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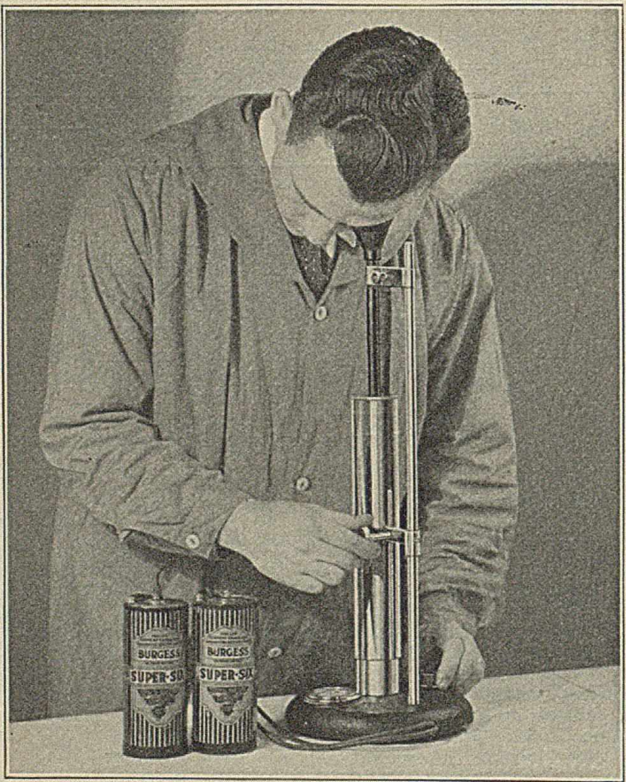

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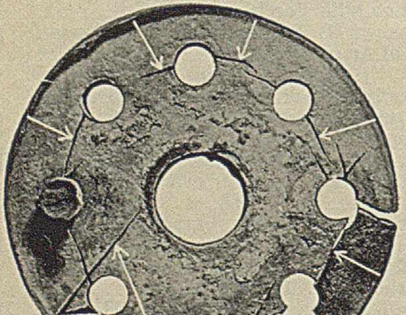

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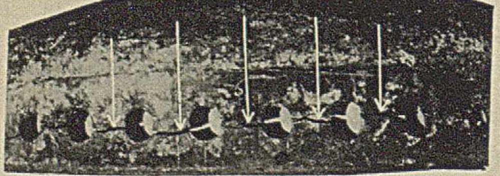
Right bottom: Cracked rivet from embrittled boiler.

Left bottom: Blow off flange showing cracks and failures caused by embrittlement.



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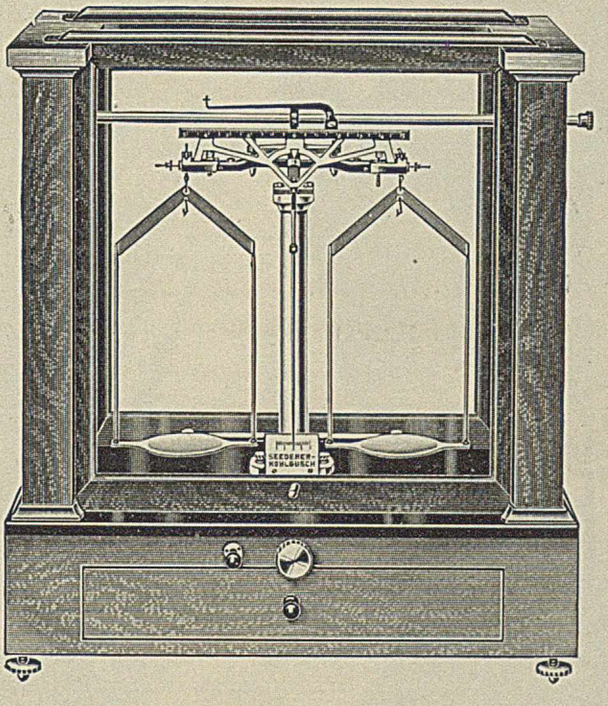
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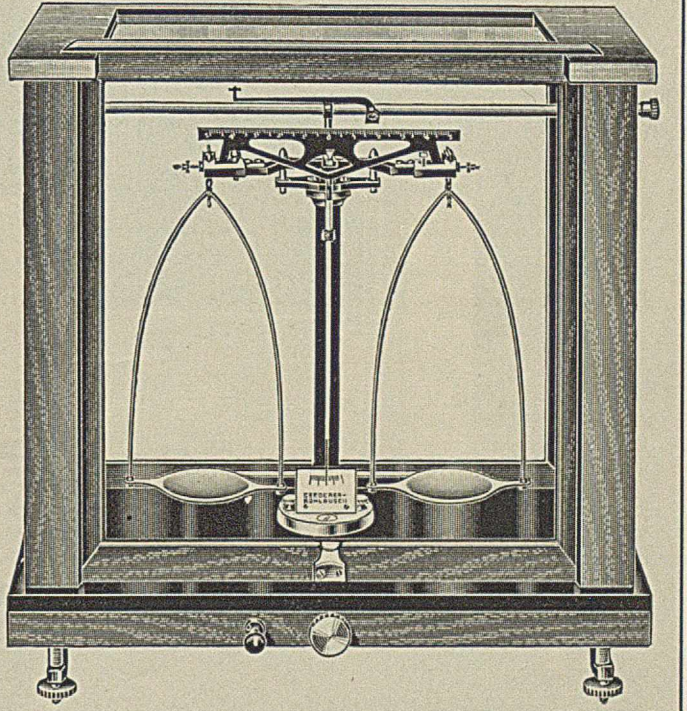
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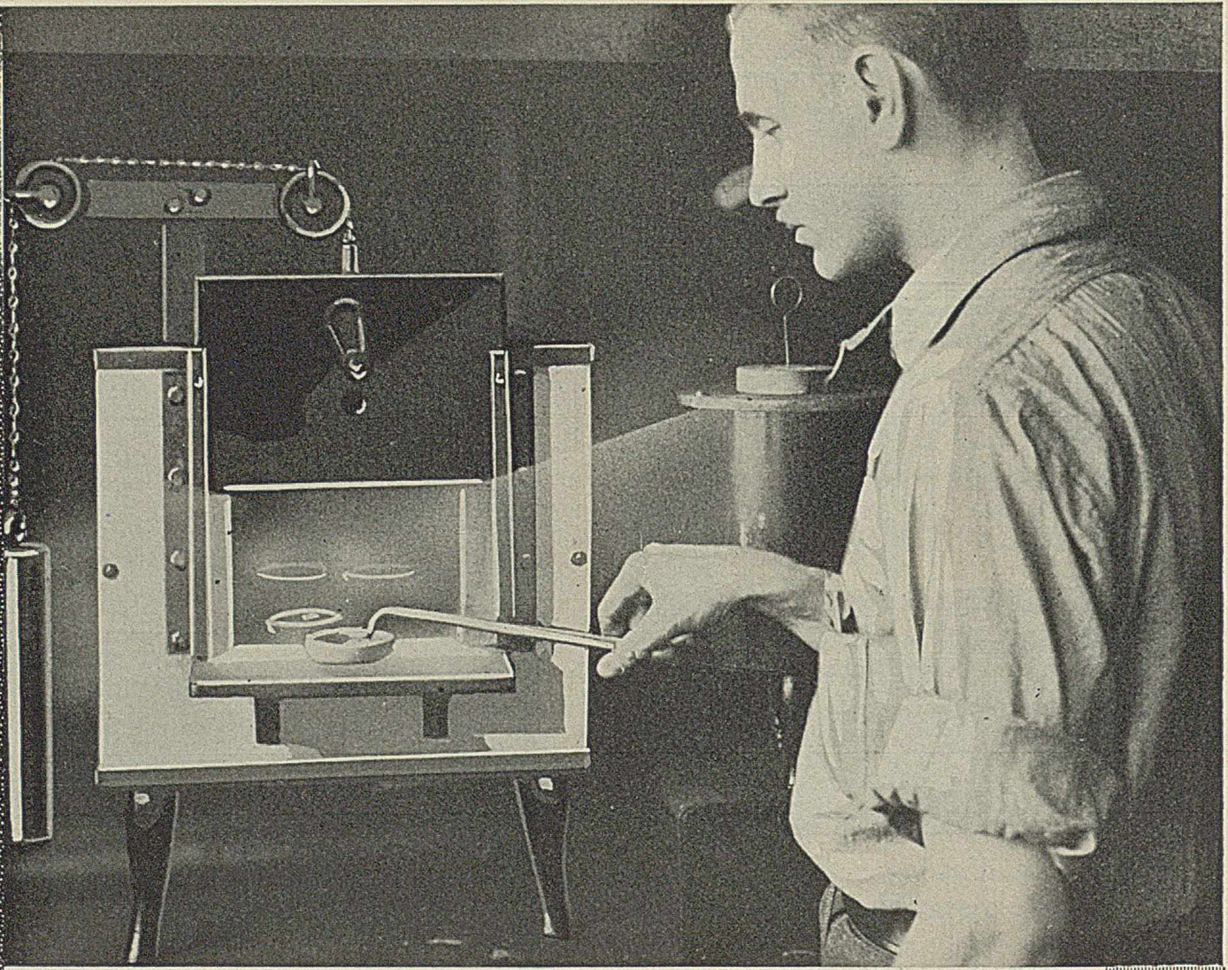

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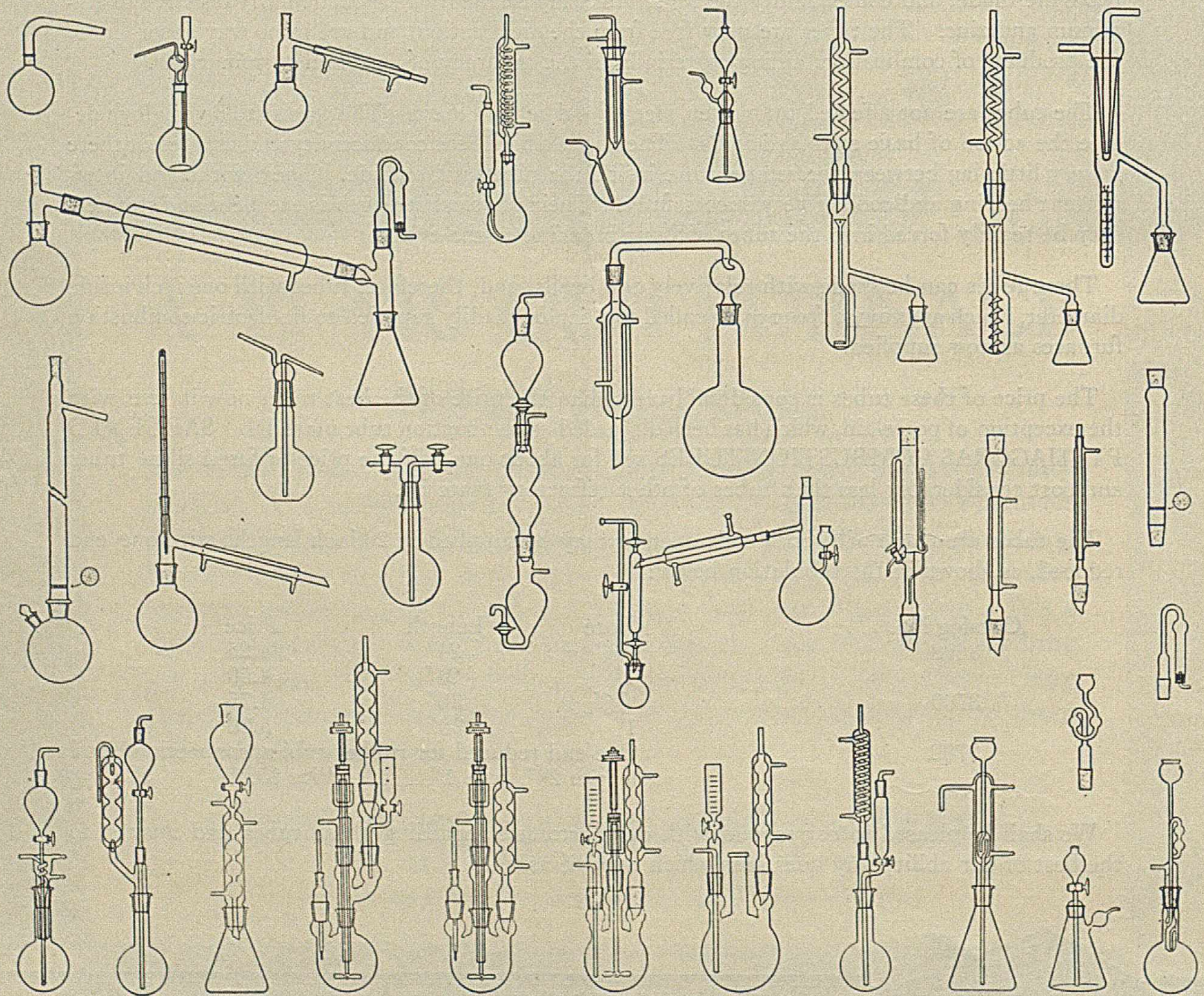

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Estimation of Diastatic Enzyme Preparations[1]

Taka-Diastase, Malt Diastase, and Pancreatic Diastase

Taichi Harada

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A method is described for the estimation of diastatic power of taka-diastase, malt diastase, and pancreatic diastase. A table for each shows Lintner's value against observed starch titrations. The starch solutions are buffered with acid potassium phthalate and sodium hydroxide solution to give more accurate results than have been previously described. A new standard unit is offered and calculated in terms of Lintner's value. The starch titration is tabulated to show the corresponding glucose content.

THE present method is a modification of Lintner's procedure (*3*), being based in principle upon the production of a definite quantity of reducing sugar by the action of a diastase upon a definite amount of Lintner's starch solution under definite conditions. Ling (*2*) has suggested a convenient modification of Lintner's method, but his calculation equation does not represent the true value since the quantity of enzyme used and the amount of sugar produced are not exactly proportional. Recently Oshima (*4*) proposed a table setting forth the relationship between Lintner's value (L. V.) and the amount of starch solution digested by the enzyme which is required to just reduce 5 cc. of Fehling's solution. Lintner's value was obtained experimentally in a series according to the original Lintner method with different strengths of diastatic solutions. In practice the calculation values from Oshima's table do not agree with the right Lintner's value when examined with a different percentage of each enzyme solution of malt and taka-diastase since his starch solution was not buffered (except with a dilute sodium hydroxide solution). The pH value of his starch solution might vary with different percentages of enzyme solution. The isoelectric point of taka-diastase has been found to be at pH 7.0.

It is very necessary to know from time to time the comparative strength of taka-diastase (*Aspergillus oryzae* diastase), malt diastase, and pancreatic diastase for the food and textile world as well as for pharmaceutical purposes in the industrial laboratory. It is also essential to establish a new standard unit for these enzymes under definite conditions. Therefore, the author presents the following method, tables, and unit devised for these three enzyme preparations to the end that more convenient and accurate results may be obtained.

Two other typical methods, those of Wohlgemuth (*7*) and of Sherman, Kendall, and Clark (*5*), are mentioned in the literature, but these are not convenient for industrial laboratory purposes for many reasons. Space does not permit a discussion of them here.

Acid Potassium Phthalate and Sodium Hydroxide Buffer Starch Solution

Twenty grams of dry soluble starch (*6*) were suspended in a little cold water in a liter beaker, then about 500 cc. of boiling water were added, and the whole boiled for 2 minutes. After cooling, 250 cc. of acid potassium phthalate and 0.2 *M* sodium hydroxide solution—150 cc. for taka-diastase, 162.5 cc. for malt, and 227 cc. for pancreatic—were added, followed by sufficient distilled water to make 1 liter. One hundred cubic centimeters of this should not completely reduce 5 cc. of Fehling's solution. This solution should be pH 5.2, as tested with chlorophenol red and methyl red. For the enzyme of *Aspergillus oryzae* (taka-diastase) this is the optimum hydrogen-ion concentration under the conditions of this method, but for malt diastase and pancreatic diastase, it should be set at pH 5.3 and 6.0, respectively (*1*).

Enzyme Solution

Exactly 0.05 to 0.5 gram, according to its strength, of finely powdered diastase is weighed out. This is first suspended in 3 to 5 cc. of distilled water in a small glass mortar, then completely dissolved by further addition of water and introduced into a 500-cc. flask by washing with distilled water until the 500-cc. mark is reached (0.01 to 0.1 per cent solutions).

Procedure and Unit

One hundred cubic centimeters of the 2 per cent Lintner's starch solution were introduced into a 150-cc. Erlenmeyer flask by means of a 100-cc. pipet. It was kept in an Ostwald thermostatic bath at 37° C. (± 0.05°) until the starch solution reached that temperature (about 30 minutes) after which 10 cc. of the enzyme solution were added and digestion carried on for exactly 30 minutes at 37° C. At the end of this time, 10 cc. of 0.25 *M* sodium hydroxide solution were added with shaking to stop further reaction. It was removed from the bath and cooled to room temperature. The total starch solution, therefore, should be 120 cc. Fehling's solution is standardized by treating 5 cc. of it with 0.5 per cent

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[1] Received June 3, 1930.

pure glucose solution drop by drop, while boiling, until the Fehling's solution becomes colorless. Five cubic centimeters of the glucose should be required. Some of the digested starch solution is transferred to a buret and gradually run into 5 cc. of the tested Fehling's solution in a test tube. The tube, held in a wire basket, is immersed in boiling water from time to time for about 10 minutes, and then the color is examined. This is continued until the solution just loses its blue color. Thus an approximate volume of the starch solution is ascertained, then the exact volume by repeating the process. When the experiment is carried out with 10 cc. of 1 per cent enzyme solution and it takes just 10 cc. of the starch solution to reduce the standardized Fehling's solution, this is taken as a new standard unit. When 0.12 gram of Lintner's enzyme preparation digested 10 cc. of 2 per cent starch solution so that just enough sugar was produced to reduce exactly 5 cc. of Fehling's solution under definite conditions, he designated this as 100 units. It has been customary to refer to this as Lintner's value (L. V.). The procedure described by the author is equivalent to 120 L. V. It is highly desirable, from a commercial standpoint, to retain the L. V. terminology. The author offers a more satisfactory method for arriving at these values.

Calculations

The enzyme solutions were prepared as follows: A sample of taka-diastase, weighing 0.118 gram and free from sugar, was dissolved in 500 cc. of distilled water. This serves as a stock solution of 0.236 per cent strength. Portions of this were further diluted with increasing amounts of distilled water to make solutions of various percentages. Each solution was treated as described above. The data are given in Table I.

Table I—Lintner's Values against Starch Titration

No. Soln.	Stock Soln. Cc.	Added Water Cc.	Strength of Starch Soln. %	Starch Soln. Required for 5 cc. Fehling's Soln. Cc.	Calcd. Value for 1% Enzyme Soln. L. V.
1	100	0	0.236	3.60	600
2	50	50	0.118	5.25	300
3	30	70	0.0708	7.40	180
4	25	75	0.059	8.50	150
5	20	80	0.0472	10.00	120
6	10	90	0.0236	15.75	60
7	10	190	0.0118	25.00	30
8	10	490	0.00472	40.00	12
9	5	495	0.00236	67.50	6

By definition, if 10 cc. of digested starch solution reduce 5 cc. of Fehling's solution, its Lintner's value is 120 provided its strength is 1 per cent. However, as shown in Table I, solution No. 5 of the enzyme solution is only of 0.0472 per cent strength. Therefore, for 1 per cent of the diastase solution, the true diastatic power of the sample diastase is

$$\begin{aligned} \text{L. V.:true L. V.} &= \text{per cent of solution:1 per cent} \\ 120:X &= 0.0472:1 \\ X &= 2542 \end{aligned}$$

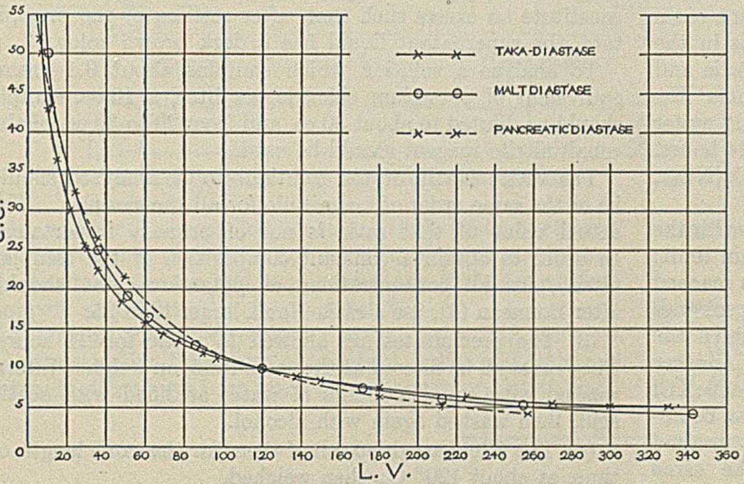
Table II—Lintner's Values of Diastatic Enzyme Preparations against the Starch Titration

Starch Titration Cc.	Taka-Diastase L. V.	Malt Diastase L. V.	Pancreatic Diastase L. V.	Corresponding Amount of Glucose %
4.30		343[a]	257[a]	
5.00	332[a]	280	224	0.5000[a]
5.25	300[a]	260	213[a]	0.4750
5.30		257.3[a]		
5.50	271[a]	240	208	0.4500[a]
5.75	254	226	198	0.4330
6.00	240	213[a]	193	0.4160
6.25	225[a]	205	187	0.4000[a]
6.50	214	197	180[a]	0.3880
6.75	203	190	174	0.3760
7.00	192	181	169	0.3625
7.25	182	176	165	
7.35				0.3500[a]
7.40	180[a]			
7.45		171.5[a]		
7.50	176	168	154	0.3380
7.75	169	162	150	0.3280
8.00	162	158	147	0.3185
8.25	155	153	143	0.3075
8.50	150[a]	146	140	0.3000[a]
8.75	143	142	136	0.2925
9.00	138[a]	137	132	0.2835
9.25	133	133	129	0.2750
9.50	129	129	126	0.2680
9.75	124	124	123	0.2615
10.00	120[a]	120[a]	120[a]	0.2550
10.20				0.2500[a]
10.25	114	114	117	0.2480
10.50	111	111	114	0.2430
10.75	108	109	111	0.2370
11.00	104	106	108	0.2320
11.25	100	103	104	0.2275
11.50	97[a]	100	101	0.2230
11.75	94	98	99	0.2180
12.00	90[a]	96	96	0.2150
12.25	88	93	94	0.2115
12.50	85	90	92	0.2070
12.75	82	88	90	0.2030
13.00	80	86[a]	88	0.2000[a]
13.25	79	84	86	0.1975
13.50	77[a]	82	85	0.1925
13.75	75	80	84[a]	0.1880
14.00	73	78	81	0.1850
14.25	70	76	80	0.1825
14.50	69[a]	74	78	0.1775
14.75	67	73	77	0.1760
15.00	65	71	75	0.1735
15.25	63	69	74	0.1710
15.50	62	68	73	0.1680
15.75	60[a]		72	0.1670
16.00	59	65	71	0.1625
16.25	57.5		70	0.1615
16.50	57	62[a]	68	0.1590
16.75			67	0.1570
17.00	54	60	66	0.1550
17.25			65	0.1525
17.50	52	58	64	0.1520
17.75			62	0.1500[a]
18.00	50	56	61	0.1480
18.25			59	0.1470
18.50	48[a]	54	60[a]	0.1450
18.75		53	58	
19.00	46	52	57	0.1415
19.25		51[a]	56.5	
19.50	45	50	56	0.1380
19.75			55	
20.00	43.5	49	54	0.1350
20.25			53	
20.50		47	52	0.1330
20.75			51	
21.00	40	46	50.5	0.1310
21.25				
21.50		44	49[a]	0.1280
21.75				
22.00	37.5		47.5	0.1260
22.25				0.1250[a]
22.50	36[a]	42		
23.00	34.5		44.5	0.1225
23.50		40		0.1210
24.00	32	38	42	0.1190
24.50			40	0.1170
25.00	30[a]	36[a]	39.5	0.1160
25.50	28.6[a]			
26.00	28	34	37	0.1140
26.50			36[a]	
27.00	26	32	34.5	0.1120
27.50				
28.00	25	30	32.5	0.1090
28.50				
29.00	23		30.5	0.1070
29.50		28		
30.00	22[a]	27	28.5	0.1030
30.50				
31.00	21	26	27	0.1010
31.50		25		0.1000[a]
32.00	19.7			0.0980
32.50			24[a]	
33.00		23	23	0.0970
33.50	18			
34.00		22	22	0.0960
34.50	17			
35.00				0.0935
36.00	16	20	20	
36.50	15[a]			0.0900[a]
37.00	14.5			0.0870
38.00		18	17	0.0850
39.00		17.2		0.0835
40.00	12		15	0.0820
41.00	11	16		0.0780
42.00			13	0.0750[a]
43.00	10[a]	14		0.0735
43.50			12[a]	
44.00				0.0725
45.00	9		10.5	0.0715
46.00		12		0.0700
47.00				0.0685
48.00	8		8	0.0670
49.00				0.0660
50.00	7.5[a]	10[a]	7	0.0645
51.00				0.0630
52.00	7		4.8[a]	0.0620
53.00				0.0600
54.00				0.0590
55.00	6.8	8.6		0.0580
65.00				0.0500[a]

[a] Experimental data.

In order to obtain the Lintner's value for 1 per cent enzyme solution for any given solutions, multiply 2542 by per cent of solution.

Table II represents complete data for the three diastases—namely, taka-diastase (A), malt diastase (B), and pancreatic diastase (C)—where the observed titration values were obtained by the above described method. The references (*a*) represent experimental data obtained by repeating with various per cent enzyme solutions. Unmarked numbers are interpolated data obtained from the curve.



Starch Titration against Calculated Values in Terms of L. V. to Per Cent Enzyme Solution

The relations between starch titration and calculated Lintner's values to 1 per cent enzyme solution of these three enzymes are also given in the figure. In testing taka-diastase, the data of Table I may also be used at 50° C. where digestion is carried on under the same conditions except that the starch solution is buffered at pH 5.4 and is made by using 250 cc. of 0.2 *M* acid potassium phthalate and 177 cc. of 0.2 *M* sodium hydroxide solution. The calculation is not altered.

In routine practice it is possible to be more economical and use more dilute buffer solutions—that is, one-fifth of the amount of each buffer solution for the starch solution. Ten cubic centimeters of 0.2 *M* sodium hydroxide solution instead of 0.25 *M* sodium hydroxide are sufficient to stop further reaction.

The last column in Table II gives the percentage of pure glucose which corresponds to the observed starch titration.

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Quantitative Determination of Potassium by Sodium Cobaltinitrite Method[1]

Pierre J. Van Rysselberge

Stanford University, Calif.

THE precipitation of potassium by the sodium cobaltinitrite reagent, studied by de Koninck (*5*), Gilbert (*4*), Adie and Wood (*1*), Cunningham and Perkin (*3*), Vürtheim (*7*), and others, has recently been thoroughly investigated by Bonneau (*2*). The difficulties of the method are reviewed in some of the bulletins of the U. S. Department of Agriculture (*8*).

Bonneau's work confirms the results obtained by Adie and Wood, who showed that the formula of the potassium-sodium cobaltinitrite is $K_2NaCo(NO_2)_6.nH_2O$. According to Bonneau, a constant composition of the precipitate (disregarding the amount of water of hydration) is obtained only if the ratio of the concentration of sodium to that of potassium is larger than 25. Below that ratio the molecule of potassium-sodium cobaltinitrite contains more potassium and less sodium than indicated by the formula given above, the composition tending towards the limiting formula $K_3NaCo(NO_2)_6.nH_2O$. The higher the temperature at which precipitation takes place, the higher the amount of potassium in the molecule. The formula found by Vürtheim is $K_{1.5}Na_{1.5}Co(NO_2)_6.nH_2O$, a result that the work of Bonneau contradicts. Gilbert gives the same formula as Vürtheim. The results of Adie and Wood and those of Bonneau show that the number of water molecules attached to each molecule of $K_2NaCo(NO_2)_6$ is usually one. According to Adie and Wood, drying the precipitate below 130° C. has a negligible influence on the final composition.

After a long series of determinations of potassium in mixed solutions of potassium and sodium chlorides, the writer was able to draw a few interesting conclusions in regard to the sodium cobaltinitrite method, which are presented here as a complement to the work of Bonneau. The reagent was the same as that used by Adie and Wood (*1*). Bonneau (*2*) used cobalt nitrate instead of cobalt acetate.

The writer usually had to determine small changes of concentration of potassium resulting from electrolytic migration (*6*). Those changes were determined by comparing the unknown samples with samples of the original solution for which the amount of potassium was known.

It was necessary to use samples having equal volumes and to add to all of them the same amount of reagent. If, moreover, the time during which the precipitates were allowed to settle was exactly the same for all the samples to be compared, satisfactory results could be obtained. The influence of the time of settling seems to have been overlooked by all the authors who investigated this method, with the exception, perhaps, of Vürtheim. He allowed the precipitates to settle for 18 hours, a time after which no increase of weight of the precipitates could be detected. Adie and Wood let the precipitates settle overnight. Bonneau speaks of "a few hours."

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[1] Received July 30, 1930.

With mixtures of potassium and sodium chlorides of a total concentration varying from 0.5 to 5 gram-equivalents per liter, the ratio of the concentration of sodium chloride to that of potassium chloride varying from 9 to 49, the writer obtained ratios of the weight of potassium–sodium cobaltinitrite to the weight of potassium varying from 5.56 to 6.43. The time of settling was at least 4 hours, and in some cases reached 66 hours; in a few exceptional cases ratios in the vicinity of 8 were obtained. The ratio given by Adie and Wood, and Bonneau, corresponding to the formula $K_2NaCo(NO_2)_6.H_2O$, is 5.81 (1:0.172), a ratio which the writer frequently obtained for a time of settling of about 24 hours. The ratio 5.58 corresponds to the formula $K_2NaCo(NO_6)$; the ratio 6.28 to the formula $K_2NaCo(NO_2)_6.3H_2O$.

In general, the weight of the precipitate increases with the time of settling and seems to tend towards a certain limit; the value of that limit and the time after which it is reached are exceedingly variable and seem to depend on the volumes of the samples, their concentration, the way in which the reagent is added, the excess of reagent used, etc. Another point noticed is that, even in the case of low NaCl:KCl ratios, high values of the ratio complex nitrite:K can be obtained. Those high ratios are evidently due to gradual hydration. Samples containing approximately the same amounts of potassium, when treated in strictly identical conditions, usually give identical ratios complex nitrite:K; sometimes, however, differences occur. They correspond as a rule to a variation of 1.3 per cent, which the writer empirically ascribes to a difference of one-third of molecule of water in the composition. Indeed, most of the results could be explained by assuming the formula $[K_2NaCo(NO_2)_6]_3.nH_2O$.

Suggested Method for Determination of Potassium

(1) The reagent is prepared according to the directions of Adie and Wood (*1*). Two solutions having, respectively, the compositions 220 grams of sodium nitrite in 440 cc. of water, 113 grams of cobalt acetate in 300 cc. of water and 100 cc. of glacial acetic acid, are mixed, thoroughly stirred, and filtered just before use.

(2) Several samples, known and unknown, are treated together in exactly the same conditions: the volumes must be the same (independently of the actual amount of potassium they contain, provided the order of magnitude be constant). The same amount of reagent is added to all of them, preferably with a pipet, stirring all the time; this amount should constitute an excess such that, after settling of the precipitate, the supernatant liquid has a dark brown color.

To analyze a solution which contains about 0.1 gram-equivalent of potassium chloride per liter, a 10-cc. sample should be diluted to about 30 cc. and from 20 to 30 cc. of the cobaltinitrite reagent should be used.

The ratios Na:K of the solutions to be analyzed should be of the same order of magnitude for all the samples. The actual value of that ratio is not of primary importance. In order to obtain a constant composition of the complex nitrite, for all concentrations of potassium, one should, after Bonneau (*2*), use a ratio Na:K larger than 25.

(3) The precipitates are allowed to settle for 24 hours. They must all be filtered at the same time, on weighed filters, washed with equal amounts of water acidified with acetic acid, then washed again with alcohol.

(4) The filters are dried, all of them for the same length of time, at about 120° C., then weighed.

(5) The ratio complex nitrite:K is deduced from the analysis of the known samples.

Very satisfactory results are obtained in this way. The accuracy of the method is 1.3 per cent, although in most cases the variations do not exceed a few tenths of one per cent.

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Micro-Absorption Tube with Mercury Seals[1]

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THE first absorption tube for organic microcombustions in the determination of carbon and hydrogen, which could be sealed, was designed by Blumer. The Blumer tube is described and discussed by Pregl (*2*). Later a micro-absorption tube was made so that the capillary ends could be sealed by drops of mercury (*1*). An objection to the Kemmerer-Hallett micro-absorption tube is the fragile nature of the ends of the tube. This objection is overcome in the new micro-absorption tube reported here (Figures 1 and 2).

Two[2] hollow glass stoppers were ground to fit the ends of a piece of Pyrex tubing about 14 cm. long and 1 cm. in diameter. The mercury trap and seal were then placed on the inside of the stopper as shown in the diagram. In this way the original straight design of the Pregl micro-absorption tube was retained.

To fill the tube, one of the glass stoppers is attached in the usual manner with Krönig's cement (*3*). A small layer of cotton (about 5 mm.) is then pressed against the stopper and the absorbing material added. This is followed by another layer of cotton and the second glass stopper is sealed to the apparatus in such a manner that the mercury traps in both stoppers occupy the same relative positions. If the Krönig cement is used correctly the ground-glass ends will be transparent. A small drop of clean mercury is then introduced into one end of the tube. This is drawn into the mercury trap by slight suction applied from the Mariotte flask. In the same manner a drop of mercury is placed in the other end. The mercury falls into the two traps, shown in Figure 1, allowing free passage of the gases during the combustion. When the tube is rotated 180 degrees, the mercury falls into the small tubing as shown in Figure 2, and thus protects the

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[2] The writer wishes to thank Arthur Shroder, director of Technical Service, Fisher Scientific Co., Pittsburgh, Pa., who had an experimental tube made for him. The apparatus can now be purchased from this company.

contents of the tube from the air. Just enough mercury is used to seal the tubes.

The tube for the absorption of water was filled with Anhydrone. Ascarite, followed by 3 to 4 cm. of Anhydrone, was used to absorb the carbon dioxide. Both tubes were kept cool during the combustion by wrapping them in wet flannel. No disadvantage resulted from having one of the sealed glass stoppers next (*4*) to the electric furnace.

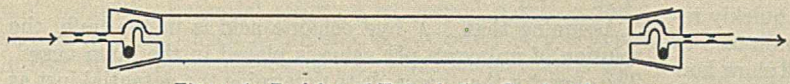

Figure 1—Position of Tube during Combustion

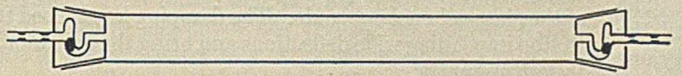

Figure 2—Tube Rotated 180° and Sealed

Following Pregl's directions exactly, but using the new micro-absorption tube, very satisfactory carbon and hydrogen determinations have been made in this laboratory for a period of 6 weeks. Practically theoretical figures can be obtained. One illustration might be of interest: 4.570 mg. (pyrogallol); 1.95 mg. H_2O, 9.583 mg. CO_2. Calcd.: H, 4.79 (8), C, 57.12. Found: H, 4.79 (2); C, 57.19.

The advantages of the micro-absorption tube here described over those already recorded are:

(1) Since both ends can be removed, the cleaning of the tube is greatly facilitated.

(2) While standing on the rack and during the weighing, the tube is sealed—yet, because of the shape it can be wiped before each weighing and handled in the manner so carefully worked out by Professor Pregl.

(3) The tube can be weighed when filled with oxygen or air.

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Hydrogen-Ion Determinations with Low-Resistance Glass Electrodes[1]

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A description is given of glass electrodes which have resistances of but 2 to 3 megohms, and are made of a commercially available glass. Such electrodes permit the use of a d'Arsonval galvanometer in hydrogen-ion estimation with fair accuracy. Their use requires little more skill than is needed with an industrial quinhydrone apparatus. Electrometers are eliminated, and electrostatic shielding becomes of little importance. Directions for construction and use of the apparatus are given.

