Weiss funnel twelve times. Care must be taken to avoid any loss of tar acids when removing the stoppers from the Weiss funnel.

This first treat is allowed to stand 2 hours, sulfuric acid being drained off at the end of this period. While the first treat is standing, the remaining tar acids extracted by petroleum ether (as outlined in the previous paragraph) are separated from the petroleum ether by 10 ml. of sodium hydroxide reagent, followed by a 10-ml. portion of water. These extracts are combined in a 150-ml. beaker, which is placed upon a steam bath under a jet of air for 30 minutes to remove petroleum ether. The cresylate solution is then cooled in an ice bath and the solution cautiously neutralized with a 50-ml. portion of sulfuric acid (sp. gr. 1.50 to 1.51), using the remainder to wash the liberated tar acids into the Weiss funnel. The tar acids and sulfuric acid now contained in the Weiss funnel are shaken, and allowed to stand 1 hour, the sulfuric acid being drained off at the end of this period.

Another treatment with 25 ml. of sulfuric acid (sp. gr. 1.50 to 1.51) is then given the tar acids, allowing them to stand 30 minutes. During this period the bath is adjusted to a temperature of 25° C. At the end of the settling period the sulfuric acid is drained off and another half hour is allowed for the last traces of sulfuric acid to settle out of the tar acids, after which the per cent of tar acids by volume is finally read at 25° C. and recorded.

Comparative results by the U. S. D. A. and liberation methods on four samples are given in Table II.

TABLE II. DETERMINATION OF TAR ACIDS

Sample	U. S. D. A. Method	Liberation Method
	%	%
1	100.0	97.5, 97.4
2	101.2	98.3, 98.4
3	100.4	96.8, 96.8
4	99.6	97.7, 97.5

An accuracy of 0.2 per cent is obtainable by the liberation method, as is demonstrated by the foregoing results. As each sample contains both water and neutral oil, the U. S. D. A. values are obviously high, since tar acids alone show 100.0 per cent or more. When per cent of water and neutral oil is added to the liberation method values, the totals are well within 99.5 and 100.0 per cent. The liberation method was

checked using U. S. P. cresol containing 0.2 per cent of water and no neutral oil, the tar acids obtained being 99.8 and 99.9 per cent.

It is firmly believed that the adoption of these improved methods of testing will result in a greater degree of accuracy, and more closely define quality in terms of specification requirements.

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Determining Organic Matter in Paddy Soils Reliability of Rapid Titration Methods

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THE volumetric determination of the soil organic matter by measuring the reducing power of the carbonaceous substance with a certain oxidizing solution is generally recognized as being much less laborious than gravimetric methods. In the former case, soils subjected to analysis are digested in a strongly acid solution with a standard solution of either potassium permanganate (2) or chromic acid (4), and the excess of oxidizing agent is then titrated with a reducing solution, frequently oxalic acid or ammonium ferrous sulfate. Previous investigation (1) has shown that results obtained by such methods agree fairly well with gravimetric ones. Owing to their simple and rapid operation, these methods are often employed when a large number of samples is at hand and high accuracy is not desired.

Rapid titration methods, such as those mentioned above, are not at all adaptable for water-logged soils, where high reduction potential usually reduces a part of the oxidizing solution. The presence in these soils of ferrous iron, which is frequently liberated in the boiling solution of strong sulfuric acid, also introduces a serious error into the resulting data.

As the total content of ferrous iron is still not measurable quantitatively, it is rather difficult to distinguish among the portions of the total oxidizing solution consumed by organic matter, ferrous salts, or other reducing substances.

A number of paddy soils have been used as testing samples, and results are given in Table I. The approximate content of ferrous salts in the soils is estimated according to Morgan's method (3).

From the data, it is obvious that erratic results have been yielded most frequently in paddy soils with gleied sub-horizons, which are usually characterized by low organic matter content and relatively high ferrous salt content. These methods are limited in value for such soils.

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TABLE I. ORGANIC MATTER CONTENT OF PADDY SOILS

(Determined by dry combustion and rapid titration methods)

Samples	Carbon by Dry Combustion Method %	KMnO ₄ Method			Chromic Acid Method			Ferrous Salts
		Sample used Gram	Carbon calcd. from result of dry combustion method Mg.	Carbon obtained by KMnO ₄ method Mg.	Sample used Gram	Carbon calcd. from result of dry combustion method Mg.	Carbon obtained by CrO ₃ method Mg.	
5-8-87 0 to 18 cm.	2.60	0.1546	4.02	4.20	0.1490	3.88	3.98	High
		0.1501	3.91	4.25	0.1487	3.88	3.94	
18 to 50 cm.	0.55	0.2508	1.38	1.44	0.2513	1.38	1.58	Very high
		0.2611	1.43	1.60	0.2544	1.40	1.50	
90 to 110 cm.	0.06	0.5043	0.30	1.01	0.4991	0.30	1.20	Very high
		0.5082	0.31	0.84	0.5024	0.30	1.01	
5-8-80 0 to 20 cm.	0.75	0.1508	1.13	1.25	0.1513	1.13	1.12	High
		0.1611	1.21	1.39	0.1537	1.15	1.28	
45 to 60 cm.	0.11	0.4981	0.55	1.58	0.5108	0.56	1.72	Very high
		0.5084	0.56	1.81	0.4931	0.54	1.63	
7-7-6 0 to 20 cm.	0.65	0.2004	1.30	1.61	0.1945	1.29	1.44	Very high
		0.2087	1.35	1.52	0.1976	1.30	1.60	
20 to 45 cm.	0.09	0.5044	0.45	1.31	0.5132	0.46	1.40	Very high
		0.5078	0.46	1.18	0.4958	0.45	1.31	

Colorimetric Evaluation of Derris and Cube Roots

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NUMEROUS qualitative color tests have been proposed for rotenone and other constituents of derris and cube roots, and several quantitative color reactions have been developed for the evaluation of these materials. The purpose of the present study is to review these tests and compare the results obtained by some of these colorimetric methods with each other and with some of the gravimetric methods.

Review of Color Reactions

Geoffroy (8) was the first to study the color reactions of rotenone with several reagents. The most characteristic of these involved treatment with bromine, followed by application of concentrated sulfuric acid to the residue. A violet color is produced.

One widely used color test is based on the reaction discovered by Durham (9) in which treatment of rotenone with nitric acid followed by ammonia produces an evanescent blue-green color. Ishikawa (14) independently discovered this reaction, using sodium hydroxide as the base. Jones and Smith (17) modified the Durham reaction, using acetone solutions of the unknown and more dilute nitric acid. In this form roughly quantitative estimates can be made. The reaction is also given by deguelin and, with a difference in hue, by toxicarol. Various alkalies may be used to develop the final blue color, and Pozzi-Escot (21) has recently found that even organic bases may be used.

Dennis (6), in a patent on cube, describes a color reaction for testing this material, using sulfuric and nitric acids followed by potassium hydroxide. The directions are not clearly stated, but tests made following the method as closely as possible showed identical color reactions to be given by roots of derris, cube, and *Tephrosia virginiana*.

A useful quantitative color procedure is that devised by Gross and Smith (12) involving treatment of an acetone extract of the sample with alcoholic potassium hydroxide, followed by nitric acid containing sodium nitrite. A fairly permanent red color is given by both deguelin and rotenone. Ambrose and Haag (1) have shortened this test using only the alkali, but in this form the test is not sufficiently specific or delicate. A more serviceable modification is that developed by Goodhue (10), in which the

nitrite is added with the alkali and sulfuric acid is used instead of nitric. This has increased the sensitivity of the original test and the stability of the color.

In 1899 van Sillevoldt (24) found that his "derrid," which undoubtedly contained a high percentage of rotenone, gave a brown-violet color with concentrated sulfuric acid. Danckwortt, Budde, and Baumgarten (5) found that sulfuric acid containing a very small amount of nitrite gives a violet color with rotenone. This suggests that van Sillevoldt's acid contained a trace of nitrite, and Goudswaard and Timmers (11) have recently stated that rotenone may be used as a very sensitive reagent for detecting nitrates and nitrites in sulfuric acid. The sulfuric acid-nitrite reaction was developed into a quantitative test for rotenone by Fischer and Nitsche (7). It has been further modified by Meyer (19), and in this form an aqueous suspension of the material to be tested is treated with the concentrated acid containing the nitrite. The reaction is given by constituents of derris and cube other than rotenone.

Rogers and Calamari (22) have discovered a reaction of rotenone in which the material, when treated with phenol, concentrated hydrochloric acid, and an oxidizing agent, gives a blue to violet color depending on the solvent. They have developed the reaction into a quantitative method using a chloroform or acetone solution of the unknown and thymol and hydrogen peroxide as the oxidizing agent. Light is used to develop the color in the chloroform solution, but in the acetone solution the color develops more rapidly and without the aid of light.

A test for rotenone developed by Pozzi-Escot (20) consists in adding Denigès reagent to a solution of rotenone in concentrated sulfuric acid, obtaining a series of reactions.

Recently Cahn, Phipers, and Boam (4) have suggested a quantitative test for toxicarol involving development of the characteristic phenol color with ferric chloride.

Comparison of Quantitative Methods

To compare results by some of the quantitative tests, four samples of derris root, three of cube and timbo, and one of *Tephrosia virginiana* were analyzed. (Solomon Love, formerly of this bureau, made some of these analyses.) The results are

TABLE I. COLORIMETRIC AND GRAVIMETRIC ANALYSIS OF DERRIS, CUBE, TIMBO, AND *Tephrosia*

Method of Analysis	Derris								Cube				Timbo		<i>Tephrosia</i>	
	No. 3002		No. 3006		No. 3007		No. 3126		No. 3004		No. 3005		No. 3230		No. 3107	
	Root ^a	Extract ^b	Root	Extract	Root	Extract	Root	Extract	Root	Extract	Root	Extract	Root	Extract	Root	Extract
	%	%	%	%	%	%	%	%	%	%	%	%	%	%	%	%
A. Total chloroform extractives	12.6	...	16.5	...	13.6	...	16.7	...	16.4	...	18.4	...	19.2	...	7.8	...
B. Rotenone (by crystallization)	2.0	16	3.6	21	0.6	4	5.8	35	2.9	18	5.6	30	3.9	20	1.4	18
C. Goodhue modification of Gross and Smith test (direct color value)	5.4	43	8.4	51	2.2	16	10.0	60	5.3	32	10.2	55	7.2	38	3.4	44
D. "Deguelin" from color test [(C - B) × 1.25]	4.2	33	6.0	36	2.0	15	5.2	31	3.0	18	5.8	32	4.1	21	2.5	32
E. Dehydro compounds, gravimetric (direct value)	5.1	40	7.8	47	1.3	10	9.1	54	6.0	37	10.7	58	7.3	38	2.0	26
F. "Deguelin" from dehydro compounds (E - B)	3.1	25	4.2	25	0.7	5	3.3	20	3.1	19	5.1	28	3.4	18	0.6	8
G. Meyer (sulfuric acid-nitrite) color test	11.4	90	14.8	90	13.3	98	13.8	83	11.7	71	15.8	86	13.4	70	6.4	82
H. Rogers and Calamari color test ^c	12.5	100	17.5	105	9	65	20	120	23.5	145	26	140	30.5	160	8	100
I. Cahn, Phipers, and Boam (ferric chloride) color test	3.2	25	3.3	20	9.2	68	0.9	5	2.8	17	1.5	8	2.5	13	1.3	17
J. Alkali-soluble material (gravimetric)	3.2	25	3.4	21	9.2	68	1.7	10	4.2	26	2.8	15	5.0	26	1.4	18

^a Percentages based on root.

^b Percentages based on extract.

^c This method appears less precise than the others, and results are not quoted to so many significant figures.

shown in Table I. All extractions were made by the chloroform-room temperature-aliquot method (16), and suitable aliquots were taken. Where necessary the aliquot was evaporated and taken up in other solvents.

Rotenone was determined gravimetrically (B) by the method of Jones and Graham (16), and total extractives (A) by evaporation of an aliquot of the chloroform extract (18).

Colors obtained by the Goodhue modification (10) of the Gross and Smith method (12) were compared in a neutral wedge photometer using a filter with its optical center at 0.56 micron (C). In general, this test is thought to be given principally by rotenone and deguelin in derris and cube. Cahn, Phipers, and Boam (4) state that pure inactive deguelin gives a color value about 80 per cent of that given by rotenone. Therefore, by subtracting from the color value for the samples under study (C) the value for rotenone (B) and multiplying this difference by 1.25, one arrives at an estimate of the deguelin content (D). According to Cahn, Phipers, and Boam (4), this value for ordinary derris roots (such as Nos. 3002, 3006, and 3126) is 27 ± 4 per cent of the extract, and for Sumatra-type roots (such as No. 3007) 9 to 15 per cent. The values obtained in this study are roughly in agreement with this, when one considers that Cahn and his co-workers calculated rotenone from the crude solvate, whereas in this work the slightly lower values for pure rotenone are used, thus making the differences greater in the present work.

The samples were also analyzed by the gravimetric method for rotenone and deguelin originated by Takei, Miyajima, and Ono (25), in which these materials are oxidized to their dehydro derivatives and separated as such, as modified by Tattersfield and Martin (26). To avoid interference from toxicarol, the alkali-soluble material was removed prior to the oxidation. No attempt was made to separate the dehydrorotenone and the dehydrodeguelin as outlined in the original method. The values obtained (E) and the differences between these and the rotenone content (B), which should represent the deguelin content, are shown in (F). The gravimetric values for the derris roots are on the average lower than those by the color method, while for the cube and timbo roots the two methods are in general agreement. The dehydrogenation in the gravimetric procedure may not be entirely quantitative, and the crystallization probably involves a slight loss. This may account for a small part of the difference between the two methods. However, the comparatively large differences for some of the derris roots suggest the possible presence in these samples of a small amount of material giving the red color test but not forming a dehydro compound.

It has not yet been definitely shown that rotenone and deguelin are the only materials in these extracts which give the red color test, or form dehydro compounds in the Takei method. Thus, Buckley (2) and, more recently, Harper (13) have isolated a new compound from derris root which forms a dehydro derivative and, since it gives the Durham test, would be expected to give the red color test, as the two tests are generally given by the same compounds. The values for deguelin by either the colorimetric or the gravimetric method may thus be in error for this reason.

It was shown several years ago (15) that the values by the Gross and Smith color test give a better indication of toxicity of derris and cube samples to insects (houseflies) than does either the rotenone or the total extractives content. Similarly Tattersfield and Martin (26) have found the value for dehydro compounds a good measure of the insecticidal value (to aphids) of derris samples. Thus, whether or not these two methods determine only rotenone and deguelin, they at least are of definite value in giving an approximate indication of toxicity. The color method is simpler and in the Goodhue modification is far more sensitive than the gravimetric pro-

cedure. It is to be hoped that some such method as these, which give a closer approach to insecticidal efficacy than do rotenone or total extractive determinations, will eventually be adopted in the commercial handling of derris and cube roots.

The sulfuric acid-nitrite test (G) was made as described by Meyer (19), and comparisons were made with a rotenone standard in a Duboseq type of colorimeter without a filter. Cahn, Phipers, and Boam (4) state that the test is given with equal intensity by rotenone, deguelin, toxicarol, and sumatrol, and by derivatives of these, and that the value for derris extracts is about 90 per cent by this method. It has been learned in a private communication from Dr. Cahn that he used a modification of the Meyer test. For the derris samples in the present work the values averaged about 90 per cent of the extract, but the cube roots gave somewhat lower values.

The Rogers and Calamari test (22) was slightly modified in these analyses. The color in acetone solution was not proportional to the rotenone present, and after a short time solutions of different rotenone concentration developed to about the same color. In chloroform solution the proportionality between color and concentration seemed to hold. Heat as well as light accelerated the color formation, but the latter was adopted. The solutions were exposed in glass cylinders to daylight at the laboratory window (never to direct sunlight) for 24 hours. Perchloric acid was found to effect a more rapid development of the color than the hydrogen peroxide used by Rogers and Calamari. The hue and intensity of the color varied with the amount of perchloric acid used as was the case with other oxidizing agents. At a rotenone concentration of 0.12 mg. per cubic centimeter, 2 drops of 60 per cent perchloric acid gave a moderately intense, pure-blue color in 24 hours. Even in this form results obtained by the test were highly erratic, and duplicate standards (run at the same time) varied as much as 10 per cent. The reaction merits further study, however. Deguelin was found to give a color about 125 per cent of that given by rotenone, whereas toxicarol gave only about one half the color given by rotenone. Since the values obtained on the root samples (H), particularly those for the cube and timbo roots, are markedly higher than the total extract values, it is apparent that some constituent in the roots gives a much greater color value than does rotenone or deguelin.

The ferric chloride test for toxicarol and sumatrol (I) was made as described by Cahn, Phipers, and Boam (4), and comparisons were made in a Duboseq-type colorimeter. Solutions were compared in pairs, consisting of a standard and an unknown, each pair being prepared fresh. A sample of toxicarol from which as much as possible of the β -toxicarol had been removed, as described by Cahn, Phipers, and Boam (3), was used as a primary standard.

This sample contained 1.5 per cent of β -toxicarol as measured by the Goodhue modification of the Gross and Smith test, in which the color value for β -toxicarol found by Cahn and his co-workers was used. [In spite of this the sample had a melting point of 217°C . (cor.). Cahn and co-workers state that pure α -toxicarol (the ordinary form) melts at $232\text{--}3^\circ\text{C}$. and that material melting at 219° contains 4.5 per cent of the β -isomeride. This matter will be further investigated.] Calculations for the ferric chloride test were made on the assumption that the sample was all α -toxicarol. Beta-toxicarol has been found to give a color with ferric chloride, but there is some doubt as to the intensity of this color compared with that given by α -toxicarol. In any event the small amount of β -toxicarol present would not appreciably affect the values obtained on most of the samples. The toxicarol standard was compared with an extract of No. 3007 (a Sumatra-type root), and this in turn was compared with an extract of No. 3006. All other extracts were then compared with

No. 3006. Tests made on only the alkali-soluble portions of some of the extracts gave substantially the same results. In this case it was possible to compare No. 3006 directly with the toxicarol standard, the others again being compared with No. 3006. Some difficulty was encountered in matching the colors from the cube samples, and the use of the alkali-soluble fraction did not improve the color matching. The ferric chloride test indicates from 1.5 to 2.8 per cent of toxicarol and sumatrol in the cube samples, although recently Rowaan and Van Duuren (23) reported that they had been unable to find toxicarol in *Lonchocarpus* (cube) roots. The color may be due to other phenolic compounds.

For comparison the amount of alkali-soluble material was determined by a method previously used (15). This value (*J*) agrees with the results of the ferric chloride test more closely in the derris roots than in the cube and timbo roots, indicating that in the latter more of the alkali-soluble material is nonphenolic.

Conclusion

In evaluating derris and cube roots it is now possible—by making use of colorimetric procedures and a determination of rotenone by the usual method to obtain at least approximate values for deguelin and toxicarol—by the Goodhue modification of the Gross and Smith color test to arrive at an estimate of the insecticidal value (for houseflies), and by the Meyer color test to get a rough idea of the total materials of the rotenone type.

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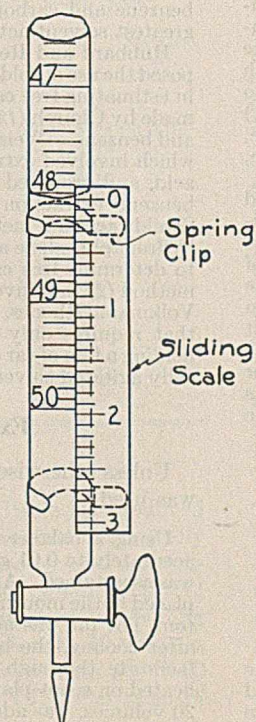
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MANY routine titrations, which require only a relatively small volume of standard solution, may be expedited by taking readings from an attached sliding scale rather than using graduations provided on the buret. Details of the auxiliary scale are shown in the figure.

The slide consists of a small brass strip to which are soldered two brass springs that clip over the buret. Division marks, similar to those on the buret, are made in ink on a piece of white paper glued to the brass strip.

In use the zero mark of the slide is set initially to coincide with the



An Auxiliary Sliding Scale for Burets

bottom of the meniscus and, after reaching the end point, the titer is read directly from the final reading on the auxiliary scale. By rotating the slide slightly toward the front, the left margin of the divisions will be aligned directly with the axis of the buret and permit better observation of the meniscus.

The use of this device for small titers obviates constant refilling to zero level of buret to eliminate subtractions. Only one numerical reading, the final, need be taken, since the first is always zero. Chance of error in subtractions is thereby avoided.

The device permits extension of usable length of buret beyond graduation limits provided by the manufacturer.

It allows direct conversion of titer into any system of expression without calculation, if the auxiliary slide is specially divided for the purpose. A buret dispensing a single standard solution may be equipped with a number of such sliding scales calibrated for each different application.

Solubility Characteristics of Tars and Pitches Produced by Coal Hydrogenation

Determination of Insoluble Matter

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IN THE continuous hydrogenation of coal, the determination of insoluble matter in the products resembling tars and pitches was desirable in calculating hydrogenation yields and as a control test. The necessity of making the determination in a few hours eliminated the Soxhlet extraction methods commonly used in examining coal tar. In the present work the centrifuge was studied as a tool (18, 21, 23) in the rapid determination of insoluble matter. The data obtained give considerable information on the solubility characteristics of heavy oils produced by coal hydrogenation and make possible comparison of coal-hydrogenation and coal-carbonization tars.

Previous Work

Although no study of the determination of insoluble matter in coal-hydrogenation products has been reported, many methods have been proposed for the estimation of "free carbon" (34, 39) in coal tar.

Kraemer (30) recommended extraction of the tar with forty times its volume of xylene. Köhler (29; 32, p. 240) heated 10 grams of tar with 25 grams of glacial acetic acid and 25 grams of toluene, poured the mixture on two filters of equal weight placed within each other, and washed with hot toluene until colorless. Kraemer and Spilker (31) mixed the tar with 20 parts of xylene, filtered off the insoluble material, washed with 5 parts of xylene, and dried the residue on the filter. The same authors gave another method which involves extracting 1 part of tar with 3 parts of aniline; it was claimed that this method gives 2 to 3 per cent lower results than the xylene method described above, owing to the greater solubility of the tar bitumens in aniline. Ceruti (11) heated 10 grams of tar with 150 cc. of castor oil, filtered, and washed the residue with carbon tetrachloride (41).

Hodurek (24, 25) distinguished between insoluble matter actually suspended in the tar, designated as C_1 , and bituminous material precipitated (C_2) by solvents such as benzene. The true "free carbon" (C_1) was determined by filtering the tar through fine-grained filter paper; C_2 was estimated by adding benzene to the filtrate. It was stated (24) that bituminous substances (C_2) are precipitated by alcohol, benzene, petroleum, toluene, xylene, ether, acetone, and acetic acid, but not by aniline, quinoline, phenol, cresol, nitrobenzene, naphthalene, and anthracene oils.

Hodurek's experiments (24, 25) were repeated and amplified by Berl and Schildwachter (9), who employed tetrahydronaphthalene as a solvent. These investigators recommended use of the latter solvent under pressure for direct determination of suspended insoluble matter, C_1 ; they also demonstrated the importance of the grain of the filtering medium employed in direct filtration of the tar. Adam and Sach (3) concluded that matter insoluble in pyridine (36) corresponds to Hodurek's C_1 and that in toluene or benzene to C_1 plus C_2 . A tar with 22 per cent of free carbon (insoluble in benzene) was found by Evans and Pickard (19) to contain only 14 per cent of pyridine-insoluble material (34).

Solvent	Insoluble, Per Cent		
	Tar	Pitch 1	Pitch 2
Light petroleum			42
Toluene	12.7	26.0	36
Benzene			22
Tetrahydronaphthalene	11.5	20.2	..
Cresylic acid	11.0	18.6	..
Aniline	11.7	18.3	..
Pyridine	10.7	16.8	10.5

Simek, Ludmila, and Helm (43) separated benzene-insoluble material (termed alpha-compounds) into fractions soluble and insoluble in anthracene oil (20). The data given above were

TABLE I. FILTRATION AND EXTRACTION OF HORIZONTAL-RETORT TARS

No.	Condition	Filtration Residue %	Insoluble, Per Cent by Weight				Petroleum ether
			Carbon bisulfide	Benzene	Acetone	Ethyl ether	
8-H	Unfiltered	23.9	5.37	7.92	11.62	18.5	64.5
	Filtered		6.52	9.62	14.12	22.5	78.4
9-H	Unfiltered	28.9	6.63	11.93	20.8	23.1	63.2
	Filtered		8.53	15.36	26.8	29.7	81.3

reported by Adam, Shannon, and Sach (4), who determined both the suspended material (C_1) and insoluble matter ($C_1 + C_2$) in several tars and pitches.

Marcusson (37) found that the benzene-insoluble components of vertical- and horizontal-retort tars, amounting to 7 and 24 per cent, respectively, consist of oxy-acids (8.6 and 0.5 per cent), pyridine-soluble resins (73 and 16.3 per cent), pyridine-insoluble resins (18.4 and 32 per cent), and partly coked material (0 and 51.2 per cent).

Volkman, Rhodes, and Work (45) determined the suspended matter in 9 tars by filtration and extracted both the filtered and unfiltered tars with carbon bisulfide, benzene, acetone, ethyl ether, and petroleum ether. About the same amounts of insoluble matter were found in both filtered and unfiltered tars; in some instances, the filtration residue exceeded the insoluble matter, as is shown in Table I. Their data, as well as those of other authors (3, 4, 19, 24, 43), show that the amount of insoluble matter found depends largely upon the nature of the solvent.

Mallison (35) and Volkman, Rhodes, and Work (45) state that the yield of "free carbon" depends upon the surface tension of the solvent. Simek, Zamrzla, and Ludmila (44) found that anthracene oil (20) was the best of a number of solvents for alpha-compounds (benzene-insoluble material). It is claimed that, although aniline or pyridine are more effective solvents than benzene and carbon bisulfide, selenium oxychloride (2) has the greatest solvent action.

Hubbard and Reeve (26) compared several methods and proposed the use of cold carbon bisulfide (28; 32, p. 321) as the solvent in estimating free carbon. Objections to this method have been made by Church (12, 13, 14), who prefers extraction with toluene and benzene. Weiss (47, 48) criticized the method of Warnes (46), which involved extraction with 90 per cent benzene and cresylic acid, and proposed the use of the currently well-known toluene-benzene extraction method (6). Bierling (10) used Berl and Schildwachter's method (9) (extraction with 4 volumes of tetrahydronaphthalene at 240° to 250° C. for 2 hours in an autoclave) to determine free carbon. Selvey (42) developed a colorimetric method (2) that involved comparison of stains left on filter papers. Volkman, Rhodes, and Work (45) described an interesting method that requires only traces of tar; the extraction is effected by holding a film of tar on a wire screen in a large volume of mechanically agitated solvent for about 45 minutes.

Experimental Procedure

Unless otherwise indicated, the following general procedure was used.

Using a balance capable of weighing several hundred grams accurately to 0.01 gram, the weight of a 250-cc. centrifuge bottle was ascertained. After a roll or funnel of ordinary paper had been placed in the mouth of the bottle to direct the tar or oil to the bottom, hot tar was added. The paper funnel was discarded and, after cooling, the bottle and contents were weighed again. To facilitate thorough mixing, the bottle and contents were then heated on a hot plate and the desired amount of solvent, usually 20 volumes, was added slowly, with manual stirring.

After all the solvent had been added, the mixture was stirred mechanically for about 3 minutes. The bottles were then centrifuged at once for 1 hour at about 2400 revolutions per minute. When solvents boiling below 100° C. were used, the supernatant liquid was poured off and the bottle dried several hours at 110° and weighed. For high-boiling solvents, a second wash was made with about 80 volumes of benzene at room temperature; after centrifuging for 0.5 hour the supernatant liquid was removed, and the bottle was dried for several hours at 110° and weighed.

Commercial grades of benzene, tetrahydronaphthalene, and cresol were used. The commercial tetrahydronaphthalene and the 5 per cent cresol-tetrahydronaphthalene solution were analyzed by extraction with 10 per cent sodium hydroxide to determine phenols. Commercial tetrahydronaphthalene (sp. gr., 0.978 at 15.5° C.) contained 2.2 per cent of alkali-soluble material that was assumed to be cresol. The solution prepared by mixing 1 volume of cresol with 19 volumes of commercial tetrahydronaphthalene underwent a volume decrease of 7.3 per cent when extracted with aqueous sodium hydroxide. The tetrahydronaphthalene (sp. gr., 0.973 at 15.5° C.) used in several experiments (Table IX) was purified by extraction with aqueous sodium hydroxide and sulfuric acid, and distillation, the fraction boiling at 205–207° C. being collected.

An independent check of the accuracy of the experiments was obtained from the ash contents of the original heavy oil and of its insoluble matter by the following formula:

$$\text{Per cent insoluble matter} = \frac{\text{per cent ash in tar (100)}}{\text{per cent ash in insoluble matter}}$$

The "free-carbon" values calculated in this manner are given below with the determined values for comparison. The agreement is usually satisfactory.

The tars and heavy oils used in the present work are described in Table II. Sample 1, Table II, which was used in most of the experiments, was a viscous oil discharged from the bottom of the converter during the continuous hydrogenation (22) of coal. Although it had been centrifuged, it contained 3.76 per cent of ash. It is likely that only negligible amounts of the remaining insoluble matter settled out during the several months consumed in collecting data. The pastes described in Table II were prepared by mixing the heavy oils from previous hydrogenations (22) with a little less than an equal amount of pulverized (200-mesh) coal.

TABLE II. PROPERTIES OF TARS, HEAVY OILS, AND PASTES

Source	No.	H	C	N	O	S	Ash	Sp. Gr.
								at 15.6° C.
Per cent by weight								
Coal hydrogenation	1	6.62	86.16	1.25	1.79	0.42	3.76	1.173
	2	6.70	...
	3	7.00	...
	4	7.52	...
	5	6.61	...
Coal carbonization	6	5.63	91.09	1.02	1.44	0.76	0.06	1.165
	7	5.46	92.37	1.15	0.54	0.45	0.03	1.207
	8	5.8	90.9	1.1	1.6	0.6
	9	5.8	91.0	1.1	1.5	0.6
	10	5.4	91.2	1.1	1.8	0.5
	11	5.4	91.1	1.2	1.9	0.4
Coal-hydrogenation paste	12	5.10	...
	13	5.50	...
	14	4.55	...

Effect of Solvent

It was found that heavy oil (sample 1, Table II) produced by coal hydrogenation has solubility characteristics generally similar to those of tars and pitches produced by coal carbonization. Table III gives the data obtained when 1 part of heavy oil was washed once with 20 volumes of low-boiling solvent. The results obtained by one wash with 20 volumes of high-boiling solvent, followed by one wash with about 80 volumes of benzene, are given in Table IV. The ratio of

TABLE III. COMPARISON OF LOW-BOILING SOLVENTS

Solvent	Surface Tension at 20° C. ^a	Insoluble, Per Cent by Weight	
		Found	Calculated
Ethanol	22.27	69.09 ^b	...
Heptane	About 20	67.59 ^b	...
Ether	17.10	37.38	37.50
Acetone	23.7	32.10	32.20
Ethyl acetate	23.9	32.05	31.72
Benzene	28.28	28.24	27.90

^a (27). ^b Fused on drying at 110° C.

