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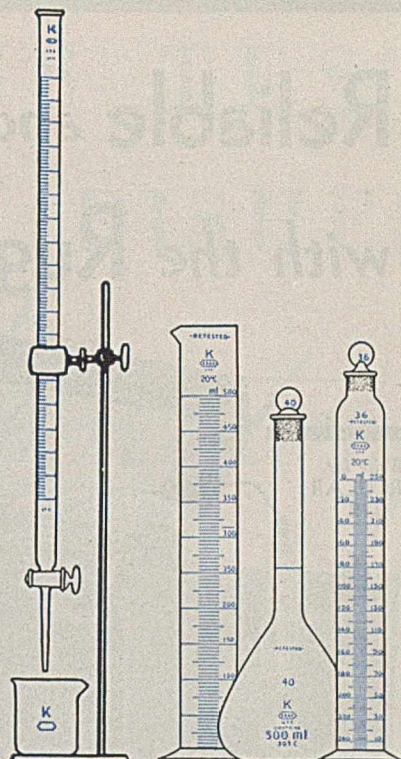
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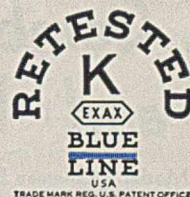
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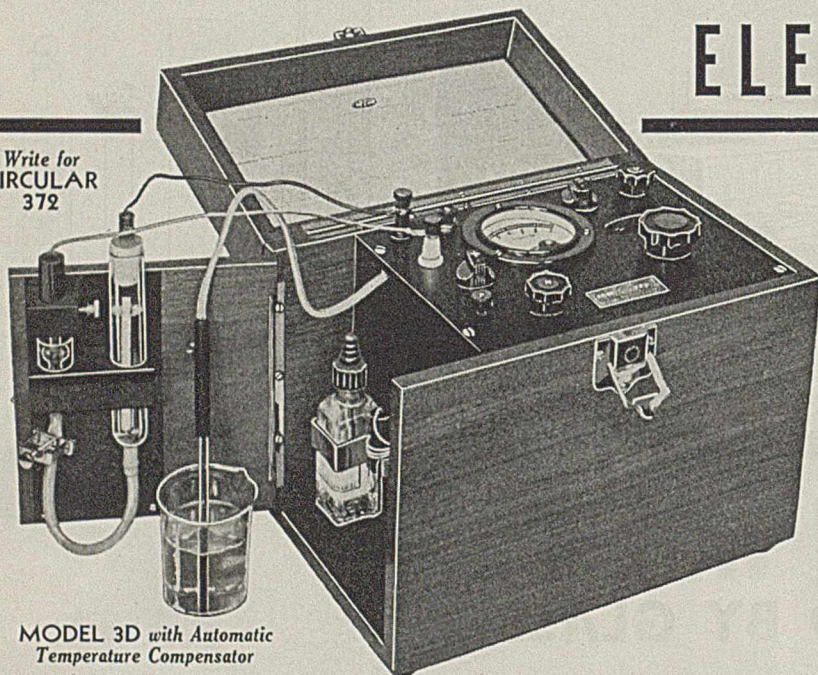


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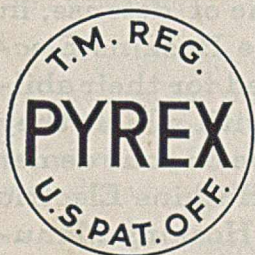
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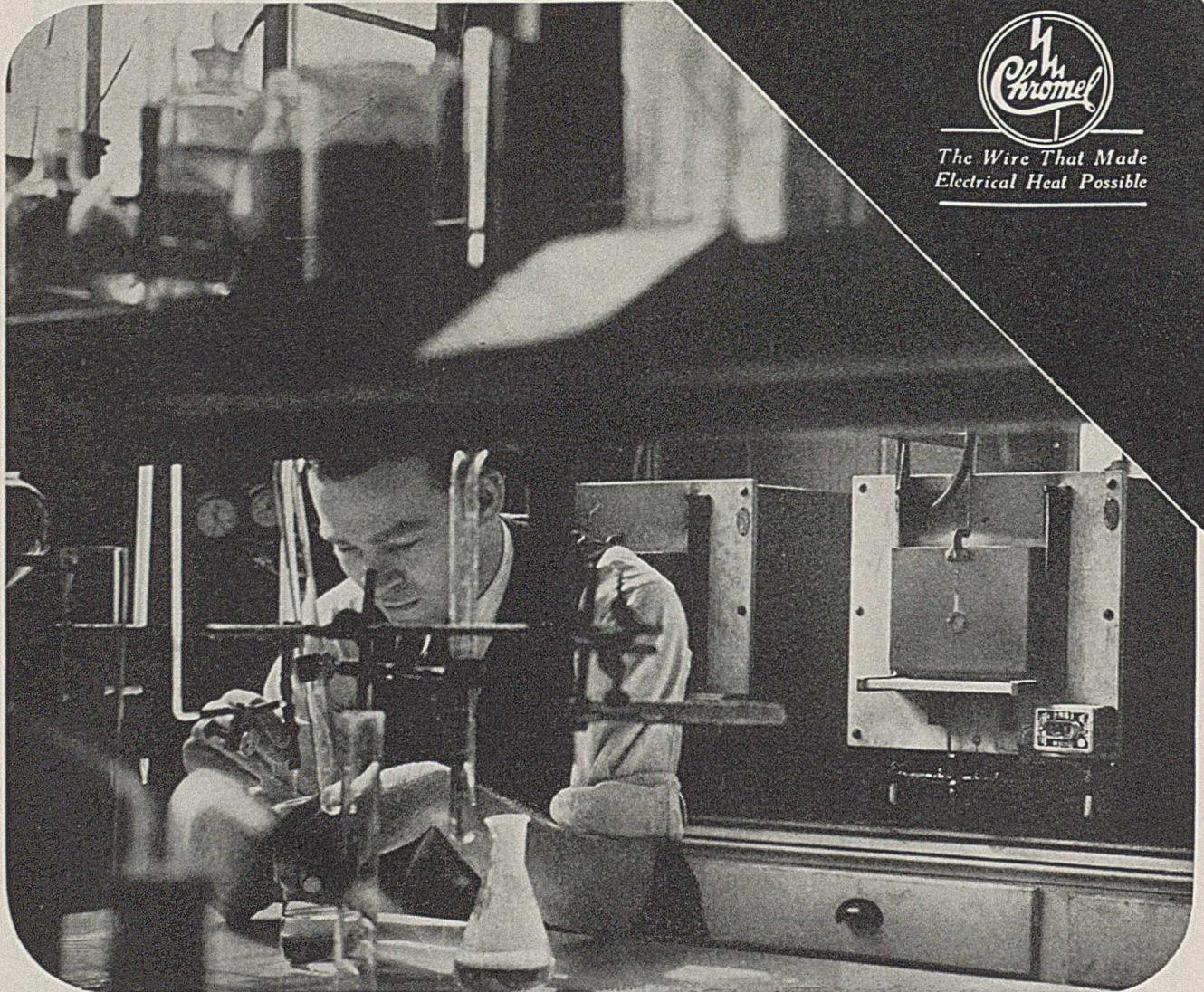
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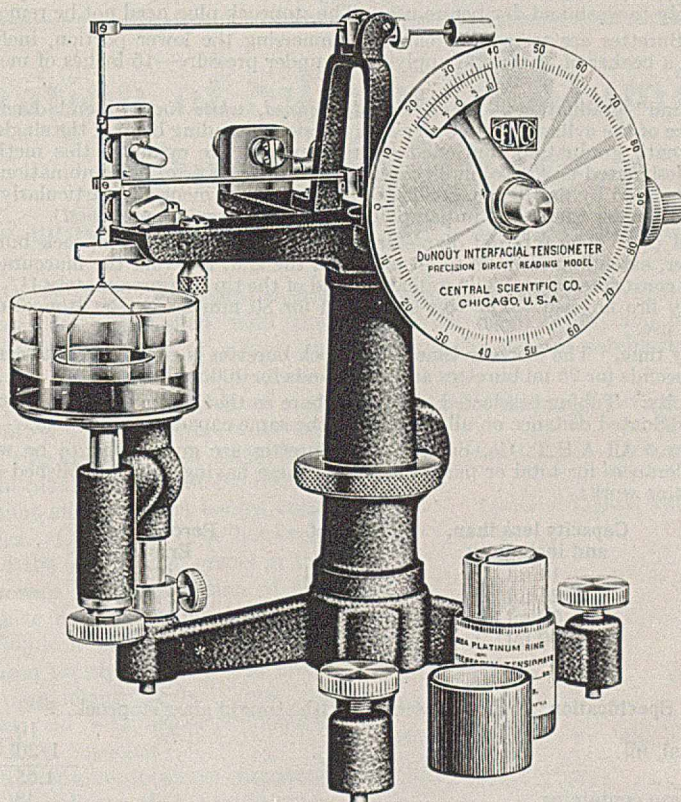
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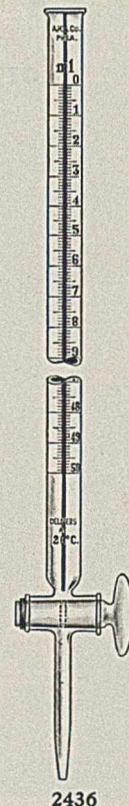
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INDUSTRIAL and ENGINEERING CHEMISTRY

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Determination of Silicon in Aluminum and Aluminum Alloys

H. V. CHURCHILL, R. W. BRIDGES, AND M. F. LEE, Aluminum Research Laboratories, New Kensington, Pa.

A REVIEW of the literature shows that analytical chemists have been more or less dissatisfied with the status of procedures for the determination of silicon in aluminum and aluminum alloys. The main basis of uncertainty lies in the fact that conventional methods of acid decomposition of the sample often yield a residue after dehydration which contains both silicon and silica. This situation is satisfactorily met by an alkaline fusion of the residue which oxidizes the silicon so that all the silicon before volatilization is present as silica. Callendar (2), however, pointed out the possibility and the actuality of errors in the determination of silicon by means of acid solution of the sample. The error was shown to be caused by a volatilization loss of silicon during solution of the sample. The possibility of such error has been tacitly recognized in most silicon methods by the use of oxidizing acids. Thus the inclusion of nitric acid in most acid mixtures recommended has silicon oxidation as one of its purposes.

Analytical work on various aluminum alloys prepared under careful control seems to indicate that acid decomposition yields satisfactory results in most cases, although in others low results seem to be produced.

It seems obvious that silicon losses would be affected by the exact kind of acid used, the physical condition of the silicon as controlled by the thermal history of the metal being analyzed, and possibly by the compounds in which the silicon occurred. Typical analytical data covering the above points are shown in Table I. In the second column *O*, *H*, *W*, and *T* have the following meaning: *O* designates metal which is fully annealed. *H* designates metal in a hard temper produced by cold working. *W* means temper of metal produced by solution heat treatment without any subsequent precipitation heat treatment. In the case of 17S, *T* refers to the temper of metal produced by solution heat treatment followed by aging at room temperature. In the case of 51S, *T* means the temper produced by solution heat treatment followed by a precipitation heat treatment. The third column refers to the use of an acid mixture made up of 485 cc. of water, 115 cc. of sulfuric acid, 200 cc. of hydrochloric acid, and 200 cc. of nitric acid. These proportions are not fortuitous but are the resultant of evolution based upon necessity. Smaller proportions of nitric acid result in low silicon recoveries.

The data in Table I are representative of a larger amount of data which cannot be presented within allowable space limitations. Data indicate satisfactory agreement between

tri-acid and sodium hydroxide results except in specific cases discussed below, and indicate a trend toward low results in the case of perchloric acid.

TABLE I. SILICON CONTENT OF ALUMINUM AND ALUMINUM ALLOYS

(As determined after three methods of decomposition)

Alloy	Temper or Thermal History	Metal Decomposed by:		
		Tri-acid %	Perchloric acid %	Sodium hydroxide %
51S	<i>O</i>	0.93	0.92	0.94
		0.93	0.93	0.93
51S	<i>W</i>	0.85	0.75	0.94
		0.86	0.73	0.93
51S	<i>T</i>	0.89	0.84	0.93
		0.88	0.84	0.94
17S	<i>H</i>	0.50	0.51	0.51
		0.51	0.51	0.51
17S	<i>O</i>	0.48	0.49	0.49
		0.48	0.49	0.48
17S	<i>T</i>	0.48	0.48	0.49
		0.48	0.47	0.49
2S	<i>H</i>	0.19	0.17	0.19
		0.19	0.17	0.19
2S	24 hours at 148.89° C. (300° F.)	0.20	0.16	0.20
		0.19	0.16	0.20
2S	24 hours at 260° C. (500° F.)	0.20	0.17	0.21
		0.19	0.17	0.21
3S	<i>H</i>	0.25	0.25	0.25
		0.25	0.24	0.25
3S	24 hours at 300° C.	0.26	0.24	0.25
		0.25	0.25	0.27
3S	24 hours at 500° C.	0.25	0.26	0.26
		0.25	0.25	0.26
43S	<i>H</i>	5.06	4.96	5.05
		5.05	4.97	5.05
43S	24 hours at 148.89° C. (300° F.)	5.06	4.97	5.03
		5.05	4.98	5.06
43S	24 hours at 260° C. (500° F.)	4.99	4.91	5.00
		5.00	4.91	5.03

Marked differences between the tri-acid and the sodium hydroxide results are shown in the case of 51S-*W* and 51S-*T*. Satisfactory agreement is shown between the two methods when 51S-*O* is analyzed for silicon. Table II shows the normal alloying constituents or impurities present in the alloys.

TABLE II. NOMINAL COMPOSITION OF METALS ANALYZED

	2S	3S	43S	17S	51S
	I ^a	I	%	%	%
Silicon	I ^a	I	5.00	I	1.00
Iron	I	I	I	I	I
Manganese	..	1.25	..	0.50	..
Copper	I	I	I	4.00	I
Magnesium	0.50	0.60

^a I indicates element present only as impurity.

It is apparent that significantly discrepant results occur only in the case of aluminum alloyed with magnesium silicide and then only when the metal is in a heat-treated condition.

In laboratories wherein aluminum and aluminum alloys are analyzed on a routine basis, the filtrate from the silicon determination is used for the determination of other elements. When the tri-acid method is used for silicon, this filtrate is a sulfate solution which is convenient for further work. The filtrate, when the sodium hydroxide method is used, may consist of either sulfates or perchlorates according to which acid is used for dehydrating silica. However, the solution contains large amounts of sodium salts which are somewhat undesirable.

The tendency toward low results found when perchloric acid is used as the decomposition reagent is somewhat disappointing; the use of this acid is usually desirable in determining silica, since dehydration of silica is satisfactory and the subsequent re-solution of salts is more easily effected than when sulfuric acid is used.

The data shown are representative of many other data, all of which indicate that while the tri-acid method is satisfactory in most cases the sodium hydroxide method should be used when aluminum-magnesium silicide alloys are analyzed for silicon.

The following methods give satisfactory service in determining silicon in aluminum and aluminum alloys.

Tri-Acid Solution Method

Place 1 gram of sample in a 250-cc. beaker. Keeping the beaker covered as much as possible, cautiously add 35 cc. of acid mixture No. 1 (485 cc. of water, 115 cc. of sulfuric acid, 200 cc. of hydrochloric acid, and 200 cc. of nitric acid). When no further action can be seen, evaporate till heavy fumes of sulfuric acid are evolved for 15 minutes, cool, add 10 cc. of 1 to 3 sulfuric acid and 100 cc. of hot water, and boil until salts are dissolved. Stir in some paper pulp, filter through a close-textured paper, and wash well with hot water. Evaporate the filtrate to fumes, cool, dissolve in water, add pulp, filter, and wash as before. Ignite the residues in a platinum thimble. After cooling, mix with 1 to 8 grams (depending on amount of residue) of sodium carbonate. Fuse cautiously until nearly quiet, then finish with a strong heat. Run the melt up the sides of the crucible, cool, and place in a beaker with 50 cc. of 1 to 3 sulfuric acid.

When the melt has dissolved, remove the crucible, washing it out into the beaker. Evaporate, continue heating until heavy fuming has taken place for at least 15 minutes, and remove from heat. While still moderately warm, add a little cold water, followed by 100 cc. of hot water. Heat to complete solution of the

soluble salts, but avoid too long treatment, as the silica tends to redissolve. Filter, after stirring in some paper pulp, and wash thoroughly with hot water. Evaporate the filtrate and heat to fuming again to separate silica, which may have escaped the former dehydration, and combine with the first residue obtained. Dry the filters with contents, then ignite in a platinum crucible at 500° C. until free from carbon, finish at 1000° C., cool, and weigh. Moisten with a few drops of diluted sulfuric acid and add several cubic centimeters of hydrofluoric acid. Evaporate dry, ignite, cool, and weigh again. The loss in weight represents silica. Deduct a determined blank. Silicon = silica \times 0.4672.

Sodium Hydroxide Solution Method

Dissolve 0.5 to 1.0 gram of sample in a covered Monel metal beaker, using 15 cc. of 30 per cent sodium hydroxide solution. When violent action ceases, place on a hot plate and heat gently until the volume of solution is reduced to about 5 cc. If the solution is still dark, add 2 or 3 cc. of 3 per cent hydrogen peroxide to hasten oxidation and again reduce the volume to about 5 cc. Transfer the concentrated sodium hydroxide solution to a Pyrex beaker containing 80 cc. of 1 to 1 sulfuric acid. Thoroughly police the Monel metal beaker and, using a few cubic centimeters of dilute sulfuric acid, wash any adhering material into the Pyrex beaker. Add 2 cc. of concentrated nitric acid. Evaporate to copious fumes and finish by the usual silica volatilization procedure. (This method with double dehydration was used to obtain results shown in last column of Table I.)

ALTERNATIVE METHOD. (This procedure is now preferred to the one given above because after dehydration salts are more easily dissolved.) Transfer the solution to a Pyrex beaker containing 65 cc. of 1 to 1 sulfuric acid and 20 cc. of 60 per cent perchloric acid. Thoroughly police the Monel beaker and cover and, using a few cubic centimeters of dilute sulfuric acid, wash any adhering material into the Pyrex beaker. Make double dehydration by evaporation to copious fumes and finish by usual silica volatilization procedure.

Another alternative procedure, substantially as published by the Aluminum Research Institute (1), is: Neutralize the concentrated sodium hydroxide solution with 1 to 1 hydrochloric acid and transfer it to a Pyrex beaker. Add 20 cc. of 60 per cent perchloric acid. Evaporate to copious fumes, cool, add 50 cc. of hot water, bring to a boil, filter at once using an ashless paper pulp, and wash with warm 1 per cent hydrochloric acid. Add 10 cc. of perchloric acid to filtrate, fume, and filter as before. Dry the filters with contents, then ignite in a platinum crucible at 1000° C. Add a few drops of sulfuric acid and ignite to constant weight. Cool and weigh. Finish by the usual silica volatilization procedure.

Literature Cited

- (1) Aluminum Research Institute, Standard Methods for Sampling and Analyzing of Aluminum and Certain Aluminum Alloys, 1932.
- (2) Callendar, L. H., *Analyst*, 58, 81 (1933).

RECEIVED February 5, 1937.

Determining the Aniline Point of Dark Petroleum Products

LEON DONN, The Texas Company, Beacon, N. Y.

THE aniline point (2) is the solution temperature of an oil with an equal part by volume of aniline. The Institution of Petroleum Technologists (1) describes a method for the determination of the aniline point of an oil, and remarks, regarding opaque oils (3), that their aniline points can usually be determined with suitable illumination or by observation of the thin film of the mixture which is splashed up on the sides of the tube during stirring.

This method works well with both transparent and not too dark oils. In the case of really opaque materials, however, it is practically impossible to obtain better than a rough ap-

proximation of the correct result. In view of this, a method has been developed particularly for dark products and has been found to give results that are in excellent agreement with those obtained by the I. P. T. method.

A consideration of the viscosity of a slowly cooling solution of two liquids in the region of their solution temperature reveals the following facts:

1. Above this temperature where true solution holds, the viscosity of the solution increases uniformly with decreasing temperature.
2. When, on cooling, the solution temperature is reached

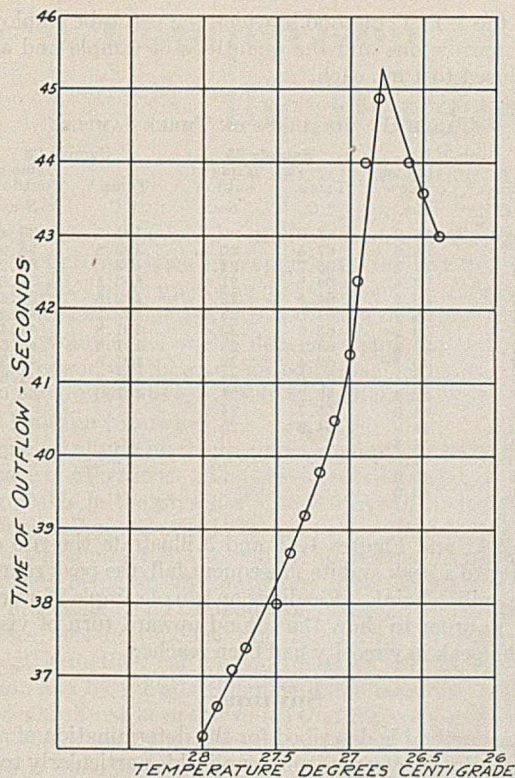


FIGURE 1. CURVE FOR SAMPLE 10

and the solution begins to separate into finely divided particles of its components, the emulsion-like mass thus momentarily formed causes a sharp increase in viscosity. This sharp peak corresponds very closely to the aniline point obtained by visual methods.

3. As the temperature continues to fall below the solution temperature, the particles of components grow rapidly in size, so that the emulsion no longer holds. During this period of cooling the viscosity is found to decrease rather than increase with cooling. This serves to accentuate the high viscosity peak.

Apparently, a study of the viscosity of a solution in the neighborhood of its solution temperature reveals its aniline point.

Procedure

Equal parts by volume of dry distilled aniline and sample are introduced into an Ostwald viscometer and the viscosity tube is heated by means of a suitable bath to a temperature sufficiently high to cause complete solution. During the heating, the mixture of sample and aniline is agitated by applying very gentle suction to the wide end of the viscometer, thereby causing a slow bubbling of air through the mixture which stirs it thoroughly. Solution having been effected, the bath is permitted to cool very slowly. At the same time relative viscosity readings are begun at this temperature above the aniline point, and continued as rapidly as possible during the cooling period. The time of outflow steadily increases with falling temperature until a maximum time of outflow is obtained. Thereafter, through a comparatively long period, the readings continually decrease with falling temperature. It has been found that the temperature corresponding to this maximum reading corresponds very closely with the aniline point obtained by the I. P. T. method.

The aniline used was of C. P. grade, and was dried by contact with anhydrous potassium carbonate for several days, and then distilled. Only the middle portion of the distillate was retained for use.

The Ostwald pipet corresponded to Eimer and Amend Catalog No. 32804 and had a time of outflow of 15 seconds at room temperature for a charge of 5 ml. of water.

The approximate temperature of complete solution can be determined in several ways, the simplest being by noting the appearance of the mixture in the capillary of the viscometer after a short stirring period. For very dark samples, whose solutions were even too opaque for observation through the

finest viscometer capillary, a micromethod was employed, which consisted in rapidly transferring a drop of hot solution to a hot but gradually cooling microscope warming stage equipped with a thermometer, and promptly covering the drop with a cover glass. Observation through the microscope of the thin film produced by the drop between the two glasses showed the aniline point by the change in appearance from a clear, transparent, though often highly colored film, to the formation of a grainy film, the grains of which grew continually larger until small droplets were definitely formed.

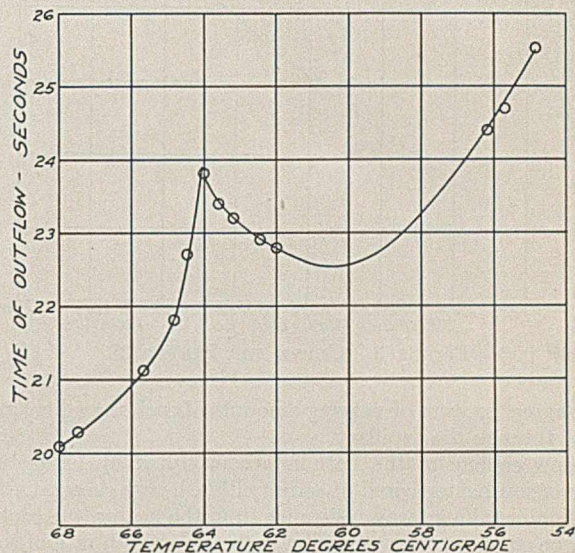


FIGURE 2. CURVE FOR SAMPLE 25

The first indication of graininess in the film was taken as the approximate aniline point, and the heating bath for the viscosity method was started at a temperature a few degrees higher than this. The behavior of the sample and aniline in the viscometer serves also to show whether the solution is complete. Successive viscosity readings of a complete solution with agitation of the solution between each reading should agree consistently with each other, while readings of an incomplete solution taken in the same way will be erratic and

TABLE I. SOLUTION TEMPERATURE

Sample	I. P. T. Method ° C.	Capillary-Tube Method ° C.	Micro-method ° C.	Narrow-Tube Method		Viscosity Method	
				Run 1 ° C.	Run 2 ° C.	Run 1 ° C.	Run 2 ° C.
1	...	71.2	71.8	71.95
2	...	Over 80	88.0	88.1
3	...	Over 90	94.1	93.9
4	...	89.8	89.9	..
5	63.6	63.7
6	56.5	57.5	57.5	57.7
7	65.0	66.0	65.8	65.7
8	48	49	48.7	48.8
9	41	41.8	41.6
10	26.5	26.8	26.85
11	35	37.3	..
12	77.5	76.8	76.9
13	72.5	75.6	75.3
14	23	22.8	22.7
15	69	67.3	67.3
16	60	57.5	58.0
17	54	49.0	49.0
18	60	58.0	59.0
19	69	64	..
20	73.5	..	73	73.3	73.5
21	68	..	68	68.1	..
22	43.8	..	45
23	46.9	..	49
24	48.4	..	49
25	63.5	64	..
26	Approx. 98	99.6	99.5
27	Over 98	104.2	104.2
28	Over 95	101.4	101.5
29	91	90.5

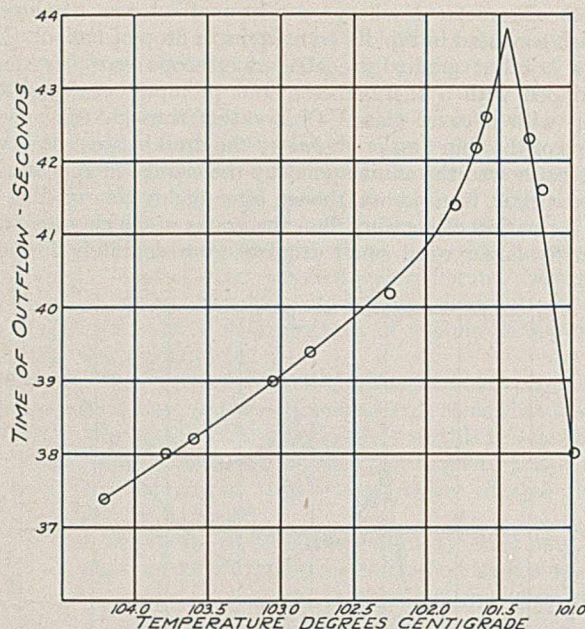


FIGURE 3. CURVE FOR SAMPLE 28

not agree, because of varying amounts of each ingredient running through the capillary.

Slow cooling of the bath is accomplished by having the immersion heater wired in series with a heavy rheostat. By adding or taking away resistance from the heater, the cooling can be cut down to a very slow rate. A smooth rate of cooling of about 1° C. in 5 to 10 minutes was found to be satisfactory. In case a sample has a solution temperature below room temperature, an immersed copper cooling coil is a convenience for further lowering the bath temperature.

Table I compares solution temperatures of different samples by various methods. The narrow-tube method is a modifica-

tion of the I. P. T. method in which the test tube employed is a very narrow one and the quantities of sample and aniline are reduced to 1 ml. each.

TABLE II. READINGS ON THREE SAMPLES

Sample 10		Sample 25		Sample 28	
Temp. ° C.	Time of outflow Sec.	Temp. ° C.	Time of outflow Sec.	Temp. ° C.	Time of outflow Sec.
28.0	36.2	68.0	20.1	104.2	37.4
27.9	36.6	67.5	20.3	103.8	38.0
27.8	37.1	65.7	21.1	103.6	38.2
27.7	37.4	64.8	21.8	103.1	39.0
27.5	38.0	64.5	22.7	102.8	39.4
27.4	38.7	64.0	23.8	102.25	40.2
27.3	39.2	63.6	23.4	101.8	41.4
27.2	39.8	63.2	23.2	101.6	42.6
27.1	40.5	62.4	22.9	101.3	42.3
27.0	41.4	62.0	22.8	101.2	41.6
26.95	42.4	56.2	24.4	101.0	38.0
26.9	44.0	55.7	24.7
26.8	44.9	54.9	25.5
26.7	44.8
26.6	44.0
26.5	43.6
26.4	43.0

Table II and Figures 1, 2, and 3 illustrate the rise of the viscosity to a peak and its subsequent fall, the peak representing the aniline point. Readings on run of sample 25 were continued in order to show the second upward turn of viscosity after the peak in viscosity had been reached.

Summary

A new method is described for the determination of aniline point or solution temperature, applicable particularly to dark-colored samples.

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Refractive Index of Strontium Nitrate

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THE use of immersion methods for determining the refractive indices of solids requires a series of immersion liquids whose refractive indices are known with an accuracy of about 0.001. The refractive indices of the immersion liquids may be determined in a refractometer or by use of a series of isotropic crystals whose refractive indices are known. Chamot and Mason (2) list such a series of isotropic crystals to be used in determining the refractive indices of liquids by immersion methods. In this list, the refractive index of strontium nitrate $[\text{Sr}(\text{NO}_3)_2]$ is given as 1.567.

While checking the refractive indices of a set of immersion oils, it was found that the value given by Chamot and Mason is incorrect. The refractive index of strontium nitrate determined by the immersion method, using white light, is 1.586. The sample of strontium nitrate used was analyzed and found to be pure $\text{Sr}(\text{NO}_3)_2$ with less than 0.1 per cent water.

A check of the literature showed that the refractive index of strontium nitrate is given as 1.5667 by International Critical Tables (7), Fry (5), and Landolt, Bornstein, and Roth (9). The compilers of these tables apparently took the value of 1.5667 from the standard work of Groth (6),

who depended upon the determinations of Fock (4) and Craw (3). The correct value is given by Behr (1) who found strontium nitrate to have a refractive index of 1.5878, using sodium light and the more accurate crystal refractometer. Keenan (8) states that he has depended on Behr's determination, which appears to be more nearly correct.

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A Comparison of Quantitative Methods for the Determination of Copper

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THE three most widely used methods for the quantitative determination of copper are the electrolytic, the gravimetric, based upon the precipitation of cuprous thiocyanate (or a combination of this with an oxidation titration), and the volumetric, which depends upon the fact that bivalent copper will liberate an equivalent amount of iodine from a soluble iodide. Each method has certain advantages and disadvantages.

The electrolytic method is most susceptible to error in the presence of other ions. The gravimetric thiocyanate method is applicable in the presence of ions other than those of lead, mercury, tellurium, selenium, and the precious metals. The iodometric method is also widely applicable, the interfering substances being arsenic, antimony, iron, hexavalent molybdenum, selenium, and the oxides of nitrogen. In the majority of cases met in practice, the interfering elements in the iodometric method can be controlled by the use of a buffer solution and by the addition of suitable reagents (5, 6).

Recently it has been shown (2) that the volumetric method is capable of giving more exact results when the usual procedure is modified slightly, and the present work has been carried out with the purpose of comparing this modified iodometric method with the standard methods. This modification consists simply of the addition of 1 to 2 grams of a soluble thiocyanate to the solution after almost all of the iodine liberated has been removed by the thiosulfate solution. With this modification the method is so nearly quantitative that the iodine standard of the thiosulfate may be calculated in terms of copper without the need for an empirical standardization with copper. In the presence of the interfering elements already noted, the arsenic, antimony, and iron are oxidized and a buffer solution is prepared, which will prevent the pentavalent arsenic and antimony from liberating iodine from the potassium iodide. The ferric iron is converted into a complex fluoride (5). Park (6) recommended the use of a phthalate buffer, for the reason that the reaction liberating iodine proceeds too slowly in the presence of the more usual acetate buffer solution. However, with the modification mentioned (2), an acetate buffer may be used. Sodium fluoride or ammonium bifluoride may be used to form the complex iron fluoride. During the progress of this work an article appeared (1) pointing out that the addition of ammonium bifluoride to an acid solution produces a buffer solution of the correct pH to prevent the interference of arsenic and antimony, as well as the interference of iron. This procedure was also included in the methods studied.

Procedures

The electrolytic method (a) was the usual procedure as described by Hillebrand and Lundell (3).

The gravimetric thiocyanate method (b) was according to Hillebrand and Lundell (3) or that recommended by Kolthoff and v. d. Meene (4).

The iodometric method (c) using an acetate buffer was carried out in the following manner:

The samples were dissolved in aqua regia with subsequent addition of potassium chlorate. The equivalent of 10 ml. of 6 N sulfuric acid was added and the nitric acid was removed completely, often with an additional evaporation with hydrochloric acid. The residue was taken up in 20 to 40 ml. of water and the equivalent of 25 ml. of 6 N acetic acid and 12 ml. of 6 N ammonium

hydroxide was added. The resulting buffer solution has a pH of approximately 3.7. Interfering elements were, in general, added before the solution of the copper ore. Following the preparation of the buffer, sodium fluoride was added directly before titration, 1 gram being used for every 0.1 gram of iron.

The iodometric method (d) using ammonium bifluoride was identical with (c) except that no acetic acid nor ammonia was added, the bifluoride being added directly to the sulfuric acid solution.

TABLE I. ANALYSIS OF ORE AND COPPER SULFIDE^a

Method	Chalcocite Ore		Maximum Deviation	Copper Sulfide		Maximum Deviation
CuCNS	74.47	0.05 (7) ^b	+0.11	64.01	0.02 (4)	-0.06
Iodoacetate	74.36	0.03 (7)	+0.08	63.98	0.03 (5)	+0.09
Electrolytic	74.44	0.04 (3)	+0.07	64.05	0.02 (3)	+0.03
Iodofluoride	63.98	0.03 (6)	+0.11

^a Deviation indicated is the mean deviation.
^b Numbers in parentheses refer to the number of experiments carried out using the particular procedure.

To the solutions resulting from procedures (c) or (d), potassium iodide was added and the liberated iodine titrated with sodium thiosulfate with the addition of ammonium thiocyanate near the end point. The sodium thiosulfate was standardized against nearly pure copper of known copper content.

The source of the copper used in the determinations was either a specially prepared sample of cupric sulfide or a chalcocite ore, kindly provided by Professor Bateman of the Department of Geology of this university. The results showed no essential differences, whichever of the two samples was used. Arsenic and iron were added together in the form of arsenopyrite, or separately as dihydrogen potassium arsenate and a solution of ferric nitrate. The antimony was in the form of potassium antimonate.

The samples of copper sulfide and chalcocite were very finely ground and as a consequence either oxidized or adsorbed moisture very slightly over the period of time during which the experiments were performed. In order always to be able to compare the results with the known copper content of the pure samples, the two sources of copper were analyzed frequently, in most cases a sample of the pure ore being run simultaneously with the analysis of the same ore to which interfering elements had been added.

Table I shows the results of analyses of the synthetic cupric sulfide or chalcocite. The term "iodoacetate" refers to the modified iodometric method in an acetate buffer, while "iodofluoride" refers to the same method using a fluoride-bifluoride buffer solution alone.

Interfering Elements

In the presence of the interfering elements normally found in copper ores or alloys, the electrolytic method is not applicable, so it was used only in analyses of the pure sulfides. Its use here, however, serves to show the high accuracy of the volumetric method; in general, the volumetric method agrees approximately within one part in a thousand with the two gravimetric methods, though it is definitely low by that amount. The possibility that there were traces of interfering elements in the chalcocite ore was considered; in fact, 0.02 per cent of silver was found and the results are corrected by that amount. All other elements which might interfere were found to be absent.

TABLE II. ANALYSES IN PRESENCE OF INTERFERING ELEMENTS^a

Substances Added	Fe	Fe	AsV	SbV	Arsenopyrite			Fe + As	Fe + As + Sb
	Gram	Gram	Gram	Gram	Gram	Gram	Gram	Gram	Gram
Amounts	0.05-0.14	0.2-0.3	0.04-0.2	0.008-0.023	0.1-0.2	0.3-0.4	0.1-0.2 + Fe 0.07-0.14	Fe 0.07-0.14 As 0.05-0.2	Fe 0.07-0.2 As 0.06-0.2 Sb 0.015-0.032
CuSCN	-0.07(8) ^b	-0.12(3)	-0.05(6)	-0.09(6)	-0.05(3)	-0.05(2)
Maximum deviation	-0.14	-0.15	-0.21	-0.19	-0.22	-0.07
Iodoacetate	-0.03(9)	-0.05(5)	+0.02(9)	-0.09(5)	-0.08(7)	-0.30(3)	-0.27(2)	-0.20(6)	-0.18(3)
Maximum deviation	-0.13	-0.15	+0.14	-0.17	-0.28	-0.40	-0.28	-0.38	-0.28
Iodofluoride	-0.20(7)	-0.93(3)	-0.08(6)	-0.02(2)	-0.24(1)	-0.24(6)
Maximum deviation	-0.41	-1.77	-0.19	-0.04	-0.41

^a Figures given for each method are mean deviations from per cent of copper in pure sample.

^b Figures in parentheses give number of determinations carried out in each particular case.

The results of nearly 100 analyses carried out in the presence of interfering elements are given in Table II. The arsenopyrite used had the following percentage composition: Fe, 33.88; As, 45.35; S, 19.62; SiO₂, 0.87. Copper, if present, amounted to less than 0.02 per cent and was disregarded.

The size of sample of ore or cupric sulfide was varied within wide limits, and about half the results were carried out using a weight buret, the other half being with a volume buret.

Several conclusions may be drawn from the results: The results are generally low by a small amount. The iodofluoride method fails in the presence of more than 0.15 gram of iron (column 2), but is slightly more accurate than the iodoacetate method in the presence of large amounts of arsenopyrite (column 6). In general, the results of the volumetric methods are excellent. In the presence of usual amounts of iron and arsenic, such as are likely to be found particularly in ore analysis, it is of no consequence which of the two volumetric procedures is used, and both are in perfect agreement with the more laborious method involving the precipitation of

copper thiocyanate (column 5). It was always noted that in using the iodofluoride method the end point was distinctly yellow rather than white, and consequently not quite so sharp as in the iodoacetate method. Column 9 shows the results of the iodoacetate method in the presence of all three commonly occurring interfering elements.

The gravimetric procedure is applicable in the presence of as much as 35 mg. of antimony; the results are not shown in the table.