THE estimation of hydrogen ion by standard methods becomes difficult or impossible when the solution under examination contains certain active oxidizing or reducing agents. In such situations the glass electrode invites consideration. Although this device has been known for over twenty years (*2*), it has been generally overlooked in American laboratories. Thanks largely to the recent work of MacInnes and Dole (*4*, *5*), and Elder and Wright (*1*), it is now attracting considerable attention.

A serious drawback of the glass electrode has been its very large electrical resistance. Values of 20 to 100 megohms are commonly reported in the literature. When such a device is placed in the ordinary potentiometer circuit in place of the common hydrogen or quinhydrone electrode, the current becomes too small for detection on a common galvanometer at adjustments near the null point.

A quadrant electrometer, or vacuum-tube potentiometer (*1*), is accordingly used instead of the galvanometer. More or less electrostatic shielding and special insulation are necessitated in such apparatus. In any case the exacting technic required in the use of these physical instruments is discouraging to an ordinary chemist who is seeking only an approximate estimation of pH value.

In the present work the resistance of the electrodes was cut to values from 2 to 3 megohms, the bulbs being blown thin. It was then found that Leeds and Northrup type R galvanometer, model No. 2500-f, an instrument of moderate cost, became useful. This galvanometer, while not of precision grade, has a sensitivity of 0.0001 microampere. It may accordingly be connected and used in a glass electrode apparatus in the same manner which one would employ with a quinhydrone electrode. Furthermore, since the resistance of the glass electrode is so low, static charges do not accumulate and disturb the galvanometer as they do an electrometer which by its very nature has no current "leak."

The sharpness of estimation of the null point is of course not so great as in a common potentiometer circuit in a hydrogen-ion determination. It is, however, sufficient to serve ordinary purposes, as seen in the following illustration:

Assume 3 megohms resistance, and the normal galvanometer deflection of 1 mm. for 10^{-10} amperes current. Suppose the potentiometer adjustment has come within just one millivolt of the null point. The current which is to actuate the galvanometer upon depression of the contact key is, therefore, by Ohm's law

$$\frac{0.001}{3 \times 10^6} = 3 \times 10^{-10} \text{ amperes}$$

Such a current deflects the No. 2500-f galvanometer marker 3 mm., and thus one may locate the null point to the accuracy of one millivolt with ease. This indicates a maximum error of ±0.02 pH in this part of the operation. On account of the relatively long period of the galvanometer any greater precision in estimation requires more time than one would care to take in rapid commercial work.

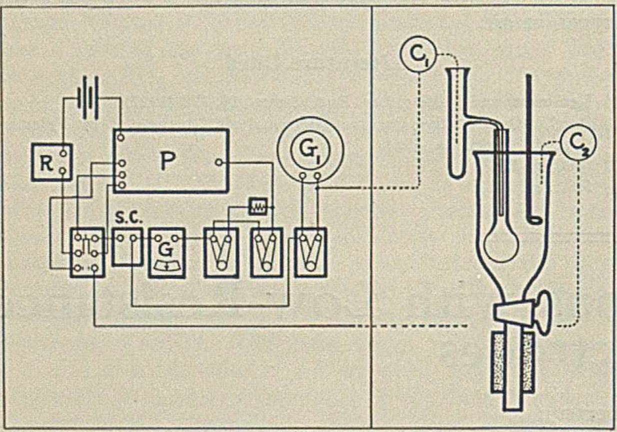
Preparation of Electrode

Corning No. 015 glass, as suggested by MacInnes and Dole (*5*), proved to be suitable for the purpose. It is obtainable from the manufacturer. A piece of 10-mm. tubing of this

[1] Received May 23, 1930.

glass, about 8 cm. long, is drawn to a tapering point in a flame. With the aid of a needle-pointed blast flame a small lump of molten glass of about 100 to 150 mg. weight is allowed to accumulate. Care is taken not to heat the glass to a temperature where gas bubbles are formed.

While the tip is at a bright red heat the tube is quickly removed from the flame and held point down. A bulb of 8 to 10 cc. volume is now blown. Experience alone will show how the air pressure may be controlled to prevent a blowout and give a very thin bulb of good mechanical strength. The writer has success when he restrains the blowing until the bulb, half blown, is getting almost too cool, and then by one hard blow stretches it to full size. This trick involves the "setting" of portions of the bulb which are already as thin as they should be, and the further spreading of other portions which are still hot enough to spread. A large part of the bulb thus becomes thin enough to conduct the electric current freely in the application to follow. Such technic will sometimes give slightly lopsided bulbs, which are nevertheless serviceable.



Apparatus for Hydrogen-Ion Determinations

After the electrode is cool, its open end is dipped momentarily into melted paraffin as deeply as may be necessary to protect the section which is to be held by a clamp on the supporting stand.

The following measurements were made of one particularly good electrode of 2 megohms resistance:

Volume of bulb section of electrode	8.5 cc.
Surface area of thin, or useful part of bulb, approx.	14 sq. cm.
Average thickness of wall	0.03 mm.
Variation in thickness	0.015 to 0.05 mm.

Arrangement of Apparatus

The whole cell and stirrer assembly, as shown in the right section of the figure, is mounted securely on one large ringstand to insure rigidity and protection of the bulb.

Calomel electrode C_1 dips into a test tube filled with dilute potassium chloride solution. The slender side stem of this test tube is filled with potassium chloride–agar jelly, and dips into the reference solution of hydrochloric acid (approx. 1 *N*) in the glass electrode. Calomel electrode C_2, presumably identical with C_1, dips into the solution under examination, placed in the main vessel. A mechanical stirrer is included.

G_1 is the type R galvanometer provided with a special tapping key used to stop the motion of the coil. This key merely serves to short-circuit the galvanometer temporarily. Some workers may prefer to include a damping resistance of from 2000 to 10,000 ohms in the key circuit, in case a retardation of the coil is desired instead of instant stoppage.

A convex lens is placed directly in front of the galvanometer mirror, and the image of a straight-line-filament incandescent lamp thus projected on an external scale.

The rest of the apparatus is Leeds and Northrup's student potentiometer outfit with slight changes in wiring to accommodate a second galvanometer.

Manipulation

Assuming that 1 *N* hydrochloric acid is in the bulb, the solution of unknown pH value is placed in the main vessel. The operator then proceeds to determine the potential just as though a hydrogen or quinhydrone electrode were in place of the glass-calomel electrode. The damping key is used freely to stop impending wide deflections and bring the galvanometer to rest promptly.

It is not advisable to attempt a calculation of pH value simply from the concentration of the hydrochloric acid and the known potential—a procedure which is correct in simple theory. Unfortunately such calculations are vitiated by glass surface potentials. The surface potential is not predictable, will change during the day, but will remain fairly constant over the few minutes required for a determination. It is thus advisable to ignore the numerical value of hydrogen-ion activity in the bulb. The plan then is to determine the potentials with three solutions: the unknown, one buffer solution of higher pH value, and one of lower. Direct linear interpolation gives a value sufficiently accurate for many industrial uses. The following example, taken from a rapid determination without thermostat or special refinement of technic, illustrates results obtainable in this manner:

A solution of commercial acid potassium phthalate (approx. 0.2 *M*), and a standard buffer solution (pH 5) were taken as unknowns. The pH value of each was estimated in reference to two standard buffers, pH 3 and pH 7. The potentials at 29° C. were as follows:

	Volt
Standard buffer pH 3	0.097
Acid potassium phthalate	0.164
Buffer pH 5	0.215
Standard buffer pH 7	0.331

Interpolation between standard buffers 3 and 7 assigns a pH value of 4.1 to the phthalate, and of 5.0 to the intermediate buffer. The apparent potential interval per pH unit between 3 and 5 was 0.059, and between 5 and 7 was 0.058.

Precautions

The three determinations of potential required in the estimation of a pH value should be run off in rapid succession. In such a case the glass potential will be constant, and can be ignored in calculation, as only the concentration potential will enter into the numerical values gotten by interpolation.

Furthermore, the electrode should not be subjected to any unusual disturbance at or near the time of the potential measurements. This advice means constancy in temperature as a prime requirement. Apparently sudden changes in temperature not only cause the small changes in potential called for by electrometric theory, but also may stimulate glass potential drift of unknown magnitude. It is not advisable to permit the electrode to come in contact with a very concentrated acid or alkali at a time near that of a regular series of three measurements. Undoubtedly the most accurate performance of this apparatus will come in a situation where pH measurements are made continuously in one fairly narrow region; where the electrode does not come into contact with a changing variety of electrolytes; and where temperatures are constant within a half degree or better.

Polarization

It was feared that an attempt to draw enough current from a glass electrode to actuate an energy-consuming instrument such as a galvanometer would polarize the electrode and throw potential readings astray. Experiments have shown, however, that no measurable error is recorded even after the contact key has been closed for a full minute, unless the potentiometer is set much more than 20 millivolts off the null point. Even when the setting was as much as 100 millivolts off the null point the potential returned to normal within a few seconds of rest. Such abuse should not occur in practice; in fact, it would actually send the galvanometer marker entirely off the scale, twist the suspension, and require a new zero setting. It is likely that the increase in conductivity provided in these electrodes has brought an increase in resistance to polarization with a given current flow.

It was noted, however, that in cases where the electrode was polarized with large currents it did not return to normal potential as rapidly as would a quinhydrone electrode. Obviously one should avoid long periods of key contact.

Silver–Silver Chloride Electrodes

Some workers may prefer to use the silver chloride electrode in place of the calomel electrodes here described. In this way one might eliminate the potassium chloride–agar bridge which, though simple and easy to prepare, is not permanent. The silver electrode would be placed directly in the glass electrode bulb. Details of the silver electrodes have been given by MacInnes and Beattie (*3*) and MacInnes and Dole (*4*).

Acknowledgment

The writer wishes to thank James B. Conant, and also the Corning Glass Company, for suggestions and materials in connection with this work.

Note—Since the writing of the foregoing account, an abstract [*C. A.*, **24**, 4188 (1930)] has been published giving a report of the work of C. Morton with glass electrodes of character similar to those described above, but with different electrical accessories and technic.

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Methods for Determining the Solubilities of Some Fluosilicates[1]

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THE fluosilicates have recently attracted considerable attention due to their use as insecticides and fungicides, in waterproofing and hardening concrete, in electroplating, etc. However, quantitative data in connection with these substances are not numerous and usually of questionable accuracy. Carter (*2*) has recently published the solubility curves for barium, potassium, and sodium fluosilicates, together with a compilation of all available solubility figures on the fluosilicates. Methods of analysis, likewise, are not all that might be desired.

This paper presents the solubilities and densities, both at 20° C., of the fluosilicates of sodium, magnesium, zinc, lead, and copper. It includes also a brief discussion of the analytical methods.

Apparatus

The apparatus deemed most suitable for the purpose was that of Bahr (*1*). The air used for stirring was first passed through a mercury pressure regulator, by which the rate of flow was maintained constant at 4 bubbles per second. Thence it passed in succession through three Drechsel gas-washing bottles (equipped with petticoat bubblers) containing sodium hydroxide solution, water, and the solution being saturated. Tests showed that the air current produced no decomposition of the fluosilicates above that taking place when the air stream was stationary. Saturator and pycnometer were arranged exactly as described by Bahr, save that a single three-way cock was used in place of two ordinary cocks. A small test tube equipped with an air vent was attached to the pycnometer so as to catch the overflow produced during filling. The whole apparatus was connected by means of ground-glass joints covered with rubber tubing and was completely immersed in an automatic thermostat adjusted to ±0.5° C. No leakage through the submerged joints was observed at any time. A small filter of packed asbestos fiber was formed in a conical tube inserted between saturator and pycnometer. The solutions, after passing the filter, were always absolutely clear. A Sprengel pycnometer of about 6.8 cc. capacity was used. All weights and volumetric apparatus were carefully calibrated. Nearly saturated solutions were made in a flask before placing in the saturator. At least 2 hours were allowed to elapse before the first sample was removed from the saturator. Successive samples never showed any trend in analysis.

Analytical Methods

The fluosilicates have the general formula $Met(SiF_6)$. The water of crystallization varies from 0 to 6 molecules. They are efflorescent and also decompose slowly, especially those of the heavy metals.

They are all decomposed rapidly by hot sulfuric acid and by hot sodium hydroxide as follows:

$$MetSiF_6 + H_2SO_4 = MetSO_4 + SiF_4\uparrow + 2HF\uparrow \quad (1)$$
$$MetSiF_6 + 4NaOH = 4NaF + 2H_2O + SiO_2\downarrow + MetF_2 \quad (2)$$

The first reaction is quantitative and the second may or may not be, depending on the extent of hydrolysis, etc.

Hydrolysis is very slight in the case of the alkali fluosilicates, but more marked with the others—e. g., $MgSiF_6$.

$$MgSiF_6 + 2H_2O = Mg(OH)_2\downarrow + 2H_2SiF_6 \quad (3)$$
$$H_2SiF_6 + 6NaOH = 6NaF + SiO_2\downarrow + 4H_2O \quad (4)$$

Since the methods of analysis used are based on Reactions 1 and 2, it is obvious that hydrolysis will occasion an error in the results when Reaction 2 is used. Reaction 2 requires 4 mols of alkali per mol of fluosilicate whereas Reaction 4 requires 6 mols. Hence volumetric methods of estimation

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[1] Received August 29, 1930. Abstracted from a thesis submitted by Katherine K. Worthington in partial fulfilment of the requirements for the degree of master of science in the Graduate School of the University of Maryland.

for fluosilicates that hydrolyze must be viewed with suspicion. The degree of hydrolysis varying with temperature and concentration, it is obvious that variable results are likely to be observed. This accords exactly with the writers' experience.

When the fluosilicates of amphoteric substances are studied, volumetric methods become still more dubious. Consider $ZnSiF_6$:

$$ZnSiF_6 + 4NaOH = ZnF_2 + 4NaF + 2H_2O + SiO_2\downarrow \quad (5)$$
$$ZnF_2 + 2H_2O = Zn(OH)_2\downarrow + 2HF \quad (6)$$
$$HF + NaOH = NaF + H_2O \quad (7)$$
$$Zn(OH)_2 + 2NaOH = Na_2ZnO_2 + 2H_2O \quad (8)$$

The extent to which Reactions 6 and 8 proceed depends on temperature, concentration, and H-ion concentration.

For these reasons the first method of analysis was used with zinc, lead, and copper fluosilicates. The sample of fluosilicate was heated to vigorous fuming with sulfuric acid containing a little nitric acid. No trace of silica was observed after this treatment. When cool, the trace of iron usually present was precipitated with ammonium hydroxide and filtered off, thus leaving a pure metal sulfate solution for appropriate analysis.

Owing to hydrolysis, free acid figures on the salts are not particularly valuable except to show the magnitude.

The method used by the writers, that of Jacobson (*4*), consists in adding ice and an excess of potassium chloride, then titrating with sodium hydroxide.

$$H_2SiF_6 + 2KCl = K_2SiF_6 + 2HCl \quad (9)$$
$$HCl + NaOH = NaCl + H_2O \quad (10)$$

Phenolphthalein was used as indicator with sodium and magnesium fluosilicate and methyl red with zinc fluosilicate.

Preparation and Analysis of Salts and Data

HYDROFLUOSILICIC ACID—This was a very pure and concentrated acid obtained as condensate from the gas tunnel from the hot dens of a phosphate rock acidulating plant.

SODIUM FLUOSILICATE—This salt was prepared in two ways:

(1) Nearly the theoretical amount of the purest sodium chloride was added to a solution of fluosilicic acid containing 100 grams of the acid per liter. Precipitation was immediate. To prevent the formation of a gel, the mother liquor was filtered off immediately and the crystals were washed with cold water on the filter. They were then dried at room temperature.

(2) The procedure was the same as under (1) save that acid sodium carbonate was added slowly.

The crystals made by the first method analyzed 100.05 per cent Na_2SiF_6, those by the second method, 99.41 per cent. Crystals made by the first method were used in the solubility determinations. They were fine, white, and opaque. No free acid was found. The solution was titrated hot with sodium hydroxide, using phenolphthalein as indicator. Carter (*2*) found 0.690 per cent (by interpolation from his table).

The results on this and the other salts will be found in Table I. Each value represents the mean of from four to thirteen determinations.

Table I—Solubilities of Some Fluosilicates at 20° C.

SALT	SPECIFIC GRAVITY 20°/4° C.	SOLUBILITY	AV. DEVIATION FROM MEAN
		%	%
Na_2SiF_6	1.0054	0.733	±0.002
$MgSiF_6.6H_2O$	1.2395	37.94	±0.29
$ZnSiF_6.6H_2O$	1.4336	49.94	±0.23
$PbSiF_6.4H_2O$	2.4314	81.90	±0.1
$CuSiF_6.4H_2O$	1.6174	59.08	±0.11

MAGNESIUM FLUOSILICATE—A very pure commercial product was used as the source of this salt. Recrystallization did not improve the purity. The salt was made by dissolving magnesite in a slight excess of dilute fluosilicic acid, evaporating at 77° C. with agitation, allowing the silica to settle out, and crystallizing at 41° C. under reduced pressure. The crystals were dried in a rotary drier. The salt analyzed 101.53 per cent $MgSiF_6.6H_2O$. The free acid was found to be 0.83 per cent. Magnesium fluosilicate forms large, water-clear crystals. Its saturated solution is slightly viscous. Although hydrolysis is not excessive, the fluosilicic acid and magnesium hydroxide are quite gelatinous and make filtration difficult.

The solutions were analyzed volumetrically in the same way as the sodium fluosilicate solutions. As a check magnesium was determined gravimetrically as the pyrophosphate according to the method described by Scott (*5*).

The volumetric results are so much more concordant that it seems safe to accept them as final. The tediousness of the gravimetric method is probably responsible for the differences observed. Only the volumetric results are given.

ZINC FLUOSILICATE—The zinc fluosilicate likewise was a very pure commercial product. It was made in the same manner as the magnesium fluosilicate, except that zinc oxide was used instead of magnesite. The analysis was 95.58 per cent $ZnSiF_6.6H_2O$. The crystals contained 0.79 per cent free acid. The crystals in appearance resemble those of the magnesium salt. The saturated solution is quite viscous. However, filtration is relatively easy, since the hydrolysis products are not very gelatinous.

For reasons already advanced, the volumetric method of analysis is not feasible with this salt. The zinc was therefore precipitated as $ZnNH_4PO_4$ in neutral solution and ignited and weighed as the pyrophosphate. The method of Fales and Ware (*3*) was used on several samples and found to give results identical with the pyrophosphate method. The data given are based on the latter method.

LEAD FLUOSILICATE—This salt was prepared by adding about 10 per cent less than the theoretical amount of red lead to a dilute fluosilicic acid solution. Strong acid produces too much decomposition of the salt because of the excessive rise in temperature. Silica and lead dioxide are formed in the reaction and must be filtered off. The solution so formed was allowed to crystallize at room temperature. The crystals analyzed 99.96 per cent $PbSiF_6.4H_2O$. This high purity was probably due to the insolubility of lead fluoride.

Lead fluosilicate is the most unstable of all those studied. Slow thermal decomposition proceeds even at room temperature. In consequence the dry salt and its solutions are very corrosive. The crystals are large, clear, and highly refractive. If allowed to stand exposed to the air, they become opaque. The saturated solution is very viscous and hydrolyzes slowly on standing, with the formation of an opaque, white precipitate.

Volumetric methods cannot be used in the analysis of these solutions, so the lead was precipitated as the chromate according to Scott (*5*). When the saturated solution was diluted, a precipitate formed which was cleared up with nitric acid.

COPPER FLUOSILICATE—This salt was prepared in four different ways:

(1) 10 per cent fluosilicic acid solution plus about 10 per cent less than theoretical C. P. cupric oxide.

(2) Same as (1) but using C. P. basic copper carbonate.

(3) and (4) Same as (1) and (2) but using 30 per cent acid.

Recrystallization of the product formed by each one of the four methods gave crystals identical in all their properties. Crystallization and drying were carried out at room temperature. The crystals are a clear, sparkling blue and are quite efflorescent. They must be preserved in a carefully stoppered bottle. The saturated solution is viscous. The crystals used analyzed 99.95 per cent $CuSiF_6.4H_2O$. Copper was determined iodometrically according to Scott (*5*).

Acknowledgment

Thanks are due to G. C. Connolly for advice and supervision during the progress of this work and to the Davison Chemical Company for the use of their analytical laboratory.

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Device for Estimation of Density of Gems and Small Amounts of Solids[1]

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IT IS frequently eminently desirable to determine rapidly the density or specific gravity of small amounts of solids too minute to be determined by the more usual methods available to the investigator. The device to be described is particularly adapted for the determination of the density of extremely small quantities of substances, cut gems, and small mineral crystals or fragments.

There are several methods available for the determination of the density or specific gravity of solids (*4*). These involve the use of: (1) the chemical balance, (2) the pycnometer, (3) heavy liquids and the Westphal balance, and (4) the Jolly balance.

These methods, with the possible exception of the third, are not adaptable to small amounts of solids. The use of heavy liquids is time consuming and the limit of accuracy seems to be 0.03 (*5*). Furthermore many substances are encountered with a higher density than the heaviest liquid obtainable. The use of a wax and red lead float or the use of clips with small specimens is not compatible with accuracy (*7*). Caley (*1*) has perfected an ingenious instrument for the determination of densities that is both accurate and rapid, but not adaptable for substances lighter than the displacing liquid nor specimens it is not desirable to crush, as in the case of gems.

The principle of this device is relatively simple. A narrow tube is filled with a suitable liquid to a mark on a side capillary tube. The sample is inserted in the liquid, and more liquid added from a weight buret to bring the liquid level with a second mark on the capillary tube. The weight of liquid required to fill the instrument from the lower mark to the higher one is previously determined. By subtracting the weight of liquid required to bring the volume from the first to the second mark when the sample is in the tube, from the weight required when the instrument is empty, gives the weight of liquid displaced by the specimen. Since the density of the liquid is known the volume of the specimen can be obtained by a simple calculation, and this value divided into the weight of the specimen gives the desired density.

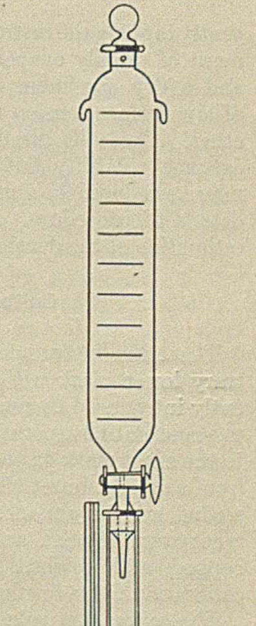
The method is simple, relatively rapid, and quite accurate.

Description of Instrument

The device is constructed of glass and is 12.0 cm. in height with an internal diameter of 0.6 to 0.8 cm. The base may be a glass or wooden block with a single hole large enough to hold the inserted tube upright. The capillary tube has an internal diameter of 1.0 mm. and should widen gradually to the point of attachment to the main body of the instrument to prevent the inclusion of air bubbles when the instrument is being filled with liquid. It is important that the internal diameter of the capillary shall not exceed 2.0 mm. or be smaller than 1.0 mm. A larger diameter means loss of accuracy when the specimen is very small while a smaller diameter leads to difficulties due to the inclusion of air bubbles when filling the instrument. The capillary should rise to a considerable height, 3.0 to 4.0 cm., above the highest liquid level in order that loss of liquid by evaporation and consequent loss in accuracy may be reduced to a minimum. It has been found by experiment that loss due to evaporation in the capillary under these conditions is negligible over short periods of time. A small weight buret was designed for the instrument bearing in mind several advantages mentioned by Friedman and LaMer (*3*). However, any weight buret of small size is adaptable to this instrument. It is essential that the buret be fitted with a glass cap and the ground surface for the cap should securely fit the top of the instrument to prevent any loss by evaporation when using very volatile liquids for displacement.

Displacement Liquids

Water may be used as the displacement liquid for relatively large specimens. In this case the capillary should be at least 1.5 mm. in internal diameter to prevent the inclusion of minute air bubbles. With very small specimens the high surface tension of water causes errors due to the inclusion of air bubbles on the surface and between the particles of solid sample. The most satisfactory displacement liquid is ethyl ether but correct results are obtained only by careful attention to the proper method of using the apparatus. With ethyl ether any minute air bubbles adhering to the surface of the specimen may be readily liberated by



Device for Estimation of Density of Gems and Small Amounts of Solids

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[1] Received September 19, 1930.

Table I—Estimation of Densities of Several Semi-Precious Gems

SAMPLE	DISPLACED ETHER		DENSITY	
	Weight	Volume	Found	Pycnometer
Grams	*Gram*	*Cc.*		
BERYL, AQUAMARINE: RUSSIA				
2.1318	0.5721	0.7957	2.68	
	0.5700	0.7928	2.69	
	0.5760	0.8011	2.66	
	0.5743	0.7987	2.67	
			Av. 2.68	2.68
BERYL, AQUAMARINE: BRAZIL				
1.1730	0.3183	0.4427	2.65	
	0.3152	0.4384	2.68	
	0.3177	0.4419	2.65	
	0.3197	0.4446	2.64	
			Av. 2.66	2.65
TOURMALINE: JAPAN				
1.9470	0.4553	0.6332	3.07	
	0.4546	0.6323	3.08	
	0.4578	0.6367	3.06	
	0.4598	0.6395	3.04	
			Av. 3.06	3.06
APPLICABILITY OF METHOD TO SMALL QUANTITIES OF SAMPLE				
BERYL, AQUAMARINE: RUSSIA				
0.3467	0.0943	0.1312	2.64	
	0.0932	0.1296	2.68	
	0.0958	0.1332	2.60	
	0.0936	0.1302	2.66	
			Av. 2.65	2.68
BERYL, AQUAMARINE: BRAZIL				
0.1864	0.0519	0.0722	2.58	
	0.0507	0.0705	2.64	
	0.0498	0.0693	2.69	
	0.0505	0.0702	2.66	
			Av. 2.64	2.65
TOURMALINE: JAPAN				
0.1191	0.0283	0.0394	3.02	
	0.0278	0.0387	3.08	
	0.0287	0.0399	2.98	
	0.0280	0.0389	3.06	
			Av. 3.04	3.06

gently tapping the instrument. Ethyl ether has the additional merit of rapidly evaporating, leaving a dry, clean apparatus and a dry specimen. Alcohol, benzene, and other liquids of low surface tension may be substituted for the use of the ether. The chief disadvantage of the use of ether lies in its extreme volatility but the errors incident to this property may be reduced to a minimum by proper attention to a few details of procedure. The use of ether permits the direct estimation of the density of most water-soluble salts.

Calibration of Instrument

The clean instrument is filled to slightly above an arbitrary lower mark with ether. The liquid is most conveniently introduced by means of a pipet. The device is allowed to stand until evaporation has reduced the level of the liquid to the exact mark on the capillary. Next ether is introduced from a weight buret till the liquid rises in the capillary to a second arbitrary mark. The marks on the author's instrument were 4.5 cm. apart. The buret is removed, quickly capped, and weighed. The loss in weight of ether is the calibration value for the particular temperature.

The calibration value is also to be determined with a lead clip in the instrument. This clip may subsequently be used to submerge specimens lighter than ether.

Method of Procedure

If the solid material is in the form of a powder, suitable fragments are selected for the determination with a forceps. In the case of a mineral the specimen is crushed and suitable fragments likewise selected. In the case of metals or alloys clippings or turnings may be used. Cut or massive gems require no sampling. Too fine powders are to be avoided since they give rise to errors from the inclusion of minute air voids between the individual particles of powder. Substances lighter than ether must be in a coherent mass so that a lead clip may be attached.

Table II—Estimation of Densities of Several Crystallized Minerals

SAMPLE	DISPLACED ETHER		DENSITY	
	Weight	Volume	Found	Pycnometer
Grams	*Gram*	*Cc.*		
CASSITERITE: BOHEMIA				
4.4516	0.4594	0.6389	6.97	
	0.4602	0.6401	6.95	
	0.4611	0.6413	6.94	
	0.4590	0.6384	6.97	
			Av. 6.96	6.96
CORUNDUM: CANADA				
3.9721	0.7206	1.0023	3.96	
	0.7211	1.0029	3.96	
	0.7200	1.0014	3.97	
	0.7197	1.0010	3.97	
			Av. 3.97	3.96
ORTHOCLASE: MONTANA				
3.1673	0.8916	1.2401	2.55	
	0.8914	1.2398	2.55	
	0.8926	1.2414	2.55	
	0.8920	1.2406	2.55	
			Av. 2.55	2.55
APPLICABILITY OF METHOD TO SMALL QUANTITIES OF SAMPLE				
CASSITERITE: BOHEMIA				
0.3015	0.0310	0.0431	7.00	
	0.0314	0.0437	6.90	
	0.0312	0.0434	6.95	
	0.0312	0.0434	6.95	
			Av. 6.95	6.96
CORUNDUM: CANADA				
0.2143	0.0391	0.0544	3.94	
	0.0388	0.0540	3.97	
	0.0379	0.0527	4.07	
	0.0390	0.0542	3.95	
			Av. 3.98	3.96
ORTHOCLASE: MONTANA				
0.1569	0.0449	0.0624	2.51	
	0.0447	0.0622	2.52	
	0.0440	0.0612	2.56	
	0.0442	0.0615	2.55	
			Av. 2.54	2.55

Table III—Estimation of Densities of Several Cut Gems

SAMPLE	DISPLACED ETHER		DENSITY	
	Weight	Volume	Found	Clerici's soln. (*2*)(*6*)
Grams	*Gram*	*Cc.*		
SAPPHIRE				
0.4003	0.0710	0.0987	4.06	4.03
TOPAZ				
0.5583	0.1121	0.1559	3.58	3.54
LAZURITE				
2.5063	0.7479	0.1040	2 41	2 41
RHODONITE				
2.0463	0.3945	0.5487	3.73	3.68

Table IV—Applicability of Method to Extreme Small Quantities of Various Substances

SAMPLE	DISPLACED ETHER		DENSITY	
	Weight	Volume	Found	Pycnometer
Gram	*Gram*	*Cc.*		
POTASSIUM CHLORIDE				
0.0600	0.0216	0.0300	2.00	
	0.0218	0.0303	1.98	
	0.0218	0.0303	1.98	
			Av. 1.99	1.98
SODIUM CHLORIDE				
0.0500	0.0166	0.0231	2.17	
	0.0159	0.0221	2.26	
	0.0162	0.0225	2.22	
			Av. 2.22	2.17
COPPER WIRE				
0.0800	0.0064	0.0089	8.99	
	0.0065	0.0090	8.88	
	0.0066	0.0092	8.70	
			Av. 8.86	8.93
CORK				
0.2098	0.6040	0.8401	0.25	0.24[a]

[a] Density of cork determined by chemical balance.

The sample being in readiness and weighed the instrument is filled with ether to the first mark by means of a pipet. The sample is quickly dropped in the instrument and the weight buret inserted. Ether is added from the buret till the liquid in the capillary rises to the second mark. The instrument is gently tapped to bring any air bubbles to the surface, and a final adjustment of levels is made. The buret is immediately removed, the stopper turned, the buret capped, and weighed. The whole operation should be performed quickly. The loss in weight of the buret, subtracted from the calibration value, gives the weight of ether displaced by the specimen. Dividing the weight of displaced ether by its density of 0.719 gram per cubic centimeter gives the displaced volume of the specimen and a simple calculation serves to give the required density.

Temperature corrections for the expansion of the glass tube over the ordinary range of working temperatures is not required as it is less than the other errors involved.

Results

The results obtained on various substances are shown in Tables I to IV. The values by the pycnometer method were determined at 15° C. on large samples of the same material as used for the other determinations. The determinations by the ether method were done at approximately 15° C. Clerici's solution was used as a check in the case of the cut gems, the same gem being used in both determinations.

No difficulty was experienced in checking against the pycnometer in the case of the larger samples.

In the case of the cut gems the values do not check quite so closely but the ether method result is probably the one nearest to the actual value.

The individual determinations of the extremely small samples vary more from the true value than do those in which a larger volume of liquid is displaced, but the average value of a series is generally quite satisfactory.

The result with cork, noted on Table IV, shows that substances lighter than ether give concordant checks with the values obtained by other procedures.

The applicability of this method to large and small samples, and to substances lighter than the displacing liquid is very satisfactory. The procedure is rapid and the results obtained check with those obtained by other methods.

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Arc Spectrographic Estimation of Chromium in Ruby[1]

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The persistence of the arc spectral lines of chromium as conditioned by concentration of the element has been studied in the range between λλ 5785.8 and 3120.4 Å. The study was extended to chromium in a mixture of fused chromic oxide and alumina, and it was observed that the sensitivity of the spectral reaction was much greater in the case of chromium in fused alumina than in the case of chromium when arcked as chromic acid. The method was applied to the estimation of chromium in rubies.

BECAUSE synthetic rubies are colored red by the addition of from 2 to 4 per cent chromic oxide, it has been assumed that the color of natural rubies is also due to this substance. The presence of chromium in rubies has long been known (*2*); it is also known that there is not as much chromium in the natural gem as there is in the synthetic. According to Wöhler and Kraatz-Koschlau (*9*) the chromium in natural rubies is analytically not determinable, as it is present in very small amounts. Doelter (*1*) also states that the amount of chromium in natural rubies is so small that it cannot be determined quantitatively. Wild and Klemm (*8*) examined the emission spectra of rubies from Siam and Montana, using a carbon arc, and compared them with that of a synthetic ruby. They found that while all of them showed lines due to chromium, the synthetic ruby contained more chromium than natural ones, as evidenced by more intense lines. They report that the chromium lines λλ 3593.5 and 3578.7 Å. were missing in the spectrogram of the Siam ruby, and λ 2653.7 A. was missing in the spectrograms of the rubies from Siam and Montana.

In the present investigation, an arc spectrographic method was adopted to estimate the amount of chromium in naturally occurring rubies. The experimental procedure has been described elsewhere (*5*, *6*, *7*), and will be outlined only briefly here.

Persistence of Arc Spectral Lines of Chromium

A solution was prepared containing 1.923 grams of chromium trioxide in 100 cc. of aqueous solution. This was analyzed by titration with 0.1 *N* potassium permanganate and $FeSO_4.(NH_4)_2SO_4.6H_2O$ in the usual way and was found to contain 0.0099 gram of chromium per cubic centimeter. Because the error was only 1 per cent of the intended amount, and because the subsequent dilutions would make it still more negligible, the value 0.0099 gram was designated as 0.01 gram of chromium per cubic centimeter. This solution was diluted in volumetric flasks to give a series of solutions containing, respectively, 0.01, 0.001, 0.0001, 0.00001, and 0.000001 gram of chromium per cubic centimeter. A one-tenth cubic centimeter sample of each of these solutions, measured from a calibrated capillary pipet, each sample containing, respectively, 1.0, 0.1, 0.01, 0.001, and 0.0001 milligram of chromium, was subjected to arc spectral excitation between graphite electrodes 7 mm. in diameter, on 110-volt direct current, using about 600 watts. The lower electrode was made the anode, and the samples were placed thereon. The spectrograph employed was of the Littrow auto-collimating type, fitted with a 30-degree quartz prism, and the spectra were photographed on d. c. ortho plates.[2]

Chromium yields a large number of arc lines in the optical spectral range that decrease in intensity and persistence with diminishing amounts of the element under excitation. The most sensitive of these lines between λλ 5785.5 and 3120.4 Å., with their persistence at varying concentrations, are listed in Table I. In this table, (v) is used to designate that a line is visible, (f) that it is faint, and (vf) that it is very faint. For the purpose of spectrographic estimation of small quantities the following lines were found most suitable: λλ 5208.4,

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[1] Received August 22, 1930.

[2] Made by Eastman Kodak Company, Rochester, N. Y.

5206.0, 5204.6, 4626.2, 4622.5, 4619.5, 4616.1, 4613.3, 4546.0, 4544.6, 4540.7, 4535.7, 4530.7, 4289.7, 4274.8, 4254.3, 3605.3, 3593.5, and 3346.7 Å.