TABLE IV. COMPARISON OF HIGH-BOILING SOLVENTS

Solvent	Surface Tension at 20° C.	Insoluble, Per Cent by Weight	
		Found	Calculated
Decahydronaphthalene ^a	26.7 (15.5°)	28.24	28.42
Diphenyl ether ^a	34.3	22.20	21.89
Tetrahydronaphthalene ^a	34.3	20.03	20.03
	34.3	17.40	17.62
	34.3 ^b	17.45 ^b	17.37 ^b
Furfural ^a	43.5	12.90	13.32
Aniline ^b	42.58	10.77	11.17
Nitrobenzene ^b	43.38	8.93	9.82
Pyridine ^a	38.0	8.85	9.27
Cresol ^b	37	8.67	9.28
Quinoline ^b	45.0	7.41	9.46

^a Solvent at room temperature.

^b Solvent at about 90° C.

solvent to heavy oil was selected on the basis of Figure 1; it does not necessarily follow that 20 volumes is the optimum ratio for each of the solvents. Moreover, the results shown in Table IV probably do not represent the solvent powers of the high-boiling solvents exactly because of the second wash with benzene.

The results in Tables III and IV, which range from 8 to 69 per cent insoluble matter, agree generally with data previously reported on coal tars and show that polar solvents give lowest values for "free carbon." In agreement with previous statements (35, 45), there is a rough correlation between surface tension and solvent power. However, this generalization obviously cannot be extended to include solvents such as glycol, glycerol, and water, which, although having high surface tensions, are poor solvents for tars and pitches.

Effect of Ratio of Solvent to Sample

Although the effect of the ratio of solvent to the tar sample has not been investigated thoroughly, 3 to 100 volumes of solvent are usually recommended. An interesting study (45) was made recently of the effect of solvent ratio for very large amounts of solvent (200 to 7100 volumes). The results showed that the solvent ratio is important; as a result of this work, concentrations above 200 mg. of sample per 100 cc. of solvent (ratio of solvent to sample, less than 500) were recommended.

The ratio of solvent to sample was found to be important for heavy oil produced by coal hydrogenation (Tables V to VII). The effect of solvent ratio for three solvents (benzene, tetrahydronaphthalene, and cresol-tetrahydronaphthalene solution) was studied for ratios up to about 40, using the centrifuge-bottle method described above. The wire-screen method of Volkmann, Rhodes, and Work (45) was employed with benzene (Table V) to determine the effect of higher solvent ratios (430 to 2000 volumes).

With all three solvents, the amount extracted increased rapidly at first with increase in solvent ratio and then more slowly (Figures 1 and 2). The stage at which further increases in solvent ratio are relatively unimportant varied with the efficiency of the solvent. For benzene, tetrahydronaphthalene, and cresol-tetrahydronaphthalene solution, these approximate values are 20, 14, and 10 volumes of solvent,

TABLE V. EFFECT OF RATIO OF SOLVENT (BENZENE) TO HEAVY OIL

Ratio of Solvent to Heavy Oil	Insoluble, Per Cent by Weight	
	Found	Calculated
5	38.32	...
10	34.51	32.65
15	31.64	30.75
20	28.24	27.90
25	29.15	28.00
26	28.16	27.72
27	27.53	27.29
30	27.77	27.15
32	26.78	26.12
34	26.90	26.10
37	27.14	27.00
39	27.66	26.61
430 ^a	21.35	...
630 ^a	19.27	...
1155 ^a	19.27	...
1400 ^a	20.02	...
1600 ^a	20.84	...
2000 ^a	20.18	...

^a Determined by wire-screen method (45).

TABLE VI. EFFECT OF RATIO OF SOLVENT (TETRAHYDRO-NAPHTHALENE) TO HEAVY OIL

Ratio of Solvent to Heavy Oil	Insoluble, Per Cent by Weight	
	Found	Calculated
4	29.47	...
6	24.53	...
8	21.59	...
10.6	19.45	19.25
12	19.28	19.33
14	18.11	18.32
16	17.76	17.95
17.2	17.94	17.88
20	17.45	17.37
25	17.07	17.05
30	17.23	17.37
33	17.74	17.85

TABLE VII. EFFECT OF RATIO OF SOLVENT (CRESOL-TETRAHYDRO-NAPHTHALENE) TO HEAVY OIL

Ratio of Solvent ^a to Heavy Oil	Insoluble, Per Cent by Weight	
	Found	Calculated
4	19.15	16.98
6	16.79	16.65
10	14.73	15.09
16.1	14.65	14.78
18.7	14.75	14.95
20	14.32	14.77
21	14.42	15.15
25	14.19	14.67
30	13.89	14.37

^a Contained 7.3 per cent (volume) of cresol.

respectively. These facts are important in devising analytical methods, since it should be easier to get consistent results by using solvent ratios above the threshold values mentioned above. It is noteworthy that well-known methods (6, 7) of determining insoluble matter employ large amounts of solvent.

The data obtained with benzene by the centrifuge-bottle method (5 to 39 volumes of solvent) and by the wire-screen method (430 to 2000 volumes) are plotted together in Figure 2, although these two sets of data are not exactly comparable. The data on acetone reported by Volkman, Rhodes, and Work (45) give a similar curve when plotted in this fashion. Figure 2 shows that the amount extracted increases rapidly with solvent ratio to about 20, slowly from 20 to about 500, and little or none above 500 volumes of solvent.

The data obtained with low solvent ratios (4 to 18), which appear on decidedly curved lines in Figures 1 and 2, gave approximately straight lines when the concentration of tar in solvent, instead of solvent ratio, was plotted against insoluble matter (Figure 3). These straight lines, whose slopes decrease with increase in extraction efficiency of the solvent, might be useful for predicting solubility by interpolation or extra-

polation when low solvent ratios are used. Figures 1 and 2 should be more useful for predicting solubility in large amounts of solvent. The straight lines of Figure 3 cannot be extrapolated to zero concentration to find the solubility of tar in extremely large volumes of solvent because, as has been demonstrated with acetone (45) and benzene (Figure 2), solubility is not even approximately a straight-line function of the concentration for concentrations lower than about 0.2 gram per 100 cc. of solvent. However, the values obtained by extrapolation to zero concentration might be useful for comparative purposes.

Extraction with Mixtures of Polar and Nonpolar Solvents

It was observed that the amount extracted with a solution of polar and nonpolar liquids cannot be predicted by the mixture law—that is, the amount extracted is not a straight-line function of the composition of the solvent (Tables VIII and IX, and Figure 4). The components of the two solutions studied in this connection are (a) benzene and pyridine and (b) tetrahydronaphthalene and cresol, all characteristic of coal-tar distillates. The amount extracted increased rapidly at first, then slowly as the concentration of the polar solvent component increased (Figure 4). These data show that the solvent power of coal-tar distillates is enhanced far more by tar acids and bases than would be expected from their concentration.

TABLE VIII. EXTRACTION WITH BENZENE-PYRIDINE SOLUTIONS

Solvent		Insoluble, Per Cent by Weight	
Benzene %	Pyridine %	Found	Calculated
100	0	28.24	27.90
95	5	22.62	21.49
90	10	19.41	18.32
80	20	16.69	16.25
0	100	8.85	9.27

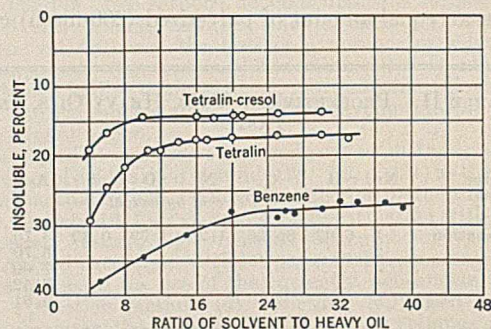


FIGURE 1. EFFECT OF RATIO OF SOLVENT TO HEAVY OIL

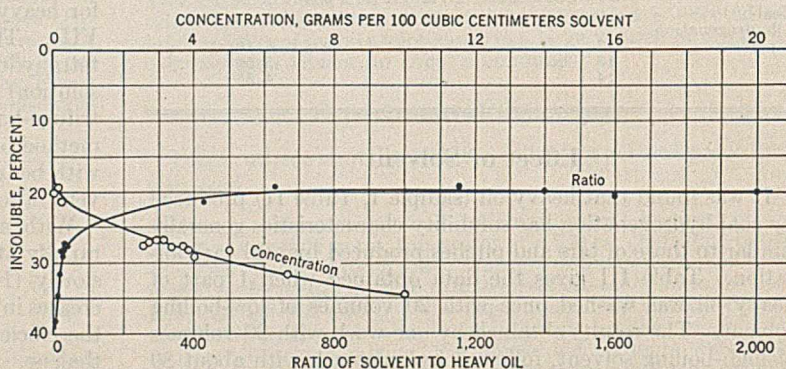


FIGURE 2. EXTRACTION OF HEAVY OIL WITH BENZENE

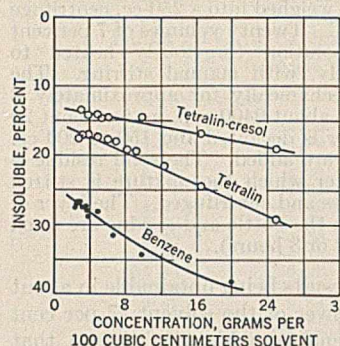


FIGURE 3. EFFECT OF CONCENTRATION OF HEAVY OIL IN SOLVENT

Table IX also contains data obtained with other tetrahydronaphthalene solutions. Since naphthalene is a probable impurity in commercial tetrahydronaphthalene, the solubility of the heavy oil in several naphthalene-tetrahydronaphthalene solutions was determined. It was found that the solubility characteristics of tetrahydronaphthalene are affected very little by the addition of as much as 10 per cent of naphthalene. On the other hand, the addition of the cresols to tetrahydronaphthalene increased the solvent power considerably, *p*-cresol being more effective than *o*-cresol. The addition of phenol to tetrahydronaphthalene also gave a more effective solvent. From these results it can be concluded that tetrahydronaphthalene-cresol solutions should give reproducible results if the tar-acid content, which can be determined easily by extraction with sodium hydroxide solution, is kept constant.

TABLE IX. EXTRACTION WITH TETRAHYDRONAPHTHALENE SOLUTIONS

Tetrahydronaphthalene %	Solvent Other component %	Insoluble, Per Cent by Weight Found	Insoluble, Per Cent by Weight Calculated
100 ^a		19.35	19.40
97.7	Tar acids, 2.3	17.45	17.37
95 ^a	Cresol, 5	15.77	15.56
		15.74	15.72
93 ^a	Cresol, 7	14.81	14.59
92.7	Cresol, 7.3	14.32	14.77
87.7	Cresol, 12.3	12.89	13.32
77.7	Cresol, 22.3	11.54	11.88
0	Cresol, 100	8.67	9.28
92.7	Cresol, 7.3	14.60 ^b	14.95 ^b
97.5 ^a	Naphthalene, 2.5	19.02	18.75
95 ^a	Naphthalene, 5	20.30	19.95
90 ^a	Naphthalene, 10	19.79	19.38
95	<i>o</i> -Cresol, 5	15.23	15.27
95	<i>p</i> -Cresol, 5	13.82	14.23
93 ^a	Phenol, 7	14.37	14.30

^a Solution prepared from purified tetrahydronaphthalene.

^b Hot tar treated with cold solvent (room temperature).

Effect of Preheating

Preheating the heavy oil at moderate temperatures had little effect on the determination of insoluble matter. When the standard heavy oil (No. 1, Table II) was heated in a centrifuge bottle at 105° to 110° C. for 20 hours the loss in weight was 2.06 per cent. However, the amount of insoluble matter found in the nonvolatile residue was 14.62 per cent (calculated value, 14.84 per cent) of the original sample. This value compares favorably with the result (14.32 per cent, Table VII) obtained in the usual manner.

This result might have been predicted from the results of Simek, Zamrzla, and Ludmila (44), who studied the rate of formation of material insoluble in benzene (alpha-compounds) from those soluble therein (beta- and gamma-compounds). The formation of alpha-compounds proceeded

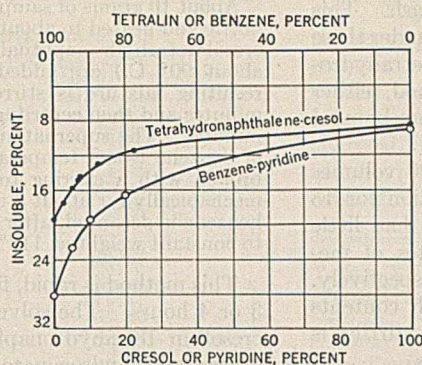


FIGURE 4. EXTRACTION OF HEAVY OIL WITH BINARY SOLUTIONS

slowly at 350° (4.95 per cent in 60 minutes, 10.91 per cent in 600 minutes). Although the formation of alpha-compounds began slowly at 450° (6.85 per cent in 60 minutes), it was markedly accelerated after the first hour (38.58 per cent in 120 minutes). Reeve (40) increased the "free-carbon" content by heating the tar at about 400° for 5 hours under a pressure of 6 to 7 atmospheres.

Effect of Temperature

The effect of temperature over a small range is illustrated by some of the data in Tables IV and IX. The experiments with tetrahydronaphthalene and 5 per cent cresol-tetrahydronaphthalene solution were made as follows: At the higher temperature, 20 volumes of hot solvent (90° to 100° C.) were stirred into the hot heavy oil, and the resulting mixture was stirred mechanically for about 3 minutes. At the lower temperature 20 volumes of solvent (room temperature) were stirred into the hot heavy oil. The resulting mixture, at a temperature of about 45°, was then stirred mechanically for about 3 minutes. There was very little difference in the results obtained by these two methods. However, when the hot, heavy oil was cooled quickly by rapid addition of cold solvent thorough mixing was hindered, and a higher value (20.03 instead of 17.4 per cent) resulted (Table IV).

Table X gives results obtained with several oils that were moderately fluid at room temperature. These results should be more significant since, in contrast with the more viscous samples, it was comparatively easy to mix sample and solvent at room temperature. The room-temperature determinations of Table X were made by adding 20 volumes of 5 per cent cresol-tetrahydronaphthalene solution to the fluid oil without previously heating either solvent or sample. Both sample and solvent were preheated to 90° to 100° C. for the high-temperature determinations. Table X shows that, with one exception, higher values for insoluble matter were obtained at room temperature. In agreement with previous work (45), it appears that small differences in temperature have little effect on the amount of insoluble matter.

Miscellaneous Variables

That continued washing is desirable under some conditions of extraction is evidenced by the fact that "free carbon" usually is determined by continuous extraction (6) in Soxhlet apparatus. Nevertheless, it is possible to avoid this time-consuming operation by working under proper conditions. Table XI shows that when 20 volumes of tetrahydronaphthalene are used most of the material soluble in tetrahydro-

TABLE X. EFFECT OF TEMPERATURE

Insoluble, Per Cent	
Room temperature	90° to 100° C.
5.79	4.74
7.00	5.42
7.09	5.49
4.76	4.76

TABLE XI. EFFECT OF REPEATED WASHING

Tetralin Washes	Benzene Washes	Insoluble, Per Cent by Weight	
1	1	17.45	17.37
2	1	14.88	15.50
2	1	15.45	16.21
2	2	15.26	16.03
1	2	15.71	16.52
1	2	15.90	16.61
1	3	16.24	16.89

naphthalene or benzene is removed in the first wash. This indicates that one or, at the most, two washings under these conditions suffice to remove virtually all the tetrahydronaphthalene-soluble material and that this method, either with tetrahydronaphthalene or a similar solvent, can be used satisfactorily as the basis of an analytical method.

Stirring the heavy oil (No. 1, Table II) with 20 volumes of 5 per cent cresol-tetrahydronaphthalene solution for 15 minutes instead of 3 minutes (the standard time) had little effect. The results found after 15 and 3 minutes of mechanical stirring are 14.52 and 14.32 per cent, respectively. The corresponding values calculated from the ash contents are 14.65 and 14.77 per cent; therefore continued stirring is not necessary and has little effect upon the results.

As has been observed previously with other methods (23, 33, 38), the insoluble matter was found to increase slowly with time of contact with the solvent. Heavy oil 1, Table II, gave 14.32 per cent insoluble matter by the standard method in which the sample is in contact with 20 volumes of the solvent for 1 hour or less. When the heavy oil was allowed to remain in contact with the solvent (after 3 minutes of stirring but before centrifuging) for 17, 241, and 386 hours the values obtained for insoluble matter are 15.26, 17.66, and 18.67 per cent, respectively. The corresponding values calculated from the ash contents are 15.57, 17.87, and 18.71 per cent. Consequently, the mixture should be centrifuged immediately after the stirring operation to get consistent results. It is claimed that the insoluble matter reaches maximum value after standing with the solvent for about 120 hours (33).

Previous workers (5, 15) showed that light causes matter to precipitate from carbon tetrachloride (41) solutions of bitumens. The amount precipitated in control experiments was considerably less, although there was some precipitation on standing in the absence of light. It was not considered necessary to study this variable in the present work, since in any analytical procedure that would be adopted the solution would be exposed to light for only a few minutes before centrifuging.

Table XII shows that centrifuging for 10 or 15 minutes will separate the 5 per cent cresol-tetrahydronaphthalene solution from the insoluble matter. Corresponding experiments for the second wash with benzene were not made, but less centrifuging should be required for benzene (sp. gr., 0.879) than for the cresol-tetrahydronaphthalene solution (sp. gr., 0.980).

TABLE XII. EFFECT OF CENTRIFUGING ON INSOLUBLE MATTER DETERMINATION

Centrifuging Time Min.	Insoluble, Per Cent Found	Per Cent by Weight Calculated from ash content
10	14.18	14.55
15	14.03	14.42
30	14.33	14.65
45	14.67	14.95
60	14.32	14.77

Method Adopted

From the foregoing account it is evident that the amount of insoluble matter depends almost entirely upon the analytical method used and that methods can be devised to give almost any desired answer. Since there is considerable latitude in choice of solvent, solvent ratio, and other conditions, it remains only to select a method that has the particular features desired for the problems at hand.

The following procedure appeared most suitable for the authors' purpose for several reasons that are here stated.

About 10 grams of sample are weighed into a 250-cc. centrifuge bottle and heated to about 90° C. Twenty volumes of 7 per cent cresol-tetrahydronaphthalene solution (previously heated to about 90° C.) are added slowly, with manual stirring. The resulting mixture is stirred mechanically for approximately 3 minutes and then centrifuged at about 2400 r. p. m. for about 20 minutes. The supernatant layer is decanted and 150 to 200 cc. of benzene (room temperature) are added. The solid residue is broken with a stirring rod, after which the mixture is stirred mechanically for about 3 minutes and centrifuged. The layer of benzene is decanted, after which the bottle and residue are dried to constant weight at 110° C. (2 or 3 hours).

This method is rapid, final results being obtainable in about 3 or 4 hours. The solvent power of the solvent (7 per cent cresol in tetrahydronaphthalene) should approximate that of tar and hydrogenated coal distillates. Enough solvent (20 volumes) is used to dissolve virtually all the reasonably soluble components. Since approximately the same results are obtained with 18 to 22 volumes of solvent, it is unnecessary to measure the solvent used with great accuracy.

TABLE XIII. INSOLUBLE MATTER IN TARS AND PITCHES DETERMINED BY DIFFERENT METHODS

No. (Table II)		(Per Cent by Weight)			
		Method ^a			
		A	B	C	D
1	Heavy oil	14.32	...	17.2	18.19
2	Heavy oil	11.94	...	{ 13.0	...
				{ 13.3	...
3	Heavy oil	15.66	...	16.1	...
4	Heavy oil	13.39	12.67
5	Heavy oil	13.99	16.25
	Coal-hydrogenation converter drainage	18.71	18.55
12	Coal-hydrogenation paste	43.70	...	40.9	...
12	Coal-hydrogenation paste	42.81 ^b	40.35	40.9	...
13	Coal-hydrogenation paste	45.87	...	43.4	...
13	Coal-hydrogenation paste	44.31 ^b	41.60	43.4	...
14	Coal-hydrogenation paste	45.75	45.25	45.70	...
	Coal tar	2.02	4.61
		2.02	4.34
		4.09	6.47
		4.57	7.74
		8.73	8.58
		3.61	4.00

^a Methods are:

A = Adopted method using centrifuge.

B = A plus Soxhlet extraction with benzene.

C = Two washes with 5 volumes of tetrahydronaphthalene, two washes with benzene, and Soxhlet extraction with benzene.

D = Gas Chemist's Handbook method.

^b Extracted twice instead of once with benzene.

Enough residue is obtained from coal hydrogenation pitches for determination of moisture, ash, etc. From the ash contents of the residue and the original sample, the percentage of insoluble matter can be calculated to check the determined value. By employing a six-place head for the centrifuge, six determinations can be made easily at one time. The efficacy of the solvent depends primarily upon the cresol content, which is easily determined by extraction with sodium hydroxide solution. The solvent is thermally stable and can be recovered by simple distillation. The residues obtained are such that the centrifuge bottles can be cleaned easily. Most tars and many pitches are fluid at 90° to 100° C. and hence easily mixed with solvent at the temperature employed. Presumably, high-melting pitches could be examined by this method after being finely pulverized.

The new method gives results somewhat lower (Table XIII) than those obtained by the well-known "free-carbon" determination (6), in which the sample is extracted with benzene in Soxhlet apparatus after a preliminary wash with warm toluene. Several of the residues obtained by the new method were extracted for 48 hours with benzene in Soxhlet apparatus. The results (column B in Table XIII) show that small percentages of the residues are extractable with hot benzene.

The reproducibility of the method is shown by Table XIV. The determined values check each other better than the values calculated from the ash content, but in nearly all instances the agreement is satisfactory.

TABLE XIV. DUPLICATE DETERMINATIONS^a

Insoluble Matter, Per Cent		Calculated from ash content
Found		
45.75	45.76	45.70
4.82	4.79	4.95
11.95	11.99 ^b	12.15
4.82	4.79	4.95
11.77	11.84	12.08
13.37	13.42	13.70
18.69	18.73	19.29
8.75	8.56	
49.95	49.15	51.10
55.33	55.20	55.70
32.04	32.06	32.27
9.57	9.64	9.41
17.06	16.97	17.42
54.94	54.98	54.90
55.94	56.08	55.90
17.45	17.49	17.73
60.85	60.88	60.80
43.44	43.95	43.85
20.98	21.04	21.15
21.74	21.78	22.00

^a Samples are heavy oils, pitches, pasting oils, and centrifuge residues produced or used in coal hydrogenation.

^b A third determination gave 11.87 per cent of insoluble matter.

Composition of Insoluble Matter

Ultimate analyses were made of the insoluble matter found in several heavy oils produced by hydrogenating coal and coal tar. As is to be expected, these insoluble products contain much ash and carbon and little hydrogen (Tables XV and XVI). Probably the precursors of most of the insoluble matter in the products of coal hydrogenation are the fusain and opaque attritus of the original coal. Both fusain and opaque attritus have high carbon-hydrogen ratios and are difficult to liquefy by hydrogenation.

For the purpose of comparison, the composition of free carbon (34) from coal tars may be considered. Hubbard and Reeve (26) analyzed several samples of free carbon and reported the following data:

Carbon	90.17 to 94.26
Hydrogen	2.59 to 3.31
Oxygen	1.81 to 5.91
Sulfur	0.50 to 1.78
Nitrogen	No trace upon qualitative test

The results of Hubbard and Reeve are roughly similar to those found by other investigators, except that considerable amounts of nitrogen are usually found (Table XVI). Mallison (35) gave the following as the composition of free carbon: C, 90.0 to 91.7; H, 3.4 to 4.0; N, 1.0 to 1.2; S, 0.7 to 1.4; and O, 2.5 to 3.3 per cent. Table XVI gives the ultimate analyses of other samples of free carbon obtained from coal tar by solvent extraction. All these samples of insoluble matter are characterized by high carbon and low hydrogen contents. From the data in Table XVI the insoluble matter from coal-hydrogenation products appears to have higher hydrogen contents and lower carbon-hydrogen ratios than that occurring in tars produced by the carbonization of coal. Since the insoluble residues (Table XVI) from coal-hydrogenation products contain 15 to 30 per cent of ash, the data calculated to the dry, ash-free basis may not represent exactly the insoluble organic matter. Insoluble matter from carbonization tars contains only traces of mineral matter, and hence their ultimate analyses are more significant.

Unpublished results obtained at the Bureau of Mines during the continuous hydrogenation of high-temperature coal tar are interesting in connection with the nature of the "free carbon" or insoluble matter. Although the tar contained nearly 9 per cent of "free carbon" (as determined by benzene extraction in Soxhlet apparatus and the cresol-tetrahydro-naphthalene method described above), the insoluble matter content of the product discharged from the bottom of the hydrogenation converter remained constant at about 1.5 per

cent. This indicates that continuous hydrogenation, in which the heavy products are recycled, converts all the tar into liquid, gaseous, or soluble products. Therefore, the "free carbon" of this tar, although of high carbon content and molecular weight, is not inert and is considerably different from carbon, charcoal, fusain, etc. One sample of "free carbon" from coal tar was found to have a molecular weight of 2000 in anthracene (16).

TABLE XV. ANALYSIS OF INSOLUBLE MATTER IN HEAVY OIL FROM HYDROGENATION OF COAL AND COAL TAR (DRY BASIS)

Volatile Matter	Fixed Carbon	Ash	H	C	N	O	S
14.60	55.55	29.85	3.05	60.49	0.98	2.91	2.72
20.20	63.78	16.02	3.96	72.80	1.33	4.41	1.48
16.75	57.79	25.46	3.46	63.86	1.08	3.83	2.31
14.70	70.54	14.76	3.60	75.30	1.55	3.36	1.43
15.75	66.85	17.40	3.53	73.07	1.41	2.79	1.80
14.60	65.02	20.38	3.42	69.63	1.28	3.50	1.79
15.90	61.59	22.51	3.37	68.14	1.18	2.99	1.81
10.4 ^a	75.7	13.9	2.3	79.4	0.8	0.7	2.9
... ^a	...	9.3	2.6	80.3	1.4	4.9	1.5
... ^b	...	2.4	3.8	83.0	2.2	7.8	0.8

^a Heavy oil from hydrogenation of coal tar.

^b Coal tar.

TABLE XVI. ANALYSIS OF INSOLUBLE MATTER IN TARS, PITCHES, ETC.

Source	Dry, ash-free basis					C/H Ratio	Reference
	H	C	N	O	S		
Heavy oil ^a	Per cent by weight						
	4.3	89.2	1.4	4.4	b	20.8	(22)
	4.7	88.3	1.6	4.7	b	18.8	(22)
	4.7	88.4	1.4	4.8	b	18.8	(22)
	4.2	89.9	1.9	3.3	b	21.4	(22)
	4.3	90.4	1.7	2.9	b	21.0	(22)
	4.3	89.3	1.6	4.1	b	20.8	(22)
4.4	89.9	1.6	3.4	b	20.4	(22)	
Heavy oil ^c	2.7	94.5	1.0	1.1	b	35.0	...
	2.9	89.5	1.6	5.3	b	30.9	...
Coal tar	3.9	85.2	2.3	7.9	b	21.8	...
	2.3	89.8	0.7	7.2	..	39.1	(17)
	3.1	91.2	29.4	(8; 32, Part 1, p. 431)
	3.2	92.7	29.0	(8; 32, Part 1, p. 431)
	3.3	91.1	1.1	3.2	1.3	27.6	(43)
	2.79	90.0	32.3	(3)

^a Produced by coal hydrogenation (22).

^b Organic sulfur assumed to be 0.7 per cent (1).

^c Produced by hydrogenation of coal tar.

Acknowledgment

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Determination of Phenols in Hydrocarbon Solvents

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IT IS well known that the presence of phenolic compounds in oleoresinous compositions tends to retard the drying rate. Certain hydrocarbon solvents have been shown to have an adverse effect on drying, due to the presence of small amounts of phenolic bodies. Since no adequate analytical method for the determination of small amounts of phenols in hydrocarbon solvents has ever been published, this work was undertaken with a view to establishing a method of controlling the phenol content of solvents used for paints.

Petroleum solvents may differ considerably in their phenolic content, depending on the source of supply and the methods of manufacture and purification. Since the major portion of the phenolic contaminants is removed at the refinery, any useful method of isolation and determination must be applicable to amounts on the order of 10 to 100 parts of the phenol per million.

Most quantitative methods suffer from the disadvantage of being inapplicable either to substituted phenols which are present in the highly aromatic type of solvents being considered or to phenols which are not effective reducing agents. Volumetric methods, such as the familiar bromate-bromide method, are essentially macro methods and insufficiently accurate for estimation of contaminants. Among the available colorimetric methods, those of Folin and Denis (1) and of Gibbs (2) have received the most attention. The former is based on reduction of phosphomolybdic-phosphotungstic acid presumably to lower oxides of molybdenum and tungsten, resulting in formation of deep blue colored solutions. It has been found specially suitable for the estimation of aminophenols and polyhydroxy phenols which are strong reducing

agents, but the reagent is less satisfactory for the estimation of the higher alkyl substituted phenols which are found in high-solvency petroleum solvents. The Gibbs method, which is based on indophenol dyestuff formation by reaction of phenols with 2,6-dibromoquinone chloroimide, is inapplicable to para-substituted phenols; in fact, even with the para position unsubstituted some phenols have failed to undergo reaction.

The procedure herein described is particularly suitable for the colorimetric estimation of the higher alkyl substituted phenols in petroleum solvents, which are only slightly soluble or insoluble in water. A method similar in principle and as applied to certain biological materials has been described by Stoughton (3).

In the present method, the phenolic bodies are separated from the hydrocarbon solvent by successive extractions with dilute aqueous alkali until the extract is phenol-free, as indicated by a negative phenol test on the final extract. Since the alkali salts of the higher alkyl substituted phenols have a limited solubility in water due to their high molecular weight, repeated extractions are essential; alkali-insoluble phenols containing 8 carbon atoms or more in the side chains are usually not encountered, because of their high boiling point, and are not apt to appear in solvents suitable for the paint and varnish industry. Steam-distillation is an ineffective means of isolation of the phenol contaminants because of the high volatility of the hydrocarbon solvent.

After extraction, an aliquot of the alkaline phenol solution is neutralized, then diluted with an equal volume of glacial acetic acid to liberate the phenols, the dilute acetic acid acting also as a solvent for the water-insoluble phenols. At least a 50 per cent concentration of acetic acid is required to maintain homogeneity. The phenol solution is treated with a few drops of sulfuric acid and nitric acid, warmed on the steam bath to effect

complete reaction as indicated by maximum development of yellow color. Making the solution ammoniacal results in rearrangement of the nitroso phenol to form the highly colored quinonoid salt. The intensity of this color is proportional to the concentration of the phenol.

The character of the color produced is somewhat influenced by the type of phenol involved; phenol itself, for instance, produces a greenish yellow color, whereas *p*-*tert*-butyl phenol produces an orange-yellow color. Since no other variations of the yellow color are encountered, either of the above two phenols may serve as standards in the colorimetric comparisons. Clear solutions are invariably obtained and direct comparison with standard phenol solutions may be made either in a Duboscq or Klett colorimeter or by the use of Nessler tubes; check results on separate extractions may be obtained within 5 to 10 parts per million. The method is rapid and direct, requiring no special apparatus other than that found in the average chemical laboratory.

Experimental Details

APPARATUS AND REAGENTS. A Duboscq or a Klett colorimeter provided with 100-mm. tubes. Dilute potassium hydroxide solution, approximately 0.2 *N* in aqueous solution. Dilute sulfuric acid solution, approximately 0.2 *N* in aqueous solution. These solutions need not be standardized.