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Determination of Rotenone in Derris and Cube Crystallization from Extracts

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SEVERAL years ago the author proposed a method for the determination of rotenone in plant material involving extraction and crystallization with the use of carbon tetrachloride (4). Since that time numerous similar methods have been proposed, usually employing other extraction solvents, but in most cases crystallizing the rotenone from carbon tetrachloride. Cahn and Boam (2) have made a detailed study of the extraction and crystallization and have proposed a modified procedure embodying several improvements. They have, however, questioned the accuracy of the crystallization, particularly for samples of low rotenone content. Other investigators (1, 3, 6) have stressed the need of more rapid extraction and have suggested other solvents, but have made no detailed study of the crystallization. The method used in this laboratory has also been changed from time to time since the procedure was published. The need for a shortened procedure and the importance of a knowledge of the accuracy of the determination have led to a more detailed study of this method for rotenone determination.

The method involves two phases, extraction and crystallization. It is necessary to decide on the latter procedure first, since errors in, or improvements of, the extraction can be studied only by means of crystallization. The present

article will be confined to a description of the crystallization procedure adopted, a discussion of its mechanism, and an evaluation of its accuracy.

Proposed Crystallization Procedure

The crystallization procedure finally adopted is similar to the original method, but the size of sample has been reduced, precautions have been taken to assure quantitative crystallization, and a test for the purity of the separated solvate has been introduced. The exact procedure is as follows:

The extract from a 25-gram sample of root in a 125-cc. Erlenmeyer flask is evaporated on the steam bath in a current of air until free of solvent. The residue is treated with exactly 25 cc. of carbon tetrachloride, the flask is loosely stoppered, and complete solution is effected by gentle warming. The extract is next cooled in an ice bath for several minutes and then seeded with a few crystals of rotenone-carbon tetrachloride solvate. The flask is then tightly stoppered and swirled until crystallization is apparent. If at this stage only a small amount of crystalline material separates, an accurately weighed quantity of pure rotenone should be added, the mixture warmed to effect complete solution, and crystallization again induced. Sufficient rotenone must be present so that the result, expressed as "pure" rotenone, is at least 1 gram. At the same time a solution of rotenone in carbon tetrachloride containing 0.27 gram per 100 cc.

of solution (the solubility at 0° C.) is prepared for use in washing. The extract and the washing solution are then placed in an ice bath capable of maintaining a temperature of 0° C. overnight.

In the morning (the method is based on a crystallization time of 17 to 18 hours) the extract is filtered rapidly through a weighed Gooch crucible in the bottom of which has been placed a disk of filter paper, the flask being removed from the ice bath only long enough for pouring a small portion of extract into the crucible. The separated crystalline material is rinsed from the flask and washed under suction with sufficient of the ice-cold saturated solution (usually 6 to 10 cc.) to remove the excess mother liquor. Suction is applied for about 5 minutes, and then the material is dried to constant weight at 40° C., which usually requires about 1 hour. This is the weight of crude rotenone-carbon tetrachloride solvate.

The contents of the crucible are then broken up with a spatula and thoroughly mixed, and a 1-gram sample is placed in a 50-cc. Erlenmeyer flask where it is treated with 10 cc. of alcohol which has been saturated with rotenone at room temperature. The flask is swirled for a few minutes and then tightly stoppered and set aside at the same temperature for 4 hours. The mixture is then filtered at the same temperature through a weighed Gooch crucible with filter-paper disk. The crystals are rinsed from the flask and washed under suction with the solution of alcohol saturated with rotenone at the temperature of the recrystallization. About 5 cc. are usually required for this. Suction is applied for about 3 minutes, and then the material is dried at 105° C. to constant weight, or for about 1 hour. The weight in grams is multiplied by the weight of crude solvate, and to the product is added 0.07 gram, representing the correction for rotenone held in solution in the 25 cc. of carbon tetrachloride used in crystallization. If any pure rotenone was added, its weight must be subtracted from the value obtained. This gives the weight of "pure" rotenone contained in the extract of the 25-gram root sample.

General Procedure of Study

In this study the general procedure was to make use of aliquots of large volumes of carbon tetrachloride extracts of several root samples, to avoid errors due to possible differences in extraction.

In preparing an extract, 250 grams of root were treated with 1 liter of carbon tetrachloride and the mixture was boiled on the steam bath under a reflux condenser for several hours. The mixture was filtered by suction and the marc washed on the filter with a small amount of hot carbon tetrachloride. The clear filtrate and washings, refiltered if necessary, were then made to exactly 1 liter. A 100-cc. aliquot of this represented approximately a 25-gram sample of the root. By using aliquots of a single extract in the comparative study of any particular point in the method, samples of exactly the same composition were assured. These aliquots were evaporated to dryness and treated by whatever procedure was being tested. The total solid content of each extract was determined by evaporation of smaller aliquots. It was found that heating the dried extract on the steam bath overnight caused considerable decomposition, and excess heating should therefore be avoided. A number of comparative determinations were made by several methods of crystallization in which one sample of a pair was evaporated in a current of air and the other in a current of carbon dioxide, with no difference in the final result.

Time of Crystallization

The rate of crystallization of the solvate is an important factor in the procedure. It has been found that the crystallization is markedly retarded by the resinous, or nonrotenone, portion of the extract. Thus, solutions of pure rotenone in carbon tetrachloride reached the point of equilibrium by crystallization, as judged by no additional separation, in a much shorter time than did similar solutions containing equal amounts of rotenone in the presence of other extractives of derris and cube. Further, in the cases of both pure rotenone and rotenone in extracts crystallization was more rapid when larger proportions of rotenone were present, in accordance with the established fact that rate of crystallization is greater with a higher degree of supersaturation. Because of this fact it seems wise to run the crystallization at as low a temperature as practical. The results also indicate that the resinous por-

tion of the extract exerts practically no solvent effect on the rotenone solvate. This point will be discussed more fully in connection with the accuracy of the method.

Purity of the Solvate

The amount of washing that should be given the separated solvate must be left to the judgment of the analyst. Sufficient wash solution should be used to remove most of the mother liquor. Additional washing effects no appreciable increase in purity and, as Cahn and Boam (2) have pointed out, causes a loss even when a saturated solution is used. It is believed that the impurity in the washed, dried solvate crystals is principally adsorbed resin.

Cahn and Boam (2) have proposed a purity test for the solvate and have found that by this test the crystals as ordinarily obtained are from 80 to 90 per cent pure. This test is based on the fact that the solvate, when treated with a small proportion of alcohol, undergoes solution and recrystallization as rotenone, a purification resulting as in any recrystallization. They used 5 parts of saturated alcohol to 1 part of solvate and allowed the mixture to stand overnight at room temperature. This method was used by the present author in preliminary work on improving the crystallization, and found to be rather satisfactory. However, a shorter method with a reasonable degree of accuracy was desired.

Attempts were first made to obtain the original solvate in a state of higher purity. Crystallization from a larger proportion of carbon tetrachloride than that usually employed gave material of higher purity, but to obtain solvate of the desired purity by this method would require volumes of solvent so large as to cause difficulty in handling and introduce a source of considerable error.

To test methods of determining the purity of the separated solvate, samples of crude solvate of known purity were prepared. It was desired to have these resemble as closely as possible the solvate obtained in the usual procedure. Therefore, extracts containing known, small amounts of rotenone (prepared as described under Accuracy of the Method) were treated with an amount of pure rotenone calculated to give the desired purity, the whole was dissolved in hot carbon tetrachloride, and the solution evaporated to a small volume. The carbon tetrachloride remaining after this evaporation was considerably in excess of that required to combine with the rotenone present as solvent of crystallization. The solution was cooled to room temperature, and stirred continuously until the solvate had crystallized to a pasty consistency. The mixture was stirred frequently until dry, was then thoroughly mixed, and all lumps were broken up.

It was found that, by heating these impure solvates to constant weight at 105° C. and assuming the loss in weight to be all carbon tetrachloride of crystallization from the rotenone, values approximating the known purities of the solvates were obtained. Considerable time was required, however, to remove the solvent of crystallization, and the method is less accurate than one based on a determination of the rotenone, since it is based on the determination of less than 28 per cent of the weight of solvate.

Comparative tests were then made of the original Cahn and Boam test and analogous procedures using different proportions of solvent and shorter periods of time. Results of some of these tests are shown in Table I.

It was found that when the proportion of alcohol was increased to 10 cc. per gram of solvate the conversion to pure rotenone was complete in 4 hours, and the values obtained, although a trifle lower than those given by the original Cahn and Boam test, in general more nearly approached the correct values for the known solvates. The modified test has been adopted, largely because it is easier to handle. It will be

TABLE I. COMPARISON OF PURITY TESTS ON SAMPLES OF ROTENONE-CARBON TETRACHLORIDE SOLVATE OF KNOWN PURITY

(Expressed as percentage of pure rotenone-carbon tetrachloride solvate)

Extract	Known Purity	Purity by Cahn and Boam Test and Modifications			
		With 5 cc. of alcohol		With 10 cc. of alcohol	
		Over-night	4 hours	Over-night	4 hours
Derris A	81	81.5	81	..	80.5
	81	81	81.5	80	80
	90.5	90	91.5	89.5	89
Cube	80.5	82	..	79.5	80
	90.5	92.5	..	90	91
Derris B	80.5	82	80
	85.5	87	85
	90.5	91	89

TABLE II. PURITY OF ROTENONE-CARBON TETRACHLORIDE SOLVATE

(Crystallized from different proportions of rotenone to nonrotenone resin in 25 cc. of carbon tetrachloride)

Extract	Nonrotenone Resin Grams	Rotenone Grams	Purity of Solvate
			%
Cube	2.93	2	96.5
		1	92.5
		0.5	91.5
		0.4	91
		0.3	90
Derris	2.26	2	94
		1	90.5
		0.5	84
		0.4	84.5
		0.3	84

noted from Table I that the test may be allowed to stand overnight, if more convenient, with practically the same results.

The data in Table II show that the purity of the solvate increases with the proportion of rotenone to nonrotenone resin.

Likewise, with a given amount of rotenone and nonrotenone resin—that is, with a given total extract—the purity is dependent on the amount of solvent. Thus, a derris extract containing about 1 part of rotenone to about 1.7 parts of nonrotenone resin when crystallized from a solution having a proportion of 1 gram of total extract to 6.5 cc. of carbon tetrachloride gave a solvate of 93 per cent purity, while the same extract crystallized from a solution having a proportion of 1 gram of total extract to 2 cc. of solvent gave a solvate of 86 per cent purity. In each case crystallizations of the solvate were made at both room temperature and 0° C., with no difference in the purity obtained.

The purity of the solvates obtained has ranged from about 70 to 95 per cent. This test is merely a recrystallization dependent on the difference in solubility between rotenone and the solvate, and therefore does not give absolutely pure rotenone. Melting points of the "pure" rotenone obtained have ranged from 155° to 162° C., and it was readily shown that its purity, as judged by the melting point, depended on the purity of the solvate from which it was obtained. Thus the error involved becomes larger with increasingly impure solvate. For this reason it is desirable to use a method in which the solvate is obtained in as pure a form as possible in the original crystallization.

Precision of the Method

The precision of the method adopted was tested with nine aliquots of an extract of derris root (No. 2). From preliminary tests it was known that the rotenone content would be somewhat above 4 per cent, and hence within the range of complete crystallization. To one of the aliquots 0.5 gram of rotenone was added, but on crystallization no excess rotenone was obtained. The "pure" rotenone ranged from 1.114 to 1.148 grams; with a mean of 1.129 grams; equivalent to 4.5 per cent of the root. The standard deviation was ± 0.013 gram, or a standard deviation of about ± 0.05 per cent in the final result.

Accuracy of the Method

PREPARATION OF EXTRACTS OF KNOWN ROTENONE CONTENT. To determine the accuracy of the crystallization method it was necessary to have extracts of known rotenone content,

preferably low, to which various amounts of rotenone might be added. There were on hand several samples of derris root that had yielded no rotenone by the old method of crystallization but were found to contain small percentages on examination by more recent and careful means. The exact amount could not be determined, however, until the accuracy of the method had been ascertained. Several attempts were made to eliminate rotenone from these and other root samples by crystallization at 0° C., or slightly below from extracts dissolved in mixtures of carbon tetrachloride and petroleum ether. These methods failed to give resins free of rotenone, but they were used in some preliminary tests.

All the work up to this point had indicated that the resins had no effect on the solubility of the solvate in carbon tetrachloride, and with this assumption as a basis the following procedure was used to obtain extracts of an approximately known rotenone content:

A carbon tetrachloride extract of a root sample with a large proportion of rotenone was freed of solvent and then dissolved in carbon tetrachloride at the rate of 1 cc. of solvent for each gram of original root sample. This extract was allowed to crystallize in a closed vessel for at least 48 hours at a constant temperature at which the solubility of rotenone in carbon tetrachloride was known. Approximately room temperature was used for the crystallization and filtration, because of the greater ease of keeping a large volume of extract at such a temperature during filtration. It is believed that the large proportion of rotenone present and the long crystallization period assured equilibrium. If the resins have no solvent effect, the amount of rotenone remaining in solution is calculable from the known solubility figure.

The extract was filtered by suction at the same temperature, and the crystalline material was pressed out to remove all possible mother liquor. Here slight errors enter which are due to solvent remaining in the mother liquor held in the separated residue and to solvent of crystallization. Approximate corrections were made on the basis of the purity of the unwashed separated solvate. The filtrate was then made to a definite volume with carbon tetrachloride, and aliquots were taken of such size as to be equivalent to a 25-gram root sample. To the dried aliquots were added various amounts of pure rotenone ranging from 0.2 to 2.0 grams, each was treated with 25 cc. of carbon tetrachloride, and crystallization was carried out at

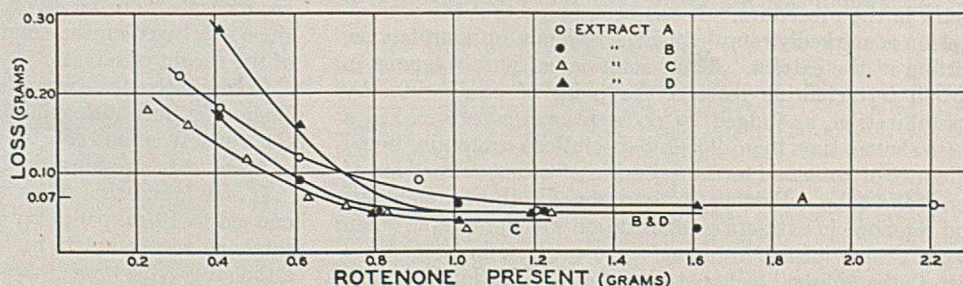


FIGURE 1. RELATION BETWEEN WEIGHT OF ROTENONE KNOWN TO BE PRESENT IN EXTRACTS OF DERRIS AND CUBE AND WEIGHT LOST ON CRYSTALLIZATION FROM CARBON TETRACHLORIDE

Normal Extracts

0° C. exactly according to the procedure outlined in the first part of this paper, except that no correction was made for the solubility of rotenone in the 25 cc. of solvent used for crystallization.

From the known solubility of rotenone in carbon tetrachloride at 0° C. we might expect a loss of about 0.07 gram. Some of the results have been plotted, and are shown in Figures 1, 2, and 3.

RESULTS WITH NORMAL EXTRACTS. Figure 1 shows the results obtained with extracts of normal root samples. The original roots had contained from about 4 to 6 per cent of rotenone. After preliminary crystallization the nonrotenone portions were as follows:

Sample	Extract	Weight per Aliquot, Grams	Per Cent of Root
Derris No. 1	A	2.07	8.3
Derris No. 2	B	2.21	8.8
Cube	C	2.56	10.2
Timbo	D	3.04	12.2

These are in the range of values normally obtained for the nonrotenone portion of such roots. As seen from the graph, the loss of rotenone in crystallization from these extracts was great when only small amounts were present, but decreased with increasing amounts of rotenone until at 0.8 to 1.0 gram it became practically constant. This constant loss approximated the loss expected from the solvent effect of the 25 cc. of carbon tetrachloride.

EFFECT OF ABNORMAL RESIN CONTENT. To determine what effect a widely different proportion of nonrotenone resin would have on these losses, either because of changing the rate of crystallization or because of possible solvent effect, portions of an extract of derris No. 1 that had been subjected to exactly the same procedure for preliminary crystallization as was given extract A were adjusted to larger and smaller volumes before taking aliquots, thus giving extracts with lower and higher resin content than in A. Similarly, an extract of derris No. 2 was prepared to give a higher resin content than B. The nonrotenone content of these extracts was as follows:

Derris Sample	Extract	Weight per Aliquot, Grams	Per Cent of Root
No. 1	E	3.25	13.0
No. 1	F	1.14	4.6
No. 2	G	4.91	19.6

The losses obtained on crystallization of aliquots of these extracts are shown in Figure 2. The losses fall in the same

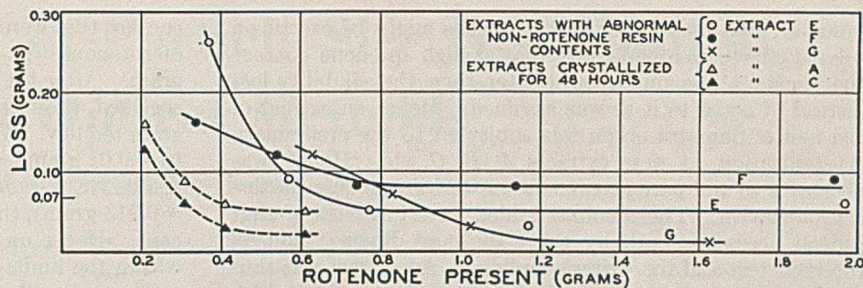


FIGURE 2. RELATION BETWEEN WEIGHT OF ROTENONE KNOWN TO BE PRESENT IN EXTRACTS OF DERRIS AND CUBE AND WEIGHT LOST ON CRYSTALLIZATION FROM CARBON TETRACHLORIDE

Extracts of abnormal rotenone content, and extracts crystallized for longer periods

region as those obtained on extracts with normal resin contents, and they reach about the same constant value, the loss then approximating that due to solubility. This indicates that, within the limits of resin content tested, which represents the range normally encountered in commercial samples of derris and cube, the retarding effect on the rate of crystallization for a given rotenone content is about the same for high, low, and normal resin contents. The results also strengthen the belief that the resin has no appreciable solvent effect on rotenone, since if such an effect were present the constant loss obtained with extracts of higher resin content would be definitely higher than that obtained with extracts of normal or lower resin content.

RESULTS WITH A LONGER CRYSTALLIZATION PERIOD. There remains the question as to whether these results are a consequence of retarded crystallization—in other words, whether an extract would crystallize quantitatively to the solubility point at a lower rotenone content if given more time. To demonstrate this, aliquots of extracts A and C were allowed to crystallize at 0° C. for 48 hours, instead of for the usual overnight period. As seen in Figure 2, complete crystallization to a value approximately equal to the solubility was obtained here with smaller amounts of rotenone.

RESULTS WITH SUMATRA-TYPE RESINS. Cahn and Boam (2) have stated that certain derris extracts in which no rotenone is obtained by ordinary crystallization are found to contain some rotenone when rotenone is added prior to crystallization. They have called these "Sumatra-type" resins or extracts and have designated the rotenone so obtained as "hidden" rotenone. Two samples of derris root giving no rotenone by the old method of crystallization (using no added rotenone), one known to be of Sumatra origin, were selected and extracts were prepared. Aliquots were taken and rotenone was added as in the foregoing tests, although no preliminary crystallization had been given the extracts. Here the amount of rotenone lost decreased with increasing

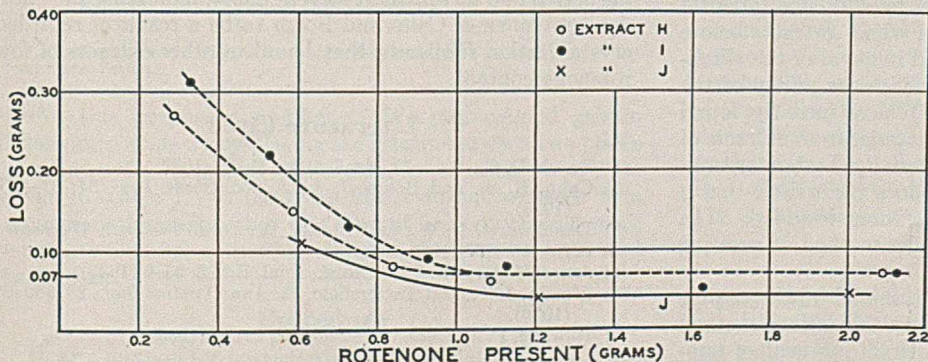


FIGURE 3. RELATION BETWEEN WEIGHT OF ROTENONE KNOWN TO BE PRESENT IN SUMATRA-TYPE EXTRACTS OF DERRIS AND WEIGHT LOST ON CRYSTALLIZATION FROM CARBON TETRACHLORIDE

amounts of rotenone added until a constant loss was attained. Since the rotenone content of these extracts was unknown, the constant loss was assumed to be equal to the solubility loss. On this basis both extracts apparently contained small proportions of rotenone (less than 0.5 per cent). The losses obtained by the recalculation were similar to those from the normal extracts tested, as shown in Figure 3, where extract H is that of the root of Sumatra origin and extract I is that of the other low-rotenone root.

The possibility still remained,

however, that these Sumatra-type resins might be exerting a solvent effect—in other words, that at high rotenone content the constant loss might be greater than the solubility loss instead of equal to it as was assumed. Hence an extract of the root of Sumatra origin was subjected to the preliminary crystallization, as were extracts *A*, *B*, *C*, etc. Here it was necessary to add pure rotenone to be certain of quantitative crystallization. The amounts added were in excess of that judged necessary both by the Cahn and Boam "hidden" rotenone test and the writer's findings. An extract was thus obtained of known rotenone content (extract *J*) to which various quantities of rotenone were added, and the losses were determined as before. At about 1 gram of rotenone and over the loss was constant and approximately equal to the solubility loss, showing these resins to be similar to ordinary derris resins in their effect on rotenone crystallization. It is believed, therefore, that the "hidden" rotenone described by Cahn and Boam is only a result of the retarded crystallization obtained with any extract of very low rotenone content and that the addition of rotenone merely hastens the crystallization as has already been pointed out.

ACCURACY OF CAHN AND BOAM METHOD. Although no attempt was made to make a careful study of the accuracy of the Cahn and Boam method of crystallization, a few aliquots of extracts *A*, *B*, *C*, and *D* with added rotenone were crystallized by this procedure. In this method the dry extract was dissolved in carbon tetrachloride at the rate of 1 gram in 2 cc. of solvent (5 to 10 grams of resin being used) and set aside for crystallization at room temperature overnight. Here the loss was approximately equal to the solubility in the amount of solvent used when 0.8 to 1.0 gram or more of rotenone was present, and increased with smaller amounts of added rotenone. The greater proportion of resin to solvent used in this method results in a definitely less pure solvate, and consequently a slightly less pure product, than is obtained when a larger proportion of solvent is used. The consequent low fluidity of the crystalline mixture renders filtration and washing difficult. For these reasons the present method is preferred, even though the Cahn and Boam procedure may be as accurate.

GENERAL DISCUSSION OF ACCURACY. Of the possible means of overcoming or accounting for the loss in crystallization of low-rotenone extracts, the addition of sufficient rotenone to bring the total amount present into the region of quantitative crystallization has been chosen as the least time-consuming and most accurate. After a little experience the analyst can readily judge at the time crystallization first occurs whether sufficient rotenone will separate to bring the final result above the desired value. Where the proportion of nonrotenone resins is not too great, it is frequently possible to increase the size of the sample to give the proper amount of rotenone in the extract.

In the case of normal samples of derris and cube (about 4 per cent rotenone) treatment of the whole extract, before crystallization, with aqueous alkali and removal of the alkali-soluble material did not increase the yield or purity of the solvate. Martin and Tattersfield (5) have recently found that separation of the alkali-soluble material from extracts of Sumatra-type derris roots does materially hasten crystallization. They believe, however, as does the writer, that a similar result is obtained when pure rotenone is added. The latter procedure seems to be the simpler method of assuring complete crystallization.

From the results shown in Figures 1, 2, and 3 it is possible to estimate the accuracy of the crystallization method adopted through a range of about 5 to 20 per cent of non-rotenone resins. For the eight extracts of known rotenone

content that were crystallized overnight, when at least 1 gram of rotenone was present the loss ranged from 0.01 to 0.08 gram. After the correction had been made for solubility as specified, the results ranged from 0.06 gram too high to 0.01 gram too low. With one exception the range was from +0.03 to -0.01 gram. In view of the precision found for replicate results on a sample of derris root (standard deviation = ± 0.013 gram), these differences cannot be considered significant. Hence on these extracts the method was accurate to within the limits of the precision.

The unusually small loss (high final result) on extract *G*, in which there was a large proportion of nonrotenone extractives, may be significant. Where the proportion of other extractives is high, sufficient impurity may be carried through to the final stage of "pure" rotenone to give slightly high results.

Because of the widely varying composition of different samples of derris and cube root, no general estimate can be made of the accuracy of the method. It is still far from the accuracy desired in most analytical procedures, but there seems no possibility of greatly improving a method that depends entirely on crystallization.

Summary and Conclusions

A modified procedure for the crystallization of rotenone-carbon tetrachloride solvate from extracts of derris and cube roots is proposed in which the author's original method has been improved from the standpoints of accuracy and speed.

Crystallization was found to be retarded by the nonrotenone portion of the extract. A test for the purity of the solvate is given. The purity has been found to depend principally upon the proportion of rotenone present and upon the proportion of solvent used in crystallization.

Accurate results by this crystallization method were obtained only when the rotenone present was equivalent to at least 4 per cent of the root or, in lieu of this, when sufficient rotenone was added, or a sufficiently large sample taken, to bring the amount present during crystallization above this value. A determination of the precision of replicate results on one sample of derris with about this rotenone content showed a standard deviation of ± 0.05 per cent. In a study of the accuracy eight extracts, containing known amounts of rotenone in the range of most accurate results, gave average values which in view of the precision were not significantly different from the actual rotenone content. In other words, results for rotenone in the region of 4 per cent should only be quoted to about 0.1 per cent.

It is probable that the nonrotenone portion of the extract only exerts a retarding action on the crystallization and has little or no actual solvent effect on the rotenone. The so-called Sumatra-type derris extracts show no unusual retarding action and no apparent solvent effect, indicating the "hidden" rotenone of Cahn and Boam to be a result of retarded crystallization similar to that found in other extracts of low rotenone content.

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Measurement of Particle-Size Distribution by Optical Methods

Effect of Light of Different Wave Lengths

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A brief study was made of the effect of light of different wave lengths upon the turbidity-concentration relation of aqueous suspensions of white and colored mineral powders using the Wagner turbidimeter. It was found that yellow and red light gave about the same slope as white light for a plot of concentration against turbidity, but that green light yielded a curve that diverged from white light in the region of low concentration. This indicates that the suspensions tend to absorb the shorter wave lengths, thereby affecting the output of the photoelectric cell with an attendant influence on the particle-size distribution as measured by this method.

OPTICAL methods for the determination of particle-size distribution offer advantages over other methods in that they are rapid and require a comparatively simple technic, but they have certain limitations which must be considered in any accurate evaluation. A convenient optical method has been developed by Wagner (4) for use in the cement industry. This instrument has been critically studied and the technic modified by Traxler and Baum (3), who found discrepancies between the size distribution in fine mineral powders as measured by an air elutriator (2) and by the turbidimeter method. In an effort to explain the differences obtained by the two methods, the present investigation was carried out to determine what effect using light of different wave lengths would have on the turbidity-concentration relation of aqueous suspensions.

TABLE I. CHARACTERISTICS OF FILTERS

Wratten Filter	Color	Total Transmission %	Principal Wave-Length Range of Gelatin ^a Millimicrons
No. 58	Green	23	490-580
No. 22	Yellow	47	560-700
No. 25	Red	22	590-700

^a Range gives wave lengths for which the filter shows greater than 10 per cent transmission.

For this purpose a number of Wratten colored gelatin filters were made up by placing the gelatin between two plates of glass. The principal characteristics of these filters are given in Table I. While these filters do not transmit true monochromatic light, they do transmit light of varying wave lengths which are somewhat different from white light and each other.

Procedure

In any method for particle-size measurement it is very important that the finely divided solid be completely dispersed in the suspending medium. Traxler and Baum (3) made an exhaustive study of this phase of the technic used with the

Wagner turbidimeter. They found, with water as the suspending medium, that a 0.0125 per cent solution of saponin or a 0.05 per cent solution of "S" brand sodium silicate gave the most satisfactory results. The rotating brush supplied with the turbidimeter has the undesirable feature of producing a vortex which entrains air in the suspension. To overcome this difficulty Traxler and Baum (3) designed a small high-speed mixer, consisting of a rotor and stator with baffle plates, which is placed below the surface of the dispersing solution.

TABLE II. TURBIDITY-CONCENTRATION DATA FOR VARIOUS MINERALS USING DIFFERENT COLORED LIGHT

Powder	Concentration W G./l.	Turbidity, $\frac{2 - \log I_d}{W}$			
		White	Yellow	Red	Green
White silica	3.0	0.58	0.56	0.56	0.59
	1.8	0.80	0.83	0.81	0.83
	1.2	0.94	0.97	0.94	1.03
	0.90	1.05	1.05	1.06	1.10
White limestone	2.5	0.72	0.70	0.70	0.72
	1.5	0.93	0.93	0.94	0.99
	1.0	1.09	1.08	1.07	1.18
	0.75	1.17	1.16	1.16	1.27
Gray trap rock	2.5	1.16	1.18	1.18	0.97
	1.5	1.07	1.03	1.06	1.10
	1.0	1.13	1.16	1.14	1.22
	0.75	1.12	1.11	1.13	1.26
Green slate	2.0	1.00	1.45	1.45	1.25
	1.0	1.52	1.52	1.55	1.62
	0.80	1.70	1.65	1.68	1.86
	0.60	1.79	1.80	1.80	1.96
Red slate	0.60	2.32	2.24	2.22	2.66
	0.30	2.58	2.59	2.58	3.02
	0.20	2.73	2.71	2.71	3.20
	0.18	2.78	2.72	2.81	3.36
	0.15	2.92	..
	0.10	3.30	..
Black slate	0.87	1.62	1.67	1.67	1.77
	0.75	1.62	1.69	1.71	1.84
	0.30	1.68	1.72	1.74	2.21
	0.26	1.74	1.87	1.92	2.13

In the present study powdered minerals of different colors were analyzed by the Wagner turbidimeter, using white and colored light. Aqueous saponin was used as the dispersing solution. The minerals were dispersed with the improved stirrer for 5 minutes, after which the dispersions were agitated by hand for 1 minute, and the cell was immediately placed on the shelf of the turbidimeter. Successive readings were obtained by adding a known quantity of water to the original concentration, thereby making successively more dilute suspensions. For colored light the technic was varied by placing the filter in the light beam behind the screen and in front of the guard, so that only colored light affected the photoelectric cell. The I_0 reading was readjusted for each filter, so that the varying sensitivity of the photoelectric cell to light of different wave lengths would not affect the readings. The data obtained are given in Table II.

Discussion

The results indicate that the turbidity-concentration relation is unaffected by the longer wave lengths, since the red and yellow filters gave practically the same results as white light except for one concentration of the green slate and one concentration of the red slate. However, when green light is used the results are definitely different from white light, and

this difference is more pronounced with the colored powders. The data for the white limestone are plotted in Figure 1 to illustrate the differences. The figure indicates that in the region of low concentration the suspension shows a higher turbidity with green light than with the light of other wave lengths.

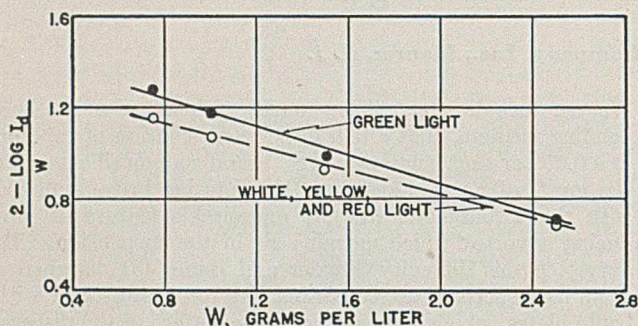


FIGURE 1. TURBIDITY CONCENTRATION CURVES FOR WHITE LIMESTONE

The difference in the slope of the turbidity-concentration curves appears to be caused by selective absorption of the shorter wave lengths of light by the suspended powders, as was suggested by Traxler and Baum (3). The green light was the shortest wave length used and it showed this effect to a significant degree. Furthermore, this selective absorption is most pronounced with the red slate, which might be expected since this mineral would tend to absorb the shorter wave lengths. If a blue filter had been used, still greater differences probably would have been obtained. An attempt was made to use a blue Wratten filter (No. 49), but the total transmission (0.5 per cent) was too low for use with the light source in the turbidimeter.

Richardson (1) in his work found that color is important in studies of suspensions. He used a photoelectric cell in his apparatus for determining the size distribution of clays, and stated that the absorption of light is independent of color for particles larger than one micron, but that for smaller particles the absorption is strongly dependent upon color. The photoelectric cell varies in sensitivity to different colored light and any selective absorption that occurs will affect the output of the cell, whether that absorption is caused by very fine or by colored particles. It may be possible, however, by using monochromatic light of the proper wave length, to eliminate this selective absorption and thereby obtain accurate results for very fine mineral powders with a turbidimeter type of instrument.

Richardson (1) also makes the rather general statement that particles smaller than one micron would tend to be held in permanent suspension by Brownian movement. This would affect the results obtained by any method utilizing rate of settling for determining particle-size distribution, especially where the distribution is calculated from the surface area as in the Wagner method. Since the major part of the surface area of a pulverized powder is dependent on the number of very small particles, Brownian movement would probably seriously affect the results on fine clays. Although pulverized powders would be less seriously affected, Brownian movement should always be considered when using the Wagner turbidimeter.

Conclusion

A number of variables affect the turbidity of a suspension as measured by optical methods. The selective absorption of light is perhaps one of the most important, and a complete understanding of this variable will do much toward simplify-

ing the use and technic of optical methods in measuring particle-size distribution.

Acknowledgment

The author wishes to express his gratitude for the assistance given by R. N. Traxler, under whose direction this study was made.

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A Simplified Sealed Stirrer

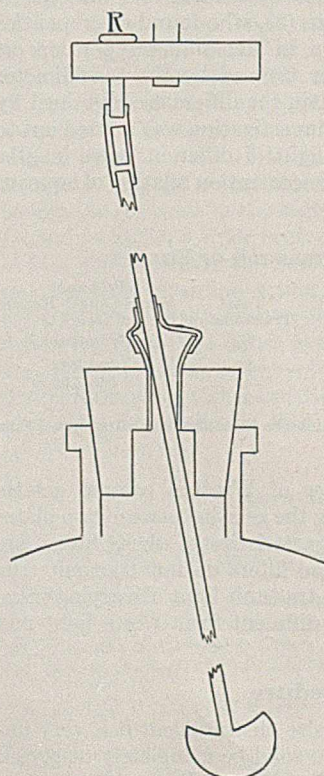
LIONEL JOSEPH

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A MODIFICATION of the sealed stirrer described by Powell (1) has been used in this laboratory for some time and has been found exceedingly useful, particularly in stirring sludges. Some difficulty was experienced in assembling the type of stirrer described, so that modifications were introduced to make the assembly of the stirrer simpler without cutting down its efficiency.

The glass bearing consists of a piece of 7-mm. tubing, 25 mm. long, spread at one end to an outside diameter of 15 mm., and inserted in the top of the cork. A hole 15 mm. in diameter is bored halfway through from the bottom of the cork. The seal is made by a short piece of rubber tubing which fits over the glass rod and makes a tight joint with the larger-bore rubber tubing attached to the glass bearing. With this arrangement it has been found unnecessary to clamp the stopper as described by Powell.

In place of the No. 12 rubber stopper the author has used a cork about 7 cm. in diameter and 2 cm. thick, through which is drilled a hole large enough to give plenty of play to rod R. Smoother operation may be obtained by drilling the hole on a slant and inserting a glass sleeve. The distance of the hole from the center of the cork may vary from 15 to 25 mm., depending upon the size of the flask used and the amount of sweep desired.



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Determination of Tar Acids and Bases by Extraction Methods

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A critical survey is presented of extraction methods for tar-acid and -base determination. The various procedures are discussed in connection with studies (presented in an earlier paper) of the important variables involved. Certain modifications which increase the accuracy of the Bureau of Mines method are recommended.

MANY methods of analyzing tar oils for their tar-acid and -base content have been employed in connection with both academic and industrial investigations. Most of these analytical procedures are based on the diminution in volume caused by extraction with alkali and mineral acids (contraction method), although other methods have been employed (14, 19, 20, 29, 30). In many instances the adoption of an analytical method was not preceded by an adequate study, and as a consequence the literature on this subject is conspicuous for its contradictory claims and recommendations. It has been shown in the case of certain synthetic solutions (6, 17) that large errors may result if the analysis is carried out by simple extraction with alkali and mineral acids.

It was the purpose of the present work to study and compare several modifications of the contraction method and to show under what general conditions tar acids and bases can be extracted accurately. Synthetic solutions, coal-tar oils, and hydrogenated coal distillates were used in this connection, and methods of determining tar acids as phenols and carboxylic acids were investigated. Methods that include washing the alkaline and acid extracts with organic solvents were not studied, since such methods are wasteful of time and subject to errors of prolonged manipulation. Furthermore, washing the aqueous extracts with organic solvents fails to accomplish the desired end, since, for example, an organic solvent removes phenols as well as nonacidic materials from alkaline solutions.

Materials and Procedure

The synthetic solutions studied were prepared from good grade chemicals. Pure toluene was used as the hydrocarbon solvent, and the cresol ("tricrosol") was a mixture of isomers.

The extractions were carried out in funnels (10, 31) graduated to 100 cc. in 0.2-cc. subdivisions. About 1 hour was allowed to elapse between agitation of the oil (100-cc. samples) with aqueous solutions and observation of volume changes.

Alkali Concentration

There is considerable disagreement concerning the concentration of alkali best suited for the accurate extraction of tar acids, and a number of alkaline reagents have been recommended. It appears certain that "maximum extractions" are obtained with rather concentrated alkali (2, 23, 25). However, it is generally recognized that the alkaline extracts thus obtained contain considerable quantities of nonacidic material, owing to the solvent power

(6, 26) of alkali-phenol solutions. In many instances nonacidic material has been removed from the alkaline layer by washing with organic solvents. Probably 10 per cent sodium hydroxide (5, 7, 9, 15, 28) is most frequently employed as the alkaline reagent, although 5 (18, 21), 15 (11, 12), 20 (1, 3, 25), and 30 per cent (24) have been used. It has been claimed (21) that the addition of sodium chloride to 10 per cent sodium hydroxide tends to prevent the dissolution of nonphenolic or nonacidic substances.

In the present work the effect of alkali concentration was studied in one series of experiments by extracting a standard amine-toluene solution (100-cc. portions) with 50-cc. portions of sodium hydroxide solution. All the sodium hydroxide solutions examined (5, 10, 20, and 30 per cent) failed to dissolve appreciable quantities of the amine-toluene solution, although all the amines present are fairly soluble in water. The potent influence of sodium hydroxide in decreasing the solubility of amines in water is shown well by the data in Table I. Although even 5 per cent alkali dissolved only negligible quantities of the amine-toluene solution, washing with three 50-cc. portions of distilled water caused a total diminution in volume of 2.5 to 3.0 cc.

	Cc.	%
Pyridine	12	1.85
Isoquinoline	32	4.9
Aniline	56	8.6
Toluene	550	84.65

The results in Table I indicate that, excluding factors other than the solubility of amines in aqueous alkali, almost any concentration of sodium hydroxide would be suitable for the analytical extraction of tar acids.