Table I—Persistence of Arc Spectral Lines of Chromium

	Milligrams of Chromium as CrO_3			
λ	1.0	0.1	0.01	0.001
5785.8 5785.0 5783.9 5783.1 5781.8 5781.2	v			
5409.8	v			
5348.3	v	f		
5345.8	v	f		
5328.3	v	f		
5300.7	v	f		
5298.3 5297.3 5296.7	v	f		
5265.7	v	f		
5264.2	v	f		
5208.4	v	v	f	
5206.0	v	v	f	
5204.6	v	v	f	
4652.2	v	v	vf	
4646.2	v	v	vf	
4626.2	v	vf		
4622.5	v	vf		
4619.5	v	vf		
4616.1	v	vf		
4613.3	v	vf		
4546.0	v	vf		
4544.6	v	vf		
4540.7	v	vf		
4535.7	v	vf		
4530.7	v	vf		
4371.3	v	v		
4363.1	v	v		
4351.8 4351.1	v	v		
4344.5	v	v		
4339.7 4339.5	v	v		
4337.6	v	v		
4289.7	v	v	v	f
4274.8	v	v	v	f
4254.3	v	v	v	f
3976.7	v	v		
3969.8	v	f		
3963.7	v			
3941.5	v			
3928.7	v			
3921.0	v			
3919.2	v			
3916.3	v			
3908.8	v			
3894.1	v			
3743.9 3743.6	vf			
3639.8	v	vf		
3636.6	v	vf		
3605.3	v	v	vf	
3593.5	v	v	vf	
3578.7	v	v		
3433.6	v	v		
3346.7	v	v	vf	
3132.1	v	v		
3120.4	v	v		

Arc Spectrographic Estimation of Chromium in Synthetic Rubies

In order to duplicate the conditions under which the natural rubies were to be examined, a number of synthetic rubies were prepared as follows:

An aqueous solution of ammonium chromium alum was prepared, containing approximately 0.01 gram of chromium per cubic centimeter. Definite portions of this solution (10, 5, and 0.5 cc.) were added to 44-gram portions of ammonium alum dissolved in water. The ammonium chromium alum solution was further diluted, and of this new solution, containing approximately 0.0001 gram of chromium per cubic centimeter, a 5-cc. and 0.5-cc. portion were added to 44-gram portions of ammonium alum dissolved in water. These amounts were calculated to yield rubies containing 2, 1, 0.1, 0.01, and 0.001 per cent chromium. The combined hydrous oxides of aluminum and chromium were then precipitated from each of the five mixtures by means of ammonium hydroxide, were filtered off, washed free of sulfate, and were ignited to aluminum oxide and chromic oxide. The hydrous oxides were precipitated together to ensure an intimate mixture with consequent uniformity of composition in the rubies.

Table II—Chromium Content of Synthetic Rubies

No.	Color	Chromium Determined
		%
1	Deep purplish red	1.84
2	Deep red	0.944
3	Pale pink	0.092
4	Very faint pink	0.009
5	White	0.0009

Table III—Persistance of Arc Spectral Lines of Chromium in Fused Alumina

	Milligrams of Chromium (as Cr_2O_3) in Fused Alumina			
λ	0.06	0.006	0.0006	0.00006
5785.8 5785.0 5783.9 5783.1 5781.8 5781.2	v			
5409.8	v			
5348.3	v	f		
5345.8	v	f		
5328.3	v	f		
5300.7	v	f		
5298.3 5297.3 5296.7	v	f		
5265.7	v	f		
5264.2	v	f		
5208.4	v	v	f	
5206.0	v	v	f	
5204.6	v	v	f	
4652.2	v	v	vf	
4646.2	v	v	vf	
4626.2	v	vf		
4622.5	v	vf		
4619.5	v	vf		
4616.1	v	vf		
4613.3	v	vf		
4546.0	v	vf		
4544.6	v	vf		
4540.7	v	vf		
4535.7	v	vf		
4530.7	v	vf		
4371.3	v	v		
4363.1	v	v		
4351.8 4351.1	v	v		
4344.5	v	v		
4339.7 4339.5	v	v		
4337.6				
4289.7	v	v	v	f
4274.8	v	v	v	f
4254.3	v	v	v	f
3976.7	v	v		
3969.8	v			
3963.7	v	f		
3941.5	v			
3928.7	v			
3921.0	v			
3919.2	v			
3916.3	v			
3908.8	v			
3894.1	v			
3743.9 3743.6	vf			
3639.8	v	vf		
3636.6	v	vf		
3605.3	v	v	vf	
3593.5	v	v	vf	
3578.7	v	v		
3433.6	v	v		
3346.7	v	v	vf	
3132.1	v	v		
3120.4	v	v		

Portions of each of the powdered mixed oxides were then put in a shallow graphite crucible, about 2.5 cm. in outside diameter, and the crucible was placed between the graphite electrodes of a horizontal arc furnace drawing 110 volts and approximately 300 amperes direct current. Separate crucibles were used for the different concentrations of chromium. The arc was then made to play on the sides of the crucible till the powdered oxides fused, this process usually requiring from 2 to 5 minutes. The resulting rubies were opaque, spherical in shape, and weighed 0.1 to 0.15 gram. Several grams of each of the different rubies were obtained in this way.

The color intensity of these rubies varied, as was to be expected, directly with their chromium content. The rubies were broken and examined microscopically; they were completely and homogeneously fused, were uniformly colored, and were crystalline aggregates, consisting of rhombohedra parallel to each other. This fact accounted in part for their opacity. They were then analyzed so as to determine the actual amount of chromium present in them after possible losses by volatilization during the fusion. They were pulverized in a "diamond steel" mortar to pass a 200-mesh sieve, and were carefully gone over with a magnet to remove any particles of steel (*4*). Samples varying from 0.3 to 4.0 grams in weight were then fused in a platinum crucible with fifteen times their weight of potassium hydrogen sulfate. The fusions were taken up in nitric acid (1:2), oxidized with sodium bismuthate in the usual way (*3*), and titrated with 0.01 *N* potassium permanganate and $FeSO_4.(NH_4)\ SO_4.6H_2O$. The fusions in nearly all cases were complete the first time, but occasionally a small insoluble residue had to be re-fused with potassium acid sulfate before oxidation and titration. The results of these analyses are given in Table II.

The pulverized rubies were next examined spectrographically to determine the sensitivity and persistence of the chromium lines when alumina played the role of solvent. The powders were loaded onto the electrodes from a small hole bored in the end of a brass rod; from the average of a number of weighings, this hole was found to deliver a sample of ruby weighing 0.0063 gram. The sample was spread evenly over the lower electrode to ensure as complete volatilization as possible of all the material during the time of photographic exposure. The results of the observations are recorded in Table III.

A comparison of Table III with Table I will point out the fact that the sensitivity of the spectral reaction of chromium was much greater in the case of the synthetic rubies than in the case of chromium trioxide. The least recognizable quantity of chromium when introduced in the arc as chromic acid was 0.001 mg., but the same element in fused alumina was recognizable to the extent of 0.00006 mg.

Spectrographic Estimation of Chromium in Natural Rubies

Eight natural rubies from five different localities were subjected to arc excitation in the manner described in connection with the synthetic rubies. In each case about 6 mg. of pulverized ruby were used and the chromium was estimated from the number as well as from the intensity of spectral lines, by comparing the spectrograms with the "standards" used in compiling Table III. The results of this examination are recorded in Table IV.

Table IV—Spectrographic Estimation of Chromium in Natural Rubies

No.	Place of Origin	Description	Weight of Chromium (estd. in 6 mg. of ruby)	Estd. Chromium
			Mg.	%
1	Mysore, India	Dark red crystal, gem variety	0.006	0.1
2	Mysore, India	Red crystals, translucent	0.006	0.1
3	Macon County, N. C.	Pink, translucent	0.0006	0.01
4	Ural Mountains	Deep red crystals, translucent	0.006	0.1
5	Mysore, India	Deep red crystals, translucent	0.006	0.1
6	Zoutpansberg, Transvaal	Deep red crystal, opaque	0.006	0.1
7	Macon County, N. C.	Deep red crystal, translucent	0.002	0.03
8	Ceylon	Bright red, transparent	0.006	0.1

To check the reliability of the spectrographic method for estimating chromium in rubies, rubies Nos. 4 and 5, of which the writers had sufficient quantities, were examined by the procedure used for determining chromium in the synthetic rubies. The chromium content of ruby No. 4 was found to be 0.120 per cent, and of ruby No. 5, 0.159 per cent.

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Elimination of Sulfur in Carbon Determinations by Direct Combustion[1]

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IN VIEW of the frequency of erroneous results in carbon determinations owing to the influence of sulfur, the discussions of the subject in the textbooks on steel analysis seem wholly inadequate, if not positively misleading.

A manufacturer of laboratory equipment has recently introduced a special carbon train designed for the elimination of sulfur. It involves the use of an electric heating unit and a catalytic cell for the conversion of sulfur dioxide to sulfur trioxide, followed by the usual zinc tower for its absorption.

The author of one of the well-known textbooks, in his latest edition, just off the press, recommends the use of red lead for all carbon determinations by combustion in steel, pig iron, and graphite, the context indicating that the object is to insure complete combustion of the carbon. In another paragraph he mentions the necessity, when dealing with materials containing an unusual amount of sulfur, of using an additional bubble tube or jar filled to a depth of 2 inches with a concentrated solution of potassium permanganate, to absorb "most of the unusual amount of sulfur dioxide which is formed."

In a series of experiments recently carried out by the writer, it was found that, under certain conditions, the sulfur can be effectively eliminated without recourse to any special additions to the conventional carbon train, even when igniting ferrous sulfide containing 27.4 per cent of sulfur.

The conditions under which this can be accomplished are as follows: The combustion tube is loosely packed in its outlet end with ignited asbestos which must extend into the hot part of the tube. After a few charges have been ignited in the tube with red lead flux, the asbestos becomes impregnated with a sublimate of this material. This is enough to oxidize to sulfur trioxide and fix in the form of lead sulfate the sulfur dioxide evolved by the average steel sample, whether a flux is used on the sample or not. If, then, red lead flux is used on pig irons and other high sulfur-bearing materials, the same reaction takes place in the combustion boat, and the effluent gases are free from sulfur dioxide.

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[1] Received September 29, 1930.

Gravimetric and Direct Volumetric Determination of Cadmium[1]

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Cadmium may be determined by precipitating as cadmium molybdate and weighing as such.

Cadmium may be determined volumetrically by titrating with a standard ammonium molybdate solution, using a saturated solution of pyrogallol in chloroform as an indicator.

CADMIUM is often determined gravimetrically by weighing the pyrophosphate or sulfate. It is commonly determined volumetrically by precipitating it as the sulfide, treating the sulfide with hydrochloric acid and then titrating with iodine solution. This of course is an indirect method.

Cadmium molybdate is very insoluble in a neutral solution. It is therefore possible to determine cadmium either by precipitating it as the molybdate and weighing it as such or by titrating a neutral solution of a cadmium salt with a standard molybdate solution. The end point of the titration may be determined by transferring some of the solution being titrated to a spot plate and bringing it into contact with a drop of chloroform saturated with pyrogallol. The solution tested must be nearly neutral. If the soluble molybdate is in excess, the aqueous drop which has been transferred will turn brown. Metals other than magnesium or the alkali metals will interfere with either method and must be removed.

Cadmium Solution Used in Determinations

A cadmium nitrate solution was prepared by dissolving 5.5150 grams of the metal in nitric acid, evaporating to dryness, and diluting to one liter. The cadmium in 25 cc. of this solution was determined as sulfate. No other metal was present.

The Gravimetric Method

The reagent ammonium molybdate is prepared by stirring up 30 grams of molybdenum trioxide with 400 cc. of water and a few drops of phenolphthalein and adding ammonia with constant stirring until the oxide is dissolved. Acetic acid is then added until the pink color disappears but the reaction is acid to litmus. After filtering, the solution is diluted to 1 liter. One cubic centimeter will precipitate 0.02 gram of cadmium.

Gooch crucibles should be prepared by covering the layer of ordinary asbestos with a layer of ground asbestos, and dried at 120° C.

Procedure for Gravimetric Method

The cadmium solution should be made just alkaline with ammonia and then just acid with acetic acid. It should then be heated to boiling and the molybdate solution added a drop at a time and with constant stirring. The presence of an excess may be determined by transferring a drop to the spot plate and testing with the pyrogallol indicator. The solution containing the precipitate is kept near the boiling temperature until the supernatant is clear or nearly so, and then allowed to stand for at least two hours and preferably overnight. It is then filtered through the Gooch, previously dried at 120° C. After the precipitate has been washed with warm water, the crucible containing it is dried at about 120° C., and weighed. The factor 0.4122 was used for converting cadmium molybdate to cadmium. The results are the following:

Cadmium present, 0.1378 gram

Cadmium found:

As sulfate, 0.1380, 0.1390, 0.1383, 0.1385; av. 0.1384 gram

Molybdate method, 0.1376, 0.1380, 0.1389, 0.1381, 0.1384, 0.1380, 0.1371, 0.1374; av. 0.1379 gram

These results show that the gravimetric molybdate is quite accurate.

In another solution there was present 0.2061 gram of cadmium and an average of four results shows 0.2062 gram present by molybdate method.

Discussion of Gravimetric Method

Cadmium molybdate as precipitated forms hard white crystals quite insoluble in water. It is, however, a little less soluble in a dilute solution of acetic acid than it is in water. Upon drying it assumes a faint pink tinge. It may readily be filtered and does not tend to clog the filter. The crystals are very small when first formed, resembling those of barium sulfate.

Too much suction should not be used in filtering, especially at the beginning, for the precipitate will tend to run through if it has not been digested long enough. This precipitate is readily washed. The use of ground asbestos in the Gooch is a precautionary measure.

Care should be used not to strike the sides or bottom of the beaker with the stirring rod when making the precipitation, since the crystals of cadmium molybdate will adhere tenaciously to the beaker at the point scratched and are detached only with great difficulty.

Cadmium molybdate is stable at 120° C. At about 500° C. it turns brown and loses about 3 per cent of its weight.

This compound is soluble in strong mineral acids and in concentrated solutions of bases. It is nearly insoluble in water, but soluble enough to give a very faint color with the pyrogallol indicator.

Volumetric Method

Prepare the standard as follows: Weigh out 7.4 grams of molybdenum trioxide, add about 100 cc. of water and some phenolphthalein. Dissolve in ammonium hydroxide and neutralize with acid. Cool and dilute to a liter with distilled water. The solution may be standardized by dissolving an exactly known amount of pure cadmium metal in nitric acid and evaporating to dryness over a water bath and then titrating the resulting cadmium nitrate against it, or it may be standardized by adding to a known volume of the solution an excess of cadmium salt and weighing the resulting cadmium molybdate as in the gravimetric method.

Procedure for Volumetric Method

The cadmium solution should be so treated that very little free acid is present. Ammonium hydroxide is then added until a precipitate begins to form. It is heated to boiling and the precipitate dissolved in the least possible amount of acetic acid. The solution is titrated and drops tested from time to time on a spot plate, the depressions of

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[1] Received August 18, 1930.

which contain a saturated solution of pyrogallol in chloroform. At the end point a deep brown color will appear. The results are the following:

Cadmium present, 0.1378 gram
Cadmium found by volumetric method, 0.1390, 0.1380, 0.1395, 0.1374, 0.1378, 0.1390, 0.1386, 0.1390; av. 0.1385 gram

The above recorded results are only a few of those obtained and are given as typical. They show that cadmium may be accurately determined volumetrically.

Comment and Discussion

Ammonium salts increase the solubility of cadmium molybdate. They should be kept at a minimum. This increase in solubility due to ammonium salts is so small as to be negligible in the gravimetric method, but due to the great sensitiveness of the indicator it is appreciable in the volumetric method.

When the end point of the titration is apparently reached it should be boiled for about 30 seconds and retested, and if necessary more standard molybdate added.

Just before the end point is reached, a very faint yellow color may be noticed in the drop tested. This color is very faint and should not be confused with the much deeper color that appears when the true end point is reached.

A standard solution of ammonium molybdate appears to give a sharper end point than the sodium salt, although either may be used.

Potentiometric Determination of Saponification Number of Mixtures of Asphalt and Drying Oils[1]

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The saponification number of linseed oil can be determined potentiometrically without a blank determination and without the standardization of the alkali.

The saponification number of asphalt can be determined potentiometrically using anisole as a solvent.

Mixtures of linseed oil and asphalt can be analyzed by the potentiometric determination of the saponification number with high precision and with no more expenditure of time than is required in other methods.

The analysis of mixtures which contain soy bean oil or Bermudez asphalt is less satisfactory.

THE determination of the saponification number of mixtures of asphalt and drying oil is of considerable importance in the testing of asphalt paints. The standard method (*1*, *2*), however, is rather difficult and inaccurate because the black color of the asphalt suspension obscures the end point of the indicator. Furthermore, when the benzene is evaporated, the asphalt is precipitated and considerable alkali is occluded by the asphalt. The method described in this paper overcomes the first difficulty by the use of the hydrogen electrode and the second difficulty by the use of anisole as a solvent.

Method

The application of the hydrogen electrode to the determination of the saponification number of the gilsonite was investigated first. To a weighed sample of gilsonite were added 50 cc. of standard alcoholic potassium hydroxide (about 0.7 *N*) and 40 cc. of pure anisole. The mixture was refluxed until saponification was complete (1 hour). After cooling it was titrated potentiometrically with standard aqueous hydrochloric acid. A normal calomel electrode and a hydrogen electrode of the usual type were used as reference and indicator electrodes, respectively. After each titration the hydrogen electrode was treated with hot concentrated nitric acid and then made the cathode in the electrolysis of dilute sulfuric acid. After this treatment it was ready for the next titration. It was found unnecessary to replatinize an electrode during the entire investigation. A Leeds and Northrup student potentiometer was used.

Anisole was found to be the best solvent for this purpose. Other asphalt solvents such as ethyl ether, propyl ether, and isopropyl ether were unsatisfactory because they failed to keep a major portion of the asphalt in solution. Nujol was unsatisfactory because it formed a thick emulsion when hydrogen was bubbled through saponified mixtures of linseed oil and asphalt. The benzene could not be used because it poisoned the hydrogen electrode. During the titration two layers separated, the upper anisole layer containing almost all of the asphalt. About 9 minutes were required to attain a steady potential after each addition of acid.

The differential curve of a typical titration is shown in Figure 1. The first maximum represents the neutralization of excess alkali. The reason for the existence of the second maximum is not clear, but may be due to the existence of acids in the gilsonite of very different ionization constants. The third maximum occurs at the same volume of acid as is required to neutralize 50 cc. of the alcholic alkali, and therefore represents the completion of the reaction between hydrochloric acid and the alkali combined with the asphalt. In this determination it is unnecessary to standardize the alkali because the amount of acid used between the first and last maxima is a direct measure of the combined alkali. The results are given in Table I.

Table I—Saponification Number of Asphalts

GILSONITE		BERMUDEZ
Blank method	Double maximum method	Blank method
11.2	12.3	26.9
9.1	8.6	28.0
9.3	8.5	27.7
10.0	...	....
Mean 9.9	9.8	27.5

Next a sample of linseed oil was saponified and titrated by exactly the same method, including the addition of the anisole. In this case only 5 minutes were required to attain a steady potential. A representative curve is given in Figure 2. Here only two maxima are found. The first

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[1] Received August 28, 1930. From a thesis submitted to the faculty of Rutgers University by James V. Demarest in partial fulfilment of the requirements for the degree of master of science.

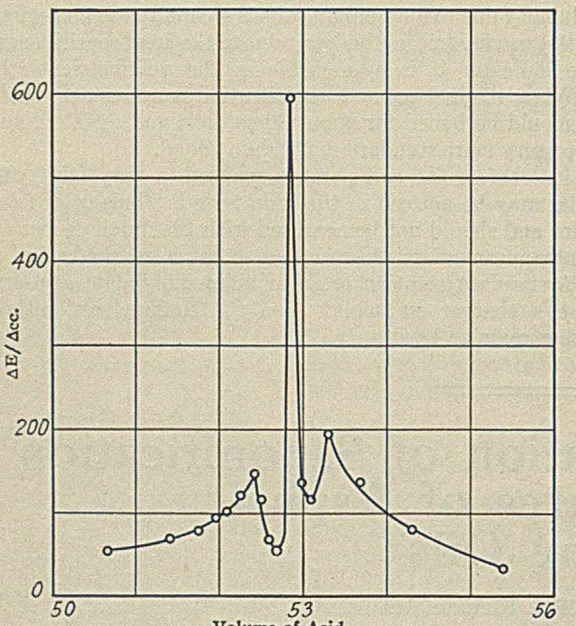

Figure 1—Gilsonite

represents neutralization of excess alkali; the second, the complete displacement of fatty acids from the soaps. The results are given in Table II.

Table II—Saponification Number of Linseed Oil

INDICATOR METHOD	POTENTIOMETRIC METHODS	
	Blank	Double maximum
191.1	192.3	192.9
191.6	192.7	194.0
190.9	193.2	191.9
192.6	192.6	...
193.1	193.1	...
192.4	192.5	...
191.5	192.4	...
191.4	192.7	...
191.6		
Mean 191.8	192.7	192.9

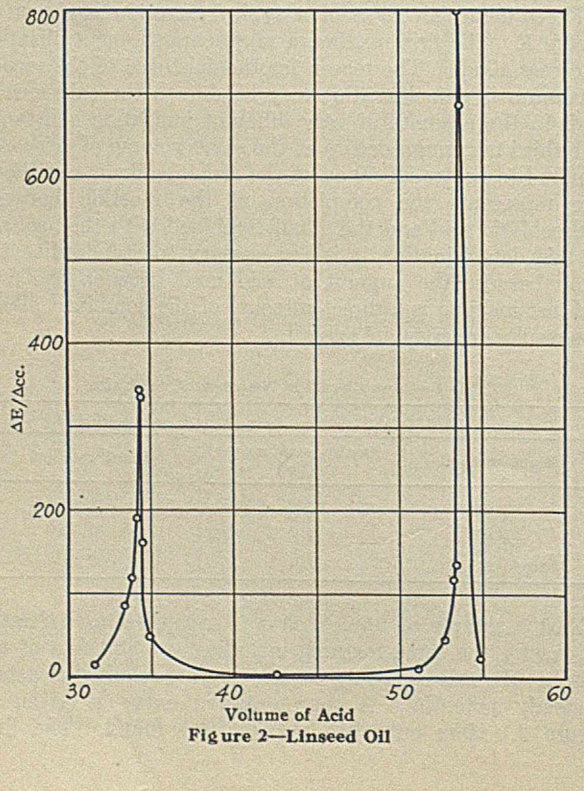

Figure 2—Linseed Oil

The saponification number of soy bean oil was determined potentiometrically in the presence of anisole, and found to be 198.0.

Mixtures of known quantities of linseed oil and gilsonite were then prepared and these mixtures were analyzed by a potentiometric determination of the saponification number. The data and curve of a typical titration are given in Table III and Figure 3.

Table III—Titration Data for Linseed Oil and Gilsonite

Cc.	*E, volts*	*ΔE/Δcc.*	*Cc.*
40.12	1.0145	...	...
41.12	0.9710	43	40.62
41.42	0.9230	160	41.28
41.52	0.9045	185	41.48
41.62	0.8870	175	41.57
41.72	0.8715	155	41.67
41.82	0.8575	140	41.77
42.13	0.8195	123	41.98
52.66	0.6790	13	47.39
52.96	0.6710	27	52.81
53.06	0.6675	35	53.01
53.16	0.6640	35	53.11
53.26	0.6570	70	53.21
53.36	0.6440	130	53.31
53.46	0.6330	110	53.41
53.56	0.5610	720	53.51
53.66	0.5150	460	53.61
54.16	0.4430	144	53.91
56.16	0.4040	19	55.16

Again only two distinct maxima are found which represent the neutralization of free and combined alkali, respectively. The results are given in Table IV.

Table IV—Analysis of Mixtures

TRUE COMPOSITION		OIL FOUND	
Gilsonite	Linseed oil	Blank method	Double maximum method
%	%	%	%
19.8	80.2	80.1	....
19.7	80.3	81.0	80.3
36.9	63.1	62.7	63.1
57.2	42.8	43.3	42.9
58.2	41.8	42.3	41.9
78.3	21.7	20.5	21.0
	Soy bean oil		
59.9	40.1	42.8	
58.7	41.3	42.4	
59.6	40.4	41.7	
Bermudez			
64.8	35.2	40.4	
61.6	38.4	44.4	
62.1	37.9	43.1	

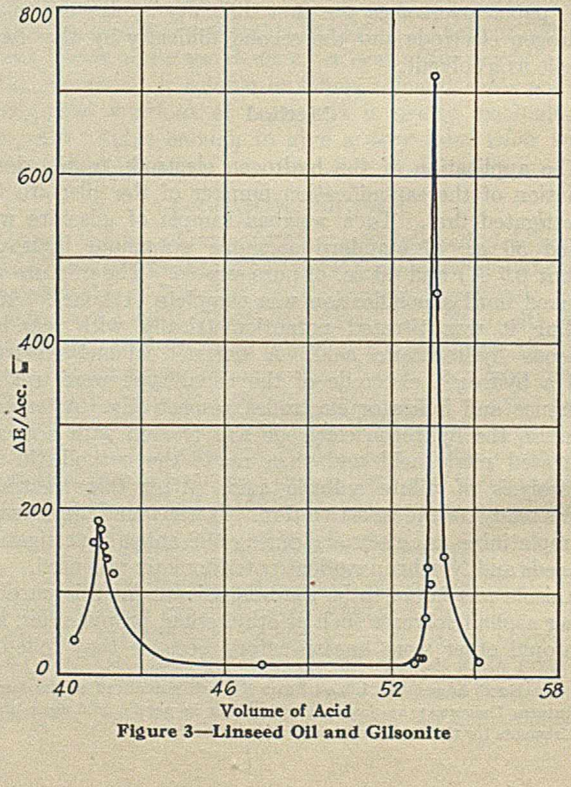

Figure 3—Linseed Oil and Gilsonite

The method was applied to mixtures of soy bean oil with gilsonite and with Bermudez asphalt with less success. Difficulty was experienced in detecting the last maximum. It is recommended, therefore, that standard alcoholic base be used in the analysis of mixtures which contain soy bean oil. These results are also given in Table IV.

Literature Cited

(1) Abraham, "Asphalt and Allied Substances," Van Nostrand, 1918.
(2) Marcusson, *Chem.-Ztg.*, **36**, 803 (1912).

Effect of Amino Acids upon Rotation of Glucose and Fructose and Its Significance to Determination of Sucrose by Double Polarization Methods[1]

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The effect of increase in alkalinity upon the combination of glucose with glycine, as previously noted by Euler and associates, has been extended with studies of the effect of temperature and different molar relationships. The extent of combination has been followed polarimetrically and by an iodometric determination of uncombined glucose.

The increase in combination with increase in pH, and the equilibrium constants for the reaction as determined by polarimetric and iodometric methods, were in agreement with each other and with results obtained by Euler from freezing point data.

At 25° C. the glycine-glucose complex was almost completely reversed by acidification while at a temperature as low as 35° C. some of the stable type of melanoidal combination, not affected by acid, was evident. Near 0° C. the extent of the reaction was very limited.

Similar experiments were carried out with asparagin and glucose and the same general effects noted although the two methods gave values of different magnitudes.

Fructose showed no optical changes in the presence of glycine and asparagin with increasing pH which could not be attributed to alkalinity alone.

The significance of the effect of pH, time of standing, and temperature upon the determination of sucrose in the presence of amino acids by double polarization method is discussed.

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The importance of more exact knowledge of the effect of certain optically active nitrogenous impurities upon simple sugars and its significance to the determination of sucrose by the double polarization method is evident from the recent referee studies reported upon this subject by Zerban (*15, 16*).

The information is especially necessary in studies of carbohydrate metabolism of plants in which the sugar concentration is quite low and the concentration of the nitrogenous materials relatively higher in proportion to the sugars than in the juice of plants used as sugar sources. Brown and Morris (*2*), who are perhaps among the earliest workers to make a detailed study of the individual carbohydrates in plants, call attention to a disparity between the value for sucrose determined by polarization as compared to chemical methods. The magnitude of the difference varied with different plant materials and with different portions of the same plant. More recently Davis and co-workers, in estimating the carbohydrates of the mangold and potato, found polarization values as much as 80 per cent greater than the reduction values and sometimes as much as 90 per cent lower. The variation was generally greatest in the stem extracts. Davis (*5*) has made the assumption that the fluctuations between the optical and chemical values is due to asparagin and glutamin. In this laboratory, in the investigation of the effect of potassium salts upon the carbohydrate metabolism of the nasturtium, the results of the determination of sucrose by polarimetric methods have been consistently higher. This has led to a series of studies in an effort to determine the causes of the differences, and to find a means of eliminating the more serious sources of error. Somers (*14*) investigated first the effect of reduction due to sucrose upon the chemical method; second, the effect of certain salts left after different defecation procedures; and finally, the influence of asparagin upon the optical values. These factors taken separately were found to have comparatively little effect, but some observations of the last mentioned are of special interest.

An asparagin solution and invert solution were prepared and portions of each were mixed with an equal volume of water. Then equal portions of each original solution were mixed together. The mixture showed an increased levorotation over the sum of the optical values of the individual constituents.

A few years later, Drake (*6*) studied the effect of the presence of a large number of amino acids upon glucose, fructose, and sucrose before and after its inversion. An effort was made to keep the solutions approximately neutral to avoid the effect of change in acidity upon the rotation of the amino acid itself. Both plus and minus differences in rotation of the mixtures were found but the value of the work suffers from lack of exact knowledge of the acidity and duration of the reaction period.

In 1925, Nueberg and Kobel (*11*) made observations of a somewhat similar character. These investigators were concerned with a probable reaction product between sugar and amino acid which accelerated the alcoholic fermentation of the sugar. Addition of *d-l*-alanine to a fructose solution increased the levorotation while with glucose very little effect was noted. Supplementary work by Neuberg and Kobel (*12*) indicated that fructose seems to react immediately with amino acids and amides at a pH of 7. Particularly striking increases in levorotation were given by aspartic

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[1] Received September 4, 1930.

and glutamic acids. With the aldol sugars the effects were much less.

It has been pointed out by Browne (*3*) and others whom he quotes that optical rotation in the ordinary sense of the term is not an additive property. It follows as a consequence that a discrepancy between the rotation of a mixture and the sum of the rotations of its constituents does not necessarily mean that a reaction has taken place between the constituents. Although the effect of the water concentration which Browne has emphasized would probably not be sufficient to account for the total differences observed by Somers and other investigators cited, additional indications of a reaction should be furnished by other methods. This has been done by Euler and his associates.

Euler and Josephson (*10*) gave attention to the effect of decreasing hydrogen-ion concentration upon the reaction of glucose with glycine. At the isoelectric point of glycine no reaction took place, but with increasing pH, the apparent combination as indicated by change in polarization was 32 per cent at a pH of 9.6. A more detailed study by Euler and Brunius (*7*, *8*, *9*) in which the reaction was followed by freezing point lowering, determination of uncombined amino acid by the Van Slyke method and glucose by the iodometric method, in addition to polarimetric change, confirmed the earlier observations. It was observed that the rate of combination of glucose with glycine is slow, but at a pH of 9.5, based on observations of freezing point lowering, it reaches equilibrium at 53 per cent combination in 48 hours. Glucose and alanine behaved in a similar fashion. The first explanation advanced for the increase in extent of reaction with increase in pH was that the alkalinity favored the change of the sugar from the lactone to the free aldehyde form which then condensed with the amino group. Preliminary treatment of the sugar with alkali had no effect on the final reaction, so any previous rearrangement to the acyclic form did not accelerate the combination. Additional evidence from refractometric observations seemed to indicate absence of a double-bonded compound, and it was concluded that the union between sugar and amino acid was of glucosidal character.

While the experiments of Neuberg and Kobel, and Euler and his associates were carried out with a biological application in view, they are not less important from the standpoint of analysis.

In the present study some of the previously reported experiments with glycine have been extended and additional experiments carried out with asparagin, a representative of one of the more common nitrogenous impurities in plant extracts.

Experimental Methods

The amino acids and sugars had been carefully purified and were of high quality. Glycine was selected as one of the amino acids for study since it is optically inactive and hence the complications due to the change in rotating power of the acid itself are eliminated.

Sodium hydroxide was added to the amino acid solution to bring it to a definite pH and then the solution made to volume with a carbonate-bicarbonate buffer. The sugar solution was similarly buffered. Amino acid and sugar solutions were then mixed in equal quantities, and for the purpose of control an equal volume of each was mixed with an equal volume of buffer solution. The hydrogen-ion concentration of each of the prepared solutions was measured. A Leeds and Northrup potentiometer was used with a Hildebrand hydrogen electrode and a 0.1 *N* calomel half-cell. The e. m. f. of the solution was measured and the pH calculated. An atmosphere of purified hydrogen was maintained above the solution to insure a steady potential. The reactions were allowed to proceed at various pH values and various temperatures until equilibrium was reached. In most of the experiments the concentrations of the mixture were in a 1 to 1 molecular ratio. In others the amino acid was reduced, keeping the molar concentration of glucose constant. In all experiments the extent of the reaction was determined by decrease in optical value. The observations were made with a Schmidt and Haensch saccharimeter. In some of the mixtures the uncombined sugar was determined by a slight modification of the Cajori (*4*) iodometric method for aldol sugars, and the uncombined amino acid estimated by the Van Slyke (*13*) method.

Calculations of equilibrium constants, glucose-amino complex ÷ glucose × amino acid, were made on the assumption that the combination is in an equal molecular ratio and that the compound formed is of negligible rotation so that the decrease in rotation is equivalent to the extent of combination. This assumption will be open to criticism. Euler has made a calculation of the probable optical activity of compound and found it to be comparatively high. However, if one accepts the theory of a glucosidal structure and if the amino acid reacts equally well with the α and β forms of glucose, one would anticipate that little change in rotation would occur if the glycine glucosides differ in rotation from their respective forms of glucose as do the methyl glucosides.

The detailed results of these experiments are given in Table I.

Table I—Effect of Glycine on Glucose at Various pH Values

Part I—Optical Changes (2 dm. tube)

Temperature, 25° C.; molar concentration, 0.0666

pH	Time	Glucose 50 cc. Glycine 50 cc.	Decrease in Rotation		Equilibrium Constant
	Hrs.	° *V.*	° *V.*	%	
8.11	0	3.60	0.00	0.00	
	24	3.53	0.07	1.94	
	48	3.50	0.10	2.77	0.43
9.52	0	3.60	0.00	0.00	
	24	3.12	0.48	13.33	
	48	3.00	0.60	16.66	3.5
10.30	0	3.60	0.00	0.00	
	7	3.51	0.09	2.50	
	19	3.14	0.46	12.77	
	26	3.03	0.57	15.83	
	42	2.94	0.66	18.33	
	48	2.80	0.80	22.22	5.5

Part II—Decrease in Apparent Glucose by Iodometric Method

Glucose-Glycine Mixture	pH	0.1116 *N* I_2 Soln.	Glucose Present	Glucose not Accounted for	Loss of Glucose
Cc.		*Cc.*	*Mg.*	*Mg.*	%
10	8.11	11.57	116.56	3.44	2.87
10	9.52	10.18	102.20	17.80	14.83
10	10.30	9.26	92.97	27.03	22.53

Part III—Uncombined Amino Acid by Van Slyke Method

Temperature, 26° C.; barometer, 749 mm. Hg

Glucose-Glycine Mixture	pH	N_2 Formed	Glycine in Sample	Total Glycine Found in Mixture (1.000 Gram Present)
Cc.		*Cc.*	*Mg.*	
10	8.11	16.64	50.10	1.002
10	9.52	16.49	49.65	0.993
10	10.30	16.56	49.86	0.997

Part IV—Summary of Results

pH	Apparent Combined Glucose		Apparent Combined Glycine
	Polarimetric	Iodometric	Van Slyke method
	%	%	%
8.11	2.77	2.87	0.0
9.52	16.66	14.83	0.9
10.30	22.22	22.53	0.5

Experiments with Asparagin

A series of experiments analogous to those with glycine were carried out with asparagin and the results are recorded in Table II.