Stock phenol solution. Exactly 2 grams, accurately weighed, of freshly distilled or crystalline phenol are dissolved in 1 liter of distilled water. From this stock solution, which contains 2000 p. p. m., standard solutions of the desired concentrations are prepared. Diluted to 1 liter:

25 ml. of stock solution =	50 p. p. m. of standard
50 ml. of stock solution =	100 p. p. m. of standard
100 ml. of stock solution =	200 p. p. m. of standard

Standard solutions containing more than 200 p. p. m. should not be used because of the intense color produced in the nitrosation reaction. The color produced from these standards is a greenish yellow.

Stock *p*-*tert*-butyl phenol solution. Exactly 1 gram, accurately weighed, of *p*-*tert*-butyl phenol (Eastman Kodak Co. organic chemical P-2465) is dissolved in 250 ml. of glacial acetic acid and the solution is diluted to 500 ml. with distilled water. Standard solutions are prepared from this solution exactly as described above for the phenol solutions. This standard produces an orange-yellow color and is the one more often used in the actual comparisons. The dilutions should not be made until they are required, since the phenol has a tendency to precipitate.

PROCEDURE. A 25-ml. sample of the hydrocarbon solvent is placed in a 100-ml. Squibb separatory funnel and extracted several times with 25-ml. portions of 0.2 *N* potassium hydroxide until additional extractions yield no color when treated as directed below. From one to five extractions are usually sufficient.

Each 25-ml. extract is separated into a 100-ml. volumetric flask, and neutralized by adding 25 ml. of 0.2 *N* sulfuric acid from a graduate. It is diluted to the mark with glacial acetic acid and mixed by shaking. Fifty milliliters of this solution are placed in a 125-ml. Erlenmeyer flask and 6 drops of concentrated sulfuric acid and 6 drops of nitric acid are added. It is heated on the steam bath until a pale yellow color develops and reaches a maximum, requiring from 5 to 30 minutes. The remaining 50-ml. aliquot of the original solution should be treated in a like manner as a check.

After cooling in ice, the pale yellow solution is cautiously made alkaline by the gradual addition of at least 35 ml. of concentrated ammonium hydroxide (sp. gr. 0.90), resulting in a considerable increase in color intensity. A greater excess of ammonium hydroxide does no harm. After dilution to 100 ml. with distilled water, the solution is compared in a colorimeter with a suitable standard, as described below. The calculated phenol contents of each of the several extractions are added to give the total phenol content of the solvent, expressed as parts per million of the particular phenol used as a standard.

As a check on the above procedure, another 25-ml. sample of the solvent is extracted with as many 25-ml. portions of 0.2 *N* potassium hydroxide as were found necessary in the previous determination. The total extracts are combined and a 25-ml. aliquot is placed in a 100-ml. volumetric flask, neutralized with 0.2 *N* sulfuric acid, and adjusted to a 100-ml. final volume by addition of glacial acetic acid. After thorough mixing, two 50-ml. aliquot portions are warmed with the mixed acids, then

made ammoniacal and otherwise treated as above. The calculated phenol content of this aliquot is multiplied by the total number of 25-ml. alkali extractions that were required to remove all phenols from the solvent; this value gives the total phenol content of the solvent and should check within 2 to 5 per cent of the previous value which was obtained by the summation of the phenol contents of the individual extractions.

PREPARATION OF THE STANDARDS. Various shades of yellow are obtained, depending on the type of phenol present in the sample of solvent. This fact makes it necessary to employ different phenols as standards for comparison. In practice, only two tints have actually been obtained. Phenol may be used if the unknown shows a greenish yellow color on treatment; *p*-*tert*-butyl phenol yields by a similar treatment an orange-yellow color. No difficulty is experienced in deciding which is the proper phenol to use in preparing the standards for the colorimetric comparison.

It is necessary to compare the unknown with a standard having approximately the same phenol concentration—that is, within 50 p. p. m. For this reason, three standards must be prepared containing 50, 100, and 200 p. p. m., respectively. Twenty-five milliliters of each standard (containing 50, 100, and 200 p. p. m., respectively) are then treated exactly as described for the unknown. The selection of the proper standard for the comparison may be readily decided by comparison with the unknown. If the first extraction of the solvent produces a color intensity corresponding to a phenol content greater than 250 to 300 p. p. m., it should be diluted with distilled water to a convenient phenol content within the range of the standards.

The colors produced are stable, the useful life of the standards being about 2 weeks, during which time they remain practically constant. After a month's standing, however, the apparent phenol content of the standards, as indicated by the color change, has decreased from 5 to 15 per cent. It is recommended that fresh standards be prepared at the time that the colorimetric comparison is to be made.

Discussion of Analytical Method

Repeated alkaline treatment of the solvent is required in order to ensure complete extraction of the phenols. Solvents containing 300 to 600 p. p. m. require at least five successive extractions; lower concentrations require only four. If the phenol content is only 10 to 20 p. p. m., one extraction suffices. This protracted extraction method has been found necessary because of the low solubility of the alkali salts of the phenols involved. Since the phenols are already in a free state in the solvents, no preliminary saponification treatment need be given.

It is unnecessary to know the identity of the phenols being estimated, since the method described is primarily for specification control or similar purposes. The fact that *p*-*tert*-butyl phenol is usually the required standard indicates that we are dealing with mixtures of alkylated phenols which have boiling points within or only slightly higher than the boiling range of the petroleum solvents in question. Stoughton (3) has indicated that hydrocarbons such as toluene might interfere. However, the authors have never encountered such interference by any of the petroleum solvents with which they have worked, most of which are highly aromatic in character. Continued alkaline treatment eventually produces an extract which yields no color whatsoever on acid treatment.

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Determination of the Molecular Weights of Oils

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An apparatus consisting essentially of a modified form of the Cottrell boiler and adapted for use with the Menzies-Wright water differential thermometer is described. Benzene or cyclohexane may be used as solvent. Benzene is to be preferred, since a good grade of commercial product requires no further purification and may be used directly. Results on pure compounds and a variety of hydrocarbon materials indicate a precision of 1 per cent or better at all times. A complete molecular weight determination requires about 2 hours; however, with the necessary equipment, two or three determinations may be carried out simultaneously.

RECENT work on the constitution of petroleum, and, in particular, the chemical structure of closely cut petroleum distillates, has shown that some rather striking relationships exist among the physico-chemical properties of an oil and the proportion of the various types of hydrocarbon molecules present. The molecular weight of an oil is important, not only for its own interest, but also because of its appearance with density, viscosity, refractive index, surface tension, etc., in a number of functions which have been developed for purposes of correlating and characterizing these materials.

Unfortunately, the molecular weight of an oil is not easy to determine. The best methods available at present involve the determination of the effective molecular weight, in some particular solvent, at several concentrations, by either a cryoscopic or an ebullioscopic method and an extrapolation of the data to zero concentration of solute. Theoretically, this value should be the weighted harmonic mean of all the constituents present.

Rall and Smith (5) of the Bureau of Mines recently conducted a survey of the cryoscopic methods in use in a number of laboratories in which research on petroleum products was being carried out. The individual results on four oils examined by each laboratory were not particularly concordant. They were analyzed and compared with the results obtained by the bureau's apparatus, with the conclusion that the only safe procedure is to use the purest solvent possible and to determine the cryoscopic constant with a known pure solute. The low solubility at the freezing point of the solvent and the tendency on the part of some solutes to form mixed crystals with the solvent introduce inherent errors in this method.

Mair (2) at the Bureau of Standards has investigated the ebullioscopic method for the molecular weights of oil fractions and has developed an apparatus capable of giving results on pure compounds which are within 1 per cent of the theoretical value. While this method obviates many of the difficulties inherent in the cryoscopic procedure, it is limited to oils having a negligible vapor pressure at the boiling temperature of the solvent. Fortunately, most waxes and lubricating oils fall in this class.

As in the case of the apparatus used by Rall and Smith, the equipment described by Mair is applicable only in research projects, its complexity making it unsuitable for routine

laboratory use. The present paper describes the construction and use of a simple ebullioscopic apparatus for the routine determination of the molecular weights of involatile oils. It was developed in this laboratory as the result of a need which arose in connection with work on the chemical constitution of oils.

Apparatus

The apparatus is essentially a modified form of the Cottrell (1) boiler adapted for use with the Menzies-Wright (3, 4) water differential thermometer. A diagram of the equipment is given in Figure 1.

The boiler is designed to hold from 25 to 30 cc. of solvent, bringing the normal liquid level to the point at which the tube begins to widen. The additions of solute during the course of a run, therefore, cause no substantial rise in the liquid level and, hence, negligible change in the pumping conditions. Surrounding the boiler is a jacket, and the annular space is under high vacuum. The use of a vacuum jacket minimizes the heat loss from the apparatus and protects the boiler from laboratory drafts.

Heat is supplied electrically through a chromel coil placed directly in contact with the liquid. The coil, formed from No. 24 wire, has a resistance of 0.9 ohm. The optimum power consumption is about 30 watts. This wire is brazed onto two tungsten leads which are brought through the vacuum jacket and into the boiler by the use of GT 70 tungsten sealing glass presses. In use, it has been found convenient to make connections with the tungsten leads by means of a small Bakelite block containing two mercury wells (Figure 1).

The vapor-lift pump is attached rigidly to the boiler at the top and bottom and thus serves to hold the water thermometer in place. The tube leading from the large bell to the inverted cup is of only 2-mm. diameter and has a relatively thin wall.

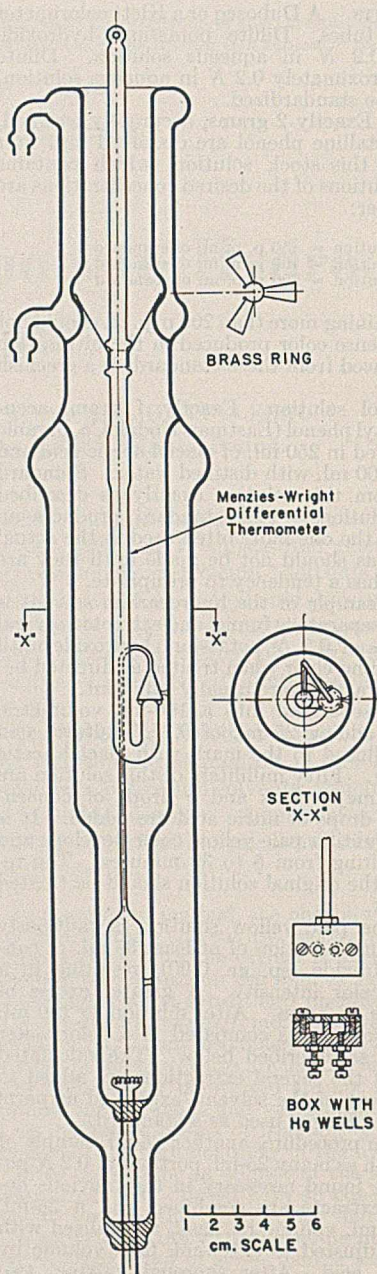


FIGURE 1. DIAGRAM

TABLE I. MOLECULAR WEIGHT DETERMINATIONS

Material	Calculated	In Benzene	In Cyclohexane	Freezing Point, Benzene
Triphenyl methane, Eastman Kodak, m. p. 93-94° C.	244.1	$K = 54.4 \pm 0.1$	$K = 61.8 \pm 0.2$...
Anthracene, sublimed and recrystallized twice from benzene	178.1	178.0 ± 1.0	179.6 ± 0.7	...
Benzil, Eastman Kodak, m. p. 94-95° C.	210.1	211.6 ± 1.3	210.6 ± 1.1	...
U. S. Bureau of Mines oil:				
No. 1	...	671 ± 5	652 ± 3^a	764
No. 2	...	450 ± 1	445 ± 2^a	442
No. 3	...	326 ± 2	312 ± 2	358
No. 4	...	208 ± 1	208.5 ± 2	218
Refined mid-continent residuum	...	1010 ± 8^a	908 ± 5^a	900
Paraffinic molecular still residuum	...	1553 ± 7^a	1459 ± 10^a	...
Heavy naphthenic distillate	...	522 ± 2^a	465 ± 2	511
Paraffin, m. p. 132° F.	...	380 ± 1	352 ± 2	...
Synthetic paraffin wax, m. p. 98° C.	...	750 ± 5	762 ± 4^a	...

^a Negative molecular weight concentration slope.

The condenser at the top of the boiler has been made fairly wide to admit the thermometer and to allow for easy addition of solute. A slight bulb is blown in the lower inner wall to act as support for the thermometer collar, illustrated in Figure 1, which is formed from 0.25-mm. (0.010-inch) brass shim stock. The three vanes rest in the depression in the condenser wall, and by adjusting the angle which they make with the stem, any degree of upward thrust can be given the thermometer. An important function of the brass collar is its action as a condenser. The vanes lying against the cold condenser wall are cooled and, during a run, an appreciable amount of solvent condenses on the brass ring and is reheated to the boiling point on the upper bulb of the thermometer. In practice, after the power input exceeds a certain critical value, rapid refluxing takes place at the base of the condenser but no vapors ever rise in the condenser. This assures, in addition to a constant vapor volume, a negligible loss of solvent. These observations were made with reference to benzene and cyclohexane as solvents.

For a successful determination, it is essential that the boiling be smooth. When functioning properly, the vapor passing up through the vapor-lift pump carries with it a heavy film of solution along the wall. The appearance of any slugs of liquid always makes for unsteady temperatures. Solution drips from the bottom bulb at the rate of 2 to 3 drops per second. After the first addition of solute is made, there is seldom any difficulty with the boiling. The type of boiling obtained with pure solvent, however, is less desirable and to get the zero point for the thermometer it may be necessary to average several readings. Once this zero point is obtained, it may be used for any determination, since its value is a function only of the dimensions of the thermometer itself and the purity and boiling point of the solvent. It has been found possible to get the zero point more quickly by dispersing a small amount of gum rubber (about 0.05 per cent) in the solvent. Good boiling results without any measurable rise in the boiling point. This rubber solution may also be used as solvent in the few cases in which poor pumping action persists after the addition of solute. The reading of the meniscus in the small bulb of the thermometer may also be dispensed with as soon as the relation between the heights of liquid in the two arms has been established. For a well-constructed thermometer, the relationship is, of course, strictly linear.

Experimental Results

A solvent chosen for the routine examination of oils should be obtainable in quantity and in a moderate degree of purity. In addition, a convenient boiling point and a large ebullioscopic constant are desirable. Adequate solvent properties for hydrocarbons and stability under the operating conditions are essential. (Owing to decomposition on the heated coil, it is not possible to use the common chlorinated solvents.) Benzene and cyclohexane are the only solvents which meet these requirements.

For this work, the cyclohexane was purified by treatment with concentrated sulfuric acid, followed by an alkali wash. This material was then fractionated in a 45-plate column still, retaining the middle third of the distillate for experimental use. The benzene used was a good grade of "nitration benzene"; no purification or drying was found necessary.

Results were obtained on a number of pure compounds, three of which are listed in Table I. In every case the precision was 1 per cent or better; the accuracy was also about 1 per cent. These three compounds were selected because they are substances which may be obtained in reasonable purity and used conveniently as calibrating compounds. The experimental values for anthracene and benzil are based on the ebullioscopic constant obtained using triphenyl methane.

To illustrate the behavior with oils and waxes, the results of a number of determinations on materials of rather widely differing properties have been tabulated in Table I. The concordance in the experimental results is again seen to be better than 1 per cent. For purposes of comparison, the four oils used by Rall and Smith (1) in their survey were examined and are listed. These oils have been preserved in tightly sealed bottles and kept in the dark. In the extreme right-hand column are listed the values obtained in this laboratory by the cryoscopic method, using purified benzene as solvent. The estimated probable error in these determinations is 3 per cent.

Throughout the work there was observed no tendency on the part of any substance to increase in apparent molecular weight with concentration. With the exception of those runs noted in Table I, the molecular weight-concentration curves were, within the limits of error, lines parallel to the concentration axis. Thus, in calculating the experimental molecular weight, a simple average of the four or five readings was taken. The limits of error noted are the mean deviations from the averaged value. Apparently the tendency of substances in general to associate is very small at the temperatures of boiling benzene or boiling cyclohexane and in the concentration range studied (maximum concentration approximately 0.15 molar).

It is evident from the tabulated results on the petroleum products that, while the values are reproducible with a precision of 1 per cent or better, it is not possible to speak of the accuracy of the determination. Differences as great as 10 per cent may exist between the values for the molecular weights of an oil or wax in boiling benzene and cyclohexane, and even greater differences are observed when the values obtained by the freezing point method are compared with those using an ebullioscopic procedure. These differences are apparently more pronounced at high values of the molecular weight. By adhering to a single solvent, however, comparable results may be expected. In this laboratory a good quality "nitration benzene" or any "reagent" product is used exclusively. Owing to the fact that they require no further purification, these solvents are preferred to cyclohexane.

It is believed that this apparatus offers a convenient and reasonably precise means for the routine examination of petroleum products. The time required for a single determination is about 2 hours. Since it is necessary to allow from 10 to 15 minutes for equilibrium to be established after each addition of solute, it would be possible for an operator, with the necessary equipment, to carry out two or three determinations simultaneously.

The method described is the best with regard to both speed and accuracy of several investigated at this laboratory, in-

cluding the original one using the Menzies-Wright differential thermometer.

Acknowledgment

The writers are indebted to William E. Barr, of the Gulf Research and Development Co., for his patient and skillful glass working.

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Photoelectric Colorimetry

An Optical Study of Permanganate Ion and of the Chromium-Diphenyl Carbazide System

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The colorimetric determination of manganese by the periodate method and the determination of chromium by diphenyl carbazide have been studied with the object of adapting them to photoelectric colorimetry. An optical method for the separation of interfering ions is discussed in connection with the manganese method.

RECENTLY, with the advent and adoption of photoelectric cells, numerous photoelectric colorimeters have been designed for chemical analysis. It now seems advisable to study several standard colorimetric methods, using a colorimeter which is constructed with due cognizance of true optical principles without the use of certain well-known refinements which none of these instruments employs (such as the use of a monochromatic source of illumination). The purpose here is to determine what precision may be expected in the use of such an instrument, what necessary changes must be made in existing methods to adapt them to photoelectric colorimetry, and the effect of certain optical properties of these systems on their use as general analytical methods.

That the fundamental law of light absorption, the Lambert-Beer relationship, should form the basis for every exact colorimetric method has been shown by Müller (6). In this investigation the conformity of the absorbing entity to this relationship was used as the criterion of an acceptable method. Only those solutions that yielded absorption values within the range of conformity were used; others were diluted until they fell within that range. This working range is that in which the extinction coefficient is invariant, within the limits of experimental error.

Apparatus

Two photoelectric colorimeters were used in this work, both of which have been described previously (6, 7). Preliminary measurements were made using the photonic cell instrument, by the use of which a photometric precision of 0.5 to 1 per cent is obtained. Final measurements were made using a colorimeter employing a vacuum photocell and triode (7), used in a slide-back type of vacuum-tube voltmeter. The compensating potential in the grid circuit is supplied by a dial and slide-wire potentiometer which can be calibrated to read transmission values directly. A photometric precision of 0.03 to 0.05 per cent can be realized by using this instrument.

Both colorimeters were subjected to physical calibration by means of nonselective wire screens of known transmission. With this assurance of linear response, conformity with Beer's law for

any system is unlikely to be the result of mutually compensating errors.

Absorption spectra of the various colored compounds and the transmission spectra of the light filters were measured with a Bausch & Lomb spectrophotometer which was calibrated periodically with a mercury arc.

Determination of Manganese

The oxidation of manganous ion to permanganate by periodate in acid solution as described by Willard and Great-house (9) is free from many of the disturbing factors arising from the use of other oxidizing agents. The reaction is given by the equation

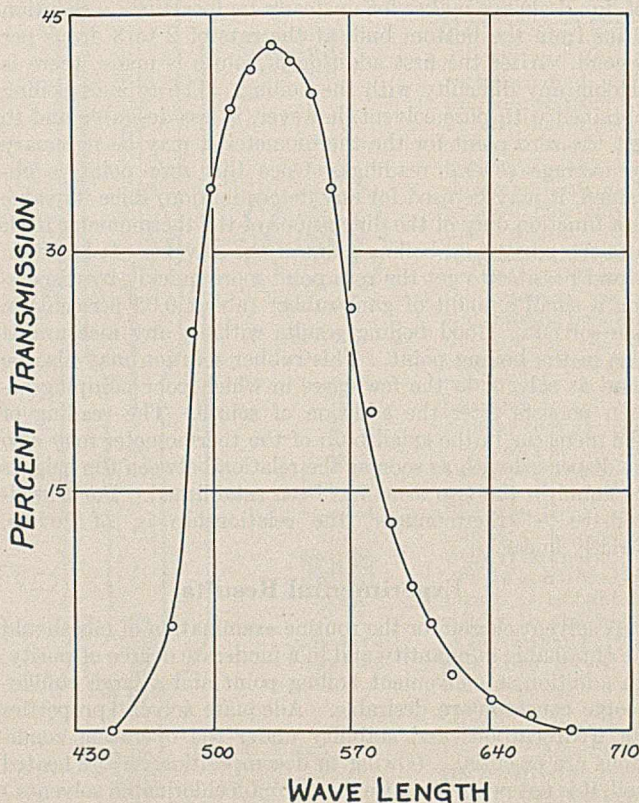


FIGURE 1. TRANSMISSION SPECTRUM OF SEXTANT GREEN FILTER

Wide application has been made of this method and it has been employed satisfactorily for a long time; therefore it seemed well adapted to the photoelectric technique.

From a consideration of the absorption spectrum of permanganate ion which has been determined by Lange and Schusterius (5), the desired region of wave lengths to be used in the determination of permanganate can be found. (The region of maximum absorption should be used in making the measurement.) The presence of a prominent absorption band at $526\text{ m}\mu$ indicates that a highly selective green light filter must be used for the measurements. A Corning sextant green filter 2 mm. thick was used to isolate this band. The transmission spectrum of this filter is shown in Figure 1. Owing to the marked change in absorption of permanganate even in this narrow ($80\text{-m}\mu$) spectral region, the validity of Beer's law must be tested using various concentrations of permanganate to ascertain the working limits for photometry.

Figure 2 shows the close agreement with Beer's law up to a concentration of 8.4 mg. of manganese per liter. The ordinates represent the extinction ($\log I_0/I$), while the abscissas are measured in milligrams of manganese per liter. From this curve the milligram extinction coefficient was calculated and this value was then used in calculating the results of the photometric measurements. If the photonic cell instrument is used, the linear behavior may be extended to 12 mg. of manganese per liter, at the expense of precision. The extension of the range is due only to the high green sensitivity of the barrier-type photocells.

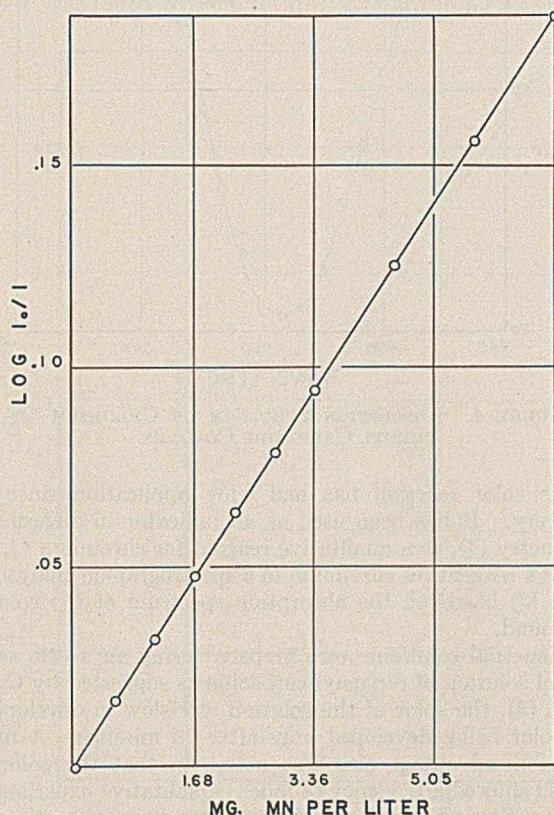


FIGURE 2

In conditioning the solution preparative to photometering it, the method of Willard and Greathouse (9) was followed. In all cases the photometric measurements were made using standard substitution technique in which a cup containing distilled water first intercepts the light beam giving the I_0 reading. The permanganate solution in a matched cup is

then substituted (giving the I reading), and finally the I_0 reading is checked.

INTERFERENCE DUE TO OTHER COLORED IONS. In many applications of this method the manganese will be accompanied by other metals which yield colored ions upon solution of the sample and subsequent oxidation with periodate. It has been customary in colorimetry to compensate for this extraneous light absorption by making some sort of arbitrary adjustment—by adding coloring materials to the standard solution, or by interposing in the light beam from the standard cup a light filter which simulates the effect of the background color. Not only do these methods depend largely upon the judgment of the analyst, but they are at best crude attempts to approximate unknown conditions and concentrations.

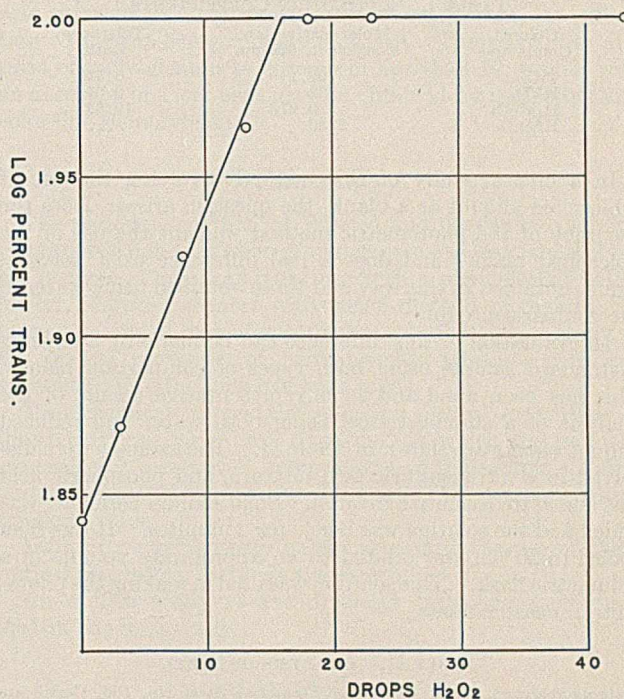


FIGURE 3. PHOTOELECTRIC TITRATION OF PERMANGANATE WITH HYDROGEN PEROXIDE

In order to circumvent this difficulty without resorting to chemical separations of the interfering ions, it was attempted to bleach a portion of the test solution and, after freeing it from permanganate, use it for obtaining the I_0 value. It was found that the addition of a few drops of very dilute hydrogen peroxide (approximately 0.01 per cent) to a portion of the oxidized solution would remove the permanganate and leave the background color.

Certain objections to this method would seem to arise: (1) reaction of excess hydrogen peroxide with periodate; (2) the formation of peroxides of other components that would in themselves color the solution; and (3) reoxidation of manganese by excess periodate (which is always present).

The first objection was met by performing a photoelectric titration of a solution containing sulfuric acid, permanganate, and periodate with dilute hydrogen peroxide. Figure 3 shows that no further color is obtained by adding to such a solution excess hydrogen peroxide after the permanganate is reduced. A fivefold excess of hydrogen peroxide (not shown in plot) over the amount necessary to reduce the permanganate gave no indication of color.

An evaluation of the magnitude of the error introduced when colored metal peroxides are present may be gained by a comparison of their molar extinction coefficients with that of

the permanganate ion. These extinction coefficients were determined at 520 $m\mu$ since the sextant green filter possesses its maximum transmission at that wave length. The values obtained are shown in Table I along with the tolerance ratio that will permit the determination of manganese to ± 1 per cent precision. However, these figures represent maximum error, since an excess of hydrogen peroxide must be added in order to develop the full color in these peroxides, while in actual work hydrogen peroxide is added only until the permanganate color is discharged.

Studies on the rate of oxidation of manganous ion to permanganate ion showed that the third objection was of no consequence, since the rate of reoxidation at room temperature is immeasurably slow.

TABLE I. EXTINCTION COEFFICIENTS

Colored Compound	Molar Extinction Coefficient, 520 $m\mu$	Tolerance Ratio
TiO ₂	98.1	0.397
HVO ₄	269	0.077
H ₂ MoO ₄	0.973	19.62
HMnO ₄	2230	...

In a critical study of this method involving the use of a bleached aliquot as a blank, the question arises: Does the accuracy of the photometric method warrant the use of the "bleached blank" and does a real difference exist between values obtained in this way and those obtained using water in the comparison cup?

An evaluation of this difference can be made by analyzing a standard sample using both types of comparison blanks. This has been done and some representative results of the analysis of a standard steel using both water and reduced aliquot blanks are shown in Table II. The samples were dissolved in a nitric-sulfuric acid mixture, and phosphoric acid was added to decolorize the iron. Solid sodium periodate was added and the solution was boiled for 2 minutes. It was then cooled to 20° C. and diluted to an appropriate volume in a volumetric flask. This solution was used in making the photometric measurements.

TABLE II. ANALYSIS OF STEEL

(Sample analyzed, U. S. Bureau of Standards Steel No. 106, Certificate Value 0.481% Mn)

Sample	Manganese Found	
	H ₂ O blank %	Reduced blank %
1	0.515	0.483
2	0.506	0.482
3	0.507	0.483
4	0.529	0.485

The results obtained from using the water blank in addition to being approximately 6 per cent high (on the average) are erratic. For this reason the popular, but always questionable, procedure of "using a factor" is doubly dangerous in this case. The reduced blank values not only agree well between themselves but also with the certified value of the sample.

TABLE III. RESULTS WITH SODIUM AZIDE

Interfering Ion	Mn Present	Mn Found
Mg./l.	Mg./l.	Mg./l.
300 Mo	3.00	3.00
600 Ti	6.00	6.12
800 V	8.00	7.80
500 Cr	5.00	4.94

ALTERNATIVE BLEACHING PROCEDURE. In the event that interfering metals are present in amounts such that the tolerance ratios are approached or exceeded, sodium azide can be used in lieu of hydrogen peroxide as the reducing agent. In this procedure a few milligrams of the solid sodium azide are added to the solution to be prepared for use as a blank.

The reduction is somewhat slower than in the case of the peroxide. The use of sodium azide, however, to produce a comparison blank gave results accurate to about 1 to 2 per cent, on the average, when used in solutions containing a hundredfold excess of interfering ion. Some typical results obtained by using this method are shown in Table III.

Chromium-Diphenyl Carbazide System

Cazeneuve (2) first suggested the use of diphenyl carbazide as a colorimetric reagent for chromium as a result of his study of the various colored metal compounds that diphenyl carbazide forms. The optics of this reaction were studied for a twofold reason. First, it is an example of the adaption of the technique of photoelectric photometry to an organic color-producing reagent; and secondly, the sensitivity of the method, or more strictly the high extinction coefficient of the chromium compound, indicates that the method is of microchemical significance. The analysis of microgram quantities of chromium by this method is therefore practical.