TABLE I. EXTRACTION OF AMINE-TOLUENE SOLUTION WITH ALKALI

Extracted with 50-Cc. Portions of	Volume Changes of Toluene Layer				
	1st 50 cc.	2nd 50 cc.	3rd 50 cc.	4th 50 cc.	1st 150 cc.
	Cc.	Cc.	Cc.	Cc.	Cc.
5% NaOH	0.0	-0.1	-0.2	...	-0.3
	0.0	-0.3	-0.1	...	-0.4
10% NaOH	0.0	0.0	-0.2	-0.2	-0.2
	-0.1	-0.1	-0.3	-0.2	-0.5
20% NaOH	+0.2	+0.1	-0.1	-0.1	+0.2
	+0.1	+0.1	0.0	-0.1	+0.2
30% NaOH	0.0	0.0	+0.1	-0.1	+0.1
	+0.1	0.0	-0.1	0.0	0.0
20% NaOH saturated with NaCl	+0.1	0.0	-0.1	-0.1	0.0
	+0.1	0.0	0.0	-0.1	+0.1
Water saturated with NaCl	+0.1	-0.1	-0.5	-0.3	-0.5
	+0.2	-0.1	-0.1	-0.3	0.0
Water	-0.8	-1.2	-1.1	-0.8	-3.1
	-0.8	-0.9	-0.9	-0.8	-2.6

In studying the solubility of amines in alkaline solutions of sodium phenolates, the same amine-toluene solution used previously was washed several times in succession with 50-cc. portions of aqueous solutions containing various amounts of sodium hydroxide and cresol. The alkali-cresol solutions were prepared by adding certain quantities of cresol (7.5, 15, 22.5, 30, 37.5, and 45 cc. to each 100 cc. of sodium hydroxide) to several different concentrations (5, 10, 15, 20, and 30 per cent) of alkali. The results (Table II and Figure 1) indicate that the solubility of amines in alkali-cresol solutions is directly proportional to the concentration of alkali, and that large amounts of amines are extracted where the concentrations of alkali and cresol are high.

The effect of varying the cresol concentration is also shown by the data in Table II and Figure 1. It is readily apparent that the volume losses of the toluene solution were directly proportional to the concentration of cresol where sufficient alkali was present to neutralize the cresol. Where the alkali present was not sufficient to react with the cresol the volume of the amine-toluene layer increased, because of the absorption of excess or "free" cresol. Because of the solvent power of concentrated alkali-phenol solutions for amines, concentrated alkali should not be used to extract tar acids where, as in analytical procedures, the simultaneous removal of amines is not desired.

Acid Reagent

The determination of tar bases is omitted in some tar-oil analyses, and consequently less is known about the efficacy of different acid reagents in the extraction of tar bases. Skirrow and Binmore (27) have observed that 2 *N* sulfuric acid extracted pyridine from pyridine-benzene solutions more efficiently than 9.63 *N* sulfuric acid. Dilute sulfuric acid appears to be the reagent (16) generally used to extract tar bases.

A number of experiments were carried out to see if phenol, as a representative of the tar acids, could be extracted in appreciable quantities by dilute mineral acids. Approximately 100 cc. of a phenol-toluene solution (80 grams of phenol in 500 cc. of toluene) were washed in succession with four 50-cc. portions of various aqueous solutions, and the acid solutions causing little change in volume of the phenol-toluene layer were considered as possible acid reagents. The presence of inorganic salts, especially sodium chloride, was found, as anticipated, to retard the removal of phenol from the toluene layer. From the data in Table III and the fact that sodium chloride would not be expected to depress the solubility of amine sulfates as much as inorganic sulfates, it appears that the most suitable reagent is 20 per cent sulfuric acid containing sodium chloride.

The following experiment, which affords a more direct comparison of hydrochloric acid and the sulfuric acid-sodium chloride solution, has shown that the latter reagent is preferable: Washing 100 cc. of a 15 per cent by volume cresol-toluene solution with three 50-cc. portions of a pyridine-hydrochloric acid solution (10 cc. of pyridine added to 100 cc. of 20 per cent acid) caused the toluene layer to suffer a total volume loss of 2.6 cc. Under the same conditions the toluene layer gained 0.4 cc. in volume when a pyridine-sulfuric acid solution (10 cc. of amine added to 100 cc. of 20 per cent sulfuric acid saturated with sodium chloride) was used.

A few experiments, which were carried out to ascertain the importance of acid concentration and the presence of amine salts on the distribution of phenols between the hydrocarbon and aqueous layers, have already been described (8). It was shown that, although the presence of aniline increased the solubility of cresol in the aqueous layer, the concentration of acid had little effect. The presence of amine salts in the aqueous layer probably has little influence on the accuracy of analytical procedures, because tar bases usually are present in relatively small amounts.

To examine the possibility that the sulfuric acid reagent would cause olefins to polymerize or to react with phenols, several reactive olefins (*d*-limonene, styrene, and pinene) were treated with 20 per cent sulfuric acid saturated with sodium chloride. There was no loss in volume of the olefins or any indication of reaction, and on distillation the hydrocarbons came over at their respective boiling points.

A comparison of the first two columns of Table II with those of Table III shows that phenol-toluene solutions absorb considerably more water than the amine-toluene solutions under the conditions employed.

TABLE II. EXTRACTION OF AMINE-TOLUENE SOLUTION WITH ALKALI-CRESOL SOLUTIONS OF VARIOUS CONCENTRATIONS

Concentration of NaOH %	Cresol Added Cc./100 cc.	Volume Changes of Toluene Layer				
		1st 50 cc. Cc.	2nd 50 cc. Cc.	3rd 50 cc. Cc.	4th 50 cc. Cc.	1st 150 cc. Cc.
5	7.5	+0.1	-0.4	-0.3	-0.2	-0.6
		0.0	-0.4	-0.4	-0.3	-0.8
10	7.5	+0.1	-0.3	-0.3	-0.4	-0.5
		+0.1	-0.2	-0.3	-0.4	-0.4
15	7.5	+0.1	-0.3	-0.2	...	-0.4
		+0.1	-0.4	-0.2	...	-0.5
20	7.5	-0.4	-0.7	-0.9	-1.0	-2.0
		-0.5	-0.5	-0.9	-0.7	-1.9
30	7.5	-3.0	-3.3	-2.8	...	-9.1
		-2.8	-3.2	-2.9	...	-8.9
5	15	+0.9	+0.2	0.0	-0.1	+1.1
		+0.9	+0.1	0.0	-0.1	+1.0
10	15	-0.3	-0.7	-0.7	-0.6	-1.7
		-0.3	-0.6	-0.7	-0.6	-1.6
15	15	-0.8	-0.9	-1.0	...	-2.7
		-0.8	-1.0	-1.1	...	-2.9
20	15	-2.0	-2.0	-1.6	-1.5	-5.6
		-1.9	-1.4	-1.7	-1.3	-5.0
30	15	-5.1	-5.2	-3.7	-2.7	-14.0
		-5.2	-4.9	-3.4	-3.3	-13.5
5	22.5	+3.1	+2.6	+2.4	...	+8.1
10	22.5	-0.4	-1.0	-1.2	-1.0	-2.6
		-0.3	-1.0	-0.9	-1.1	-2.2
15	22.5	-1.8	-2.1	-1.7	...	-5.6
		-2.0	-1.9	-1.7	...	-5.6
20	22.5	-2.6	-2.3	-2.1	-1.8	-7.0
		-2.8	-2.6	-2.3	-2.0	-7.7
30	22.5	-6.3	-5.1	-4.3	-2.8	-15.7
		-6.4	-5.3	-4.1	-3.0	-15.8
5	30	+5.5	+7.0	+4.3	...	+16.8
10	30	-0.8	-1.4	-1.6	-1.3	-3.8
		-0.8	-1.4	-1.6	-1.3	-3.8
15	30	-2.1	-2.3	-1.9	...	-6.3
20	30	-3.7	-3.4	-2.5	-2.1	-9.6
		-3.8	-3.1	-2.7	-2.3	-9.6
5	37.5	+8.1	+7.4	+7.5	...	+23.0
10	37.5	+1.9	+1.7	+1.6	...	+5.2
		+2.0	+1.4	+1.6	...	+5.0
15	37.5	-2.8	-2.7	-2.2	...	-7.7
20	37.5	-4.7	-3.9	-2.8	-2.4	-11.4
		-4.8	-3.9	-3.0	-2.3	-11.7
10	45	+4.2	+4.3	+2.7	...	+11.2
		+4.4	+4.1	+3.0	...	+11.5
15	45	-2.8	-3.0	-2.5	...	-8.3
20	45	-5.9	-4.5	-3.3	-2.7	-13.7
		-6.4	-4.6	-3.4	-2.3	-14.4

TABLE III. EXTRACTION OF PHENOL-TOLUENE SOLUTION WITH VARIOUS AQUEOUS SOLUTIONS

Extracted with 50-Cc. Portions of	Volume Changes of Toluene Layer				
	1st 50 cc. Cc.	2nd 50 cc. Cc.	3rd 50 cc. Cc.	4th 50 cc. Cc.	1st 150 cc. Cc.
20% H ₂ SO ₄	+0.2	-0.8	-0.8	-0.7	-1.4
	+0.2	-0.8	-0.8	-0.8	-1.4
20% H ₂ SO ₄ saturated with cryst. K ₂ SO ₄	+0.3	-0.5	-0.7	-0.4	-0.9
20% H ₂ SO ₄ saturated with anhyd. Na ₂ SO ₄	+0.6	-0.2	-0.3	-0.1	+0.1
20% H ₂ SO ₄ saturated with NaCl	+0.8	-0.2	-0.1	-0.3	+0.5
20% H ₂ SO ₄ saturated with NaCl and K ₂ SO ₄	+0.3	-0.1	-0.3	0.0	-0.1
	+0.5	-0.3	-0.3	-0.5	-0.1
20% H ₂ SO ₄ saturated with NaCl and K ₂ SO ₄	+0.7	-0.1	-0.2	-0.3	+0.4
	+0.4	-0.2	-0.3	-0.1	+0.1
20% HCl	-0.3	-0.9	-0.9	-0.7	-2.1
	-0.6	-0.9	-0.8	-1.0	-2.3
20% HCl saturated with NaCl	-0.2	-0.8	-0.4	-0.6	-1.4
	0.0	-0.9	-0.7	-1.0	-1.6
Water	-0.4	-1.7
	-0.6	-1.4
Water saturated with K ₂ SO ₄	-0.1	-1.3	-1.2	-1.3	-2.6
	-0.2	-1.3	-1.1	-1.0	-2.6
Water saturated with NaCl	+0.4	-0.4	-0.3	-0.4	-0.3
	+0.5	-0.2	-0.2	-0.6	+0.1

Bureau of Mines Method

After analyzing several synthetic mixtures under different conditions with various acid and alkaline reagents, Kester and Rockenbach (17) adopted the following method (5) for determining tar acids and bases: The tar oil (100 cc.) is extracted with acid and alkali in the following order: (1) three 50-cc. portions of 20 per cent sulfuric acid saturated with potassium sulfate, (2) three 50-cc. portions of 10 per cent sodium hydroxide, and (3) three 50-cc. portions of 20 per cent sulfuric acid saturated with potassium sulfate. This method, which employs reagents conforming to the requirements defined above (Tables II and III), has been used

repeatedly with good results, and is interesting in that the unusual procedure of extracting tar bases first is employed.

Numerous analyses of coal-tar distillates by the Bureau of Mines method have confirmed (communication from J. D. Davis and L. P. Rockenbach) the claim of Hatcher and Skirrow (13), which is in agreement with the experience of coal-tar workers, that tar bases cannot be extracted conveniently in the presence of tar acids. Since mineral acids bring about only a partial extraction of tar bases in the presence of tar acids, it seemed likely that washing with acid, then alkali, and finally with acid (as in the Bureau of Mines method) would separate the tar bases roughly into two types: (1) amines having distribution ratios favorable to the acid layer and (2) amines with a distribution ratio more favorable to the hydrocarbon-phenol layer. The ratio between quantities extracted in the presence and absence of tar acids should depend on the composition of the tar oil and thus be a characteristic property. These ratios have been calculated for several tar oils; the oils from low-temperature tars yielded ratios ranging between zero and 0.1, while the high-temperature tar oil (see Table V) gave a higher ratio (0.54). As might be expected from their composition, the synthetic solutions described in Table V gave still higher ratios (1.2 to 1.4). Since high-temperature tar oils contain larger proportions of low-molecular-weight amines than oils from low-temperature tars it follows that, considering the amine ratios given above, more of the low-molecular-weight amines are removed in the first acid washings—i. e., before the tar acids are removed. Experimental evidence that supports this view has been given elsewhere (6). Cheng and Morgan (2) have shown that chiefly low-molecular-weight phenols are removed where tar acids are incompletely extracted from tar oils.

In view of the results obtained by extracting amine-toluene solutions with sodium hydroxide containing cresol (see Table II), it might be expected that oils containing high concentrations of tar acids and bases could not be analyzed accurately by extraction methods. To find the maximum concentration amenable to accurate analysis by contraction methods, several synthetic mixtures were extracted by a modification of the Bureau of Mines method. Uneven portions (100, 35, and 15 cc.) of the reagents were employed, and sodium chloride was used instead of potassium sulfate to saturate the 20 per cent sulfuric acid. The synthetic solutions were prepared by mixing known volumes of an amine mixture (equal parts by volume of pyridine, quinoline, isoquinoline, and aniline), cresol, and toluene. The results of these analyses, given in Table IV, show that the solutions containing large amounts of phenols and amines gave high results for phenols and low results for amines. However, fairly accurate data were obtained with the synthetic mixtures having the concentration of amines and phenols usually found in coal tars. In view of the fact that the solutions of low amine and phenol content gave satisfactory analyses, it might be expected that dilution of coal oils before extraction would be beneficial. (Dilution of oils of high tar-acid and -base content to obtain improved analyses has been suggested by Hill 15, and by Fridli and Raffay, 8.)

It appears that the ratio of amines to phenols, as well as total content, is important. As an example, where the ratio (amines to phenols) was 1 to 1 good results were obtained with a total amine-phenol content of 40 per cent, but with a ratio of 1 to 5 errors appeared with a total amine-phenol content as low as 25 per cent.

It will be noted (Table IV) that in most cases low results were obtained for the neutral oil. This probably indicates that usually small, and in some cases considerable, amounts of the neutral oil also were extracted.

Comparison of Extraction Methods

Using both synthetic solutions and coal-tar distillates, a comparison was made of the Bureau of Mines method and several other typical extraction procedures. In view of the generally satisfactory results obtained previously with the Bureau of Mines method (Table IV), the data obtained with coal oils by this procedure (Table V) were considered fairly accurate, and hence of some value as a standard for evaluating the other methods. The "liberation method" of Morgan and Meighan (22) gave more accurate results for two synthetic solutions (Table V) and was therefore employed to obtain the true tar-acid content of the coal oils.

The several oils and synthetic mixtures described in Table V were analyzed as follows:

1. Bureau of Mines method, considered above in some detail.
2. Modified Bureau of Mines method (sodium chloride instead of potassium sulfate in 20 per cent sulfuric acid, and uneven portions of reagents), used previously to obtain the data in Table IV.
3. Essentially the Bureau of Mines method backward. The oil (100 cc.) was extracted with three 50-cc. portions of 10 per cent alkali, and then with three 50-cc. portions of 20 per cent sulfuric acid (saturated with sodium chloride). These alternate

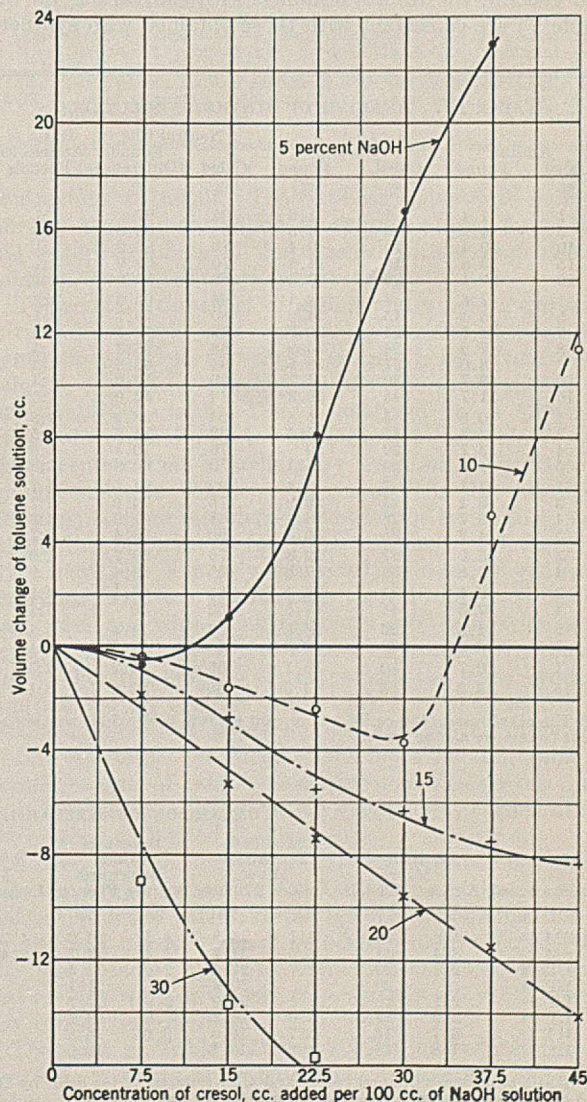


FIGURE 1. AMINES IN TOLUENE WASHED WITH 150 Cc. OF ALKALINE-CRESOL SOLUTION

extractions were repeated until all tar acids and bases were removed.

4. A special method based on the use of 5 per cent sodium hydroxide, which, in the presence of sodium phenolates, dissolves smaller quantities of amines and forms worse emulsions than 10 per cent alkali. The following extraction procedure was designed to benefit from the advantages of both concentrations of alkali; the bulk of the phenols was removed with 5 per cent alkali and the last traces of phenols were removed with 10 per cent alkali, which generally causes a good separation of layers. This method gave troublesome emulsions with some tar oils, and hence is of little value.

- a, b. 100 cc. of 5 per cent sodium hydroxide
 c. 50 cc. of 10 per cent sodium hydroxide
 d. 50 cc. of 20 per cent sulfuric acid (sodium chloride)
 e, f. 25 cc. of 20 per cent sulfuric acid (sodium chloride)
 g. 25 cc. of 10 per cent sodium hydroxide
 h. 25 cc. of acid reagent

5. Liberation method. The oil was extracted with 20 per cent alkali, the alkaline extract was acidified, the acidic solution was extracted with benzene, and the benzene washings were diluted to 100 cc. and extracted with 10 per cent sodium hydroxide; the volume loss of the benzene layer indicated the tar-acid content.

6. The volume loss of 100 cc. of tar oil to 20 per cent sodium hydroxide, as carried out in method 5. It was observed in several cases that 20 per cent alkali removed all the tar acids—that is, no further quantities of tar acids could be obtained by removing the tar bases and extracting again with alkali.

In general, the results obtained with the various tar oils (Table V) are consistent with those obtained with synthetic

mixtures. As might be expected, the greatest volume losses were caused by washing with 20 per cent sodium hydroxide (method 6), which undoubtedly removed considerable quantities of amines, and probably some of the neutral oil, along with the phenols. The values afforded by the liberation method were lower than those obtained by simple extraction with 10 or 20 per cent alkali; this result was to be anticipated and is in agreement with a generalization made previously by Weiss (31).

Methods 1 and 2, differing from each other only in minor details, gave almost identical results in all cases. In view of the good agreement with the values of the liberation method and the results obtained with synthetic solutions, it appears that methods 1 and 2 generally give satisfactory results. It seems likely that in most cases the true value of the tar-acid content lies between the results afforded by methods 1 (or 2) and 5. Methods 1 and 2 generally are preferable to 5 (liberation method) because of their simplicity and the fact that values are obtained for both the tar-acid and -base content. Method 4 was superior to the other procedures with synthetic mixtures, but could not be used conveniently with the tar oils.

In a few cases (data not shown) 5 and 10 per cent sodium hydroxide solutions saturated with sodium chloride were employed in extractions, but appeared to have no advantage over alkali alone.

A number of facts have been established which present a rather clear picture of the Bureau of Mines method and explain the beneficial effect of extracting first with acid. The following interpretation of the Bureau of Mines type of tar-acid and -base analysis is consistent with the data thus far presented in this paper and in an earlier paper (6):

Extraction first with acid removes principally the amines of lower molecular weight, and saturates the tar-oil layer with water. (This is partly responsible for the low amine and high phenol values usually obtained.) As indicated above, the amines of higher molecular weight have distribution ratios more favorable to the hydrocarbon-phenol layer, and hence are not removed by acid (6). Only negligible quantities of phenols are removed in the acid wash because (1) a suitable acid reagent (20 per cent sulfuric acid saturated with an inorganic salt) is used, (2) relatively small quantities of amines are present, (3) only a portion of the amines present (certain amines of low molecular weight) as salts in acid solution is capable of extracting phenols in appreciable quantities from hydrocarbon solutions, and (4) only the phenols of low molecular weight are easily extracted by acid-amine solutions.

Extraction with alkali in the second stage of the analysis removes the phenols, and probably most of the water absorbed in the first washing. Possibly traces of certain highly alkylated phenols (4) (such as thymol and phenols difficultly soluble in alkali) are not extracted. Only small quantities of amines are removed along with the sodium phenolates because (1) moderately dilute alkali is used, (2) only high-molecular-weight amines, sparingly soluble in sodium phenolate solutions, are present, and (3) the amine content, relatively low at the beginning, is lower than its original value. In the third stage of the analysis the remaining amines of high molecular weight are removed easily by mineral acid extraction since phenols are not present. In several cases of the present work a second extraction with alkali, as a fourth stage of the analysis, caused slight diminution in volume, indicating that such a procedure might be necessary in some cases to remove all traces of tar acids.

Where tar oils are extracted first with alkali, practically all the tar acids are removed, since tar bases have little retarding effect. The highly alkylated, weakly acidic phenols are less easily extracted, especially in the presence of tar bases. Con-

TABLE IV. ANALYSIS OF SYNTHETIC SOLUTIONS

Caled.	Amines		Phenols		Neutral Oils		Ratio of Amines to Phenols
	Found	Found	Found	Found	Found	Found	
%	%	%	%	%	%	%	
1	1.4	1	1.6	98	97	1.1	
5	4.9	5	4.5	90	90.6	1.1	
10	10.4	10	9.4	80	80.2	1.1	
15	15.3	15	14.8	70	69.9	1.1	
20	20.1	20	20.3	60	59.6	1.1	
1	1.6	3	3.1	96	95.3	1.3	
5	5.4	15	14.9	80	79.7	1.3	
7	6.7	21	20.9	72	72.4	1.3	
8	7.9	24	23.8	68	68.3	1.3	
9	8.0	27	28.5	64	63.5	1.3	
10	8.7	30	31.7	60	59.6	1.3	
15	11.7	45	46.3 ^a	40	42.0	1.3	
1	0.8	5	5.3	94	93.9	1.5	
3	2.8	15	15.5	82	81.7	1.5	
4	3.7	20	20	76	76.3	1.5	
5	4.0	25	26.1	70	69.9	1.5	
1	1.1	7	7.4	92	91.5	1.7	
3	3.1	21	20.9	76	76.0	1.7	
4	3.7	28	28.4	68	67.9	1.7	
5	4.3	35	36.3	60	59.4	1.7	
3	3.0	27	27.3	70	69.7	1.9	
4	2.8	36	37.8	60	59.4	1.9	
3	2.5	33	34.4	64	63.1	1.11	
4	2.5	44	47.5	52	50	1.11	
2	1.8	26	26.8	72	71.4	1.13	
3	1.9	39	40.3	58	57.8	1.13	
1	0.7	30	30.1	69	69.2	1.30	
15	13.5	5	4.3	80	82.2	3:1	

^a The alkali used (150 cc. of 10 per cent sodium hydroxide) was not sufficient to remove all the cresol.

TABLE V. COMPARISON OF EXTRACTION METHODS

Oil Examined	Bureau of Mines		Modified Bureau of Mines		Bureau of Mines Backward		5% NaOH Method		Liberation Method	20% NaOH Method		Amines Ratio ^a
	Amines	Phenols	Amines	Phenols	Amines	Phenols	Amines	Phenols		Phenols	Phenols	
	%	%	%	%	%	%	%	%	%	%	%	
SM 1 ^b	4.3	25.9	4.1	25.8	4.5	26.0	4.7	25.3	24.4	27.1	1.2	
SM 2 ^c	8.4	31.7	8.5	31.7	7.4	32.7	8.4	31.4	30.6	35.6	1.4	
LT 1 ^d	2.7	22.1	2.7	22.1	2.9	22.5	21.2	24.2	0.0	
LT 2 ^e	..	20.4	..	20.4	..	21.1	..	20.6	19.2	22.4	..	
LT 3 ^d	2.1	22.2	2.4	21.9	2.9	22.7	21.5	23.5	0.1	
LT 4 ^d	2.9	19.3	3.0	19.2	3.6	19.4	19.0	21.6	0.07	
HT 1 ^e	3.7	16.1	3.7	16.3	3.6	16.8	0.54	
HC 1 ^f	1.8	13.6	1.6	13.8	..	13.6	12.0	15.1	0.29	

^a Ratio of amines obtained before and after removal of tar acids by Bureau of Mines method.

^b Synthetic solution, 5 per cent amines, 25 per cent phenols.

^c Synthetic solution, 10 per cent amines, 30 per cent phenols.

^d Low-temperature tar distillates.

^e High-temperature tar distillate.

^f Hydrogenated coal distillate.

siderable amounts of tar bases are removed along with the phenols, and usually the amount of water going into the oil layer is small. The amount of tar bases removed in the alkali wash is directly proportional to the concentration of tar acids, alkali, and tar bases and inversely proportional to the molecular weight of the tar bases. The structure of the tar bases and acids also is a factor. After the tar acids have been removed, the tar bases, as is well known, are easily removed with mineral acid.

Analysis of Oils Containing Carboxylic Acids

To determine the amount, generally small, of carboxylic acids and other acids of similar strength in tar oils, the extract obtained by washing with alkali usually is saturated with carbon dioxide and then acidified with hydrochloric or sulfuric acid (21). The weakly acidic phenols are liberated by carbon dioxide and the stronger acids by mineral acid. Methods of this kind are time-consuming and necessitate the acidification of considerable amounts of carbonate solutions. A study of synthetic solutions and tar oils containing various amounts of benzoic and acetic acids has shown that the strong tar acids may be determined directly by extraction with sodium or potassium carbonate solutions. The synthetic solutions were prepared by mixing the desired amounts of cresol, a carboxylic acid, toluene, and an amine mixture (equal parts by volume of pyridine, quinoline, isoquinoline, and aniline). The amount of carboxylic acid added was judged by the increase in volume of the solution. The solution and tar oils were analyzed by the following reagents and order of extraction:

1. 100 cc. of 20 per cent sulfuric acid (sodium chloride)
2. 50 cc. of 20 per cent sulfuric acid (sodium chloride)
3. 50 cc. of 10 per cent sodium carbonate
4. 100 cc. of 10 per cent sodium hydroxide
5. 35 cc. of 10 per cent sodium hydroxide
6. 15 cc. of 10 per cent sodium hydroxide
7. 50 cc. of 20 per cent sulfuric acid (sodium chloride)
8. 25 cc. of 20 per cent sulfuric acid (sodium chloride)
9. 15 cc. of 20 per cent sulfuric acid (sodium chloride)
10. 10 per cent sodium hydroxide

The volume of oil was recorded at extractions 2, 3, 6, 9, and 10. The last extraction was made to remove any trace of phenols not accounted for previously. In the case of the synthetic solutions, the volume loss at this point was only 0.2 to 0.3 cc., and was disregarded. In the case of the tar oils, appreciable volume losses were often observed in the last extraction with alkali.

The results obtained (Table VI) indicate that carboxylic acids may be determined satisfactorily, the values found agreeing very well with the amounts present. Nothing new was revealed concerning the determination of amines and phenols. As observed in previous analyses, the amine values are low and the phenol values high.

Correction for Water Absorption

The suggestion has been made previously (6) that absorption of water by the tar oil is partly responsible for the fact that the values obtained for amines and phenols are usually low and high, respectively. It has been observed in many cases that washing 100 cc. of tar oil with 50 cc. of 20 per cent sulfuric acid (saturated with inorganic salt) causes the oil layer to undergo a volume increase of about 1 cc. During this operation some quantity of tar bases must have passed into the aqueous layer unobserved, causing the amines value to be erroneously low. It is likely that most of the water dissolved in the oil layer is removed in the alkaline extraction along with the phenols, resulting in a high value for the tar acid content.

It has been found that errors arising from water absorption may be obviated somewhat by adding 2 to 3 cc. of aqueous sodium chloride solution to the oil as the first stage of the analysis. The increase in volume caused by this washing was noted, and later subtracted from the volume

TABLE VI. SYNTHETIC SOLUTIONS CONTAINING BENZOIC ACID

Present	Amines		Total	Phenols		Carboxylic Acids	
	First wash	Found Second wash		Present	Found	Present	Found
Volume-Per Cent							
5.1	3.0	1.7	4.7	20.0	20.4	0.0	0.0
5.2	2.9	1.8	4.7	20.5	21.2	0.7	0.7
4.6	2.6	1.7	4.3	20.1	20.9	1.2	1.1
4.8	2.7	1.8	4.5	19.9	20.2	2.6	2.7

TABLE VII. ANALYSIS FOR ACIDIC AND BASIC CONSTITUENTS WITH PRELIMINARY ADDITION OF SALT-WATER SOLUTION

No.	Modified Bureau of Mines Method		Salt-Water Solution Added		Liberation Method
	Amines	Phenols	Amines	Phenols	
%					
1	2.6	37.9	3.6	37.0	0.0
2	2.7	13.4	1.0
3	1.7	27.3	2.2	26.8	0.0
4	1.9	28.9	2.0	28.6	0.0
5	2.4	31.8	1.6
6	5.5	19.7	5.2	19.4	0.0
7	6.2	26.1	6.3	24.9	0.6
8	2.8	15.1	3.4	12.6	1.2

1. Synthetic solution: 4% amines, 36% cresol, and 60% toluene; 0.9 cc. of water absorbed.
 2. Hydrogenated coal distillate; 0.2 cc. of water absorbed.
 3. Coal tar (500° C. carbonizing temp.) distillate; 0.6 cc. of water absorbed.
 4. Coal tar (600° C. carbonizing temp.) distillate; 0.4 cc. of water absorbed.
 5. Coal tar (700° C. carbonizing temp.) distillate; 0.6 cc. of water absorbed; 1.2% of benzoic acid added.
 6. Coal tar (800° C. carbonizing temp.) distillate; 0.2 cc. of water absorbed.
 7. Coal tar (800° C. carbonizing temp.) distillate; 0.3 cc. of water absorbed.
 8. Coal tar (900° C. carbonizing temp.) distillate; 0.4 cc. of water absorbed; 0.8% of benzoic acid added.
- 1 to 4. Ten per cent sodium carbonate used to remove carboxylic acids.
5 to 8. Almost saturated potassium carbonate solution used to remove carboxylic acid.

contraction to alkali. The tar-base value was indicated directly by the contraction in volume caused by washing the water-containing oil (oil washed with sodium chloride solution) with the sulfuric acid reagent.

To ascertain the effect of adding water before extracting with sulfuric acid and sodium hydroxide solutions, one synthetic solution (prepared as previously from cresol, toluene, pyridine, quinoline, isoquinoline, and aniline) and several tar-oil distillates were analyzed by a procedure identical with that used to obtain the data in Table VI, with the exception that a preliminary wash with 2 to 3 cc. of sodium chloride solution was employed. It was found necessary to allow considerable time for the layers to separate where the oil was washed with carbonate solutions. In some instances a nearly saturated solution of potassium carbonate was less troublesome than 10 per cent sodium carbonate, and with either reagent a good separation of the layers must be effected to determine traces of carboxylic acids. For the purpose of comparison the same synthetic solution and tar oils (see Table VII) were analyzed by the modified Bureau of Mines method and the liberation procedure of Morgan and Meighan (methods 2 and 5, Table V). Small amounts of benzoic acid were added to tar oils 5 and 8, but in all cases the liberation method was carried out on the original, untreated distillates.

As may be seen from Table VII, washing the oil with salt solution before extracting the tar acids and bases caused higher and lower values, respectively, to be obtained for the amines and phenols. Such values are more accurate than the ones obtained by simple extraction methods; hence the preliminary wash with salt water is a worthy addition to the contraction method.

The data in Table VIII show that oils containing appreciable amounts of water-soluble amines and carboxylic acids give erroneous results when analyzed by the procedure described previously and used to obtain the data in Table VII. This is due to the fact that the water-soluble car-

boxylic acid (acetic acid) is extracted along with the amines in the sulfuric acid wash. More accurate results (see solutions 3 and 4, Table VIII) were obtained by extracting the acetic acid just after the sodium chloride-water treatment and before removal of the amines.

TABLE VIII. ANALYSES OF SYNTHETIC SOLUTIONS^a CONTAINING ACETIC ACID

Synthetic Solution No.	Water Absorbed Cc.	Amines		Phenols		Carboxylic Acids	
		Present	Found	Present	Found	Present	Found
		Volume-Per cent					
1 ^b	0.4	5.2	6.3	20.4	20.6	1.6	0.5
2 ^c	0.5	5.3	7.5	20.4	20.5	2.8	0.7
3 ^d	0.5	5.2	5.2	20.1	19.9	2.0	2.6
4 ^e	0.4	5.5	5.0	20.0	20.2	1.6	2.1

^a Synthetic solutions prepared from toluene, cresol, acetic acid, and an amine mixture (equal parts by volume of pyridine, quinoline, isoquinoline, and aniline).

^b Carboxylic acid extracted with saturated potassium carbonate after sulfuric acid extraction.

^c Carboxylic acid extracted with 10 per cent sodium carbonate after sulfuric acid extraction.

^d Carboxylic acid extracted with saturated potassium carbonate after sodium chloride-water treatment.

^e Carboxylic acid extracted with 10 per cent sodium carbonate after sodium chloride-water treatment.

Conclusions

Dilute alkali (about 10 per cent) is a suitable reagent for determining tar acids by contraction methods. In the presence of tar acids, more concentrated alkali dissolves considerable quantities of nonacidic material, chiefly tar bases, and gives erroneous results; more dilute alkali (about 5 per cent) is not satisfactory because of its tendency to form emulsions with tar distillates.

Reagents such as 20 per cent sulfuric acid saturated with certain inorganic salts (sodium chloride, potassium sulfate, etc.) are suitable for extracting tar bases in contraction methods. The other acid reagents examined were found to dissolve considerable quantities of the lower boiling tar acids.

The common procedure of extracting with alkali and then with mineral acid gives high and low results, respectively, for tar acids and bases. More accurate results are obtained by extracting first with mineral acid, and then alternately with alkali and mineral acid until all tar acids and bases are removed.

The high and low values obtained for tar acids and bases, respectively, are due to (1) the solvent power of alkaline phenolate solutions for amines and (2) absorption of water by the oil layer. Errors from these two causes may be partly eliminated by extracting with dilute alkali and by making a correction for the water absorbed.

In agreement with the conclusions of Weiss (31) but contrary to those of Hill (15), it was found that contraction methods give higher tar-acid values than liberation methods.

The more efficient and convenient method of extracting first with alkali is almost as accurate as extracting first with mineral acid, if dilute alkali (about 10 per cent) is employed.

Tar acids may be determined as strong (polyhydric phenols and carboxylic acids) and weak (monohydric phenols) acids by extraction with both sodium (or potassium) carbonate and alkali.

The procedure described below is recommended for determining tar bases, carboxylic acids, and phenols in tar oils (using about 100 cc. of oil in a graduated separatory funnel, 10, 31).

The oil is shaken with 2 to 3 cc. of an approximately saturated sodium chloride solution; the increased volume of the oil layer is noted and used subsequently in calculating volume contractions.

Extracted with 5 to 10 cc. of approximately saturated potassium carbonate solution; diminution in value of oil layer is indication of carboxylic acid content.

Extracted in succession with 100- and 50-cc. portions of the sulfuric acid reagent (20 per cent sulfuric acid, approximately saturated with sodium chloride).

Extracted in succession with 100-, 35-, and 15-cc. portions of 10 per cent sodium hydroxide.

Extracted in succession with 50-, 25-, and 15-cc. portions of the sulfuric acid reagent.

Extracted with 15 to 20 cc. of 10 per cent sodium hydroxide. The amounts of tar bases and phenols present are indicated by the total volume contractions to sulfuric acid and sodium hydroxide, respectively. The tar acid value is corrected by subtracting from it the water-absorption value (obtained in the first step).

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Determination of the Moisture Content of Tobacco

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IT HAS been pointed out by Cone (4) that the control of the moisture content of tobacco is one of the most important phases of manufacture. While some hygroscopicity data are available (9, 15), they are insufficient for the types chiefly used in this country, and the writers had planned additional work to measure the equilibrium vapor pressure of various types, over a wide range of temperatures and moisture values.

It was realized, however, that there is no such thing as an "absolute" moisture content for any sample of tobacco; the value obtained depends on the method used, and few laboratories agree on the same method. Methods include drying the samples in ovens, for varying times, at different temperatures, with or without forced air circulation; drying at room temperature over various desiccants, under atmospheric pressure or vacuum; various distillation procedures with solvents immiscible with water; and indirect procedures involving conductivity or dielectric constant. In this work an attempt has been made to compare six methods in common use.

No experiments on the various "indirect" methods were made. The Tag-Heppenstall moisture meter, methods based on a change in dielectric constant (7), and others depending on the evolution and measurement of acetylene when the tobacco is mixed with calcium carbide (10) must all be calibrated against some such method as those discussed here. Attempts to deduce the moisture content from the humidity of the air in the tobacco were ruled out by the writers' experience, by that of other observers (12), and by the slowness with which equilibrium is reached (15). Other methods which have been suggested (1, 11) do not lend themselves to use on a large number of samples with a minimum of effort.

Selections of Samples for Drying

It is generally agreed that the greatest source of error in moisture determinations on tobacco is the heterogeneity of the material. Any manufactured sample is a blend of several grades, if not of several widely different types, and the proportions are not the same in every part of a large lot. The types vary in hygroscopicity, and as the more hygroscopic shreds rob the others of their moisture, variations of the water content are produced. Most tobacco ready for smoking also contains added substances (sugars, glycerol, diethylene glycol) which increase its natural hygroscopicity (4); any minor maldistribution of such material can cause a disproportionately large local concentration of water. If one attempts to pulverize and mix a sample of tobacco, moisture is usually lost in handling, and the sample must be very dry before it can be powdered. Moreover, a loose, fluffy mass of cigaret filler may be dried more rapidly and uniformly by most methods than an equal weight of fine powder. It is desirable to dry as much as possible at each determination; the writers have found 20 grams about the maximum for convenient use and the minimum for sufficient accuracy. Any method, therefore, which is restricted to a much smaller sample has been ruled out.

It was accordingly decided to compare single grades, representative of the most important types. Flue-cured, "bright," or "Virginia" tobacco amounts to half the domestic production, and Burley is next in importance. Since by the criteria

of Dixon and his associates (6) tobacco 30 months old may be considered fully aged, a sample of 1933 tobacco from Wilson, N. C., U. S. Grade C4F, was selected to represent flue-cured, and a sample of 1933 tobacco from Lexington, Ky., same grade, was chosen as typical Burley. These samples will be designated as "flue-cured" and "Burley," respectively. Flue-cured tobacco is generally more hygroscopic than air-cured Burley or Maryland, and contains up to 25 per cent of sugars, whereas the latter two contain almost none (5, 8).