Table II—Effect of Asparagin on Glucose at Various pH Values
Part I—Optical Changes (2 dm. tube)
Temperature, 25° C.; molar concentration, 0.0666

pH	Time	Glycine 50 cc. Glucose 50 cc.	Decrease in Rotation	
	Hrs.	° *V.*	° *V.*	%
8.75	0	3.65	0.00	...
	24	3.50	0.15	4.11
	48	3.50	0.15	4.11
	72	3.50	0.15	4.11
10.64	0	3.65	0.00	...
	24	3.20	0.45	12.33
	48	2.71	0.94	25.75
	72	2.67	0.98	26.85
11.55	0	3.65	0.00	...
	24	1.35	2.30	63.01
	48	0.41	3.24	88.76
	72	0.23	3.42	93.72

Part II—Decrease in Apparent Glucose by Iodometric Method

Glucose-Asparagin Mixture	pH	0.1116 *N* I_2 Soln.	Glucose Present	Glucose not Accounted for	Loss of Glucose
Cc.		*Cc.*	*Mg.*	*Mg.*	%
10	8.75	11.97	120.10	...	...
10	10.64	10.70	107.40	12.60	10.50
10	11.55	7.26	72.89	47.11	39.26

Part III—Uncombined Amino Acid by Van Slyke Method
Temperature, 26° C.; barometer, 749 mm. Hg

Glucose-Asparagin Mixture	pH	N_2 Formed	Asparagin in Sample	Total Asparagin in Mixture = 0.440 gm.
Cc.		*Cc.*	*Mg.*	*Gm.*
10	8.75	4.16	22.04	0.441
10	10.64	4.07	21.57	0.431
10	11.55	4.10	21.73	0.434

Part IV—Summary of Results

pH	Apparent Combined Glucose		Apparent Combined Glycine
	Polarimetric	Iodometric	Van Slyke method
	%	%	%
8.75	4.11	0.00	0.0
10.64	26.85	10.50	2.04
11.55	93.72	39.26	1.36

Effect of Acidification on the Reversibility of the Reaction

Euler and Brunius (*8*) found that, when solutions of alanine and glucose with a pH of 10.4 had been allowed to stand until equilibrium was reached and then acidified with sulfuric acid, after 25 hours the iodine consumption was almost the same as the initial value, indicating a reversibility of the reaction. Such reversibility should characterize all glucose-amino compounds. To demonstrate this point solutions were prepared in double the concentration indicated in Table I, Part I, and polarized. They were allowed to stand 48 hours, polarized, and acidified with an equal volume of dilute hydrochloric acid. After 48 hours the solutions were again polarized. The results are given in Table III.

Table III—Effect of Acidification upon Glucose-Amino Acid Condensation Product
Molar concentration, 0.1332

pH	Glucose 50 cc. Glycine 50 cc.	After 48 Hours	Add Equal Volume Dil. HCl	After 48 Hours
	° *V.*	° *V.*	° *V.*	° *V.*
8.11	7.20	7.00	3.50	3.60
9.52	7.20	6.30	3.15	3.50
10.30	7.20	5.60	2.80	3.40

Effect of Variation in Glucose-Glycine Ratio upon Their Combination

The next experiments were designed to determine the effect of altering the ratio of the glucose and glycine upon the optical value at different pH values. The majority of sugar juices or sirups contain sugar in large excess of the amino acids so that the mass action effect of the sugar is quite high, and one would expect almost all the amino acid to be in combination. In this study the glucose concentration was kept constant, and that of the glycine reduced. The general method of procedure was the same as previously outlined. After equilibrium was reached, solid oxalic acid was added, and the rate of reversion to the original constituents followed. These experiments were carried out at room temperature during an exceedingly warm summer and the thermometer registered close to 35° C. during the whole period. The results are given in Table IV.

Table IV—Effect of Changes in Glucose-Glycine Ratio and pH upon Rate of Change in Optical Value of Solution. Rate of Change on Acidification

Part I—Original pH, 9.52; Temperature, 35° C.; Molar Concentration of Glucose, 0.222

Reaction Period	Rotations				Apparent Combination			
	Initial glucose-glycine ratio				Initial glucose-glycine ratio			
	1:1	1:0.5	1:0.25	1:0.125	1:1	1:0.5	1:0.25	1:0.125
Hrs.	° *V.*	° *V.*	° *V.*	° *V.*	%	%	%	%
0	12.24	12.24	12.24	12.24	0.0	0.0	0.0	0.0
6	9.66	10.85	11.39	11.84	21.0	22.7	27.7	26.2
18	8.39	10.35	11.17	11.56	31.4	30.9	35.0	44.4
24	8.12	10.16	10.86	11.55	33.7	33.9	45.1	45.1
30	8.32	9.93	10.77	11.55	32.0	37.7	48.0	45.1
42	8.04	9.83	10.78	11.28	34.3	39.3	47.7	62.7
48	8.12	9.93	10.89	11.44	33.7	37.7	44.1	52.3
AFTER ADDITION OF SOLID OXALIC ACID								
0	8.12	9.93	10.89	11.44	33.7	37.7	44.1	52.3
6	10.97	11.35	11.43	11.60	10.3	14.5	26.4	41.8
18	11.18	11.23	11.38	11.53	8.7	16.5	28.1	46.4
66	11.06	11.57	11.39	11.66	9.6	10.9	27.7	37.9
(A) Per cent reduction of rotation due to destruction of glucose or formation of a non-dissociable compound.					9.6	10.9	27.7	37.9
(B) Per cent combined at equilibrium after correction for (A).					24.1	26.8	16.4	15.5

Part II—Original pH, 10.3; Temperature, 35° C.; Molar Concentration of Glucose, 0.222

Reaction Period	Rotations				Apparent Combination			
	Initial glucose-glycine ratio				Initial glucose-glycine ratio			
	1:1	1:0.5	1:0.25	1:0.125	1:1	1:0.5	1:0.25	1:0.125
Hrs.	° *V.*	° *V.*	° *V.*	° *V.*	%	%	%	%
0	12.24	12.24	12.24	12.24	0.0	0.0	0.0	0.0
6	9.50	10.63	11.35	11.80	22.4	26.3	29.0	28.9
18	8.10	10.38	10.98	11.28	33.8	30.4	41.2	62.7
24	7.89	9.63	10.70	11.16	35.5	42.6	50.3	70.6
30	7.85	9.63	10.56	11.00	35.8	42.6	54.9	81.0
42	7.77	9.65	10.60	11.07	36.5	42.3	53.6	76.4
48	7.82	9.63	10.51	11.03	36.1	42.6	56.6	79.1
AFTER ADDITION OF SOLID OXALIC ACID								
0	7.82	9.63	10.51	11.03	36.1	42.6	56.6	79.1
6	11.01	11.21	11.07	11.03	10.0	16.8	38.2	79.1
18	11.01	11.03	11.10	10.86	10.0	19.8	37.2	90.2
66	10.93	11.21	11.00	10.89	10.7	16.8	40.5	88.2
(A) Per cent reduction of rotation due to destruction of glucose or formation of a non-dissociable compound.					10.7	16.8	40.5	88.2
(B) Per cent combined at equilibrium after correction for (A).					25.4	25.8	16.1	..

Method of Calculations

Calculation of the apparent percentage of glycine in combination may be indicated as follows: In Table IV, Part II, the ratio of glucose to glycine is 1 to 0.5. The decrease in rotation indicates an apparent loss of glucose equal to 21.3 per cent. Since one mol of glycine combines with one mol of glucose and its initial concentration is only half that of the glucose, then 42.6 per cent of it may be considered as in combination.

The equilibrium values at 48 hours would seem to indicate that as the glucose is increased in proportion to glycine, a greater percentage of glycine is brought into combination. However, when the solutions are acidified, they fall far short of returning to their original values. Apparently, at this higher pH and temperature the type of melanoid reaction recently discussed by Ambler (*1*) begins to take place between sugar and amino compound. In addition there may be some alteration of the glucose itself. Consequently calculations of even apparent equilibrium constants are out of the question.

Effect of Temperatures of 0° C. and 50° C. upon Reaction of Glucose and Glycine at pH 10.3

The temperature of 35° C. having given a non-dissociable compound of sugar and amino acid, a couple of experiments were carried out to determine the effect of a greater range from ordinary room temperatures. The glycine and glucose were again used in equivalent amounts, and the solutions buffered at a pH of 10.3. Blanks containing sugar and buffer alone were examined at the same time. Experiments were run in duplicate, one series of flasks being placed in a refrigerator at 0° C., and the other in an oven at 50° C. The observations of rotation are given in Table V.

Table V—Effect of Different Temperatures upon Reaction of Glucose and Glycine at a pH of 10.3

Part I—Temperature, 0° C.; Molar Concentration, 0.222

REACTION PERIOD	CONTROL: GLUCOSE AND BUFFER				GLUCOSE-GLYCINE AND BUFFER			
	Rotation		Change		Rotation		Change	
	(*a*)	(*b*)	(*a*)	(*b*)	(*a*)	(*b*)	(*a*)	(*b*)
Hrs.	° *V.*	° *V.*	%	%	° *V.*	° *V.*	%	%
0	12.24	12.24	0.0	0.0	12.24	12.24	0.0	0.0
12	12.20	12.18	0.3	0.4	11.80	11.78	3.5	3.7
24	12.16	12.16	0.6	0.6	11.80	11.78	3.5	3.7
36[a]	12.02	12.02	1.6	1.6	11.76	11.76	3.9	3.9
72	12.00	12.00	1.8	1.8	11.76	11.76	3.9	3.9

Part II—Temperature, 50° C.; Molar Concentration, 0.222

REACTION PERIOD	CONTROL: GLUCOSE AND BUFFER				GLUCOSE-GLYCINE AND BUFFER			
	Rotation		Change		Rotation		Change	
	(*a*)	(*b*)	(*a*)	(*b*)	(*a*)	(*b*)	(*a*)	(*b*)
Hrs.	° *V.*	° *V.*	%	%	° *V.*	° *V.*	%	%
0	12.24	12.24	0.0	0.0	12.24	12.24	0.0	0.0
3	9.44	9.88	22.9	19.3	8.14	8.42	33.5	31.2
6	8.38	8.50	31.5	30.5	7.76	7.78	36.6	36.4
12	7.22	7.22	41.0	41.0	6.98	7.02	42.9	42.6
24	6.46	6.54	47.2	46.5	6.02	6.02	50.8	50.8
36	6.52	6.52	46.7	46.7	Dark	Dark	..	..

[a] At end of 36-hour period the temperature had risen somewhat due to trouble with mechanical refrigerator. Experiments were continued in an ice chest a few degrees above zero.

At the lower temperatures, the solutions remained perfectly clear and uncolored throughout the experiment. Even at relatively high pH values, the amino acid and sugar react to a very limited extent and the equilibrium value at the low temperature is practically reached within the first 12 hours.

At the higher temperature, both the control and the mixture became dark colored, but the mixture was very much darker than the control containing no amino acid. Addition of oxalic acid caused but little change in rotation, indicating that the products of the reaction were of a very stable character.

Effect of Amino Acids on Fructose at Various pH Values

Neuberg and Kobel (*12*) have demonstrated that at a pH of 7, fructose tends to react immediately with amino acids to give products of a lower rotatory value. It seemed desirable to determine the effect of increasing alkalinity upon such sugar mixtures. Accordingly experiments were tried with glycine and asparagin. The results are given in Table VI.

Table VI—Effect of Glycine and Asparagin upon Optical Value of Fructose at Various pH Values

Temperature, 25° C.; molar concentration, 0.222

pH	TIME	ROTATION (4-DM. TUBE)		
		Levulose and buffer	Levulose-glycine	Levulose-asparagin
	Hrs.	° *V.*	° *V.*	° *V.*
8.15	0	−19.69	−19.61	−19.87
	79	−19.55	−19.52	−19.78
9.52	0	−19.48	−19.54	−19.79
	79	−19.44	−19.50	−19.82
10.30	0	−19.41	−19.46	−19.74
	79	−19.42	−19.44	−19.72

Discussion of Results

As can be noted in Table I, and in agreement with observations of previous workers, the effect of decreasing the hydrogen-ion concentration is to increase the tendency of the sugar and amino acid to react, and the rate of reaction is fairly slow. The very satisfactory agreement between the values for the extent of combination of glucose and glycine, as determined by polarimetric and iodometric methods, and the almost complete recovery of amino acid when the mixture is analyzed by the Van Slyke method, are, however, somewhat at variance with the results of Euler and his associates for the same pH values. It should be pointed out that their mixtures of glycine and glucose were in the ratio of 2 mols of the former to 1 of the latter, and their iodometric method necessitated a much more strongly basic solution. The difference in the Van Slyke values may be attributed to a longer period of time consumed in the analyses here reported, with the result that under these conditions the amino-acid sugar complexes had almost completely reverted to the original constituents.

The equilibrium constants, as calculated, lie close to the curve which Euler and Brunius (*7*) obtained by the freezing point method for the extent of combination at different pH values. This fact, in addition to the agreement between the polarimetric and iodometric values of Table I, Part IV, lends support to the assumption that the glucose-glycine compound is of negligible optical activity.

A complete dissociation of the glucose-glycine complex is evident after acidification of the solutions of low alkalinity, but in the solutions of higher alkalinity there appears to be either a slight destruction of glucose or the formation of some non-dissociable product.

The results with asparagin are similar except that an enormous change in optical value takes place which is probably due to the effect of the alkali upon the amino acid itself in addition to the favoring of the condensation reaction.

As can be noted in Table VI there is little change in increasing alkalinity upon the keto sugar-amino acid complex. Any differences observed are probably due to the effect of the alkaline solution upon the sugar itself.

Significance of Effect of Amino Acids upon Determination of Sucrose by Double Polarization Methods

The effects of change in the optical value of the amino acids and fructose with change in acidity of the solution, hydrolysis of reversion products, and chemical change in some of the amino acids themselves, upon the determination of sucrose by the double polarization method with different hydrolytic procedures, have been discussed by Zerban (*15*, *16*). However, he states that a preliminary study of the methods following lead clarification gave such divergent results by two chemists working in the same laboratory that work along this line was postponed temporarily.

Since raw sugar solutions are usually defecated with lead acetate and the excess lead removed with sodium carbonate or a similar reagent before the determination of sucrose, the pH of the solution may be very markedly increased by both the excess of deleading agent and the soluble acetate salt produced in the lead precipitation process. This may be expected to favor the amino acid–aldol sugar combination, the extent depending on the relative quantities of each present, the alkalinity of the solution, and the time the solutions are allowed to stand before polarizing. Even if acid be added to bring to some definite pH near the neutral point, the rate of reversion of the complex to its original components in low acid concentration is slow and the time required to reach an equilibrium value may be several hours. In addition, the temperature of the solution exerts a marked influence upon the extent and nature of the complex formed. Thus the apparent change due to the hydrolysis of the sucrose can vary widely and be either higher or lower than the theoretical value. The variations between polarimetric and reduction previously mentioned as observed by Brown and Morris, Davis, and others probably result from all those factors.

It is evident that satisfactory results for sucrose by the double polarization method must involve very careful consideration of this tendency of amino acids and glucose to combine as well as the many other factors which have received attention previously.

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Determination of Glucose in Presence of Fructose and Glycine by Iodometric Method[1]

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A study has been made of the effect of the presence of fructose and glycine upon the determination of glucose by oxidation with alkaline iodine solution in the presence of sodium hydroxide, sodium carbonate, and phosphate buffers.

The rate of oxidation is so rapid that the extent of condensation of the glucose and glycine is negligible under the conditions of the experiments, and there is no tendency for low results due to this cause if the solution is neutral when the analysis is begun.

The results obtained are always higher than those due to glucose alone because of reduction of iodine by the fructose and glycine.

Even if fructose may react immediately with the glycine, the compound has little protective action against the oxidizing agent.

Of the various basic reagents used with iodine, sodium phosphate has a number of advantages and gave the most satisfactory results.

THE selective oxidation of aldol sugars by iodine in alkaline solution has received renewed attention on account of the ease and rapidity of the method (*10*) and its special application to the analysis for glucose in plant materials used as sources of fructose (*9*, *3*).

One of the objections assigned to the iodometric method is that it gives high results because of the fact that substances other than sugars take up iodine under the conditions of the analysis. On the other hand, certain factors may tend to cause low results. It has been demonstrated by Euler and Brunius (*5*, *6*), and Englis and Dykins (*4*) that when amino acids are present and the solution is alkaline, a stable condensation product of the monosaccharide sugars with the amino substances takes place and prevents its oxidation by iodine in alkaline solution. With glucose the rate of condensation is relatively slow near the neutral point but increases rapidly in rate and extent as the alkalinity is increased. With levulose the combination is immediate and at a lower alkalinity. If the amino substance can then combine with only an equal molecular quantity of sugar, it might be expected that since fructose is the predominating sugar in the hydrolyzed extracts of inulin-containing plants, it might combine with all the amino material and thus leave the aldol sugar to react as it normally would in the absence of the amino substance. If the amino substances still tend to react with the aldol sugar, the rate will be a function of the time, temperature, and alkalinity, and different values may be expected for the iodometric methods using different degrees of alkalinity and different reaction periods. To secure definite information upon these points was the object of these experiments.

Experimental Procedure

Three methods involving different basic reagents for the iodometric procedures were used. In the first, sodium hydroxide was the base and the conditions approximated those outlined by Kolthoff (*7*). In the second, sodium carbonate was utilized under about the same conditions as specified by Cajori (*1*) except that the quantities of reacting materials were increased about 2.5 times. In the third, a disodium phosphate–sodium hydroxide buffer mixture of about the same pH value as the sodium carbonate mixture was used.

The iodine and sodium thiosulfate solutions used were approximately 0.1 normal. The sodium thiosulfate solution was standardized against pure potassium dichromate and its value in terms of glucose was found to be 9.515 mg. per cc. In each series of determinations, blank runs were made in which distilled water replaced the sugar solution.

A concentrated stock solution of a high purity glucose containing 10.000 grams in 100 cc. was made the source of the glucose for all experiments. When 10 cc. of this were

[1] Received September 12, 1930.

Table I—Determination of Glucose in Presence of Fructose and Glycine by Iodometric Method

Alkali Used		Initial pH	Time Interval	Contents of 25 cc. Soln.	$Na_2S_2O_3$ Used		$Na_2S_2O_3$ Equiv. to I_2 Reduced	Apparent Glucose Found Attributed to:			
					Blank	Sugar soln.		Total	Glucose	Fructose	Glycine
	Cc.		*Minutes*	*Mg.*	*Cc.*	*Cc.*	*Cc.*	*Mg.*	*Mg.*	*Mg.*	*Mg.*
ALKALINE MEDIUM PRODUCED BY SODIUM HYDROXIDE											
0.5 *N* NaOH	8	12.40	10	Glucose 100	25.93	15.35	10.58	100.7	100.7	...	..
				Glycine 25	25.93	24.83	1.10	10.5	...	...	10.5
				Glucose 100 Fructose 200	25.93	14.50	11.43	108.8	100.7	8.1	..
				Glucose 100 Glycine 25	25.93	14.66	11.27	107.2	100.7	...	6.5
				Glucose 100 Fructose 200 Glycine 25	25.93	14.22	11.71	111.4	100.7	10.7	
ALKALINE MEDIUM PRODUCED BY SODIUM CARBONATE											
15% Na_2CO_3	5	11.43	25	Glucose 100	25.92	15.17	10.75	102.3	102.3	...	..
				Glycine 25	25.92	25.69	0.23	2.2	...	...	2.2
				Glucose 100 Fructose 200	25.92	14.30	11.62	110.6	102.3	8.3	..
				Glucose 100 Glycine 25	25.92	15.10	10.82	102.9	102.3	...	0.6
				Glucose 100 Fructose 200 Glycine 25	25.92	14.39	11.53	109.7	102.3	7.4	
ALKALINE MEDIUM PRODUCED BY SODIUM PHOSPHATE–SODIUM HYDROXIDE MIXTURE											
25% Na_2HPO_4 + $12H_2O$	10	11.48	60	Glucose 100	25.95	15.46	10.49	99.8	99.8	...	..
0.5 *N* NaOH	5			Glycine 25	25.95	25.49	0.46	4.4	...	...	4.4
				Glucose 100 Fructose 200	25.95	15.36	10.59	100.8	99.8	1.0	..
				Glucose 100 Glycine 25	25.95	15.20	10.75	102.3	99.8	...	2.5
				Glucose 100 Fructose 200 Glycine 25	25.95	15.22	10.73	102.1	99.8	2.3	

diluted to 250 cc., the solution was of a concentration such that 25 cc. then contained 100 mg. glucose. For the mixtures containing glycine and fructose, these reagents were added to the diluted glucose solution before it was made up to volume.

A sample of Pfanstiehl 90 per cent levulose was recrystallized from glacial acetic acid, washed with absolute alcohol, and dried in a vacuum oven. The crystals were perfectly white and the purity by polarization using Vosburgh's (*11*) formula was 99.7 per cent.

The purity of the glycine was first tested by observation of the melting point which was found to be 225–9° C. Reported values of 231–5° C. are given in the literature. However, due to the fact that decomposition takes place near the melting point, the test is not very satisfactory. To confirm further the purity of the sample used with the sugars in the experimental work which follows, comparative tests of its reactivity with iodine solution were made upon five different samples of glycine from both natural and synthetic sources. One of these had been analyzed for amino nitrogen by the Van Slyke method and the theoretical value found. All showed practically the same reducing power toward iodine as that of the sample indicated in the table. It seems safe to conclude that the reducing action is due to glycine and not to any impurity in the samples. The fact that alanine and aspartic acid show a similar reactivity adds evidence to this conclusion.

As pointed out by Kolthoff (*8*) it was found necessary to mix the sugar and iodine solutions before adding the alkali. Twenty-five cubic centimeters of each were measured into glass-stoppered flasks and to the mixture the alkali was added. The time of making the mixture alkaline was considered as zero time. The flasks were then stoppered and placed in the dark. After the reaction had proceeded the specified number of minutes, the solution was acidified with 0.5 *N* sulfuric acid and titrated at once with the standard thiosulfate solution. Details as to the amount and kind of alkali used, and the time allotted, as well as the results obtained, are tabulated in Table I.

Discussion

In Table I the same value for iodine reduced is assigned for the glucose of the sugar mixture as is obtained where glucose is present alone, and the difference from the total reduction obtained is attributed to the accompanying fructose or glycine or both. This figure is given for the purpose of indicating the error only, since the presence of the amino acid or fructose probably alters the reduction value of the glucose itself, and even greater values than those which are attributed to the accompanying substances in the table, are likely due to them.

As shown in the first section, the error due to the fructose and glycine is greatest when the alkalinity is highest and due to sodium hydroxide. In all cases the error is in the direction of high results rather than lower values as was anticipated. The glycine itself seems to have some reducing action which may be analogous to the Hoffman hypobromite reaction. The time interval for the reaction with the sugar is such that oxidation takes place before the condensation of glucose and glycine is appreciable. The fact that fructose combines immediately with amino substances may account for the decrease in the total reduction when both are present together with glucose, as is shown by the fact that the summation of the increments assigned to each is greater than the increment when both are present in the mixture.

Table II—Rate of Oxidation of Glucose in Alkaline Medium Produced by Sodium Phosphate–Sodium Hydroxide Mixture

Alkali used, 10 cc. 25% Na_2HPO_4 + $12H_2O$; initial pH, 11.48; 5 cc. 0.5 *N* NaOH

Time	$Na_2S_2O_3$ Used Glucose	$Na_2S_2O_3$ Used Blank	$Na_2S_2O_3$ Equivalent to I_2 Reduced[a]	Glucose Present
Minutes	*Cc.*	*Cc.*	*Cc.*	*Mg.*
0	25.98	25.98	0.00	0.0
10	16.32	25.97	9.65	91.8
20	16.05	25.97	9.92	94.4
30	15.65	25.95	10.30	98.0
40	15.60	25.95	10.35	98.5
50	15.52	25.94	10.42	99.1
60	15.45	25.95	10.50	99.9
75	15.39	25.95	10.56	100.5
90	15.30	25.93	10.63	101.1

[a] 1 cc. = 9.515 mg. glucose.

Although Colin and Lievin (*2*) in 1918 have used a phosphate buffer in connection with iodometric sugar determinations, they have made no critical study of it. Most of the recent work has been with sodium hydroxide or sodium carbonate. With the latter the brisk effervescence of carbon dioxide upon acidification increases the danger of loss of iodine by volatility. This fact, in addition to other favorable aspects, led to an experiment as to the effect of the time interval upon the extent of oxidation of the pure glucose with the phosphate buffer. The results are given in Table II.

Conclusion

It seems safe to conclude that the presence of amino substances will tend to give slightly higher values for glucose by the iodometric method and that the condensation reaction between the aldol sugar and amino acid will not have a significant effect unless the solution has been allowed to stand for some time in an alkaline condition before the analysis is made. Such a situation might follow a defecation procedure as has been pointed out in a previous paper.

On the whole the phosphate buffer gives more satisfactory results than a carbonate buffer of the same pH. The results vary but little over a considerable time interval; there is less danger of loss of iodine on acidification of the reaction mixture and less error due to the presence of fructose and amino substances.

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Determination of Phosphates in Presence of Silica in Boiler Water[1]

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THE greatest source of error in the colorimetric determination of phosphate in boiler waters and in other alkaline solutions is the interference of silica or silicate. Relatively minute quantities of silica cause the production of a blue color similar to the color due to phosphate. This interference has recently been noted by many workers in the boiler field. The present paper describes a method that minimizes this difficulty and produces reliable results in the presence of silica.

When the colorimetric method for phosphate determination was first used in this laboratory certain samples developed a clear blue color more like the blue of copper sulfate solution than the characteristic violet-blue of the phosphate when treated with slightly acidified molybdate and hydroquinone solutions, and subsequently neutralized with sodium carbonate in the presence of sodium sulfate. It had been suggested that iron interfered, but this was found not to be the cause of the clear blue color in the samples of boiler water, zeolite-softened well water, or certain untreated natural waters which contained no phosphate.

Investigation showed the color to be due to silica. The presence of silica also intensified the color due to phosphates in samples of known phosphate content, causing errors in the phosphate estimation as great as 100 per cent.

Since the blue color is proportional to the amount of phosphate or silicate ion in solution in the sample, it was obviously necessary to remove the silicate if the phosphate was to be determined accurately. It was not convenient to dehydrate or precipitate the silicate, but by acidifying to the right degree it was found possible to repress the ionization of the weak silicic acid to a point where it developed no noticeable blue color, while the stronger phosphoric acid remained sufficiently ionized to react with the molybdate and produce a blue color proportional in intensity to the concentration of phosphate present.

It is important to make up the phosphate standards with the same amount of acid used in testing the samples, as the quantity of acid used influences the depth of color produced.

Solutions Required

(1) Standard sodium phosphate, $Na_3PO_4.12H_2O$—0.320 gram per liter. 1 ml. = 2 p. p. m. PO_4 in 40 ml. H_2O.

(2) Sulfuric acid—600 ml. H_2O plus 300 ml. 95% c. p. H_2SO_4.

(3) Ammonium molybdate, $(NH_4)_6 Mo_7O_{21}.4H_2O$—92.3 grams per liter plus 38 ml. concd. H_2SO_4.

(4) Hydroquinone, $C_6H_6(OH)_2$—23 grams per liter plus 5 ml. concd. H_2SO_4.

(5) Alkaline sodium sulfite—183 grams NaOH + 16 grams Na_2SO_3 per liter H_2O.

Procedure

To a 40-ml. sample to be tested for phosphate, add 5 ml. sulfuric acid and mix thoroughly. Add 1 ml. of molybdate solution and 1 ml. of hydroquinone solution. Again shake vigorously and allow to stand 5 minutes. Then add 15 ml. of the alkaline sodium sulfite. If phosphate is present a blue color will form which is then compared with standards of known PO_4 content prepared in exactly the same way as the sample being analyzed.

For general laboratory analysis it is found convenient to make up standards of 5, 10, 20, 30, 40, and 50 p. p. m. In the boiler room, however, it is usually sufficient to prepare only two standards representing the upper and lower limits of allowable PO_4 concentration. If the color developed in the boiler water is less than 20, for example, more sodium phosphate should be fed. If the color is greater than 30, the addition of phosphate may be curtailed.

Large test tubes of uniform size or 100-ml. Nessler tubes will be found convenient for comparing the colors. The comparison should be made at once since the phosphate color begins to fade after about 10 minutes. There is also a tendency for the silicate color to appear if the sample is allowed to stand 5 to 10 minutes after neutralizing the acid with the alkaline sulfite solution.

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[1] Received September 4, 1930.

Determination of Copper in Dairy Products[1,2]

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A new method for the determination of copper in foodstuffs and biological material has been devised. It was found that the method of Elvehjem and Lindow could be shortened considerably, the separation of copper sulfide improved, and the danger of losses in transfers minimized, by shaking out the precipitated copper sulfide with chloroform instead of separating it by filtering. It was found that the ashing temperature and time used may be the source of large errors in copper determinations. The ashing temperature should not exceed 565° C. for 3 to 4 hours.

Detailed directions for the procedure, embodying precautions as to ashing conditions, and the modification mentioned, are given. The detailed method as outlined gives results that agree closely with those obtained by the original Elvehjem-Lindow method, when the latter is used with the necessary precautions as to ashing conditions.

IN THE past, copper has been considered toxic or undesirable in foods, but today it is generally known that copper is an essential constituent of most plant and animal material, and that it plays an important role in life processes. This has been definitely shown by the recent work by Hart and co-workers (*5*) on the function of minute amounts of copper in foods in the cure of nutritional anemia. This recent work has opened an important field for further studies of the functions of this element in life processes, and its distribution in living material.

However, in the manufacture of many foodstuffs, it is still desirable to keep the copper content at a minimum for technical, if not legal, reasons. This is especially true in the case of dairy products, where the detrimental effect of copper has long been known, but not fully appreciated until the recent work of Guthrie (*4*). A method for determining the copper content of foodstuffs is therefore of general and current interest.

The method given in this paper was developed in connection with experimental work to determine the solubility of copper in milk. However, the details evolved are applicable to the analysis of other foodstuffs and biological materials. The method as given is a modification of the Elvehjem-Lindow (*3*) method for the determination of copper in biological materials, which in turn was based on the method of Biazzo (*2*) for the copper determination in canned vegetables.

Methods Previously Used

Recent work on the distribution of copper in foodstuffs and biological materials has become possible only through the development of the colorimetric methods which permit the estimation of minute amounts of copper in relatively small samples. Previous to this, electrolytic methods had been used most frequently, but for samples containing mere traces of copper these methods were unsatisfactory because of the large samples required to obtain a weighable deposit, and because of the other ash constituents which frequently interfered with the copper deposition.

The colorimetric methods which have been developed to overcome these difficulties have been used in analyses to determine the copper content of raw milk and the amount of copper dissolved by milk from dairy equipment. The potassium ethylxanthate method was adapted to the determination of copper in milk by Supplee and Bellis (*9*) and this adaptation was used by King and Etzel (*6*), Quam and coworkers (*7*), and, in combination with the electrolytic method, by Rice and Miscall (*8*). The colorimetric method developed by Elvehjem and Lindow for the determination of copper in biological materials is more recent. It is based on the color reaction given by copper with potassium thiocyanate and pyridine, which is very specific, and the color in the chloroform solution is proportional to the amount of copper present.

Observations Leading to Modified Method

The method of Elvehjem and Lindow was tentatively selected mainly because the reagents were available.

The accuracy of the method was tested by making a large number of recovery determinations; but the results were disappointing. Not more than 55 to 70 per cent of the added copper was recovered, even when the directions of the method were followed in detail.

To find the cause of the losses of copper during the procedure, efforts were made to induce more complete and rapid flocculation of the copper sulfide, but no improvements in the percentage of recovery were attained. Removing the iron and phosphate in the manner of Supplee and Bellis (addition of an excess of ammonium hydroxide to the ash solution and filtering) and making the colorimetric determination directly on the concentrated filtrate did not give the desired recovery, thus indicating that copper was lost at some other step in the procedure.

When the copper was added to the milk ash solution, recovery was greatly improved. This finding, together with the observation that any attempt to obtain a whiter ash by using higher ashing temperatures and longer times was followed by lower results, called for improvement of the ashing procedure.

In further determinations the ashing temperature was confined to a range of between 510° and 565° C. Using this temperature, ashing was completed in about 3 to 4 hours. Under these conditions results given in Table I were obtained.

Table I—Copper Determinations in Skim Milk with and without Added Copper Using Ashing Temperature of 510° to 565° C.

Sample	Skim Milk Used	Copper Added	Colorimeter Readings: Standard[a]	Colorimeter Readings: Unknown	Copper Indicated	Added Copper Recovered
	Cc.	*Mg.*	*Mm.*	*Mm.*	*Mg.*	%
1	250	0.0	5.00	12.27	0.041	91.0
	250	0.0	5.00	12.88	0.039	
	250	0.1[b]	13.00	9.98	0.130	
	250	0.1[b]	13.00	9.87	0.132	
2	250	0.0	2.90	10.50	0.028 (0.0235)[d]	96.65[d]
	250	0.0	3.45	11.53	0.030 (0.0252)[d]	
	210	0.1[c]	10.00	8.27	0.121	

[a] Color standard 0.1 mg. copper in 5 cc. chloroform.
[b] Copper added to ash solution.
[c] Copper added to skim milk before ashing.
[d] Figured to basis of 210-cc. milk sample.

The addition of 0.1 mg. copper to the ash solution of sample 1 increased the result of the analysis from 0.040 to 0.131 mg., or an increase of 0.091 mg. This represents a recovery of the added copper of 91 per cent. In sample 2

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[2] Published with the permission of the Director of the Wisconsin Agricultural Experiment Station.

the addition of 0.1 mg. copper to the skim milk before ashing increased the result of the analysis from 0.02435 to 0.1210 mg. copper, or an increase of 0.09665 mg. This represents a recovery of added copper of 96.65 per cent. These results indicate that the ashing procedure used had not caused the loss of any copper. The possibility of losing copper in ashing and the suitability of a low ashing temperature is further illustrated in Table II.

Table II—Effect of Ashing Conditions on Copper Determinations

Whole Milk[a] Used	Copper Added	Ashing Temp.	Ashing Time	Colorimeter Readings: Standard[b]	Colorimeter Readings: Unknown	Copper Indicated	Added Copper Recovered
Cc.	*Mg.*	° *C.*	*Hrs.*	*Mm.*	*Mm.*	*Mg.*	%
250	0.0	700–840	3	1.00	7.22	0.014	
250	0.1	700–840	3	5.00	11.22	0.045	31.0
250	0.0	510	8	3.00	8.89	0.034	
250	0.1	510	8	5.00	4.43	0.113	79.0

[a] The same milk was used throughout.
[b] The color standard contained 0.1 mg. copper in 5 cc. chloroform.

From the results in this table it is clear that a large fraction of the copper may be lost in ashing due to high ashing temperature or excessive time. The low percentage recovery of added copper, even where an ashing temperature of 510° C. was used, is due to the prolonged ashing, the results differing from those of Table I where the ashing time was 3 to 4 hours. It is probable that part of this loss is caused by the copper fusing with the silica dishes that were used, and part to volatilization.

With the importance of the ashing temperature and time recognized and carefully controlled, it was now decided to compare the original method of Elvehjem and Lindow with the modified form of this method, the modification consisting, as already stated, in the removal of the interfering iron and phosphate in the manner of Supplee and Bellis. The comparison of the results obtained by the two methods showed good agreement in a reasonably large number of experiments. On the average the original Elvehjem-Lindow method gave slightly higher results.

In the study to which this work on methods was incidental, both methods have been used, and both served quite well for the routine determinations, provided the precautions as to ashing temperature and time were observed. However, both methods require considerable time. The desire to shorten the time finally led to the use of chloroform to shake out the copper sulfide precipitated from the ash solution instead of allowing it to stand to flocculate, and then filtering.

Chloroform has been used for removing the colloidal copper sulfide to facilitate the reading of the end point in the volumetric titration of copper with ammonium sulfide (*1*). It was found that this procedure could be applied advantageously instead of filtering for the removal of the copper sulfide precipitate from the milk ash solution. A considerable saving of time is effected and, as will be shown, there is no sacrifice in accuracy.