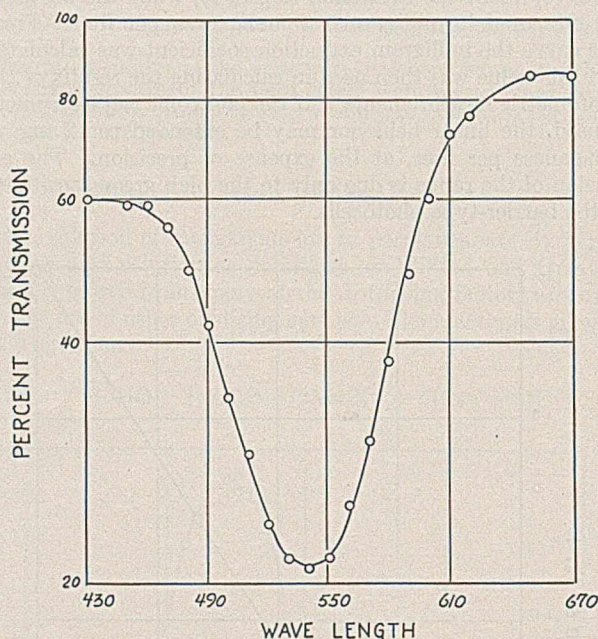


FIGURE 4. ABSORPTION SPECTRUM OF CHROMIUM-DIPHENYL CARBAZIDE COMPLEX

This color reaction has had wide application since its discovery. It has been used as an indicator in dichromate oxidimetry (1), as a qualitative reagent for chromium (4, 8), and as a reagent for chromium in a spectrographic analysis of tissue (3) based on the absorption spectrum of the colored compound.

When trial solutions were prepared using an acetic acid-alcohol solution of diphenyl carbazide as suggested by Cazeneuve (2), the color of the solution was slow in developing, full color being developed only after 20 minutes. A more serious disadvantage also was noted, in that the color so formed showed a tendency to fade. Qualitative experiments bore out Stover's conclusion that the presence of acetic acid was the disturbing factor. Further experiments indicated that acidification with sulfuric acid increased the color stability and brought about instantaneous development of full color. Furthermore, it was found that solutions acidified in this manner and containing mercury, copper, and ferric iron (the interfering metals mentioned by Cazeneuve) developed no color. For these reasons a saturated solution of diphenyl carbazide in 95 per cent ethyl alcohol was used as the color

reagent in the following experiments, and for each 100 cc. of dichromate solution (made approximately 0.1 molar with sulfuric acid) 1 cc. of this reagent was used. That the color stability is sufficient for accurate analysis under these conditions is shown in Table IV, the data covering the concentration range where Beer's law is valid for this system under the optical conditions indicated.

TABLE IV. USE OF DIPHENYL CARBAZIDE

Chromium Micrograms/l.	I/I_0 on Addition of Reagent	I/I_0 after 0.5 Hour	I/I_0 after 15 Hours
125	83.1	82.7	84.4
250	69.8	70.2	72.2
375	59.8	60.1	63.0
500	50.2	50.3	54.9
625	42.8	42.8	46.2

In order to determine the proper filter to use for photometry, the absorption spectrum of the chromium-diphenyl carbazide complex was determined using a 2.06×10^{-6} molar potassium dichromate solution which had been treated before final dilution in the manner previously described to develop the color. The compound was found to have a fairly broad absorption band in the green (Figure 4) as found by Dingwall, Crosen, and Beans (3). The molar extinction coefficient calculated on the basis of the molarity of the dichromate solution resulted in a value of 8.14×10^4 at 540 $m\mu$. From these data it is seen that the sextant green filter used in the permanganate studies should also be used in this case. Using this filter with the vacuum photocell vacuum-tube voltmeter colorimeter, the diphenyl carbazide-chromium system was found to conform to Beer's law in all concentra-

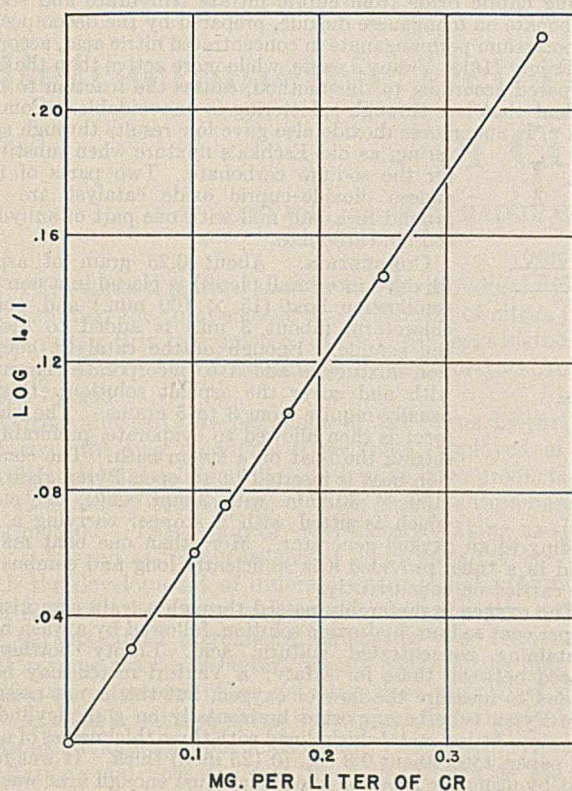


FIGURE 5

tions below 3.6×10^{-4} molar dichromate. This corresponds to a concentration of 375 micrograms of chromium per liter. The conformity of this system to Beer's law is shown graphically in Figure 5.

INTERFERENCE OF OTHER METALS. If for any reason the use of sulfuric acid is inadvisable and the sample to be ana-

lyzed is known to contain a high percentage of iron, is it possible to neglect the iron color under the conditions of photometry used in these experiments? Other investigators (3) measured the absorption spectrum of the iron compound and found that its maximum occurred at about 380 $m\mu$. From the transmission value read from their curve of the absorption spectrum (for a solution containing 100 mg. of ferric iron per liter, measured through a 2-cm. depth) the molar extinction coefficient at 460 $m\mu$ was calculated to be 5. The approximate cutoff of the sextant green filter is 460 $m\mu$. At 500 $m\mu$ the solution transmits 100 per cent of the incident light. Hence, interference due to iron may be neglected entirely when this green filter is used.

In addition to the interfering metals noted by Cazeneuve, molybdenum when present as molybdate in 0.1 molar sulfuric acid solution yields a violet colloidal suspension, its extinction coefficient being roughly 5×10^2 . Therefore with any ratio of molybdenum to chromium less than 10, results with an accuracy of 1 per cent may be obtained by neglecting any color due to molybdenum.

Summary

The periodate method of Willard and Greathouse for the colorimetric determination of manganese has been studied for the purpose of adapting it for use with a photoelectric colorimeter. Since the most convenient method of making the measurements is that of substitution photometry, a study of the optical properties of permanganate solutions with and without interfering ions has been made.

Two chemical methods of effecting optical separation of interfering ions have been developed in which the permanganate color is removed in an aliquot of the sample solution and this solution used to furnish the I_0 (100 per cent transmission) value.

Data of a confirmatory nature regarding the use of these optical separatory methods are shown.

An optical study of the diphenyl carbazide-dichromate system has been made.

Acknowledgment

The author is greatly indebted to Ralph H. Müller who suggested this work and under whose able direction it was carried out.

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TAKEN from a thesis submitted by George P. Rowland, Jr., in partial fulfillment of the requirements for the degree of doctor of philosophy at New York University.

Correction

In the article on "Determination of Tetraethyllead in Gasoline" [*IND. ENG. CHEM., Anal. Ed.*, 11, 324 (1939)] there is an error in the second sentence of the fifth paragraph under "Procedure." This sentence should read:

"To the dry lead chloride add 3 ml. of nitric acid."

CHARLES M. GAMBRILL

Determination of Total Sulfur in Asphalts

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YOUNG (22) recently applied the method of Brunck (6) to the determination of organic sulfur and stated that accuracy was obtainable even by the employment of relatively simple apparatus.

In 1923 the author became interested in the determination of sulfur in asphalt and other bitumens in connection with a study of the reaction of sulfur with free magnesia present in asbestos used in the manufacture of bituminous cold-molded compositions. As the bomb equipment was not available, it became necessary to seek and develop a simple and accurate method for determining sulfur in bitumens by utilizing inexpensive and readily available apparatus. Accordingly, a thorough search of the literature relating to the determination of sulfur in organic substances was made.

Methods Investigated

The methods of Falcicola (8), David and Fourcar (7), and Losana (17), as well as the alumino-thermite procedure (2, 3) and a method depending on the oxidation of sulfur vapor from the volatilized asphalt by passing with air through highly heated alundum (13), were thoroughly investigated; for various reasons it was found necessary to discard all of these. A method of combustion developed by Brunck (5) and Marderna (18) proved to be the most promising.

Development of Method

A detailed study of the catalytic method discussed by Brunck, involving the preparation of nickel sesquioxide and cobalt sesquioxide by various procedures, including activation, was made. Combustion behavior was also carefully investigated.

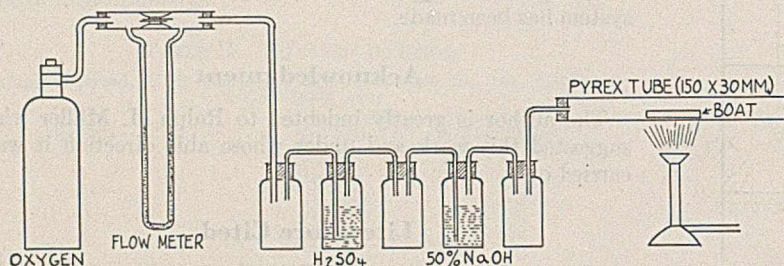


DIAGRAM OF APPARATUS

It was observed, however, that sulfides persistently formed with these oxides—probably nickel sulfide, cobalt sulfide, and some sodium sulfide. Because of the insolubility of nickel and cobalt sulfides, a loss resulted. Activation by the presence of a rare metal was ineffective. It was found impossible to oxidize these sulfides by digesting with water containing the common oxidizing agents (such as bromine and hydrogen peroxide). Commercial oxides, as purchased, proved unsatisfactory and were discarded.

In view of the strong oxidizing activity of a mixture of 60 parts of manganese dioxide and 40 parts of cupric oxide, which has been described in the literature (1, 4, 9-11, 15, 16, 19-21), its possible use as a catalyst in this case was investigated. Numerous trials were made with this catalyst and in none of the large number of determinations was the formation of sulfides detected. Also, the results agree closely with the sulfur content as determined by the bomb method. This is clearly evident from an examination of Table I.

TABLE I. DETERMINATION OF SULFUR IN ASPHALTS

	Sample 2173-24-A	Sample 2173-24-B	Sample 2173-24-C
S by bomb method, %	5.62, 5.80	3.27, 3.50	0.93, 1.01
S by method described, %	5.92, 5.75	3.48, 3.53	1.01, 1.01
	5.87, 5.94	3.53, 3.48	0.98, 0.98
	5.83, 5.84
	5.58, 5.67
	5.90, 5.88
	5.78, 5.90
	5.86, 5.96

Method of Determining Total Sulfur in Asphalts

Based on the results of the investigation as outlined above, the following procedure was finally devised.

PREPARATION OF THE CATALYST. Manganese chloride tetrahydrate (411 grams) is dissolved in 500 ml. of water; to this is added a solution of 255 grams of cupric chloride dihydrate in 400 ml. of water. The solutions are thoroughly mixed, warmed, and stirred. A solution of 500 grams of potassium hydroxide in 500 ml. of water is then added drop by drop, stirred with uniformity, washed by decantation several times, filtered on a Büchner funnel, and washed free of alkali and chlorides. The mixed oxides are then dried in the steam bath overnight and finally at 200° to 225° C. until all the moisture has been driven off.

No advantage is gained by preparing this catalyst by precipitating cupric oxide from cupric nitrate trihydrate and sodium carbonate on manganese dioxide, prepared by the decomposition of potassium permanganate in concentrated nitric acid, according to Frémy (12). Frémy's oxide, while more active than the oxide prepared according to this method, causes the reaction to be so violent that loss through splattering is unavoidable. Commercial c. p. manganese dioxide also gave low results through splattering, as did Eschka's mixture when substituted for the sodium carbonate. Two parts of manganese dioxide-cupric oxide catalyst are then ground in a ball mill with one part of anhydrous sodium carbonate.

COMBUSTION. About 0.25 gram of asphalt (divided into small pieces) is placed in a porcelain combustion boat (15 × 100 mm.) and enough chloroform (about 3 ml.) is added to dissolve the sample. Enough of the catalytic combustion mixture is added to incorporate thoroughly with and cover the asphalt solution; this will usually require from 3 to 5 grams. The chloroform is then allowed to evaporate, preferably by setting the boat on a steam bath. The combustion boat is inserted in an open Pyrex glass tube (150 × 30 mm. with 2-mm. wall), one end of which is fitted with a stopper carrying a tube leading to an oxygen generator. More than one boat may be used in a tube, provided it is sufficiently long and combustions are carried on concurrently.

The oxygen is preferably passed through a train comprising a 50 per cent sodium hydroxide solution, followed by a wash bottle containing concentrated sulfuric acid. Empty bottles are placed between these for safety; a Venturi meter may be included to measure the flow of oxygen, but this is not essential. The Pyrex tube is supported horizontally on a semicylindrical and close-fitting metal shield lined with three thicknesses of asbestos paper, total about 0.3 cm. (0.125 inch) thick. It was found that by using the asbestos lined shield just enough heat was conducted for a smooth quiet combustion. The heat is insufficient to cause fusion between the glass and porcelain; thus the life of the Pyrex tube is greatly prolonged.

The oxygen is passed through the tube in a fairly rapid stream, about 10 ml. per second, and the tube is heated, at the zone where the boat is located, with a fishtail burner with a low flame at the start. When the combustion starts, as evidenced by the glowing of the asphalt-catalyst mixture, the flame is removed until the glowing ceases. To ensure complete oxidation, the tube is again heated for about one minute over a full flame. The oxy-

gen is then shut off and the tube and boat are allowed to cool. When cool, the boat and contents are digested with boiling water, filtered through double ordinary filter paper, and washed with boiling water (containing 1 to 2 per cent of sodium carbonate in order to prevent turbid washings due to carrying through of colloidal matter, 14). The filtrate is then made acid to Congo red with hydrochloric acid and refiltered on quantitative filter paper. A double filtration is desirable in order to free the filtrate completely from any colloidal matter that may have been carried through in the first filtration; quantitative paper is desirable. On the basis of a study of 26 determinations of the residue left on the filter in the second filtration, an average result of 0.0017 gram was obtained, which is too large to be neglected. The sulfates are precipitated in the filtrate with barium chloride according to standard practice. Blank determinations for sulfur content of the catalytic combustion mixture should be made and corrections applied.

Conclusion

This modification of Brunck's method for sulfur determination, as applied to bitumens and asphalts, gives results concordant with the bomb method, and uses simple and readily available equipment. This modified method has been found entirely satisfactory.

Acknowledgment

This work was performed during the years 1923 to 1927 in the laboratory of the Garfield Manufacturing Company, Garfield, N. J. Acknowledgment is gladly made to all who assisted in this work, and particularly to L. S. Miller of the Barber Asphalt Company, who furnished the asphalts.

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Refractometric Determination of Soluble Solids in Citrus Juices

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THE standard method used in the citrus industry for estimating the total soluble solids content of citrus juices employs the Brix hydrometer. This is the legal method for testing maturity, by determining the ratio of total soluble solids to acid.

During the early development of the citrus by-products industry, the Brix spindle was generally employed in estimating the total soluble solids content of juice products, and the standards of composition of these products were based on this method. This was fairly satisfactory so long as simple products such as reamer-extracted juices were involved, but with the development of different types of natural-strength and concentrated juices and compounded products containing various added ingredients, difficulties were encountered and in some cases satisfactory results could not be obtained.

The refractometer offers an alternative method of determining soluble solids in citrus juice. In spite of a number of obvious advantages, this is also subject to certain errors and limitations and does not give the same results as the Brix spindle.

A number of factors are involved in the use of both methods. The Brix spindle method is based on changes in density of aqueous sucrose solutions with changes in the sucrose content. Actually, solutions of sugars other than sucrose have densities so near those of sucrose solutions that the Brix hydrometer may be considered accurate in them. Soluble materials other than sugars have variable and in most cases unknown effects on the Brix readings.

In the measurement of degrees Brix it is necessary, for best results, first to check the calibrations of the hydrometer, since many of those on the market are not accurately calibrated. The spindle should be thoroughly clean and dry. Measurements should be made in regulation hydrometer cylinders filled level with the ground-glass rim. The sample is preferably deaerated. In the case of finely screened, dilute juices this may not be necessary if the hydrometer is twirled to detach air bubbles as it is lowered into the liquid. A highly concentrated juice must be deaerated, and even then, if it is thick or viscous because of high soluble or insoluble solids or pectin, much time is required for the hydrometer to assume the equilibrium position. The sluggishness caused by excessive viscosity may result in serious error. Such difficulties may be partially eliminated by use of the dilution method, but this procedure has obvious objections in routine testing. Finally, the temperature should be close to the standard of 20°C., since the usual temperature corrections do not apply equally to sugar and nonsugar solids.

Similar precautions are necessary in the use of the refractometer. The prisms must be perfectly clean to be evenly wet by the solution under test and must be perfectly dry to prevent dilution of the test solution. Screening and deaeration of the sample improve the sharpness of the shadow and thereby enhance the precision and accuracy. For accurate results the readings should be made at 20°C. The errors introduced in applying temperature corrections are similar to those occurring with the Brix spindle.

The refractometer, used either with the sucrose scale or the regular refractive index scale and sugar table, and the Brix spindle should give identical results with pure sucrose solutions. Other solutes do not have the same effects as sucrose, however, and consequently when the two methods

are applied to complex solutions, such as citrus juices, different results are obtained.

In adapting the refractometer to various fruit juice products, several workers have recognized that its use is complicated by the diverse compositions of these products. Macara (2) recognized that errors are caused by citric acid, glucose solids, and invert sugar and gave data for applying corrections for these components. McRoberts (3) did a large amount of work on the determination of soluble solids in fruit products and showed that the refractometer is satisfactory for the purpose. He also obtained data by which corrections for citric or tartaric acid might be made.

The authors' work with citrus juices, involving analysis by the two methods of numerous samples of citrus juices and juice products and of prepared solutions of the different juice constituents, has indicated that the Brix spindle gives high values and that the refractometer gives low results. The constituents of citrus juices known to be important in this respect are citric acid, invert sugar, ash, insoluble solids, and essential oils. Since several factors are involved, the relation of the results obtained by the two methods is changed by natural variation in composition among different products. The greatest single variation is caused by citric acid and, consequently, the greatest difference between refractometer and Brix spindle values appears with highly acid products such as lemon juice, concentrated citrus juices, and certain types of beverage bases.

Because this error may amount to several per cent, it is necessary to apply some form of correction if the refractometer is to be used for routine analysis. There is some question as to whether this correction should be applied to give true soluble solids or degrees Brix, but since the use of the hydrometer method is well established, it appears desirable to correct to degrees Brix.

The over-all corrections to make refractometer sucrose scale values comparable with Brix values may be made in at least three ways: (1) by applying separate corrections for each of the above factors, determined on synthetic mixtures; (2) by applying empirical corrections determined for a large number of representative products with some constituent such as citric acid as an index of the magnitude of the correction; or (3) by applying a correction for citric acid only, this being the greatest single factor.

When these three methods and modifications of them were considered, it became obvious that none would be entirely

satisfactory because of the wide natural variation in composition of citrus juices. Method 1 would necessitate a fairly complete analysis of every sample before the correct solids could be ascertained and this would defeat the very purpose of the use of the refractometer. Methods 2 and 3 have been used experimentally, applying corrections based on data obtained on a large number of samples of orange, lemon, and grapefruit juices of different types and on synthetic solutions of sugar and citric acid. The corrections were used in both tabular and nomographic forms. This experience led the authors to adopt method 3 as tabulated herein for all routine work with citrus juice products, other than maturity testing.

Procedure and Data

In obtaining data for correction tables a number of solutions of pure citric acid were prepared and the soluble solids, as sucrose, of the solutions were determined with the refractometer and the Brix spindle.

The citric acid was prepared by recrystallization of the ordinary U. S. P. grade of acid (from lemons). The acid was recrystallized four times from water by vacuum concentration in Pyrex glass apparatus at about 35° C. The final crystals, after being rinsed with cold water and drained as free of liquor as possible by suction, were dried to about 3.5 per cent moisture at about 40° C.

Solutions of different strengths, as shown in Table I, were prepared from this recrystallized acid with boiled, carbon dioxide-free distilled water. The strength of these solutions in terms of anhydrous citric acid by weight was determined by titration with 0.1 N sodium hydroxide solution which had been standardized with National Bureau of Standards benzoic acid according to directions furnished with the acid.

In making these analyses, a portion of the acid solution containing approximately 1.64 grams of anhydrous acid was weighed in a weighing bottle on the analytical balance, transferred to a 500-ml. volumetric flask, and diluted to the mark with boiled distilled water. Several 50-ml. aliquots of this final solution were titrated in 150-ml. Erlenmeyer flasks with 0.1002 N sodium hydroxide solution, using 3 drops of neutralized 1 per cent phenolphthalein solution as the indicator. About 25.5 ml. of sodium hydroxide solution were required to neutralize each portion.

As a further check, duplicate 1.64-gram portions of the citric acid dried to constant weight under vacuum at 60° C. were weighed out and made into 500 ml. of solution as described above. Portions of these solutions were titrated as above and it so happened that the average of the two determinations gave the exact theoretical value. (The error of a single determination was indicated as not greater than 1 in the third decimal place.)

The refractometer (Zeiss Abbe type with refractive index and sucrose scales) and the Brix spindles used in determining the soluble solids of the citric acid solutions were checked for accuracy. Boiled distilled water and solutions of highly purified moisture-free sucrose of 1, 5, 10, 20, and 30 per cent theoretical strength, respectively, were used in checking the refractometer. The Brix spindles were checked with solutions of pure sucrose at points on the scale coinciding very closely with those used with the citric acid solutions. These readings were made at 20° C. with the room temperature approximately the same.

Each of 24 citric acid solutions, varying in strength from 0.545 to 30.07 per cent, was checked with the refractometer and Brix spindle with results as shown in Table I. At least five readings were made on each of three or more portions, on two or more different days, with the refractometer, at 20° C. Duplicate checks of five readings each were made with the Brix spindle also at 20° C. The room temperature was 19° to 22° C. when most of the determinations were made.

The refractive indices were recorded to the nearest fourth decimal as indicated by the average reading. The sucrose values, based on Schonrock's data (1), were recorded as indicated by the average. The Brix values shown are the average of the different readings.

The values of Table I were plotted on a large-scale graph (20 mm. = 1 per cent on each ordinate) to obtain data for preparing a correction table. In the case of the refractometer data,

TABLE I. RELATIONSHIP OF TOTAL SOLIDS, REFRACTIVE INDEX, AND ° BRIX OF PURE CITRIC ACID SOLUTIONS

Anhydrous Citric Acid by Titration %	Refractive Index, 20° C.	Soluble Solids as Sucrose (1) %	° Brix, 20° C., by Hydrometer
0.000	1.3330	0.00	0.00
0.545	1.3337	0.48	0.61
1.007	1.3343	0.90	1.09
2.010	1.3355	1.77	2.17
3.021	1.3369	2.68	3.26
4.002	1.3381	3.52	4.32
4.904	1.3393	4.33	5.27
4.995	1.3394	4.42	5.38
5.805	1.3405	5.10	6.23
7.055	1.3421	6.20	7.27
7.701	1.3430	6.80	8.27
9.011	1.3447	7.92	9.63
9.674	1.3456	8.50	10.35
9.981	1.3460	8.76	10.67
10.96	1.3473	9.62	11.75
11.95	1.3487	10.50	12.75
13.42	1.3506	11.77	13.75
14.92	1.3527	13.10	15.90
18.19	1.3573	15.97	19.34
19.87	1.3596	17.40	20.75
22.08	1.3628	19.33	23.40
24.04	1.3656	21.06	24.75
25.94	1.3684	22.72	27.46
27.05	1.3701	23.68	28.75
30.07	1.3746	26.34	31.78

TABLE II. CORRECTIONS FOR OBTAINING ° BRIX OR ACTUAL SOLUBLE SOLIDS FROM REFRACTOMETER READINGS

(Based on citric acid content of citrus juices or other acid-containing sugar solutions)

Citric Acid, Anhydrous, % by Weight	Correction to Be Added to Refractometer Sucrose Value		Citric Acid, Anhydrous, % by Weight	Correction to Be Added to Refractometer Sucrose Value		Citric Acid Anhydrous, % by Weight	Correction to Be Added to Refractometer Sucrose Value	
	To obtain ° Brix	To obtain true soluble solids		To obtain ° Brix	To obtain true soluble solids		To obtain ° Brix	To obtain true soluble solids
0.0	0.00	0.00	11.0	2.10	1.33	22.0	4.05	2.73
0.2	0.04	0.02	11.2	2.14	1.36	22.2	4.09	2.75
0.4	0.08	0.04	11.4	2.18	1.38	22.4	4.13	2.77
0.6	0.12	0.06	11.6	2.21	1.40	22.6	4.17	2.79
0.8	0.16	0.08	11.8	2.24	1.43	22.8	4.20	2.81
1.0	0.20	0.11	12.0	2.27	1.46	23.0	4.24	2.84
1.2	0.24	0.13	12.2	2.31	1.49	23.2	4.27	2.87
1.4	0.28	0.16	12.4	2.35	1.51	23.4	4.30	2.89
1.6	0.32	0.18	12.6	2.39	1.54	23.6	4.34	2.92
1.8	0.36	0.21	12.8	2.42	1.56	23.8	4.38	2.95
2.0	0.39	0.23	13.0	2.46	1.59	24.0	4.41	2.97
2.2	0.43	0.26	13.2	2.50	1.61	24.2	4.44	2.99
2.4	0.47	0.29	13.4	2.54	1.64	24.4	4.48	3.02
2.6	0.51	0.31	13.6	2.57	1.67	24.6	4.51	3.04
2.8	0.54	0.33	13.8	2.61	1.70	24.8	4.54	3.07
3.0	0.58	0.35	14.0	2.64	1.72	25.0	4.58	3.10
3.2	0.62	0.38	14.2	2.68	1.74	25.2	4.62	3.13
3.4	0.66	0.40	14.4	2.72	1.76	25.4	4.66	3.15
3.6	0.70	0.42	14.6	2.75	1.79	25.6	4.69	3.18
3.8	0.74	0.45	14.8	2.78	1.81	25.8	4.73	3.20
4.0	0.78	0.47	15.0	2.81	1.84	26.0	4.76	3.23
4.2	0.81	0.49	15.2	2.85	1.86	26.2	4.79	3.25
4.4	0.85	0.52	15.4	2.89	1.89	26.4	4.83	3.28
4.6	0.89	0.54	15.6	2.93	1.92	26.6	4.86	3.30
4.8	0.93	0.56	15.8	2.97	1.95	26.8	4.90	3.33
5.0	0.97	0.59	16.0	3.00	1.97	27.0	4.94	3.35
5.2	1.01	0.62	16.2	3.03	1.99	27.2	4.97	3.38
5.4	1.04	0.64	16.4	3.06	2.02	27.4	5.00	3.40
5.6	1.07	0.66	16.6	3.09	2.04	27.6	5.03	3.43
5.8	1.11	0.69	16.8	3.13	2.07	27.8	5.06	3.45
6.0	1.15	0.71	17.0	3.17	2.10	28.0	5.10	3.48
6.2	1.19	0.73	17.2	3.21	2.13	28.2	5.14	3.50
6.4	1.23	0.76	17.4	3.24	2.16	28.4	5.18	3.53
6.6	1.27	0.78	17.6	3.27	2.18	28.6	5.22	3.55
6.8	1.30	0.81	17.8	3.31	2.21	28.8	5.25	3.58
7.0	1.34	0.84	18.0	3.35	2.23	29.0	5.28	3.60
7.2	1.38	0.86	18.2	3.38	2.25	29.2	5.31	3.63
7.4	1.42	0.88	18.4	3.42	2.27	29.4	5.35	3.66
7.6	1.46	0.91	18.6	3.46	2.30	29.6	5.39	3.69
7.8	1.50	0.94	18.8	3.49	2.33	29.8	5.42	3.71
8.0	1.54	0.96	19.0	3.53	2.35	30.0	5.46	3.73
8.2	1.58	0.98	19.2	3.56	2.37	30.2	5.49	3.76
8.4	1.62	1.01	19.4	3.59	2.40			
8.6	1.66	1.03	19.6	3.63	2.43			
8.8	1.69	1.05	19.8	3.67	2.45			
9.0	1.72	1.08	20.0	3.70	2.47			
9.2	1.76	1.11	20.2	3.73	2.49			
9.4	1.80	1.13	20.4	3.77	2.52			
9.6	1.83	1.16	20.6	3.80	2.54			
9.8	1.87	1.18	20.8	3.84	2.56			
10.0	1.91	1.21	21.0	3.88	2.59			
10.2	1.95	1.24	21.2	3.91	2.62			
10.4	1.99	1.26	21.4	3.95	2.64			
10.6	2.03	1.28	21.6	3.99	2.67			
10.8	2.06	1.30	21.8	4.02	2.70			

the true per cent of anhydrous citric acid, as shown by titration, was plotted as ordinate against the corresponding refractometer sucrose value as abscissa. This resulted in practically a straight line and was plotted as such. The acid-degrees Brix relationship plotted in a similar manner gave a slight curve, bending upward. A 45° angle straight line was drawn to represent true or theoretical per cent of solids. This line fell between the other two but was nearer that of degrees Brix.

The data of Table II were obtained from this graph. This shows for each per cent of citric acid by titration the correction to be added to the corresponding refractometer sucrose scale reading to obtain the proper Brix value. Table II also includes a column of data for correcting refractometer sucrose scale values to true soluble solids or, in the case of pure acid solutions, the true per cent of acid, as would be shown by titration.

Discussion

The use of the correction data of Table II is simple.

For example, a sample of lemon juice, containing 5.60 per cent of anhydrous citric acid by titration, may give a refractometer

sucrose scale or sucrose table value of 8.20. By referring to the table the correction to be added for 5.60 per cent acid is found to be 1.07, when it is desired to correct the refractometer reading to degrees Brix. The approximate Brix value of the juice is, thus, 8.20 + 1.07 or 9.27. If it is desired to correct the refractometer reading to true per cent of soluble solids, the correction is 0.66 and the final corrected value becomes 8.20 + 0.66 or 8.86.

Table II may also be used to correct Brix readings to true solids when the acid content is known by subtracting the corresponding correction in the second column and adding that in the third column.

Tests made with solutions containing both citric acid and sucrose verified the corrections for acid shown in Table II.

In general the corrected refractometer sucrose values on citrus juices are slightly lower than the corresponding Brix spindle values.

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Change in Solvency during Evaporation of Thinners

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A rapid film evaporator for "mineral spirits" and related naphthas permits the measurement of change in solvency of hydrocarbon thinner blends as 100 ml. are evaporated in the form of a film during less than 3 hours at room temperature.

OLEORESINOUS protective coatings are frequently cut hot with a high-solvency naphtha and later thinned with a material of considerably lower solvency—e. g., "mineral spirits." When a difficultly soluble resin forms a part of the coating, it is important that solvency should not fall away too rapidly during application and setting. Maintenance of solvency during evaporation also makes possible a better leveling of the film and generally improves the physical characteristics of the coating.

An apparatus has been devised wherein 100 ml. of a thinner or a mixture of thinners, which boil within or near the mineral spirits boiling range, can be evaporated in less than 3 hours, at room temperature, and as a film. Characteristics of the evaporation differ from those accompanying actual coating application in two respects—viz., the film is in motion, and no nonvolatile component is present.

A number of evaporation methods whereby changes in solvency during evaporation can be determined have been described (1, 4, 6-8). Most were designed to deal with lacquer thinners, and have provided for evaporation and sampling from pools of liquid contained in a beaker, paint-can cover, or crystallizing dish. When comparatively high-

boiling materials, such as mineral spirits, are evaporated from pools in sufficient quantity for sampling during the progress of the evaporation, too much time is required. Further, it seems reasonable that evaporation as a film should more nearly simulate actual conditions than evaporation from a pool, in some cases inches deep.