Two samples of cut cigaret tobacco (blends A and B) were also used. These were blends of various types and grades, and their hygroscopicity had been increased by the addition of diethylene glycol. The cut tobacco was usually taken from the middle of a large, fairly tight container, and was mixed as well as possible in an atmosphere close to the equilibrium humidity. In general physical and hygroscopic properties it was felt that these blends were fairly representative of the popular American brands.

Experimental

All samples were cut by machine into shreds the usual width of cigaret filler (0.75 mm.), thoroughly mixed, and packed into plug-tins (1600 cc., 16-ounce size). All seams were sealed with paraffin. Samples from the same tin taken at intervals of several weeks showed no measurable change in moisture content. For each determination except by distillation, about 20 grams of tobacco were weighed quickly into a covered aluminum dish 63 mm. in diameter and 45 mm. deep. The electric oven used was a Freas No. 601, the temperature of which can be kept at 100° ± 0.5° C. all over the oven. A strong current of air was drawn by a fan horizontally through the drying chamber at such a velocity that it did not quite blow tobacco out of the dishes. For the British tests, on the basis of which duty is levied, small steam-jacketed ovens were kept very close to 100°, but the only circulation obtained was by convection.

After the oven-drying, the samples were cooled in desiccators over porous barium oxide for at least an hour.

For the samples dried over sulfuric acid, enough acid was used to maintain the acid concentration above 90 per cent after it had absorbed all the moisture it would. Three days after introducing the samples, the acid was stirred to prevent stratification of the layers of different concentrations.

The vacuum desiccators were exhausted by a water aspirator to 26 mm., and it was found that this pressure was maintained without leakage.

The toluene distillation apparatus was essentially that of Bidwell and Sterling (2). The cylindrical measuring tube was 0.782 cm. in diameter; the menisci were read from a reference point by a vernier caliper and the volumes were computed. Use of a smaller tube was attempted, but complete separation of layers was impossible. Distillation was continued until no more water could be driven over, although it was difficult to decide just when this desideratum occurred. Every sample, however, was distilled at least 2 hours.

In the 3-hour oven test the size of the sample influences the results obtained. With a given container, the larger the sample, the lower the result; but the results are not much lower until it is necessary to pack the tobacco to get the whole sample in. When tobacco is dried in vacuum, however, the size of the sample is of little effect. By any method, the time of drying is a factor which must be decided empirically, for it is practically impossible to dry to constant weight (14).

In vacuum desiccators the loss in weight after the first few days is very slow; the authors opened their desiccators at 5, 9, and 15 days with one sample of tobacco, weighing the dishes and reëvacuating each time (Table I). The period of

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TABLE I. MOISTURE DETERMINATIONS

(Sample of cigaret blend No. 1, from cut-filler storage)

Oven Drying, 3 Hours at 100° C.

Weight of sample, grams	13.5	21.0	29.3
Per cent of water	11.59	11.50	11.04
Vacuum Drying over P ₂ O ₅			
Weight of sample, grams	10.0	20.0	30.0
Per cent of water, 5 days	9.67	9.84	9.66
9 days	9.84	9.91	9.74
15 days	10.03	10.10	9.93

7 days was chosen simply because it is about as long as most workers are willing to wait (Table II).

Discussion of Results

Table II shows that for a given sample of tobacco moisture values may vary as much as 50 per cent, depending on the method used, and that the differences between the methods are by no means constant with all types of tobacco or for all moisture values. The choice of methods, therefore, depends simply on how much water the experimenter wishes to remove. The sulfuric acid apparently takes out only that held mechanically by capillarity; when something as hygroscopic as diethylene glycol has been added to the tobacco, perhaps even this water is not completely removed, for diethylene glycol itself is a fairly good desiccant. Vacuum drying at room temperature seems to remove all the water held by absorption and adsorption, which apparently is all that contributes to the mechanical pliability of the leaf.

Barium oxide was substituted for phosphorus pentoxide as the desiccant in these experiments; it seems to be as good a drying agent (8) and there is less chance of its taking up the volatile bases of tobacco. The writers found a reduction in the nicotine content of tobacco dried over phosphorus pentoxide and measurable amounts of nicotine (about 5 per cent of that in the tobacco dried) in phosphorus pentoxide over which tobacco has been dried, and got slightly higher results

for the moisture when phosphorus pentoxide was used as the desiccant (Table II).

At 100° C. in a good draft salt hydrates and hydrates of the sugars present begin to decompose. Flue-cured tobacco which contains up to 25 per cent of sugars (5) gives values 1.16 to 1.5 per cent higher on drying 3 hours at 100° C. than with vacuum drying over barium oxide; the 16-hour British test gives a value 2.85 per cent higher. With air-cured Burley which contains practically no sugar, the 3-hour oven test gives a value only 0.1 per cent higher than vacuum drying, and the British test gives 0.26 per cent higher. Since the chief chemical difference between flue-cured and Burley is the sugar content, this factor is probably responsible for the different values obtained.

It is also likely that at 100° C. other substances than these hydrates are decomposed. In a sample of cigaret blend A containing 11.52 per cent of moisture (oven), the writers found that in 3 hours at 100° C. the percentage of nicotine on the basis of the original moisture content was reduced from 2.45 to 2.16 per cent—a known error of around 0.3 per cent. The writers believe that the humidity of the room air also influences the results. At the conclusion of the 16-hour British test the tobacco had been considerably darkened and had lost most of its original hygroscopic power.

The toluene distillation simply dries at the boiling point of toluene (111° C.). The appearance of the tobacco indicates that even greater decomposition has taken place and while the authors agree with other observers (2, 13) that this method obviates the possibility of oxidation, it also probably decomposes some of the carbohydrate present. Bidwell and Sterling (2) claim that water of crystallization is separated from some substances, and the authors' results show that this may be the case with some compounds present in tobacco. Since water was still being slowly liberated after 2 hours' distillation, the decision to stop at any particular time makes this method as purely empirical as any of the others. In addition, there was very poor separation of water and toluene in the tube the authors finally used, and all the water does not descend from the condenser into the graduated section.

Since any method is more or less empirical and since all except distillation give consistent results with little trouble, the selection of a procedure becomes largely a matter of convenience. The authors feel, therefore, that the speed of the 3-hour oven test and the fact that a single worker with a fast balance can handle nearly 100 samples a day makes this the most useful for general control work. For calibration and comparison, vacuum drying for a week over a good neutral or alkaline desiccant (magnesium perchlorate, calcium sulfate, or porous barium oxide) is to be recommended.

TABLE II. MOISTURE DETERMINATIONS

Type	7 Days ^a over H ₂ SO ₄	7 Days ^a over P ₂ O ₅ (Vacuum)	7 Days ^a over BaO (Vacuum)	3 Hours in Electric Oven at 100° C.		16 Hours in Steam-Heated Oven at 100° C. (British Test)		Toluene Distilla- tion
	%	%	%	%	%	%	%	%
Flue-cured	9.92	12.66	12.32	13.84	13.88	14.92	15.17	...
	10.13	12.61	12.50	13.88	13.80	15.38	15.12	...
	10.07	12.72	12.18	13.72	14.00	15.10	15.40	...
	13.63	13.88
	Av.	10.04	12.66	12.33	13.83	...	15.18	...
Same kept 18 hours at 22.22° C. (72° F.), 61% relative hu- midity	8.90	...	10.56	11.59
	8.70	...	10.38	11.55
	8.75	...	10.43	11.73
	Av.	8.78	...	10.46	11.62
Burley	9.00	...	13.03	13.09	...	13.32	13.13	13.97
	9.07	...	12.92	12.96	...	13.08	13.24	14.15
	9.03	...	12.84	13.03	14.22
	Av.	9.03	...	12.93	13.03	...	13.19	...
Same kept 18 hours at 22.22° C. (72° F.), 60% relative hu- midity	7.75	...	10.04	10.23
	7.54	...	10.11	10.32
	7.56	...	10.29	10.17
	Av.	7.62	...	10.15	10.24
Cigaret blend A	6.46	...	9.33	10.92	...	12.37	12.62	11.74
	6.35	...	8.91	10.70	...	12.80	11.91	11.94
	6.62	...	8.85	10.66	11.78
	Av.	6.48	...	9.03	10.76	...	12.43	...
Same kept 18 hours at 22.22° C. (72° F.), 62% relative hu- midity	8.62	...	9.97	11.83	11.76
	8.76	...	10.38	11.74	11.68
	9.00	...	10.03	11.78
	Av.	8.79	...	10.13	11.78
Cigaret blend B, wet from cutters	13.45	...	16.30	18.02	18.90
	13.29	...	16.79	18.20	18.56
	13.41	...	16.70	17.72	18.97
	Av.	13.38	...	16.60	17.98
Cigaret blend A, too dry for use	4.42	...	5.77	7.08	8.12
	4.30	...	5.88	7.08	8.08
	4.41	...	5.88	7.08	8.47
	Av.	4.38	...	5.84	7.08

^a At 22° to 30° C.

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Separation of Beryllium in the Presence of Complex Tartrates

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OWING to statements in the literature (1, 4) that solutions of beryllium salts in the presence of tartrate are stable to strong alkali, the idea has arisen that beryllium cannot be precipitated as the hydroxide in the presence of tartrate. The author has found, however, that beryllium may be precipitated from its complex tartrate solution by means of an optimum hydroxyl-ion concentration provided by the addition of ammonium hydroxide. In this way it is possible to separate beryllium, to a fairly quantitative extent, from such elements as aluminum, iron, copper, and chromium, which form complex tartrates from which the hydroxides of the metals are not precipitable upon addition of an optimum quantity of ammonium hydroxide.

Recently Jilek and Kota (2) demonstrated that beryllium could be separated quantitatively from aluminum by adding a known quantity of ammonium tartate solution to the

salts of aluminum and beryllium; subsequent addition of an excess guanidine carbonate precipitates beryllium as the basic carbonate while the aluminum remains in solution.

The method herein proposed eliminates the use of guanidine carbonate by employing ammonium hydroxide.

A solution of beryllium nitrate, containing a known quantity of beryllium, was accurately pipetted into a 250-cc. beaker, to which was added a measured portion of 0.5 M potassium tartrate solution. The contents of the beaker were well mixed, after which a specified amount of 16 M ammonium hydroxide was added dropwise. After standing at room temperature (25° C.) for 10 hours, the precipitate was filtered on No. 44 Whatman paper, washed with water containing a trace of ammonium nitrate (3), dissolved with dilute nitric acid, reprecipitated as many times as indicated in the Tables I and II, washed as described above, ignited, and weighed as beryllium oxide.

Tables I and II are illustrative of typical results. It is significant that the amount of beryllium recovered depends, to within certain limits, on the quantity of ammonium hydroxide added to a given quantity of the salt solution. If the final solution is too feebly alkaline with ammonium hydroxide, all the beryllium may not be precipitated, thus leading to low results.

Precipitation of Beryllium

Eight determinations of beryllium were made by precipitating beryllium as beryllium hydroxide in the presence of the complex tartrates of aluminum, iron, copper, and chromium.

To 50 cc. of solution containing $\text{Be}(\text{NO}_3)_2 \approx 140.0$ mg. BeO , $\text{AlCl}_3 \approx 11.2$ mg. Al , $\text{FeCl}_3 \approx 20.7$ mg. Fe , $\text{CuCl}_2 \approx 47.3$ mg. Cu , and $\text{CrCl}_3 \approx 19.5$ mg. Cr , were added 30 cc. of 0.5 M potassium tartrate, followed by the dropwise addition of 16 cc. of 16 M ammonium hydroxide. From this point on the procedure described above was followed. The precipitates were redissolved three times and reprecipitated. An average of 143.6 ± 1.3 mg. BeO (theoretical, 140.0 mg. BeO) was obtained.

The principal disadvantage of this method of analysis is the tendency of gelatinous precipitates to co-precipitate crystalloidal matter. For this reason it is not recommended for very precise and accurate separations and determinations.

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TABLE I. PRECIPITATION OF BERYLLIUM FROM ITS COMPLEX TARTRATE

BeO Theoretical Mg.	0.5 M Potassium Tartrate Cc.	16 M NH_4OH Cc.	BeO Found Mg.
146.3 ^a	20	8	113.8
146.3 ^a	20	10	126.0
146.3 ^a	20	14	144.4
146.3 ^a	20	16	146.4
146.3 ^a	25	15	146.2
146.3 ^a	25	16	145.1
146.3 ^a	25	16	145.1
146.3 ^a	25	16	144.1
146.3 ^a	25	16	143.7
146.3 ^a	25	16	144.2
140.0 ^a	25	15	140.0
14.0 ^b	3	5	14.2
14.0 ^b	3	5	14.0
14.0 ^b	3	5	14.0
14.0 ^b	3	5	14.0

^a 50.00 cc. of $\text{Be}(\text{NO}_3)_2$ solution ≈ 146.3 mg. of BeO , etc.

^b 5.00 cc. of $\text{Be}(\text{NO}_3)_2$ solution + 20 cc. $\text{H}_2\text{O} \approx 14.0$ mg. of BeO . In each case the precipitate was dissolved in dilute nitric acid and reprecipitated.

TABLE II. PRECIPITATION OF BERYLLIUM FROM ITS COMPLEX TARTRATE^a

(In the presence of aluminum ≈ 33.5 mg.)		
0.5 M Potassium Tartrate Cc.	16 M NH_4OH Cc.	BeO Found Mg.
20	8	75.0
20	10	117.8
20	15	151.0
20	15	146.3
25	14	146.2
30	14	146.2
25	16	145.0

^a For each determination 50.00 cc. of solution containing $\text{Be}(\text{NO}_3)_2 \approx 146.3$ mg. of BeO and $\text{AlCl}_3 \approx 33.5$ mg. of Al . Each precipitate was dissolved in nitric acid and reprecipitated.

Interference of Phosphorus in the Determination of Fluorine

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SINCE the discovery that fluorine is a causal factor of the dental defect known as mottled enamel on teeth, the literature of analytical chemistry has abounded with papers describing methods for its determination in small amounts—that is, up to a few parts per million. More recently the increased use of fluorides as insecticides has stimulated interest in such methods and, since the U. S. Food and Drug Administration placed the maximum allowable limit for fluorine content of food at 0.01 grain per pound (1.4 p. p. m.), the need for an accurate method to determine it in the range of 1 to 2 parts per million is paramount.

Workers in this field have used various procedures for the determination of fluorine. Churchill (2), when investigating the occurrence of fluorine in some waters of the United States, determined fluorine by a modified Fairchild method and verified the results by means of the spectrograph. Willard and Winter (7) developed a method for the determination of fluorine by distilling it with perchloric or sulfuric acid and titrating it with thorium nitrate, using the zirconium sodium alizarin sulfonate lake as an indicator.

Armstrong (1) improved this method by using alizarin sulfonate only as the indicator. Thompson and Taylor (5) developed a colorimetric method using the zirconium alizarin lake for the determination of fluorine in sea water. Sanchis (4) modified the procedure for the determination of fluorine in natural waters. Winter (8) used it for the determination of fluorine in alfalfa and grass, and Wichmann and Dahle (6) developed an improved titanium bleach method (Steiger Merwin reaction) and determined the most suitable pH for color development and the effect of many interfering ions and various solution concentrations. Hoskins and Ferris (3) made a study of the thorium nitrate titration, determining the most suitable pH at which it should be made and the minimum concentration at which the ions of halogens, NO₃, ClO₄, SO₃, AsO₃, SO₄, AsO₄, and PO₄ interfere.

It is well known that phosphates interfere with the determination of fluorine by the above colorimetric and thorium nitrate titration methods, but it generally has been considered that the Willard-Winter distillation made a complete separation of fluorine from phosphate. However, in determining fluorine in some foods having a high phosphorus content, by the thorium nitrate titration of a distillate made from the ash of the food, results for fluorine were obtained which varied from "not detected" to 11 parts per million. Investigation showed that such varying results obtained on navy beans were caused by titration of phosphate carried over into the distillate. When the first distillate was made alkaline with sodium hydroxide to phenolphthalein, evaporated to small volume, and redistilled, satisfactory results for fluorine were obtained which indicate the fluorine content to be less than 1 part per million.

It was evident that some variable factor caused the phosphate contamination. It seemed plausible that the contamination was caused by the presence of unburned carbonaceous matter or that possibly during ashing phosphate was reduced to a form which is readily carried over in the distillate. This is indicated by the following experimental analysis of navy beans:

Thorium nitrate titration of a distillate using sulfuric acid on the ashed sample indicated 7.2 p. p. m. of fluorine. In this distillate phosphate was present in appreciable amount, sulfate a trace.

When the distillate from sulfuric acid was concentrated and redistilled, using perchloric acid, less than 1 p. p. m. of fluorine was indicated. Phosphate and sulfate were not detected in this distillate.

To another distillate from sulfuric acid, which indicated 7.2

p. p. m. of fluorine, phosphate was added as phosphoric acid in amount equal to that present in the original ash. Concentration of the distillate followed by distillation, using perchloric acid, gave a titration indicating less than 1 p. p. m. of fluorine. In this distillate phosphate and sulfate ions could not be detected.

Satisfactory recovery of added fluorine was made by the double distillation. It, therefore, seems necessary to make a double Willard-Winter distillation of the fluorine from the ash of foods, for satisfactory determination of fluorine. The first is made with sulfuric acid rather than perchloric acid to eliminate hazard, as some carbonaceous matter is usually present. The second should be made with perchloric acid at 135° C., which gives a distillate free from phosphate and sulfate.

Fluorine in a number of food products, mostly purchased in retail stores, was determined by the above double-distillation procedure and titration with thorium nitrate, with the following results: Less than 0.2 p. p. m. of fluorine was indicated in dried beans, wheat bran, crushed oats, peanuts, mackerel (boned), carrots, turnips, sweet potato, Irish potato, canned corn, beef, mutton, and pork. Less than 1.0 p. p. m. of fluorine was indicated in baking powder C, pure wheat germ, alfalfa, wheat, wheat straw, yellow corn, and whole rice.

More than 1.0 p. p. m. of fluorine was found as follows:

Mackerel (with bones)	3.9	Corn germ	15.0
Salt pork	1.1	English Breakfast tea	66.0
Baking powder A	220.0	Gun Powder tea	67.0
Baking powder B	19.0	Oolong tea	41.0
Commercial wheat germ A	1.7	Canned salmon	4.5
Commercial wheat germ B	4.0	Canned sardines	7.3
Cottonseed meal	12.0		

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Correction

In the article entitled "Physical and Chemical Properties of Petroleum Fractions. I. Behavior in Dilute Benzene Solutions" [*IND. ENG. CHEM.*, **Anal. Ed.**, **8**, 324 (1936)] by Harry T. Rall and Harold M. Smith, *C* in the equations in Table I should be multiplied by 100. Thus, the equation for A-1, Wet, should be

$$K = 64.98 - 0.16 C \times 100$$

In the second article of the series, "II. Relations between Molecular Weight and Concentration in Dilute Solution" [*Ibid.*, **8**, 436 (1936)], *S* for oil O-1 in C₂H₄Br₂ should be 11,600.0 instead of 1160.0.

HARRY T. RALL

Direct Determination of Oxygen in Organic Compounds by Hydrogenation

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RUSSELL and Fulton (8) and Russell and Marks (9) reported an improved method for the direct determination of oxygen in organic compounds containing only carbon, hydrogen, and oxygen and in compounds also containing nitrogen. Later Marks (4) applied the method to the determination of total oxygen in oxidized oils in the presence of small amounts of sulfur contained in the oils. The method is the hydrogenation method of ter Meulen (7); it has enjoyed the best success of all the direct methods for oxygen, although some workers have reported difficulties with it, one of the latest being Gauthier (2). It seemed desirable to render the method more dependable and capable of wider application.

With the present procedure and apparatus it has been successfully applied, without any modifications, to a similar variety of compounds containing carbon, hydrogen, oxygen, nitrogen, and sulfur. Moreover, the reproducibility was found to be generally as good as the accuracy—that is, about 0.1 per cent for the oxygen.

Apparatus

The apparatus of Russell and Fulton (8) was modified only slightly (Figure 1).

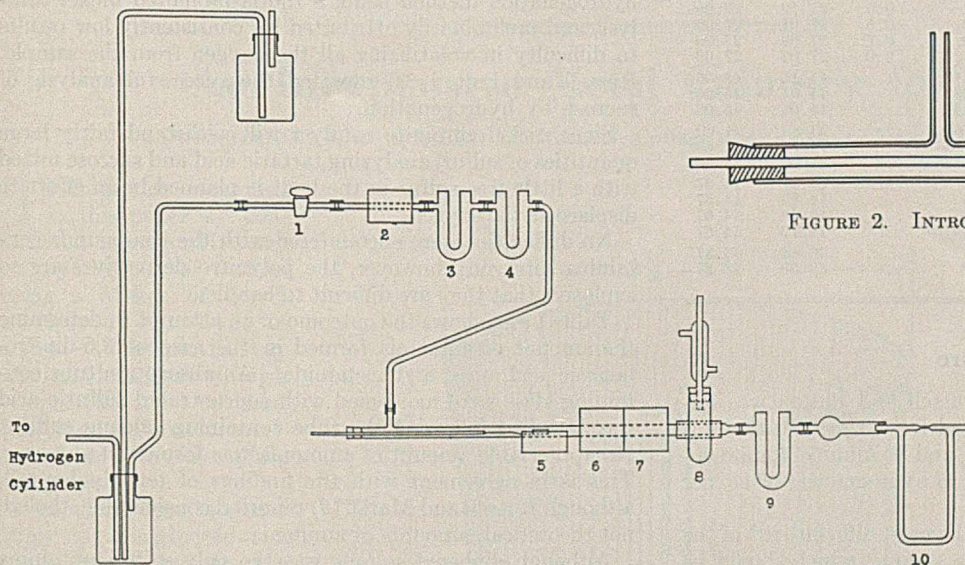


FIGURE 1. DIAGRAM OF APPARATUS

The cracking, 6, and catalyst chambers, 7, and preheater, 2, were electrically heated by specially prepared furnaces each 20 cm. long. A 2.5 × 5 × 10 cm. (1 × 2 × 4 inch) cast-aluminum block, 5, with a groove along the center of a large face and a longitudinal hole for a thermometer, was used in vaporizing the sample. A glass mortar, 8, 8 cm. long in which toluene was refluxed to maintain a temperature of 111° C. was used to heat a 2-cm. plug of silver sulfate in the case of halogen-containing compounds. This silver sulfate was omitted in all runs where halogen was not involved.

A capillary stopcock, 1, was used to adjust the flow of hydrogen; the hydrogen was dried by sodium hydroxide pellets, 3, and anhydrous calcium sulfate, 4, and was delivered to the apparatus under a pressure of about 2 meters (6 feet) of water siphoned from one 19-liter (5-gallon) carboy to another. The water formed

during the analysis was absorbed by anhydrous calcium sulfate contained in a 150-mm. Schwartz U-tube, 9, attached to the quartz tube by a rubber connection. The exit hydrogen was passed through a flowmeter, 10, open to the atmosphere. The clear quartz tube had a total length of 70 cm. and an internal diameter of 7 mm.

The means employed for the introduction of the regular platinum microboat, during an exit flow of hydrogen of more than 200 cc. per minute, is illustrated in Figure 2. A one-hole rubber stopper contained a solid glass rod which extended into the quartz tube about 10 cm. Sealed into the end of this rod was a double length of Nichrome wire having a loop on the end the right size and shape for the microboat to fit snugly. The rod and wire remained in the tube during the analysis and attendant vaporization of the sample. The boat was removed by pulling it to the end of the quartz tube with the rod and wire and then picking it up with clean forceps. The boat containing the next sample was immediately placed in the wire loop and pushed into place in the tube.

Catalyst and Cracking Surface

The nickel chromite catalyst is quickly prepared from readily available materials and is easily handled even after reduction. The freshly prepared catalyst, after reduction at 400° C. for 10 or 12 hours (overnight) and then at operating temperatures for 1 hour, gave a constant blank of about

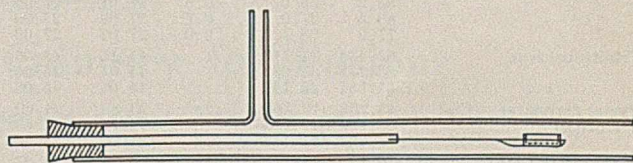


FIGURE 2. INTRODUCTION OF MICROBOAT

0.2 mg. per liter of hydrogen. Russell and Fulton (8) reported that it took 2 or 3 days to reduce their thoria-promoted nickel catalyst to a point where it gave a similar constant blank.

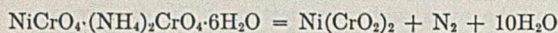
Of especial significance is the fact that the activity of the nickel chromite catalyst is unaffected by sulfur (3) up to relatively large amounts, and as sulfur is completely retained by this substance (3) the method is applicable to sulfur-containing compounds. Marks (4) has shown that the thoria-promoted nickel catalyst is also resistant to poisoning by sulfur.

Nickel chromite was also found to make the best cracking surface when heated to red heat. Some carbon dioxide escaped when platinized quartz beads were tried as cracking surface with nickel chromite as catalyst, whereas when nickel chromite was used as cracking surface (at 750° C.) and as catalyst (at 400°) the carbon dioxide was completely hydrogenated. Under these conditions the nitrogen in nitrogen-containing compounds is cracked directly to free nitrogen and practically no ammonia is formed (Table I).

The catalyst was prepared by weighing 31 grams of am-

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monium chromate $[(\text{NH}_4)_2\text{CrO}_4]$ into one beaker and 29 grams of nickel nitrate $[\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}]$ into another; the nickel nitrate was dissolved in 50 cc. of distilled water and the solution poured over the dry ammonium chromate with stirring. This produces the double salt, $\text{NiCrO}_4 \cdot (\text{NH}_4)_2\text{CrO}_4 \cdot 6\text{H}_2\text{O}$ (1). After about 10 minutes of stirring, the precipitate was filtered off with suction, dried over a low flame, and decomposed in small portions in a porcelain casserole over a Bunsen burner at 200°C . with stirring.



The catalyst so obtained was in fluffy particles which were put directly into the quartz tube for a distance of 40 cm. and into the preheater tube and packed slightly with light tapping. Approximately 10 grams of the catalyst were used in the combustion tube and 5 grams in the preheater.

TABLE I. DETERMINATION OF OXYGEN

Substance	Sample Mg.	Water Mg.	Ammonia Mg.	Oxygen	
				Found %	Cal- culated %
Benzoic acid	81.2	23.9	...	26.14	26.22
	99.2	29.3	...	26.23	26.22
Succinic acid	110.8	67.5	...	54.11	54.21
	112.6	68.6	...	54.11	54.21
Tartaric acid	110.6	37.6	...	30.19	63.96
	117.9	47.0	...	35.41	63.96
Picric acid	46.7	25.7	...	48.88	48.89
	60.2	33.0	...	48.69	48.89
3,5-Dinitrobenzoic acid	102.1	52.0	0.5	45.23	45.27
	101.6	51.8	0.6	45.28	45.27
Urea	89.5	26.8	0.2	26.60	26.64
	88.1	26.5	0.0	26.71	26.64
Acetamide	83.2	25.4	0.0	27.12	27.09
	82.2	25.0	-0.5	27.01	27.09
	88.5	27.0	0.7	27.09	27.09
Trinitrobenzene	77.9	23.7	0.0	27.02	27.09
	62.434	31.748	...	45.17	45.06
	65.278	33.032	...	44.94	45.06
Pyrrol derivative (C ₁₀ -H ₁₁ NO ₃)	51.551	26.144	...	45.05	45.06
	45.202	12.160	...	23.89	24.60
	63.962	17.683	...	24.55	24.60
Diphenyl sulfone	62.062	17.116	...	24.50	24.60
	70.1	11.5	...	14.57	14.67
	76.5	12.6	...	14.63	14.67
	68.2	11.2	...	14.58	14.67
Chloroacetic acid	71.2	11.8	...	14.72	14.67
	135.6	55.7	...	36.48	33.87
	127.6	54.7	...	38.08	33.87

Procedure

In general, the procedure of Russell and Fulton was followed. Fifty minutes were allowed for a run: 20 minutes for the vaporization of the sample, and 30 minutes for sweeping out the tube. The rate of flow of hydrogen was 60 cc. per minute.

The most important and by far the most difficult part of the analysis is the vaporization of the sample, which should be done slowly and evenly by heating the aluminum block under the sample with a microburner. A thermometer in the block registers the approximate temperature of the sample and a practice run is often advisable to learn the peculiarities of the individual substance when volatilized; the vaporization of the sample should be conducted about 20° above its melting point the first time it is run.

Substances will distill from the hot to the cold portion of the tube and in many cases distillation countercurrent to the flow of hydrogen was observed. This is effectively prevented by keeping the tube hotter (with an oxygen blowtorch) 6 or 8 cm. preceding the sample than in the region surrounding the boat. When all the substance has been volatilized from the boat, the aluminum block should be lowered and the boat heated with the free flame from the microburner before the oxygen blowtorch is applied.

With picric acid (Table I), when easily decomposable or explosive substances are used, it was found necessary to keep the temperature of the sample as low as possible during the vaporization and to spend a longer time than usual on this process. It is advisable to increase the rate of flow of the hydrogen to at least 90 cc. per minute.

With diphenyl sulfone (Table I), when difficultly decomposable substances are analyzed it is necessary to slow the rate of flow down to about 30 cc. per minute, so that the vapors may remain in contact with the cracking surface for a longer period of time.

Discussion of Results

In the case of compounds containing only carbon, hydrogen, and oxygen the results were satisfactory with one exception: with tartaric acid the percentage of oxygen found was very much too low. This was true for another hydroxy compound, sucrose, the results for which were thrown out because of an inactive catalyst.

It seems impossible to vaporize either tartaric acid or sucrose without carbonization of most of the sample. Other substances will carbonize, but when they are heated in the full blast of the oxygen blowtorch all the oxygen is given up and the results are satisfactory. In the case of sucrose, test runs with benzoic acid proved that the catalyst was inactive at the time of the sucrose runs. This may also be true for tartaric acid, though it is believed that all the oxygen was not volatilized from the residue in the boat. However, Gauthier (2) reported a successful analysis of this substance.

In a private communication, W. R. Kirner stated his inability to get satisfactory results with sucrose by a microhydrogenation method using a thoria-promoted nickel catalyst, and preliminarily attributed his consistently low results to difficulty in volatilizing all the oxygen from the sample. Russell and Fulton (8) reported the successful analysis of sucrose by hydrogenation.

Since nickel chromite catalyst will withstand fairly large quantities of sulfur, analyzing tartaric acid and sucrose mixed with a little free sulfur in the boat is planned in an effort to displace all the oxygen.

No difficulties were encountered with the compounds containing nitrogen; however, the polynitro derivatives are so explosive that they are difficult to handle.

Table I also shows the outcome of an attempt to determine the amount of ammonia formed in the case of 3,5-dinitrobenzoic acid, urea, and acetamide. An absorption tube containing glass wool moistened with concentrated sulfuric acid was attached following the tube containing calcium sulfate. No appreciable amount of ammonia was formed in any case. This is in agreement with the findings of ter Meulen (5), although Russell and Marks (9) reported considerable, though not theoretical, amounts of ammonia.

Although diphenyl sulfone was the only sulfur-containing compound tried, it is believed to be a sufficient test of the method. With this substance it was demonstrated that sulfur in reasonable amounts does not poison the catalyst completely.

Halogen compounds (chloroacetic acid) cannot be successfully analyzed with nickel chromite catalyst prepared as directed. This is in agreement with ter Meulen's findings (6) that a thoria-promoted catalyst is attacked by halogen acid, liberating water from the thorium oxide present. The chromite catalyst prepared according to the method outlined contains a small amount of free oxide, which presumably is never completely reduced.

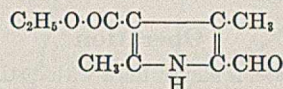
The introduction of a slight modification should make the method applicable to halogen-containing compounds when nickel chromite is used. When this catalyst is pure it is insoluble in boiling concentrated hydrochloric acid (3), so that

if the catalyst, as prepared with a small excess of chromic oxide, were boiled or leached with several portions of boiling hydrochloric acid, it should no longer react to produce water under operating conditions in the quartz tube. Preliminary results from work now in progress indicate this to be true.

It has been shown definitely (Table I) that ammonia is not formed in the presence of this catalyst, even from a substance like urea; it is therefore planned to use phosphorus pentoxide as the absorbent for water, with no silver sulfate in the tube when analyzing halogen compounds. It is then possible that halogen may be determined simultaneously.

With these two modifications, the leaching of the catalyst with hydrochloric acid and the substitution of phosphorus pentoxide for calcium sulfate as the absorbing agent for water, it is believed the method will be readily applicable to halogen-containing compounds and therefore general with one simple setup.

The pyrrol derivative



and the trinitrobenzene, furnished by A. H. Corwin, were run as unknowns for Frazer; a Kuhlmann microbalance was used for these runs with no modification of apparatus or procedure except the use of micro absorption tubes weighing about 15 grams when filled.

Summary

The method of hydrogenation has been successfully employed for determining the percentage of oxygen in organic

compounds containing carbon, hydrogen, oxygen, nitrogen, and sulfur, using an active nickel chromite catalyst at 400° C. The low results obtained in the analysis of tartaric acid and sucrose indicated extreme difficulty in driving all the oxygen from the residue in the boat.

The accuracy and reproducibility are each about 0.1 per cent for the oxygen, or about that with which carbon is determined in ordinary combustions, and the apparatus and procedure are almost as simple as for combustions. The time allotted to a single run was 50 minutes.

A modification has been suggested which will probably make the method applicable to halogen-containing compounds.

Acknowledgment

The authors are indebted to A. H. Corwin for many suggestions.

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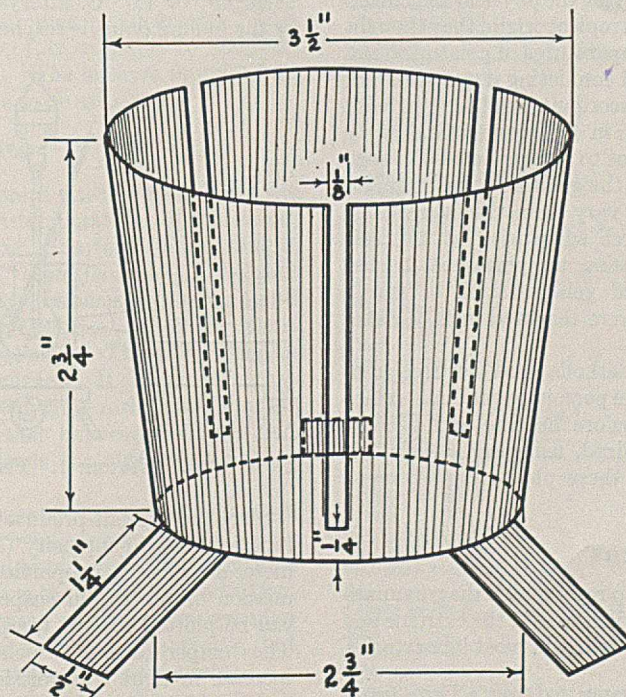
RECEIVED October 30, 1936. Taken from the dissertation submitted by Mr. Goodloe to the Board of University Studies, The Johns Hopkins University, in partial fulfillment of the requirements for the degree of doctor of philosophy.

An Inexpensive Metal Chimney for Fusions

LOUIS J. CURTMAN AND LEO LEHRMAN, College of the City of New York, New York, N. Y.

THE device described in this paper was constructed to expedite the carrying out of fusions using a Meker or Tirrill burner as a source of heat. It is particularly serviceable where a high temperature must be maintained, as in the decomposition of a silicate with sodium carbonate.

For a long time the blast lamp was employed for most fusions, but it was noisy and troublesome. Later it was found that if an asbestos cylinder was placed over the crucible, a sufficiently high temperature could be obtained with a Tirrill or Meker burner; however, after a few heatings the asbestos crumbles and must be discarded. The authors' device, being made of metal, can be used for a long time, is inexpensive, and can be employed with any type of burner. Numerous experiments



have shown that it is as effective as the asbestos cylinder.

The chimney is constructed of ordinary tin-plated sheet steel, such as is used for tin cans. Three slots are cut equidistant from each other to hold conveniently a Vitreosil or clay triangle upon which the crucible can be supported. At the bottom of the device and spaced between the slots are three projections, by means of which the apparatus can be set on a ring or tripod. The drawing clearly shows the construction of the chimney.

Acknowledgment

The authors wish to thank Harold Wilson of the stock division for his kindness in making the various models that were tried out.

RECEIVED February 25, 1937.

Determining the Gelatinization Temperature of Starches

A Photoelectric Method

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A simple photoelectric method for the determination of the gelatinization temperatures of starches has been developed. The results can be plotted against temperatures to form smooth curves. Three types of characteristic curves have been found. One, typical of starches of tropical origin, has a very steep slope; the second, typical of northern grain starches, has a more gradual slope and irregular rate of gelatinization; the third is intermediate and is produced by a few northern and tropical starches. The slope of the curves seems to be determined by the fragility of the starch granule. The significance of these curves in determining the dietetic value of starches when fed to patients suffering from the tropical disease, sprue, is pointed out. The method may be used as an aid in identifying starches or following changes produced by swelling and hydrolyzing agents and may even find practical application in industrial starch plants.

WHILE the authors were studying the physical and chemical properties of starches of tropical origin, they thought it desirable to determine their temperatures of gelatinization. A search of the literature revealed conflicting data; different investigators failing to secure concordant results, even with the same method. Reichert (4), in his monumental work on starches, gives several references to workers who, between 1861 and 1909, tried to determine the gelatinization temperature of starches. Their methods vary from the microscopic examination of samples of a starch suspension at intervals when subjected to slowly increasing temperatures, to the visual estimation of swelling and gelatinization of starch suspensions in test tubes which were removed from a water bath at 5° C. intervals.

It appeared that none of the methods used was free from errors of manipulation, or from the personal equation. Since starch suspensions are opaque before heating and become translucent or clear when gelatinized, using a photoelectric method for the measurement of these physical phenomena appeared feasible.

Apparatus

After some trials, the final setup represented diagrammatically in Figure 1 was devised. It is simple in the extreme and can be assembled from equipment found in most laboratories.

It consists of a 60-watt tungsten lamp, fed from a Delta transformer to smooth out line voltage fluctuations, and a condensing lens to bring the beam of light to a focus in the reaction vessel, which is a wide-mouthed flask of 150-cc. capacity, containing a

thermometer and small motor-driven stirrer. The reaction vessel is suspended in a 1-liter Pyrex beaker that serves as a water bath. The photoelectric cell is of the copper oxide or photonic type, and is directly connected with a 0-50 microammeter. A three-heat hot plate completes the assembly. The beaker water bath is covered with black paper in which two holes 3.75 to 5 cm. (1.5 to 2.0 inches) in diameter are cut to allow the beam of light to pass through the water bath and reaction vessel and into the photocell, and at the same time to cut out interfering light from the laboratory.

Operation

The reaction vessel is almost filled with distilled water and the heater is adjusted so that the temperature rise is around 0.5° C. per minute. When the temperature in the reaction vessel has reached about 40° C., the light is turned on, focused, and adjusted to give at least a full-scale reading on the microammeter. Sufficient dry starch—1 or 2 grams—is suspended in 25 cc. of water and slowly poured into the reaction vessel till the microammeter reading drops to 3 to 5 microamperes. As the temperature increases there will be a slow drift of the microammeter needle of two or three divisions. Most starches show a slight decrease in light transmission at this point, which generally is several degrees below the temperature of gelatinization, but this change is so gradual that it may be disregarded.