Method for Determination of Copper in Milk

A 250-cc. portion of the sample is carefully evaporated over a low flame in a quartz evaporating dish. The addition of 10 to 15 drops of glacial acetic acid prevents film formation and foaming, and thus hastens evaporation. After evaporation of most of the moisture, the drying is completed in an oven at 150° to 200° C. When the sample has been thoroughly dried, as indicated by the caramelized or even charred appearance, it is transferred to an electric ashing furnace, the temperature of which should not exceed 565° C. The use of a pyrometer so that the ashing may be conducted at a known temperature is advisable. At this temperature ashing is usually complete in 3 to 4 hours, and a grayish white ash is obtained.

The ash is moistened with 4 cc. of dilute hydrochloric acid (1 to 1), and diluted to about 100 cc. with distilled water. To bring about complete solution, the solution in the quartz evaporating dish is heated and kept near the boiling point for about 20 minutes. It is then filtered, the dish and filter carefully washed with distilled water, and the filtrate and washings collected. The undestroyed carbon together with the filter paper is returned to the quartz dish and ashed for 30 minutes; the ash is dissolved in a few drops of dilute hydrochloric acid, diluted with distilled water, and warmed, filtered, and washed as before, the filtrate and washings being added to the main ash solution.

The total ash solution, or an aliquot thereof, if the copper content is expected to be high, is evaporated to about 10 cc. and transferred to a 25-cc. volumetric flask. Complete transfer is aided by adding a drop of dilute hydrochloric acid (1 to 1) to the first rinsing, and by heating this solution to boiling. After cooling to about room temperature, hydrogen sulfide is passed into the solution in the volumetric flask for 5 minutes through a capillary glass tube (a 4- or 5-mm. glass tube drawn out to a capillary of about 1 mm. outside diameter). The capillary should not be immersed in the solution until the hydrogen sulfide has been turned on, to prevent the solution from rising in the capillary; for the same reason it is advisable to remove the capillary from the solution before shutting off the hydrogen sulfide. The outside of the capillary is rinsed with 0.5 cc. of saturated hydrogen sulfide water. The flask is stoppered and set in cold water or otherwise cooled to about 10° C. To this cooled solution containing the precipitated copper sulfide, 5 cc. of chloroform, which has previously been cooled to about 10° C., are added, the flask is securely stoppered and shaken vigorously for about 1 minute. The flask is then set in cold water and the chloroform allowed to settle out. The water layer becomes perfectly clear, and the copper sulfide is now contained in the chloroform at the bottom of the flask.

The water solution is drawn off by means of a capillary tube, leaving enough to avoid the possibility of drawing out some of the chloroform. The remainder is diluted with 15 to 20 cc. of cold, saturated hydrogen sulfide water, and this is again drawn out as completely as possible. This one washing has been found sufficient in all cases; it can be omitted entirely if the aliquot does not represent more than the ash of 50 cc. of milk. The small amount of phosphate which is left in the solution in this case dissolves completely in the acetic acid added later in the colorimetric determination. Gas bubbles may make the removing of the water portion difficult if the temperature during the operations is too high.

It is desirable to limit the volume of the ash solution to 10 cc. as directed above, so that after the addition of the chloroform there is ample space for thorough shaking. The capillary tube which is used to draw out the water solution should not touch the side of the neck, because a fine film of chloroform containing copper sulfide usually covers the glass.

After the copper sulfide is shaken out with chloroform, the water solution drawn off, and the residue rinsed as directed, the chloroform is evaporated by placing the flask in a hot water bath for 10 minutes, increasing the temperature to boiling towards the end. The residue in the flask is dissolved by adding 1 cc. of concentrated nitric acid, placing the flask in the hot water bath for 20 minutes with occasional shaking to bring the acid in contact with the entire inside surface of the flask. The solution is then neutralized with dilute sodium hydroxide (200 grams in 1 liter of solution) so that the reaction is just alkaline phenolphthalein. The neck of the flask must be rinsed carefully to remove every trace of nitric acid (also oxides of nitrogen) which would interfere with the color reaction later. The indicator should not be added too soon, because the compound formed by the destruction of phenolphthalein by strong acid or alkali dissolves in chloroform with a yellow color, and thus interferes with the colorimetric determination even if present only in traces. In the above neutralization, the indicator may be added after the first permanent turbidity develops due to the precipitation of traces of phosphate remaining in the flask. When this point has been reached, one drop of dilute sodium hydroxide solution then usually suffices to make the solution just alkaline to phenolphthalein.

From this point in the procedure the colorimetric determination as given by Elvehjem and Lindow is followed. To the neutralized solution in the flask, containing the dissolved copper sulfide, 1 cc. of glacial acetic acid, 1 cc. of a 10 per cent solution of potassium thiocyanate, and 10 drops of pyridine are added in the order given, with slight shaking after each addition. Finally 5 cc. of chloroform, accurately measured, are added, and the volume made up to the mark with distilled water. After thorough shaking, the chloroform has taken up the green copper-thiocyanate-pyridine compound. The water portion is then removed by drawing off with a capillary tube, and the chloroform solution is used for the colorimetric comparison with a standard in a suitable colorimeter.

Table III—Results Obtained by New Method and Elvehjem-Lindow Method Using Ashing Temperatures of 510° to 565° C. and Ashing Times of 3 to 4 Hours

Sample	Elvehjem-Lindow Method (A): Aliquot taken of ash soln. of 250 cc. milk	Copper detd. in aliquot	Copper	New Method (B): Aliquot taken of ash soln. of 250 cc. milk	Copper detd. in aliquot	Copper	Deviation of B from A: Copper detd. in aliquot	Copper
		Mg.	Mg./l.		Mg.	Mg./l.	Mg.	Mg./l.
1	0.25	0.054	0.864	1/4	0.054	0.864	0.000	0.000
2	0.25	0.251	4.016	1/4	0.251	4.016	0.000	0.000
3	0.25	0.226[b]	3.616	1/4	0.263	4.208	+0.0370	0.592
4	0.40	0.050	0.500	2/5	0.053	0.530	+0.0030	0.030
5[a]	0.20	0.048	0.480	2/5	0.049	0.490	+0.0025	0.025
				2/5	0.052	0.520		
6[a]	0.25	0.054	0.432	1/4	0.055	0.440	+0.0015	0.012
				1/4	0.056	0.448		
7[a]	0.25	0.104	0.832	1/4	0.103	0.824	+0.0005	0.004
				1/4	0.105	0.848		
8[a]	0.25	0.065	0.520	1/4	0.067	0.536	+0.0075	0.060
				1/4	0.078	0.624		
9	0.25	0.041	0.656	1/4	0.043	0.688	+0.0025	0.040
				1/4	0.044	0.704		
10	0.25	0.019	0.304	1/4	0.020	0.320	+0.0015	0.024
					0.021	0.336		
11	0.25	0.096	1.536	1/4	0.103	1.648	+0.0110	0.168
				1/4	0.110	1.760		
12	0.40	0.070	0.700	2/5	0.072	0.720	+0.0020	0.020
				1/5	0.036	0.720		
13	0.25	0.094	1.504	1/4	0.104	1.664	+0.0100	0.160
14	0.25	0.073	1.168	1/4	0.066	1.056	−0.0070	0.120
15	0.016	0.051	12.750	2/125	0.047	11.750	−0.0040	1.000
16	0.02	0.047	9.400	1/50	0.050	10.000	+0.0030	0.600

[a] 500 cc. milk had been used for ashing.

[b] Sample was turbid and colorimetric readings less exact. This accounts for wide discrepancy in results. With amounts of copper as in samples 2 and 3, turbidity is likely to develop in 5-cc. chloroform solution. Exact point at which this occurs varies with temperature and salts present.

The standard for comparison is made from a stock solution made by dissolving 0.3928 gram of pure crystalline copper sulfate, $CuSO_4.5H_2O$, in distilled water and diluting to 1 liter. This stock solution contains 0.1 mg. of copper in each cubic centimeter. In making up the standard for comparison, enough of this stock solution should be used so that the standard contains approximately the same amount of copper as the unknown. If the copper content of the unknown is from 0.05 to 0.15 mg., take 1 cc. of the stock solution, add 1 cc. of glacial acetic acid, 1 cc. of 10 per cent potassium thiocyanate solution, and 10 drops of pyridine, and proceed as already described for the unknown sample. The standard for comparison will finally consist of 5 cc. chloroform with an amount of copper-thiocyanate-pyridine compound dissolved in accordance with the amount of stock solution used.

In working at low room temperatures, the colorimetric comparisons are frequently seriously influenced by the tendency of the standard to become turbid. Slight warming will cause the standard to become clear, but on cooling it again becomes cloudy. This difficulty may be overcome entirely by adding 1 cc. of concentrated nitric acid in making up the standard; the solution is then neutralized to phenolphthalein with dilute sodium hydroxide before adding the glacial acetic acid, potassium thiocyanate and pyridine, and shaking out with chloroform.

Comparison of New Method with Elvehjem-Lindow Method

Before the method, as outlined above, was finally adopted for the routine analyses in the problem under investigation, the copper content of a number of samples of milk, contaminated by varying amounts of copper, was determined by both methods. These results are given in Table III.

When the results given in this table are compared, it it must be considered that minute amounts of copper are being dealt with and that the final determinations are by colorimetric comparisons. In view of this, it may be concluded, first, that the results obtained by the two methods agree closely, and, second, that the results obtained by method B are slightly higher in the majority of cases and in the average. This slightly higher result by method B must be expected because there is obviously less opportunity for losses by transfers in method B, and because it was observed that the chloroform removed additional copper sulfide from the filtrate of the copper sulfide precipitation as used in method A.

From the above, and from results of recovery determinations made with the new method, and as shown in Table IV, it is apparent that the modifications introduced in the new method do not impair the accuracy of the original method. The advantages of the new method appear to be the saving of considerable time, reduced danger of contamination and of losses in transfers, and more complete separation of the copper sulfide.

Table IV—Copper Determinations in Milk with and without Added Copper Using Ashing Temperatures of 510° to 565° C.

Sample	Milk Ashed	Copper Ashed to Milk	Colorimeter Readings: Standard: Copper	Standard: Reading	Unknown reading	Copper Indicated	Added Copper Recovered
	Cc.	Mg.	Mg.	Mm.	Mm.	Mg.	%
1	250	0.00	0.05	10.0	12.22	0.0409	
	250	0.10	0.10	10.0	7.34	0.1363	95.4
	250	0.10	0.10	10.0	6.47	0.1545	113.6
2	250	0.00	0.10	2.0	14.00	0.0143	
	250	0.15	0.10	10.0	6.73	0.1487	89.6
	250	0.20	0.10	10.0	4.85	0.2062	96.0
3	250	0.00	0.03	10.0	11.39	0.0264	
	250	0.10	0.10	10.0	8.50	0.1177	91.3
	250	0.10	0.10	10.0	8.37	0.1195	93.1
	250	0.05	0.10	8.0	10.56	0.0758	98.8

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Electrolytic Determination of Lead as Lead Dioxide[1]

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The electrolytic method for the determination of lead has been studied and the best results were obtained when the following conditions were observed: The sample should be electrolyzed for $1^1/_2$ to 2 hours with a current of 3 amperes and placed on the board at a temperature of 90° C. The anodes should be sand blasted and clean and the amount of lead present between 5 and 150 mg. The solution should contain from 20 to 30 per cent free nitric acid and about $^1/_4$ cc. of sulfuric acid. Interfering elements should be absent.

The effects of interfering impurities were investigated and silver, bismuth, manganese, tin, arsenic, antimony, mercury, chromate, and phosphate were found to cause poor results. If these elements are present in any great amount, a separation should be made before electrolyzing. Potassium, sodium, ammonia, calcium, magnesium, cadmium, copper, zinc, and iron were found to have no effect unless the solution contains large amounts of the salt.

The precision of the method was determined. It was found that the average variation obtained was less than 0.2 mg. provided the lead content of the sample is between 5 and 150 mg. Samples of higher lead content can be run but the error is usually somewhat larger. The error is practically always negative. The theoretical factor should always be used with this method in order to avoid low results.

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THE electrolytic method for lead has been adopted as a control method especially for ores in which the lead content is less than 7 per cent. The method is rapid and accurate under certain conditions but variations in conditions produce erratic and irregular results which may check each other but will not check the true lead content.

Because of this fact a thorough study of the conditions affecting the electrolytic deposition of lead dioxide was undertaken. The following factors may affect the determination of lead: (1) apparatus, (2) temperature, (3) time of electrolysis, (4) concentration of acid, (5) current, (6) amount of lead present, (7) added reagents, and (8) type of material analyzed.

Apparatus and Solutions

A slight modification of the apparatus first used by Guess (*1*), and further described by Holmes and Morgan (*2*), was used in this work. A diagram of the apparatus is given in Figure 1.

The anodes should be made of 0.005-inch (0.0127-cm.) sand blasted sheet platinum. Sleeves of rubber tubing placed over the split terminals furnish contact pressure to hold the anodes and cathodes in place. The cathodes are firmly held in place by an additional bakelite sleeve placed over the end of the terminal. The cathodes are stiffer and last longer if crimped as shown. The terminals should be of rolled hard drawn aluminum in order to resist the acid fumes to which they are exposed. The base may be either cast or machined but the terminals should be welded to it to insure against poor contact. The wiring should be so arranged that any number of cells may be removed from the board without disturbing the remaining cells. The wiring in the diagram has this advantage.

Lead nitrate was prepared by dissolving pure lead in nitric acid. The solution was filtered through a quartz filter, and precipitated with concentrated nitric acid. The recrystallization was repeated several times and the salt dried. Solutions of known lead content were prepared from this purified lead nitrate and checked gravimetrically by the sulfate method.

Preliminary Procedure

In the preliminary experiments the conditions were selected which had been recommended by other workers and had been used in this laboratory. All factors were held constant save one which was varied and the effect of this variable was studied. The procedure at first used was to take a suitable weight of the sample and digest with 20 cc. of nitric acid. When brown fumes ceased to be evolved, 15 cc. of a saturated solution of ammonium nitrate was added and the solution boiled for approximately 1 minute. The sample was then diluted with cold water and electrolyzed for $1^1/_2$ to 2 hours. If a pure lead solution were used instead of a

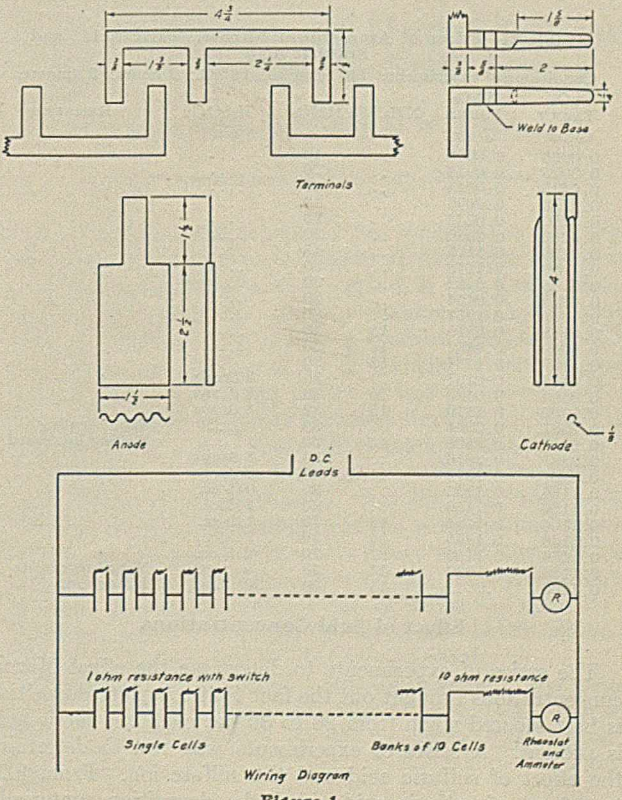

Figure 1

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[1] Received September 5, 1930. Presented before the Division of Rubber Chemistry at the 80th Meeting of the American Chemical Society, Cincinnati, Ohio, September 8 to 12, 1930.

standard sample, the procedure was approximately the same.

Effect of Time and Temperature

The usual value for current with the type of anodes used in these experiments is 3 amperes (a current density of about 7 amperes per square decimeter), giving good results in $1^1/_2$ to 2 hours. It was found that complete deposition in the cold could only be secured by electrolysis over a period of 8 or more hours, the slowness of deposition being due to the plating of lead on the cathode. Electrolysis of a solution at an initial temperature of 90° to 95° C. yielded a quantitative deposition of lead in a period of $1^1/_2$ to 2 hours. The temperature during this time dropped to about 50° C. The lead is not completely deposited from the solution if the high temperature is maintained during the electrolysis.

Table I—Effect of Time and Temperature

Conditions of experiment: 140 cc. soln.; 30 cc. HNO_3; 3 amperes

	Gram
PbO_2 taken	0.0288
Average of 8 determinations (cold) $1^1/_2$ hours	0.0254
Maximum deviation from average	0.0003
Error	0.0034
PbO_2 taken	0.0250
Average of 6 determinations (cold) 8 hours	0.0249
Maximum deviation from average	0.0002
Error	0.0001
PbO_2 taken	0.0250
Average of 22 determinations (hot) $1^1/_2$ hours	0.02501
Maximum deviation from average	0.0002
Error	0.00001

These results, given in Table I, indicate that the temperature is one of the most important factors in the electrolysis of a lead solution. Results in the cold are poor unless a long period of electrolysis is used, while results with a hot solution are very good in $1^1/_2$ to 2 hours. The experiments also brought out the fact that checking results could be obtained under practically all conditions, even though all of the lead was not deposited from the solution. This emphasizes the fact that checking results do not mean quantitative results.

Table II—Effect of Ammonium Nitrate, Nitric Acid, and Sulfuric Acid

Conditions of experiment: 140 cc. soln.; 90° C.; 2 hours; 3 amperes

PbO_2 TAKEN	PbO_2 FOUND	NH_4NO_3	HNO_3	H_2SO_4	REMARKS
Gram	*Gram*	*Cc.*	*Cc.*	*Cc.*	
0.0025	0.0009	..	10	....	
0.0025	0.0016	..	20	....	
0.0025	0.0014	..	30	....	
0.0250	0.0096	..	10	....	
0.0250	0.0238	..	20	....	
0.0250	0.0250	..	30	....	
0.1156	0.1125	..	15	....	
0.1156	0.1148	..	30	....	
0.0188	0.0182	..	30	....	
0.0469	0.0454	..	30	....	
0.1407	0.1351	..	30	....	
0.0188	0.0175	15	30	....	
0.0469	0.0452	15	30	....	
0.1407	0.1384	15	30	....	
0.0188	0.0187	..	30	8 drops	
0.0469	0.0470	..	30	8 drops	
0.1407	0.1410	15	30	8 drops	
0.2887	0.2864	..	30	....	Slight scaling
0.2887	0.2806	15	30	....	Scaling increased
0.2887	0.2876	..	30	8 drops	
0.2887	0.2878	15	30	8 drops	
0.1156	0.1155	..	30	0.5 cc.	
0.1156	0.1156	..	30	1.5 cc.	
0.1156	0.1154	15	30	1.5 cc.	
0.1156	0.1155	15	30	2.5 cc.	
0.1156	0.1156	..	30	2.5 cc.	
0.1156	0.1080	15	30	5 cc.	Very low results
0.1156	....	15	30	30 cc.	No deposit

Effect of Acid Concentrations

The series of experiments to determine the effect of acid concentrations brought out the fact that complete deposition is best secured when from 20 to 30 per cent free nitric acid is present. A series of experiments was run to determine the effect of sulfuric acid and the sulfate ion. From 0.25 to 0.5 cc. of sulfuric acid aided the deposition materially by giving a firmer and more coherent deposit and increasing the amount of lead dioxide which could be quantitatively determined. A concentration of sulfuric acid in greater amounts than 2.5 cc. produces incomplete deposition. The concentration of sulfate ion produced by the addition of sodium sulfate, potassium sulfate, or calcium sulfate produced the same effect as did sulfuric acid. When running a sulfide ore there is always a little sulfate present, either from the original ore or formed by the action of the nitric acid during the solution of the sample. This sulfate probably explains the excellent results usually obtained in the electrolytic analysis of sulfide ores.

In these experiments, noted in Table II, it was demonstrated that ammonium nitrate is not essential and in larger amounts tends to produce scaling. Also it has been found that satisfactory results are obtained when the electrodes are dried rapidly on a hot plate or in an oven at a temperature between 150° and 200° C. The anodes are removed from the hot plate as soon as dry.

Interfering Elements

The effect of certain salts on the deposition of lead dioxide was studied. The salts were those which might be obtained in the solution of a lead ore. Calcium nitrate, cadmium nitrate, zinc nitrate, potassium nitrate, sodium nitrate, cupric nitrate, ferric nitrate, and perchloric acid were without effect when sulfuric acid was present.

Certain elements, however, do interfere with the determination. An investigation of the effects of silver, bismuth, arsenic, antimony, mercury, manganese, tin, chromate, and phosphate shows them to be harmful to the determination. Some of these impurities deposit with the lead while others prevent deposition or cause scaling of the lead dioxide deposit. In any case in which these elements are present in an amount large enough to cause trouble, a separation must be performed. Traces of these impurities may be present without the production of any appreciable interference. The results of this investigation are given in Table III.

A small amount of chromate does not harm the determination so that it would be possible to precipitate lead from solution as lead chromate, redissolve, and deposit electrolytically as lead dioxide.

Table III—Effect of Interfering Elements

Conditions of experiment: 30 cc. HNO_3; 1.5–2 hours; 3 amperes; 0.25 cc. H_2SO_4; 90° C.; 140 cc. soln.

IMPURITY PRESENT	WEIGHT OF IMPURITY	PbO_2 TAKEN	PbO_2 FOUND	REMARKS
	Gram	*Gram*	*Gram*	
As	0.0050	0.0100	0.0064	
	0.0100	0.0500	0.0416	
Mn	0.0300	0.0100	0.0108	Deposit with PbO_2 loosens deposit
	0.0200	0.0500	0.0504	
	Scaling with large amounts of Mn			
Bi	0.0050	0.0500	0.0524	Deposit with PbO_2 may loosen deposit
	0.0100	0.0500	0.0550	
	0.0500	0.0500	Scaling	
Sn	0.2500	0.0500	0.0552	
	0.5000	0.0500	0.0590	
Sb	0.0100	0.0500	0.0520	
	0.1000	0.0500	0.0494	
Ag	0.0100	0.0500	0.0506	Deposits with PbO_2
	0.1000	0.0500	0.0510	
Hg	0.0100	0.0500	0.0426	Hg on cathode holds Pb
	0.1000	0.0500	0.0422	
CrO_4	0.0500	0.1156	0.1157	Occluded
	0.2500	0.1156	0.1168	
	1.0000	0.1156	0.1186	
H_3PO_4	1 cc.	0.0500	Very low	
	5 cc.	0.0500	No deposit	
Na_2HPO_4	0.0500	0.1156	0.1147	
	0.2500	0.1156	0.1100	
	0.5000	0.1156	0.0980	

Amount of Lead

The amount of lead which may be quantitatively deposited was determined and the data presented in Table IV and Figures 2 and 3. These indicate that the method gives excellent results when the lead content of the sample is between 5 and 150 mg. Within this range the average error of the method is less than 0.2 mg. of lead. When the sample contains less than 5 mg. of lead, low results are obtained. Should the lead content of the solution be more than 150 mg., as much as 1 mg. of lead may remain in solution.

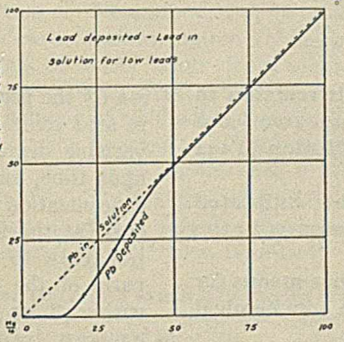

Figure 2

Other workers have recommended factors less than theoretical. According to this the method should give high results when the theoretical factor is used, but in these experiments high results were never obtained unless some interfering element, such as bismuth or tin, were present. The factor lead taken over lead dioxide deposited, is always 0.8662 if the proper conditions are observed. Hydrogen sulfide was used to test for the complete deposition of lead and only traces were found after electrolysis.

Table IV—Deposition of Various Amounts of PbO_2

Conditions of experiment: 140 cc. soln.; 0.25 cc. H_2SO_4; 2 hours; 3 amperes; 90° C.; 35 cc. HNO_3

PbO_2 Taken	PbO_2 Found	No. of Detns.	Average Deviation
Gram	Gram		Gram
0.0015	0.0000	2	.....
0.0020	0.0010	3	.....
0.0025	0.0012	5	0.0013
0.0030	0.0022	1	0.0008
0.0035	0.0028	1	0.0007
0.0040	0.0036	5	0.0004
0.0045	0.0044	1	0.0001
0.0050	0.0049	4	0.0001
0.0075	0.0076	2	0.0001
0.0100	0.0100	2	0.0000
0.0250	0.02501	22	0.00001
0.1156	0.11555	18	0.00005
0.1732	0.1727	5	0.0005
0.2309	0.2295	3	0.0014
0.2887	0.2876	5	0.0012
0.3464	0.3451	4	0.0013
0.4041	0.4024	5	0.0017

Procedure

The procedure as finally adopted and recommended for use when there is no interference from other elements is as follows: A sample, the amount depending upon the per cent of lead, is weighed into an ordinary 150 cc. electrolytic beaker, 30 to 35 cc. of nitric acid are added, and the sample is boiled until brown fumes cease to be evolved. The sides of the beaker are washed and 0.25 cc. sulfuric acid added. The solution is boiled again for 1 to 2 minutes, diluted to 140 cc., and heated to a temperature of 90° C. It is then electrolyzed for 2 hours at 3 amperes. The anodes are removed from the board, washed in water, alcohol, dried rapidly in an oven or on a hot plate, cooled, and weighed. The weight of lead dioxide deposited is equal to the per cent of lead when a factor weight of the sample has been used. When interfering elements are present, it is necessary to perform a separation before electrolyzing.

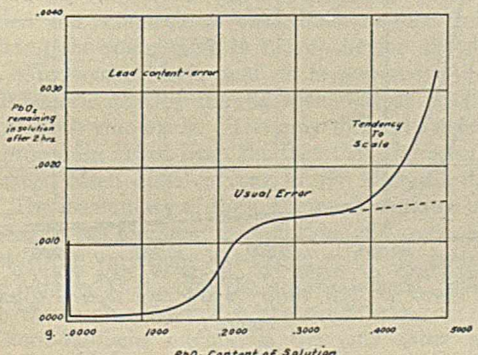

Figure 3

In applying this method to the analysis of lead concentrates it is usually best to take a one-fourth factor weight sample. A one-half factor weight sample may be run but the error is usually greater. Care must be taken to assure a homogeneous sample. In some instances it is necessary to grind the sample to pass a 200-mesh screen before satisfactory results can be obtained.

This is illustrated by the data given in Table V.

Table V—Analysis of Lead Concentrates

Original Sample 100-Mesh	Sample 150-Mesh	Sample 200-Mesh
%	%	%
51.76	53.88	53.92
53.76	53.68	53.92
53.96	53.60	54.04
53.92	53.76	53.88[a]
54.46	53.88	53.84[a]
53.72	54.08	53.84[a]
53.44		Av. 53.91 ± 0.05
53.48		
54.46		
53.42		
53.90		
53.90		

[a] Run by A. W. Holmes, Bureau of Mines.

Literature Cited

(1) Guess, *Bull. Am. Inst. Mining Eng.*, 1239 (1905).
(2) Holmes and Morgan, Ind. Eng. Chem., Anal. Ed., 1, 210 (1929).

Determination of Hydrogen Sulfide in Refinery Still Gases[1]

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THE iodine titration method has always been a standard method for the determination of hydrogen sulfide, but with refinery still gases this method is inaccurate because of the reaction of the gaseous unsaturated hydrocarbons with the iodine. The following method has been used in our laboratory: 100 cc. of 0.1 *N* acid lead nitrate is placed in a Fisher gas washing bottle or any convenient scrubber. The gas to be tested is passed through the bottle and metered with a gas meter, or a known volume of water is displaced. A second wash bottle with 100 cc. of 0.1 *N* lead nitrate is placed directly after the first wash bottle. With the slightest discoloration of the second bottle, the rate of flow of the gas is reduced to insure all of the hydrogen sulfide being caught in the first bottle. The second bottle is useful also when testing a gas in which the quantity of hydrogen sulfide is unknown, as the second bottle will be an indicator when the first bottle becomes spent.

The first bottle is filtered, made up to volume, and aliquot portions titrated with ammonium molybdate solution. With convenient factors on the solutions, the method is rapid and accurate.

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[1] Received November 3, 1930.

Proposed Modification of Oxygen Consumed Method for Determination of Sea Water Pollution[1]

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By applying the Zimmerman-Reinhardt reaction to alkaline permanganate consumption, an easy and reliable method for the estimation of pollution in sea water is obtained.

Each set of determinations must be calibrated against the blank sample of the purest sea water in the locality of the pollution.

The method may be correlated with other means for the detection of pollution such as the biochemical oxygen demand, bacteria, and plankton.

IN USING the standard method (*2*) for the determination of pollution in briny waters, considerable difficulty was experienced in this laboratory in obtaining a sharp end point. Also results were not consistent with the known pollution in given samples and the values were several fold too high. Table I shows the variations obtained in samples of sea water from several bays of Puget Sound. These samples were all taken by means of a deep sea tester at a uniform depth of 10 feet. The biochemical oxygen demand was determined after 5 days' incubation in a thermostat at 25° C., and computed to a 20-day basis by use of the sewage factor 0.68.

Table I—Variations in Pollution Data

Sample	B. O. D. *Mg./liter*	Oxygen Consumed by $KMnO_4$ *Mg./liter*	Chlorides *Mg./liter*
1	1.82	18.54	14,750
2	3.49	17.89	14,200
3	0.87	20.29	14,184
4	2.75	17.45	15,905
5	2.21	14.76	15,975
6	4.15	29.34	16,110
7	1.82	13.13	16,075
8	5.88	19.60	15,150

Table II—Comparison of Results by Old and New Methods

Sample	New Method *Mg./liter*	Old Method *Mg./liter*
BLANK SEA WATER BEFORE INCUBATION		
1	13.0	37.4
2	12.8	46.4
3	12.7	45.0
4	12.5	49.0
5	12.7	40.5
Av.	12.7	43.7
AFTER INCUBATION FOR 96 HOURS AT 23° C.		
1	6.8	38.3
2	6.7	27.8
3	6.7	28.5
4	7.0	20.2
5	6.8	34.2
Av.	6.8	33.0
DIGESTER LIQUOR DILUTIONS AFTER 96 HOURS' INCUBATION AT 23° C.		
Ratio Liquor to Sea Water		
1:1000	74.5 73.8	80.9 81.9
1:5000	21.7 20.7	40.1 23.2
1:10000	14.6 13.8	34.3 30.8
1:50000	7.2 7.2	40.3 25.3
DIGESTER LIQUOR DILUTIONS AFTER 24 HOURS' INCUBATION AT 23° C.		
1:7500	25.2 25.2	38.2 36.2
1:30000	16.1 15.9	36.2 37.2

It is evident that no correlation exists between the organic content of these samples as measured by the biologic and permanganate oxygen consumptions, respectively. The differences are rather suggestive of slight variations in technic which would permit other reactions than the oxidation of organic matter to proceed. In the presence of iron as a catalyzer it seems probable that the oxidation of the chloride ion by the permanganate ion in acid solution occurs to a variable degree dependent upon time, temperature, and concentration factors. However, at times it was found possible to check aliquot parts of the same sample within 2 or 3 p. p. m. of oxygen by allowing an arbitrary length of time (20 seconds) from the addition of a single drop of permanganate (in back titrating) until the disappearance of its color. Even so, the values obtained for oxygen consumed appear much too large.

In order to enable the accurate reproduction of results in a given sample and to limit the reaction more nearly to the oxidizable organic matter contained in sea water, use is made of the Zimmerman-Reinhardt (*5*) method for the titration of permanganate in the presence of hydrochloric acid.

Proposed Procedure

The digestion is carried out in exactly the same manner as in the standard method (*2*). The modification lies in the determination of unconsumed permanganate. After digestion, the sample is acidified with 25 ml. of the preventative solution containing manganous sulfate, sulfuric acid, and phosphoric acid. Immediately thereafter 10 ml. of standard ferrous sulfate solutions are added. The sample is brought to room temperature and standard permanganate added until the addition of one drop changes the solution from colorless to light pink. This end point is sharp enough so that two identical samples may be checked within 0.02 ml. Tenth normal permanganate standardized against either

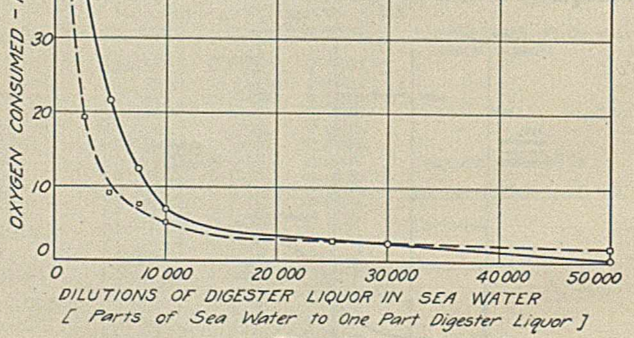

Figure 1

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[1] Received September 10, 1930.

iron wire or sodium oxalate is used. The iron solution contains ferrous ammonium sulfate and sulfuric acid in concentrations of 0.1 *N* and 0.3 *N*, respectively. The preventative solution contained 67 grams of $MnSO_4.4H_2O$, 138 ml. of 85 per cent phosphoric acid, and 130 ml. of sulfuric acid (concd.) diluted to the volume of 1 liter.

The comparison of this method with the standard method is given in the determinations, used in Table II, which utilized various dilutions of waste liquor from sulfite digesters in sea water obtained from Seattle harbor.

With this constancy of results it is obvious that the oxygen-consumed values may be used to indicate the concentrations of sulfite liquor when it is known that it is the polluting agent in sea water. By making up the various dilutions and taking the mean of five determinations on each dilution the results used in Table III were obtained.

Table III—Oxygen Consumed with Sulfite Liquor as Polluting Agent

DILUTION OF LIQUOR IN SEA WATER	OXYGEN CONSUMED BY MIXTURE	OXYGEN CONSUMED BY DIGESTER LIQUOR
	Mg./liter	*Mg./liter*
Blank	11.3	0.0
1:1000	73.7	62.4
1:5000	32.8	21.5
1:7500	23.7	12.4
1:10,000	18.3	7.0
1:30,000	13.7	2.4
1:50,000	11.5	0.2
1:100,000	11.3	0.0

When these values are plotted against concentrations the resulting curve (Figure 1) is either identical or nearly so with that obtained by dividing the 5-day biochemical oxygen demand (*3*) by the sewage factor 0.68 commonly used to express complete biological oxygen consumption. Inasmuch as Rudolfs (*4*) has shown that there is a direct relation between the biochemical oxygen demand, bacteria, and plankton, it would seem that the oxygen consumed as determined by this modified method correlates with the other factors ordinarily used for detection of pollution.

Abbot (*1*) has proposed a modified acid dichromate absorption test as a more sensitive index of oxidizable matter than the permanganate absorption test. His values of the percentage oxidation of various organic substances range from 98 per cent in the case of sodium oxalate to 66 per cent for gelatin. To ascertain the degree of completion of oxidation of organic substances somewhat similar to lignin and the other components of digester liquor, the following compounds were submitted to the modified permanganate consumed test: vanillin, tannic acid, starch, sucrose, and pyrogallol. Complete oxidation is defined according to the following reactions:

Vanillin: $C_8H_8O_3 + 17\ (O) \longrightarrow 8CO_2 + H_2O$
Tannic acid: $C_{14}H_{10}O_9 + 24\ (O) \longrightarrow 14CO_2 + 5H_2O$
Starch: $C_6H_{10}O_5 + 12\ (O) \longrightarrow 6CO_2 + 5H_2O$
Sucrose: $C_{12}H_{22}O_{11} + 24\ (O) \longrightarrow 12CO_2 + 11H_2O$
Pyrogallol: $C_6H_6O_3 + 12\ (O) \longrightarrow 6CO_2 + 3H_2O$

After making correction for the oxygen consumed by the blank, the results given in Table IV were obtained by the modified method.