During the setting and drying of a protective coating film the effect of solvent retention occurs. Dorsch and Stewart (3)

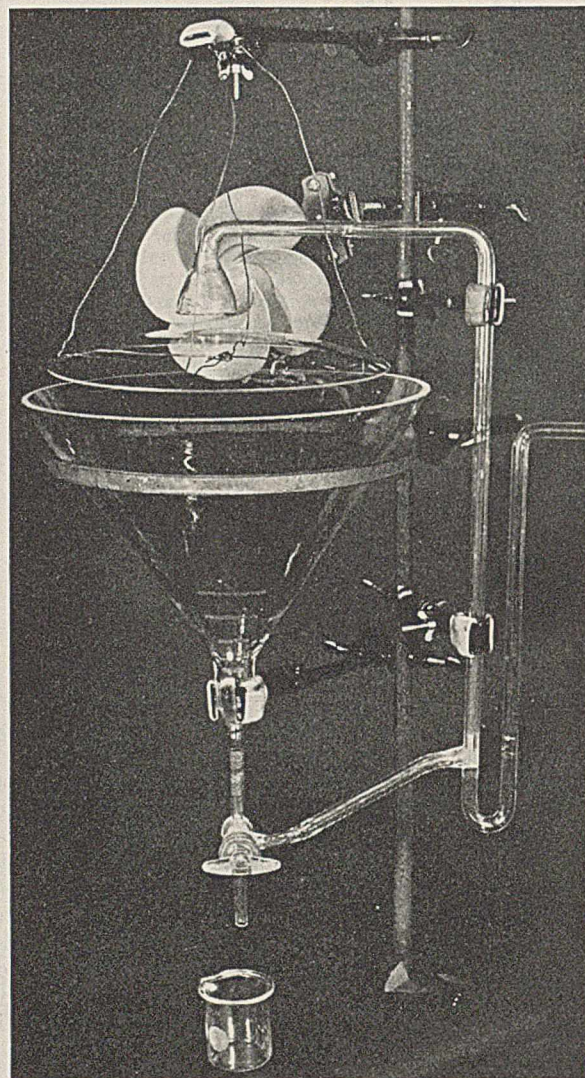


FIGURE 2. APPARATUS

have shown that the retention of hydrocarbons by nitrocellulose films differs from retention of esters and alcohols of the same evaporation rate. For most oleoresinous and synthetic resinous coatings, however, hydrocarbons alone are employed as thinners, and thus the error introduced by the total absence of nonvolatile vehicle may be assumed to be fairly constant and of lower magnitude in the case of mineral spirits than with lacquer volatiles.

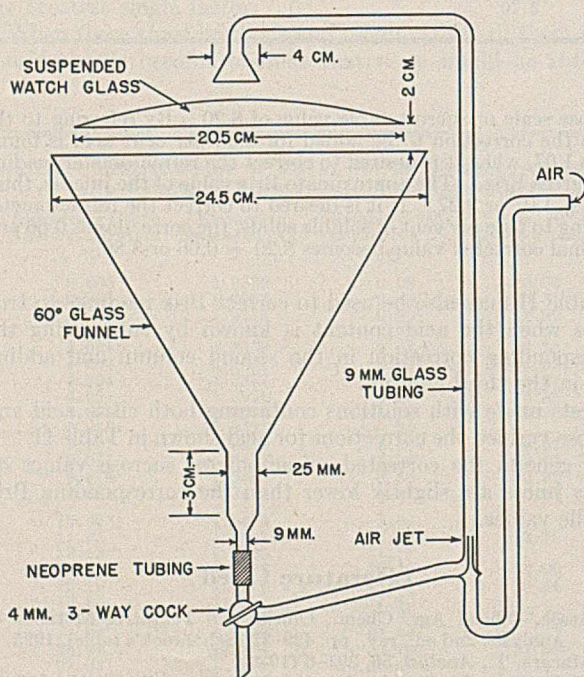


FIGURE 1. SOLVENT FILM EVAPORATOR

Estimation of Solvency

A convenient method of determining solvency as the thinner evaporates is to abstract small samples (1 ml.) after one half, three quarters, and seven eighths are off, and take the aniline points. Aniline point is so generally accepted as a measure of solvency of a hydrocarbon thinner of a given boiling range that several large producers and consumers of naphthas use it as a specification solvency test. It requires neither temperature control nor costly equipment.

To abstract three 1-ml. samples, and yet not greatly upset the composition of the fractions, it is desirable to evaporate 100 ml. of naphtha.

Since most oleoresinous or resinous coatings retain considerable thinner after reaching their set point (2), no measurements of a residual portion less than one eighth were taken.

Precision of Method

The precision attainable in the apparatus was originally tested by making two runs with the same thinner mixture under different conditions. Run 1 was made with 200 ml. during 207 minutes for seven eighths evaporated, and in a steam-heated room without other temperature or humidity control. Run 2, and subsequent runs detailed below, were made with 100 ml., in about half the time (112 minutes for seven eighths evaporated in run 2), in a room maintained at 25° C. and 50 per cent relative humidity. That time and temperature, within fairly narrow limits, were not factors affecting the operation of the apparatus is indicated in Table I. Thinner mixture, of 31.4° C. aniline point, was blended from two volumes of Stoddard solvent and one volume of No. 2 aromatic naphtha (Table III).

The rate of evaporation is not considered. The method is limited to the determination of change in solvency during evaporation at a speed of the same order of magnitude as that encountered in the setting of oleoresinous varnishes and enamels.

TABLE I. ANILINE POINTS

	Last Half ° C.	Last Quarter ° C.	Last Eighth ° C.
Run 1	47.2	55.5	61.0
Run 2	47.6	55.8	61.0

Apparatus

It may be found convenient to modify the apparatus (Figures 1 and 2), but the present setup is quickly assembled, sufficiently rapid for most purposes, and automatic. The small glass-sealed air jet may be replaced by a Neoprene-connected T-tube arrangement. The funnel need not necessarily be of glass, although liquid level reading is thus facilitated. The flared overhead discharge tube should be large enough, and close enough to the watch glass, to prevent spattering as the bubbles break. The fan should be

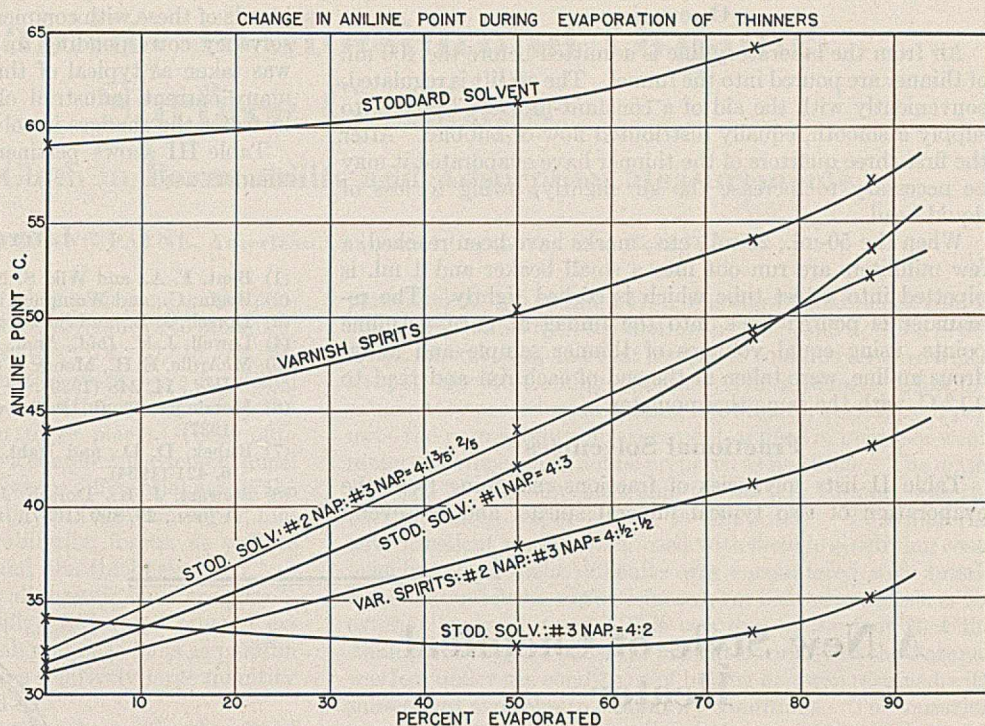


FIGURE 3

TABLE II. ANILINE POINTS

Thinner or Blend	Original ° C.	Last Half ° C.	Last Quarter ° C.	Last Eighth ° C.
Stoddard solvent	58.0	61.3	64.2	66.0
Varnish spirits	44.0	50.4	54.0	57.2
Stoddard solvent, 4 volumes No. 1 naphtha, 3 volumes	31.6	42.0	48.9	53.7
Stoddard solvent, 4 volumes No. 3 naphtha, 2 volumes	34.0	32.6	33.3	35.1
Stoddard solvent, 4 volumes No. 2 naphtha, 1.6 volumes	32.4	44.0	49.0	52.2
Varnish spirits, 4 volumes No. 2 naphtha, 0.5 volume	31.4	37.9	41.1	43.2
No. 3 naphtha, 0.5 volume				

TABLE III. INSPECTIONS

	Stoddard Solvent	Varnish Spirits	Aromatic Naphtha		
			No. 1	No. 2	No. 3
Gravity, ° A. P. I.	49.4	45.6	35.9	33.6	29.8
Specific gravity	0.782	0.799	0.845	0.857	0.877
Initial boiling point, ° C.	155	154	133	131	175
5% off	162	159	142	137	178
10%	163	161	143	139	180
50%	172	170	152	147	186
90%	192	185	171	163	197
95%	201	191	177	169	202
Dry point	208	202	183	176	210
Final boiling point, ° C.	210	202	184	177	210
Tag closed-cup flash, ° C.	41	41	28	29	55
Mixed aniline point, ° C. ^a	28.0	17.6	22.4
Aromatics, %	73.5	91.8	89.2

^a A control test now run in several laboratories, measuring the critical solution temperature of a mixture of 10 ml. of anhydrous aniline, 5 ml. of sample, and 5 ml. of any naphtha whose aniline point is 60° C.

^b As determined by method of Philadelphia Paint and Varnish Production Club (5).

of such power and distance from the apparatus (20 cm. in the present instance) that no droplets of liquid are carried away. An air current which requires only a 2° or 3° tilt of the watch glass toward the fan for equal film distribution over the surface appears to be satisfactory. The lower speed of a conventional rubber-bladed automobile defrosting fan is used in this laboratory. Air current should be directed underneath the watch glass, to scavenge vapors inside the funnel, as well as above.

The funnel is graduated, with the fan shut off, while the air lift is in operation. Liquid holdup of the apparatus as shown amounts to 9.5 ml.

Operation

Air from the laboratory line is admitted before the 100 ml. of thinner are poured into the funnel. The air lift is regulated, conveniently with the aid of a constant-pressure by-pass, to supply a smooth, equally distributed flow of bubbles. After the first three quarters of the thinner have evaporated it may be necessary to increase the air slightly, owing to loss of liquid head.

When the 50-ml., 25-ml., etc., marks have been reached, a few milliliters are run out into a small beaker and 1 ml. is pipetted into a test tube which is corked tightly. The remainder is poured back into the funnel at once. Aniline points, using equal volumes of thinner sample and anhydrous aniline, were taken at the end of each run and read to 0.1° C. with the same thermometer.

Fractional Solvencies

Table II lists solvencies of fractions remaining from the evaporation of two typical mineral spirits, and of several

blends of these with commercial high-solvency naphthas. The solvency corresponding to an aniline point of about 32° C. was taken as typical of that of the total thinner present in many current industrial oleoresinous finishes. Figure 3 illustrates the changes in solvencies.

Table III shows pertinent inspections of the commercial thinners used.

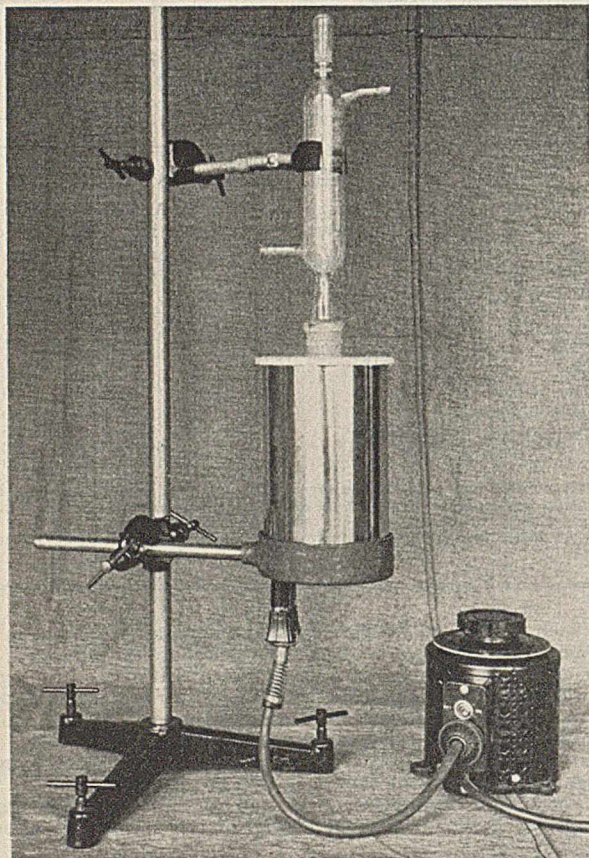
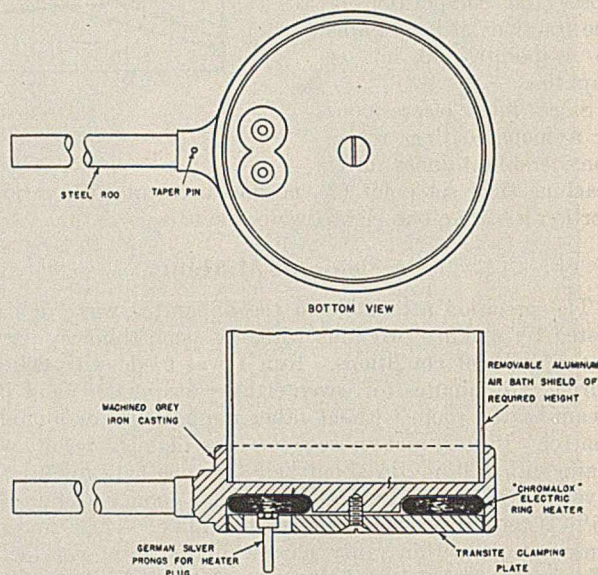
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A New Style of Chemical Heater

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A NEW style of electric heater, developed several years ago by the Research Bureau of the Consolidated Edison Company, has proved very satisfactory in severe chemical laboratory service. It may be used as an ordinary hot plate or as an "air bath" when provided with a removable heat-reflecting jacket. In the latter form, shown in the photograph,



it is an excellent substitute for water, oil, or glycerol baths with the added advantage of eliminating liquids. Under ordinary conditions the air-bath temperature may be maintained within a few degrees by means of a rheostat, transformer, or thermostat. In a draft-free location or by the use of a double jacket, regulation within a fraction of a degree is possible. It is exceptionally rugged and to date no trouble has been experienced from corrosion so frequently encountered in chemical heaters.

Various sizes may be made using stock heating units. The diagram shows the construction of a good general-purpose heater built around a 500-watt Chromalox A-20 ring unit. This type of unit is inherently resistant to corrosion and is further protected from spilled chemicals by the lip around the bottom of the casting and the transite clamping plate which holds it in intimate contact with the casting. Prongs of nickel silver are substituted for the wire-holding nuts on the unit, care being taken not to disturb the nuts next to the sheath. The holding rod is 18-8 stainless steel 0.5 inch in diameter and the jacket is anodized 2S aluminum alloy tubing of 4-inch diameter.

Permeability to Moisture of Organic Surface Coatings

Use of Glass Cloth in Permeability and Adsorption Measurements

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A GREAT deal of excellent work has been done on the permeability of various films and coated fabrics to moisture, organic liquids, and several gases (3-7, 12, 13, 15, 19, 22, 23, 31). The data obtained from this work have furnished considerable evidence in support of the theory regarding the mechanism by which permeation takes place. These data have shown the phenomenon to be a complex physico-chemical process, affected by the vapor pressure differential across the film, the relative polarity and solubility of film and vapor, film structure and its resistance to imbibition forces, as well as the physical dimensions of area and film thickness.

The data have also shown that all organic films are permeable to moisture. The permeability will vary from an extremely small amount through such nonpolar films as paraffin wax and rubber (20, 21, 29, 30) to a relatively large quantity through such a film as raw linseed oil.

In general, the moisture adsorption of a coating is related to its permeability, but there are many exceptions to this. For example, a short oil-limed rosin varnish will have a high moisture adsorption but a fairly low permeability, but the most striking contrast may be found in shellac which has a very high moisture adsorption and surprisingly low permeability (8, 9, 20, 21). These variations in permeability and moisture adsorption, together with the demand for high water resistance in surface coatings, have made necessary more precise methods for measuring the water sensitivity of a coating under all possible conditions. This has resulted in a technique which will measure the time required for moisture to permeate a film—the actual amount of water which will pass through a film under specified conditions, and the amount of water which will be adsorbed by the film.

Specific methods are available for certain industries, types of film, or materials to be coated. For example, the time required for electrical breakdown of a film under constant potential and varying humidity conditions is taken as a measure of the permeability of the film in the electrical insulating industry (1, 11). The Forest Products method (2) uses the time rate of increase in weight of coated wooden panels subjected to specific humidity conditions to indicate the permeability of the coatings to moisture. A method which has a much more general applicability is the Gardner jar method or one of its many modifications as used by Muckenfuss (16), Gettens (10), Payne and Gardner (21), the New Jersey Zinc Co. (14), the Bell Telephone Laboratories (29, 30), the New York Paint and Varnish Production Club (17), and many others.

At the convention of the Federation of Paint and Varnish Production Clubs in Cincinnati in 1937 the New York club proposed a standard method for permeability measurement. The method measures the rate at which moisture will pass through a film under specific conditions of vapor pressure differential, temperature, and area of film. Using a specially designed metal cup, known as the Payne

permeability cup (Figure 1), it was shown that check results could be obtained with this method by operators working in different laboratories, and that a support could be used on which to apply the film-forming material. This avoids the rather unsatisfactory procedure of making free films for testing, and permits the permeability measurement of films of brittle or weak materials which could not be prepared as free films. The material used by the New York club for the film support was the parchmentized paper known as "Patapar." This material gave excellent results when used with flexible air-drying coatings, but some slight difficulty was encountered with brittle materials and it was not satisfactory for baking materials or for exterior exposure tests. This was due to the fact that the small percentage of moisture present normally in the Patapar was lost under the conditions of baking and was regained with subsequent exposure to laboratory conditions. The variation in moisture content produced variation in volume of the Patapar with consequent distortion of the film it was supporting.

The purpose of the present paper is to show that a fine grade of glass cloth may be used as the support for films intended for permeability and adsorption measurements. This support does not change in volume in contact with moisture, and it may be used satisfactorily at the baking temperatures required in the surface coating industry.

Glass Cloth

The glass cloth used was obtained from the Owens-Corning Fibreglas Corp., Toledo, Ohio, and is known as Fibreglas Cloth No. 01-175. It is described as follows:

Specific gravity, 2.60 ounces per square yard
Thickness, 0.003 inch
Thread size, warp 900-2/2, filling 900-1/2
Number of threads per inch, warp 60, filling 64

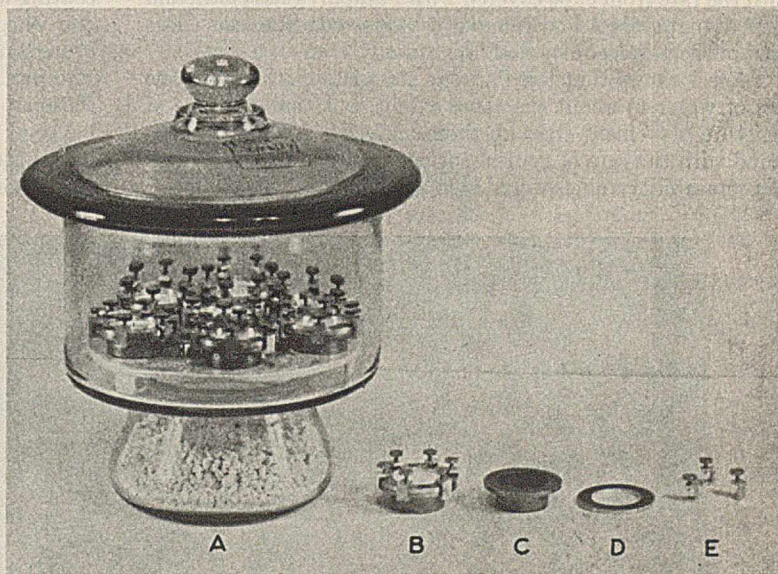


FIGURE 1. PERMEABILITY APPARATUS

A. Desiccator with cups
B. Payne permeability cup, loaded
C. Cup
D. Flange
E. Clamps

The material is made from a glass composition which possesses excellent electrical properties because it is intended for electrical use, but it is not sufficiently resistant to chemical attack for use in contact with corrosive chemicals.

The difference in structure of glass cloth and Patapar is shown clearly in Figures 2 and 3. The individual filaments of the glass cloth are very fine, but a number of them are twisted together to form a thread. The threads are woven in the normal manner with the warp running the length of the cloth and the filling across the cloth. There are small regular

Any of the standard application methods may be used to apply the film-forming material to the glass cloth, but the most satisfactory procedure is to apply the first coat by dipping the glass cloth into the material and allowing it to drain and dry in the normal manner. Subsequent coats may be applied by brushing, spraying, or dipping. If the first coat must be applied by spraying or brushing, a very satisfactory holder may be made by cutting the rim off a 1-gallon triple-seal friction-top paint can and also cutting out the metal from the lid of the same can, leaving the rim of the lid only.

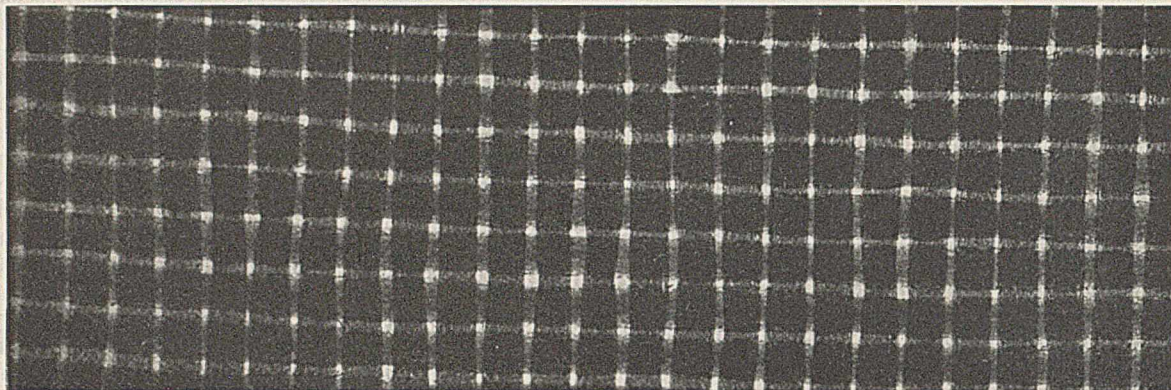


FIGURE 2. GLASS CLOTH BY TRANSMITTED LIGHT ($\times 15$)
Dark sections, threads. Light sections, spaces between threads

spaces at the intersections of the threads, as shown by transmitted light in Figure 2. The Patapar has a matted structure with interstitial spaces of irregular dimensions distributed throughout its mass. Figure 3 shows the spaces in the Patapar to be smaller than those in the glass cloth but this does not affect the rate of moisture movement through it, as shown in Table I.

TABLE I. MOISTURE LOSS

	Gram/hr.
Open cup	0.0830
Patapar	0.0625
Glass cloth	0.0618
Film A	0.0014
Film E	0.0002

The rate of moisture loss from an open cup was compared with the rate from cups covered with Patapar, glass cloth, and films of materials A and E under the same conditions as those used in the permeability determinations.

Table I shows that the Patapar and glass cloth retard the loss of water to about the same extent, but that the rate of moisture movement through these materials is so large compared with the rate of typical surface coatings that the effect on permeability values would be insignificant.

If the glass cloth is placed between the two rims and the rim from the lid forced into position, the glass cloth will be drawn tight and held very firm, but care must be taken to adjust the material and spray conditions so that a continuous coating is formed free from pinholes.

The glass cloth is wetted easily by surface coatings, but Figure 2 shows the possibility of pinhole formation at the intersections of the threads. This is eliminated entirely when the glass cloth is dipped into the coating, as shown in Figure 4, by the excellent penetration of the coating into the cloth.

The photomicrograph of the cross section of glass cloth which has been coated on both sides shows the ends of two warp threads with their individual filaments embedded in the coating with very few voids, and a filling thread running under one warp and over the other in intimate contact with the coating over its entire length. In contrast to this the coated Patapar, Figure 5, shows the two films in contact with the Patapar at isolated places only, with considerable voids between the Patapar and the film and no penetration of the film material into the Patapar. Water permeating through this structure could accumulate in the voids and saturate the

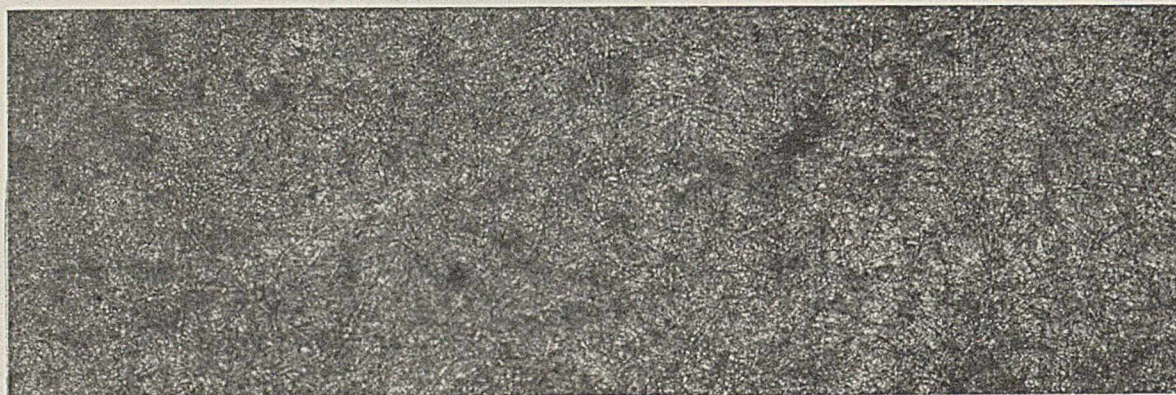


FIGURE 3. PATAPAR BY TRANSMITTED LIGHT ($\times 15$)

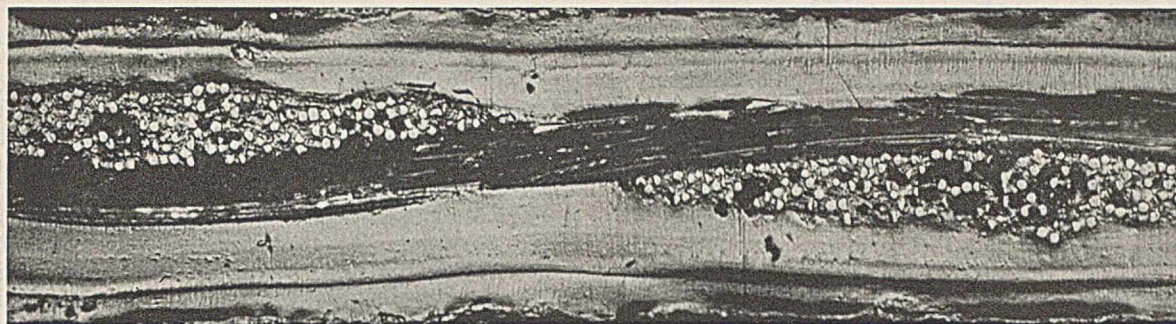


FIGURE 4. GLASS CLOTH, COATED ON BOTH SIDES (CROSS SECTION, $\times 250$)

Patapar, with subsequent swelling and distortion of the films and increase in permeability. This condition is avoided in the New York club method by coating only one side of the Patapar.

The film thickness on the Patapar is apparently more uniform than on the glass cloth, but the almost complete penetration of the cloth by the film ensures a film uniformity not apparent from the photomicrograph. The coated cloth is practically a solid film reinforced with glass fibers. In this respect it approaches more nearly its condition on a metal

The thickness of the film on glass cloth is calculated by the same procedure (weight-area-specific gravity relationship) as used in the New York club method. It is recognized that there is a variation in film thickness due to the woven structure of the glass cloth and this is shown clearly in Figure 4, but permeability has been shown to be inversely proportional to film thickness over the range of thickness in question; therefore, there would be no discrepancy in the calculation of specific permeability from an average value of film thickness. The coated glass cloth is practically a solid film reinforced

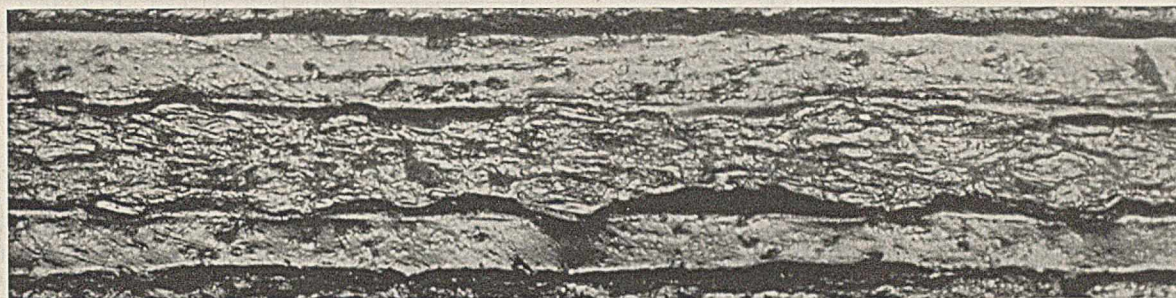


FIGURE 5. PATAPAR, COATED ON BOTH SIDES (CROSS SECTION, $\times 250$)

panel, although the orientation at the film-glass interface would differ slightly from the orientation on metal. The film on Patapar is more nearly like a free film.

Permeability Measurement

The New York Paint and Varnish Production Club standard method (17) was used for permeability measurement, but glass cloth was substituted for the Patapar.

The film-forming materials under investigation are applied to one side of the Patapar support by any of the general methods—brush, spray, or flow on—but not by dipping because both sides of the Patapar must not be coated. The film is allowed to dry on the support for any specified length of time and a disk is then cut from it. A similar disk is cut from the uncoated Patapar, both are weighed, and the difference is the weight of the film on the Patapar. The thickness of the film may be calculated from its weight, area, and specific gravity. The coated disk is placed between the flanges of a Payne permeability cup after about 5 grams of water have been placed in the cup. The flanges are then clamped together tightly and the loaded cup is weighed and placed in a desiccator with phosphorus pentoxide as the desiccant. The desiccator is kept in an oven maintained at 38°C . (100°F .) and the cup is weighed periodically to determine the amount of water which has permeated through the 10 sq. cm. area of film.

The dimensions of the Payne cup are such that the specific permeability rating may be obtained simply by multiplying the loss in weight from the cup in grams by 100 and by the film thickness in millimeters if the weighings are made each 24 hours. The specific permeability is defined as the milligrams of water permeating through 1 sq. cm. area of film of 1-mm. thickness in 1 day under specified conditions of temperature (38°C .) and vapor pressure differential.

with glass fibers and the difference in weight of uncoated and coated glass is the weight of the coating which may be converted into thickness from the relationship existing between specific gravity and area.