With a little experience one can tell when the starch has almost reached the temperature of gelatinization, as the suspension, which up to this time is of a dull flat white color, begins to take on an opalescent appearance, with a faint bluish tinge. When this stage is reached, the microammeter should be watched closely and the instant the needle begins to show an increased reading the temperature should be recorded. The microammeter readings are then taken for each 0.5° or 1.0° C. interval, till readings become constant or the boiling point is reached.

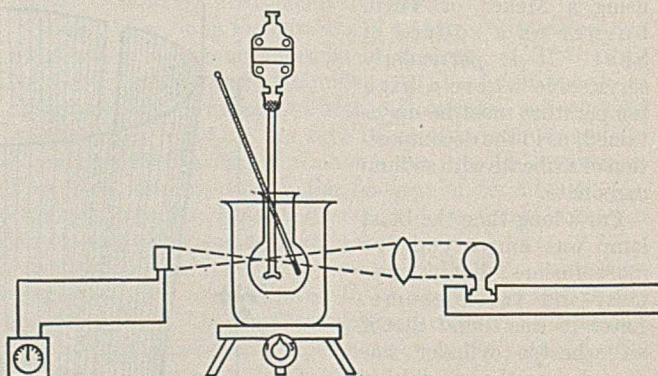


FIGURE 1. PHOTOELECTRIC SETUP

Since the current produced by the photonic cell is a lineal function of light intensity (3), the readings of the microammeter are directly proportional to the changes in light transmission of the starch suspension. The readings, therefore, can be plotted against temperatures to form smooth curves. The temperature at which the suspension shows its first increase in light transmission, or the beginning of swelling and gelatinization, is called the temperature of transition. This point and the rate of gelatinization as shown by the slope of the plotted curves are characteristic of the sample of starch

under investigation. Results are duplicable if the conditions of the experiment are kept constant. In fact, the temperature of transition and the slope of the curve can be used as a means of identification of many starches, if the starch samples have all been obtained by the same process of manufacture. The method is a delicate means of testing the treatment to which a starch has been subjected previous to gelatinization, as treatment with acids, or alkalies, desiccation over dehydrating agents, or drying at temperatures of 50° to 60° C. may modify both the temperature of transition and the slope of the curve.

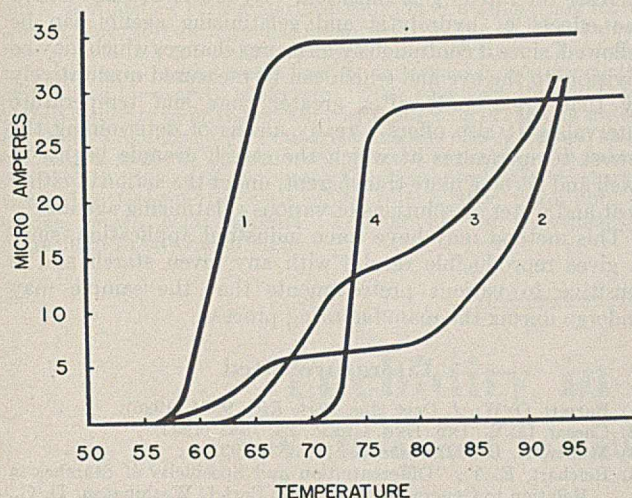


FIGURE 2. TYPICAL STARCH GELATINIZATION CURVES

1. Arracacha starch
2. Wheat starch
3. White potato starch
4. Taro starch

Results are duplicable if the conditions of the experiment are kept constant. The principal condition to watch is the rate of heating the water bath. The rate of heating affects the temperature of transition, but does not change the slope of the curve. By experiment the temperature of transition of a cassava starch was shifted 3° C. higher by changing the rate of heating from 6.3 to 0.8 minutes per degree C. It is therefore advisable in any series of experiments to maintain a fairly constant rate of heating. The authors found 1.5 to 2.0 minutes per degree Centigrade to be satisfactory.

Results

Taylor (6) suggested that different sizes of granules in the same starch might have different temperatures of transition, or varying rates of gelatinization. To test this, a sample of yautia starch [*Xanthosoma sagittifolium* (L.) Schott] was separated by flotation into two batches averaging 4 and 12 microns, respectively. The classification of all plant species used in this paper is Barrett's (1). These two samples showed no difference in their curves. It is possible that with wheat starch, which shows such wide variation in granule size, there might be some difference between the large and small granules, but experience leads the authors to believe that it would be slight.

The fact that taro, with a granule of only about 2 μ average diameter, gives exactly the same type of curve as the edible canna with an average size of 60 μ would indicate that granule size is not important in determining the rate of gelatinization. Within a given sample the largest and smallest granules might have slightly different transition temperatures, but apparently they rupture and gelatinize at the same rate.

One of the most interesting points brought out by this investigation is the wide difference exhibited by the curves of starches obtained from temperate and tropical zone plants.

The temperature of transition of the temperate zone starches tested lies between 55° and 65° C. and they give curves of long duration with, first, a moderate increase of transmission, then a latent period or slowing up of the rate between 65° and 85° C., and then an increasing rate of transmission up to 90° to 95° C. The temperature of transition of the tropical starches generally lies between 60° and 78° C., with curves of short duration or very steep slope till transmission becomes constant, which generally occurs below a temperature of 85° C. Figure 2 illustrates this with characteristic curves for the starches of arracacha (*Arracacia xanthorrhiza* Baner), taro [*Caladium colocasia* (L.) W. F. Wight], white potato, and wheat obtained from the north. This peculiarity of starches from plants grown in different climates appears to be associated with the fragility of the granule envelope.

Taylor (7) mentions the difficulty of rupturing potato and wheat granules even by continued boiling, and Caesar (2), in his ingenious method of measuring the viscosity of 20 per cent starch pastes, mentions the same phenomenon. It is to be regretted that the only tropical starches included in his investigations were tapioca and sago. The former is one whose curves, in the authors' work, lie midway between those of truly tropical nature and northern, and which more nearly approaches potato in its type. This is confirmed by the viscosity curves which Caesar gave for these two starches. The authors have not investigated sago starch. It would be interesting to see if the tropical root starches with which the authors worked would give earlier and lower viscosity changes than the northern starches.

TABLE I. GELATINIZATION DATA

Starch Source	Size		Transition Temperature ° C.	Temperature Finish ° C.	Difference ° C.
	Min.	Max.			
Ñame hícamo (<i>Dioscorea polygonoides</i> H. & B.)	5	32	48	78	30
Apio (<i>Arracacia xanthorrhiza</i> , Baner)	4	22	56	66	10
Ñame mapuey (<i>Dioscorea trifida</i> L. f.)	19	58	61	72	11
Cassava [<i>Manihot manihot</i> (L.) Cockerell]	4	20	62.5	82.5	20
Edible canna (<i>Canna edulis</i> Ker.)	32	108	63	69	6
Yellow sweet potato [<i>Ipomoea batatas</i> (L.) Lam.]	4	25	66	72	6
Yellow yautia [<i>Xanthosoma sagittifolium</i> (L.) Schott]	4	19	69	79	10
White yautia [<i>Xanthosoma caracu</i> C. Koch & Bouché]	4	12	73	79	6
White sweet potato [<i>Ipomoea batatas</i> (L.) Lam.]	8	35	73	79.5	6.5
White yam (<i>Dioscorea alata</i> L.)	14	50	73	81	8
Taro [<i>Caladium colocasia</i> (L.) W. F. Wight]	1	5	73	77	4
Sweet potato [<i>Ipomoea batatas</i> (L.) Lam.]	4	29	72.5	80	7.5
Arrowroot (<i>Maranta arundinacea</i> L.)	7	49	74	96	22
Green plantain (<i>Musa paradisiaca</i> L.)	13	59	75	96	21
Wheat (<i>Triticum aestivum</i> L.)	2	35	55	94	39
Barley (<i>Hordeum vulgare</i> L.)	3	37	56	94	38
Oats (<i>Avena sativa</i> L.)	2	18	57	93	36
Rice (<i>Oryza sativa</i> L.)	4	12	59	92	33
White potato (<i>Solanum tuberosum</i> L.)	7	80	62	97	35
Corn (<i>Zea mays</i> L.)	4	22	65	96	31

Microscopic examination at 5° C. intervals indicate that with tropical starches the granules are ruptured completely in almost all cases below a temperature of 85° C., while white potato, cassava, wheat, corn, rice, and barley, on the contrary, show many swollen but unruptured granules even at 90° to 95° C. The interesting photomicrographs of Sjostrom (5) bear out this observation, showing the swelling and disintegration of sweet potato and canna, at temperatures lower than that of corn and wheat.

The importance of the distinction between the starches of northern and tropical origin has apparently a correlation in the ability of patients suffering from the tropical disease, sprue, to digest and assimilate starches from various sources. This phase of the problem will be discussed in a paper soon to be published.

Certain starches, such as cassava, white potato, and the starch of the green plantain (*Musa paradisiaca* L.), give curves which are intermediate in character between those of the northern and main tropical starches investigated (Figure 2). This brought out a curious observation which will require further investigation to verify completely. Starch from white potatoes grown in Puerto Rico seems to give a curve more like the other tropical starches than starch from the same variety of potato grown in the north. It is possible that acclimatization of the plant may bring about changes in the physical and chemical properties of such a complex material as starch.

Some 30 varieties of starch have been run by the photoelectric method; the transition points vary from 48° to 78° C., but all produce curves of the three types illustrated in Figure 2. Most fall in the true tropical or northern group curves, with 3 or 4 in the intermediate cassava or white potato group.

Table I gives the granule size, temperature of the transition point, and the temperature at which no further increase of transparency occurs with rising temperature. The difference

column is simply a measure of the slope of the gelatinization curve and indicates that the starches can be grouped in three classes: those with a temperature difference up to 10° C.; those of the intermediate class in the 20° to 22° C. range; and the third, mostly composed of northern starches, with differences of 30° to 40° C. for completion of gelatinization.

The effects of gelatinizing agents such as acids, alkalis, sodium thiocyanate, and calcium chloride have been tested by the photoelectric method, and in general, their effect is to increase the temperature of the transition point, and in the case of the intermediate and northern group starches, greatly increase the rate of gelatinization. By means of this method the effects of hydrolytic and gelatinizing agents can be followed, since it continuously measures changes which may be invisible to the eye and which can be measured qualitatively by that organ only after greater time and temperature intervals. It also offers a ready means of determining the lowest temperatures at which the starch granule begins to swell and become more transparent, under the action of either heat and water or solutions of various gelatinizing agents.

This method may have some industrial application, since it gives reproducible results with any given starch and is sensitive to various pretreatments that the sample may undergo during the manufacturing process.

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RECEIVED February 15, 1937.

Determination of Sugars in Plants By Oxidation with Ferricyanide and Ceric Sulfate Titration

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IN A PREVIOUS paper the writer (1) published a method for the determination of sugars in plants by oxidation with potassium ferricyanide and titration with ceric sulfate, using *o*-phenanthroline ferrous sulfate as an indicator. Further observation showed that in some cases certain plant extracts presented difficulty in obtaining a distinct end point with this indicator, especially when the amount of reducing sugar in the sample was small and a large excess of the ferricyanide was left in solution after oxidation of the sugar.

The difficulty was remedied by using Setopaline C instead of *o*-phenanthroline ferrous sulfate and by modifying the concentration of the alkaline ferricyanide solution. In order to avoid a large excess of ferricyanide when the quantity of reducing sugars in the sample was small, the amount of the alkaline ferricyanide used for the oxidation was reduced. This modified method is applicable to quantities between 0.3 and 3.5 mg. of reducing sugars.

Reagents

INDICATOR. Setopaline C (0.1 gram) is dissolved in 100 cc. of water and 7 to 10 drops of the indicator are used for the titration. The end point is a sharp change from pale green to a golden brown. The indicator consumes practically no ceric sulfate:

1 drop of 0.01 *N* ceric sulfate is sufficient to impart a golden brown color to the blank. (Setopaline C is manufactured in Switzerland and its formula at present is a trade secret. It may be obtained through Eimer & Amend, New York, N. Y., at a very small cost.)

ALKALINE POTASSIUM FERRICYANIDE. A mixture of 8.25 grams of potassium ferricyanide and 10.6 grams of sodium carbonate is dissolved in cold water and made up to 1 liter. The solution is poured into a dark bottle and kept in a cool place, preferably in a refrigerator above freezing. Quantities of the solution are taken out as needed.

CERIC SULFATE. A 0.25 *N* ceric sulfate stock solution is made as follows: 75.5 grams of ceric sulfate (55 per cent pure) are placed in about 300 cc. of water to which 30 cc. of concentrated sulfuric acid have been added. The mixture is heated on a steam bath until all of the ceric sulfate is dissolved. The solution is filtered, cooled, and made up to 500 cc.

The ceric sulfate is conveniently standardized against a 0.1 *N* solution of ferrous ammonium sulfate (Mohr's salt). This standard solution is made up by dissolving 39.214 grams of the salt in about 300 cc. of water, to which 25 cc. of 1 to 1 sulfuric acid have been added, and diluting to 1 liter. The Mohr's salt, $\text{Fe}(\text{NH}_4)_2(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}$, must be of high purity suitable for use as an analytical standard.

Fifteen cubic centimeters of the approximately 0.25 *N* ceric sulfate solution are diluted with 50 cc. of water and 3 cc. of 1 to 1 sulfuric acid and titrated with the 0.1 *N* standard Mohr's solution until the color of the ceric sulfate is almost bleached out.

Eight drops of Setopaline C indicator solution are then added and the titration is continued to a sharp change from golden brown to a light yellow color.

A 0.01 *N* solution of ceric sulfate is made up for the use of sugar analysis by diluting 20 cc. of the 0.25 *N* stock solution and 50 cc. of 1 to 1 sulfuric acid to 500 cc. The 0.01 *N* ceric sulfate solution may also be standardized against Mohr's salt. A 0.01 *N* standard solution of the ferrous ammonium sulfate should be used for this purpose. The stock solution is kept in a cool place and the dilute 0.01 *N* ceric sulfate is made up as needed.

Procedure

The plant extract is clarified as previously described (1). Five cubic centimeters of the clarified solution containing not more than 3.5 mg. of reducing sugar are mixed with 5 cc. of the alkaline ferricyanide in a 145 × 28 mm. Pyrex glass test tube. The tube is heated in a boiling water bath or immersed in a steam bath and heated for exactly 15 minutes. The tube with the contents is then cooled to room temperature by immersing in running water for about 3 minutes. Five cubic centimeters of 5 *N* sulfuric acid are added and the contents are mixed by shaking the tube. Seven to 10 drops of the Setopaline C indicator are introduced and titrated with the 0.01 *N* ceric sulfate from a 10-cc. buret until a golden brown color appears. Estimations are conveniently carried out in batches of eight.

The ceric sulfate used is standardized against a pure grade of glucose by the same procedure, using 5-cc. aliquots of solution containing known amounts of the sugar. From the titration of pure glucose the number of cubic centimeters of ceric sulfate equivalent to 1 mg. of glucose is calculated. It was found that 3.00 cc. of 0.01 *N* ceric sulfate solution are equivalent to 1 mg. of glucose. It is convenient to have on hand a solution of pure 1 per cent glucose made up in 0.25 per cent benzoic acid. When prepared in this way the glucose will keep for several months. Whenever needed, a few cubic centimeters of this standard solution are diluted to the proper strength and used for standardization of the dilute ceric sulfate solution. Standardization of the ceric sulfate solution against glucose is necessary whenever it is made from the 0.25 *N* stock solution.

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RECEIVED March 15, 1937.

Turbidity in Sugar Products

V. Color and Turbidity of Hard Refined Sugars

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THE previous two articles of this series (3, 5) dealt with the determination of coloring matter and turbidity in raw cane sugars. This investigation has now been extended to hard refined sugars. Of the twenty-nine samples examined, twenty-six were granulated cane sugars, two were powdered cane sugars, and one was a beet sugar. Three analytical procedures were used in this work: (1) Balch; (2) Zerban, Sattler and Lorge; (3) Landt and Witte.

Balch Method

In the method of Balch (1) a 60-Brix solution of the sugar is prepared, and a portion of it is filtered. The unfiltered solution is read in the spectrophotometer against the filtered solution at one or more wave lengths, and the result is expressed in terms of the specific absorptive index, $-\log t$. The concentration of the coloring matter is found by reading the filtered solution against water, and converting the result also into $-\log t$.

In applying this method to white sugars, the writers used the same filtering materials as before: Celite analytical filter aid, specially prepared asbestos, and purified silica gel.

Since hard refined sugars contain very little coloring matter and turbidity, long absorption cells must be employed. The cells used by the writers were 100 mm. in length, the maximum available for the Keuffel and Esser spectrophotometer. Still longer cells would be preferable. The readings were taken at wave length 529 $m\mu$, in order to permit direct comparison with the measurements made according to the other two procedures.

Zerban, Sattler, and Lorge Method

In the method of Zerban, Sattler, and Lorge (4) the transmittancy, T , and the Tyndall beam intensity, R , of the unfiltered 60-Brix solution are measured with the Pulfrich photometer in a 2.5-mm. cell. R is expressed in per cent of the Tyndall beam intensity of the standard turbid glass block

of the instrument. Color filters are used for measurements at various wave lengths.

The concentration of turbidity, N , and of coloring matter C , are then found by means of Equations 1 and 2.

$$\begin{aligned} R &= aNk^{-C} & (1) \\ -\log T &= N + C & (2) \end{aligned}$$

The numerical values of the constants a and k are given in the paper referred to (4). In practice it is easier to find N and C from a graph based on the two equations rather than by calculation. N and C are thus expressed in terms of $-\log T$ for a 60-Brix solution and a cell thickness of 2.5 mm. In refined white sugars the color is generally so close to zero that the expression k^{-C} in Equation 1 is almost equal to unity, and N becomes directly proportional to R , or nearly so.

An attempt was made to measure the Tyndall beam intensity of the refined sugar solutions in the cells of 2.45- and 2.46-mm. thickness, previously used in raw sugar work, but the turbidity was so small and the correction for the turbidity of the water used for dissolving the sugar was relatively so large that reliable results could not be obtained. The measurements were therefore repeated in a 26-mm. Zechmeister beaker, the effective depth of which is 16.3 mm. The transmittancy of the unfiltered solutions was measured in a 100-mm. tube with the spectrophotometer, the same figure being used as in the method of Balch. The results for $-\log T_{100}$ and for $R_{16.3}$ are shown in Table I, columns 2 and 3, respectively, for wave length 529 $m\mu$.

In order to calculate N and C from $-\log T$ and R by means of Equations 1 and 2, it was necessary first to reduce $-\log T_{100}$ and $R_{16.3}$ to a depth of 2.455 mm. It was found that over such a wide range of thickness the optical density, $D (= -\log T)$, is not directly proportional to the depth, b , but a power function of it, according to the equation

$$D_1 : D_2 = (b_1 : b_2)^n \quad (3)$$

The exponent n was found to equal 0.955. Consequently, $-\log T_{100}$ had to be multiplied by 0.02901 to reduce it to $-\log T_{2.455}$. Similarly, $R_{16.3}$ had to be multiplied by 0.16401.

TABLE I. EXPERIMENTAL DATA AND CALCULATED VALUES FOR METHODS OF ZERBAN, SATTTLER, AND LORGE, AND OF LANDT AND WITTE

1	2	3	4	5	6	7	8	9
No.	$-\log T$, 100 mm.	$R = 100 A$, 16.3 mm.	$-\log T$, 2.455 mm.	$\log R$, 2.455 mm.	N , 2.455 mm.	C , 2.455 mm.	f_k , 16.3 mm.	Absolute Turbidity, Landt and Witte
1	0.1757	73.49	0.0051	1.0811	0.0021	0.0030	1.106	0.0023
2	0.2746	179.70	0.0080	1.4694	0.0049	0.0031	1.171	0.0059
3	0.1634	65.85	0.0047	1.0334	0.0018	0.0029	1.098	0.0020
4	0.0415	25.58	0.0012	0.6228	0.0007	0.0005	1.026	0.0007
5	0.0901	23.45	0.0026	0.5850	0.0006	0.0020	1.053	0.0007
6	0.2409	138.49	0.0070	1.3563	0.0038	0.0032	1.149	0.0045
7	0.1428	135.40	0.0041	1.3465	0.0038	0.0003	1.086	0.0042
8	0.0992	40.03	0.0029	0.8173	0.0012	0.0017	1.059	0.0012
9	0.1307	55.44	0.0038	0.9587	0.0015	0.0023	1.079	0.0017
10	0.2577	94.71	0.0075	1.1913	0.0027	0.0048	1.160	0.0031
11	0.0832	35.26	0.0024	0.7621	0.0010	0.0014	1.049	0.0010
12	0.1036	60.43	0.0030	0.9961	0.0017	0.0013	1.062	0.0018
13	0.1025	53.85	0.0030	0.9460	0.0015	0.0015	1.060	0.0016
14	0.4250	65.51	0.0123	1.0312	0.0019	0.0104	1.277	0.0024
15	0.1574	162.10	0.0046	1.4246	0.0044	0.0002	1.094	0.0050
16	0.1331	96.28	0.0039	1.1984	0.0028	0.0011	1.080	0.0029
17	0.1262	102.70	0.0037	1.2264	0.0029	0.0008	1.075	0.0031
18	0.0965	58.84	0.0028	0.9845	0.0017	0.0011	1.057	0.0018
19	0.1662	101.55	0.0048	1.2215	0.0028	0.0020	1.100	0.0032
20	0.0904	51.41	0.0026	0.9259	0.0014	0.0012	1.053	0.0015
21	0.0766	74.00	0.0022	1.0841	0.0020	0.0002	1.044	0.0022
22	0.0918	71.70	0.0027	1.0704	0.0019	0.0008	1.054	0.0021
23	0.0443	46.93	0.0013	0.8863	0.0013	0.0000	1.025	0.0014
24	0.2377	235.21	0.0069	1.5863	0.0064	0.0005	1.146	0.0076
25	0.1785	88.23	0.0052	1.1605	0.0025	0.0027	1.108	0.0028
26	0.0935	69.13	0.0027	1.0545	0.0019	0.0008	1.055	0.0021
27	0.1347	94.11	0.0039	1.1885	0.0027	0.0012	1.081	0.0029
28	0.1952	112.73	0.0057	1.2669	0.0032	0.0025	1.118	0.0036
29	0.1638	115.12	0.0048	1.2760	0.0033	0.0015	1.099	0.0036

The values of $-\log T_{2.455}$ and of $R_{2.455}$, calculated in this manner, are given in columns 4 and 5 of Table I. The corresponding values of N and C were next found from a greatly enlarged graph, similar to that shown in Figure 1 of Part II of this series (4), and the results are given in columns 6 and 7 of Table I.

Landt and Witte Method

In the method of Landt and Witte (2) the turbidity alone is determined with the Pulfrich photometer, in the same manner as in the procedure of Zerban, Sattler, and Lorge. The Tyndall beam intensity is expressed as A , which is equal to $0.01 R$. The so-called "absolute" turbidity is then calculated by the formula

$$\text{Absolute turbidity} = A \times f_k \times D \times t \quad (4)$$

where f_k is a correction factor which is a function of the transmittancy. The values of this factor are shown in Table I, column 8, for each of the 29 samples. D is a factor varying with the depth of layer used. For the 26-mm. Zechmeister beaker D equals 1. t is the absolute turbidity of the standard glass block—i. e., the Tyndall beam intensity—for a 1-cm. depth of layer, expressed as a fraction of the incident light intensity, under the assumption that the primary light is completely scattered, and that there is no multiple reflection. The t of the glass block used in this investigation, for wave length 529 $m\mu$, is 0.00282. The absolute turbidities of the sugar solutions, calculated by means of Equation 4, are shown in Table I, column 9.

Comparative Results

In order to make a direct comparison between the results obtained by methods 1 and 2, it is necessary to reduce them all to a common basis, and the specific absorptive index, $-\log t$, was chosen for this purpose. The results of the method of Landt and Witte cannot be converted directly into $-\log t$, but the relationship between the two will be discussed.

The $-\log T$ values for the total absorption and for that due to turbidity alone, obtained by Balch's method with 60-Brix solutions and a 100-mm. tube, were reduced to 1-cm. thickness by multiplying by 0.11092 ($0.10^{0.955}$), and to a concentration of 100 grams in 100 ml. by multiplying by 1.296. Beer's law was assumed to hold within the limits of error, for the increase in concentration was only about 30 per cent. The concentration of coloring matter was then found by deducting the turbidity, expressed as $-\log t$, from the total $-\log t$ of the unfiltered solution. The turbidity and coloring matter, calculated in this manner, are shown in Table II, columns 2 to 7, for filtration with Celite, asbestos, and silica gel, respectively.

The $-\log T$ and N values, obtained by method 2 for a cell thickness of 2.455 mm. and 60-Brix concentration, were similarly converted into $-\log t$, multiplying by 3.8238 ($4.0734^{0.955}$), and the product by 1.296. The C values were again found by difference. The N and C figures are given in Table II, columns 8 and 9.

The absolute turbidities, found by the Landt and Witte method, were multiplied by 1.296, to base them also on a concentration of 100 grams in 100 ml., and the values thus calculated are shown in Table II, column 10.

A comparison of the results obtained with the three filtering materials confirms the previous findings with raw sugars. The color concentration, arrived at by asbestos filtration, averages higher than that found by Celite filtration, and silica gel gives the lowest average color figures, but in many individual cases filtration with asbestos results in lower color values than filtration with Celite. Silica gel gives lower color figures than asbestos in all cases but one, and lower ones than Celite in all but four.

In the preceding paper, dealing with raw sugars, it was shown that the discrepancies in the results obtained with the three filtering agents may be explained by their selective effect. All remove both turbidity and coloring matter, but to a varying degree, depending on particle size. The same is true for white sugars.

Table II also shows that the method of Zerban, Sattler, and Lorge, employing only unfiltered solutions for the measurements, usually gives lower turbidity values and correspondingly higher color values than the filtration methods. In a few individual cases the reverse is true. Both higher and lower color values may be explained by the selective effect of the filtering agents. In the former case the filtering material removes relatively more coloring matter from the solution; in the latter a relatively large portion of the turbidity goes into the filtrate, and, causing absorption, is registered as coloring matter.

It remains to inquire whether the methods utilizing the transmittancy and Tyndall beam intensity of unfiltered solutions give a reliable measure of the color and turbidity, for white sugars at least. Information on this point may be obtained by a comparison between the results of the method of Zerban, Sattler, and Lorge and that of Landt and Witte. The latter method has a sound theoretical foundation when coloring matter is absent or very small in quantity, as is the case with white sugars. Under these conditions the turbidity

concentration is practically proportional to the Tyndall beam intensity, but a correction must be applied for absorption.

TABLE II. COMPARISON OF RESULTS WITH FILTERED AND UNFILTERED SOLUTIONS^a

1	2		3		4		5		6		7		8	9	10	
	No.	Turbidity	Color	Turbidity	Color	Turbidity	Color	Turbidity	Color	Turbidity	Color	<i>N</i>			<i>C</i>	Landt and Witte
1	0.0183	0.0070	0.0176	0.0077	0.0203	0.0050	0.0104	0.0149	0.0030							
2	0.0359	0.0036	0.0361	0.0034	0.0394	0.0001	0.0242	0.0153	0.0077							
3	0.0165	0.0070	0.0136	0.0099	0.0192	0.0043	0.0090	0.0145	0.0026							
4	0.0041	0.0019	0.0018	0.0042	0.0047	0.0013	0.0035	0.0025	0.0010							
5	0.0094	0.0036	0.0098	0.0032	0.0177	0.0013	0.0030	0.0100	0.0009							
6	0.0275	0.0071	0.0297	0.0049	0.0307	0.0039	0.0190	0.0156	0.0058							
7	0.0179	0.0026	0.0178	0.0027	0.0183	0.0022	0.0190	0.0015	0.0054							
8	0.0098	0.0045	0.0101	0.0042	0.0102	0.0041	0.0059	0.0084	0.0016							
9	0.0162	0.0026	0.0150	0.0038	0.0163	0.0025	0.0074	0.0114	0.0022							
10	0.0336	0.0035	0.0303	0.0068	0.0331	0.0040	0.0134	0.0237	0.0040							
11	0.0077	0.0043	0.0089	0.0031	0.0096	0.0024	0.0050	0.0070	0.0014							
12	0.0134	0.0015	0.0138	0.0011	0.0134	0.0015	0.0084	0.0065	0.0024							
13	0.0115	0.0032	0.0123	0.0024	0.0130	0.0017	0.0073	0.0073	0.0021							
14	0.0549	0.0062	0.0517	0.0094	0.0555	0.0056	0.0094	0.0517	0.0031							
15	0.0196	0.0030	0.0168	0.0058	0.0210	0.0016	0.0216	0.0010	0.0065							
16	0.0153	0.0038	0.0140	0.0051	0.0171	0.0020	0.0137	0.0054	0.0038							
17	0.0154	0.0027	0.0165	0.0016	0.0175	0.0006	0.0142	0.0039	0.0040							
18	0.0113	0.0026	0.0103	0.0036	0.0117	0.0022	0.0085	0.0054	0.0023							
19	0.0197	0.0042	0.0175	0.0064	0.0203	0.0036	0.0137	0.0102	0.0041							
20	0.0095	0.0035	0.0070	0.0060	0.0114	0.0016	0.0070	0.0060	0.0020							
21	0.0103	0.0007	0.0080	0.0030	0.0107	0.0003	0.0100	0.0010	0.0028							
22	0.0127	0.0005	0.0117	0.0015	0.0130	0.0002	0.0093	0.0039	0.0028							
23	0.0062	0.0002	0.0035	0.0029	0.0055	0.0009	0.0064	0.0000	0.0018							
24	0.0307	0.0034	0.0290	0.0051	0.0312	0.0029	0.0316	0.0025	0.0099							
25	0.0219	0.0037	0.0214	0.0042	0.0243	0.0013	0.0123	0.0133	0.0036							
26	0.0674	0.0060	0.0086	0.0048	0.0087	0.0047	0.0094	0.0040	0.0027							
27	0.0148	0.0045	0.0113	0.0080	0.0155	0.0038	0.0133	0.0060	0.0037							
28	0.0220	0.0060	0.0187	0.0093	0.0223	0.0057	0.0158	0.0122	0.0046							
29	0.0206	0.0030	0.0173	0.0063	0.0202	0.0034	0.0164	0.0072	0.0046							
Av.	0.0177	0.0037	0.0166	0.0048	0.0188	0.0026	0.0120	0.0094	0.0035							

^a Results are expressed as $-\log t$, except for the Landt and Witte method, where they are given as absolute turbidity for a concentration of 100 grams of solids in 100 ml. of solution.

This is done in the method of Landt and Witte by multiplying by the f_k factor, derived from theory, and in that of Zerban, Sattler, and Lorge by the use of the empirical formulas 1 and 2, based on experimental evidence. If the two methods give the same results, when reduced to a common basis, this constitutes strong presumptive evidence that these results are correct. An examination of the figures given in Table II, columns 8 and 10, shows that there is a nearly constant ratio, averaging 3.47, between the N values and the absolute turbidities. Table III, column 3, shows the values obtained by multiplying the absolute turbidity by this factor 3.47. The results check closely with those found directly by the method of Zerban, Sattler, and Lorge (column 2), and the averages agree within 1.6 per cent.

The largest percentage discrepancies between N found directly, and N calculated from the absolute turbidity, are found in samples 14 and 2. Both samples show high total absorption, as may be seen from Table I, column 2. Under this condition the f_k values of Landt and Witte are evidently a little too high, and the theoretical assumptions on which they are based no longer hold strictly. As a matter of fact, a closer analysis of the figures in columns 8 and 10 of Table II shows that the ratio between N found and N calculated decreases from 3.70 to 3.22 with an increase in the absolute turbidity from 0 to 0.01. N has been calculated from the absolute turbidity by this varying ratio also, and the results are shown in column 5 of Table III. The individual values as well as the average value of N calculated in this manner check with the found values only slightly better than those obtained by means of the average ratio 3.47, and nothing is gained in practice by using the sliding ratio for calculating N from the absolute turbidity of white sugars.

While the results of the method of Zerban, Sattler, and Lorge are confirmed by those of the Landt and Witte method, both give an exact measure of the turbidity concentration only if the distribution of particles of different size, shape, etc., is always the same. In the method of Zerban, Sattler, and Lorge, the distribution must be the same as in the standard sugar used by the writers to establish their formulas

1 and 2. It stands to reason that this condition is the exception rather than the rule, and it follows that the method of the writers, using unfiltered solutions, does not give absolute

figures for color and turbidity any more than the filtration methods, and that the results are in both cases merely comparative. However, the time required for an analysis by the method of Zerban, Sattler, and Lorge is much shorter because the tedious filtration process is avoided, while the number of optical observations is the same in both methods. The only drawback of the method without filtration is that the measurements of Tyndall beam intensity must be made with the greatest care and attention to details, as has been pointed out by Landt and Witte as well as by the writers.

Since both turbidity and coloring matter absorb light selectively and differ merely in degree of dispersion, a line of demarcation must be drawn arbitrarily, and either any one of the filtra-

tion methods or the method of the writers may be chosen for this purpose. This applies to raw sugars also, and in the light of the results recently obtained by the writers there is no need to use unfiltered solutions for turbidity determination and filtered solutions for color determination in raw sugars, as previously proposed, because it is now known that the color determined after previous filtration is no more reliable than that derived, by the method of the writers, from the Tyndall beam intensity and transmittancy of the unfiltered solution. The method of Landt and Witte cannot be used for this purpose on raw sugars, because the assumptions on which the f_k values of these authors are based, while

TABLE III. COMPARISON BETWEEN N , AS $-\log t$, FOUND DIRECTLY AND CALCULATED FROM ABSOLUTE TURBIDITY, BY AVERAGE AND BY VARIABLE RATIO

No.	N , Found by Zerban and Sattler	N , Calcd. by Average Ratio 3.47	Deviation %	N , Calcd. by Variable Ratio	Deviation %
1	0.0104	0.0103	-1.0	0.0105	+1.0
2	0.0242	0.0267	+10.3	0.0254	+5.0
3	0.0090	0.0092	+2.2	0.0094	+4.4
4	0.0035	0.0033	-5.7	0.0035	0.0
5	0.0030	0.0032	+6.7	0.0033	+10.0
6	0.0190	0.0202	+6.3	0.0198	+4.2
7	0.0190	0.0187	-1.6	0.0184	-3.2
8	0.0059	0.0054	-8.5	0.0056	-5.1
9	0.0074	0.0076	+2.7	0.0078	+5.4
10	0.0134	0.0136	+1.5	0.0140	+4.5
11	0.0050	0.0047	-6.0	0.0049	-2.0
12	0.0084	0.0081	-3.6	0.0084	0.0
13	0.0073	0.0073	0.0	0.0075	+2.7
14	0.0094	0.0106	+12.8	0.0108	+14.9
15	0.0216	0.0225	+4.2	0.0218	+0.9
16	0.0137	0.0132	-3.6	0.0133	-2.9
17	0.0142	0.0140	-1.4	0.0140	-1.4
18	0.0085	0.0079	-7.1	0.0081	-4.7
19	0.0137	0.0141	+2.9	0.0142	+3.6
20	0.0070	0.0069	-1.4	0.0071	+1.4
21	0.0100	0.0098	-2.0	0.0100	0.0
22	0.0093	0.0096	+3.2	0.0098	+5.4
23	0.0064	0.0061	-4.7	0.0063	-1.6
24	0.0316	0.0341	+7.9	0.0318	+0.6
25	0.0123	0.0124	+0.8	0.0126	+2.4
26	0.0094	0.0092	-2.1	0.0094	0.0
27	0.0133	0.0129	-3.0	0.0130	-2.3
28	0.0158	0.0159	+0.6	0.0159	+0.6
29	0.0164	0.0161	-1.8	0.0160	-2.4
Av.	0.01200	0.01219	+4.0	0.01216	+3.2

holding for sugars with little or no coloring matter, do not apply when large quantities of coloring matter are present. The experiments of the writers have shown that even with white sugars f_k is slightly too high when absorption is high, and that with dark raw sugars it becomes so much too high that absolute turbidities greatly in excess of 1 are found, which is an impossibility, since the intensity of the scattered or reflected light cannot be greater than that of the incident light. But the objections to the method of Landt and Witte in the case of raw sugars do not apply to that of Zerban, Sattler, and Lorge, which is based on experiments with high concentrations of both turbidity and coloring matter, and is therefore applicable to raw as well as to white sugars.

In this simplified method, without any filtration whatever, the "quality index" (δ) loses its meaning, being equal to 1 in all cases. The nature of the turbidity may be characterized by making measurements at different wave lengths and calculating the dispersion quotients; that of the coloring matter may be similarly defined by the Q - or R -ratios of Peters. Further refinements may be introduced by independent measurement of the various particle properties, but for routine purposes this would hardly be necessary.

The suggestion is again advanced that the International Commission for Uniform Methods of Sugar Analysis undertake a comparative study of the various methods proposed and recommend one for general adoption.

Summary and Conclusions

The previous investigation on raw cane sugars has been extended to hard refined sugars. A comparison has been made between the method of Balch, in which the turbidity and

coloring matter are found from the transmittancy of the solution before and after filtration, and the method of the writers, in which both are calculated from the transmittancy and Tyndall beam intensity of the unfiltered solution. The method of Landt and Witte for determining turbidity has also been included in this study.

The previous finding, that filtering agents act selectively, has been confirmed. Generally, Celite gives lower color values than asbestos, and silica gel still lower ones; the opposite is true for the turbidity figures. But there are exceptions to this rule, depending on the nature of the turbidity and of the coloring matter. The method of the writers usually gives higher color values than any of the filtration methods. While this also indicates that the filtering agents remove coloring matter, it must be considered that both turbidity and coloring matter absorb light selectively and that any line of demarcation between the two must necessarily be arbitrary. The choice between the two types of methods thus becomes a matter of agreement. The method without filtration has the advantage of greater speed, but requires greater care in manipulation. It is suggested that the decision be left to the International Commission for Uniform Methods of Sugar Analysis.

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Estimation of Potassium in Silicates and Soils

A Low-Melting Alkali Carbonate Flux

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DIFFICULTIES in completely decomposing highly aluminous minerals by the J. Lawrence Smith fusion (2) have been pointed out by Lamar, Hazel, and O'Leary (1), and have been experienced by the present authors in working with soils, clays, and similar materials. This led to the search for a more desirable flux, which, to be suitable for potassium determinations in silicates, (1) should have a low melting point, (2) should be reactive with silicates at the melting point, and (3) must not leave a residue of salts difficult to separate from potassium. A mixture of two parts of sodium carbonate and one part of lithium carbonate was found to have these characteristics, if potassium is determined by the cobaltinitrite method. This flux appears to be very similar to the composition of a eutectic compound of sodium and lithium carbonates. It melts between 470° and 480° C. and is very effective in decomposing soil silicates at temperatures between 500° and 600° C. Sodium and lithium salts do not interfere with the determination of potassium by the cobaltinitrite method.

The following experimental procedure was applied to a number of soils in connection with the potassium determination:

A 1-gram sample of 100-mesh soil is weighed into a 40-ml. platinum crucible. In order to destroy the organic matter in the

sample, 0.5 to 1 ml. (depending on organic matter content) of concentrated perchloric acid is added. The crucible is placed on a hot plate and heated until the last trace of perchloric acid is removed. To the sample, free of organic matter, are added 8 grams of a mixture of 2 parts sodium carbonate and 1 part lithium carbonate. The sample and carbonates are mixed thoroughly by means of a glass rod and then covered with an additional gram of the carbonate mixture. The crucible is covered and the sample is fused in a muffle furnace at a temperature between 500° and 600° C., this temperature being maintained until all bubbling has ceased.