Table IV—Modified Permanganate Consumed Tests

SUBSTANCE	WEIGHT OF SAMPLE	OXYGEN REQUIRED Theoretical	OXYGEN REQUIRED Actual	COMPLETE OXIDATION
	Gram	*Gram*	*Gram*	%
Vanillin	0.0159	0.0285	0.0282	99.0
Tannic acid	0.0056	0.0067	0.0044	65.5
Starch	0.0527	0.0626	0.0451	72.0
Sucrose	0.0408	0.0446	0.0372	83.5
Pyrogallol	0.0130	0.0196	0.0152	77.5

From the similarity of these substances to those present in digester liquor it would be reasonable to expect that their oxidation is from 85 to 90 per cent complete.

Literature Cited

(1) Abbot, IND. ENG. CHEM., **19**, 919 (1927).
(2) American Public Health Assocn., "Standard Methods for Examination of Water and Sewage," 6th ed., p. 24, footnote.
(3) Benson, *Paper Trade J.*, **90**, No. 24, 69 (1930).
(4) Rudolfs, IND. ENG. CHEM., **21**, 256 (1929).
(5) Treadwell and Hall, "Analytical Chemistry," Vol. II, pp. 515-8, footnote 2.

Modified Ford-Williams Method[1]

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THE following procedure is applicable to the determination of manganese in high chrome-nickel alloys which are practically insoluble in nitric acid. Such alloys are, however, soluble in nitro-hydrochloric acid.

If either the persulfate or bismuthate method is used for determining the manganese in nickel-chrome alloys soluble only in nitro-hydrochloric acid, it is necessary to remove the hydrochloric acid by fuming with sulfuric acid and the chromium with zinc oxide. The only difficulty encountered in this procedure arises from the fact that the complex sulfates formed often dissolve very slowly after dilution with water. The insolubility of these chromium sulfates probably increases with the temperature and time of fuming, although rather startling variations have been met with in regard to the time required to dissolve the sulfates formed, while working with the same alloy under like conditions.

The Ford-Williams method is the only other practical alternative method used to determine the manganese in such alloys. It is not necessary to separate the chromium in this method, but the hydrochloric acid must be removed by at least two evaporations with nitric acid to a sirupy consistency. Evaporations of this kind are always somewhat troublesome and time-consuming.

The proposed method eliminates the objectionable features of the above-mentioned procedures if the alloy is insoluble in nitric acid, as it is easily carried out, reasonably accurate, and much faster than the methods usually employed. However, if the material to be analyzed is soluble in nitric acid, obviously the following modification cannot be used to any advantage as the Ford-Williams method in its present form has always been recognized as entirely reliable.

Method

Weigh 2 grams of sample into a 500-cc. tall form beaker. Add 15 cc. of hydrochloric acid (sp. gr. 1.19), 5 cc. of nitric acid (sp. gr. 1.42), and 20 cc. of water. Boil until dissolved and add 20 cc. of perchloric acid (60 per cent). Continue to boil until the perchloric acid fumes and insoluble salts start to separate. Cool, dissolve in 30 cc. of nitric acid (sp. gr. 1.42), and heat just to boiling. Add a few crystals of sodium chlorate in order to avoid excessive foaming and then precipitate with four additions of 2 grams each of sodium chlorate adding each portion after the effervescence produced

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[1] Received September 3, 1930.

by the last addition has about ceased. This precipitation properly carried out should take about 20 minutes during which time the solution should always be saturated with free chloric acid in order to precipitate the manganese completely. If the solution is overheated at this point, the sodium chlorate decomposes too rapidly and the manganese may not be entirely precipitated. Remove the solution from the hot plate before the effervescence from the last addition of sodium chlorate has entirely ceased, filter on an asbestos pad with suction, and wash thoroughly with water. It is not necessary to allow the solution to cool and settle before filtering although it does no harm. Transfer the pad to the beaker in which the precipitation was made and wash any adhering manganese dioxide from the funnel into the beaker with 100 cc. of water. Dissolve the manganese dioxide in 20 cc. of 0.1 N ferrous sulfate containing 100 cc. of sulfuric acid (sp. gr. 1.84) per liter, and titrate back to a permanent pink end point with 0.1 N potassium permanganate.

Calculate the manganese by means of the following formula:

$$\text{Per cent Mn} = \frac{[(A \times B) - C] \times 0.2747 \times D}{\text{Weight of sample}}$$

A = cc. of 0.1 N ferrous sulfate
B = permanganate solution equivalent of the 0.1 N sulfate
C = cc. of 0.1 N potassium permanganate
D = normality factor of 0.1 N potassium permanganate

In order to estimate the accuracy of this method, the manganese in two stainless steels containing approximately 1.5 per cent silicon, 8 per cent chromium, and 22 per cent nickel, was carefully determined by both the persulfate and bismuthate methods, after separating the chromium with zinc oxide. The average percentage obtained from four determinations on each steel was assumed to be the correct manganese content of these two samples which are designated in the table as 1 and 2.

Determination of Manganese in Eight Samples

SAMPLE	MANGANESE OBTAINED					MANGANESE PRESENT
	1	2	3	4	Av.	
	%	%	%	%	%	%
1	0.85	0.81	0.81	0.83	0.83	0.83
2	0.49	0.50	0.49	0.51	0.50	0.51
12*c*	0.41	0.39	0.38	0.43	0.40	0.409
72	0.64	0.64	0.65	0.62	0.64	0.651
32*a*	0.25	0.24	0.25	0.24	0.25	0.244
30*b*	0.49	0.48	0.48	0.50	0.49	0.499
10*c*	1.12	1.15	1.14	1.13	1.14	1.13
7*a*	0.42	0.41	0.42	0.42	0.42	0.446

The manganese in five Bureau of Standards standard steel samples and one iron (7*a*) was also determined and included in this table in order to compare further the accuracy of the above method with the commonly used procedures. The results on iron (7*a*) were obtained without separating the silicon or graphitic carbon.

Four determinations on each sample were run at the same time without employing any more care or refined apparatus than is ordinarily used to obtain reasonably accurate results in routine steel work. The theoretical titer was used as shown in the preceding formula to calculate the results thus obtained, which were tabulated without rejecting the percentages obviously inaccurate. These values, however, considered as a whole would be closer to the theoretical percentages if multiplied by 1.02 as an empirical factor.

Investigation of Ammonium Acetate Separation of Sulfates of Lead, Barium, and Calcium[1]

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A METHOD commonly given by standard texts upon quantitative chemical analyses for separating lead from barium and calcium depends upon the solubility of lead sulfate and the insolubility of barium and calcium sulfates in ammonium acetate solution. It is the intention of this piece of work to test out that method as regards its completeness of separation.

Previous Investigations

In speaking of the precipitation of lead as a sulfate in the determination of lead in ores and metallurgical products, Treadwell and Hall (*7*) claim that the precipitate of lead sulfate containing silica and barium sulfate (also strontium and sometimes calcium sulfate) can be purified by redissolving the lead in hot ammonium acetate solution. They suggest that the lead extraction be made with 20 cc. of hot 2 N ammonium acetate.

Low (*2*) suggests the use of ammonium or sodium acetate solution in dissolving lead sulfate. He would titrate the lead solution with standard ammonium molybdate solution while the calcium remains out of solution.

In the analysis of fluorspar Sisco (*6*) claims that lead and barium sulfates are separated by the acetate extraction using a 20 per cent solution of ammonium acetate.

Scott (*5*) considers the barium sulfate slightly soluble in ammonium acetate and hence a possible contaminant of the extracted lead.

The problem has two main parts—namely, (1) is barium extracted with the lead; and (2) is calcium extracted with the lead when ammonium acetate, hot and concentrated, is used upon a precipitated mixture of the sulfates of lead, barium, and calcium?

A subdivision of the problem, however, of minor importance was added by the claim of Majdel (*3*) that the separation of lead from barium in the presence of barium, by precipitating both components with sulfuric acid and dissolving lead sulfate in ammonium acetate, is not possible as the double salt of lead and barium sulfate is formed which is insoluble in ammonium acetate, and, therefore, a part of the lead remains with barium. The error is greater as the ratio of barium to lead increases. In proportion of Pb:Ba as 1:0.6, 9 per cent lead remains in the undissolved barium sulfate; as 1:1, 45 per cent; as 1:2, 88 per cent; as 1:7, 100 per cent; and is thereby lost. The separation must be accomplished, therefore, with hydrogen sulfide.

The ratio of 1 lead to 100 barium was taken. The precipitated mixture of their sulfates was extracted ten times with boiling 50 per cent ammonium acetate as given below. The filter and its residue then were boiled with 100 cc. of 50 per cent ammonium acetate until spattering commenced. Fifty cubic centimeters more of ammonium acetate were added, the mixture heated to boiling and allowed to settle.

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[1] Received August 12, 1930.

Experimental Data

DETERMINATION	(1)	(2)	(3)	(4)	(5)	(6)	(7)	(8)	(9)	(10)	(11)	(12)	(13)	(14)	(15)
Solution of ammonium acetate, per cent	50	50	50	50	50	50	50	50	25	25	50	Hot water	Hot water	50	50
Number of extractions made	6	6	6	6	8	8	8	8	8	8	12	8	8	8	8
Volume used in each extraction, cc.	25	25	25	25	25	25	25	25	25	25	30	25	25	25	25
Lead in sample, gram	0.0200	0.0200	0.0200	0.0200	0.0200	0.0200	00.020	0.0200	0.0200	0.0200	0.0100	....	....	....	....
Lead in extract, gram	0.0199	0.0200	0.0199	0.0199	0.0199	0.0198	0.0198	0.0199	0.0198	0.0198	0.0095	....	....	....	....
Lead extracted, per cent	99.5	100	99.5	99.5	99.5	99.0	99.0	99.5	99.0	99.0	95.0	....	....	....	....
Barium in sample, gram	0.0100	0.0100	0.0200	0.0200	0.0800	0.0800	0.0900	0.0900	0.0600	0.0600	1.000	....	....	....	....
Barium extracted	None	None	None	None	None	None	None	None	None	None	....	....	....	....	....
Calcium in sample, gram	0.0100	0.0100	0.0200	0.0200	0.0800	0.0800	0.0900	0.0900	0.0600	0.0600	None	0.0600	0.0600	0.0600	0.0600
Calcium extracted, per cent	....	....	....	....	3.37	3.62	0.66	0.77	8.50	5.00	....	26.3	35.3	3.16	19.5

It was then filtered, the filtrate being passed into the filtrate of the first ten extractions. The results of this extraction may be found under column 11 of the data.

In all extractions the filter paper with its precipitated sulfates was transferred to a casserole, 25 cc. of concentrated ammonium acetate added, and heated to boiling. The acetate solution was filtered through a Swedish filter paper. This was repeated six or eight times until the paper in the casserole and funnel did not darken when touched with a rod containing a drop of hydrogen sulfide solution. The filter paper in the funnel was washed four times with hot water and squeezed well to remove all liquid.

Method of Procedure

Known mixtures of lead nitrate, barium nitrate, and calcium carbonate are dissolved in water acidulated with nitric acid. An excess of sulfuric acid is added to the mixture and taken to sulfuric acid fumes. This is cooled, diluted, filtered on Swedish filter paper, and washed well with water containing 10 per cent sulfuric acid. The filter paper with its residue is placed in a casserole and extracted with 30 cc. of hot, concentrated ammonium acetate, and the solution decanted through filter paper. This extraction is repeated until the filtrate indicates no lead when a drop of the filtrate is put in some potassium chromate solution. It requires about six to eight extractions to get negative tests for lead on the filtrate.

Filtrate I. This contains the lead and possibly some of the barium and calcium. The filtrate is made faintly acid with hydrochloric acid and hydrogen sulfide is passed through it for 30 minutes. It is then heated on a steam bath for same period of time and filtered.	*Residue I.* Contains most of the barium and calcium. This was discarded in this problem.
Filtrate II. Contains barium and calcium. This filtrate is evaporated nearly to dryness and the sulfides dissolved in the least amount of hydrochloric acid, and the excess acid expelled by evaporation. The residue is taken up in 300 cc. of water containing 5 drops of acetic acid. Sufficient ammonium acetate solution is added to make the solution neutral. An excess of potassium chromate solution is added after heating the solution to boiling. The solution is allowed to settle until cold. It is filtered through a Gooch crucible.	*Residue II.* Contains the lead as a sulfide. This residue is washed well with water saturated with hydrogen sulfide gas. It is then treated with hot hydrochloric acid and then nitric acid and heated to boiling. Ten cubic centimeters of concentrated sulfuric acid are added and the solution evaporated to strong sulfuric acid fumes. It is cooled, diluted with water, and filtered on an asbestos mat in a weighed Gooch crucible. The residue is washed with dilute sulfuric acid and with alcohol, and dried at a dull red heat. It is weighed as lead sulfate.
Filtrate III. Contains calcium. To the neutral solution after heating to boiling, 10 cc. of acetic acid are added and 15 cc. of a saturated solution of oxalic acid, and after 5 minutes, a slight excess of ammonia. It is allowed to cool an hour, then decanted through a filter. The precipitate is ignited wet in a weighed crucible and strongly heated to constant weight. It is weighed as calcium oxide.	*Residue III.* Contains barium as a chromate. It is washed with a dilute potassium chromate solution until free of calcium and with water until free of potassium chromate. It is then washed once with dilute alcohol, dried at 110° C., and weighed as barium chromate.

Results

The data of the first ten columns (of the table of experimental data) are the result of twenty-two determinations on lead. If the lead did not check with the amount in the original sample, the sample was discarded and another one begun. In case the amount of lead sulfate ran high, further heating sometimes brought the amount of lead down to the amount in the sample. The general tendency, however, was for the lead to run low. The work was done with extreme care. Each sample was weighed separately and carefully. Considering the slight solubility of lead sulfate and the small amount of lead in the sample, a slight loss of lead is to be expected, as is shown in the table.

Outstanding Findings of the Work

(1) In a ratio of calcium to barium of 1 to 1: (*a*) all lead is extracted, (*b*) no barium is extracted, (*c*) as much as 8.5 per cent of calcium is extracted.

(2) In a ratio of calcium to barium of 1 to 9.3, no barium is extracted.

(3) In a ratio of lead to barium of 1 to 100, 95 per cent of lead is extracted.

Conclusions

(1) Lead may be separated from barium by ammonium acetate extraction of their sulfates, the barium not passing into the lead solution in appreciable amounts.

(2) Lead cannot be separated entirely from calcium by ammonium acetate extraction, the calcium passing into the lead solution in considerable quantity.

(3) The amount of calcium passing into the lead solution seems to depend upon certain physical factors not in control of the operator. The writers suggest these as possible factors: the time required in filtering each extract, the amount of cooling during filtration, small changes in the density of the acetate solution during boiling.

(4) As the amount of barium is increased there seems to be an increasing difficulty in extracting all the lead. This may be due to physical occlusion of the lead sulfate by the barium sulfate or to the formation of a definite lead-barium salt which is insoluble. The writers are inclined to believe from the data in column 11 of the table that this noticeable difficulty may be due to occlusion.

(5) Less calcium is extracted in the presence of lead and barium than when it is the only constituent of the sulfate precipitate.

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Measurement of Drillability of Fertilizers[1]

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The drillability of a fertilizer affects its flow from most distributors in two ways: It determines (1) the quantity of fertilizer that will be applied on any given field with a fixed setting of the mechanism, and (2) the degree of uniformity or quality of its distribution. The comparative rate of flow of a fertilizer under a given force may be determined if its angle of repose, apparent specific gravity, and average particle diameter are known. Of these the angle of repose is of greatest and particle size of least importance. Under the conditions prevailing in the field application of ordinary fertilizer the effect of particle size is often negligible. The angle of repose of a fertilizer is also an indication of the degree of uniformity attainable with distributors in its application to crops. Directions are outlined for measuring the angle of repose, apparent specific gravity, and average particle diameter of fertilizers. A method is given by which a coefficient of the rate of flow of the fertilizer may be obtained by substituting these three measurements in an equation.

THE term drillability is used to denote the resultant of all the properties of fertilizers that affect the manner in which they flow. The properties and therefore the drillabilities of different fertilizers vary widely and the drillability of even the same fertilizer is apt to change from time to time with variations in external conditions (*4*). The drillability of a fertilizer affects its flow from most distributors in two ways: It determines (1) the quantity of fertilizer that will be applied on any given field with a fixed setting of the mechanism, and (2) the degree of uniformity or quality of its distribution.

For maximum efficiency fertilizers must be applied uniformly (*1*) and at the proper rate. These conditions are difficult, if not impossible, to obtain at present. A method of measuring drillability would facilitate obtaining desired rates of application and thus lead to greater efficiency in the use of fertilizers.

With a little experience good and poor drillability in a fertilizer can be distinguished just as readily as hot and cold weather, but small differences in drillability like small differences in temperature and humidity can only be detected by instruments.

A search of the literature has revealed only one method (*3*) for measuring drillability. This was devised by Doctor Wichern in Germany and is intended only for superphosphates. The apparatus used is shown in Figure 1. To make a determination, 25 grams of superphosphate previously passed through a 2-mm. sieve are placed in each bowl and 10 glass marbles, weighing exactly 100 grams, are placed on top of each sample. The reciprocating motion of the apparatus causes the marbles to roll back and forth until they finally pack the fertilizer into a cake which will not fall from the bowl when it is inverted. The time required to do this is used as the measure of the drillability of the superphosphate.

This apparatus distinguishes between superphosphates of satisfactory and unsatisfactory drillability and assigns numerical values to the drillability which is very desirable. It will not, however, work satisfactorily with certain kinds of fertilizers, nor give a numerical value that can be relied upon with superphosphates of the best drillability. Three samples tested by it in this laboratory showed no signs of packing after one hour although all the conditions laid down for the test were rigorously met. They did pack down, however, after still longer periods of time. The drillability of a fertilizer depends to a large extent upon its content of moisture and very fine particles. These also determine the length of time required to pack the sample in the apparatus, but under the conditions of this test both the moisture and fine powder content are apt to change very greatly during the test. The amount of exposure to the air in the screening, weighing, and shaking is so great in proportion to the size of the sample that unless already approximately in equilibrium with the atmosphere, its moisture content is bound to change. Thus the length of time required to pack the sample may depend upon the relative humidity of the atmosphere much more than upon the condition of the material being tested. The amount of fine powder in the sample is usually increased during the determination because the marbles have much the same effect as the balls in a ball mill. Thus a granular superphosphate may be reduced to an impalpable powder in this apparatus and when this occurs the sample will pack tightly, although it would not pack tightly so long as it remained in a granular condition. The length of time required for packing depends upon the original size and hardness of the particles, which may or may not affect the drillability.

To be of greatest value a method of measuring drillability should apply to all kinds of fertilizers and over the entire range of drillability, give reliable results that can be duplicated, be easily and quickly carried out, and not involve the use of equipment that is expensive or difficult to procure. This paper gives a method for measuring the drillability of fertilizers which promises to meet these requirements.

Theoretical Considerations

Drillability consists of two elements, the rate of flow (unit of mass per unit of time) through a fixed opening, and the degree of uniformity of flow when subjected to a given amount of force. This force in all fertilizer distributors except the top delivery type consists of two components in varying proportions according to the type of mechanism. These components are the pressure supplied by the dispensing mechanism and the force of gravity.

In the top delivery type the rate of delivery is independent of the force of gravity, and thus all fertilizers are delivered at the same rate when calculated on a volume basis. Application rates, however, are computed by weight per unit of area, and on this basis rates by the top delivery type of distributor vary with the apparent specific gravity of the fertilizer. There is no flow in the hopper of the top delivery type and therefore the rate of delivery on a weight basis can be determined if only the apparent specific gravity of the fertilizer is known.

The vast majority of distributors now in use deliver the fertilizer from an orifice at the bottom of the hopper. With this type the fertilizer flows to the delivery opening and the

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delivery rate with a given setting of the quantity-regulating devices depends upon the angle of repose, apparent specific gravity, and average diameter of the particles composing the mass.

The kinetic angle of repose is the slope which a substance forms with the horizontal when it has come to rest after being carefully poured into a pile. It measures the point at which the forces tending to continue the flow exactly balance the forces opposing the flow, or in other words, the friction between the particles. The effect of cohesion caused by the presence of moisture and of very small particles, and part of the effect of specific gravity on the rate of flow also affect the angle of repose. The rate of flow of comminuted solids and consequently the delivery rate of fertilizers by most distributors varies inversely with the angle of repose. No flow from an orifice can be caused by gravity alone when the kinetic angle of repose is greater than 45 degrees, but fertilizer distributors in operation exert pressure upon the material being dispensed by means of paddle wheels, revolving plates, or other devices. This pressure increases the rate of flow and thus many distributors can dispense materials with angles of repose considerably higher than 45 degrees.

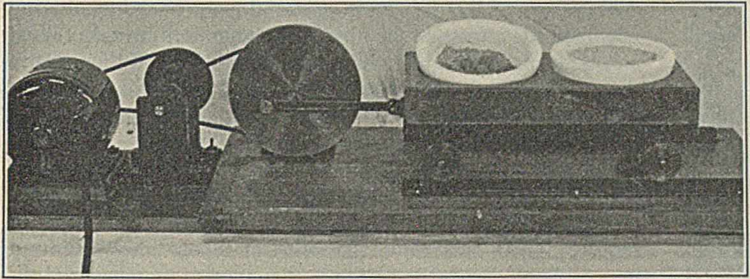

Figure 1—Wichern Apparatus for Measuring Drillability of Superphosphates

Rate of flow varies directly with the apparent specific gravity. With most fertilizer distributors the variations in rate of delivery caused by differences in apparent specific gravities are less than those caused by differences in the angles of repose.

Average particle size is not an appreciable factor in the rate of flow of materials when they are not in a confined space, as, for example, when poured from a vessel or flowing down an inclined chute. It becomes important when the flow is in a confined space and the diameter of the particles approaches in size that of the opening through which they flow. Most materials fail to flow through an opening with a diameter less than 5 times the average diameter of its particles. Under field conditions the effect of size of the particles of the fertilizer on rate of delivery is often negligible.

The second element of drillability is the degree of uniformity of distribution. Irregular distribution of a homogeneous fertilizer is caused, first, by the fact that cohesion of the particles of the mass is greater than the forces available for separating them, and second, by various mechanical imperfections in the distributor. The irregularities caused by cohesion may be measured by the angle of repose of the material.

Measurements of the temperature, relative humidity, and wind velocity of the atmosphere are each important in interpreting the weather, but no simple means exists for measuring the effect of all these simultaneously so that a single figure will answer for all purposes. Drillability, like the weather, cannot be completely measured by a single determination, because it is composed of two elements. These, as explained before, are the rate of flow and degree of uniformity of flow.

Measurement of Rate of Flow

The factors that affect the rate of flow of a subdivided solid are the coefficient of friction, apparent density, and size of the particles composing the mass. Rates of flow of fertilizers that have low angles of repose may be determined directly by measuring with a stop-watch the time required for a definite weight of material to flow by gravity from a specially constructed funnel. Many fertilizers now in use, however, will not flow by gravity alone so that this method is of limited usefulness. Although a machine could be devised to exert constant pressure upon them and thus cause most materials to flow, yet certain of the materials that flow well by gravity alone do not flow at all when subjected to pressure in such a machine. The material is crushed or the machine is broken. The only method so far known that will apply to all fertilizer materials and mixtures is the use of a formula, requiring measurements of the angle of repose, the average particle diameter, and the apparent density of the fertilizer.

In a previous study (*2*) of the flow of masses of solid particles as the result of the force of gravity the following formula was derived:

$$t = \frac{\mu}{B^{5/2}d}\left[34.6 + (67.4 + 444 \sin {}^{1}/_{2}\,\phi)\,(D/B + 0.130 - 0.161\mu)\right] \quad (1)$$

where t is the time in minutes required for 100 grams to flow through an orifice, μ is the kinetic coefficient of friction or natural tangent of the angle of repose, B is the diameter of the orifice in millimeters, d is the apparent specific gravity of the material, ϕ is the vertical angle of the hopper bottom, and D the average diameter of the particles in millimeters. The rates of flow calculated for various materials by use of this equation agreed remarkably well with experimentally determined rates. The materials included a number of fertilizers, sand, lead shot, various seeds, marbles, etc., and thus embraced a wide range of physical properties. The variation between the calculated and observed time required for a given weight of any material to flow was no greater than the experimental errors involved in determining the time and it is therefore concluded that measurements of the angle of repose, apparent specific gravity, and average particle size are sufficient to determine completely the comparative rate of flow of a fertilizer.

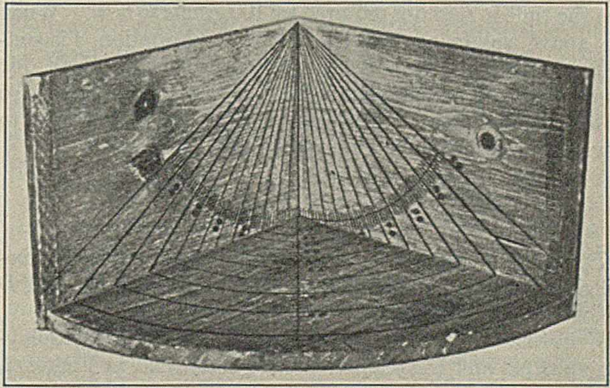

Figure 2—Easily Constructed and Convenient Apparatus for Measuring Angle of Repose of Fertilizers

Although Equation 1 gives excellent results for materials that flow by gravity, it does not hold good for those that require pressure to flow. Empirical Equation 2, however, appears to be satisfactory for all fertilizers.

$$t = \frac{\mu}{B^{5/2}d}\left[34.6 + (67.4 + 444 \sin {}^1/_2\,\phi)\left(D/B + \frac{0.005}{\mu^3}\right)\right] \quad (2)$$

For all materials that will flow by gravity t is the actual time consumed. Although t is a hypothetical figure when measurements of a material that will not flow by gravity are substituted in the equation, it nevertheless has a value corresponding to the delivery rates actually given by distributors.

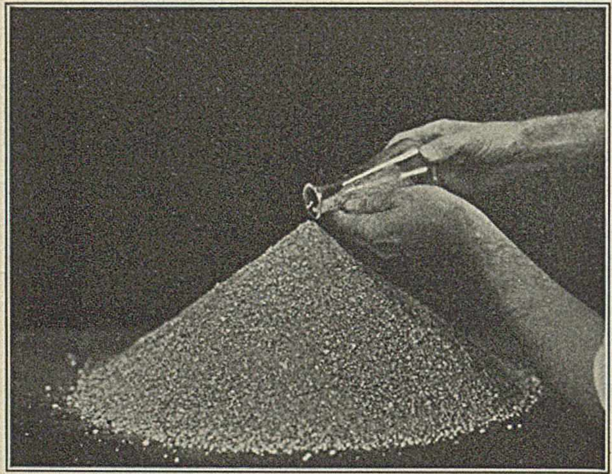

Figure 3—Proper Position of Pouring Vessel in Relation to Apex of Cone

The values of t may be used as coefficients of rate of flow if arbitrary values are assigned to B and ϕ. If this is done the same values should be used by all who employ the method so that the results of one worker may be compared with those of others. For this purpose $B = 15$ and $\phi = 60$ degrees seem reasonable since these figures represent about average conditions found in the use of fertilizer distributors. Other values might answer equally well. t in Equations 1 and 2 was the time in minutes required by 100 grams to flow. When the above values are substituted in the Equation, t is generally a fraction with a zero in the first decimal place. It would therefore be more convenient to change the formula so as to obtain T, the time necessary for 1 kg. of fertilizer to flow. By making these changes we get Equation 3.

$$T = \frac{\mu}{87.146\,d}\left[34.6 + 289.4\left(\frac{D}{15} + \frac{0.005}{\mu^3}\right)\right] \quad (3)$$

T may be considered as a coefficient of rate of flow. Detailed instructions for obtaining the values of μ, d, and D follow.

MEASUREMENT OF ANGLE OF REPOSE—A method employing a simple and convenient device, illustrated in Figure 2, has been used for a number of years in the Bureau of Chemistry and Soils (*4*) for making kinetic angle of repose measurements where an accuracy of ±0.5 degree was sufficient.

For more accurate work the following method may be used: The sample should be measured preferably in the same room in which it has been stored, since it is apt to be more nearly in equilibrium with this than with some other atmosphere. About 5 pounds is a convenient amount to measure but it need not be weighed, since after taking the sample no time should be lost in making the determination. About three-fourths of the sample should be rapidly but carefully poured into a conical heap upon a rigid and approximately level surface, such as a table, placed out of all drafts or air currents. The balance of the material must be poured slowly and very carefully. The final pouring may be done from an Erlenmeyer flask or cylinder held as shown in Figure 3, and slowly rotated so that a very thin stream of material will fall from a distance of no greater than 5 mm. directly upon the apex of the cone. If the pouring is too fast or from too great a height the velocity acquired by the particles will reduce the slope of the pile and the resulting determination will be too low. The pile must not be touched or jarred in any way. If this does occur accidentally more material may be added to the pile until the effects of the disturbance are obliterated. With a few fertilizers the pile will build up rapidly and then slump down followed by a repetition of these events in a cyclic manner. When this occurs the cone should be measured as nearly as possible at its highest point in the cycle. The apex of the cone should be as sharp as possible. The height of this pile divided by the average radius of its base is the coefficient of friction of the material, μ, or the tangent of its angle of repose. From this value the angle of repose may be found in a table of natural tangents. It may also be measured directly with a protractor level such as is commonly used by machinists and carpenters. The face of the instrument shown in Figure 4 was extended for greater accuracy by attaching a strip of metal to it. To make a measurement the limb of the protractor should be clamped in a level position in a ring stand. The face of the protractor should then be made to coincide in direction with the slope of the cone in the manner shown in Figure 5, but care must be used that it does not touch the pile. The angle of repose is then read off from the scale on the instrument. If the material is homogeneous and the pouring has been properly done, the angle will be the same wherever it is measured. On the other hand, heterogeneous mixtures will give variable angles and a sufficient number of measurements on different parts of the pile must be made and averaged to secure a true mean value. In every case at least four readings should be averaged for a determination.

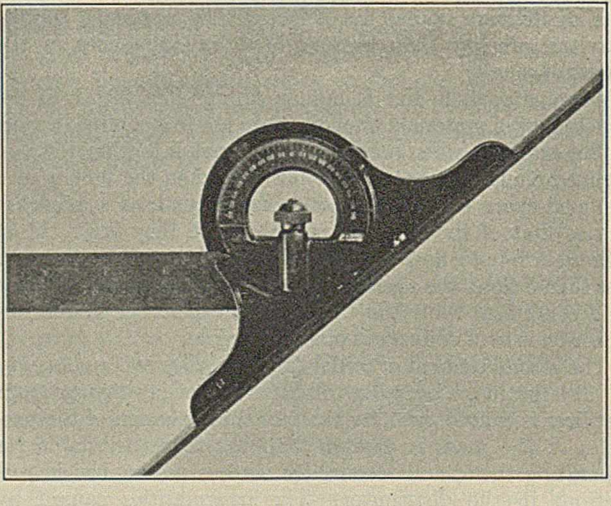

Figure 4—Protractor Level Used for Measuring Angle of Repose of Fertilizers. The Face Was Extended by Screwing a Strip of Metal to It

Mixtures containing particles varying in size and specific gravity when poured into a pile in the manner described above sometimes produce cones with dished sides, as shown in Figure 6. The slope is steeper near the apex than it is near the base. Large round particles also may roll beyond the real base of the cone. The proper slope to measure is that of a line connecting the apex and any point in the circumference of the base.

Duplicate readings made as above on materials with angles of repose up to 45 degrees made by different operators or the same operator at different times on the same material should agree to within 0.5 degree. The degree of accuracy varies with the size of the pile measured as shown by Table I. The angle of repose becomes increasingly difficult to measure accurately as its value is raised above 45 degrees although approximate measurements may be made up to values of about 65 degrees. For practical purposes it is usually sufficient to know the angle of repose to the closest whole number. With some distributors it is impossible to secure satisfactory distribution of materials with angles of repose of 55 degrees or above. The minimum value for a fertilizer material encountered in this laboratory is 22 degrees. The average mixed fertilizer when measured in the manner described above has an angle of about 40 degrees.

Table I—Effect of Size of Sample upon Accuracy of Angle of Repose Measurements

WEIGHT OF SAMPLE	MEASUREMENT BY FIRST OPERATOR	MEASUREMENT BY SECOND OPERATOR
Pounds	*Degrees*	*Degrees*
1	34.6	34.1
5	34.5	34.3
25	34.31	34.37
200	34.39	34.37
2000	34.380	34.375

MEASUREMENT OF APPARENT SPECIFIC GRAVITY—The apparent specific gravity is the weight of a unit volume of the material. It is measured in connection with the testing of various classes of materials, either with or without tamping. Since fertilizers are never tamped down in the hopper of a distributor but on the contrary are often kept in a loose uncompacted condition by the agitator of the distributor it is felt that for fertilizers this measure will be of greatest value if the material is not compressed. The following procedure has been found satisfactory: Fill a 100-cc. graduated cylinder to the 50-cc. mark and lightly tap the bottom of the cylinder on the palm of the hand three times. Then fill to the 100-cc. mark and tap three times more. Refill to the mark and tap as before until the material does not settle further with light tapping. The weight in grams of the contents of the cylinder divided by 100 is the apparent specific gravity. To be comparable this determination must always be made in the same manner.

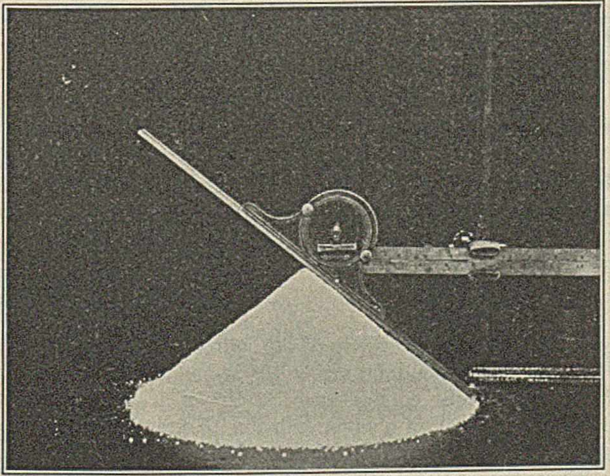

Figure 5—Manner of Making Angle of Repose Measurements with Protractor Level

MEASUREMENT OF AVERAGE PARTICLE SIZE—When the particles composing a mass are all or nearly all of the same relative size, the average diameter may be quickly determined by screening and use of the equation $D = {}^1/_2 (D_1 + D_2)$ where D is the average diameter of the particles, D_1 is the diameter of the openings in a screen through which the bulk of the material will pass, and D_2 is the diameter of the openings in a screen which will hold it.

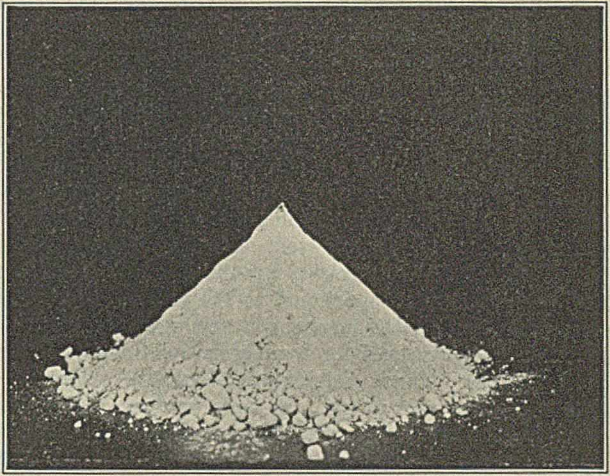

Figure 6—Irregular Slopes Obtained with Heterogeneous Mixtures

It requires the exercise of judgment to determine the correct angle of repose in such cases.