A series of tests was made, with the above method, to determine the relation between Patapar and glass cloth, using the following materials:

A. CLEAR FLEXIBLE COATING. Rezyl resin¹ 869-1 with cobalt drier.

B. CLEAR BRITTLE COATING. Orange shellac.

C. SHORT OIL-PHENOL MODIFIED RESIN VARNISH. Phenac resin² 622N, 100; tung oil, 80; mineral spirits, 170 parts by weight. Heat-processed in the normal manner and thinned with mineral spirits.

D. NITROCELLULOSE LACQUER. Nitrocellulose, 0.5 second, 100; Rezyl resin¹ 99-4, 100; and dibutyl phthalate, 20 parts by weight on the solid basis. Thinned with appropriate solvents.

E. WHITE BAKING PRIMER. Titanium dioxide, 80; zinc oxide, 80; and Rezyl resin¹ 412-1 (50% solids), 200 parts by weight. Mineral spirits to correct viscosity.

F. WHITE BAKING ENAMEL. Titanium dioxide, 97; zinc oxide, 3; and Beetle resin² 592-8 (50% solids), 200 parts by weight. Xylene to correct viscosity.

Patapar No. 30, Paterson Parchment Paper Company, Bristol, Penna.

Fiberglas Cloth No. 01-175, Owens-Corning Fiberglas Corp., Toledo, Ohio.

Payne permeability cup, R. P. Cargille, New York, N. Y.

¹ Registered trade-mark of the American Cyanamid Co.

² Trade-mark of the American Cyanamid and Chemical Corp.

Comparison of Patapar and Glass Cloth

A comparison was made of the permeability of four typical air-drying surface coatings, *A*, *B*, *C*, and *D*, on Patapar and on glass cloth. Two coats of each material were applied as shown in Table II, and each coat was air-dried for one week.

TABLE II. COMPARATIVE PERMEABILITY

Material	Method of Application	Specific Permeability	
		Patapar	Glass cloth
<i>A</i>	Dip, both sides	1.370	0.868
	Flow, one side	0.813	0.835
	Spray, one side	0.830	0.876
<i>B</i>	Dip	0.510	0.292
	Flow	0.310	0.298
<i>C</i>	Dip	0.598	0.243
	Flow	0.306	0.212
<i>D</i>	Dip	1.091	0.872
	Flow	0.890	0.884

In each case where the material was applied by dipping and thereby coating both sides, the permeability on the Patapar was higher than on the glass cloth. The permeability readings for the same material on Patapar and glass cloth check satisfactorily when only one side of the Patapar was coated. The high permeability reading on the Patapar was caused by adsorption of water by the layer of Patapar between the two layers of coating. The adsorbed water swelled the Patapar and distorted the film, producing minute cracks in brittle materials and weak places in flexible materials. The large increase in area of the film on Patapar was apparent from its wrinkled appearance, while the film on the glass cloth was perfectly smooth and unaffected.

These results show that the same permeability values may be obtained for films on Patapar or on glass cloth, but that the glass cloth is not subject to the limitation of being coated on one side only.

Glass Cloth for Baking Materials

To illustrate the value of the glass cloth as a support for baking coatings, the permeabilities of the white baking primer, *E*, and the white baking finish enamel, *F*, were determined. The results are shown in Table III.

The physical characteristics of a baking coating vary with the time and temperature of the bake, and it is desirable to determine the minimum schedule consistent with optimum characteristics such as color, gloss, hardness, and chemical and water resistance. The permeability and water adsorption of the baked film are indications of its water resistance. The variation in permeability of the white baking enamel, *F*, with variation in baking schedule is also shown in Table III.

TABLE III. PERMEABILITY OF WHITE BAKING COATINGS

Material	Bake		Specific Permeability
	Hour	° F.	
<i>E</i>	0.75	350	0.116
1 coat <i>E</i>	0.75	350	0.103
1 coat <i>F</i>	1	275	
<i>F</i>	1	225	0.276
	1	275	0.113
	0.5	325	0.108
	1	325	0.084

The permeability determinations were all run in duplicate with results which did not vary more than ± 1.5 per cent. It is apparent from the above values that glass cloth is a very satisfactory support for permeability determinations on films of materials which require baking at elevated temperatures.

It is also apparent that permeability determinations may be used to indicate the baking schedule required to give a material the necessary degree of water resistance. These values check very nicely the water adsorption results obtained on these same films as described below. The best method of applying the film-forming material to the glass cloth is to dip the first coat; the succeeding coats may be dipped, sprayed, or brushed.

Water Adsorption

The time required and the extent to which a film structure will adsorb water are indications of its water resistance. The adsorption is not necessarily proportional to the degree of softening and whitening of the film when immersed in water, nor to the permeability of the film, but it serves a useful purpose in the evaluation of a surface coating.

The McBain-Bakr quartz fiber spring balance (18) may be used to determine adsorption-desorption isotherms with extreme precision over a wide range of relative humidities, but a simple water immersion test with periodic weighings will determine very satisfactorily the amount of water taken up by a film under this condition.

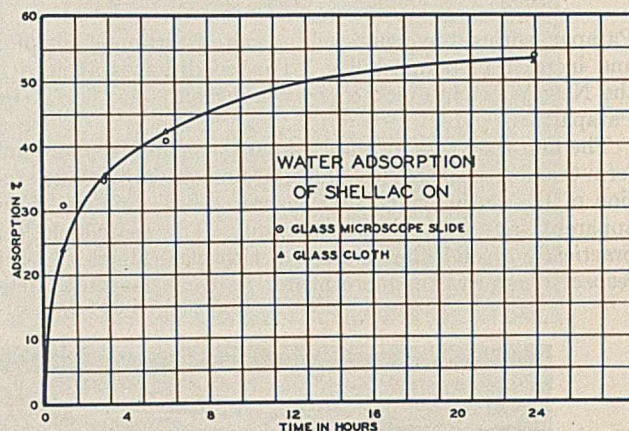


FIGURE 6

The British Ministry microscope slide test for water adsorption specifies that a glass slide be dipped into the material being tested and, after proper drying of the film, the coated slide immersed in water. The slide is weighed before and after coating and after immersion, and the gain in weight is expressed as per cent water adsorbed by the film. The glass slide is better than a metal panel because of the absence of corrosion, but it has some disadvantages. Materials, such as nitrocellulose lacquers, lose their adhesion to the slide after a short period of immersion and cannot be handled satisfactorily. In some cases where the material is fairly water-sensitive the water tends to accumulate in blisters between the slide and the coating and it is very difficult to remove this water without disrupting the film. The test requires that all surface adhering water be removed, so that only the water adsorbed by the film shall be weighed, but it is obviously impossible to remove a thin layer of water which may be between the film and the glass slide. The disadvantages of the glass slide are overcome entirely by the use of glass cloth. There is no loss of adhesion because the coating is enmeshed completely in the fibers of the cloth, and there is also no possibility of forming blisters underneath the coating. The water adhering to the surface is removed easily by placing the wet coated cloth between heavy blotting paper, but care should be taken to make the time required for weighing the sample uniform, so that the surface water only and no adsorbed water will be lost.

The water adsorption of a number of materials on glass slides and on glass cloth was compared and in every case the results were found to check satisfactorily.

Table IV and Figure 6 show the water adsorption of shellac. The mechanism of adsorption is not simple diffusion in the film (24-28) or it would be represented by some form of Fick's diffusion law

$$X = D \frac{(C) \text{ time}}{\text{thickness}}$$

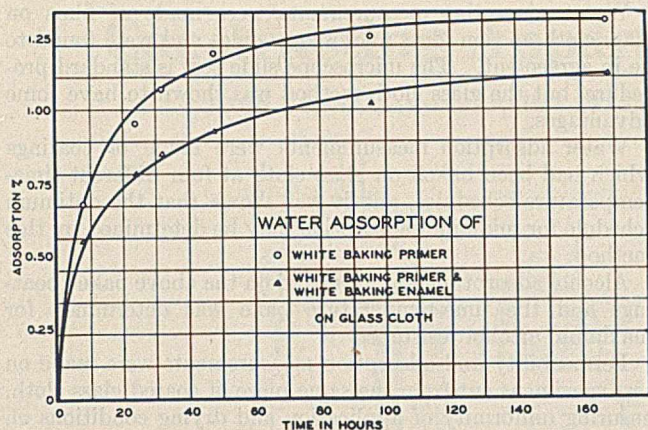


FIGURE 7

where X , the amount of water diffusing, is directly proportional to D , the diffusion constant for the particular material, C , the concentration, and the time, and inversely proportional to the film thickness. This law states that the amount diffusing is a linear function of the time, but the curve is parabolic, showing that both film structure and simple diffusion are factors in this phenomenon.

TABLE IV. WATER ADSORPTION OF SHELLAC

Hours	Microscope Slide			Glass Cloth		
	Film 1, 0.0954 g.	Film 2, 0.0921 g.	Av., 0.0937 g.	Film 1, 0.1018 g.	Film 2, 0.1051 g.	Av., 0.1035 g.
1	30.2	31.8	31.0	23.8	25.0	24.4
3	34.2	35.4	34.8	35.1	36.1	35.6
6	40.1	41.3	40.7	41.8	42.6	42.2
24	53.4	54.4	53.9	52.7	53.5	53.1

Another distinct advantage of the glass cloth over the glass slide is the fact that permeability and adsorption may be determined on the same strip of film. This ensures identical application, film thickness, and conditions of drying, all of which are important factors in these determinations or in establishing any relationship between them.

A strip of glass cloth was dipped in the white baking primer, E , and baked as shown in Table V; then a coat of the baking enamel, F , was sprayed on one side of the primed cloth and baked as shown. The coated glass cloth had practically the same appearance as a metal panel finished in the same manner, very good gloss, color, and hardness. Disks were cut from the coated cloth and permeability measurements made as shown previously, and strips the size of a microscope slide (7.5×2.5 cm., 3×1 inch) were also cut and the water adsorption determinations made.

TABLE V. WATER ADSORPTION OF WHITE BAKING PRIMER AND ENAMEL

Hours	Primer Bake 0.75 Hour at 177° C. (350° F.)			Enamel Bake 1 Hour at 135° C. (275° F.)		
	Film 1, 0.2253 g.	Film 2, 0.2168 g.	Av., 0.2110 g.	Film 1, 0.4295 g.	Film 2, 0.4283 g.	Av., 0.4289 g.
8	0.69	0.66	0.675	0.52	0.58	0.55
24	0.95	0.96	0.955	0.76	0.79	0.775
32	1.09	1.05	1.07	0.82	0.86	0.84
48	1.26	1.18	1.22	0.90	0.93	0.915
96	1.25	1.25	1.25	1.03	1.01	1.02
168	1.33	1.29	1.31	1.12	1.12	1.12

The same shaped curve was obtained as with the shellac, but of course on a very different scale. The curve for the primer and enamel shows a lower adsorption than for the primer alone, owing to the additional baking period on the primer while the enamel was being baked over it and to the excellent water-resisting characteristics of this combination.

Variation of Water Adsorption with Baking Schedule

It was shown in Table III that the permeability of films baked at different times and temperatures could be used to determine the optimum baking schedule for the characteristics desired. Table VI and Figure 8 indicate that adsorption determinations may be used for the same purpose or as a check on the permeability results.

TABLE VI. VARIATION IN WATER ADSORPTION WITH BAKING CONDITIONS

Hours	(White baking enamel) Bake 1 Hour at 107° C. (225° F.)			Bake 1 Hour at 135° C. (275° F.)		
	Film 1, 0.6157 g.	Film 2, 0.5982 g.	Av., 0.6069 g.	Film 1, 0.5180 g.	Film 2, 0.5162 g.	Av., 0.5121 g.
8	0.88	0.92	0.90	0.82	0.71	0.765
27	1.22	1.34	1.28	1.03	0.93	0.98
48	1.42	1.50	1.46	1.03	1.01	1.02
72	1.48	1.52	1.50	1.04	1.02	1.03

Hours	Bake 0.5 Hour at 163° C. (325° F.)			Bake 1 Hour at 163° C. (325° F.)		
	Film 1, 0.5513 g.	Film 2, 0.5395 g.	Av., 0.5454 g.	Film 1, 0.5109 g.	Film 2, 0.4975 g.	Av., 0.5042 g.
8	0.72	0.72	0.72	0.64	0.65	0.645
27	0.89	0.91	0.90	0.68	0.74	0.71
48	0.92	0.92	0.92	0.73	0.75	0.74
72	0.93	0.95	0.94	0.75	0.77	0.76

The same strip of coated cloth was used for determining both permeability and adsorption. The results check except for a reversal of X and Y , but this might be expected from the closeness of the figures and in view of the fact that permeability and adsorption are not necessarily directly proportional to each other. The results affirm the fact that, within limits,

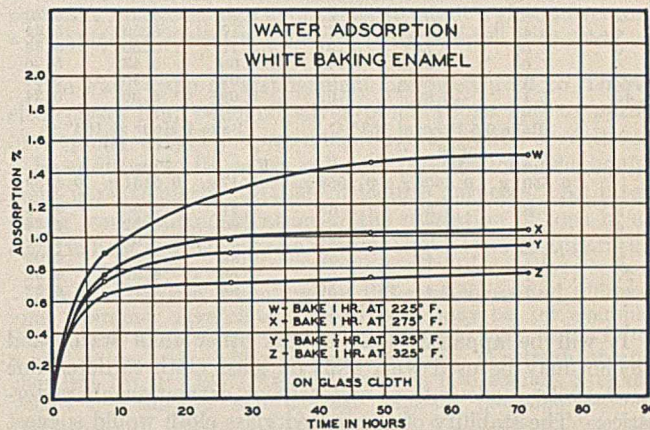


FIGURE 8

an increase in time or temperature of baking will increase the resistance of a film. This is shown even more emphatically in the following section.

Alcohol Adsorption

The permeability and water adsorption results shown in Tables III and VI were used to indicate the optimum baking schedule necessary for water resistance, and it will be seen from Table VII and Figure 9 that adsorption of liquids other than water may be used for this same purpose. The advantage of being able to cut portions from the same strip of coated glass cloth for these various determinations will be apparent.

The shape of the curves obtained from the adsorption of alcohol is not the same as those obtained from water. This is no doubt due to incomplete conversion of the film at the X baking schedule; the film still retained a small proportion of alcohol-soluble material which was leached out by the alcohol with consequent loss in weight.

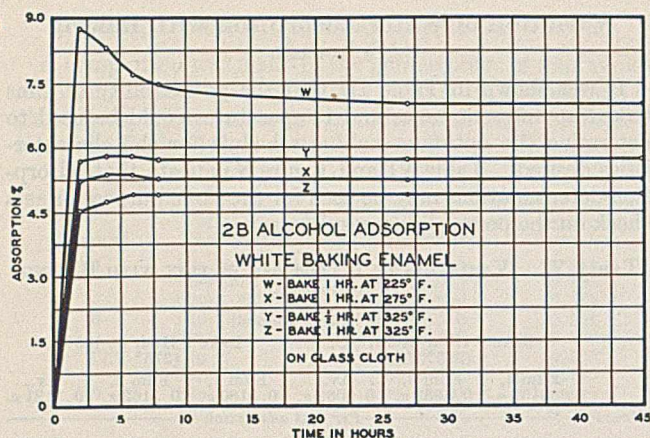


FIGURE 9

These determinations were not made primarily to determine the characteristics of any particular material but to illustrate a method only. For example, a longer baking schedule at 107° C. (225° F.) may have converted the film completely to the insoluble stage and this could have been determined by the method indicated, but that is not the purpose of the present paper.

TABLE VII. VARIATION IN ALCOHOL ADSORPTION WITH BAKING CONDITIONS

Hours	(White baking enamel)					
	Bake 1 Hour at 107° C. (225° F.)			Bake 1 Hour at 135° C. (275° F.)		
	Film 1, 0.6109 g.	Film 2, 0.5801 g.	Av., 0.6005 g.	Film 1, 0.5141 g.	Film 2, 0.5133 g.	Av., 0.5137 g.
	Per cent adsorption					
2	8.81	8.69	8.75	5.06	5.34	5.20
4	8.45	8.21	8.33	5.17	5.50	5.34
6	8.04	7.78	7.91	5.17	5.50	5.34
8	7.60	7.35	7.48	5.09	5.43	5.26
27	7.15	6.89	7.02	5.09	5.36	5.24
45	7.14	6.89	7.02	5.09	5.36	5.24
	Bake 0.5 Hour at 163° C. (325° F.)			Bake 1 Hour at 163° C. (325° F.)		
	Film 1, 0.5501 g.	Film 2, 0.5606 g.	Av., 0.5553 g.	Film 1, 0.5147 g.	Film 2, 0.5131 g.	Av., 0.5139 g.
2	5.82	5.55	5.68	4.41	4.66	4.53
4	5.94	5.69	5.81	4.66	4.82	4.74
6	5.94	5.69	5.81	4.86	4.99	4.92
8	5.74	5.44	5.59	4.86	4.99	4.92
27	5.74	5.44	5.59	4.86	4.99	4.92
45	5.74	5.44	5.59	4.86	4.99	4.92

It will be apparent that liquids other than water and alcohol may be used with films on glass cloth to determine permeability, adsorption, and solvent extraction characteristics. The stability of the coated glass cloth would suggest its use in determinations of change of permeability with exterior or accelerated exposure. The coated cloth could be held rigidly in a metal frame which would be noncorrosive, and could be exposed in the same manner as is now customary with coated metal or wooden panels.

Summary

The value of glass cloth in permeability and adsorption measurements has been shown. The permeabilities of four air-drying materials were compared on Patapar and glass cloth and were found to be in agreement. The glass cloth may be coated on both sides, but the coating may be applied to only one side of the Patapar. The permeabilities of two baking materials were determined satisfactorily on glass cloth. This is not possible on the Patapar because of volume changes due to loss and regain of moisture.

The permeability of a baking material was determined after baking at four different time-temperature schedules, and it was shown that this method may be used to indicate the best baking schedule for maximum resistance.

Water adsorption measurements were made of films on glass cloth and on glass microscope slides and were found to be in agreement. The microscope slide test is standard procedure, but the glass cloth method was shown to have some advantages.

Water adsorption measurements were made of coatings which had been baked on glass cloth at four different time-temperature schedules, and it was shown that the optimum schedule for minimum adsorption may be determined by this method.

Alcohol adsorption was measured on the above baked coatings and the time-temperature bake was determined for maximum alcohol resistance.

Permeability and adsorption measurements were made on test specimens cut from the same piece of coated glass cloth, ensuring uniformity of application and drying conditions on all test specimens.

Evidence has been provided to show the possibilities of glass cloth as a support on which to form films for test purposes. The tests were made with this object in view and no attempt was made to compare the characteristics of the materials used.

Acknowledgment

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Constructing Apparatus for Electrodialysis

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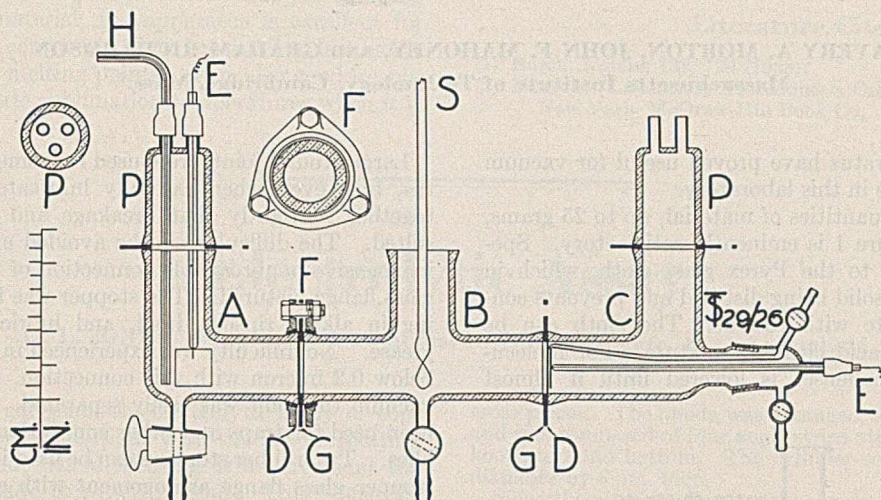


FIGURE 1. TWO TYPES OF THREE-COMPARTMENT CELLS

THE procedure of electrodialysis is of considerable value in many fields of scientific and technological activity. Various types of apparatus for use in electrolysing substances have been described from time to time in the literature, and some of these are available commercially through laboratory supply houses. Almost all of these commercial outfits possess one or both of two serious drawbacks. In the first place, many are largely constructed of rubber or some similar material which is entirely unsuitable for use in electrolysing operations on many substances. Most apparatus which is available is so limited in its flexibility of design that no modifications can readily be made in the size or arrangement of its essential features.

In the course of some work in these laboratories, the authors have had occasion to use procedures involving electrodialysis. In a search for suitable apparatus for their purposes, they have devised a method of constructing electrodialysis cells, which they believe is novel and useful because of its flexibility of design and ease of manipulation.

The important feature of their method of constructing electrodialysis apparatus is the use of stock fittings of Corning industrial flanged Pyrex pipe. These fittings, which are available in a wide variety of shapes and sizes, have been described in considerable detail (1). Figure 1 gives in one composite drawing two types of three-compartment cells which have been built and used by the authors, and serves to illustrate the method of construction.

The middle compartment, *B*, is a 3.75-cm. (1.5-inch) Pyrex T-fitting to which was sealed a stopcock to act as a drain for the compartment. Simple electrode compartments can be made in the form labeled *A* from 90° L-fittings of the same size by attaching a stopcock to act as a drain, or a somewhat more elaborate type of electrode compartment can be built as shown by *C*. This latter design, which is similar to the type of cell devised by Pauli (2), is particularly suitable for removing electrolytes from colloidal substances. Caps, *P*, for the electrode compartments, were made by drawing down a 15-cm. (6-inch) length of 3.75-cm. (1.5-inch) flanged Pyrex pipe. Three short pieces of 10-mm. Pyrex tubing were sealed to each cap to provide openings for the introduction of electrodes, gas delivery tubes, or funnels, as desired.

The various parts of the apparatus are clamped together by means of the standard metal joint flanges, *F*, which are supplied for this purpose by the Corning Glass Works. Between the sections, gaskets, *G*, of various materials may be used to ensure a

tight joint. A very satisfactory gasket can be cut from 0.05-cm. (0.020-inch) thick Eastman acetate sheet. Diaphragms, *D*, of any suitable membrane material are clamped between the three compartments of the cell in conjunction with the gaskets. The capacity of a cell constructed from 3.75-cm. (1.5-inch) piping is 225 to 275 ml. in the middle compartment, and 125 to 200 ml. in the electrode compartments. The side limb of the center compartment is large enough in diameter to admit a glass stirrer and a Beckman glass electrode and reference half-cell with ease.

The Pauli type of arrangement has been used to remove electrolytes from colloidal silver preparations and to purify hydrophilic colloid preparations, such as starch derivatives.

In addition to its use in colloidal preparations, the equipment is particularly suitable for lecture purposes. An interesting lecture demonstration of the migration of ions in an electric field can be performed with either type of apparatus.

For this purpose, three dyes of different colors and different ionic character were chosen. Such dyes may be, for example, Safranin O (Eastman organic chemical No. 1753), which forms a red cation and a chloride ion; tartrazine (Eastman organic chemical No. P 1163), which dissociates into sodium ions and yellow dye anions; and Chicago Blue-6B (National Aniline Chemical Co., Niagara Sky Blue-6B), which dissociates into sodium ions and blue associated dye anions. If a mixture of these three dyes in solution is electrolysing in the above cell fitted with membranes of No. 600 0.0045-cm. (0.0018-inch) Cellophane swelled for 12 hours in distilled water, a clean-cut migration occurs. The safranin goes into the cathode compartment and tartrazine into the anode compartment, with retention of the Chicago Blue in the center compartment. The catholyte is tinted red and the anolyte yellow in from 5 to 20 minutes by applying a potential of 110 volts across the cell. Because of the tendency of the dyes to precipitate one another in certain concentration ratios, care must be taken in making up the mixed solution. This was satisfactorily prepared from the dyes on hand by making stock solutions of safranin containing 0.50 gram per liter, tartrazine containing 2.5 grams per liter, and Chicago Blue containing 0.25 gram per liter. Equal volumes of each were taken and were mixed by adding the safranin to the tartrazine, and then adding the Chicago Blue to the mixture. The electrode compartments contained 0.001 *N* sodium chloride at the start of the demonstration.

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COMMUNICATION No. 725 from the Kodak Research Laboratories.

Vacuum Sublimation and Molecular Distillation Apparatus

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TWO kinds of apparatus have proved useful for vacuum distillation of solids in this laboratory.

For relatively large quantities of material, up to 25 grams, the type shown in Figure 1 is eminently satisfactory. Special attention is called to the Pyrex glass cloth, which in practice rests upon the solid being distilled and prevents contamination of sublimate with residue. The cloth can be cleaned with the usual acid cleaning mixture. For molecular distillations the condenser is lowered until it almost touches the cloth.

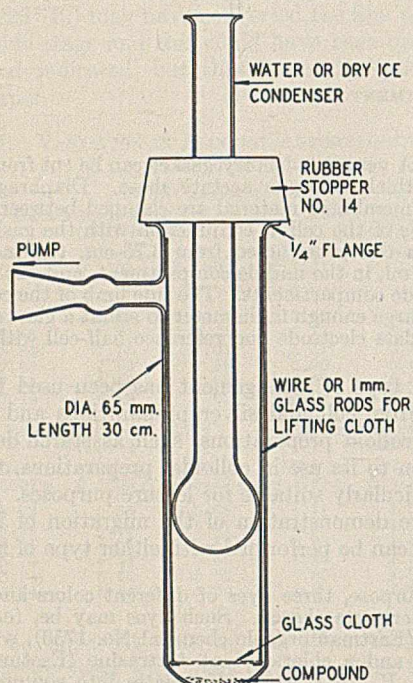


FIGURE 1. VACUUM SUBLIMATION APPARATUS

Large ground joints were used for some time in the apparatus, but, even when carefully lubricated, became jammed together so tightly that breakage and loss of product resulted. The difficulty can be avoided entirely by using the inexpensive nonbreakable connection of rubber stopper and glass flange pictured. The stopper was first cleaned by boiling in alkali, rinsed, dried, and lubricated with stopcock grease. No difficulty was experienced in obtaining a vacuum below 0.2 micron with this connection. Upon releasing the vacuum the joint was easily separated. Similar joints have been used for traps and other connections in vacuum assemblies. Two rubber stoppers can be used in place of the rubber stopper-glass flange arrangement with equal success. It is possible also to rotate the stoppers on each other without destroying the vacuum.

Ordinary stopcock or common lubricating grease has been used as the lubricant, but even more satisfactory is the vaseline residue obtained by distilling the low-boiling components from about 400 ml. of vaseline in a 2-liter flask arranged as a horizontal flask still (2) with air instead of water as the condensing liquid. From about 40 to 65 per cent of low-boiling material is removed before a final temperature of 360° (pressure at 40.50 mm.) is reached in the sand bath used as the heater. Such a lubricant has been mentioned by Burch (1) as admirably suited for work at low pressures. Its freedom from inorganic residues and from low-boiling compounds and its fusion to a clear liquid when warmed make it superior to the common types.

A second apparatus is shown in Figure 2. In this unit the innermost tube containing the sample to be distilled is heated in a jacketed tube, so that the solid is vaporized through the whole length of the tube and collected in a band just beyond the heated portion. A narrow strip of cloth wound around the tube several times and kept cold with water or ice serves as a condenser. A solid carbon dioxide pack or basket may be placed further along the tube to act as an auxiliary condenser or trap. When a fraction is collected at one temperature the heater jacket is moved back about 6 cm., the con-

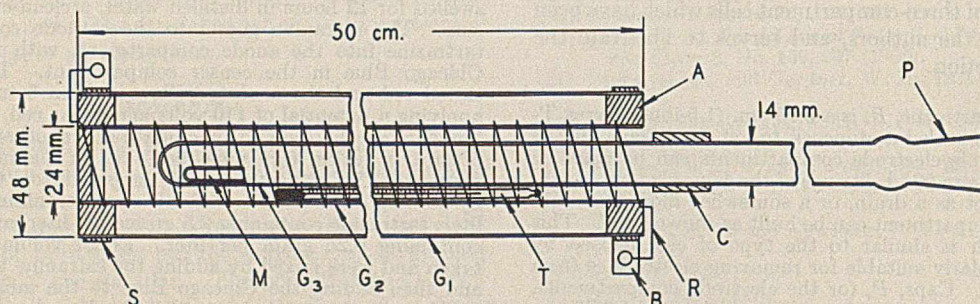


FIGURE 2. FRACTIONAL SUBLIMATION APPARATUS

- A. Asbestos tape
- B. Binding post and fastener
- C. Condenser
- G₁, G₂, G₃. Glass tubes 48, 24, and 14 mm. in diameter, respectively
- M. Material being sublimed, contained in glass capsule
- P. Pump connection
- R. Resistance wire
- S. Strip of metal to prevent breakage and serve as support for binding posts
- T. Thermometer

denser moved onto the vacant position, the temperature raised a little, and a new fraction collected. This process is repeated a number of times until a series of bands has been formed. The effect is particularly striking when colored substances are distilled. Apart from its value for distilling small quantities of material, the apparatus is excellent for testing the purity of a compound, since the first and last bands should have identical melting points. It is also good for observing the approximate sublimation temperatures when it is

desired to obtain data preliminary to handling a large batch. Passage of the sublimate through the long tube has little effect on raising the temperature of sublimation if the heating is not too rapid.

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- (1) Burch, *Nature*, **122**, 729 (1928).
- (2) Morton, "Laboratory Technique in Organic Chemistry," p. 120, New York, McGraw-Hill Book Co., 1938.

Electrolytic Assay

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IT IS customary to carry out the electrolytic assay of copper, nickel, and other solutions with the aid of rotating cathodes or anodes, but where their use is inconvenient the electrolyte may be made to rotate instead. This is usually done by placing an electromagnet beneath the electrolyte, thus producing a vertical field, which, in the presence of a current moving radially gives rise to a stirring motion. Several workers have adopted this method of agitating the solution (1-4). When the employment of an electromagnet is impracticable, the same result may be obtained by means of a permanent magnet, within the air gap of which the electrolyte is situated. The following short study is an account of such a magnet and of some results obtained with it.

The magnet was of the four-claw pot type used in loud speakers, but the center pole was truncated and the annular pole enlarged, as depicted in Figure 1. The field produced was substantially vertical at the center pole, becoming almost radial towards the outer one. A pot magnet of the size shown is capable of accommodating beakers of 400-ml. capacity.

The magnet was of 15 per cent cobalt steel, having the following approximate percentage analysis: carbon, 1; cobalt, 15; chromium 9 to 10; molybdenum, 1. The steel was crucible-melted and sand-cast. The casting was sand-blasted, machined, and heat-treated by annealing and hardening. The magnet used for the experiments was devoid of pole pieces; these, when fitted, gave a gap 38 mm. in inside diameter, 41 mm. in outside diameter, and 0.6 cm. (0.25 inch) deep, and an associated flux density of 8500 to 9000 lines, the total flux being 64,000 to 68,000 lines.