The crucible is removed from the furnace and given a rotary motion to distribute the fused mass on the sides of the crucible during solidification, thus facilitating the removal of the cake which, after cooling, is placed in a 250-ml. beaker. The cake and residue left in the crucible are dissolved together (in a covered beaker) by adding 25 ml. of water and 50 ml. of 6*N* hydrochloric acid. A shell of silica will form on the cake, which must be broken off from time to time to hasten solution of the inner portion. If it dissolves too slowly the beaker may be placed on a steam bath.

After the carbonates have completely dissolved from the cake, the crucible and lid are washed and removed from the beaker and the contents are taken to dryness on the steam bath. The residue is treated with 10 ml. of concentrated perchloric acid and taken to dryness on the hot plate. The perchloric acid treatment is repeated with the addition of 1.0 ml. of concentrated hydrochloric acid and 0.5 ml. of concentrated nitric acid to ensure complete dehydration of the silica and decomposition of a trace of ammonium salts which might be present. The residue is treated

TABLE I. RECOVERY OF POTASSIUM AFTER FUSION WITH SODIUM AND LITHIUM CARBONATE

Potassium Added Gram	Potassium Recovered Gram
0.00143	0.00141
0.00143	0.00146
0.00143	0.00143
0.00143	0.00141
0.00143	0.00145

TABLE II. POTASSIUM REMAINING IN SILICA RESIDUE FROM SODIUM-LITHIUM CARBONATE FUSION

Source of Sample	Potassium Found ^a		
	Silica residue %	Filtrate from silica residue %	Total potassium ^b %
Purdue University, Soils Department	0.33	1.24	1.57
	0.31	1.27	1.58
	0.34	1.24	1.58
	0.32	1.27	1.59
Bureau of Chemistry and Soils	0.32	1.04	1.36
	0.32	1.04	1.36
	0.30	1.04	1.34
	0.31	1.01	1.32
Illinois Experiment Station, sample 5767	0.32	1.04	1.36
	0.37	1.53	1.90
	0.37	1.53	1.90
	0.32	1.53	1.85
Illinois Experiment Station, sample 5788	0.33	1.56	1.89
	0.32	1.56	1.88
	0.32	1.56	1.88
	0.33	1.56	1.89
U. S. Bureau of Standards, sample 97	0.39	1.56	1.95
	0.03	0.42	0.45
	0.03	0.49	0.52
	0.03	0.46	0.49
U. S. Bureau of Standards, sample 98	0.03	0.46	0.49
	0.07	2.67	2.74
	0.08	2.64	2.72
	0.10	2.67	2.77
	0.10	2.64	2.74
	0.09	2.70	2.79

^a Per cent of dry sample.^b Blank, 0.003 per cent.

TABLE III. COMPARISON OF SODIUM-LITHIUM CARBONATE WITH J. LAWRENCE SMITH FUSION ON SOILS

Source of Sample	Potassium Found		Average Difference	Per Cent Dif- ference
	J. L. Smith %	Na ₂ CO ₃ -Li ₂ CO ₃ %		
Purdue University, ^a Soils Department	1.47	1.57	0.10	6.8
	1.49	1.58		
		1.58		
		1.59		
Av.	1.48	1.58		
Bureau of Chemistry and Soils ^b	1.27	1.36	0.06	4.7
	1.39	1.36		
	1.30	1.34		
	1.27	1.32		
Av.	1.21	1.38		
	1.30			
Illinois Experiment Station, sample 5760	1.91	2.16	0.25	13.2
	1.87	2.09		
		2.12		
		2.18		
Av.	1.89	2.14		
Illinois Experiment Station, sample 5767	1.36	1.90	0.54	40.3
	1.32	1.90		
		1.85		
		1.86		
Av.	1.34	1.88		
Illinois Experiment Station, sample 5788	1.65	1.89	0.27	16.6
	1.61	1.88		
		1.88		
		1.89		
Av.	1.63	1.90		
U. S. Bureau of Standards, sample 97	0.45	0.45	0.04	8.9
	0.46	0.52		
	0.46	0.49		
	0.42	0.49		
Av.	0.47	0.49		
U. S. Bureau of Standards, sample 98	0.45	0.49	0.12	4.6
	2.64	2.74		
	2.67	2.72		
	2.70	2.77		
Av.	2.62	2.74		
	2.60	2.79		
Av.	2.63	2.75		

^a Sample furnished by G. H. Enfield.^b Sample furnished by W. O. Robinson.

with 25 to 50 ml. of 5 per cent hydrochloric acid and heated on the steam bath for a few minutes.

After the crust of iron salts has dissolved, the solution is filtered, and the residue of silica is washed twice with 2 N hydrochloric acid, and with hot water until free of chlorides. The filter paper, after removing the dried silica, is ignited in a platinum crucible. The silica is added to the residue in the crucible, moistened with 2 ml. of water and 3 drops of perchloric acid, and 5 ml. of hydrofluoric acid are added. The contents of the crucible are taken to dryness in a well-ventilated hood. This acid treatment is repeated without the addition of water. The residue left in the crucible is dissolved in 2 ml. of hot 5 per cent hydrochloric acid and the resulting solution is added to the filtrate from the silica. The filtrate is evaporated until salts begin to crystallize, and is then transferred to a 100-ml. volumetric flask and made up to volume. From this volume 10-ml. aliquots are taken, the excess acid is neutralized with 10 per cent sodium hydroxide, using phenolphthalein as an indicator, and after the addition of 10 ml. of 0.15 N acetic acid, potassium is determined by the cobaltinitrite method of Volk and Truog (3). The remainder of the solution may be used for the determinations for which the sodium carbonate fusion is applicable.

Experimental Results

To determine the effect of the salts left by the carbonate fusion mixture on the potassium determination, a known amount of potassium sulfate was added to 9 grams of the sodium-lithium carbonate flux. Potassium was determined after fusing by the proposed procedure. Potassium was satisfactorily recovered, as shown by Table I.

In order to check on the effectiveness of this method of

decomposing silicates, the filtrate from the silica and the residue from the silica after the hydrofluoric acid treatment were analyzed separately. These results are presented in Table II. In the case of the soil samples three-fourths or more of the potassium was made acid-soluble by the fusion, while in the case of the clays, supplied by the U. S. Bureau of Standards, the potassium was made very nearly completely soluble.

Table III gives the results of comparisons of the proposed method with the J. Lawrence Smith method. The data by the J. Lawrence Smith method have all been obtained by other analysts working at the various stations indicated. Each value reported on the samples from the U. S. Bureau of Chemistry and Soils and the U. S. Bureau of Standards was obtained by a different analyst. In every case the average value obtained by the low-melting flux method is higher than the corresponding average obtained by the J. Lawrence Smith method. The samples from the bureaus show that this difference between the two methods is of the same order of magnitude as the differences within the J. Lawrence Smith values.

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Pretreatment of Wood with Hot Dilute Acid

Effect on Lignin Values

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The influence of pretreatments of wood to remove, by means of hydrolysis, carbohydrate substance which allegedly causes errors in the lignin determination, has been studied to determine whether or not lignin is dissolved during such treatments. Hot water, to some extent, and boiling 3 per cent sulfuric acid, to a much greater extent, dissolved lignin from maple wood. An examination of methoxyl contents demonstrated that the substance removed was lignin and not some carbohydrate material which might polymerize to an insoluble resi-

FOR the purpose of removing carbohydrate substances which allegedly polymerize when subjected to the conditions employed in the estimation of lignin, various forms of pretreatments, using hot dilute acid, have been suggested. Norman and Jenkins (4), for example, recommended that the wood be boiled with dilute sulfuric acid for a definite period, making this recommendation with the reservation that nothing was known of the effect of such treatment on lignin as it occurs in the wood. Campbell and Bamford (1) stated that such treatment resulted in the polymerization of some carbohydrate substances with a consequent small but definite increase in the lignin yield. Therefore they recommended that dissolved carbohydrate substances be removed immediately from the sphere of action by the application of several acid treatments, each of only a few minutes' duration. In neither of the above instances was the possibility of an accompanying lignin extraction considered. An investigation of this was therefore initiated and the results are presented in this paper.

Experimental Procedure

Maple wood, ground to 40 mesh in a Wiley mill, was extracted in succession with cold alcohol-benzene (1 to 2), cold alcohol, cold water, and water at 98° C. The alcohol-benzene and alcohol extractions were made in a continuous, percolating extractor (each for 24 hours' duration), and the water treatments were applied in a glass-lined mayonnaise mixer, the former for 24 hours and the latter in two periods of 3 hours each. The wood was finally washed on a suction filter until the hot wash water remained colorless. Corresponding quantitative treatments, using glass apparatus, indicated that the total loss by extraction amounted to 4.3 per cent. The wood was then extracted continuously for 50 hours with water at 98° C. in an apparatus which emptied through a siphon tube once every hour. A similar quantitative treatment in glass showed a further loss of 6.3 per cent, making a total loss by extraction and, possibly, by mild hydrolysis of 10.6 per cent.

Preparatory to subsequent treatments the wood was dried at room temperature (20° to 25° C.), and then ground in an attrition mill until all of it passed through a No. 80 sieve.

Separate portions of the prepared wood were then boiled under reflux with a 3 per cent solution of sulfuric acid (50 ml. per gram of wood) for periods of 2, 4, 8, 16, and 30 hours. Another portion was mixed in a filter crucible with a boiling 5 per cent solution of sulfuric acid (10 ml. per gram of wood) for 4 minutes and the acid solution was then withdrawn by suction and renewed. This procedure was continued until the wood had received ten such treatments.

due. All the filtrates gave significant color reactions for lignin with chlorine and sodium sulfite. In addition, the acid filtrates deposited a brown flocculent substance which contained 20.3 per cent of methoxyl and which behaved like lignin when chlorinated and subsequently dissolved in sodium sulfite. Spruce wood is reported to be affected in a similar manner. It is recommended that all forms of mild hydrolysis, including treatments with hot water, be avoided when preparing woods for either the determination or isolation of lignin.

Following each of the foregoing treatments, the acid was removed by suction and the wood washed free of acid by means of hot water. All samples were subsequently dried at room temperature.

Corresponding treatments, using weighed samples and under identical conditions, furnished data relative to the losses caused by acid hydrolysis.

Determinations of lignin, using the U. S. Forest Products Laboratory's modified procedure, and of furfural yield, using the Tollens method with phloroglucinol as precipitant, were made on all samples. Additional samples of lignin were prepared and dried at room temperature preparatory to the determination of methoxyl content.

The data, corrected to the basis of unextracted, moisture-free wood, are presented in Table I.

Discussion

While the furfural yield was only slightly decreased by water treatments, acid hydrolysis caused a rapid decrease which continued steadily with time of hydrolysis until finally, after 30 hours' treatment, only about 1 per cent of furfural was obtained. Lignin values showed significant decreases when the wood was heated with hot water, but the losses were not of the same order as that caused subsequently by boiling 3 per cent sulfuric acid. The latter, in 2 hours, decreased the lignin value to 17.7 per cent which seemed to be the limit, because longer periods of boiling, up to 30 hours, caused no significant losses of lignin. The results (Table I, D to H) suggested a solubility relationship, the acid solution (a) having become saturated with the slightly soluble lignin in the first 2 hours, (b) having reached a condition of equilibrium between dissolution of lignin and its deposition as a less soluble polymerized material, or (c) having dissolved all the soluble lignin during that period.

The methoxyl content of the isolated lignin remained uniform throughout and, therefore, demonstrated that lignin, rather than carbohydrate substances which might polymerize to an insoluble residue, was being removed. This was verified when the lignin methoxyl contents were calculated as percentages of wood.

It was evident that lignin is soluble in hot dilute acid and an examination of the various filtrates supported this contention. These filtrates were chlorinated and, on the addition of sodium sulfite in excess of that required to react with the acid present, a wine-red color, characteristic of chlorin-

TABLE I. EFFECT OF BOILING DILUTE SULFURIC ACID ON THE LIGNIN VALUE OF MAPLE WOOD

Reference	Pretreatment	Loss by Solvent Extraction ^a	Loss by Hot-Water Treatment ^a	Loss by Acid Hydrolysis ^a	Furfural Yield ^a	Lignin Content ^a	Methoxyl in Lignin ^a	
		%	%	%	%	%	% ^b	%
A	Extraction with alcohol-benzene, alcohol, and cold water	3.2	12.8	23.2	20.2	4.69
B	Extraction with alcohol-benzene, alcohol, cold water, and hot water	4.3	12.5	21.5	20.5	4.40
C	Same as B, plus 50 hours' treatment with hot water as described	4.3	6.3	..	12.1	20.2	20.6	4.16
D	Same as C, plus hydrolysis for 2 hours with boiling 3% H ₂ SO ₄ aq.	4.3	6.3	24.8	3.6	17.7	20.4	3.61
E	Same as C, plus hydrolysis for 4 hours with boiling 3% H ₂ SO ₄ aq.	4.3	6.3	29.0	2.3	17.3	20.7	3.58
F	Same as C, plus hydrolysis for 8 hours with boiling 3% H ₂ SO ₄ aq.	4.3	6.3	31.3	1.6	17.6	20.3	3.58
G	Same as C, plus hydrolysis for 16 hours with boiling 3% H ₂ SO ₄ aq.	4.3	6.3	32.2	1.3	17.5	20.5	3.59
H	Same as C, plus hydrolysis for 30 hours with boiling 3% H ₂ SO ₄ aq.	4.3	6.3	35.4	0.9	17.3	20.6	3.56
I	Same as C, plus 10 treatments with boiling 5% H ₂ SO ₄ aq. (10 ml. per gram) each for 4 minutes	4.3	6.3	13.7	10.8	19.7	20.7	4.08

^a Expressed as percentages of unextracted, moisture-free wood.

^b Expressed as percentage of lignin.

ated lignin dissolved in sodium sulfite, developed. Furthermore, after standing at room temperature for a few days, a brown flocculent substance resembling lignin separated out from the filtrates. Some of this was collected and chlorinated. It brightened in color to orange yellow and dissolved in sodium sulfite to a wine-red solution which changed to a brown color on heating. The methoxyl content of this substance was found to be 20.3 per cent.

Apparently the dissolved lignin polymerized to a less soluble form when left in contact with the dilute sulfuric acid for several days. Campbell and Bamford (1) postulated such a reaction involving carbohydrate substances when they recommended the short successive treatments to which reference has already been made (Table I, I). It is conceivable that the phenomena are identical and that the substance which Campbell and Bamford found to be redeposited was really lignin. Although their method, when used in this study, did not decrease the lignin yield as much as did the other acid treatments, the filtrate gave a definite color reaction for lignin. Probably continued treatment by their method would eventually have decreased the lignin yield to about 17.7 per cent.

The results obtained with dilute acid naturally directed attention to the possibility of similar effects resulting from milder forms of hydrolysis, such as extractions with hot water which had been used in preparing the wood. The lignin content had been appreciably decreased by the prolonged extraction (Table I, C) and the effluent from the extractor gave a slight color reaction for lignin with chlorine and sodium sulfite. This reaction, although slight as compared with that obtained with the acid filtrates, was very significant because about 40 liters were used in the course of the extraction and, as the effluent was run to waste rather than concentrated, the lignin concentration was consequently small. Digestion with water at 98° C. for shorter periods such as 3 hours also resulted in some dissolution of lignin (Table I, B) because the filtrate from this treatment gave a very definite color reaction for lignin.

The action of boiling dilute sulfuric acid on wood is comparable with that of methanol-hydrochloric acid when it is used in the extraction of soluble lignin. In both instances, there is an acidic condition which enhances hydrolysis of some carbohydrate substances. These are apparently associated chemically with the soluble lignin and their removal sets it free to dissolve in water on one hand, or in methanol

on the other. In fact, the difference between the lignin yields (1) from wood which has been subjected only to alcohol-benzene, alcohol, and cold water (Table I, A), and (2) from wood which, in addition, has been treated with hot water and dilute sulfuric acid (Table I, D), is approximately 6 per cent—that is, of the same order as the yield of soluble lignin by the methanol-hydrochloric acid process (3).

The influence of mild hydrolysis in releasing soluble lignin to a solvent was demonstrated by one of the authors (2) when describing the effects of alkaline extraction on the lignin yield. Sodium hydroxide (0.5 per cent) was found to have a much greater solvent action on lignin if the wood was first subjected to an extended extraction, amounting to mild hydrolysis, with hot water.

The polymerization of the dissolved lignin to a less soluble aggregate under the influence of cold dilute sulfuric acid may be regarded as a milder form of the action of the 72 per cent sulfuric acid employed in the lignin determination. It is significant that the filtrate from a lignin determination does not give any form of color reaction with chlorine and sodium sulfite.

Although this investigation was limited to maple wood, similar results, indicating that in addition to maple some spruce lignin was dissolved by dilute sulfuric acid, have been recorded in an unpublished report of the U. S. Forest Products Laboratory by R. L. Mitchell.

It is concluded that any form of pretreatment involving hydrolysis will cause significant errors in lignin determinations and may even result in the complete loss of that portion of lignin which is known as soluble lignin. It is believed that all forms of pretreatment using hot dilute acids are not only unnecessary for the purpose of removing carbohydrate material, but that they should be avoided, and that, if water must be used to remove interfering extraneous matter, cold extraction should preferably be employed.

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Determination of the Common and Rare Alkalies

Note on Wells and Stevens' Method

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RECENTLY Wells and Stevens (1) published a detailed modification of the analytical procedure for the alkali group to include accurate determination of lithium, cesium, and rubidium. In analyses on samples of pollucite containing over 30 per cent of cesium oxide it became obvious that the method of Wells and Stevens was not directly applicable in such a case. The purpose of this note is to draw attention to certain facts which they did not sufficiently emphasize, and to suggest a modification of their procedure for cases in which a large percentage of cesium or rubidium is present.

The basis of their separation of these elements from potassium is the extraction of the alkali chlorides with a mixture of alcohol and hydrogen chloride in which the solubility of potassium chloride is reduced as far as possible. Their Table I is here reproduced with the addition of values for the ratio of solubility of cesium chloride to potassium chloride.

TABLE I. SOLUBILITY OF ALKALI CHLORIDES AT 25° C.

Solvent	Solubility			Ratio of CsCl to KCl
	KCl Grams	RbCl Grams	CsCl Grams	
1. 10 ml. of water	3.08	7.28	12.7	4.1
2. 10 ml. of concentrated HCl (1 part) and alcohol (2 parts)	0.0031	0.021	0.31	100.0
3. 0.4 ml. of water and 10 ml. of alcohol, both saturated with HCl	0.0006	0.0027	0.024	40.0

It is obvious that solvent 2 is the most efficient for separating the two chlorides. However, since it would not be convenient to reduce the volume much below 10 ml., the fact that solvent 3 dissolves the smallest mass of potassium chloride per 10-ml. portion is adequate reason for its adoption in their method. Its solvent action for cesium chloride is adequate for any sample ordinarily encountered.

In the case encountered by the author, however, a 1-gram sample yielded over 300 mg. of chlorides of the alkali group, substantially all cesium chloride. Using an aliquot containing 100 mg. of alkali chlorides, at least four and probably six extractions would be necessary with solvent 3. These would remove more potassium chloride than the one extraction required with 2, and for the total amount of chlorides the amount extracted by 3 would far exceed that by 2, and the volume of solvent would become inconveniently great. In general, any sample containing enough cesium or rubidium to require four or more extractions with solvent 3 is better extracted by solvent 2.

In case a sample has a high percentage of cesium or rubidium, two courses are open. One is to take a small aliquot and proceed according to the method of Wells and Stevens; when a fair percentage of potassium is also present this is the best and simplest procedure. However, when the percentage of potassium is known to be low, the use of an aliquot satisfactory for cesium chloride reduces the mass of potassium chloride present in the aliquot to such a small value that no degree of accuracy could be claimed for the determination. In such cases, the other course is to use solvent 2, followed by the same procedure.

Where the potassium content is previously known to be very low, a third and simpler procedure is suggested by the work of Wells and Stevens: The extraction of cesium chloride

from the mixed chlorides may be omitted and these potassium group chlorides treated as "cesium chloride," containing a trace of potassium extracted with it. The ammonium sulfate separation may then be carried out as directed by them. Experiments with synthetic mixtures of cesium and potassium chlorides containing up to 5 per cent of potassium chloride gave satisfactory results with this separation. The chloroplatinate separation given by these authors should also be applicable at this point, if the amount of potassium chloride can be assumed to be less than 2 mg.

Bearing these facts in mind, a judicious choice of reagents and the use of aliquots should make Wells and Stevens' excellent method applicable to any combination of alkalies encountered in practice, with good precision for each.

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The Analysis of Pollucite

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HILLYER (1) has discussed the method of determining rare alkalies devised by the present writers (2), showing that it must be revised when analyzing materials of high rare-alkali content. His notes are an interesting and needed addition to the method, which was devised for the majority of samples encountered in mineral analyses, in which rare alkalies are absent or present only up to moderate quantities. Obviously the procedure should be different for large percentages of the rare alkalies.

In the analysis of pollucite from Tin Mountain, S. Dak., the method was also changed by the authors because of the high content of cesium. The results for the complete analysis are given in Table I.

TABLE I. ANALYSIS OF POLLUCITE FROM TIN MOUNTAIN, S. DAK.

SiO ₂	45.66	K ₂ O	0.13
Al ₂ O ₃	18.64	Rb ₂ O	None
Fe ₂ O ₃	0.22	Cs ₂ O	31.80
FeO	0.10	H ₂ O ⁺	2.17
MgO	0.29	H ₂ O ⁻	0.42
CaO	0.36	TiO ₂	None
Li ₂ O	0.22		100.13
Na ₂ O	2.12		

The separated chloroplatinates of potassium, rubidium, and cesium obtained from 0.5000 gram of the mineral were subjected to several fractional crystallizations. The chloroplatinates of potassium and rubidium were thus obtained in solution because of their greater solubility and scarcity, while the bulk of the cesium remained as undissolved chloroplatinate. From the extracted chloroplatinates platinum was removed with formic acid and the resulting chlorides were treated with the alcoholic ammonium sulfate reagent to separate potassium and rubidium from the remaining cesium. The precipitated sulfate was ignited and its weight found to be 0.0011 gram. Careful spectroscopic examination showed the absence of rubidium both in the potassium fraction precipitated by alcoholic ammonium sulfate and in the soluble cesium fraction. From the weight of potassium sulfate obtained, K₂O was calculated to be 0.12 per cent.

The percentage of Cs_2O was found from the weight of mixed chloroplatinates, after correcting for K_2PtCl_6 , to be 31.80.

An alternate method based only on fractionation of the chloroplatinates gave a result in close agreement. The chloroplatinates were fractionally precipitated in water, and the soluble part was evaporated and extracted with 15 per cent alcohol to separate the K_2PtCl_6 . This method gave 0.14 per cent K_2O and the average of the two results is 0.13 per cent K_2O .

Pollucite is unusual, as it is the only mineral compound of cesium found in nature. Cesium may replace potassium in minerals, but its content seldom exceeds a few per cent and usually it is absent. No mineral has been found in which ru-

bidium is an essential constituent. Rubidium may proxy potassium in some minerals and in these it seldom exceeds 2 per cent. Few minerals contain rare alkalies, and their absence is quickly and definitely shown by the method as originally described.

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RECEIVED March 2, 1937. Published by permission of the Director, U. S. Geological Survey.

Borax as an Acidimetric Standard. II

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A RAPID method for purifying and drying borax by means of alcohol and ether for use as a standard substance has been described (2), and preliminary experiments bearing on its stability have been reported. The present paper describes further experiments on the stability and also some tests of the accuracy, precision, speed, and convenience of borax in comparison with sodium carbonate as an acidimetric standard for routine technical and student use.

Stability of Borax

The principal problem which arises in the use of borax, $\text{Na}_2\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O}$, as a standard relates to the fact that it is hydrated, and thus is susceptible to changes in composition due to variation in its water content. It has long been known that borax loses some of its water of hydration on standing in air at ordinary temperatures. This loss proceeds very slowly at first and increases gradually, requiring about 30 days to amount to a total loss of 0.1 per cent (2).

In order to prevent this slow decomposition, Menzel (3) proposed that borax be kept in a desiccator over a solution saturated with respect to sucrose and sodium chloride. The vapor pressure of this solution is such that borax will remain in the decahydrated state over a wide range of temperature. Menzel found that a sample of borax kept over this solution lost only 0.02 per cent in weight in 12 months. An experiment in verification of Menzel's findings was performed by placing a 3.5-gram sample of borax, dried with alcohol and ether, in a desiccator over the sugar-salt solution and weighing it from time to time over a long period. After 55 days in the desiccator the sample showed a loss of 0.026 per cent in weight, but no further change occurred during a subsequent period of 15 months. It thus appears that borax may be kept indefinitely over saturated sugar-salt solution without undergoing decomposition.

Because borax decomposes so very slowly in air, it seemed likely that it could be stored simply in tightly stoppered bottles for a very long time before sufficient decomposition occurred to have an appreciable effect in ordinary acid standardizations, where an accuracy beyond 0.1 per cent is seldom sought. To test this possibility about 13 grams of recrystallized borax, dried by the alcohol-ether method, were placed in two weighing bottles having tight-fitting ground-glass stoppers. Samples of this material weighing about 0.5 gram were titrated with 0.1 *N* hydrochloric acid at intervals during a 12-month period. All but one of these titrations were run in duplicate, and in all, 23 titrations representing 12 intervals of time were made. The mean value for the ratio of the weight of borax to the volume of acid for all 23 runs was 1.928×10^{-2} gram per milliliter, and the average deviation of a single run was $\pm 0.0010 \times 10^{-2}$ (0.05 per cent). The largest

deviation was 0.2 per cent, obtained only once, the remainder being 0.1 per cent or less. The measurements were made with weights and volumetric instruments calibrated to give an accuracy of 0.1 per cent.

If the borax sample had lost some of its water, the calculated ratio would, of course, decrease with time. No trend of this sort could be discovered, nor could any relating to the temperature, which varied from 25° to 33° C.

From these results it appears that borax crystallized and dried in the manner referred to is extraordinarily stable, and that for ordinary analytical purposes where an accuracy greater than 0.1 per cent is not required, it is sufficient to keep the material in a tightly stoppered container.

An experiment testing the stability of 0.1 *N* borax solutions was also performed. Such a solution was prepared from pure borax and stored in a soft glass bottle. Portions were titrated with 0.1 *N* hydrochloric acid every 2 weeks for 4 months and once a month for 3 months longer. During the first 4 months the apparent concentration of borax increased very slowly to a value 0.1 per cent greater than its original value, and in the last 3 months increased more rapidly to a value 0.7 per cent greater. A number of other observations on the stability of 0.1 *N* borax solutions which were not so systematically analyzed are in general agreement with this experiment.

Comparison of Borax and Sodium Carbonate

A number of criteria for the selection of analytical standards for routine technical use are given by Dodge (1). Although no substance appears to fulfill all these requirements, it is somewhat surprising that of all the acidimetric standards proposed, anhydrous sodium carbonate, which fails to meet several, should be the most popular, while borax, which seems to fulfill all but one, is little used. The principal objection to sodium carbonate is that it is very difficult to weigh accurately because it is hygroscopic. In addition, it has a rather low equivalent weight (53.00), and the end point of the titration with acid is somewhat indistinct when methyl orange, the usual indicator, is employed.

Borax, on the other hand, has a number of advantages which make its use desirable: It has a high equivalent weight, 190.72; it is inexpensive and easily available; it is easily and economically purified by recrystallization; heating to constant weight is not required; no loss or gain of water occurs during weighing; the end point of the titration with acid is sharp and easily detected with methyl red; the titration error may be eliminated by the use of a simple color standard.

As Dodge has pointed out, the only objection to borax is that it is hydrated, but in view of the ease of the recrystallization and drying with alcohol and ether, and also the unusual stability of the purified material, this objection is largely

overcome, and borax would seem to be superior to sodium carbonate in almost every way.

A direct test of the merits of these two standards was carried out by a class of students in quantitative analysis who were to perform as their first analytical experiment the preparation and standardization of 0.1 *N* hydrochloric acid, followed by analyses of carbonate solutions as unknowns.

The students prepared pure sodium carbonate by the method of Reinitzer (4), and pure borax as previously described (2). The carbonate was dried in the usual way by heating to constant weight at 270° to 300° C. The borax was dried in two ways, one group of students using alcohol and ether and another the saturated sugar-salt solution of Menzel. While this latter method of drying is hardly to be recommended for ordinary use because of the time factor, it was introduced into the experiment to provide an independent check on the borax.

The standardization of the acid against borax was performed by the titration of 0.5-gram samples. Methyl red indicator was used, and the end point was matched with a boric acid-sodium chloride color standard (2). To standardize the acid against the sodium carbonate, a standard 0.1 *N* solution was prepared and samples were titrated with the acid, using methyl orange. The weights and volumetric instruments used in preparing the solutions and in the titrations were calibrated by the students to give an accuracy of 0.1 per cent.

Since each student had prepared his own hydrochloric acid by dilution of reagent acid, no direct comparison of the two standardizations was possible. Such a comparison was, however, obtainable by means of a carbonate solution which was analyzed by the students with their acid. This analysis was performed exactly like the carbonate standardization. Each student had two values for the normality of his acid, one from borax and one from sodium carbonate; hence two values for the unknown could be calculated. A comparison of the two values thus obtained affords a means of comparing the merits of the two standards.

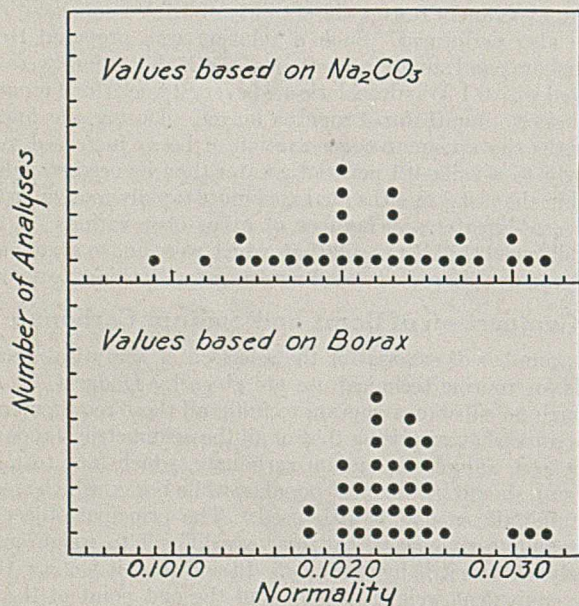


FIGURE 1. NORMALITY OF CARBONATE SOLUTION

The results obtained are shown graphically in Figures 1 and 2. One carbonate value (0.0997 *N*) does not appear. A summary of the results is given in Table I.

TABLE I. NORMALITY OF CARBONATE SOLUTION

	No. of Analyses	Mean Normality	Average Deviation
Borax ^{a, b}	35	0.1023	0.00022
Na ₂ CO ₃	32	0.1022	0.00045
Borax ^a	16	0.1024	0.00024
Borax ^b	19	0.1023	0.00021

^a Dried with alcohol and ether.
^b Dried over sugar-salt solution.

The good concordance of the mean values for the normality of the carbonate shows again the suitability of borax as an acidimetric standard and gives added confirmation to the validity of the alcohol-ether method of drying. The average deviation gives a measure of the variability in the preparation and use of the two standards. Since the average deviation for the sodium carbonate values is twice that for borax, even with the most aberrant result excluded, it may be concluded that borax, when properly purified and dried, gives more reproducible results than sodium carbonate in the hands of students. Such a conclusion is also supported by other student results not reported.

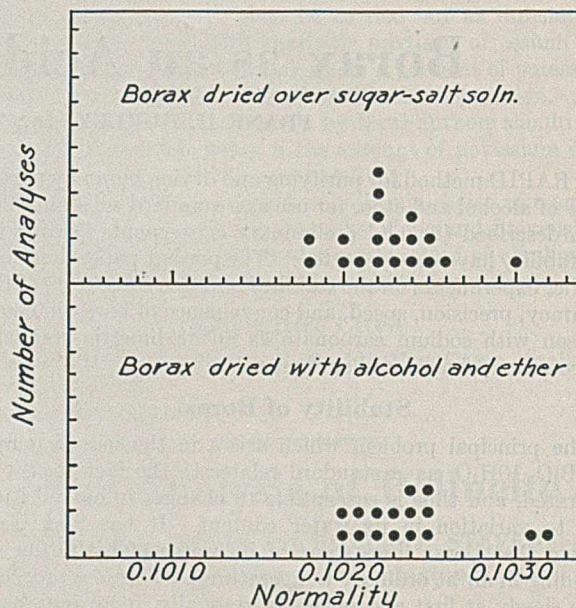


FIGURE 2. NORMALITY OF CARBONATE SOLUTION

With regard to the speed of the two methods of standardization, it would seem at first thought that borax, because it requires recrystallization, is less rapid than sodium carbonate. Actually this is not the case. In the experiment described, the recrystallization and treatment with alcohol and ether required at most 1.5 hours' work, while the heating of the carbonate to constant weight, the most time-consuming operation in the entire experiment, required at least twice this length of time.

Acknowledgment

The writer wishes to thank Arthur F. Scott for his interest and coöperation in this work.

Summary

In accordance with the findings of Menzel, borax may be kept indefinitely over a saturated sugar-salt solution without any change in composition.

Dry, recrystallized borax may be stored in tightly stoppered bottles for as long as a year without undergoing any change in composition greater than 0.1 per cent.

Borax is superior to sodium carbonate as an acidimetric standard for general use, since it is equally accurate, more precise, faster, and more convenient.

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The Calibration of Weights

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THE calibration of a set of weights is usually performed by the well-known method of Richards (3). The essential feature of this method is the device used for obtaining the corrections for the individual weights without the use of simultaneous equations such as are required in older calibration methods (5). In his original description of the procedure Richards stated that this method of obtaining the corrections was based on an approximation regarding the properties of small numbers in the presence of large ones, and in many of the subsequent expositions of the method which appear in textbooks and in the literature the procedure is explained on this basis (4). However, in recent years Eaton (1) has shown that in reality no approximation is involved, and therefore the weight corrections obtained by Richards' method are identical with those calculated by substitution in systems of algebraic equations relating the various weights.

In the present paper, a complete and rigorous analysis of Richards' method is made in a way which serves to clarify a number of points regarding the theory of the process, especially the approximation on which the method was for so long a time thought to rest. In addition, a careful study of the observational errors in weight calibration is presented, and the way in which they affect the weight corrections is analyzed.

The Sensitivity

In building up the "preliminary values" of the weights by progressive intercomparison, the small differences in mass between the various weights and combinations are usually measured by the rest-point displacement and translated into terms of the rider by means of the sensitivity. For this reason a determination of the sensitivity of the balance at various loads must precede the calibration or be made while the calibration is in progress.

We may define the sensitivity, s , as the displacement in rest-point caused by the effective mass of the rider at its 1.0-mg. position on the beam. The exact value of this mass in grams is not known (though it is in the neighborhood of 1.0 mg.), and to avoid making any assumption regarding its value, we may call it B . If we assume that for small deflections the rest-point displacement is proportional to the added load, we may calculate the masses corresponding

to small displacements by means of the sensitivity. Thus the mass x , corresponding to a rest-point displacement d , is

$$x = \frac{d}{s} B$$

The extent to which this assumption is valid depends on the construction of the balance.

Observed Masses of the Weights

The calibration proper consists in the experimental determination of the masses of the various weights in terms of the mass of the smallest weight and the effective mass of the rider at the 1.0-mg. position, B . In Richards' terminology these masses were called "preliminary values," but this term is here discarded in favor of "observed masses."

Let us assume that the smallest weight in a set being calibrated is 0.01 gram, the rider also being 0.01 gram. Choosing the first 0.01-gram weight as the standard of comparison, let its mass be A . On comparison of the rider at its 10-mg. position, R , with the standard, let the observed weight difference correspond to a rest-point displacement of d_R . Then the observed mass of the rider at its 10-mg. position is $A + \frac{d_R}{s} B$. Similarly, the observed mass of the 0.01' when compared with the standard is $A + \frac{d_{0.01'}}{s} B$. The mass of the 0.02-gram weight, compared with the standard and the 0.01', is $2A + \left(\frac{d_{0.01'}}{s} + \frac{d_{0.02}}{s}\right) B$. The observed masses of the other weights are similarly obtained.

In Table I the calibration data for a set of weights are tabulated. These data are taken from Eaton's paper, the only change being that the weight designated as 0.01" by him is here called the rider at its 10-mg. position, R .

It is clear from Table I that the observed masses of the weights are given in terms of two standard masses, A and B , between which no relationship has been determined experimentally. In order to evaluate the masses of the weights in grams, the values of both A and B in grams must be found. It is obvious that these can be calculated only if the masses of two of the weights in the set are known in grams. This is also true of any other system of mass units. This calculation could be made by setting the expressions for the observed masses of the two known weights equal to their values in grams. This would give two equations

TABLE I. CALIBRATION DATA

Weight	Weights Used for Comparison	Weight Difference $d/s B$	Observed Mass	Face Value	Weight Correction
0.01	A	$A - 0.07 B$	$+0.07 B$
0.01'	$-0.06 B$	$A - 0.06 B$	$A - 0.07 B$	$+0.01 B$
R	0.01	$-0.09 B$	$A - 0.09 B$	$A - 0.07 B$	$-0.02 B$
0.02	$0.01 + 0.01'$	$-0.04 B$	$2A - 0.10 B$	$2A - 0.14 B$	$+0.04 B$
0.05	$\Sigma (0.05)^a$	$-0.13 B$	$5A - 0.38 B$	$5A - 0.35 B$	$-0.03 B$
0.1	$\Sigma (0.1)$	$-0.13 B$	$10A - 0.76 B$	$10A - 0.70 B$	$-0.06 B$
0.1'	0.1	$+0.06 B$	$10A - 0.70 B$	$10A - 0.70 B$	$0.00 B$
0.2	$0.1 + 0.1'$	$+0.02 B$	$20A - 1.44 B$	$20A - 1.40 B$	$-0.04 B$
0.5	$\Sigma (0.5)$	$+0.05 B$	$50A - 3.48 B$	$50A - 3.51 B - 0.00001 g.$	$+0.03 B + 0.00001 g.$
1.0	$\Sigma (1.0)$	$-0.08 B$	$100A - 7.09 B$	$100A - 7.02 B - 0.00002 g.$	$-0.07 B + 0.00002 g.$
1.0'	1.0	$+0.13 B$	$100A - 6.96 B$	$100A - 7.02 B - 0.00002 g.$	$+0.06 B + 0.00002 g.$
1.0"	1.0	$+0.03 B$	$100A - 7.06 B$	$100A - 7.02 B - 0.00002 g.$	$-0.04 B + 0.00002 g.$
2.0	$1.0 + 1.0'$	$+0.02 B$	$200A - 14.03 B$	$200A - 14.04 B - 0.00003 g.$	$+0.01 B + 0.00003 g.$
5.0	$\Sigma (5.0)$	$+0.04 B$	$500A - 35.10 B$	$500A - 35.09 B - 0.00008 g.$	$-0.01 B + 0.00008 g.$
10	$\Sigma (10)$	$-0.14 B$	$1,000A - 70.38 B$	$1,000A - 70.19 B - 0.00016 g.$	$-0.19 B + 0.00016 g.$
10'	10	$+0.30 B$	$1,000A - 70.08 B$	$1,000A - 70.19 B - 0.00016 g.$	$+0.11 B + 0.00016 g.$
20	$10 + 10'$	$+0.43 B$	$2,000A - 140.03 B$	$2,000A - 140.38 B - 0.00032 g.$	$+0.35 B + 0.00032 g.$
50	$\Sigma (50)$	$+0.24 B$	$5,000A - 350.49 B$	$5,000A - 350.95 B - 0.00079 g.$	$+0.46 B + 0.00079 g.$
100	$\Sigma (100)$	$-0.67 B$	$10,000A - 701.89 B$	$10,000A - 701.89 B - 0.00158 g.$	$+0.00158 g.$

^a The meaning of this notation is $\Sigma (0.05) = 0.01 + 0.01' + R + 0.02$.