Commercial fertilizers are usually composed of particles widely varying in size. Under these circumstances the rate of flow will be different from that of a material composed of uniformly sized particles and a set of sieves or screens should be used in which the size of the openings form a series in which each member is about one-half the value of the preceding. The effective size may then be calculated by use of the equation

$$D = 0.8\,\frac{(D^5{}_1 - D^5{}_2)P_1 + (D^5{}_2 - D^5{}_3)P_2 + (D^5{}_3 - D^5{}_4)P_3 + \ldots.}{(D^4{}_1 - D^4{}_2)P_1 + (D^4{}_2 - D^4{}_3)P_2 + (D^4{}_3 - D^4{}_4)P_3 + \ldots.} \tag{4}$$

where D_1, D_2, D_3. . . are the diameters of the sieve openings, and P_1, P_2, P_3. . . are the percentages of material found in the indicated intervals. Less than 5 per cent of any of the sizes may be omitted from the calculation without any material effect upon the result. When the effective particle size is determined in this way its value is equal to that necessary, in a mass composed entirely of particles with uniform diameters, to flow at the same rate.

Measurement of Degree of Uniformity of Flow

In a previous study (*4*) the relation between the angles of repose of fertilizers and the degree of uniformity of flow was determined by collecting the amount of fertilizer deposited in each foot of row and calculating the average deviations from the mean rate of delivery. These deviations were complicated by variations in delivery caused by the machines, but this work coupled with numerous other observations of distributors in action shows that the angle of repose gives a good indication of the degree of uniformity of distribution attainable with ordinary distributors. Directions for making this determination have already been given in connection with the measurement of the comparative rate of flow. The same determination will answer for both purposes.

When the angle of repose is less than 40 degrees, cohesion is imperceptible and any homogeneous fertilizer with an angle of repose below this value will flow uniformly if the forces applied to it remain constant. When in practice they do not, it is because of imperfections of the distributor.

As the angle of repose of a fertilizer increases above 45 degrees it flows more and more irregularly. With most distributors the degree of irregularity of distribution increases at a more rapid rate than the angle of repose until finally a point is reached at which flow ceases altogether.

Discussion

Whether more than one or all of the measurements outlined above should be made in any particular case must depend upon the circumstances and the purpose in view. If a complete statement of the drillability of a fertilizer is desired in mathematical terms, the angle of repose, apparent density, and average particle diameter should be measured and T computed by substitution of the proper terms in Equation 3. All four values should be reported. In the case of distributors depending largely upon gravity for the flow of the fertilizer, T will be inversely proportional to the rates of delivery at each adjustment of the mechanism and this holds good for all fertilizers, not merely for commercial mixtures with average properties. These distributors constitute a large proportion of those now in use. In the proportion that the delivery of the fertilizer is effected by mechanical force, the apparent density will determine the delivery rate. Delivery is brought about entirely by the pressure supplied by the mechanism of the top delivery type and largely so by that of the auger type. In every case the angle of repose will indicate the degree of uniformity of distribution likely to be obtained independently of that caused directly by the machine.

The ratio of the average particle diameter of the majority of commercial mixed goods to the size of the delivery opening of the ordinary distributor when making average applications remains approximately constant. Therefore the delivery rates of such mixtures can be determined, if suitable standard calibrations of the implement are available, from the angle of repose and apparent density only.

For some purposes the angle of repose measurement alone will be satisfactory as a rough measure both of rate of flow and degree of uniformity of flow; for example, when several samples of the same kind of material are compared, since they are likely to have nearly the same apparent densities, or when measurements are made at different times upon the same fertilizer. Variations in the apparent specific gravity of more than ±0.1, however, must not be neglected even in rough work.

In comparing the effects of different fertilizer formulas or of various sources of a single fertilizing element upon crops in the field it is important that each plot should be fertilized with the same degree of uniformity and at the proper rate. It has been difficult to do this with machinery in the past. The use of the measurements outlined above will give control of the drillability of the fertilizer and should assist in getting better results from such agronomic experiments.

Drillability measurements may also be used by implement manufacturers to calibrate distributors more accurately, by fertilizer manufacturers to standardize their products and to maintain uniform drillability, and in other ways.

Acknowledgment

Credit is due W. E. Deming, associate mathematician of this division, for assistance in deriving the formulas in this work.

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Conductometric Formula for Determining Ash in Both Raw and Refinery Sirups and Molasses[1]

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A conductometric method has been provided for the determination of ash in both raw and refinery sirups and molasses. It is applicable to those products regardless of their geographical source or their factory and refinery treatment.

IN PREVIOUS papers the writers have pointed out the difficulties entailed in attempting to predict the per cent ash in raw sugars from the electrical conductivity of their solutions. The crux of the problem lay in the variability of the chemical composition of the conducting substances. This variability was found to be considerable in samples which came even from the same district, and so larger variations in the ratio of ash divided by conductance—that is, the C-ratio—were to be expected for different geographical sources.

In those cases where the C-ratio was found to vary within narrow limits, an average ratio was all that was necessary in order to determine the per cent ash in a given sample. The specific conductance of the solution containing 5 grams of raw sugar in 100 ml. was multiplied by the specific C-ratio of the particular community, and the ash was thus at once obtained (*1*).

When the origin of the sugar was unknown, the simple conductance method was inadequate, and it was shown (*2*) that the equation

$$\text{Ash} = 0.001757(0.913\,K + 193.5 - 0.1\,K_1) \quad (1)$$

gave good results regardless of the source of the sugar. Here K is the simple conductance $\times 10^6$ as mentioned before, and K_1 is the specific conductance $\times 10^6$ of a solution made by taking 200 ml. of a sugar solution (5 grams per 100 ml.) and adding to it 5 ml. of 0.25 N hydrochloric acid.

When the above method was applied to other sugar products, Formula 1, with the factor in it multiplied by 10, was found to hold under specific experimental conditions (0.5 gram product plus 4.5 grams sucrose in 100 ml.) for sirups and molasses produced in the raw cane sugar factory, but it did not give good results for refinery sirups (*3*). The factor in the equation was lower than 0.01757 for final refinery sirups, lower still for unfiltered sirups and still lower for filtered sirups. Not only that, but the factor varied from refinery to refinery, and so the simple conductometric Formula 1 was found to be quite unsatisfactory. Obviously the difficulties due to the variability in the chemi-

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[1] Received September 18, 1930. Presented before the Division of Sugar Chemistry at the 79th Meeting of the American Chemical Society, Atlanta, Ga., April 7 to 11, 1930.

cal composition of the conducting substances were aggravated by the treatment in the refinery. It was apparent that the decrease in the value of the factor kept pace with the increase in the extent of the bone black treatment. This was experimentally verified (*4*), and the conclusion was drawn that the results could be accounted for by the selective adsorption of cations as well as of anions by the bone black.

Conductometric studies with 0.25 *N* potassium hydroxide instead of 0.25 *N* hydrochloric acid were made on the 175 remaining samples in the hope that some information might be secured regarding the nature of the cations in the various types of sugar products under investigation. This equation was developed:

$$\text{Per cent ash} = 0.01757(1.33\,K + 498.3 - 0.091\,K_1 - 0.5\,K_2) \quad (2)$$

where K and K_1 are the specific conductances $\times\ 10^6$ without and with 0.25 *N* hydrochloric acid, respectively, and K_2 is the specific conductance $\times\ 10^6$ with 0.25 *N* potassium hydroxide.

Although the formula gave excellent results with refinery products, it was exceedingly poor for Porto Rican blackstraps. The equation was not at all as general as had been desired, and so the problem was attacked from a slightly different angle.

Orthophosphoric acid is only a moderately strong acid, and it could be expected to do two things—to displace the weak organic acids which were present as salts, and to react with the di- and tri-valent metallic ions. The use of this acid in place of the hydrochloric acid has apparently solved the general problem of ash determination, and the present paper provides a method which is applicable to various cane sirups and molasses regardless of their geographical source or their factory and refinery treatment.

The range in the per cent ash in the products studied varied between 4.84 and 14.23 per cent, and for the 133 samples which were still available for the conductometric determinations with phosphoric acid, the maximum deviation between chemical ash and ash calculated from the conductivity measurements was ±0.30 per cent compared to 1 per cent when Formula 2 was used. With an average chemical ash of 9.209 per cent the average deviation of the conductometric ash was found to be ±0.134 per cent for the entire series taken as a supposedly homogeneous group.

Method

The experimental procedure was, in general, the same as in the determinations made previously with hydrochloric acid. Duplicate ash determinations were made in silica dishes on samples which had been filtered by suction through a mat of filter paper pulp covered with asbestos. The important change consists in the addition of 5 ml. of normal orthophosphoric acid to 200 ml. of solution in place of the 0.25 *N* hydrochloric acid which had been used previously in the other investigations. The phosphoric acid is standardized by adding 5 ml. of it to 200 ml. of conductivity water. The corrected specific conductance at 20° C. is 1925×10^{-6} reciprocal ohm. In order to have comparable analytical conditions, one liter of solution was made from each sample by diluting 40 ml. of the 25 grams in 200 ml. sirup filtrate. As in the previous studies, 4.5 grams of Domino tablet sugar were added per 100 ml. of solution before making up to the mark at 20° C. For routine work, there is a possibility that a smaller volume of solution would be sufficient, but if the cell is to be rinsed three times before each reading, it is better to have larger volumes of material.

Three conductivity determinations were made: the specific conductance of the solution, that of a solution made by taking 200 ml. of the sugar solution and adding to it 5 ml. of 0.25 *N* potassium hydroxide and finally the specific conductance of a solution containing 200 ml. of the sugar solution plus 5 ml. of normal orthophosphoric acid. These three values, multiplied by 10^6, will be designated as K, K_2, and K_3, respectively.

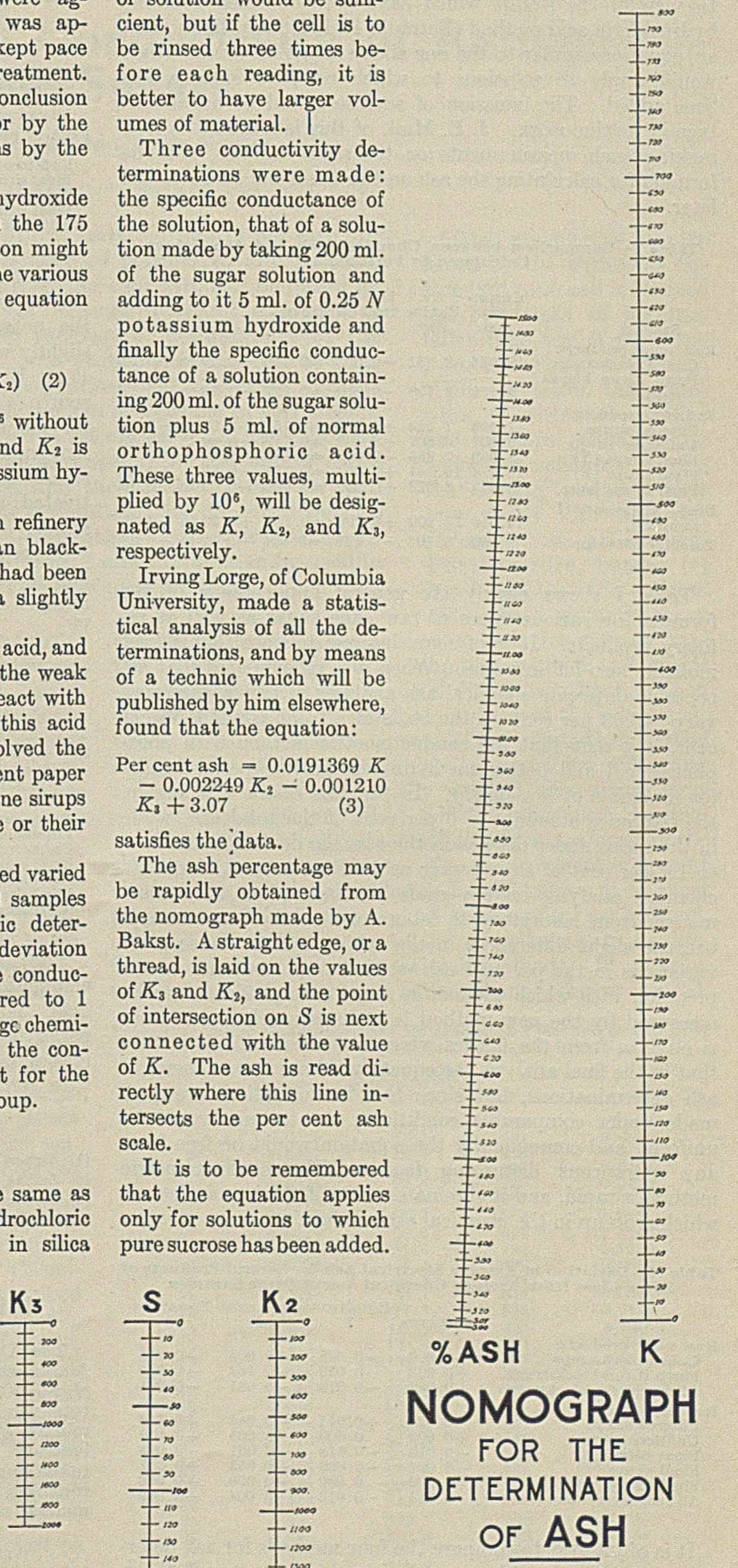
Irving Lorge, of Columbia University, made a statistical analysis of all the determinations, and by means of a technic which will be published by him elsewhere, found that the equation:

$$\text{Per cent ash} = 0.0191369\,K - 0.002249\,K_2 - 0.001210\,K_3 + 3.07 \quad (3)$$

satisfies the data.

The ash percentage may be rapidly obtained from the nomograph made by A. Bakst. A straight edge, or a thread, is laid on the values of K_3 and K_2, and the point of intersection on S is next connected with the value of K. The ash is read directly where this line intersects the per cent ash scale.

It is to be remembered that the equation applies only for solutions to which pure sucrose has been added.



NOMOGRAPH FOR THE DETERMINATION OF ASH

K = INITIAL CONDUCTIVITY
K₂ = CONDUCTIVITY WITH KOH
K₃ = CONDUCTIVITY WITH H₃PO₄
S = REFERENCE LINE

In view of the results which have been obtained with the hydrochloric acid method (Formula 1), it is very likely that an equation similar to the one above might be found which would apply to solutions to which no pure sucrose has been added. The omission of sucrose would be an advantage in routine work. J. E. Mull, of this laboratory, is now making such measurements on the same samples, and the formula for calculating the ash on this basis will be published later.

Table I—Comparison between Chemical Ash and Ash Values Calculated by Formula 3

Sample	Av. Chemical Ash	Av. Calcd. Ash	Deviation of Av.	Av. Deviation	Max. Variation
Raw sugar products:					
Cuban blackstraps	9.986	9.931	−0.055	±0.146	−0.29 to +0.21
Porto Rican blackstraps	9.176	9.106	−0.070	±0.117	−0.28 to +0.17
Refinery products:					
Filtered sirups	7.393	7.552	+0.159	±0.159	+0.06 to +0.27
Unfiltered sirups	6.707	6.807	+0.100	±0.117	−0.03 to +0.19
Final sirups (*X*)	8.089	7.996	−0.093	±0.140	−0.30 to +0.15
Final sirups (*Y*)	10.274	10.281	+0.007	±0.121	−0.29 to +0.27
Final sirups, misc.	8.613	8.673	+0.060	±0.080	−0.03 to +0.19
Beet molasses (1 sample)	13.510	13.800	+0.290	±0.290	+0.29 to +0.29
Total for 133 samples	9.209	9.196	−0.013	±0.134	−0.30 to +0.29

Table I shows clearly the general applicability of the formula for various types of raw cane sugar as well as refinery products. It is of some interest to note that a beet molasses also fell into line. When it is remembered that acceptable duplicate chemical ash analyses of raw sugars may vary ±0.03 per cent on the basis of a total ash of 0.50 per cent, it is seen that the conductometric method with phosphoric acid and potassium hydroxide gives superior results for materials of low purity. In the case of the raw sugars, the tolerance amounts to 6 per cent of the total ash, while in the series under discussion the average deviation amounts to 1.4 per cent of the average ash. Furthermore, duplicate chemical analyses on low-grade products often vary enormously from laboratory to laboratory on the same sample because slight differences in the ashing technic cause great variations in the per cent ash which is reported, and so the precision with which the ash in sugar cane products can be measured by the new method is perhaps much higher than is obvious from the figures which are reported. It is true that in the final analysis the equation is based upon chemical ash determinations, but since the determinations were all made under comparable conditions, the technic would be uniform, and consequently the equation would be free from any extraneous disturbing factors. The conductometric method is rapid, and it eliminates most of the human factors which crop up in the chemical ash method.

Table II—Deviation of Average Electrical Ash for Several Products of Same Class from Average Chemical Ash of Same Samples

Sample	C-Ratio	Equation 1	Equation 2	Equation 3
Raw sugar products:				
Cuban blackstraps	+0.006	−0.098	+0.005	−0.055
Porto Rican blackstraps	+0.053	−0.023	−0.187	−0.070
All raw sugar blackstraps	+0.022	−0.078	−0.061	−0.061
Refinery products:				
Filtered sirups	−0.021	+0.011	−0.048	+0.159
Unfiltered sirups	+0.003	0.000	−0.066	+0.100
Final sirups (*X*)	−0.016	−0.018	−0.001	−0.093
Final sirups (*Y*)	−0.024	−0.026	+0.053	+0.007
Final sirups, misc.	+0.032	0.000	−0.020	+0.060
All refinery sirups	−0.015	−0.013	+0.004	+0.009

It is of interest to compare the four methods for ash determination which have been studied in this laboratory. They have been the following: the C-ratio method, the simple conductometric formula (Equation 1), the potassium hydroxide–hydrochloric acid method (Equation 2), and finally the most general method—namely, the potassium hydroxide–phosphoric acid method (Equation 3).

Table III—Average of Individual Deviation from Chemical Ash Figure for Each Kind of Product or Class of Products

Sample	C-Ratio	Equation 1	Equation 2	Equation 3
Raw sugar products:				
Cuban blackstraps	0.278	0.155	0.188	0.146
Porto Rican blackstraps	0.128	0.125	0.296	0.117
All raw sugar blackstraps	0.227	0.145	0.224	0.135
Refinery products:				
Filtered sirups	0.147	0.070	0.140	0.159
Unfiltered sirups	0.114	0.083	0.126	0.117
Final sirups (*X*)	0.140	0.093	0.121	0.140
Final sirups (*Y*)	0.240	0.158	0.112	0.121
Final sirups, misc.	0.100	0.123	0.083	0.080
All refinery sirups	0.170	0.111	0.120	0.137

As shown in Table II the potassium hydroxide–hydrochloric acid method was best for refinery products, but the potassium hydroxide–phosphoric acid method is only slightly worse whereas it shows marked improvement for the Porto Rican blackstraps as well as for the final sirups from source (*Y*). The C-ratio and the simple conductance methods for the Porto Rican blackstraps are even better than the new method, but the disadvantage is overcome by the consideration that the Porto Rican blackstraps now can be treated as members of the same family as the refinery sirups.

There is considerable variation among the various methods, but again it is seen that raw and refinery products are now brought quite close together. This is even clearer from Table IV.

Table IV—Maximum Individual Deviations from Chemical Ash for Each Kind of Product or Class of Products

Sample	C-Ratio	Equation 1	Equation 2	Equation 3
Raw sugar products:				
Cuban blackstraps	0.7	0.4	0.5	0.3
Porto Rican blackstraps	0.4	0.3	1.0	0.3
All raw sugar blackstraps	0.7	0.4	1.0	0.3
Refinery products:				
Filtered sirups	0.4	0.2	0.2	0.3
Unfiltered sirups	0.3	0.2	0.2	0.2
Final sirups (*X*)	0.4	0.3	0.3	0.3
Final sirups (*Y*)	0.6	0.5	0.3	0.3
Final sirups, misc.	0.2	0.2	0.2	0.2
All refinery sirups	0.6	0.5	0.3	0.3

The most striking thing about the new method is the elimination of the distinction between raw and refined products. Not only that, but in every case the method is superior to the C-ratio method where the individual idiosyncrasies of the products were taken into consideration.

Literature Cited

(1) Zerban and Sattler, *Facts about Sugar*, **21**, 1158 (1926).
(2) Zerban and Sattler, *Ibid.*, **22**, 990 (1927).
(3) Zerban and Sattler, Ind. Eng. Chem., Anal. Ed., **2**, 32 (1930).
(4) Zerban and Sattler, *Ibid.*, **2**, 322 (1930).

Mineral Production of Alaska in 1930

The Department of the Interior announces that mines in Alaska are estimated to have produced minerals to the value of $13,602,000 in 1930 as against $16,066,000 in 1929. The total value of the mineral output of Alaska since 1880 is approximately $629,000,000. The figures for 1930, which are preliminary estimates and consequently subject to revision, are taken from the Geological Survey's annual report on the mineral resources of Alaska, now in preparation. The source of this mineral wealth was approximately as follows:

Value of Mineral Output of Alaska in 1930 and 1929

	1930	1929
Gold	$ 8,394,000	$ 7,761,000
Copper	4,100,000	7,130,000
Silver	158,000	252,000
Coal	609,000	528,000
Other minerals (lead, petroleum, marble, tin, platinum, etc.)	341,000	395,000
	$13,602,000	$16,066,000

Ash and Electrical Conductivity of Refined Cane Sugars[1]

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The percentage of ash (sulfated less 10 per cent) in refined cane sugars such as granulated and remelts, containing less than 0.3 per cent ash, can be found by dissolving 25 grams of the sugar in 100 ml. conductivity water, determining the specific conductance of the solution at 20° C., and multiplying the result, after correcting for the conductivity of the water, by the factor 530. To find the ash percentage in soft sugars, only 5 grams are used in 100 ml. solution, as in the case of raw sugars. The appropriate factor, which varies from place to place, may then be determined for each refinery, or else the general method described may be employed. The article concludes with practical recommendations for equipment and methods to be used in routine work on all types of cane products.

THIS final chapter of our investigation on the relation between ash and electrical conductivity of sugar cane products (*3* to *9*) deals with the sugars made in cane sugar refineries, and either sold or returned to process.

Work on similar products of beet sugar refineries has been reported in Europe, especially by Lundén (*1*), and on American granulated beet sugars by Nees (*2*). The last named author used a concentration of 25 grams of sugar in 100 ml., and found that for granulated beet sugars from three different states the ratio between the specific conductance × 10^5 and the per cent sulfated ash (less 10 per cent) averages 231.5 if the conductivity determinations are made at 25° C. and corrected for the conductance of the water used as a solvent. The concentration of 25 grams in 100 ml. was chosen because the specific conductance passes through a maximum in the neighborhood of that point.

Granulated and Remelt Cane Sugars with Low Ash

The first group of refined cane sugars taken up by the writers comprised granulated and remelt sugars with an ash content up to 0.3 per cent. Nees' concentration of 25 grams was adopted for these low ash sugars, but the normal temperature for sugar laboratories, 20° C., has been adhered to. The same equipment was used as in all previous work, and all the solutions were filtered through a mat of filter paper and asbestos to exclude the effect of the ash contained in the insoluble portion of the sugar on the chemical ash determination. The limit of 0.3 per cent ash was arbitrarily chosen because with sugars of high ash content our standard concentration of 5 grams of sugar in 100 ml. can be used, as has been done in the case of raw sugars and also of soft sugars.

The results for 34 samples from four different refineries are given in Table I, where the sugars are arranged in the order of ascending ash content. The column headed "Chemical Ash" shows the sulfated ash, less 10 per cent, determined in the usual manner on the filtered solution of the sample. The next column shows K, the specific conductance × 10^6, of the solution at 20° C., corrected for the conductance of the water. The figures in the succeeding column, headed "C-Ratio," represent the quotient of the ash percentage divided by the specific conductance itself (not × 10^6). The last column gives the ash percentage calculated by multiplying the specific conductance with the average C-ratio 530, or K with 0.000530.

For the proper interpretation of these results it must be kept in mind that the different chemical ash methods themselves are all entirely empirical and do not give concordant results among each other. It will be recalled that the sulfated ash method was selected by the writers as the standard because it is affected less by details in manipulation than any of the "carbonated" ash methods. With the latter, the quantities of chlorine, sulfur, and perhaps phosphorus which are volatilized during the heating process may vary widely with slight differences in procedure. Furthermore, Lundén (*1*) has found that the sulfated ash method gives the most concordant figures when used as a basis for refinery control. Yet it is after all an empirical method and yields discrepant results in the hands of different analysts. When the ash content is very small, as in many of the samples recorded in Table I, the results even of the sulfated ash method are quite unreliable, because usually only a few milligrams or even less of ash are actually weighed, unless very large quantities of sugar are ashed, which is precluded in actual practice. In such cases the possible percentage error in the ash figure becomes enormous. The measurement of specific conductance, on the other hand, is well known to be most precise, and for this reason alone the electrical ash method, although admittedly empirical, is, nevertheless, to be preferred over the other empirical ash methods. In addition to this, it is much more rapid, and much more easily executed.

Table I—Ash and Conductivity of Unwashed and Washed Granulated and Remelt Sugars, with Ash up to 0.3 Per Cent

SAMPLE	CHEMICAL ASH	SPECIFIC CONDUCTIVITY × 10^6 (K)	C-RATIO	K × Av. C-Ratio
	%			
1	0.0059	11.7	504	0.0062
2	0.0077	16.1	478	0.0085
3	0.0088	19.6	449	0.0101
4	0.0095	22.6	420	0.0120
5	0.0110	16.5	671	0.0087
6	0.0112	16.5	679	0.0087
7	0.0128	20.6	621	0.0109
8	0.0158	31.8	497	0.0169
9	0.0292	59.1	492	0.0313
10	0.033	63.4	524	0.034
11	0.035	63.1	554	0.033
12	0.039	77.5	503	0.041
13	0.052	111.8	441	0.059
14	0.071	124.4	571	0.066
15	0.073	134.3	544	0.071
16	0.079	147.9	534	0.078
17	0.083	178.4	465	0.094
18	0.084	156.9	536	0.083
19	0.096	189.5	507	0.100
20	0.110	247.5	445	0.131
21	0.114	204.5	558	0.108
22	0.118	181.3	651	0.096
23	0.124	206.4	602	0.109
24	0.130	233.9	556	0.124
25	0.134	253.1	530	0.134
26	0.146	293.3	498	0.155
27	0.167	334.5	500	0.177
28	0.169	319.9	528	0.170
29	0.172	357.4	481	0.189
30	0.175	314.0	557	0.166
31	0.177	346.9	510	0.184
32	0.225	431.7	521	0.229
33	0.226	367.2	599	0.195
34	0.269	460.0	585	0.244
35	0.295	566.2	521	0.300
		Av.	530	

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[1] Received September 18, 1930. Presented before the Division of Sugar Chemistry at the 80th Meeting of the American Chemical Society, Cincinnati, Ohio, September 8 to 12, 1930.

One difficulty arises in the case of specially purified sucrose, and some refined sugars of the very highest grade. With sugars of this type the specific conductance of the solution may be less than the specific conductance of the water, owing to the depressing effect of sucrose on the conductivity of electrolytes. In cases like this, specially purified water might be used, but even then the difficult question of correction would remain. With such sugars the ash content can be found only approximately, yet with greater precision than by the chemical method.

It is interesting to inquire how the C-ratio of 530 found for refined cane sugars compares with the C-ratio of granulated beet sugars. At 25° C., the temperature used by Nees, the value 530 would be reduced to 470. Nees' divisor, 231.5 at 25° C., is equal to a C-ratio of 432. This confirms the statement of Nees that the ratio between ash and conductivity for cane sugars is probably different from that for beet sugars, because the latter contain a large proportion of highly ionizable alkali salts. This would involve a lower C-ratio for granulated beet sugars, in agreement with the facts.

With this class of sugars it is obviously unnecessary to resort to the more complicated conductometric procedures of ash determination, developed by the writers for raw sugars and for sirups and molasses.

Soft Sugars

The chemical ash in the samples of soft sugars received by the writers from three different refineries ranged from 0.18 to 2.31 per cent. The conductivity determinations were therefore run on solutions containing 5 grams of total sugar in every 100 ml. of solution, as in the case of raw sugars. Within the ash range up to 1 per cent, 5 grams of the soft sugar were used, and above 1 per cent, 2.5 grams of soft sugar plus 2.5 grams of sucrose; in the latter case the result of the conductivity determination was multiplied by 2. Parallel determinations were made in the presence of acid, 5 ml. of 0.25 *N* hydrochloric acid being added to 200 ml. of the 5-gram-per-100-ml. sugar solution, and measuring the specific conductance again, exactly as in the previous work. The results of the measurements are shown in Table II. Columns 1 to 5 are the same as in Table I. The average C-ratio was found to be 1580 which is lower than the value found previously for any group of refinery products, but this fact has little significance because it has been shown before that the C-ratio may vary within extremely wide limits. Column 6 gives the individual deviations of the electrical ash (in column 5) from the chemical ash. The values for K_1, which is the specific conductance $\times 10^6$ of the acidified solution, are found in column 7. In column 8 are shown the figures for the ash calculated by the simple conductometric expression developed previously ($0.913\ K + 193.5 - 0.1\ K_1$), multiplied by the factor 0.001695. This factor agrees closely with the average factor obtained for refinery sirups (*8*).

The individual errors by the C-ratio method exceed 0.03 per cent in seven cases, amounting to 0.04 in two, 0.05 in one, 0.08 in two, and 0.12 in one. The total deviations for this method are −0.52 and +0.51, or 1.03 in all. The conductometric formula results in only two deviations of 0.04 per cent and two of 0.05 per cent; the total deviations are −0.30 and +0.41, or 0.71 altogether. The simple conductometric formula method is evidently more reliable than the C-ratio method, and still better results could probably be obtained by the general conductometric formula based on three conductivity determinations (*9*), one on the solution itself, a second after addition of *N* orthophosphoric acid, and a third after addition of 0.25 *N* potassium hydroxide solution. But it is believed that this would have no practical advantage, and in the control of a single refinery even the C-ratio method will probably prove quite satisfactory for most purposes.

Table II—Ash and Conductivity of Soft Sugars

Sample	Chemical Ash %	K	C-Ratio	$K \times$ Av. C-Ratio	Error %	K_1	Ash Calcd. by Formula %	Error %
1[a]	1.30	829.6	1567	1.31	+0.01	1824	1.32	+0.02
2[a]	1.43	900.2	1589	1.42	−0.01	1776	1.45	+0.02
3[a]	1.53	983.4	1556	1.55	+0.02	1755	1.58	+0.05
4[a]	1.84	1149.4	1601	1.82	−0.02	1717	1.85	+0.01
5[a]	2.31	1385.8	1667	2.19	−0.12	1573	2.27	−0.04
6	0.43	280.5	1497	0.44	+0.01	2143	0.40	−0.03
7	0.46	308.3	1492	0.49	+0.03	2184	0.44	−0.02
8	0.60	399.4	1502	0.63	+0.03	2098	0.59	−0.01
9	0.79	506.2	1561	0.80	+0.01	2045	0.77	−0.02
10	0.89	563.4	1580	0.89	0.00	1931	0.87	−0.02
11[a]	1.07	695.6	1538	1.10	+0.03	1945	1.07	0.00
12[a]	1.23	807.8	1523	1.28	+0.05	1970	1.24	+0.01
13[a]	1.26	813.0	1550	1.28	+0.02	1889	1.27	+0.01
14[a]	1.50	963.8	1556	1.52	+0.02	1821	1.53	+0.03
15[a]	1.49	940.2	1585	1.49	0.00	1767	1.51	+0.02
16[a]	1.63	1013.8	1608	1.60	−0.03	1756	1.63	0.00
17	0.27	178.2	1515	0.28	+0.01	2077	0.25	−0.02
18[a]	1.47	892.0	1648	1.41	−0.06	1528	1.52	+0.05
19	0.42	276.6	1518	0.44	+0.02	2020	0.41	−0.01
20	0.21	136.4	1540	0.22	+0.01	2067	0.19	−0.02
21[a]	1.84	1110.6	1657	1.76	−0.08	1474	1.87	+0.03
22	0.80	509.4	1570	0.80	0.00	1770	0.82	+0.02
23[a]	1.52	942.4	1613	1.49	−0.03	1633	1.56	+0.04
24	0.63	413.9	1522	0.65	+0.02	1946	0.64	+0.01
25[a]	1.26	777.2	1621	1.23	−0.03	1770	1.26	0.00
26	0.83	541.9	1532	0.86	+0.03	1898	0.84	+0.01
27[a]	1.72	1036.4	1660	1.64	−0.08	1613	1.71	−0.01
28	0.28	199.1	1406	0.32	+0.04	2113	0.28	0.00
29	0.19	126.8	1498	0.20	+0.01	2135	0.17	−0.02
30	0.45	299.4	1503	0.47	+0.02	2054	0.44	−0.01
31	0.22	167.7	1312	0.26	+0.04	2153	0.22	0.00
32	0.59	375.1	1573	0.59	0.00	2044	0.56	−0.03
33	0.18	132.7	1356	0.21	+0.03	2150	0.17	−0.01
34	0.87	533.2	1632	0.84	−0.03	1795	0.85	−0.02
35	0.48	309.3	1552	0.49	+0.01	1942	0.48	0.00
36	0.60	387.6	1548	0.61	+0.01	1934	0.60	0.00
37	0.75	490.3	1550	0.77	+0.02	1855	0.77	+0.02
38	0.89	565.8	1573	0.89	0.00	1748	0.91	+0.02
39[a]	1.31	832.2	1574	1.31	0.00	1811	1.33	+0.02
40[a]	1.29	824.6	1564	1.30	+0.01	1825	1.31	+0.02
41[a]	1.31	812.2	1613	1.28	−0.03	1815	1.30	−0.01

[a] The conductance determinations on these samples were made at a concentration of 2.5 grams sample plus 2.5 grams sucrose, and the results were multiplied by 2.

High Ash Remelt Sugars

The samples collected by the writers included six remelt sugars with an ash content within and also above the soft sugar range. The conductivity determinations were therefore made at the concentration adopted for soft sugars—that is, on 5 grams sample in every 100 ml. up to an ash content of about 1 per cent; at an ash content between 1 and 3 per cent, 2.5 grams sample plus 2.5 grams sucrose were taken, and when the ash exceeded 3 per cent, 0.5 gram sample plus 4.5 grams sucrose were used. The results are given in Table III.

Table III—High Ash Remelt Sugars

Sample	Chemical Ash %	K	C-Ratio	$K \times$ 1580	Error %	K_1	Ash Calcd. by Formula %	Error %
1	0.39	245.1	1591	0.39	0.00	1936	0.38	−0.01
2	0.66	375.3	1759	0.59	−0.07	1723	0.62	−0.04
3	1.35	814.2	1658	1.29	−0.06	1709	1.34	−0.01
4	2.05	1193.2	1718	1.88	−0.17	1443	2.01	−0.04
5	3.25	1985.0	1637	3.14	−0.11	1891	3.15	−0.10
6	4.63	2761.0	1677	4.36	−0.27	1734	4.61	−0.02

The discrepancies found by the C-ratio method, with the average C-ratio of 1580 for soft sugars, are rather large, but, as has been explained above, without significance. The results calculated by the simple conductometric formula, with the soft sugar factor 1695, are very much better, considering that an error of 0.10 on 3.25 per cent ash is really only about 3 per cent of the total. Just as with the soft sugars, the general conductometric formula mentioned above would probably reduce the errors, but in practice it is unnecessary to go to such refinements.

Summary of Recommendations for Routine Electrical Ash Determinations in Sugar Cane Products

EQUIPMENT—For routine conductivity measurements it is advisable to use a self-contained instrument with as little outside wiring as possible, to prevent current leaks and other inconveniences. If it is operated by a battery this should also be enclosed in the instrument case. With this type a telephone receiver is necessary as a null indicator. In a noisy factory laboratory the telephone is practically useless, and if alternating line current is available or can be provided, it is better to use an instrument to be connected to the a. c. line with a galvanometer as null indicator. The only other outside connection should be with the conductivity cell. The instrument should be calibrated in terms of specific conductance at 20° C.; this necessitates a compensator for variations in the cell constant. For cane products it is not advisable to have the scale calibrated directly in ash percentage, on account of the variations in the C-ratio, but an additional blank scale might be provided which could be calibrated by the individual worker for the C-ratio most frequently used. The instrument should also be provided with a compensating device for variations in temperature. Since the temperature coefficient itself varies to some extent as has been shown by the writers, especially when conductivity determinations are made also in the presence of acid and alkali, it is safest to keep the temperature of the solution as close as possible to the standard of 20° C. This is most readily accomplished by the use of the Lange type of cell provided with a water jacket, as employed by the writers. This cell has the further advantage for routine work that the solution which has been tested can be run out rapidly and the next solution be filled in without delay. Dipping cells may also be used if preferred, but they are not as convenient as the Lange type of cell.