Solutions of electrolytic copper were electrolyzed under various conditions of acidity and current density, and for three different times. The volume in each case was 100 ml. The cathode consisted of a circular cylinder of platinum gauze, 2.4 cm. in diameter by 3 cm. high, attached to a central stem by means of cruciform

cross pieces. The anode was arranged to surround the cathode, and was composed of four angle strips attached to a side stem by hoops top and bottom. The cylinder so formed was 4.5 cm. in diameter by 3 cm. high.

Since the stirring effect would clearly be weak at low current densities, experiments under these conditions were not carried out. In the case of mixed acid solutions 1 gram of urea was added to the electrolyte towards the end of the assay. Good, firm deposits were obtained, particularly in the instance of mixed acid solutions.

TABLE I. DEPOSITION OF COPPER

Time Hours	Acidity		Current Amp.	Copper Present Gram	Copper Deposited Gram
	H ₂ SO ₄ %	HNO ₃ %			
0.5	5	..	5	0.4995	0.4783
1.0	5	..	5	0.4995	0.4993
1.5	5	..	5	0.4995	0.4998
0.5	5	..	7.5	0.4995	0.4757
1.0	5	..	7.5	0.4995	0.4993
1.5	5	..	7.5	0.4995	0.4994
0.5	10	..	5	0.4995	0.4696
1.0	10	..	5	0.4995	0.4982
1.5	10	..	5	0.4995	0.4995
0.5	10	..	7.5	0.4995	0.4914
1.0	10	..	7.5	0.4995	0.4993
1.5	10	..	7.5	0.4995	0.4995
0.5	5	5	5	0.4995	0.4814
1.0	5	5	5	0.4995	0.4979
1.5	5	5	5	0.4995	0.4996
0.5	5	5	7.5	0.9990	0.9879
1.0	5	5	7.5	0.9990	0.9954
1.5	5	5	7.5	0.9990	0.9986
0.5	5	5	10	0.9990	0.9940
1.0	5	5	10	0.9990	0.9979
1.5	5	5	10	0.9990	0.9983

The results (Table I) indicate that, although most of the copper is deposited within half an hour, complete removal of the copper from solution does not take place until electrolysis has proceeded for a further hour. At the end of every experiment the electrolyte was tested for copper by means of potassium ferrocyanide; those solutions which had been electrolyzed for the full period (90 minutes) gave a negative reaction. Assays carried out in nitric acid solution yielded poor deposits, and deposition of the metal was incomplete.

The stirring effect of the magnet is appreciable at moderate current densities, and becomes vigorous at high densities. A more powerful magnet than that used in the present study would, of course, enhance the action. Since the magnet is working at a large air gap, it is possible that loss of magnetism may occur in the course of time, although this is unlikely to be serious.

Literature Cited

- (1) Ashcroft, *Electrochem. Met. Rev.*, **4**, 145 (1906).
- (2) Frary, *J. Am. Chem. Soc.*, **29**, 1592 (1907).
- (3) Hurmuzescu, *Elec. Rev.*, **42**, 322 (1898).
- (4) Knot and Work, *J. IND. ENG. CHEM.*, **4**, 534 (1912).

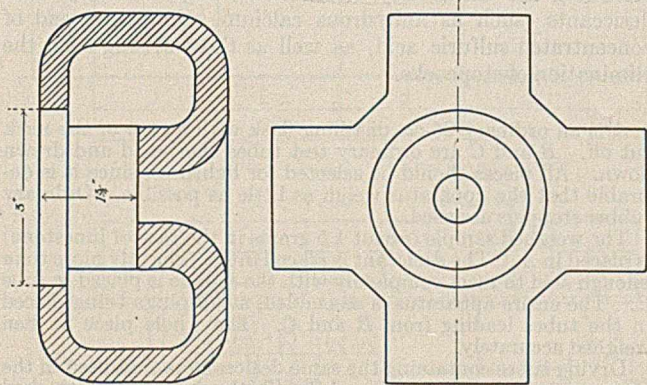


FIGURE 1. PLAN AND SECTIONAL ELEVATION OF MAGNET

An Improved Thermometer Guard

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A COMMON laboratory problem is the installation of thermometers so that they may be easily removed and at the same time well guarded. In the course of research it was necessary to install ten thermometers on a double-pipe heat interchanger and a guard was developed which is believed to have considerable merit.

The complete guard is shown in Figure 1. The body of the guard, *B*, is a 1-inch length of $\frac{7}{8}$ -inch hexagonal brass stock, drilled and tapped for a standard $\frac{3}{8}$ -inch pipe thread. At the bottom of the tapped hole a concentric hole is drilled through of a diameter at least $\frac{1}{16}$ inch greater than that of the thermometer, *C*, being installed. In addition, three holes are drilled for $\frac{3}{16}$ -inch welding rods, *D*, which constitute the guards. These rods, of proper length, are threaded or soldered in place and a short piece of $\frac{1}{8}$ -inch pipe, *E*, is brazed or soldered inside the rods as shown. For the packing, about $\frac{3}{16}$ inch is cut from the large end of a No. 00 one-hole rubber stopper, so that the remainder, *G*, will not bind in the threads when on the thermometer. Last, a washer, *H*, with $\frac{9}{16}$ -inch outside diameter

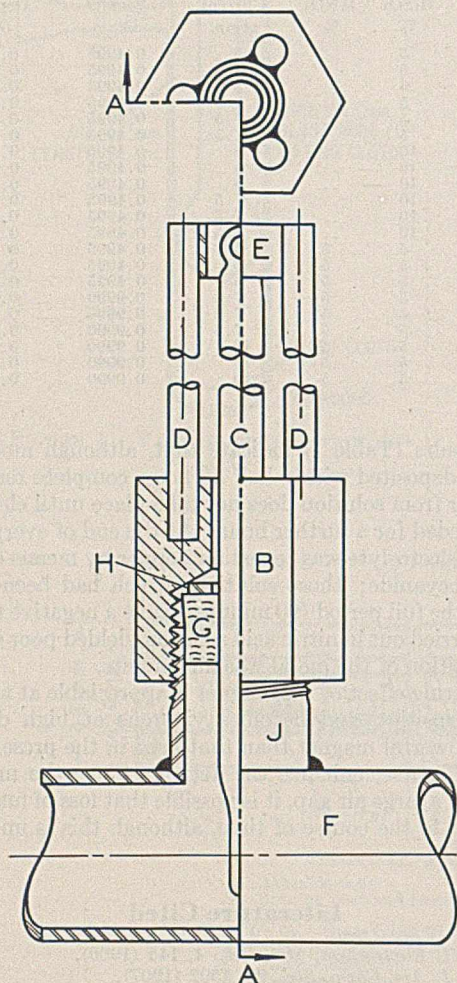


FIGURE 1. DETAILS OF GUARD

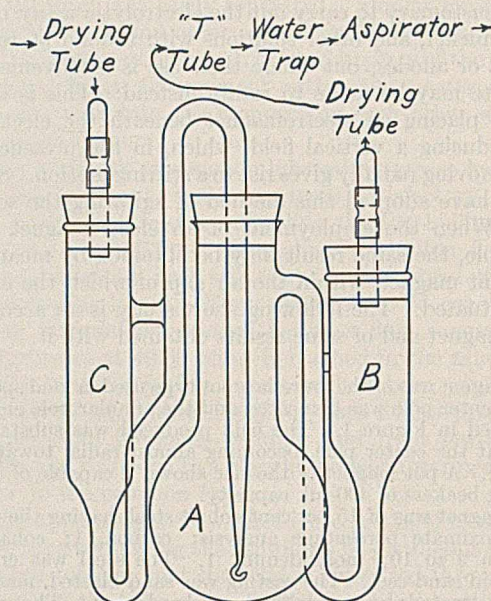
and inside diameter the same as drilled in the body, is slipped on the thermometer above the stopper to prevent the stopper's jamming into the body and turning the thermometer as the guard is screwed on.

The assembled guard may be screwed on a $\frac{3}{8}$ -inch nipple which is in turn screwed into a tee, but a much neater method for permanent installations is shown in the figure. A short length of $\frac{3}{8}$ -inch pipe, *J*, threaded at one end, is brazed or welded into a hole drilled in the main pipe, *F*, as shown.

An Alkalimeter

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THE indirect determination of carbon dioxide by means of a simple alkalimeter merits consideration whenever extreme accuracy is not required and speed is of some importance.

Such an alkalimeter of somewhat original design has been used with considerable success in the author's laboratory for the past 3 years. In it are incorporated the advantages attending the use of any of the newer high-efficiency solid desiccants (such as anhydrous calcium sulfate), instead of concentrated sulfuric acid, as well as those arising from the elimination of stopcocks.

A is an ordinary 25-cc. distilling flask with a part of the neck cut off. *B* and *C* are ordinary test tubes shortened and drawn down. All pieces should be selected for lightness, since it is desirable that the apparatus weigh as little as possible. Ordinary rubber stoppers are used.

The weighed sample (about 1.5 grams in the case of limestone) is placed in *A*. The desiccant is placed in *B*. Slightly more than enough acid to react completely with the sample is placed in tube *C*. The entire apparatus is assembled, small plugs being placed in the tubes leading from *B* and *C*. The whole piece is then weighed accurately.

Drying tubes containing the same desiccant as that used in the apparatus are attached to *B* and *C*. To the drying tube attached to *B* are connected a T-tube, a water trap, and an aspirator as indicated.

With the aspirator going slowly, the open arm of the T-tube is closed momentarily to start the flow of acid into the reaction chamber, *A*. It is best that the acid be added slowly with some shaking. When all the acid has been added, the open arm of the tube is closed and a slow stream of air is drawn through to remove all the carbon dioxide.

After the apparatus has again reached room temperature, the plugs are attached to *B* and *C* and the apparatus is weighed again. The loss in weight represents the carbon dioxide evolved.

For more detailed general instructions concerning the manipulation, the reader is referred to such texts as Kolthoff and Sandell (1).

Literature Cited

- (1) Kolthoff, I. M., and Sandell, E. B., "Textbook of Quantitative Inorganic Analysis," pp. 360-2, New York, Macmillan Co., 1936.

Crucible Support

GILBERT E. SEIL AND H. A. HEILIGMAN, E. J. Lavino and Company, Norristown, Penna.

THE crucible support shown in the drawing offers many advantages to the laboratory in which evaporations, fumings, and ignitions are done in platinum crucibles.

When platinum crucibles are heated on a sand bath or supported in a triangle, many determinations are lost because of the spattering of the residue. Moreover, determinations in adjacent crucibles must be discarded because no near-by crucible is free of suspicion of contamination.

The creep of salts up the sides and over the top of the crucible during the fuming of a residue is a frequent source of annoyance and error. The salts may bake to the outside of the crucible and become contaminated with the sand of the sand bath. Portions of the baked residue may crack and

drop off. A crucible support which eliminates spattering and creep is a valuable adjunct to any laboratory.

The equipment described in this article supports the crucible so that accidental overturning is impossible. The support is easily cleaned and kept clean and, unlike a sand bath, can be moved as required to any convenient location. Filter papers can be quickly and thoroughly dried without charring before ignition.

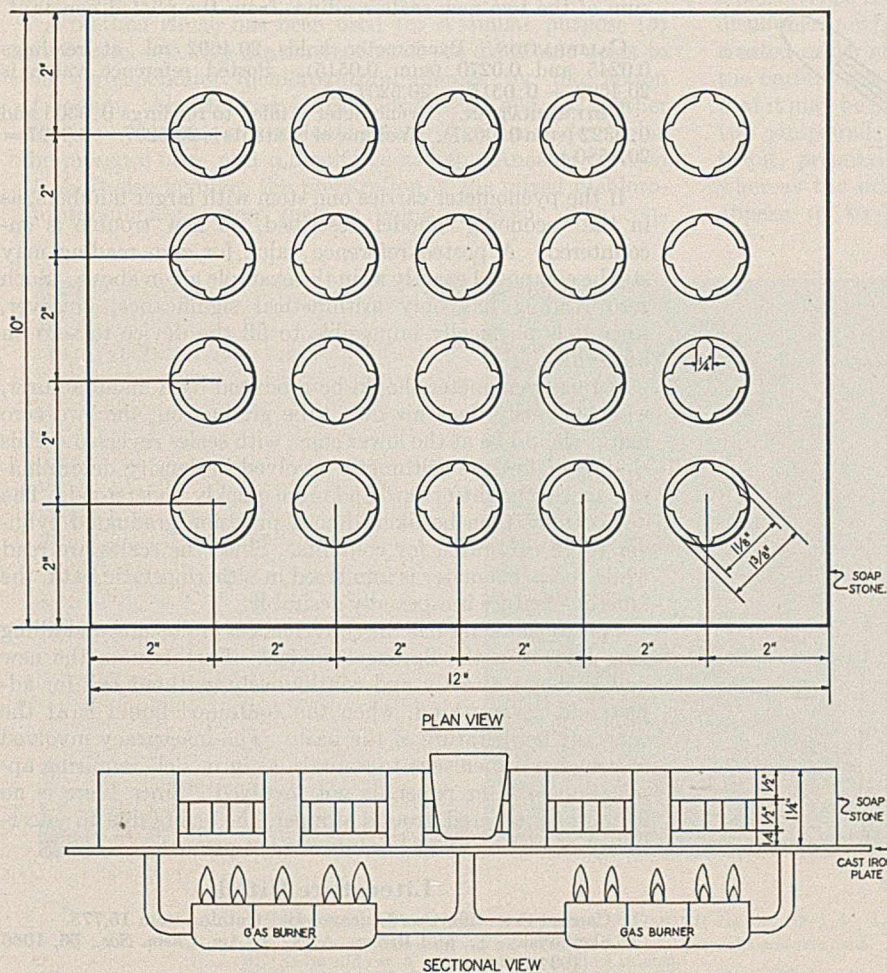
The time required for carrying out a drying, an evaporation, or a fuming in a platinum crucible is reduced by one half as compared with the usual methods. The authors found, for example, that in doing several hundred fluorspar analyses, the time required for volatilizing the silicon tetrafluoride, fuming

the residue with sulfuric acid, and then igniting the calcium sulfate was cut in half by the use of this support. More important, the creep of the salts up the sides and over the top of the crucible was eliminated. No samples were lost because of creep.

The crucible support described is in reality an air bath which distributes the heat around the sides as well as to the bottom of the crucible. It can be conveniently placed on one corner of a hot plate. The authors obtain excellent results with a support placed on an iron plate over a circular gas burner such as is frequently used in kitchen ranges. The size of the support and of the openings can be varied to suit the needs of the individual laboratory.

The authors use several supports in which twenty crucibles (30-ml. capacity) can be treated simultaneously. The supports are easily made from a piece of soapstone $25 \times 30 \times 3$ cm. ($10 \times 12 \times 1.25$ inches) drilled as shown in the drawing. First the 0.6-cm. (0.25-inch) holes are drilled at the center of each circle and at the points indicated on the circumference of each circle. Next the 2.8-cm. (1.125-inch) holes are drilled through the stone, and finally the 3.4-cm. (1.375-inch) holes are drilled 1.25 cm. (0.5 inch) from the top of the stone and 0.25 inch from the bottom of the stone.

The crucible will rest in the opening, and the heat will go through the holes along the sides of the crucible, thus heating the sides as well as the bottom. The crucible rests low in the opening and cannot be turned over.



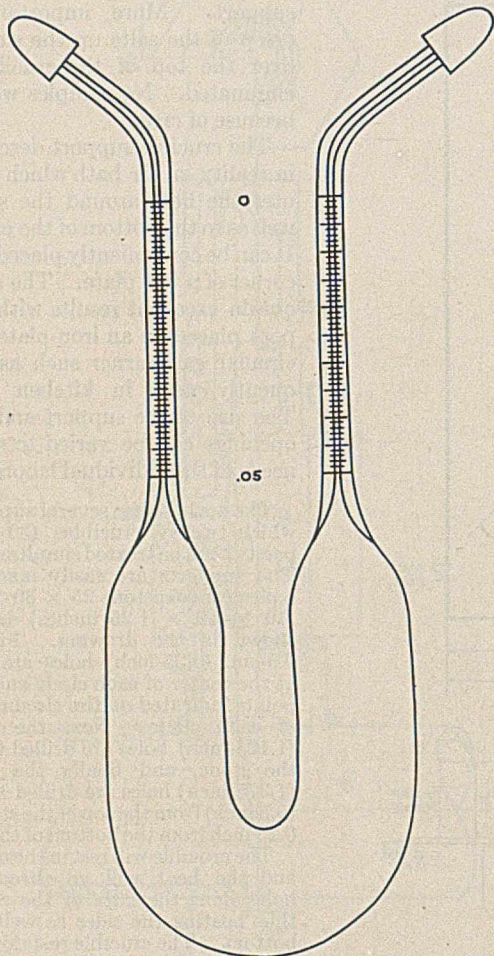
A Graduated Pycnometer

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IN AN article concerned primarily with another topic Shedlovsky and Brown (2) incidentally described a new quartz pycnometer featuring two graduated stems. Apparently this item has not been recorded in abstract indexes under "pycnometer" or like caption, and has thus probably escaped deserved attention. The technique of tube graduation needed with the quartz device requires, however, facilities not commonly at hand. The substitution of a standard commercial graduated tube for the quartz tube, as described below, readily permits the construction of a glass pycnometer of the type mentioned. Only ordinary glass-blowing skill is required.

As suggested in the accompanying figure, the upper parts of two graduated pipets are incorporated in a U-tube assembly of 20- to 25-ml. capacity. The current Kimble blue-line Kahn serological pipet, total delivery 0.2 ml., graduated in 0.001-ml. divisions spaced about 1 mm. apart, is used. Probably the most substantial construction is effected by sealing the two segments of pipets to the intervening piece of large tubing first in a straight line. The U-bend is next made, and finally the 45° bends. For workers of limited glass-blowing skill it will probably be easier to prepare the body of the pycnometer in two equal sections connected by a U-tube of small caliper, as illustrated in a commercial Sprengel pycnometer now on the market (1). Such a modification is not quite so easily filled, however.



Economy may be attained by sacrificing only one pipet, from which two graduated sections are cut. The resulting irregularity in numerical markings detracts from the appearance of the finished pycnometer, but not from its usefulness. The 45° angles at the top facilitate drainage, in contrast to certain older Sprengel-type pycnometers, but make filling more difficult where a rubber connecting tube is not permissible. In the latter case a ground-on glass angle tube may be prepared to fit in place of one of the glass caps.

The pycnometer is suspended in a thermostat with side window or equivalent, and is read with complete immersion of the filled portion. In calibration it is filled with the usual air-free distilled water approximately to mid-positions on the graduated stems. The true volume, presumably at 20° or 25° C., is then calculated for the contents represented by the two stem readings. It makes no difference whether these stem readings are at the same horizontal level. In 1-mm. capillary tubes very slight irregularities cause decided differences in position of meniscus.

When the pycnometer is ready to receive the liquid under investigation, it is not necessary to fill to the same marks recorded for water. Even should the level on each side be as far as 0.010 ml., or 10 scale divisions, from the position of calibration, and the temperature of the thermostat be 5° from the standard 20° at which the pipet was graduated, the error is negligible.

It is convenient to post a reference value for the volume of the pycnometer filled on both sides to the zero marks. In each subsequent determination one need only subtract the sum of the two new scale readings from the posted constant.

CALIBRATION. Pycnometer holds 20.4692 ml. at readings 0.0245 and 0.0270 (sum 0.0515). Posted reference value is $20.4692 + 0.0515 = 20.5207$ ml.

DETERMINATION. Pycnometer is filled to readings 0.0305 and 0.0322 (sum 0.0627). Volume of contents is $20.5207 - 0.0627 = 20.4580$ ml.

If the pycnometer carries one stem with larger numbers, as in the "economy" model described, no new trouble is encountered. A posted reference value for zero reading may still be computed exactly as in the example given above. Such zero reading has only arithmetical significance, however, since it is physically impossible to fill the device to zero on both sides.

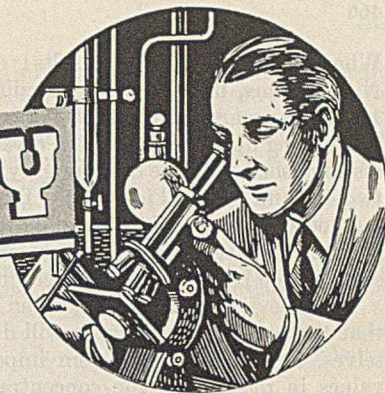
If this pycnometer should be produced by a manufacturer, who obviously does his own tube graduation, the two zero marks should be at the lower ends, with scales reversed. This change makes the arithmetic involved in density determination more straightforward and more quickly understood. The device may then be likened to a precision graduated cylinder to be calibrated for contents. Since the scales are read while the pycnometer is immersed in a thermostatic bath, the blue-line feature is especially desirable.

This pycnometer has the conveniences of flushing and filling long known in the Sprengel models. Furthermore the new device shows directly and continuously, without call for adjustment of any kind, when the contained liquid is at the constant temperature of the bath. The inaccuracy involved in bringing a meniscus to a mark, as in models requiring application of filter paper, is not involved. Since there is no fitting of a tapered ground stopper, the errors due to uncertainty of seating of such joints are not present.

Literature Cited

- (1) Central Scientific Co., Chicago, Ill., Catalog item 15,775.
- (2) Shedlovsky, T., and Brown, A. S., *J. Am. Chem. Soc.*, 56, 1066 (1934).

MICROCHEMISTRY



Estimation of Anthraquinone-1,8-Disulfonic Acid

Microscopic Method for Use in the Presence of Certain Other Anthraquinone Sulfonic Acids and Sulfuric Acid

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WHEN anthraquinone is sulfonated in the presence of mercury in order to form the disulfonic acids, a mixture is formed which is composed mainly of 1,5-disulfonic acid and 1,8-disulfonic acid with some 1,6- and 1,7-acids. A method was needed for the identification and estimation of the 1,8-acid in a mixture of the 1,8-acid, the 1,5-acid, and sulfuric acid, from which the 1,6-acid and the 1,7-acid had already been removed.

A method which has been used for a similar purpose (3) involves as one step the conversion of the disulfonic acids to the corresponding dichloroanthraquinones by the action of sodium chlorate and hydrochloric acid, and as another step the hydrolysis of α -sulfonic groups (in order to determine the presence of α - and α,β -sulfonic acids). Another method (1, 4, 6) also involves the preparation of the mixed dichloroanthraquinones, whose melting point is taken. The con-

centration of 1,8-acid is determined from a mixed melting point diagram for 1,5- and 1,8-acids. These methods are time-consuming. Furthermore, the melting point would be depressed by impurities other than the 1,8-dichloroanthraquinone; consequently a high value for 1,8-acid would be obtained.

The method which is reported here is based on a new principle. When a mixture of sulfuric acid, anthraquinone-1,5-disulfonic acid, and anthraquinone-1,8-disulfonic acid is treated under standardized conditions with barium chloride, the barium salt of the 1,8-acid is precipitated in such a form that it may be distinguished from the barium salts of the other two compounds by microscopic examination. It forms anisotropic, prismatic crystals, which exhibit parallel extinction, whereas the other two barium salts form aggregates which appear to be amorphous under ordinary magnifications.



FIGURE 1. PHOTOMICROGRAPHS OF BARIUM SALTS OF 1,5-, 1,8-, AND SULFURIC ACIDS
A. 18 per cent 1,8-acid; 62 per cent 1,5-acid; 20 per cent sulfuric acid. Bright-field illumination.
B. Same slide as A between crossed Nicol prisms.
C. 4 per cent 1,8-acid; 76 per cent 1,5-acid; 20 per cent sulfuric acid. Between crossed Nicol prisms.

When the mixture of barium salts is examined between crossed Nicol prisms, under suitable conditions of illumination, the 1,8-salt appears as brilliantly glistening specks or prisms (depending upon the size of the crystals) which can be readily distinguished from the black or grayish aggregates of the other two barium salts (Figure 1). By means of a systematic method of counting, it is possible to get a quantitative relationship between the number of crystals of the 1,8-barium salt and the percentage of 1,8-acid in the original mixture.

It is inevitable, of course, when a precipitation is made, that the precipitated crystals will differ in size among themselves, and so it might seem impossible to get consistent values in relation to the concentration of 1,8-acid without some system of weighting the counted crystals. Actually this is not necessary, because when the precipitation is carried out under standardized conditions, the small and the large crystals seem to be formed in some constant proportions, so that it is possible by counting all crystals alike regardless of size to obtain a linear relationship between the count and the percentage of 1,8-acid, within certain limits of concentration of the latter (Figure 2).

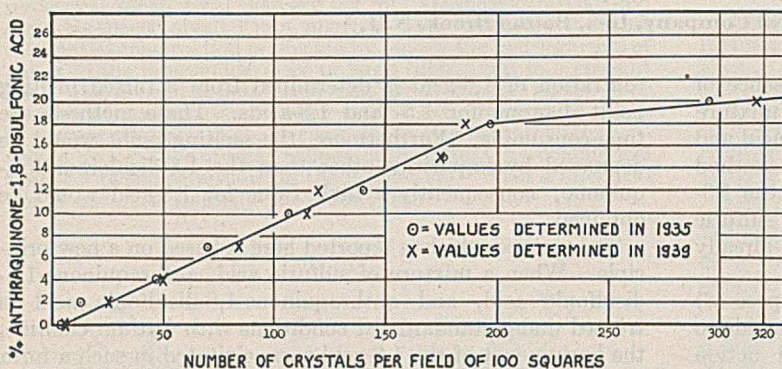


FIGURE 2. RELATIONSHIP BETWEEN COUNT AND PERCENTAGE OF 1,8-ACID

The method was worked out in detail for mixtures containing 20 per cent of sulfuric acid and 80 per cent of variously proportioned 1,5- and 1,8-acids. The latter varied between 0 and 20 per cent. For such mixtures it was found that the 1,8-acid could be estimated with a probable error for a single determination of ± 0.5 per cent (absolute) of 1,8-acid. This error represents both precision and accuracy. Of course, more accurate values can be obtained by averaging more than one value. In this case the probable error of the mean would be $\pm 0.5\%/\sqrt{n}$, where n is the number of values averaged.

This work was aimed primarily at a method for distinguishing 1,8-acid from 1,5-acid, but incidentally three other sulfonic acids were tried: the 2,6- and 2,7-disulfonic acids and the 2-monosulfonic acid. (The 1,6- and 1,7-disulfonic acids and the 1-monosulfonic acid were not available.) It was found that the 2,7- and the 2-acids behaved like the 1,5-acid and sulfuric acid, when they were in the presence of the 1,5-acid and sulfuric acid alone; but in the presence of the 1,8-acid too, they seemed to lower the values which were found for the 1,8-acid.

Not enough work has been done with these mixtures to enable the author to draw definite conclusions concerning the likelihood of perfecting a method to eliminate these interferences. The 2,6-acid interferes, since its barium salt forms anisotropic needles under the conditions of the method, which are counted with the crystals of the barium salt of the 1,8-acid. The effect of the 2,6-acid was only of incidental interest, and too few experiments were made with it to permit drawing many conclusions, but it would seem possible to

devise a technique for estimating the total percentage of 1,8- and 2,6-acids when they are present together with the 1,5-acid and sulfuric acid. It should also be possible to estimate the percentage of the 2,6-acid in the absence of the 1,8-acid but in the presence of the 2,7-acid or the 2-acid, or both (Table II). Since conditions of sulfonation which lead to the production of 1,8-acid do not lead to the production of 2,6-acid (3, p. 220), these two would not normally interfere with each other.

It is reported that the barium salt of the 1-sulfonic acid crystallizes in needles (5). Since the author has found that the 2-acid precipitates in a form similar to the 1,5- and 2,7-acids, it may be possible to develop a method for the estimation of the 1-acid in the presence of the 2-acid, based on the principle described here.

Procedure

A curve is first constructed which is based on the precipitation of the barium salts of a mixture of such acids as would be present in the samples which are to be analyzed.

CHEMICALS. *Barium Chloride.* The ordinary reagent grade of barium chloride dihydrate was used.

Anthraquinone-1,8-disulfonic Acid. The crystals of the 1,8-acid, which had separated from a sulfuric acid wash liquor obtained in the preparation of the 1,5-acid, were precipitated from aqueous solution by means of concentrated hydrochloric acid. The precipitate was recrystallized three times from a mixture of 19 parts by weight of acetic acid and one part of water, with the addition of decolorizing carbon. The product, after drying for 2 hours in a steam oven and then in a vacuum desiccator, melted at $299.5\text{--}300.5^\circ\text{C}$. (cor.) with decomposition. An additional recrystallization from 19 to 1 acetic acid did not change the melting point. Titration with 0.1 N sodium hydroxide (methyl red indicator) gave a value of 82.7 per cent of $\text{C}_{14}\text{H}_6\text{O}_2(\text{SO}_3\text{H})_2$ or 102.9 per cent of $\text{C}_{14}\text{H}_6\text{O}_2(\text{SO}_3\text{H})_2 \cdot 5\text{H}_2\text{O}$. The drying at steam-oven temperature had partially dehydrated the pentahydrate.

Barium Salt of 1,8-Acid. An aqueous solution of the 1,8-acid was precipitated with a solution of barium chloride. The barium salt was filtered and washed with water.

Anthraquinone-1,5-disulfonic Acid. An alcoholic solution of the crude 1,5-acid was treated with an alcoholic solution of monomethylaniline. The precipitated monomethylaniline salt of the 1,5-acid was washed with alcohol and recrystallized from a mixture of 4 parts by volume of alcohol and 5 parts by volume of water. This product, as well as a small portion which was recrystallized again from the 4 to 5 alcohol, melted with decomposition at $252.5\text{--}253^\circ\text{C}$. (cor.) when the melting point tube was immersed in a bath previously heated to 240°C . The monomethylaniline salt was warmed gently with a slight excess of dilute sodium hydroxide solution, and the liberated monomethylaniline was steam-distilled.

The 1,5-acid was precipitated from the solution of its sodium salt in the form of the barium salt, and this was decomposed with sulfuric acid. After removing the precipitated barium sulfate, the solution of the 1,5-acid was concentrated and then treated with hydrochloric acid to precipitate the free 1,5-acid. This was recrystallized from 19 to 1 acetic acid and dried in the steam oven. The product, as well as a small portion which was recrystallized once more from acetic acid (19 to 1), melted with decomposition at about 313°C . (cor.). Titrations with 0.1 N sodium hydroxide (methyl red indicator) gave a value of 84.0 per cent of $\text{C}_{14}\text{H}_6\text{O}_2(\text{SO}_3\text{H})_2$ or 100.4 per cent of $\text{C}_{14}\text{H}_6\text{O}_2(\text{SO}_3\text{H})_2 \cdot 4\text{H}_2\text{O}$.

Anthraquinone-2,6-disodium Disulfonate. The ethylbenzyl-aniline $[\text{C}_6\text{H}_5\text{N}(\text{C}_2\text{H}_5)\text{CH}_2\text{C}_6\text{H}_5]$ salt of the 2,6-acid was prepared by treating a hot aqueous solution of the crude 2,6-acid with a dilute hydrochloric acid solution of ethylbenzyl-aniline. The salt was recrystallized from methyl and ethyl alcohols (1 to 1 by volume) three times. The melting point [$238.4\text{--}238.7^\circ\text{C}$. (cor.)] did not change upon recrystallization from butyl alcohol. The purified salt was hydrolyzed with sodium hydroxide solution and the last trace of ethylbenzyl-aniline was removed by steam distillation. The disodium salt of the 2,6-acid was recovered by concentrating the residual solution which was left after steam distillation. It was then recrystallized from water.

Analysis. Sodium (calculated from the sulfated ash), 11.04, 11.16; average, 11.10 per cent. Sulfur, 15.55, 15.55 per cent. Calculated for $C_{14}H_6O_2(SO_3Na)_2$: sodium, 11.16 per cent; sulfur, 15.55 per cent.