TABLE II. CALIBRATION DATA, 1 TO 100 GRAMS

Weight	Weights Used for Comparison	Weight Difference, $d/s B$	Observed Mass	Face Value	Weight Correction
1.0	100 $A - 7.09 B = C$	$C + 0.07 B - 0.00002$ g.	$-0.07 B + 0.00002$ g.
1.0'	1.0	+0.13 B	$C + 0.13 B$	$C + 0.07 B - 0.00002$ g.	+0.06 $B + 0.00002$ g.
1.0''	1.0	+0.03 B	$C + 0.03 B$	$C + 0.07 B - 0.00002$ g.	-0.04 $B + 0.00002$ g.
2.0	1.0 + 1.0'	+0.02 B	2 $C + 0.15 B$	2 $C + 0.14 B - 0.00003$ g.	+0.01 $B + 0.00003$ g.
5.0	$\Sigma (5.0)$	+0.04 B	5 $C + 0.35 B$	5 $C + 0.36 B - 0.00008$ g.	-0.01 $B + 0.00008$ g.
10	$\Sigma (10)$	-0.14 B	10 $C + 0.52 B$	10 $C + 0.71 B - 0.00016$ g.	-0.19 $B + 0.00016$ g.
10	10 $C + 0.52 B = D$	$D + 0.19 B - 0.00016$ g.	-0.19 $B + 0.00016$ g.
10'	10	+0.30 B	$D + 0.30 B$	$D + 0.19 B - 0.00016$ g.	+0.11 $B + 0.00016$ g.
$\Sigma (10)$	10	+0.14 B	$D + 0.14 B$
20	10 + 10'	+0.43 B	2 $D + 0.73 B$	2 $D + 0.38 B - 0.00032$ g.	+0.35 $B + 0.00032$ g.
50	$\Sigma (50)$	+0.24 B	5 $D + 1.41 B$	5 $D + 0.96 B - 0.00079$ g.	+0.45 $B + 0.00079$ g.
100	$\Sigma (100)$	-0.67 B	10 $D + 1.91 B$	10 $D + 1.91 B - 0.00158$ g.	+0.00158 g.

which could be solved simultaneously for A and B . Substitution of these values for A and B in the expressions for the observed masses would give the values in grams for all the weights in the set. The calculation of A and B in this way is, however, so inaccurate that this method of obtaining gram values for the weights is rendered useless. A further objection will appear in the consideration of observational errors.

Richards' method of calculation differs considerably from that described above in that the weight corrections, rather than the observed masses, are evaluated in grams. In order to begin this calculation we must know the mass of one of the weights in grams. For the sake of accuracy the known weight should be the largest in the set. In the example chosen, the mass of the 100-gram weight is known to be 100.00158 gram. Therefore, from the observed mass of this weight we may write

$$10,000 A - 701.89 B = 100.00158 \text{ grams}$$

from which we have

$$10,000 A - 701.89 B - 0.00158 \text{ gram} = 100.00000 \text{ grams}$$

Since 100.00000 grams is the nominal or face value of this weight, the left-hand member of this equation gives an expression in A and B which is equal to this nominal or face value. Dividing this equation by 2, by 5, etc.—i. e., taking the proper aliquot parts of the expression—will then give expressions in A and B which are equal to the face values of the other weights in the set (column 5 of Table I). In Richards' terminology they are called the "ideal values."

Now the correction for any weight is equal to the amount that must be added to its face value to give its actual or observed mass; in other words, its correction equals its observed mass minus its face value. Therefore the corrections for the weights are given by subtracting the quantities in column 5 from those in column 4. The resulting corrections are given in column 6.

In the expressions for the corrections, the terms in A have vanished, leaving only terms in B and in grams, the latter becoming too small to be added in the small weights. If relative rather than absolute weight corrections are used, the terms in grams do not appear at all. The A terms may, of course, be completely omitted from the table in the interests of brevity, once a thorough understanding of the process has been gained.

In order to evaluate the corrections in grams it is necessary to know the value of B in grams, but an inspection of the multipliers of B in the corrections reveals that it need be known only to three significant figures. The evaluation of B requires either that the mass of one of the weights other than the 100-gram be known in grams, or that it be assumed that the beam is marked correctly to within about 1 per cent. (If the rider is actually used on the beam to determine the weight differences, it is necessary to make this assumption at the outset in order to calculate the observed masses of the weights.)

If the first condition is fulfilled, it is easy to see how B may be calculated from the expression for the correction. In the interest of accuracy, the known weight should be the one whose weight correction has the largest term in B . If, on the other hand, the second condition is assumed to hold, the value of B is calculated from the weight of the rider at its end position on the beam. This may be obtained from the correction for R given in the last column of Table I. From this correction

$$R = 0.010000000 \text{ gram} - 0.02 B$$

We assume $10 B = R$, and substitute in the above expression

$$10 B = 0.010000000 \text{ gram} - 0.02 B$$

from which

$$10.02 B = 0.010000000 \text{ gram}$$

and

$$B = 0.000998 \text{ gram}$$

Or, rounding off to three significant figures,

$$B = 0.00100 \text{ gram}$$

Substitution of this value for B in the corrections gives the values of the corrections in grams. While the value obtained for B in the example was 1.00 mg., this depends directly on the correction for R . Thus a correction of $+0.10 B$ (about 0.1 mg.) for the rider would increase the value of B by 1 per cent.

If the weight corrections are desired only to the nearest 0.1 mg., the evaluation of B need hardly be carried out, since a rider with a correction large enough to affect the calculations (0.5 mg. or more) is unlikely to be used at all.

The assumption made regarding the beam divisions really amounts to assuming a value in grams for one of the weights other than the 100-gram—namely, the weight B , its value being assumed as 0.100 R gram. This is the second approximation which has been made in the calibration, the first being that the deflections of the pointer are proportional to the added load. It is apparent, however, that the second approximation need not be made at all if the masses of two of the weights in the set are known in grams. (The assumptions of proportionality of deflections to added load and $R = 10 B$ can be checked directly, after the calibration has given a set of values for the weights.)

A device for keeping small the numerical coefficients of B in the observed masses, and thus making the calculations less subject to errors in arithmetic, is to divide the table into three parts: (1) the fractional weights, including the first 1.0-gram weight, (2) the weights from 1 to 10 grams, (3) the weights from 10 to 100 grams. The first division is identical with the first part of Table I, and the way in which the other two divisions are made is illustrated in Table II. This arrangement of the computations is highly recommended as a timesaver.

Assignment of Values to A and B

In the preceding analysis, no preliminary scale of mass units was used, and no numerical values were assigned to the two standard masses, A and B , at the outset. In this way a clear picture of the process was obtained.

In Eaton's treatment of the calibration procedure, he assigned to *A*, the mass of the smallest weight, the value zero, and, by implication, gave *B* the value 0.00100000 gram. In this way he obtained "preliminary values" (observed masses) which involved only the observed weight differences. While the assignment of the value zero to *A* in no way affects the weight corrections obtained, it must be objected to on the grounds of logic, since the mass of any weight can hardly be called zero in any system of units. That it is possible to give *A* the value zero (or any other value) without affecting the weight corrections is only due to the fact that *A* disappears by subtraction in the calculation of the corrections, a point not clearly shown by Eaton. The assignment of the value 0.00100000 gram to *B*, which is implied when Eaton writes the preliminary value of the 100-gram weight as 0.70189 gram, must also be objected to because it is untrue. However, in spite of the manifest error made in assigning *B* this value, the weight corrections calculated from these preliminary values would not be significantly in error unless the true mass of *B* differed by about 1 per cent from that assigned. An inspection of the coefficients of *B* in the correction terms of Table I reveals why this is so.

In the ordinary Richards procedure, *A* is assigned a value of exactly 0.01 unit of mass, and *B*, by implication, is assigned the value of exactly 0.001 "unit." Thus the preliminary value of the 100-gram weight would be written

$$100.00000 - 0.70189 = 99.29811$$

The units of this preliminary value are supposed to be 100 × the mass of the 0.01-gram weight. This, however, is an erroneous idea, for the figure 99.29811 is not a homogeneous number, being actually composed of two parts—namely, 10,000 *A* and -701.89 *B*—which cannot be added unless the relationship between *A* and *B* is known. To add them in the way indicated is to imply that *B* = 0.100000 *A* unit, an assumption not justified by the facts. Again, however, the assignment of these values to *A* and *B* has little effect on the weight corrections which are calculated from the nonhomogeneous preliminary values. *A*, of course, is completely without effect, since it subtracts out, and the assignment of the value 0.00100000 "unit" to *B* has no significant effect in the example chosen unless the real value of *B* lies outside the region 0.00100 ± 0.00001 gram.

The real objection to the assignment of values to *A* and *B* in the calculation of the observed masses is that it may lead to incorrect ideas regarding the theory of the calibration process. This is especially true of the ordinary procedure, which, because its preliminary values appear to be homogeneous when they are not, has led to the mistaken idea that an approximation is involved in the calculation of the corrections. The source of this mistake may be seen if the observed masses of Table I are translated into "preliminary values" in the supposed "units" by the ordinary Richards procedure. Having obtained preliminary values in this way, the units are next translated into grams by means of a known weight. For the 100-gram weight,

$$99.29811 \text{ "units"} = 100.00158 \text{ grams}$$

$$\text{Or, } 1 \text{ "unit"} = \frac{100.00158}{99.29811} \text{ grams}$$

By multiplying the preliminary value of each weight by this

factor, it appears that its value is converted into grams. This is, to be sure, an entirely factitious conversion because of the nonhomogeneity of the factor. It was pointed out by Richards that the conversion of each preliminary value from units to grams by the use of this conversion factor would involve a large amount of calculation and necessitate the use of seven-place logarithms. To avoid this he suggested an "approximation" which may be illustrated with the 50-gram weight, the preliminary value of which is 49.64951 units. Although Richards did not clearly state his method of reasoning, it must have been along these lines:

$$\text{Mass of 50 in grams} = M_{50} = 49.64951 \times \frac{100.00158}{99.29811} \text{ grams}$$

Dividing the numerator and denominator of the "factor" by 2,

$$M_{50} = 49.64951 \times \frac{50.00079}{49.64906}$$

This calculation is performed by the use of an approximation theorem which is that, when *a* and *b* are small relative to *N*,

$$N \left(\frac{N+a}{N+b} \right) \cong N + a - b$$

In the numerical expression

$$\begin{aligned} N &= 49.64951, \text{ the "preliminary value"} \\ a &= 50.00079 - N \\ b &= 49.64906 - N \end{aligned}$$

If instead of the mass of the 50-gram weight we calculate its correction, we obtain

$$\begin{aligned} \text{Corr.}_{50} &= N + a - b - 50.00000 \\ &= N + (50.00079 - N) - (49.64906 - N) - 50.00000 \\ &= N - (49.64906 - 0.00079) \end{aligned}$$

which may be rewritten as

$$\text{Corr.}_{50} = N - \frac{1}{2} (99.29811 - 0.00158)$$

or, in words,

$$\text{Correction} = \text{"preliminary value"} - \text{"ideal value"}$$

The argument is identical for all other weights in the set.

Observational Errors

The full beauty of Richards' calibration method is not apparent until we examine the way in which observational errors are handled. Richards himself made no comment on this point in his original paper, but subsequent writers (2) have described the method of calculating the corrections as one for "redistributing" the accumulated error in the "preliminary value" of the heaviest weight "according to

TABLE III. OBSERVATIONAL ERRORS

Weight	Error in Weight Difference	Error in Observed Mass	Maximum Error in Observed Mass
0.01	..	a	1
0.01'	a	b	2
R	b	c	5
0.02	c	d	10
0.05	d	2a + b + c	11
0.1	e	4a + 2b + 2c	22
0.1'	f	8a + 4b + 4c	53
0.2	g	20a + 10b + 10c	106
0.5	h	40a + 20b + 20c	107
1.0	i	j + X	107
1.0'	j	k + X	214
1.0''	k	l + 2X	535
2.0	l	m + 5X	1,070
5.0	m	n + 10X	1,071
10	n	o + 20X	2,142
10'	o	2m + 2n + 2o + 20X	5,353
20	p	8j + 4k + 4l + 2m + 2n + 2o + 20X	5,353
50	q	20j + 10k + 10l + 5m + 4n + 2o + 2p + q + 50X	10,706
100	r	40j + 20k + 20l + 10m + 8n + 4o + 2p + q + r + 100X	10,706

the relative values of the weights." It is not always clear what is meant by this. A rigorous examination of the observational errors which occur in the calibration is extremely interesting and fruitful, especially if the errors are considered individually.

Observational errors in weight calibration occur from two sources, the determination of the rest-point differences and the sensitivity. Since the one is divided by the other in obtaining the weight differences, we may consider the net effect of the errors on these differences. Thus for the 0.01', the weight difference on comparison with the 0.01 may be written $\left(\frac{d_{0.01'}}{s} + a\right) B$, where a is a

term of unknown value correcting the observational error in $\frac{d_{0.01'}}{s}$. The other weight differ-

ences contain similar correction terms. These terms are listed in column 2 of Table III, the factor B being omitted. The way in which these errors accumulate in the course

of calculating the observed masses is shown in column 3. The expressions here are the terms which, when multiplied by B , must be added to the observed masses to correct for their observational errors and thus obtain the true masses of the weights. The true mass of the 100-gram weight is thus: $10,000A - 701.89B + (100X + 40j + 20k + 20l + 10m + 8n + 4o + 2p + q + r)B$.

In calculating the face values, the term -0.00158 gram is added to the above expression and aliquot parts of the whole are taken. The next step is the subtraction of the face values from the observed masses (or true masses, if the error correction terms are added) to obtain the weight corrections. The result of this subtraction on the observational errors is shown in column 3 of Table IV. (The aliquot parts of the error term are not shown.) These are the net observational error corrections for each weight, and when multiplied by B are to be added to the weight corrections of Table I.

An inspection of the error expressions of Table IV reveals several interesting facts. In the first place, the most important individual errors affecting any weight correction are seen to be those made in the comparison of weights near the one being considered. For example, the correction term for the 0.1-gram weight involves all the observational errors from 0.1 to 100 grams, but only those of the 0.1, 0.1', 0.2, 0.5, and 1.0 ($e, f, g, h,$ and i) are of much importance, the others being corrections of the second or third order. If the observational error made in the comparison of the 100-gram weight, r , were as large as 5 mg. (assuming $rB = 5$ mg.) this would affect the 0.1-gram correction only by 0.005 mg.

Another interesting fact is that if we assume the observational errors to be of the same absolute magnitude in every comparison, the maximum error in the correction of any weight (assuming the most unfavorable distribution of signs) is between one and two times a single error. This is shown in column 4 of Table IV, where the maximum errors

TABLE IV. OBSERVATIONAL ERRORS

Weight	Error in Weight Difference	Error in Weight Correction	Maximum Error in Weight Correction
0.01	..	$-\frac{1}{100}X - \frac{1}{10000}Y$	$1.0706 \times \epsilon$
0.01'	a	$\frac{1}{100}(60a - 20b - 20c - 10d - 8e - 4f - 2g - h - i) - \frac{1}{10000}Y$	1.2706
R	b	$\frac{1}{100}(-40a + 80b - 20c - 10d - 8e - 4f - 2g - h - i) - \frac{1}{10000}Y$	1.6706
0.02	c	$\frac{1}{50}(10a - 20b + 30c - 10d - 8e - 4f - h - i) - \frac{1}{5000}Y$	1.7412
0.05	d	$\frac{1}{20}(10d - 8e - 4f - 2g - h - i) - \frac{1}{2000}$	1.353
0.1	e	$\frac{1}{10}(2e - 4f - 2g - h - i) - \frac{1}{1000}Y$	1.106
0.1'	f	$\frac{1}{10}(2e + 6f - 2g - h - i) - \frac{1}{1000}Y$	1.306
0.2	g	$\frac{1}{5}(2e + f + 3g - h - i) - \frac{1}{500}Y$	1.812
0.5	h	$\frac{1}{2}(h - i) - \frac{1}{200}Y$	1.53
1.0	i	$-\frac{1}{100}(40j + 20k + 20l + 10m + 8n + 4o + 2p + q + r) = -\frac{1}{100}Y$	1.06
1.0'	j	$\frac{1}{100}(60j - 20k - 20l - 10m - 8n - 4o - 2p - q - r)$	1.26
1.0''	k	$\frac{1}{100}(-40j + 80k - 20l - 10m - 8n - 4o - 2p - q - r)$	1.66
2.0	l	$\frac{1}{50}(10j - 20k + 30l - 10m - 8n - 4o - 2p - q - r)$	1.72
5.0	m	$\frac{1}{20}(10m - 8n - 4o - 2p - q - r)$	1.3
10	n	$\frac{1}{10}(2n - 4o - 2p - q - r)$	1
10'	o	$\frac{1}{10}(2n + 6o - 2p - q - r)$	1.2
20	p	$\frac{1}{5}(2n + o + 3p - q - r)$	1.6
50	q	$\frac{1}{2}(q - r)$	1
100	r

for each of the weight corrections have been tabulated. These were calculated by assuming that each of the observational errors amounts to ϵ , and the most unfavorable distribution of signs was taken for every weight.

A consideration of the errors to which the observed masses are subject is also instructive. These are tabulated in column 4 of Table III. Here it is assumed that each error amounts to $+\epsilon$. These errors accumulate extremely rapidly in the calculation of the observed masses, as can be seen from the table, and by the time the 100-gram weight is reached, the error in the observed mass amounts to 10,706 ϵ . This, of course, explains how it happens that two persons calibrating the same set of weights may obtain sets of preliminary values which differ widely and yet come out with weight corrections which are sensibly the same. It also shows how inaccurate the calculation of A and B from the observed masses of two known weights may be. Thus the calculation and substitution of values of A and B in the expressions for the observed masses to obtain gram values for the weights might give values which would be grossly in error. In Richards' method for obtaining the gram values, however, the observational errors disappear to a large extent by subtraction. It is this feature which gives the method its real importance.

Summary

1. A complete and rigorous explanation of Richards' method for the calibration of weights has been presented, and the approximations involved have been pointed out.

2. The calculation of "preliminary values" in the usual manner has been shown to be an illogical procedure which has led to confusion regarding the theory of the method, though it is ordinarily without serious effect on the results obtained.

3. An analysis of the observational errors in the calibra-

tion process has been made and the effect of the individual errors on the separate weight corrections has been determined.

Acknowledgment

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An Apparatus for Determining Odor in Water

A Practical System of Dilutions for Establishing Threshold Zone

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THE odor of water is a highly revealing, though broad, criterion of its quality. The presence of substances having intense and characteristic odor is often detectable through the sense of smell. The odor test is frequently applied as a part of the examination of raw water for domestic supply or to determine the effectiveness of purification processes and is also extensively used in the examination of industrial wastes. Under these circumstances, the odor of an individual substance is involved only in unusual instances. Instead, the odors encountered are those caused by minute organisms, vegetable decay, earthy suspended matter, domestic sewage, industrial wastes of various kinds, or combinations of these.

Various procedures for determining the odor of a sample of water have been proposed from time to time, most of them developments of water-purification plant laboratories. The

original method (1) is familiar to all. Later, Gullans (4), in using Spaulding's threshold system for odor testing, developed the "snuzzle" tube which he held down in the neck of the flask. The top of the tube was flared and formed a more or less close fit for the operator's nose. This was a noteworthy improvement. Recently, Fair developed the osmometer, followed by the types A and B osmoscopes.

The Atlantic Refining Company, at its Philadelphia Refinery, has established a laboratory for control of processes used to condition waste water for proper disposal and for general research in pollution prevention by petroleum refining processes. These studies must of necessity take into consideration prevention of pollution not only by petroleum and its products but also by various chemical compounds. Types of odors in waste water and persistence after further dilution in a stream have received particular attention.

During the past several years, all the methods so far developed for taking the odor of water have been tried or given serious consideration. Some were particularly applicable to control of water purification processes and unsuitable for liquid wastes. Each method had some feature which did not seem to meet the requirements. Usually this feature involved the apparatus recommended.

A constant search has been carried on to find a method that is practical, general in application, easy and rapid in manipulation, and as free as possible from error. It is well known that individuals vary in their sensitivity to odors. This variation cannot be entirely overcome by any apparatus or procedure. A satisfactory apparatus and method should meet certain conditions: It should make possible taking the odor of the sample with the minimum danger of contamination by odors in the atmosphere where the test is being conducted. Taking the odor should not involve any violence in inhalation but, instead, the same quiet intake of breath that is normal to breathing. There should be no tubes extending into the nose, nor close-fitting nosepiece, for any discomfort or unnatural feeling seriously interferes with the sense of smell. The equipment should be simple in design, inexpensive, and if possible it should be portable. It cannot be emphasized too strongly that the apparatus must be so designed that each part subject to contact with the sample odor must be readily removable so that it may be washed thoroughly, easily, and

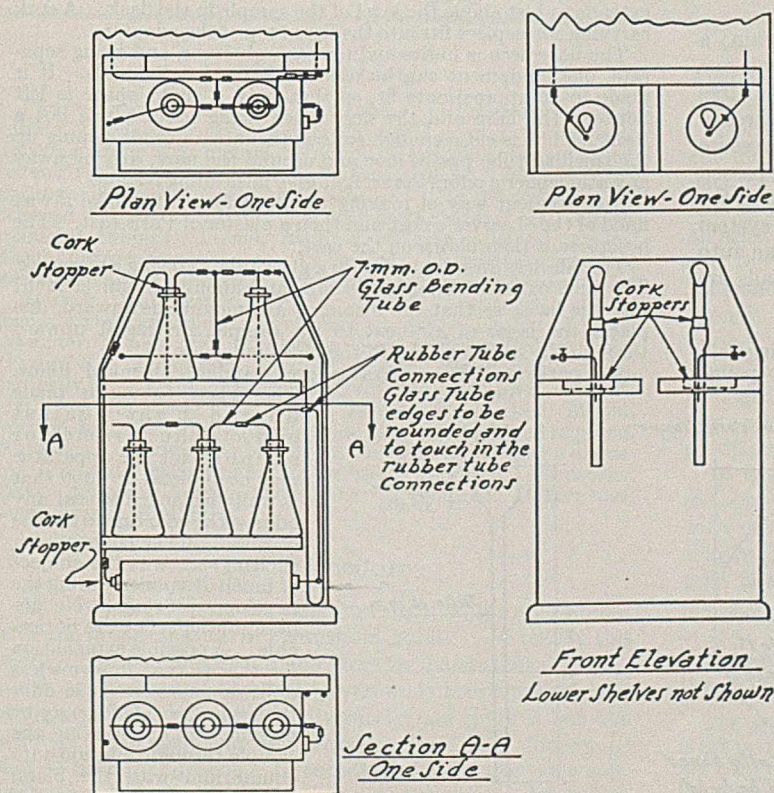


FIGURE 1. ODOR DETERMINATION APPARATUS

All stoppers rubber, except as shown

Note A - Brass Hinges approx. $38 \times 75 \times 2.5$ mm.
 Note B - See Detail
 Note C - Brass Hook and Screw Eye - to fit.
 Note D - 90° Brass Brackets - approx. 16×75 mm.

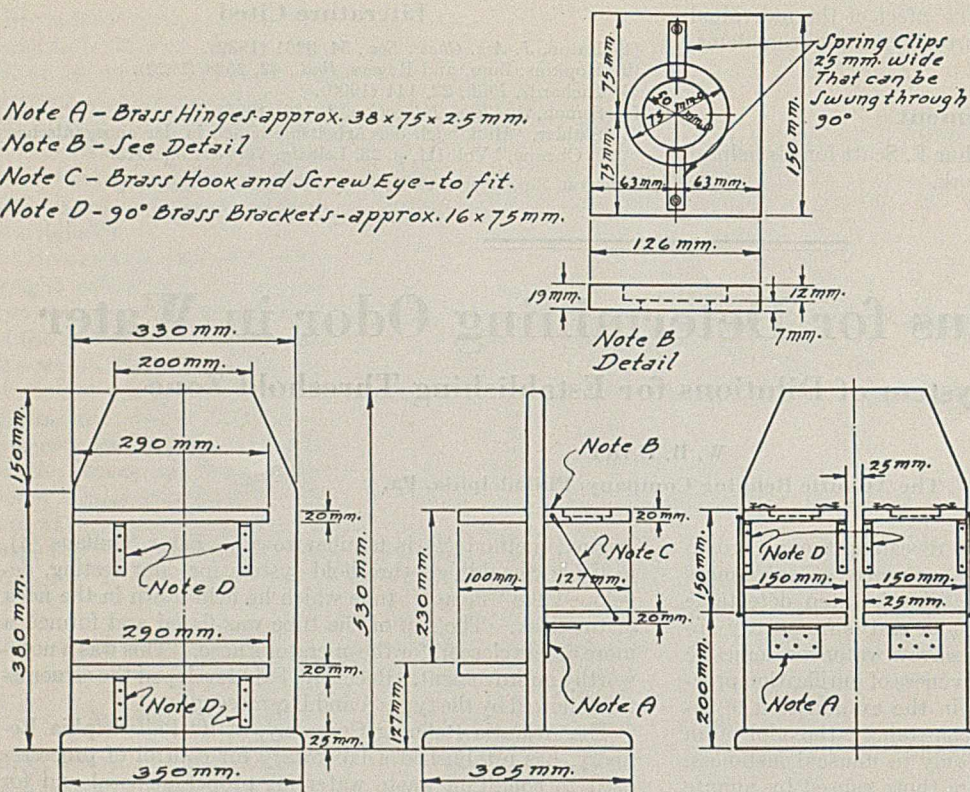


FIGURE 2. STAND FOR ODOR DETERMINATION EQUIPMENT

quickly. The importance of each of these features was well demonstrated while developing the equipment described below.

Apparatus

The apparatus consists essentially of a purification train; a means of supporting two flasks, one for the sample and one for a blank of odor-free water; a support for the odor-free air inlet and smelling tube for each flask; a combined mercury seal and pressure-relief valve to maintain the required pressure in the system and allow the escape of air when not being passed into the flasks; and a manometer to show the pressure in the system. The source of the air used is a compressor system or, in one portable design, a truck-tire inner tube and an auto pump. The apparatus is briefly described, since details are better shown by Figures 1 to 6.

PURIFICATION TRAIN. For deodorizing the incoming air, which should not exceed 70.3 grams per sq. cm. (one pound per square inch) in pressure, a train of three flasks and an activated carbon canister is used. The first flask contains about 75 ml. of standard formula dichromate-sulfuric acid oxidizing solution. The second flask contains about the same amount of strong caustic soda solution, and the third about 2 grams of 300-mesh activated carbon suspended in water. The canister is of the standard gas-mask type. The air is passed through the train in the usual manner and then through an empty flask which serves as a trap. Just beyond it divides into three streams, one leading to the

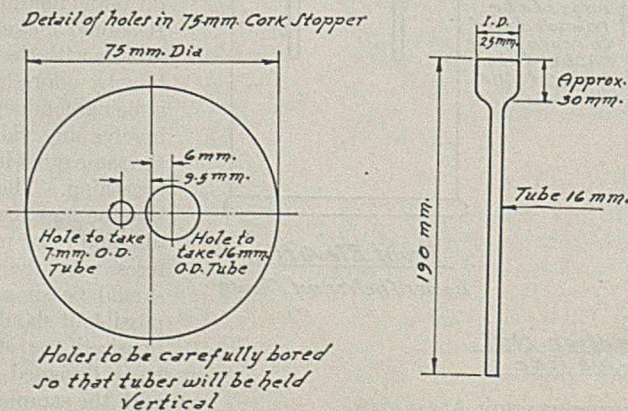


FIGURE 3. DETAIL OF ADAPTER

sample flasks, one to the mercury-seal relief valve, and one to the manometer.

SAMPLE FLASK SUSPENSION. Two separate shelves carrying corks approximately 75 mm. in diameter extend horizontally from the main vertical support of the apparatus. To hold the corks the shelves are recessed and supplied with clip springs. Concentrically within the recess the shelves are drilled with a hole through which the flanges of the sample flasks will pass and press against the under side of the corks. Two hinged shelves are located lower on the main vertical support at a point where they will swing out horizontally and hold the flasks against the corks with a slight pressure which is taken up by the spring clips. These shelves are then supported by hooks which swing from the sides of the main support. Rubber pads on the swinging shelves take up any irregularity in the height of the flasks which are of 250-ml. capacity and the wide-mouth type.

PRESSURE-RELIEF VALVE AND MANOMETER. The pressure relief valve is simply an open-end tube extending into some mercury in a container,

far enough to keep about 100 mm. (4 inches) of water pressure in the system when the stopcocks to the flasks are closed.

The manometer is of the simple U-tube type.

SMELLING TUBE AND AIR INLET. The smelling tubes for the sample flask and for the blank flask are identical. There are two parts. An adapter tube is used for the lower section and extends to just above the level of the sample in the flask. A cork carrying a nose-piece fits into the flared top of the adapter.

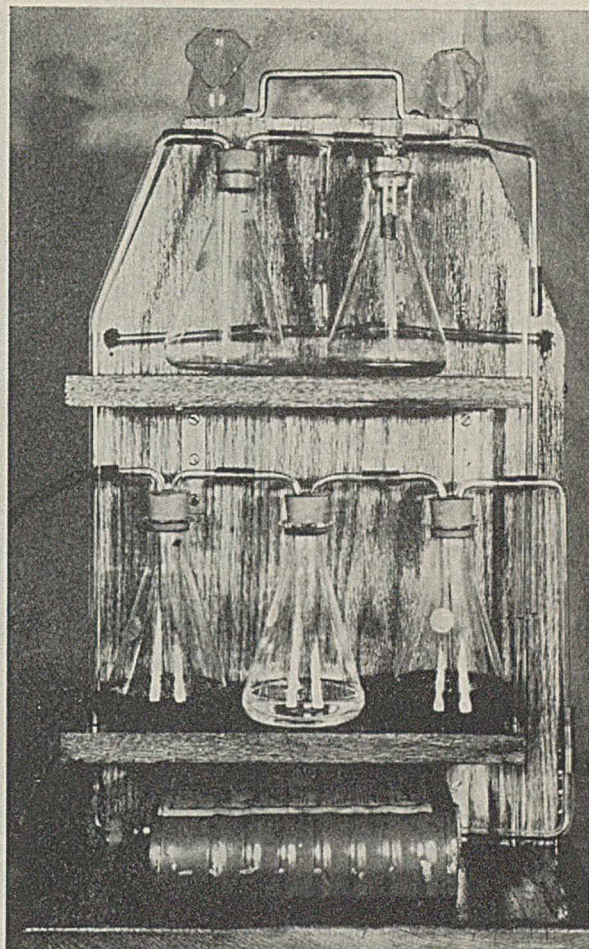
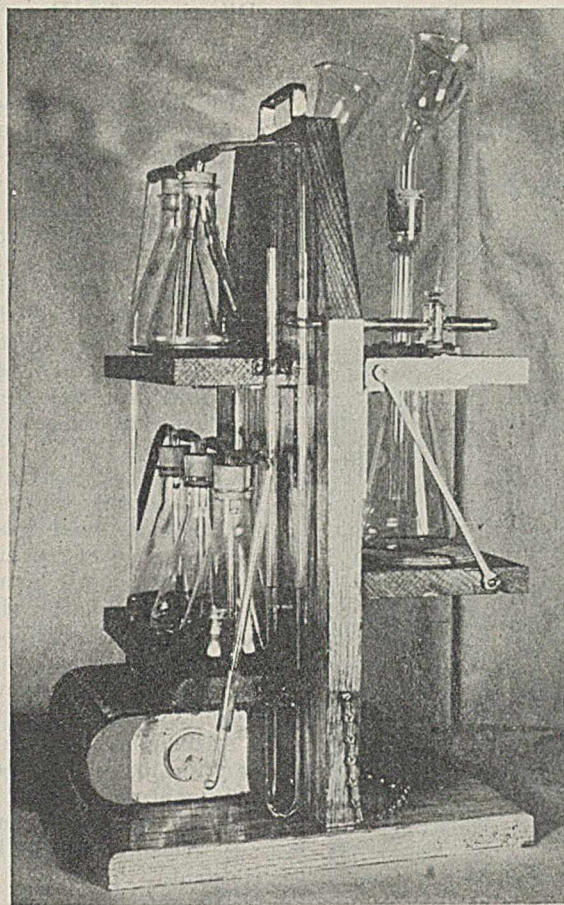
The nose-piece is individual for each observer, and being separate, one equipment can be used by several individuals. It is made to an approximate fit, so that only a slight space is left between the flare and the nose when being used. It is not a tight fit, but is close enough so that the stream of air coming up the smelling tube passes into and around the nose, driving away any atmospheric odors that might give misleading results.

A convenient way of making the nose-piece is to make a wax mold of the observer's nose and then a plaster of Paris cast. The nose-piece is then blown on the cast.

The odorless air inlet is simply a glass tube carrying a stopcock. The tube extends through the cork and about 2.5 cm. (1 inch) into the flask, so that the incoming air, moving downward, displaces the layer of air next to the sample, driving it upward through the smelling tube to the observer's nose.

All parts of the apparatus are standard chemical items.

The glass tubing is made up end tight against end. The frame or support for the apparatus may be of metal or wood that is well shellacked to seal any odor. The odor due to the use of corks, rubber connections, shellac, etc., was the subject of much discussion during the development stage. No undesirable effects were noticeable. A possible explanation for this is that it seems less difficult to detect some odor than no odor. Odor may be present, but in bringing the sample through dilution into equilibrium with the blank through the sense of smell, some slight odor may help.



FIGURES 4 AND 5. PHOTOGRAPHIC VIEWS OF APPARATUS

Material List

PURIFICATION TRAIN. Glass tubing: laboratory bending tubing of soda-lime glass, 7-mm. outside diameter, 1-mm. wall; approximately 4.5 meters required. Rubber tubing: transparent rubber tubing, thin wall, 6-mm. bore, 1.75-mm. wall; approximately 45 cm. required. Corks: 1 No. 12 and 1 No. 16, selected dense stock; bored centrally one hole for 7-mm. outside diameter tubing; 1 each required. Flasks: 250-ml. conical flasks, narrow-mouth type; 5 required. Cannister: standard gas-mask carbon canister; 1 required; replaced as needed.

SAMPLE EQUIPMENT. Flasks: 250-ml. capacity, conical flasks, extra wide mouth; 12 or more required. Corks: 75-mm. diameter, 16 mm. high, of selected dense stock; drilled two holes (Figure 3); 2 required. No. 12, selected dense stock, drilled centrally for 16-mm. outside diameter tube; 2 required. Adapters: 190 mm. long from top of flare to end of tube, 16-mm. outside diameter tube, 25-mm. inside diameter flare; 2 required. Nosepiece: made special for operators of 16-mm. outside diameter lime-soda glass tube; 2 or more required. Stopcocks: glass; plugbore 5 mm., bent to fit; 2 required. Glass tees: bore, 5 mm.; 3 required.

Test Procedure

All those engaged in the examination of water are familiar with the determination of "threshold point." In reality this is not a point to more than one observer but rather a "zone" and is so designated here. To even one observer, the exact point would be determined only rarely and there is but one absolute point that can be checked by several: the condition of no odor present. In samples of very low odor concentration the zone becomes more and more constricted as zero odor is approached and may seem to be a point. Group opinion is valuable under all conditions and particularly

when numbers of individuals are concerned with the purity of the water.

The ability to detect faint odors varies not only with different individuals but at times with the same individual, depending upon physical condition. Also, when odor is present to a certain slight extent, one observer may detect it and not another. Between the low intensity detectable to the first and the higher intensity detectable to the other, there is a "threshold zone" which is the indication that the water "smells." This "zone" has practical value to many; the "point" has value to only the one who finds it. The average sensitivity will be well within the zone, but it is probable that in a group of observers the individual threshold finding of any one will range from 5 to 10 per cent on either side of the group average.

In carrying out the threshold zone determination using the equipment described, dilutions are made of the sample with odor-free water and a tentative threshold is found by simply smelling at the mouth of the flask. This tentative zone is established at a point of no odor, well beyond the real zone. Dilutions for this purpose are made in multiples of ten. Then, after a rest period, intermediate dilutions are made up and tested in the equipment, always approaching the threshold zone from the no-odor side to assure a clear nose.

The manipulation is simple. An odor-free blank of 100 ml. is set up on one side of the apparatus and the unknown dilutions are tried on the other. The flask is held up under the cork, making sure that the flanges rest evenly, and the bottom shelf is brought up and hooked in place. With the air turned on through the apparatus the stopcock is opened for a few seconds to sweep out any room atmosphere. Then the stopcock is closed, the

flask is removed and shaken gently to contact the air and water and replaced. This agitation is important. Then the nose is placed just comfortably in the nosepiece and, opening the stopcock just before a normal inhalation, the odor is taken. There should be air escaping from the relief valve when the stopcock is closed and also, to some extent, when it is open.

Where an absolutely odor-free atmosphere exists, no protection against outside odors is necessary. This is not often the case, particularly where waste waters are being tested in industrial laboratories. Very satisfactory results have been obtained with the procedure described under conditions purposely made difficult.

Evaluation of Odors

The original method of evaluating odors as devised by the late Professor Whipple is described in Standard Methods (1). Spaulding's threshold-point method (5, 6) was a great improvement. More recently the exponential method of Fair (2, 3) was developed. These methods, or variations of them, are all in use today. But in making threshold determinations, and in studying the results of others, a uniform procedure that will eliminate as many variables as possible is badly needed, particularly when the final result depends upon the differing sensitivity of various individuals. Also, as the intensity or persistency of the odor increases, the dilutions constituting the boundaries of the threshold zone may diverge to a greater extent without great importance attaching.

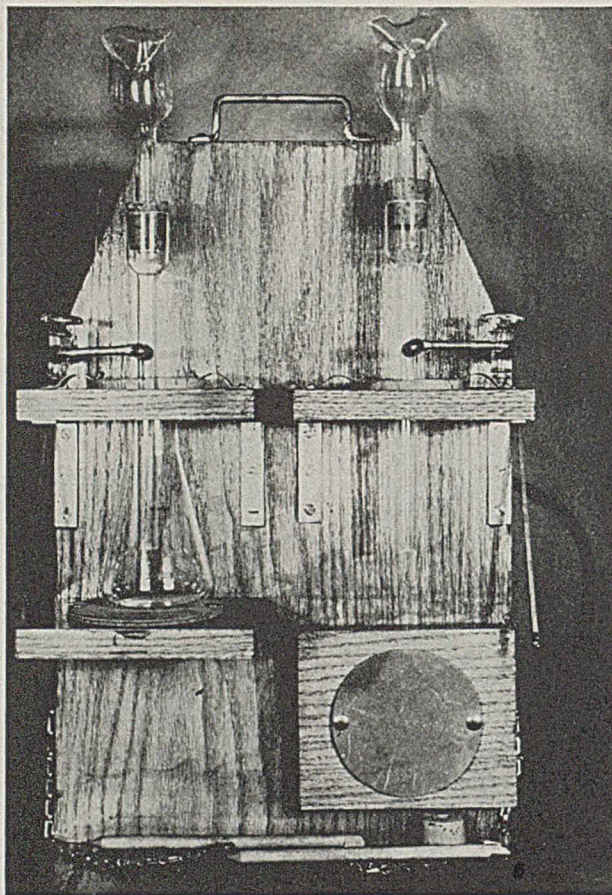


FIGURE 6. PHOTOGRAPHIC VIEW OF APPARATUS

Dilutions for Determination of Threshold Zone

The dilutions are made up as shown in Table I, extending the series until it is found that the threshold zone has been passed. This establishes the tentative threshold.