Anthraquinone-2,7-disodium Disulfonate. The ethylbenzyl-aniline salt was prepared in a manner similar to that described for the 2,6-acid. It was recrystallized twice from a solvent made up of one part by volume of alcohol and 3 parts of water. The melting point [149.8–151.2° C. (cor.)] did not change upon an additional recrystallization from butyl alcohol.

Analysis. Micro Dumas nitrogen, 3.45 per cent; calculated for $C_{14}H_6O_2(SO_3H)_2(C_6H_5N.C_2H_5.CH_2C_6H_5)_2$, 3.54 per cent.

The salt was treated with sodium hydroxide solution in order to liberate the ethylbenzylaniline. The last traces of the latter were removed by extraction with ether, the solution was concentrated, and the 2,7-disodium disulfonate was thrown out by the addition of alcohol. It was redissolved, then reprecipitated by means of alcohol, and dried at 110° C.

Analysis. Sodium (calculated from the sulfated ash), 11.08, 11.18; average, 11.13 per cent. Sulfur, 15.64, 15.49; average, 15.57 per cent. Calculated for $C_{14}H_6O_2(SO_3Na)_2$: sodium, 11.16 per cent; sulfur, 15.55 per cent.

Anthraquinone-2-sodium Sulfonate (Silver Salt). The crude anthraquinone-2-sodium sulfonate was precipitated as the monomethylaniline salt by treating its hot solution with an aqueous hydrochloric acid solution of monomethylaniline and cooling. The methylaniline salt was recrystallized from dilute alcohol, and a portion of these crystals was recrystallized from benzene. Both products melted at 201.2–202.0° C. (cor.) with slight decomposition, when the melting point was taken in a bath previously heated to 185° C.

The methylaniline salt was hydrolyzed by means of sodium hydroxide solution and the anthraquinone-2-sodium sulfonate was recrystallized from water.

Analysis. Sodium (calculated from sulfated ash), 7.41, 7.41 per cent; calculated for $C_{14}H_7O_2SO_3Na$, 7.41 per cent.

REAGENT SOLUTIONS. A. Saturate distilled water with the barium salt of 1,8-acid at room temperature and filter. The solution should be perfectly clear. The solubility of the barium salt is reported as 1 part in 3600 parts of water at 18° C. and 100° C. (2), yet even this slight solubility would interfere sufficiently with the complete precipitation of the barium salt of the 1,8-acid, so that it is necessary to use A for all solutions which are to be used in the method.

B. Dilute 0.590 gram of barium chloride dihydrate with A to 100 ml., with the addition of a little barium salt of 1,8-acid. Shake well and allow whatever barium salt will precipitate from A, because of the common-ion effect of the barium chloride, to do so over a period of several hours. Filter and use the clear solution.

C. Make up 0.0125 gram of anthraquinone-1,8-disulfonic acid to 100 ml. with A. This solution contains 0.1 mg. of anhydrous 1,8-acid per ml.

D. Make up 0.1190 gram of anthraquinone-1,5-disulfonic acid to 100 ml. with A. This solution contains 1.0 mg. of anhydrous 1,5-acid per ml.

E. Make up 0.0112 gram of anthraquinone-2,6-disodium disulfonate to 100 ml. with A. This solution contains, as the sodium salt, the equivalent of 0.1 mg. of anhydrous 2,6-acid per ml.

F. Make up 0.0112 gram of anthraquinone-2,7-disodium disulfonate to 100 ml. with A. This solution contains, as the sodium salt, the equivalent of 0.1 mg. of anhydrous 2,7-acid per ml.

G. Make up 0.0108 gram of anthraquinone-2-sodium sulfonate to 100 ml. with A. This solution contains, as the sodium salt, the equivalent of 0.1 mg. of anhydrous 2-acid per ml.

H. 0.1 N sulfuric acid; 0.4 ml. is equivalent to 2 mg. of sulfuric acid.

STANDARD SOLUTIONS. Make up mixtures of the reagent solution so that each solution will contain a total of 10 mg., distributed between the sulfuric acid and the various sulfonic acids. In all this work each solution had 0.4 ml. of 0.1 N sulfuric acid (2 mg. of sulfuric acid) plus 8 mg. of total sulfonic acids. Each milligram of sulfonic acid is equivalent to 10 per cent of the total sulfuric acid plus sulfonic acids. Add sufficient A so that the total volume of the solution will be 30 ml.

PRECIPITATION OF BARIUM SALTS. Place 10 ml. of B in a 50-ml. beaker provided with a small stirring rod. Place the 30 ml. of standard solution in a buret or pipet and, with continuous vigorous stirring, add it to B drop by drop, very slowly at first, and somewhat faster as the solution becomes turbid, in such a manner that it takes about 4 to 5 minutes to add the entire 30 ml. Continue stirring vigorously for 10 minutes, scratching the sides of the beaker at the same time. Allow the beaker to stand overnight, stirring occasionally, before taking a sample for a crystal count.

PREPARATION OF CELL AND COUNTING OF CRYSTALS. Prepare a counting cell by cementing a flat ring upon a microscope slide. The cell which was used in this work was 9.5 mm. in diameter and 0.29 mm. in depth. Cells of any other practical dimensions may be used, provided that the curve is based upon the use of the same cell as will be used for the analysis.

Agitate thoroughly with a stirring rod the beaker which contains the precipitated crystals, and remove a drop of the mixed liquid on the end of the rod. Touch the drop to the center of the cell. Remove another drop, after thorough agitation, and touch this to the first drop. Immediately place a cover glass upon the cell, pressing it down as soon as it is in position, in order to squeeze out excess liquid before the crystals in the excess have had much time to settle. Allow the cell to stand for 2 minutes before examining.

Examine the cell between crossed Nicol prisms with a visual magnification of X70. In this work there was used a Leitz X10 objective, a tube length of 170 mm., and a X7 micrometer ocular with a Whipple disk. Under these conditions of magnification, a side of each of the 100 small squares corresponded to a length of 0.124 mm. as measured by comparison with a stage micrometer.

First focus the microscope upon the crystals with the analyzer removed. Then insert the analyzer in the crossed position with respect to the polarizer. Adjust the illumination so as to bring the crystals of the 1,8-barium salt into the greatest prominence and lower the condenser sufficiently so that the aggregates of barium sulfate and of the 1,5-barium salt will appear as dull, grayish particles. If the condenser is raised too high, these barium salts will appear bright and confuse the counting of the 1,8-barium salt crystals.

Count the 1,8-barium salt crystals systematically in each field of 100 squares. Count as one crystal every particle in each small square which appears brilliantly illuminated, regardless of its size. Some particles will appear merely as barely perceptible bright specks and others may extend across several small squares. There will be some well-formed prismatic crystals which happen to be lying in the positions of extinction and so, although not illuminated, are nevertheless perceptible and obviously different from the background of barium sulfate and 1,5-barium salt. Count these together with the illuminated crystals. In counting, count one small square at a time, and count as one crystal every crystal in a small square and any part of a crystal which crosses a line into a small square. In this way many crystals are counted more than once, but this partially compensates for the variations in the sizes of the individual crystals.

Sometimes, for samples with a high crystal count, some crystals remain out of focus when the count is taken by focusing upon the crystals at the surface of the slide. By focusing up, these crystals are brought into view, and should be included in the count for a given field. It has been found necessary to focus twice in this way only occasionally, and then only for fields with high counts. Record the total count for 100 small squares. Examine six fields on each slide, changing the position of the slide without looking at the field through the microscope, so as to avoid being influenced in placing the slide by the number of crystals in a field. Calculate the average number of crystals per field and plot the number of crystals against the percentage of 1,8-disulfonic acid (Figure 2).

Up to a crystal count of 200 the per cent of 1,8-acid can be calculated by the following equation, which fits the curve:

$$\% \text{ of 1,8-acid} = \frac{\text{number of crystals}}{11}$$

ANALYSIS OF SAMPLES. Weigh 0.100 gram of the sample, which contains sulfuric acid and the 1,5- and 1,8-disulfonic acids. Make up to 50 ml. with A. Pipet a 5-ml. aliquot and dilute with 25 ml. of A. Then treat as described for the standard solutions. Read the value of 1,8-acid from the curve or calculate by means of the equation.

RATE OF PRECIPITATION. It is necessary to standardize the method of precipitation of the barium salts; otherwise the crystal count may not be reproducible. Some experiments were made in which the solution of the acids was added to the barium chloride solution directly from a 50-cc. beaker over a period of about 5 minutes. The difference in this method from that described in the procedure lay mainly in the fact that the additions of the solution were in quantities more than a drop at a time. This procedure resulted in counts which for two mixtures were lower than those for normal precipitations, whereas with one mixture the count was normal. Table I gives the values obtained. The reason

TABLE I. EFFECT OF METHOD OF PRECIPITATION UPON CRYSTAL COUNT

Method of Precipitation	1,8-Acid %	Crystal Count
Normal	5	58
Abnormal	5	51
Normal	12	134
Abnormal	12	75
Abnormal	12 ^a	97

^a This sample had 5 per cent of 2,6-acid in addition to the 1,8-acid and should consequently have had an even higher count than that which was normal for 12 per cent of 1,8-acid.

for this behavior may possibly lie in the fact that, when the solution is added too rapidly, the relatively lower concentration of barium chloride which meets the sulfonic acids, as compared with that in the slower addition, results in the formation of fewer nuclei and consequently larger crystals.

TABLE II. EFFECT OF SULFONIC ACIDS OTHER THAN 1,5- AND 1,8-ACIDS

[All solutions contained 0.4 ml. of 0.1 N H₂SO₄ (2 mg. of H₂SO₄)]

Solution	1,5-Acid Mg.	1,8-Acid Mg.	2,6-Acid Mg.	2,7-Acid Mg.	2-Acid Mg.	1,5-Acid %	1,8-Acid %	2,6-Acid %	2,7-Acid %	2-Acid %	Crystal Count	Crystal Count Calculated as % 1,8-Acid
XVII	6	0	2	0	0	60	0	20	0	0	Many fine needle crystals. Slide not counted.	
XVIII	6	1	1	0	0	60	10	10	0	0	228	18
XIX ^a	4	0.5	1.5	0	0	50	6.25	18.75	0	0	221	18
XX ^a	7	1.5	0.5	0	0	63.6	13.6	4.55	0	0	104, 83	8
											Av. 94	
XX ^b	6	1.5	0.5	0	0	60	15	5	0	0	177	16
XXI	6	0	0	2	0	60	0	0	20	0	None	0
XXII	6	0	0	0	2	60	0	0	0	20	None	0
XXIII	6	1	0	0.5	0.5	60	10	0	5	5	22	2
XXIV	6	0.5	0	0.8	0.7	60	5	0	8	7	24	2

^a Contained a total of sulfonic acids and sulfuric acid which differed from the normal 10 mg.

^b This sample inadvertently did not have sulfuric acid added at start of precipitation; it was added after about half of solution had been added to barium chloride solution.

Evidence that reproducibility does not depend upon an unconscious duplication of a technique which is not susceptible of adequate description is offered by the fact that the curve in Figure 2 represents determinations made four years apart; no determinations were made in the intervening period.

TIME OF STANDING BEFORE COUNTING. Frequently a preparation will attain its maximum count if it is allowed to stand with occasional stirring for 2 hours after precipitation. Sometimes, however, the count after 2 hours will be low. If the mixture is allowed to stand overnight, the count will always have attained a maximum value which is constant, since an additional period of one day causes no increase.

INTERFERING SUBSTANCES. Table II indicates the results of some experiments which were made to test the effect of acids other than the 1,8- and 1,5-acids in the method. These acids were added in the form of the sodium salts, but the percentages were calculated on the basis of the free acids.

Several conclusions may be drawn. The 2,6-acid interferes with the estimation of 1,8-acid, since it precipitates as anisotropic needles in the absence of the 1,8-acid (XVII). Experiments XVIII, XIX, XX, and XX' indicate that the values for 1,8- and 2,6- are not additive under the conditions of the estimation of 1,8-acid, but it may be possible to devise conditions such that the two would be additive. One such condition would, of course, be to use as diluent water which has been saturated with the barium salt of both the 2,6-acid and the 1,8-acid. It appears that, although when the 2,7-acid and the 2-acid are each present separately with the 1,5-acid and without the 1,8-acid, they deposit no crystals which can be counted, yet when they are both present together with the 1,8-acid, they lower the count of 1,8-acid. The use of the sodium salts of the 2,6-, 2,7-, and 2-acids may

have had some influence upon the results, since the curve was based upon material which contained no sodium salts.

Precision and Accuracy

In counting crystals, it was found that if six fields from one slide are counted, the values for the individual fields may vary considerably, yet the average count for the six fields will agree well with the average for six fields from another slide prepared from the same mixture. Table III illustrates the agreement which may be expected.

From the slope of the curve (Figure 2) between the range of 0 to 200 crystals, it can be calculated that, within that range about 11 crystals are equivalent to 1 per cent of 1,8-acid; between about 200 to 300 crystals the ratio is about 50 crystals for 1 per cent of 1,8-acid. The mean crystal count for two slides differs from the count for each slide by a value which is equivalent to less than ± 1 per cent of 1,8-acid (absolute).

The points which are plotted on the curve represent separate determinations. One set of points was made four years after the other set. The mean deviation of these points from the curve in terms of per cent of 1,8-acid is ± 0.5 per cent (absolute) for 18 values. The probable error for a single value may also be calculated as ± 0.5 per cent of 1,8-acid (absolute). This represents both the precision of the method and the deviation from the true value of 1,8-acid. The method does not involve any constant error. If more than one determination is made, the mean value will have a probable error of $\pm 0.5/\sqrt{n}$ per cent, where n equals the number of values averaged to get the mean value.

TABLE III. CRYSTAL COUNTS IN INDIVIDUAL FIELDS AND AVERAGES

Solution A		Solution B		Solution C	
Slide 1	Slide 2	Slide 1	Slide 2	Slide 1	Slide 2
36	34	163	153	279	292
48	32	163	171	272	315
41	37	158	112	256	298
40	34	164	141	266	268
34	40	164	148	311	296
43	34	177	162	292	261
Av. 40	35	165	148	279	288
Grand av. 38			157		284

Summary

A method has been devised for the estimation of anthraquinone-1,8-disulfonic acid in admixture with sulfuric acid and anthraquinone-1,5-disulfonic acid which involves precipitating the barium salts of the three acids and counting

the crystals of the barium salt of the 1,8-acid under the microscope between crossed Nicol prisms. The method was investigated for mixtures containing 20 per cent of sulfuric acid, 0 to 20 per cent of 1,8-acid, and 60 to 80 per cent of 1,5-acid. The probable error of a single value is ± 0.5 per cent of 1,8-acid (absolute). The method involves no constant error.

Anthraquinone-2,6-disulfonic acid interferes and is estimated together with the 1,8-acid. The method might be developed for mixtures containing 2,6-acid in the presence or absence of 1,8-acid. Anthraquinone-2,7-disulfonic acid and anthraquinone-2-sulfonic acid may cause low values for the 1,8-acid. It might also be possible to develop a method for the estimation of anthraquinone-1-sulfonic acid in the presence of anthraquinone-2-sulfonic acid, based upon the principle described.

Acknowledgments

Acknowledgment is made of the cooperation of A. R. Norton in furthering the study of the method; of the assistance of G. L. Royer in preparing the photomicrographs; and of the assistance of W. J. Mader in preparing the sodium salts of anthraquinone-2,6-, -2,7-, and -2-sulfonic acids.

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A Distillation Capillary

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MIXTURES of low boiling liquids, in volumes as small as 0.02 to 0.1 ml., can be fractionally distilled by means of the apparatus described below.

Preparation of Distillation Capillary

A piece of Pyrex glass tubing, *A*, about 8 mm. in outside diameter, and with 1-mm. wall, is heated in the blast lamp and drawn out to a capillary, *B*, somewhat longer than 10 cm., with a uniform inner bore of approximately 2 mm. A 10-cm. section, *C*, of this capillary is cut off. About 5 cm. from one end, the capillary is drawn out to a much finer capillary, *D*, 0.25 to 0.5 mm. in outside diameter, and about 7 cm. long. Any excess length is cut off. The end of the finer capillary is sealed by heating in the flame.

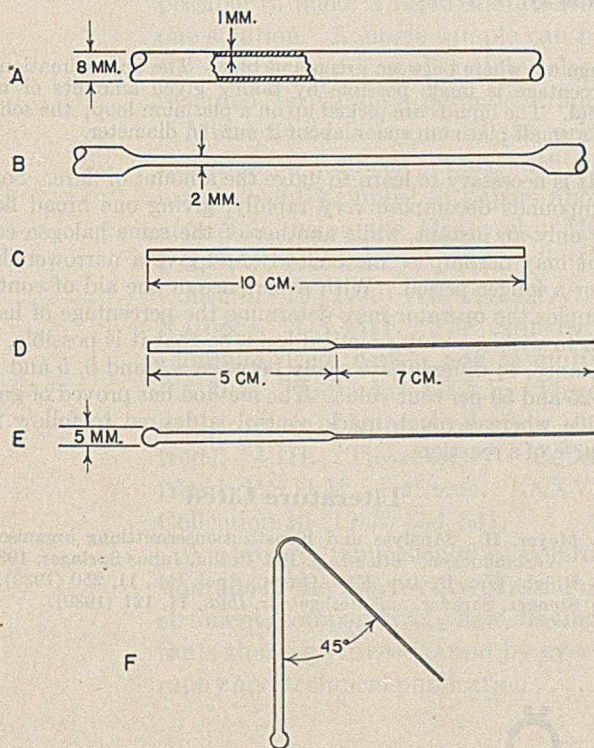


FIGURE 1

The end of the larger capillary is then also sealed, using a small blast flame, and the glass kept soft by holding it in the flame until a hollow bulb about 5 to 6 mm. in diameter (0.06- to 0.1-ml. capacity) forms, *E*, owing to the increased pressure of the heated air within. The size of the bulb will depend upon the length of time that it is kept in the flame. Excessive heating must be avoided, since this will gradually enlarge the bulb to the point of bursting. When cool, the tip of the fine capillary is broken off. The stem of the fine capillary at a point 1 to 2 cm. from the larger capillary is softened by heating in a luminous flame, and bent to an angle of about 45°, *F*. The distillation capillary is now ready for use.

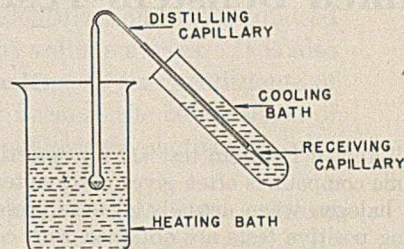


FIGURE 2

Filling the Distillation Capillary

The drop of liquid to be fractionated is introduced into the distillation capillary in the following manner:

The bulb of the distillation capillary is warmed by immersing for a few moments in boiling water. While the bulb is still warm, the fine capillary tip is dipped into the drop of liquid to be fractionated, and then a cooling bath (solid carbon dioxide and acetone) is applied to the bulb. The decreased air pressure within, due to the cooling, causes the liquid to flow up the fine capillary, down the larger capillary, and into the bulb of the apparatus. Should any of the liquid remain in the stem, it is easily forced into the bulb by shaking the apparatus two or three times, as is customary with clinical thermometers. For a successful distillation the bulb should not be more than half full of liquid. In order to remove all traces of adhering liquid from the fine capillary arm, the arm is carefully warmed, while the bulb containing the bulk of the liquid is kept in the cooling mixture.

The Distillation

A test tube, 6 cm. long, partly filled with ice water is used to cool the distillate-receiving capillary. For very low boiling liquids (30° C. or less) a small Dewar flask containing liquid air is used.

A capillary, 9 cm. long, having an inside diameter just a trifle larger than the outside diameter of the fine arm of the distillation capillary, is introduced into the cooling bath, with its sealed end resting on the bottom of the test tube. The fine stem of the distillation capillary is introduced into the receiving capillary as far as it will go. The entire setup is held by means of the water-containing test tube during the distillation. The bulb of the distillation capillary is now inserted into cold water contained in a small beaker. The water is then gradually and very slowly heated until a ring of condensate is seen rising up the column and condensing in the receiving capillary. At this point the flame should be at once removed, in order to keep the temperature of the water from rising too high. The distillation meanwhile is allowed to continue until a layer not more than 2 mm. thick (0.01-ml. volume) has collected in the receiving capillary. At this point the distillation capillary is quickly withdrawn from the receiving capillary by means of a glass rod supporting the curved part of the distillation capillary, and the bulb is quickly placed in the solid carbon dioxide-acetone cooling mixture, in order to suck back into the bulb any liquid remaining in the capillary portion of the apparatus.

The receiving capillary containing this first fraction is stored in the cooling mixture until ready for identification tests, such as the boiling point determination. Fractional distillation of the remaining liquid in the bulb is then continued as described above. Not more than 2 mm. of each fraction should be collected in the receiving capillaries. Five to six fractions can be obtained in this way from 0.06 ml. of liquid.

Results Obtained by Fractional Distillation

Various mixtures of low boiling liquids were prepared, and small volumes, as indicated in Table I, were fractionated by the method described. The boiling points of the several fractions were determined by Emich's boiling point micro-method (1). The first fractions contain the lower boiling liquid, and the last fractions the higher boiling liquid, in a form pure enough to be identified by their respective boiling

TABLE I. EXPERIMENTAL RESULTS

Ml.	Mixtures of Liquids Used	Boiling Points of Pure Liquids ° C.	Expt.	Boiling Points of Successive Fractions ° C.	
0.02	Ethyl ether	34.5	1	34.5, 35.0, 49.5, 55.8	
0.02	Acetone	56.5	2	34.5, 35.3, 43.0, 55.5, 56.0	
0.03	Methyl alcohol	64.6	1	33.0, 35.5, 37.0, 41.5, 60.5, 63.5	
0.03	Methyl formate	31.5	2	32.0, 33.5, 38.5, 42.5, 63.2, 64.0	
0.03	Ethyl ether	34.5	1	21.5, 21.5, 22.0, 33.0, 34.0	
0.03	Acetaldehyde	21.5	2	21.0, 21.0, 22.5, 33.5, 34.0	
0.03	<i>n</i> -Propyl chloride	46.4	1	37.5, 37.5, 42.5, 43.5, 45.0	
0.03	<i>iso</i> -Propyl chloride	36.5	2	36.0, 37.0, 40.5, 44.0, 46.5, 46.8	

points. The intermediate fractions contain mixtures of the two liquids.

If it becomes desirable to redistill some of the fractions, they may be introduced into the bulb of the apparatus as described and refractionated.

For corroborative identification, since there is no loss of material during the boiling point determination, the liquid in the receiving capillary can be used to determine its molecular weight by the method of Niederl *et al.* (2).

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Modified Beilstein Test for Halogens in Organic Compounds

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THE well-known Beilstein test (1) for detecting halogens in organic compounds often gives positive tests for small amounts of halogen when actually none is present—for example, strong positive tests are obtained with certain types of pyrimidines, pyridines, and oxyquinolines (1).

Modified tests (2, 3) have been described for gases and volatile liquids.

A⁴ method has been in use in this laboratory for about 5 years which accurately detects the presence of halogens in organic compounds. With experience the operator may approximate the halogen to within 20 per cent of the actual value. The test has never given positive results on any compound not containing halogen, with the exception of materials containing copper.

A section of Monel metal tubing 0.9 cm. (0.375 inch) in outer diameter is heated to a cherry red color with a Bunsen burner equipped with a fishtail. The compound to be tested is brought up to within 1 cm. of the under side of the Monel tube. The material decomposes in the flame and the decomposition products are automatically swept up against the hot metal. If the compound contains halogen, a colored flare will appear which may

range anywhere between green and blue. The approximation of percentage is made possible by taking given amounts of material. The liquids are picked up on a platinum loop; the solids, on a small platinum spoon about 2 mm. in diameter.

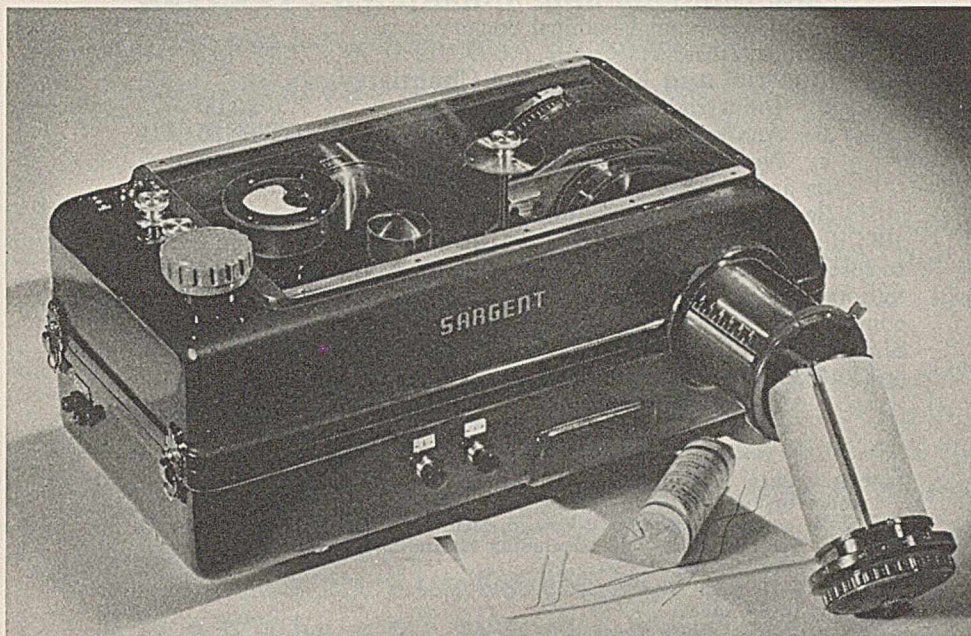
It is necessary to learn to judge the amount of flare. Some compounds decompose very rapidly, giving one broad flare for only an instant, while another of the same halogen content may decompose more slowly and give a narrower flare over a longer period. With experience or the aid of control samples the operator may determine the percentage of halogen to within a very practical limit, so that it is possible, for instance, to differentiate easily between a 2 and 6, 5 and 10, or 25 and 50 per cent value. The method has proved of great value where a rough quick control is desired to follow the course of a reaction.

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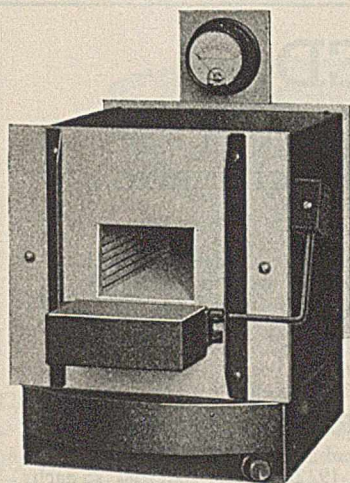
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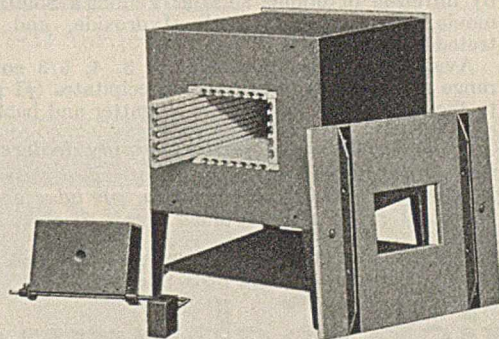
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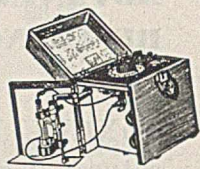
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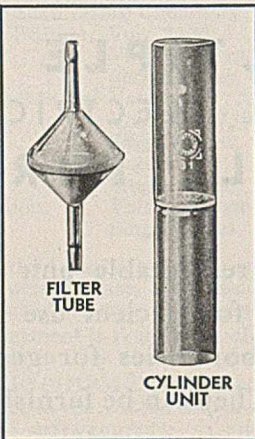
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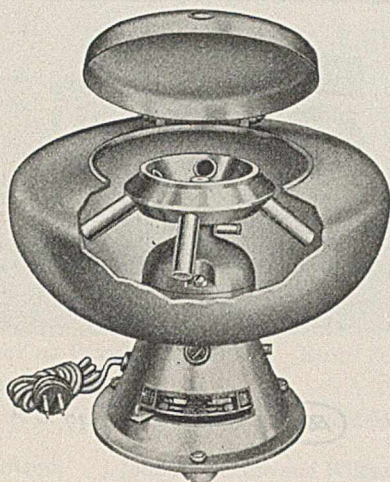
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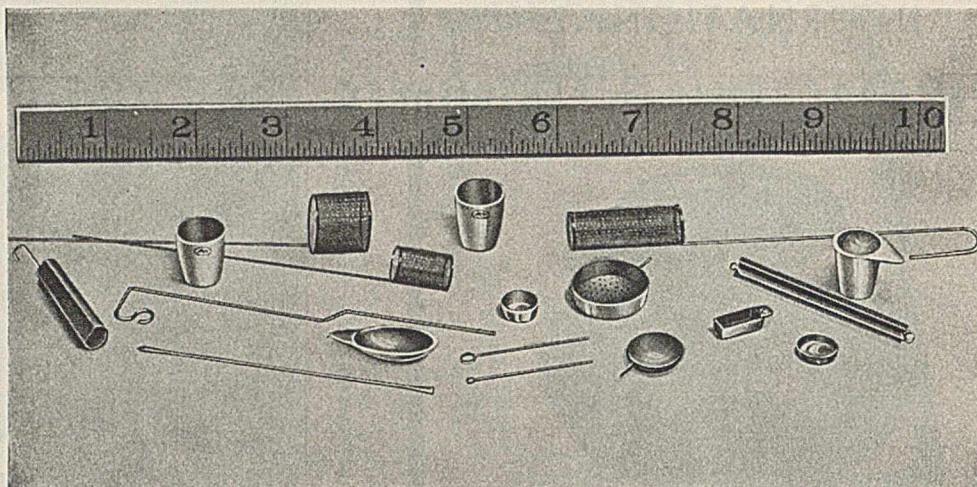
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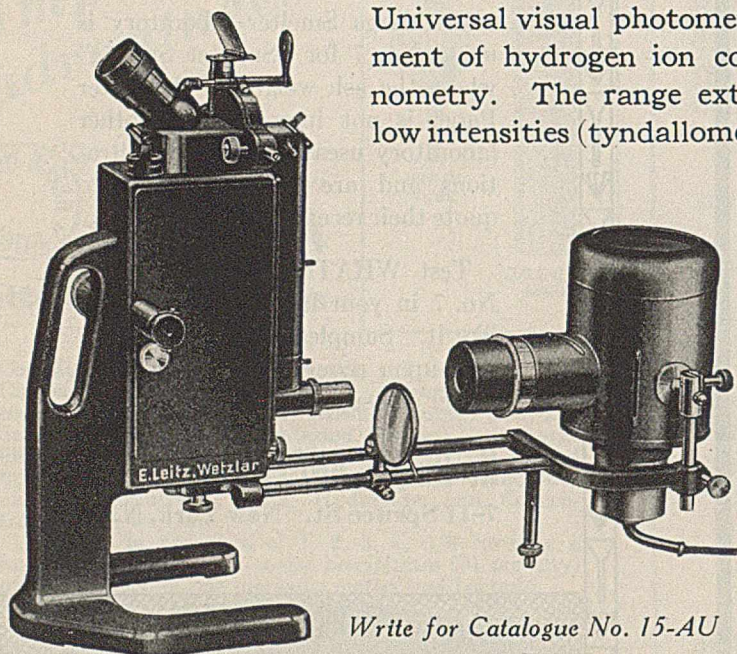
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