Having found two dilutions, the lower having odor and the higher no odor, it is obvious that the real threshold zone lies between. The limits are then reduced as shown in Table II.

Certain precautions should be observed in making dilutions. Since waste waters may carry suspended matter or oily suspensions that cannot readily be washed from a pipet, clean measuring equipment should be used wherever conditions indicate.

All dilutions are made to as nearly 100 ml. as is possible for accurate ratios, so that the air-water volume ratio remains practically constant.

The threshold zone reported is the dilution in which odor is first detected.

TABLE II. DILUTIONS

Dilution Identification	Sample Ml.	Odor-Free Water Ml.	Dilution
1A	12 L. D. ^a	96	1 in 90% of H. D. ^b
2A	12 L. D.	84	1 in 80% of H. D.
3A	15 L. D.	90	1 in 70% of H. D.
4A	16 of L. D.	80	1 in 60% of H. D.
5A	20 of L. D.	80	1 in 50% of H. D.
6A	25 of L. D.	75	1 in 40% of H. D.
7A	33 of L. D.	66	1 in 30% of H. D.
8A	50 of L. D.	50	1 in 20% of H. D.

^a Lower dilution, L. D. ^b Higher dilution, H. D.

TABLE I. DILUTIONS

Dilution Identification	Sample Ml.	Odor-Free Water Ml.	Dilution
1	10	90	1 in 10
2	10 (Dilution 1)	90	1 in 100
3	10 (Dilution 2)	90	1 in 1,000
4	10 (Dilution 3)	90	1 in 10,000
5	10 (Dilution 4)	90	1 in 100,000

Since such zones actually exist, it is important that they be limited. Such limitation makes for uniformity that will add value to the reports of various observers. It will in reality make possible check determinations at the expense of very little accuracy, for there will be a definiteness about the observation that is not present when a "point" is looked for. The point found by one observer will be questionable to another. A systematic series of dilutions, that will step by step establish zones such as described and is particularly adaptable to waste waters, follows.

This information then will indicate water quality: need or no need for further treatment or any other purpose required.

Acknowledgment

Although not included in the references the author wishes to acknowledge the very valuable assistance and information given by M. W. Cowles, Health Officer, Hackensack Water Co., and L. F. Warrick, State Sanitary Engineer, Wisconsin.

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RECEIVED April 25, 1936. Presented before the Division of Water, Sewage, and Sanitation Chemistry at the 91st Meeting of the American Chemical Society, Kansas City, Mo., April 13 to 17, 1936.

Twenty-Plate Laboratory Bubble-Cap Still

For Low-Boiling Materials

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THE object of the present investigation was to develop a laboratory still suitable for the preparation of low-boiling (below room temperature) compounds of extremely high purity. The main requirements for such a still are:

1. The efficiency of the fractionating column, expressed in the number of theoretical plates, should be such that even small amounts of a volatile impurity can be removed. A study of the vapor-liquid equilibrium diagrams of binary mixtures will reveal that it is normally much more difficult to effect an enrichment in concentration from 95 to 100 mole per cent than from 50 to 95 mole per cent.

2. The capacity of the still should be large enough so that comparatively large amounts (500 to 1000 ml.) of material can be distilled in a single distillation.

The low-temperature columns of Podbielniak (6), Davis (4), and Bosschart (1) have been used successfully for establishing approximate compositions of low-boiling mixtures. For the purpose

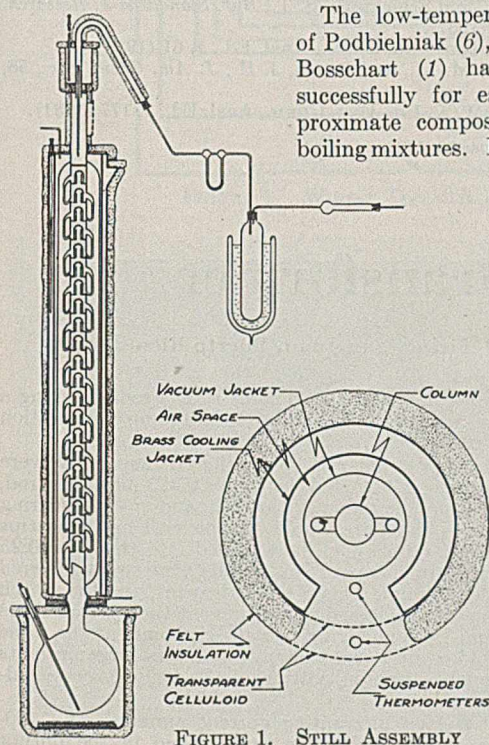


FIGURE 1. STILL ASSEMBLY

of preparing pure low-boiling compounds, however, it was felt that an improved still could be designed which would meet the above mentioned requirements better than the older columns.

Description of Still

Figure 1 shows the assembly of the still. The still pot has a capacity of 1000 ml. and is provided with a thermometer well into which is suspended a toluene thermometer. It is surrounded by a Pyrex beaker, the outside of which is heavily insulated with felt pad. In the bottom of the beaker is placed an electric heater similar to that described in an earlier publication (3).

The fractionating column, which is 80 cm. long, consists of twenty bubble-cap plates of glass of the type shown in Figure 2 and described in a recent paper (2). As indicated in Figure 1, a vacuum glass jacket (72 mm. o. d.) was sealed to the column in order to minimize radiation. During distillations of low-boiling compounds, such as propane, it was

found that better results could be obtained if the glass vacuum jacket was surrounded by a C-shaped brass cooling jacket provided with a vertical celluloid window along its entire height. The bottom, the outside, and the top of the cooling jacket were insulated with heavy felt pad. The column was supported by an angle iron frame by means of a Transite support.

The reflux head consisted of a half-inch copper tube surrounded by a short 2-inch brass cooling jacket. All of the exposed parts of the reflux head were insulated by felt.

The receiver consisted of small pressure cylinders immersed into a Dewar flask.

The flowmeter shown between the reflux head and the receiver was used to indicate the rate of distillation for fractions such as propane and may be omitted if desired.

Operation

The brass cooling jacket around the column was filled about three-fourths full with a cooling mixture such as carbon tetrachloride and chloroform, and solid carbon dioxide was introduced through the spout near the top until the temperature in the brass jacket was low enough to cool the vacuum jacket and the column and to minimize radiation through the glass vacuum jacket. In order to ensure complete visibility of the column and of the thermometer between the column and the inside celluloid window, it is important to prevent water vapor from freezing on the vacuum jacket and on the windows. For this reason Dehydrite tubes were connected to the top and bottom of the air space between the brass jacket and the vacuum jacket, as well as to the space between the two celluloid windows.

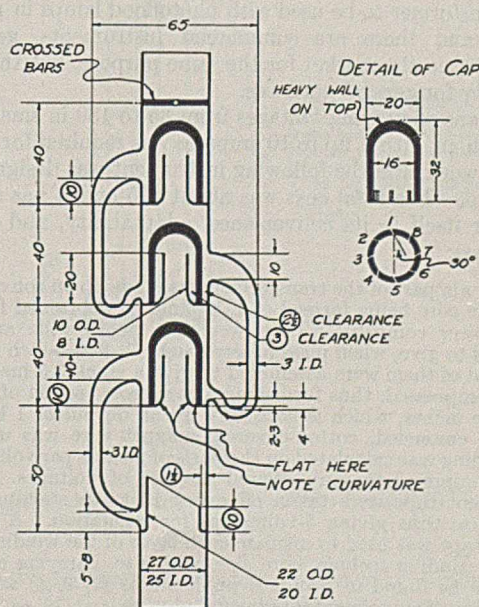


FIGURE 2. REDESIGNED BUBBLE-CAP COLUMN, 4-CM. SECTIONS

Slots in bubble cap, as shown, about 0.5 to 1 mm. wide and 5 mm. deep, at an angle of 30° with radius, fire-polished. Material, Pyrex laboratory glass. All dimensions are in millimeters. Exact dimensions are circled.

For charging purposes the still pot was cooled by surrounding it with a large Dewar flask containing cooling liquid. The material to be distilled was then introduced into the still pot as a liquid. As soon as the reflux head had been cooled sufficiently to ensure complete condensation, the Dewar flask under the still pot was replaced by the heating unit shown in Figure 1. During distillation of very low-boiling fractions such as propane, the operation of the bubble-cap column will not commence until a sufficient quantity of liquid has condensed on the plates. If flooding should occur during this initial starting period, some pressure should be applied on the top of the column by blowing through a drying tube located at the end of the distillation train. This procedure will force the condensed liquid down to the empty plates and will enable the operator to start a distillation in about 10 or 15 minutes.

A thermometer suspended from the reflux head at the top of the column was used to read the temperature of the distillation. Other thermometers were placed in the still pot, in the air space between the vacuum jacket and the brass jacket, and in the cooling mixtures surrounding the column and the reflux head.

The distillate fractions may be taken either by temperature or by volume. When the latter method was used, the volume of distillate in the receiving cylinder was measured by means of a small glass tube (about 2 mm. o. d.) which was inserted into the liquid distillates for 1 or 2 seconds. A calibrated

glass receiver could obviously be used for most hydrocarbons, but for low-boiling liquids, such as propane, steel cylinders were preferred since they were used also as pressure storage containers for the distilled fractions.

Efficiency

Carefully conducted tests with different liquid mixtures and under different rates of distillation showed that the height of the equivalent theoretical plate for the bubble-cap column shown in Figure 2 is slightly above 4 cm. (2). Consequently, the separation obtained by means of the new column is equivalent to an efficiency of nearly twenty theoretical plates.

The column shown in Figure 1 was used for the purification of *n*-propane. The time-temperature cooling curve of the distilled middle fraction of this propane indicated an unusually high degree of purity (5).

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RECEIVED November 28, 1936.

A Variable-Voltage Autotransformer

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A SOURCE of variable alternating current voltages would often be convenient in laboratory work. Low voltages of 2 to 24 volts can, of course, be supplied by toy or bell-ringing transformers, but their current-carrying capacity is small. Greenleaf (3) described the construction of a simple autotransformer to be used with photoflood lamps in photography, and there are commercial instruments, generally rheostats, on the market for the same purpose, but they lack flexibility for general purposes.

A means of varying voltages from 35 to 180 in small steps and with an output up to 10 amperes was required for experimental work, and the following instrument was designed and made up. The total cost was about \$25 and it has already paid for itself in its convenience, adaptability, and general usefulness.

The main part of the transformer was made up on conventional lines, the core being formed of L-laminations obtained from the local power company. They were 1.5 inches wide and were trimmed to give, when piled in a rectangle, a 1 × 6 inch window. Sufficient of them were assembled to give a stack 3.5 inches high when compressed, thus furnishing a core cross section of at least 4 square inches, which is necessary for an output of 1 kilowatt. No. 14, enameled, cotton-covered, magnet wire was used and the winding was calculated on the basis of 2 turns per volt. Taps can be supplied for any desired number of voltages. In this instrument taps were taken off every 10 turns starting at the 70th turn, thus giving 5-volt steps for regulation. A layer of empire tape was used to insulate each layer of the winding. Details of winding technic, core size, wire size, carrying capacity, etc., can be found in standard publications (1, 2, 4) and many other texts of experimental radio and physics.

The power line connection which normally would, in this case, be connected to the 220th turn (transformer calculated for 2 turns per volt) was made variable by the addition of a 7-point rotary switch, allowing connection to be made to every 20 turns of the transformer winding, from the 180th to 300th turn, inclusive. This increased the range and usefulness of the appara-

tus. The main regulator was a 20-point rotary switch giving a variation of 3 to 5 volts per contact, depending on the position of the 7-point switch.

Since switch points could not be purchased here, they were easily made by cutting 0.25-inch disks from a 0.375-inch brass rod, drilling a 0.1875-inch hole partway through, and sweat-soldering to the heads of 0.1875-inch brass bolts 1.25 inches long. The tips of these bolts had a 0.0625-inch hole drilled into them for 0.25 inch, and the transformer taps of No. 14 wire were sweat-soldered to them after assembling. This is not a rheostat, and the switch points must be spaced wide enough to prevent the contact shoes of the switch arms from engaging two switch points at the same time, which would cause a short circuit, and very large currents would flow through a limited portion of the transformer windings.

A 10-ampere Weston alternating current ammeter and 150-volt alternating current voltmeter were placed in the output circuit, together with a 10-ampere fuse plug and two porcelain plug outlets. A Cutler Hammer single-pole single-throw heavy-duty toggle switch was placed in the output side ahead of the ammeter. The voltmeter was so wired that when this switch was in the off position, the meter still registered the voltage that can be thrown into the output circuit. These wiring details are clearly seen in Figure 1. The instruments and switches were mounted on a 12 × 14 inch Bakelite panel and the whole was screwed to a 2-inch mahogany base 12 × 15 inches. The outfit weighed about 50 pounds and was capable of delivering 8 amperes at any voltage from 35 to 190 continuously and 10 amperes for an hour without heating up above 45° C. Figure 2 shows panel mounting.

It is ideal for closely regulating the output of heating devices, such as small furnaces, hot plates, and immersion heaters. The speed of any Universal laboratory motor used for stirrers, centrifuges, or grinders, can be controlled. Ordinary light bulbs flashed at 180 or 190 volts can be used in place of photoflood lamps for photography. Projection machines and arc lamp microprojectors can be maintained at efficient voltages on power lines that are delivering only 90 to 100 volts. A 17-volt tap could be added, if desired, to use the General Electric S₁ and S₂ lamps for ultraviolet work. In fact, the device is useful for any purpose where close regulation of voltage to an apparatus is

Siphon-Starting Device

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THE starting of a siphon, particularly with corrosive liquids in an open container, often cannot be achieved conveniently and safely by expedients commonly used. Siphoning from a wide-mouthed bottle, pail, or drum may present such difficulty, and to meet this condition in handling a corrosive solution the device shown in Figure 1 was made.

Essentially, the apparatus consists of a siphon centered in a reservoir tube, of sufficient capacity to fill and start the siphon by pressure on the liquid in the reservoir. A rubber stopper around the bottom of the larger tube acts to seal the reservoir until the siphon has been started; then tilting the assembly allows the siphon to drain the container. A flat disk of gasket rubber placed on the bottom of the containing vessel may help to form a better seal while the siphon is being started.

The drawing is self-explanatory, except that it does not indicate the relation between the tube sizes. The length of the siphon and height of the reservoir are determined by the container with which they are to be used. If it is assumed that the length of the siphon is three times the height of the reservoir, and if the reservoir is to provide four times the volume of the siphon tube, the relationship of the inside tube diameters is: $D = \sqrt{12d^2}$, where D is the diameter of the reservoir and d is the diameter of the siphon. These relationships provide for sufficient reservoir capacity to ensure an excess of liquid over that just sufficient to start the siphon.

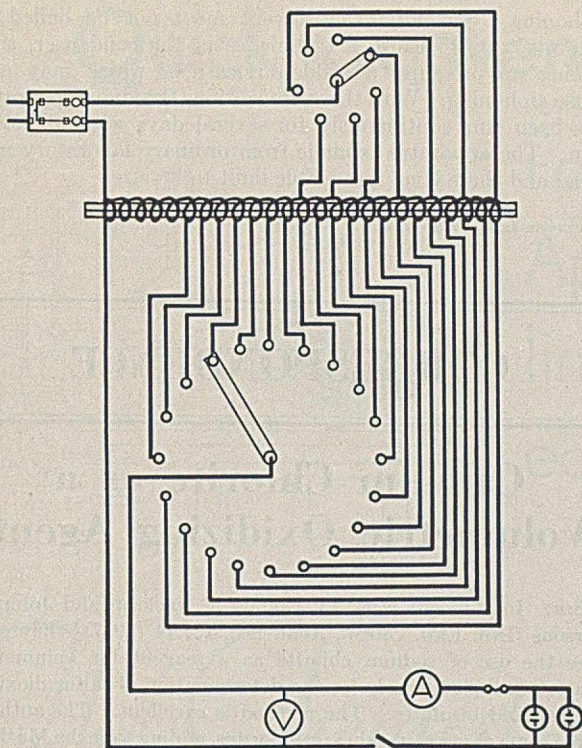


FIGURE 1. WIRING DETAILS

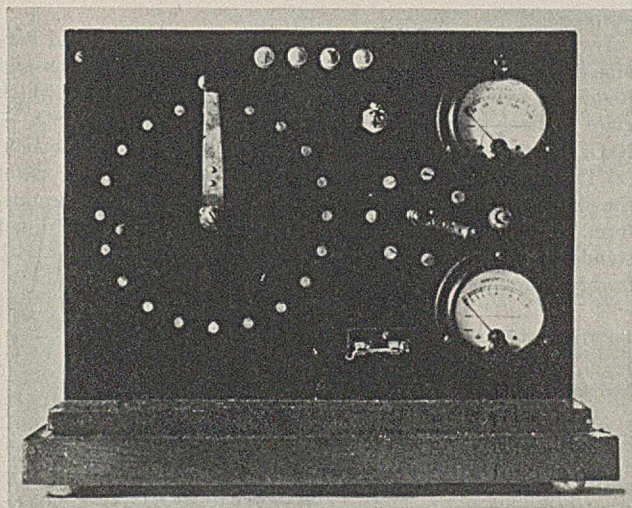


FIGURE 2. PANEL MOUNTING, FRONT VIEW

desirable. It does not regulate in the sense of keeping down voltage fluctuations in the main line supply. Unlike a rheostat, there is no power lost in heat; all the current is used in producing the effect desired and regulation is closer than with the average rheostat. On this instrument, 4 binding posts are mounted on the panel to furnish current for a hot wire loop for glass cutting. They are connected to any successive 10-turn taps of the transformer, thus giving voltages from 3 to 20, depending on the position of the 7-point rotary switch.

This device has been in constant service in the laboratory for two years and has given entire satisfaction.

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RECEIVED March 16, 1937.

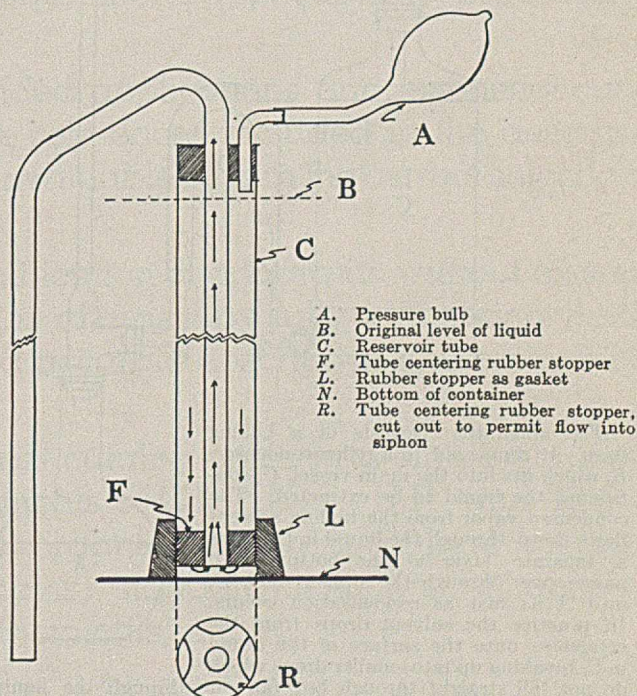


FIGURE 1. DEVICE FOR STARTING SIPHON IN OPEN VESSELS

If the liquid level is too low to provide a volume great enough to fill the siphon tube, suction may be applied to fill the reservoir tube before the pressure is applied to start the siphon. A tee with vacuum connection and pressure bulb attached could well be provided if the need is anticipated.

RECEIVED February 20, 1937.

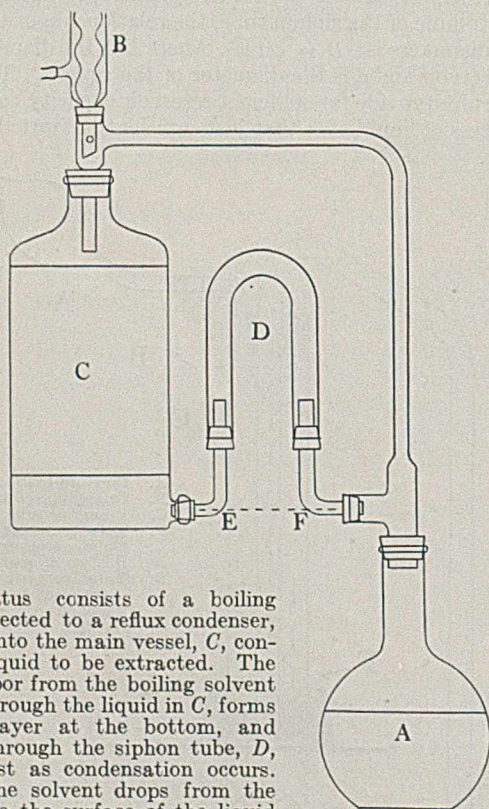
Apparatus for the Extraction of Liquids with Immiscible Solvents of Greater Density

LINDSAY H. BRIGGS

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AN ORDINARY "siphon" apparatus similar to the Soxhlet extractor may be used for extraction of liquids with immiscible solvents of greater density, provided the return tube is sufficiently wide to prevent siphoning, the solvent flowing over continuously as fast as it condenses. The main disadvantage of such apparatus is in arranging the height of the siphon tube, which must vary from experiment to experiment according to the density of the solvent and the amount of liquid to be extracted.

The following apparatus has been found useful in extracting comparatively large amounts of aqueous solutions containing plant material with heavy solvents such as chloroform or trichloroethylene.



The apparatus consists of a boiling flask, A, connected to a reflux condenser, B, which fits into the main vessel, C, containing the liquid to be extracted. The condensed vapor from the boiling solvent flows down through the liquid in C, forms a separate layer at the bottom, and passes over through the siphon tube, D, into A as fast as condensation occurs. In practice the solvent drops from the condenser onto the surface of the liquid in C, breaking up into smaller drops which do not fall straight through but fan out through the liquid. The essential feature is that the siphon tube can swing about the axis E-F, enabling the height of liquid in the tube to be adjusted according to the amount of aqueous extract in C and the density of the solvent. Major adjustments may be made by sliding the inverted U-tube up or down and minor adjustments by tilting the U-tube, which is then clamped to hold it steady.

There are two essentials in the construction. Firstly, the siphon tube must be of sufficient width to allow the condensate to run over freely. Blocking with solvent owing to the use of smaller bored tubing will immediately cause complete

siphoning. Secondly, the solvent must not be boiled so vigorously as to cause a turbulence in the condenser, thus setting up pressure, a sudden release of which may also cause siphoning. With these precautions the above apparatus has been run continuously for several days without attention. The apparatus is made from ordinary laboratory material and there is no reasonable limit to its size.

RECEIVED January 5, 1937

CORRESPONDENCE

Calcium Chlorite as a Volumetric Oxidizing Agent

SIR: In a recent work by Donald T. Jackson and John L. Parsons [IND. ENG. CHEM., Anal. Ed., 15, 14 (1937)] they propose the use of sodium chlorite as a reagent for volumetric analysis and particularly for the determination of sulfur dioxide, sulfites, and bisulfites. The method is excellent. The authors quote some of my researches on chlorites, adding that the Mathieson Alkali Works, Inc., now manufactures a product containing 97 to 98 per cent of sodium chlorite which may be used for this purpose.

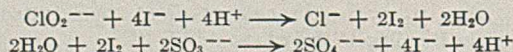
I would like to make two observations: (1) Jackson and Parsons do not mention my article on "Reactions of Oxidation and Reduction with Chlorites" [Gazz. chim. ital., 52, 58 (1922)] which gives precisely the reaction, $2\text{H}_2\text{SO}_3 + \text{NaClO}_2 = 2\text{H}_2\text{SO}_4 + \text{NaCl}$, that the authors assume as the basis of the titration. (2) The ability to obtain 100 per cent calcium chlorite because of the solubility of calcium chlorate and chloride in alcohol, permits, from my point of view, its more convenient use as the direct standard. The calcium chlorite solution must be made with freshly boiled water free of carbon dioxide.

GIORGIO RENATO LEVI

ISTITUTO DI CHIMICA GENERALE
R. UNIVERSITÀ
PAVIA, ITALY
March 16, 1937

SIR: The pioneering work in the preparation, properties, and uses of the chlorites by G. R. Levi and his associates is fully appreciated by Dr. Jackson and myself with reference to our article on sodium chlorite as a volumetric oxidizing agent in the ANALYTICAL EDITION for January 15. Unfortunately the Italian journals are not readily accessible to us. For many of Mr. Levi's references, therefore, we have had to depend on the abstract journals and the equation to which he refers in his comments was not covered by the abstract.

It has been our experience, however, that the reaction $2\text{H}_2\text{SO}_3 + \text{NaClO}_2 = 2\text{H}_2\text{SO}_4 + \text{NaCl}$ is rather slow and not particularly suited to volumetric analysis. By the addition of a small amount of potassium iodide the reaction is markedly accelerated and is very satisfactory for the purpose we had in mind. In the presence of the iodide ion the reactions appear to be:

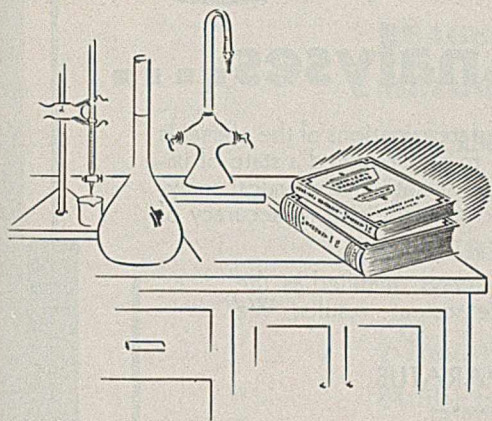


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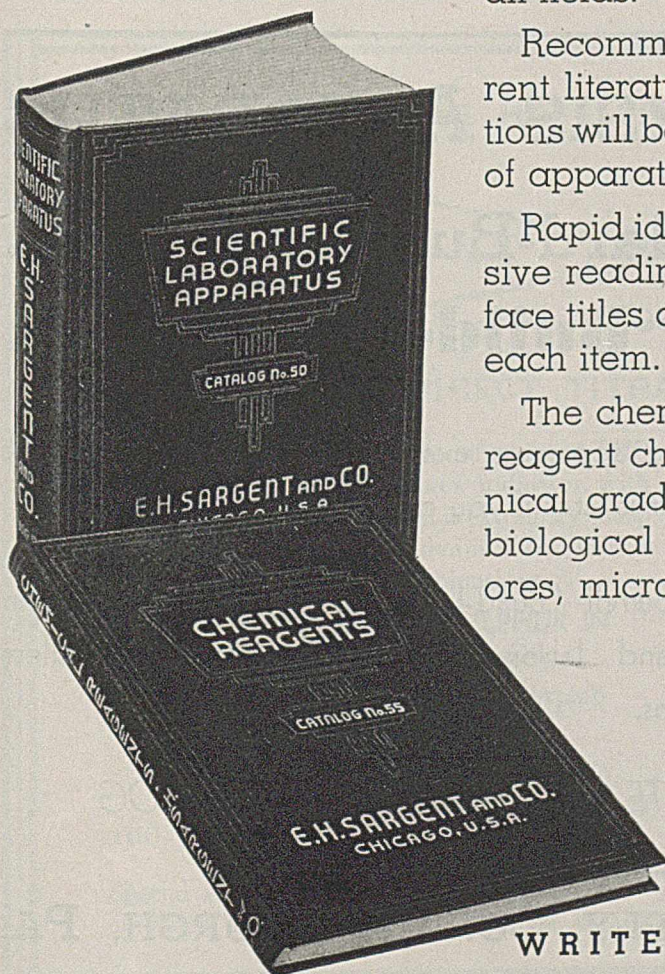
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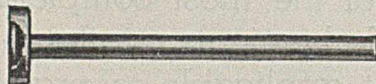
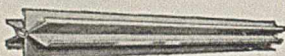
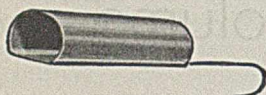
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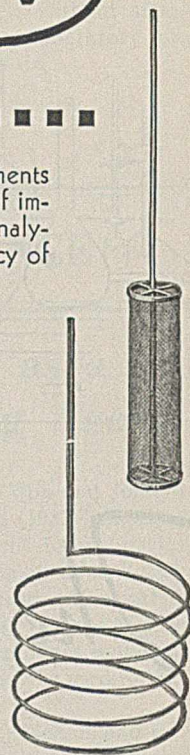
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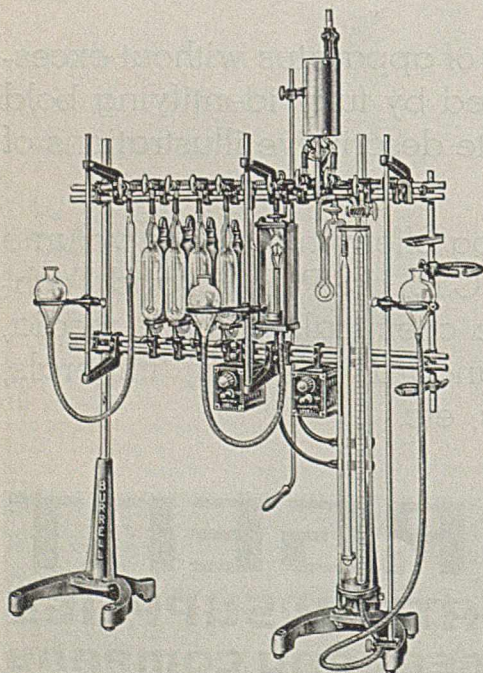
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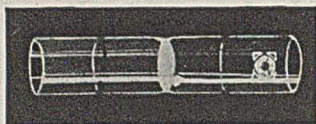
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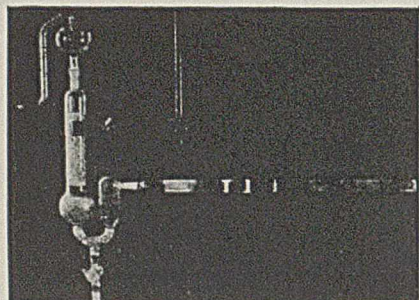
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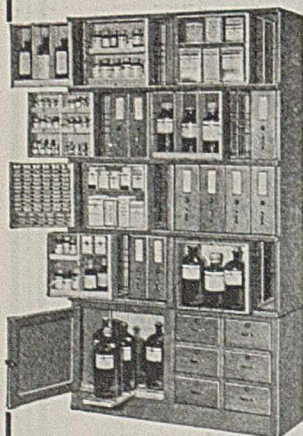
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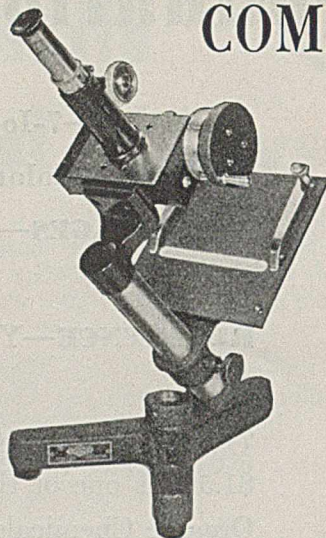


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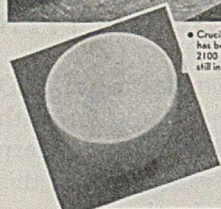
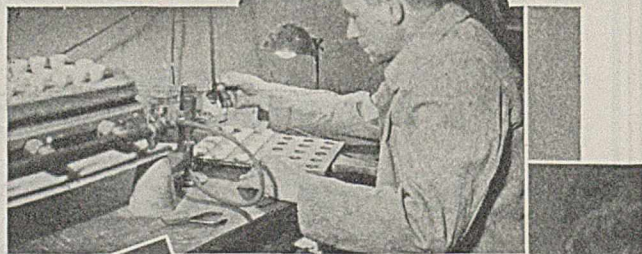
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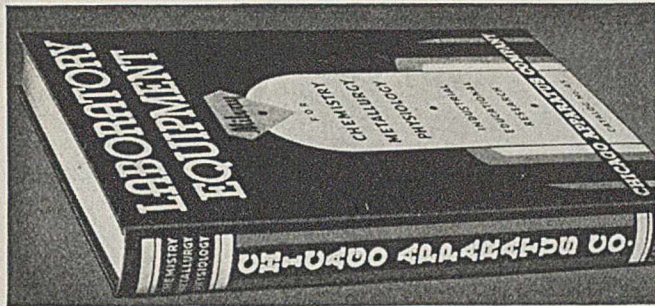
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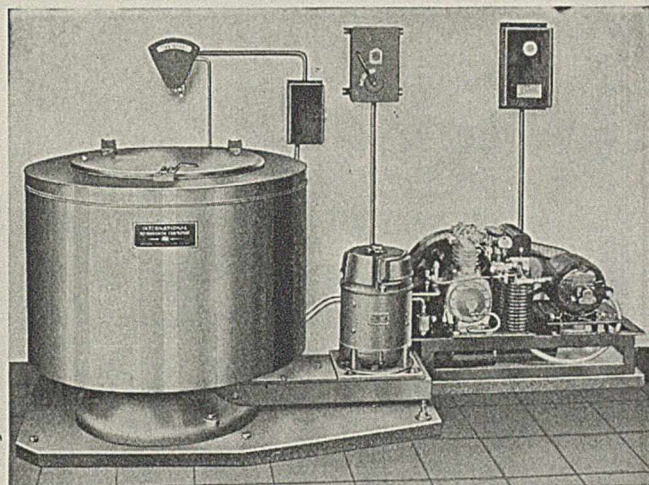
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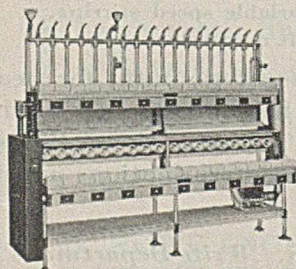
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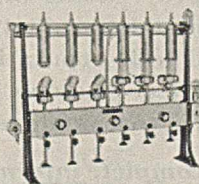
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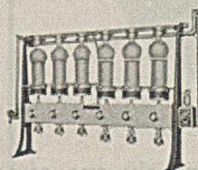
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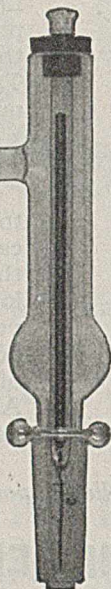
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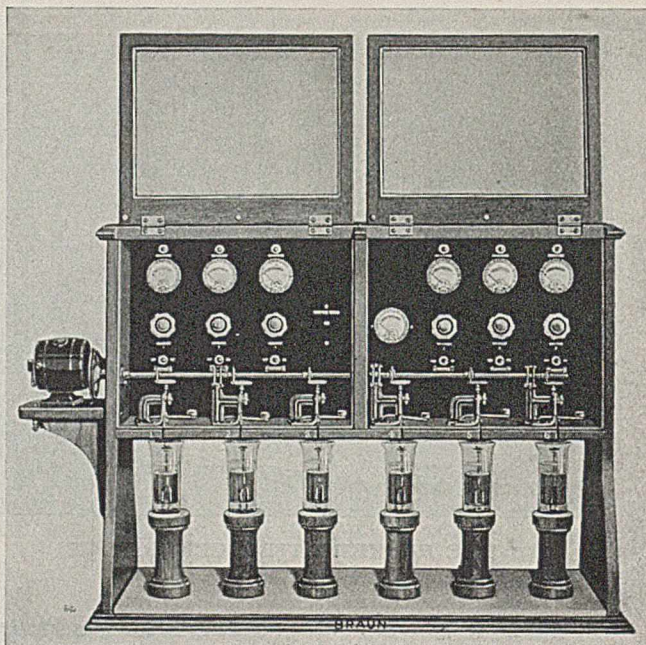
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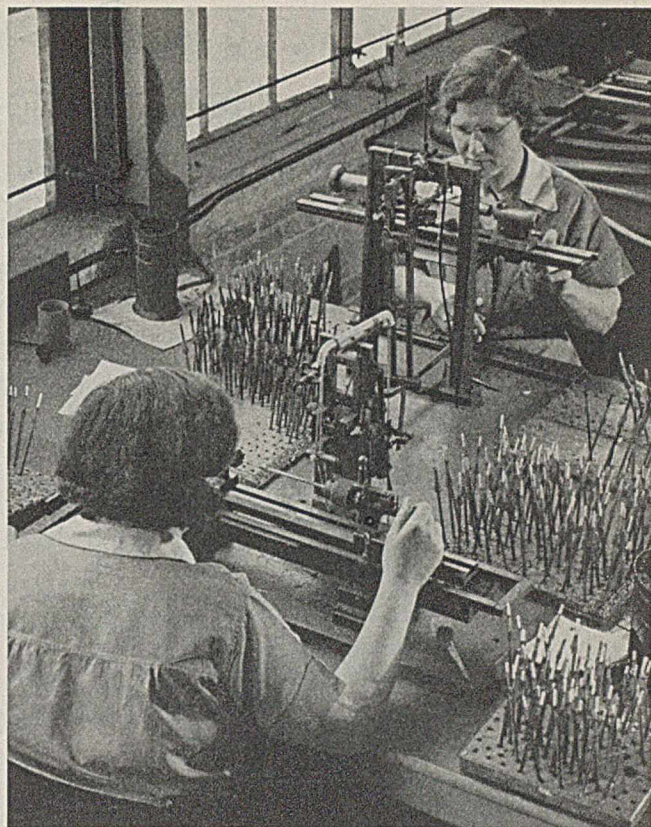
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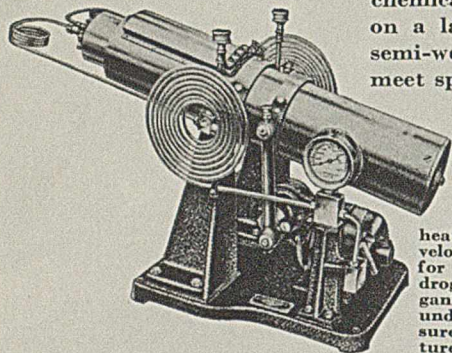
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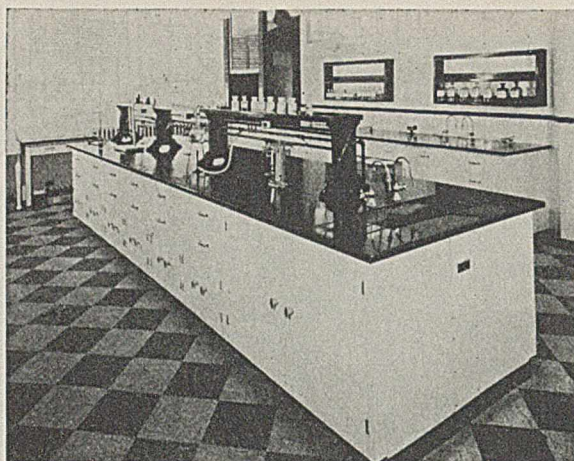


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