METHOD—For the control work of individual factories it is desirable and quite possible to use the ordinary C-ratio procedure, with only one conductivity determination, based on actual comparisons of chemical ash and specific conductance of the various products. These should include not only the materials studied by the writers, but should be extended to the several types of juices.

When samples are received from many different sources, such as in regulatory and similar work, the choice of the proper method will depend on the type of product analyzed. For granulated and other refined sugars of low ash content, the simple C-ratio method outlined in this paper is sufficiently accurate. For raw cane sugars and soft sugars the simple conductometric formula with two conductivity determinations should be used, the factor being 0.001757 for raw sugars (*7*), and 0.001695 for soft sugars. The same method, with the factor 0.01757, will also suffice for sirups and molasses known to have been produced without char treatment (*8*), but otherwise it is safest to resort to the general conductometric formula based on three conductivity determinations, one on the solution itself, one with the addition of phosphoric acid, and one with the addition of potassium hydroxide (*4*).

Acknowledgment

The writers are indebted to various sugar refining companies in the New York district for the samples used in this investigation.

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The Plastometer[1,2]

A New Instrument for Measuring Plastic Properties of Coal

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BETWEEN certain limiting temperatures, depending on its rank and to some extent on its origin, a coking coal assumes a semi-fused or plastic state. Destructive distillation of the coal substance and of those constituents which fuse, begins as soon as or before fusion sets in and is greatly accelerated by rising temperature; the mass may assume a more or less plastic state before solidifying as coke. As the temperature rises to the limit of the plastic range (or state), most of the volatile matter is driven off and the mass sets into coke. Plasticity develops, however, only when a favorable heating rate, such as that prevailing in industrial coking practice, is chosen. Audibert (*2*) has shown, for example, that it is possible to choose a heating rate so slow that the fusible matter is decomposed before it has actually fused. In such a case the coal does not become plastic and coke is not formed. On the other hand, heating may be so rapid that, although fusion does take place, decomposition is accelerated to such an extent that plasticity cannot be measured and a frothy coke results. The instrument to be described was designed in connection with the Bureau of Mines Survey of the Gas- and Coke-Making Properties of American Coals, for heating rates within the range of those prevailing in industrial practice under these conditions. Coke is invariably produced, provided that the coal is suitable for coke-making.

Previous Methods for Studying Plastic State of Coal

The method devised by Foxwell (*3*) and modified by Layng and Hathorne (*4*), and that of Agde and von Lyncker (*1*) will serve as examples of experimental methods previously used for study of the plastic state of coal.

Layng and Hathorne carbonize a standard column of sized coal at a suitable rate in an electric tube furnace while passing nitrogen through it. Sufficient nitrogen for the test is confined in a bottle connected to the tube containing the coal. This is caused to flow by water displacement at constant head, so that resistance to its passage develops when the coal fuses. A manometer connected to the nitrogen

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[1] Received September 19, 1930. Presented before the Division of Gas and Fuel Chemistry at the 80th Meeting of the American Chemical Society, Cincinnati, Ohio, September 8 to 12, 1930.

[2] Printed by permission of the Director, U. S. Bureau of Mines. (Not subject to copyright.)

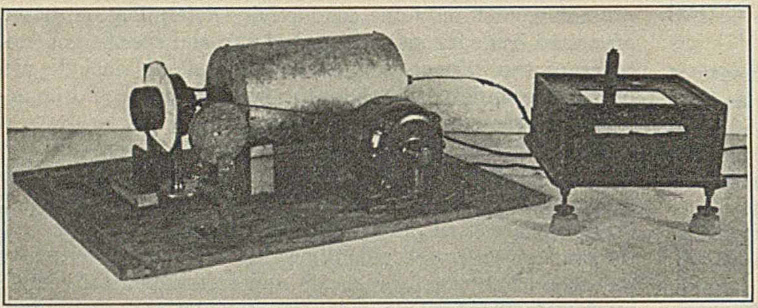

Figure 1—The Plastometer

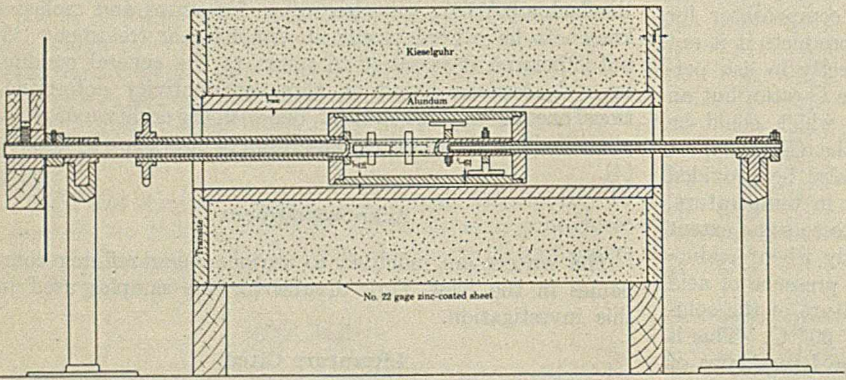

Figure 2—Diagram of Plastometer

bottle serves to indicate the amount of resistance and the rate at which it develops. This is plotted against the temperature (or time) and defines the plastic range of the coal.

Agde and von Lyncker carbonize a small sample of coal packed in a vertical tube furnace at a constant heating rate. A weighed needle, which is free to move vertically, rests on the coal. When the coal fuses the needle begins to sink and the rate of sinking is noted on a vertical scale provided for the purpose. The more plastic the coal the more rapid is the rate of sinking. When the charge sets into coke the needle comes to rest.

Although the Layng-Hathorne method with most coals serves to define approximately the limits of the plastic range, it does not give a direct measure of the plasticity of the charge within this range. The Agde-von Lyncker method, on the other hand, gives a figure which corresponds with the ease with which the charge yields to a needle. It is in effect a penetrometer, and the result obtained is not necessarily a measure of plasticity. In addition, it defines the limits of the plastic range with more or less precision.

In the hands of the writer this method proved difficult to carry out, yielding results difficult of close reproduction.

Without discussing the relative merits of these methods it is perhaps sufficient to observe that, when properly carried out, both will yield specific information of considerable value to one studying the coking process. Of course great care must be employed in interpretation of such results.

The specific information sought by the plastometer is the plasticity of the charge within the plastic range, together with close definition of the temperature limits.

Description of Plastometer

Figure 1 is a photograph of the plastometer and Figure 2 shows a vertical section through the instrument. The plastometer consists of a steel retort 5 inches (127 mm.) in length by $1^7/_8$ inches (22 mm.) in diameter, mounted on a tubular axle through the center of a 2-inch (51-mm.) tube furnace 12 inches (305 mm.) in length, and arranged for rotation at constant speed by a $^1/_4$-horsepower motor through a reduction gear and chain drive. The retort, whose wall is $^3/_{16}$ inch (4.8 mm.) in thickness, is provided with screw caps. A tubular shaft is passed through the gear-driven axle into the retort. Five rabble arms are fixed to the end of this shaft within the retort. These arms clear the retort wall by $^1/_{32}$ inch (0.4 mm.). The protruding end of the shaft is fitted with a circular brass disc whose rim carries a scale similar to that of a torsion viscometer head. A pulley is also fixed to the end of the shaft and a chain is attached to its face. The other end of the chain is fixed to a spiral tension spring; as long as the rabble arms within the retort encounter no resistance in the rotating retort, the shaft does not turn and the spring is under no tension.

Method of Making Test

Eight grams of the 20- to 40-mesh coal sample[3] to be tested are charged into the retort and the heads are screwed in place, a thick paste of graphite and oil being used to prevent the threads from "freezing" on subsequent heating. The charged retort is now placed in the furnace, the drive chain is attached, and a thermocouple is inserted in the hollow shaft. The temperature is given continuously by a recording milli-

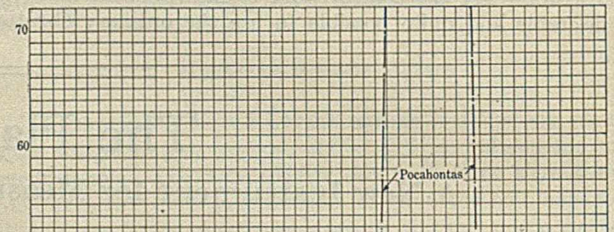

Figure 3—Resistance Developed in Heating Coal in Plastometer

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[3] It is recognized that the selection of a size fraction of coal is not representative of the entire coal, and it is hoped to modify the apparatus so that a strictly representative sample in which the fine coal is not rejected may be used.

voltmeter. The motor is now started and the furnace is rapidly heated (7° C. per minute) to approximately 375° C., below which point no tension of the coil spring develops. From 375° C. through the plastic range (480° to 500° C.) the heating rate is maintained constant (± 0.2°) at 3.4° C. per minute. A note of the scale reading is made at 1-minute intervals during the plastic range and at the end of the experiment the readings, reduced to pound-inches of torque, are plotted against the temperature. Tension develops at 400° to 460° C. depending on the coil, and drops sharply at temperatures ranging from 450° to 480° C. The plastic range is defined by these limiting temperatures for each coal.

Behavior of Different Kinds of Coal under Test

By the manner of development of tension on the plastometer head several kinds of coking coals have been distinguished:

(1) Coals that fuse at a low temperature, have a wide plastic range, and become very plastic at intermediate temperatures. These coals fuse together well and should produce well-fused coke—i. e., the Powellton coal of Figure 3.

(2) Gas coals containing splint that have a short plastic range and exhibit little or no plasticity, as the Elkhorn coal.

(3) Semi-bituminous coals having a high fusing temperature, very little plasticity, and a short plastic range which gives an exceedingly high plastic tension, as shown by the Pocahontas coal of Figure 3.

(4) High oxygen, weakly coking coals of which the limiting temperatures of the plastic range are just distinguishable by the plastometer. Hocking coal represents this type.

Practical Value of Plastometer

Only a few coals have been tested by this method and no broad generalization can be made as to indication of coke quality. However, with coals so far tested it may be observed that: (1) Class 1 coals produce a fine-grained coke which does not fracture badly when exposed to high coking temperatures; (2) class 2 coals have large cells and when coked without admixed low-volatile coals give a more fractured high-temperature coke than class 1 or class 3 coals; (3) class 3 coals produce strong fine-grained coke but one which does not shrink appreciably after setting and which offers resistance to pushing from ovens.

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Determination of Alkalinity of Reclaimed Rubber[1]

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A new method is given for determining the relative alkalinity of reclaimed rubber. The extraction of the alkaline material is based on a digestion of the sample in a mixture of ethanol, benzene, and water. The method is compared with the previous method described by the authors in 1928. The experimental figures given show that the new method gives results which are dependable, and approximately four times as accurate as the previous method. The higher degree of accuracy is due to the elimination of much of the personal error, the extraction of a larger percentage of alkaline material, and a more accurate titration end point.

THE purpose of this paper is to present a method for determining the relative alkalinity of reclaimed rubber which, in the authors' opinion, has certain advantages over other methods in use at present.

In general other methods current for determining alkalinity consist of a digestion in water of various sizes of samples for times varying from 3 to 48 hours. In the discussion of an article by Shepard, Palmer, and Miller (*2*) in 1928, the relative control method then in use by the authors was described. This method has recently been referred to by Stafford (*3*) in an article on the testing of reclaimed rubber. Briefly this method consists in digesting a 25-gram sample in water for 3 hours, after which the sample is squeezed and thoroughly washed during squeezing. The sample is further digested, and the liquor titrated with normal acid using methyl red as the indicator. A disadvantage of this method is that it involves a personal factor in the squeezing of the sample after digestion. Another disadvantage of the method and other unpublished methods known to the authors, is that a relatively small quantity of the total alkali is extracted which naturally means that errors in the method will magnify the differences in alkalinity. Further, the solution to be titrated is often brown enough in color so that the end point of the usual indicators is masked. The method developed and described below overcomes these difficulties since a relatively higher percentage of alkaline material is removed and a more efficient titration method is applied.

Method of Titration

Inasmuch as the color of the solution often causes the end point of usual indicators such as methyl red to be very indistinct, an application has been made of the iodine-starch end point. The procedure after the sample is prepared for titration is as follows:

To the solution 0.1 *N* HCl is added from a buret until the solution is distinctly acid. This point may be most definitely determined by using litmus paper. Approximately 5 cc. each of 3 per cent KIO_3 solution and of 1 *N* KI solution are then added. The mixture is allowed to stand 3 minutes and the same volume of 0.1 *N* $Na_2S_2O_3$ as 0.1 *N* HCl is added. The mixture is allowed to stand for 15 minutes after which 5 cc. of fresh starch solution are added. Titration is then made with 0.1 *N* iodine solution until the appearance of the usual iodine-starch blue color. This color may of course be black due to the brown color of the solution.

The particular advantage of this method of titration is that the end point can always be distinguished and even the darkest solutions can be diluted so that the end point is visible. In cases of reclaim of low alkalinity the solutions are less deeply colored and the end point may often be de-

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termined by the use of methyl red instead of the iodine-starch combination.

It should be mentioned that before arriving at the above method an effort was made to use the two following methods:

(1) Use of $K_2Al_2(SO_4)_4.24H_2O$: Since $K_2Al_2(SO_4)_4$ hydrolyzes in water to H_2SO_4 and $Al(OH)_3$, the H_2SO_4 reacts to neutralize the alkali and the $Al(OH)_3$ carries down a considerable amount of colloidal matter in the solution, but not enough to render the solution sufficiently clear to discern methyl red indicator.

(2) Use of $FeCl_3$ and $K_4Fe(CN)_6.3H_2O$: When $FeCl_3$ hydrolyzes in water to form HCl and $Fe(OH)_3$, the HCl will neutralize the alkaline material. Any soluble ferric salt gives with $K_4Fe(CN)_6$ a very deep blue color. In using this method $FeCl_3$ was added until all the alkali was neutralized, the blue color being formed by the excess $FeCl_3$ with $K_4Fe(CN)_6$. The color was masked considerably, however, by the presence of the $Fe(OH)_3$. The addition of HCl to diminish the amount of $FeCl_3$ necessary was not effective since the indicator was not sensitive to such a small amount of $FeCl_3$.

Extraction of Alkaline Material

Since other methods in vogue have extracted a relatively small amount of the total alkaline material, an effort was made to evolve a method which would give a higher percentage of the total alkali present. This has been achieved by the use of the following procedure:

The sample of reclaim is sheeted to a thickness of 0.127 mm. (0.005 inch) plus or minus 0.0254 mm. (0.001 inch) in thickness. A 5-gram sample is torn in pieces about 25 mm. (1 inch) in diameter and placed in a liter Erlenmeyer flask to which have been added 60 cc. of benzene, 40 cc. of ethanol (denatured with 0.5 per cent benzene),[2] and 100 cc. of distilled water. These reagents must, of course, be neutral. A reflux condenser is attached to the flask and digestion is made for 2 hours on a hot plate which is at 110° C. After the digestion 500 cc. of distilled water are added and the heating continued for 1$^1/_2$ hours without the reflux condenser attached. At the end of this time the benzene and the larger percentage of the ethanol will be completely distilled off. If benzene is still present at the end of this time, the heating, with a periodic shaking, should be continued until all benzene is removed. The total heating time will not exceed 1$^3/_4$ hours. The solution is then decanted leaving the rubber sample in the flask. Seventy-five cubic centimeters of boiling distilled water are added and the flask whirled rapidly to wash the sample. This water is added to the original liquid and two more washings are made as above after which the solution is allowed to cool preparatory to titration.

In developing this method of extraction the following observations have been made on factors which affect the results:

Thickness of Sample—The same sample of reclaim was refined once and twice at the thicknesses of 0.0762 and 0.1778 mm. (0.003 and 0.007 inch) with the results shown in Table I. The results reported in all tables are in terms of NaOH. These results show that the thickness between these limits may be tolerated and that the second refining did not affect the amount of alkaline material extracted. An attempt was made to prepare the sample by cutting it into very small pieces but the results in Table II show that this is not a suitable method of preparation.

Effect of Benzene, Ethanol, and Water—Various proportions of benzene, ethanol, and water were tried. The first tests were run with 100 cc. benzene, 100 cc. water, and 20 cc. ethanol. The benzene functions to swell and break up the rubber and the ethanol acts as a carrier. With these proportions it was found that the emulsion formed made it difficult to boil off the benzene without much bumping, foaming, and spattering. The benzene was decreased and the ethanol increased to the proportions named in the method with the result that the above-mentioned difficulties disappeared.

The effect of these reagents in different proportions is given in Table III. It will be noted that increasing the volume of water gives no higher results. The ethanol is necessary as a carrier and the benzol as a swelling agent. Tests on another sample of reclaim A show 0.242 per cent alkalinity when the regular volume of reagents was doubled, against 0.238 per cent for the prescribed volume.

Table I—Effect of Refining (Reclaim A)

Thickness of Sample		Number of Refinings	Alkalinity		
			Test 1	Test 2	Av.
Mm.	*Inch*		%	%	%
0.0762	0.003	1	0.312	0.300	0.306
0.0762	0.003	2	0.283	0.293	0.288
0.1778	0.007	1	0.272	0.279	0.276
0.1778	0.007	2	0.280	0.292	0.286

Table II—Comparison of Methods of Preparing Sample (Reclaim G)

Method of Preparation	Alkalinity	
	Test 1	Test 2
	%	%
Sheeted on refiner mill	0.420	0.412
Cut into $^1/_8$-inch (3-mm.) cubes	0.365	0.216

Table III—Effect of Digesting Reagents

Reclaim	Test	Alkalinity				
		Benzene, cc.	60	60	100	..
		Ethanol, cc.	40	40	..	100
		Water, cc.	100	200	100	100
			%	%	%	%
A	1		0.304	0.318	0.127	0.179
	2		0.305	0.304	0.122	0.212
D	1		0.505	0.462	0.248	0.453
	2		0.507	0.462	0.248	0.406

Effect of Time of Digestion—A sample of reclaim A was digested for 2 and 3 hours with the extraction of 0.164 per cent and 0.165 per cent alkali, respectively. Observation showed that times less than 2 hours are insufficient to break up the sample thoroughly.

Amount of Water Added after Digestion—Whether the water added after digestion is cold or hot did not affect the alkalinity value. The water caused the finely divided and benzene-swollen sample to form a semi-solid mass so that the benzene could be boiled off without any danger of loss of sample or liquor due to spattering. Five hundred cubic centimeters gave higher alkalinity results than lower volumes and were used as a practical upper limit convenient to handle.

Number of Washings—After decanting the liquor from the sample it was convenient to wash the sample in the flask. In washing with 75-cc. portions of hot water, it was found that the alkaline material became constant after the first washing. The alkalinity determination on the various washings will be found in Table IV.

Table IV—Effect of Washing

	Alkalinity			
	Reclaim B		Reclaim C	
	Test 1	Test 2	Test 1	Test 2
	%	%	%	%
Determined from decanted liquor only	0.094	0.106	0.470	0.466
Washings with 75 cc. hot water:				
(1)	0.004	0.008	0.010	0.010
(2)	0.004	0.004	0.004	0.004
(3)	0.004	0.004	0.004	0.004

Error Caused by Retention of Liquor by Sample—It is obvious that the sample retains some alkaline liquor, and since in the new method the sample is not squeezed, this is a source of error. In Table V is shown the approximate amount of liquor retained and the percentage error introduced by its retention.

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[2] 2B Formula, U. S. Industrial Alcohol Co.

Table V—Error Due to Liquor Retained by Sample

	Reclaim B	Reclaim C
	Cc.	*Cc.*
Decanted liquor plus washings	825	825
Liquor retained by sample	25	23
Total liquor	850	848
	%	%
Alkalinity as determined on available liquor	0.114	0.486
Corrected alkalinity based on total liquor	0.118	0.503
Error due to liquor held by sample	3.4	3.2

EFFECT OF IRON AND ANTIMONY COMPOUNDS ON RESULTS—The fact that trivalent antimony may be titrated with iodine led to the following experiment to determine whether iron or antimony would affect the results as obtained by an iodometric titration.

Two per cent of crimson antimony (Sb_2S_3) were added to a whole tire scrap (reclaim A) and refined on the laboratory mill. To another sample of scrap, 5 per cent of red oxide (Fe_2O_3) were added and the reclaim finished as before. These were tested against a control reclaim made from the same sample of well-blended scrap. The figures given in Table VI show that trivalent antimony in the reclaim affects the titration with iodine while red oxide has no effect.

Table VI—Effect of Iron and Antimony Compounds Added to Reclaim A

	Alkalinity			
	Test 1	Test 2	Av.	Variation
	%	%	%	%
Control	0.350	0.354	0.352	....
5% Red oxide (Fe_2O_3)	0.351	0.354	0.353	+0.001
2% Crimson antimony (Sb_2S_3)	0.299	0.301	0.300	−0.052

Table VII—Comparison of Old and New Methods on Several Samples of Different Reclaims

Reclaim	Sample	Operator	Old Method			New Method		
			Test 1	Test 2	Variation	Test 1	Test 2	Variation
A	1	Z	0.047	0.050	0.003	0.272	0.261	0.011
	2	Z	0.028	0.040	0.012	0.225	0.225	...
	3	Z	0.103	0.099	0.004	0.242	0.251	0.009
B	1	Z	0.019	0.020	0.001	0.100	0.097	0.003
	2	Z	0.022	0.014	0.008	0.116	0.116	...
	3	Z	0.044	0.037	0.007	0.167	0.167	...
	4	W	0.034	0.038	0.004	0.100	0.110	0.010
	5	W	0.056	0.055	0.001	0.136	0.139	0.003
	6	W	0.044	0.049	0.005	0.141	0.140	0.001
	7	W	0.041	0.046	0.005	0.111	0.122	0.011
	8	W	0.060	0.056	0.004	0.157	0.163	0.006
D	1	X	0.429	0.397	0.032	0.507	0.505	0.002
E	1	Z	0.180	0.164	0.016	0.374	0.382	0.008
	2	Z	0.216	0.217	0.001	0.386	0.386	...
F	1	X	0.013	0.012	0.001	0.064	0.055	0.009
H	1	X	1.68	1.94	0.260	1.91	1.83	0.08
I	1	X	0.819	0.585	0.234	0.96	1.05	0.09

Table VIII—Reproducibility of Results by Different Operators

Reclaim	Operator	Alkalinity		
		Test 1	Test 2	Variation
NEW METHOD AND SAME SAMPLE				
		%	%	%
B	X	0.123	0.126	0.003
B	Y	0.130	0.126	0.004
C	X	0.487	0.484	0.014
	Y	0.488	0.474	0.014
	Z	0.488	0.488	...
G	X	0.406	0.400	0.006
	Z	0.420	0.412	0.008
OLD METHOD AND SAME SAMPLE TITRATED WITH METHYL RED				
		Test 1	Test 2	Test 3
		%	%	%
A	X	0.083	0.099	0.062
A	Z	0.110	0.158	0.163

The experimental work given below was carried out on reclaims which will be designated as follows:

A—a regular production whole tire reclaim
B—a specially washed whole tire reclaim
C—an experimental whole tire reclaim
D—an experimental whole tire reclaim
E—a carcass reclaim
F—a digester tube reclaim
G—a whole tire reclaim processed in another factory
H and I—tube reclaims processed in another factory

Table IX—Continuous Total Extractions

Time of Extraction	Alkalinity	
	Reclaim A	Reclaim B
	%	%
First 24 hours	0.375	0.089
Days		
6	0.716	0.345
11	0.837	0.508
16	0.899	0.608
21	0.953	0.684
26	0.999	0.750
31	1.018	0.783
36	1.030	0.814
41	1.038	0.837
46	1.045	0.860
51	1.048	0.865
55	1.048	0.865
Percentage extracted:		
Old method	0.150[a]	0.034[a]
New method	0.307[b]	0.126[a]
Percentage of total:		
Old method	14.31	3.93
New method	29.29	14.57

[a] Average of 2 tests.
[b] Average of 4 tests.

The tests given in Table VII show a comparison of the method of extraction previously used (*2*), except that the redigestion for 2 hours was not used, with the benzene-ethanol method described above. All titrations were made with the iodine-starch end point. This table shows the variation which occurs with the old method in comparison with the new method. It will be noted that the new method extracts two to five times as much alkaline material and consequently the percentage error in the new method is much less than in the old method, assuming equivalent actual error in the test. However, examination of the figures in Table VII will show a less actual error in the new method, and consequently a much higher accuracy. The average error shown by these figures is 15.62 per cent for the old method and 4.06 per cent for the new method. The results show also that the new method lines up different samples of the same reclaim better than the old method, which shows considerable variation between different samples.

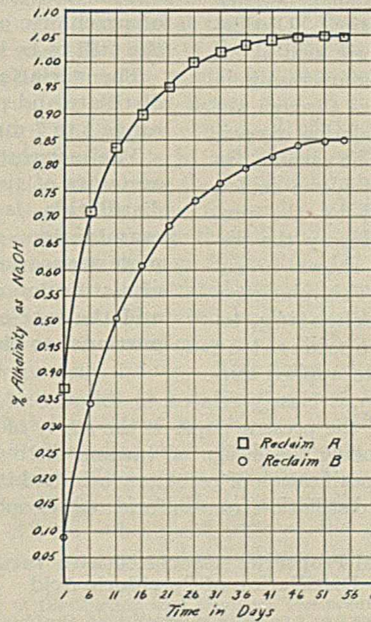

Figure 1—Complete Extractions of Reclaims A and B

Tests run on the same sample of reclaim by different operators show that this method is not subject to the personal error which is caused primarily by the squeezing. The old method, however, cannot be depended upon to give reproducible results by the same or different operators as Table VIII shows.

In order to compare the amount of alkaline material actually present with that extracted by the old and new method, a complete extraction was made on reclaims A and B. It was necessary to run this for 55 days until the percentage of alkaline material removed corresponded to the blank. Twenty-five-gram samples were digested in 800 cc. of boiling water continuously. At first the water was changed every 24 hours, while near the end of the experiment it was changed every 48 hours. Kilbourne and Miller (*1*) required about 60 days for determination of total alkalinity. Samples of the same reclaims were also run by the old and new method. The results, given in Table IX, show that the old method extracts 14.31 per cent and the new method 29.29 per cent in reclaim A, and in the case of reclaim B, 3.93 per cent of the total was extracted by the old method and 14.57 per cent by the new. While it is possible to achieve as high results as are given by the benzene-ethanol method by continued extraction in water for at least 24 hours and upwards to 48 hours, this length of time is hardly practicable. The benzene-ethanol method may be completed in approximately 5 hours.

Acknowledgment

The authors are indebted to O. C. Moyer for his helpful suggestions and analytical work.

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Purification of Perchloric Acid by Vacuum Distillation[1]

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Special designs of stills for the purification of perchloric acid by vacuum distillation are described including besides conventional designs a cold target type. Special features involved in the vacuum distillation of perchloric acid are shown to govern the design of the still to be used in its purification.

The variation in the acid concentration of both distillate and residue with change in pressure over the range 1 to 7 mm. is given.

The separation of perchloric acid from various amounts of sulfuric and phosphoric acids by vacuum distillation is subjected to a careful quantitative examination, and the conditions under which complete separations result are described. The time rate of distillation of various designs of stills is determined and the rate of distillation shown to be directly proportional to the degree of superheating employed.

The preparation of pure perchloric acid by all methods of manufacture requires that it be purified by distillation. Distillation of perchloric acid at atmospheric pressure results in too great a loss through the formation of chlorine, oxygen, and water. The vacuum distillation of perchloric acid is complicated by the pronounced tendency the distilling liquid shows to superheating. This phenomenon of superheating, together with consideration of the pressure applied during distillation, is closely related to the rate of distillation. The object of the present paper is the study of the various factors influencing the design of vacuum distillation equipment for the purification of perchloric acid and its use in the separation by distillation from sulfuric and phosphoric acids.

Special Properties Associated with Vacuum Distillation of Perchloric Acid

The vacuum distillation of concentrated perchloric acid of approximately the constant boiling composition (72.4 per cent at 760 mm.) up to the composition of the dihydrate (73.60 per cent) shows the following distinctive features: The distilling acid can be superheated to the extent of 30° to 60° C. depending upon the pressure and the rate of application of heat. A thermometer placed in the liquid being distilled and another placed at varying heights in the vapors over the liquid will show wide differences in temperature depending upon the amount of superheating and the difference in level of the thermometer bulbs within and above the distilling liquid. The acid, therefore, is not in simple equilibrium with the vapors formed. The complex nature of the mixture of different forms of perchloric acid in this vapor phase is the subject of a subsequent paper. By regulating the pressure between the limits 0.0 to 18.0 mm., the temperature of the distilling liquid can be varied between 50° and 120° C. The distillate under these conditions collects at the rate of 0.5 to 10 cc. per minute. No ebullition accompanies such distillations. Even with agitation of the strongly superheated distilling acid, no ebullition results.

If the perchloric acid being distilled under reduced pressure contains dissolved gases some preliminary ebullition results. There are two methods of eliminating these dissolved gases: Chill the strong (71 to 72 per cent) acid before distillation to a temperature of $-5°$ to $-10°$ C. or lower. This method has the additional advantage that solids in solution, such as sodium, potassium, or other perchlorates, are also removed. Or first concentrate the perchloric acid to be distilled at atmospheric pressure until a temperature of approximately 200° C. is attained and the acid concentration has reached 71.5 to 72 per cent using the same still for the concentration as that to be employed in the vacuum purification. The temperature of the concentrated acid is then allowed to fall to from 80° to 90° C. and the distillation continued at reduced pressure.

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[1] Received August 23, 1930. Presented before the Division of Physical and Inorganic Chemistry at the 80th Meeting of the American Chemical Society, Cincinnati, Ohio, September 8 to 12, 1930.

Control of Factors Leading to Rapid Distillation by Changes in Still Design

Several factors govern the design of a still for the purification of perchloric acid. The main ones are: First, the efficient condensation of the distilling vapors. This problem is made the more important by the fact that the vapors are at a temperature much higher than minimum distillation temperature because of the superheated condition of the distilling liquid. Second, the use of a target type of condenser can be predicted as most efficient in both condensation of the vapors emitted and in avoiding return flow of condensate. Third, the control of the degree of superheating by regulation of the pressure. This last factor is influenced in turn by the first two.

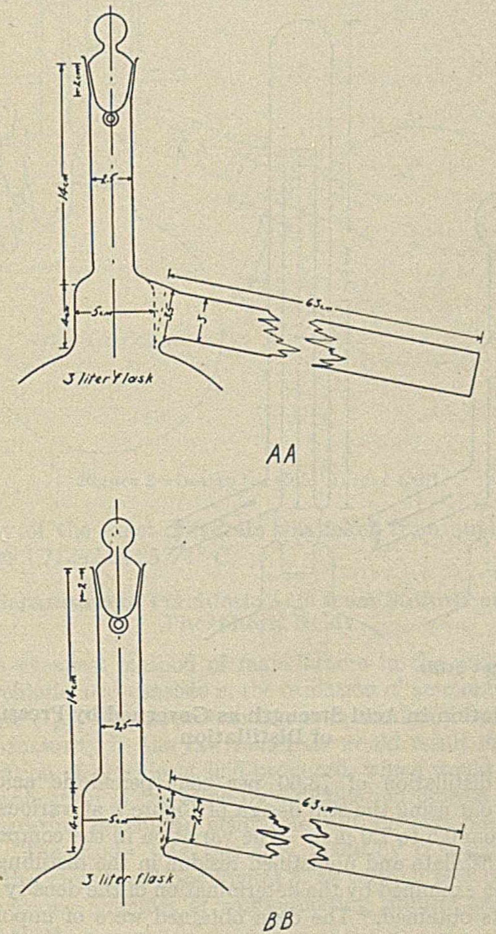

Figure 1—Stillheads of Conventional Design

Dimensions Applied to Stills of Conventional Design

Figure 1 shows two stillheads with dimensions included. The important dimensions are those of the inside diameter of the condenser tube and its length. As shown, the point of contact between the condensing side arm and the neck of the flask is placed as close to the balloon of the flask as indicated. This is possible because the liquid is distilling without ebullition and is advisable to prevent return flow of condensed acid vapors. A 5-liter flask has been used successfully in connection with this design of still. This design does not provide for recovery of the condensed acid forming on the inside of the neck above the side arm. The length of the condenser arm was found to be suited to the use of ordinary tap water for cooling.

As a result of the tests upon stills *AA* and *BB* given in Table I, it is observed that the latter gave both the best yield of finished product per unit of time and resulted in the greatest degree of superheating. A maximum application of heat which just failed to produce ebullition was employed.

Modification of Cold Target Design of Still

According to the explanation of the mechanism accounting for the phenomenon of superheating to be given in a later paper, the molecules of gaseous perchloric acid are projected through a probable film of oxonium perchlorate (OH_3ClO_4) upon the surface of the distilling liquid. In taking advantage of this phenomena and for the additional advantage of making the distillation apparatus more compact the cold target type of still illustrated in Figures 2 and 3 were designed and tested. These are of two types, those of *A* and *B*, Figure 2, which provide for the application of the pump connection at the end of a vertical condensing column and a refluxing of the condensed acid vapors to be drained out at the lower horizontal outlet shown. Neither type *A* nor *B* was found to be suited by comparison with the conventional form of still shown in Figure 1. This type of still has a further disadvantage that if operated at pressures greater than 7 mm. there is some probability that anhydrous perchloric acid may be formed in some quantity and fail to be condensed before passage through the pumping system. The stillheads *C* and *D*, Figure 2, and the design shown in Figure 3 were found more efficient in condensing the distilling vapors and in addition are more compact. The drawings of Figure 2 do not show the condenser chamber water-cooling jackets in place. The performance of these (Figure 2) stills, with the exception of type *A*, is shown in Table I.

The most satisfactory still design of all those studied is shown in Figure 3. This type differs from those of Figure 2 in that the double ring seal at the top of the distilling flask is eliminated and the length of the tubular from the top of the distilling flask into the condensing chamber is changed. It was observed in the cold target type of condenser that practically all of the vapors condensed at the upper end of the cooled target which is in accordance with the fundamental principles underlying the construction of such a still. The cooling surface is thus materially diminished. The ground stopper used to charge the still and support the thermometer (an Anschütz of range 50° to 105° C.) also provides for the use of a little concentrated perchloric acid to seal the stopper against leaks. The receiving flask is attached using a rubber stopper and the connection made to the vacuum pump using rubber pressure tubing. This form of still provided for the greatest degree of superheating and the best time rate of distillation, as shown in Table I. It is the most easily charged and recharged of those designs shown and is by far the most compact. It is more expensive than the conventional type of Figure 1, which is practically its only disadvantage. All the subsequent tests of the present paper were made using this type of distillation equipment.

Table I—Rate of Distillation and Working Temperature of Various Types of Perchloric Acid Vacuum Stills at 1 to 2 mm. Pressure

Type	Distillation Rate	Temperature Maximum	Temperature Average	Distillation Rate 50° C.
	Kg. per hour	° *C.*	° *C.*	*Kg. per hour*
AA	1.05	77	75	0.20
BB	1.14	89	85	0.18
B	0.90	86	84	0.10
C	1.04	90	88	0.10
D	0.93	91	85	0.10
Fig. 3	1.19	94	93	0.08

An examination of the data of Table I shows the superiority of the distillation apparatus designed according to Figure 3. The maximum rate of distillation is seen to accompany the greatest degree of superheating and the highest average temperature of distillation. The strength of the acid distilled in these tests was 71 to 72 per cent.

Further Considerations in Purification of Perchloric Acid

Crude perchloric acid made from technical grades of ammonium perchlorate after concentration to from 70 to 72 per cent strength at atmospheric pressure will have, after cooling and gravity separation of the solid perchlorate impurities (potassium, sodium and ferric perchlorates, and dehydrated silica), variable amounts of soluble impurities to be removed by vacuum distillation. The degree of dehydration of silicic acid and the extent to which soluble impurities are removed will depend upon the temperature applied during the concentration at atmospheric pressure and the temperature to which the acid is chilled prior to the separation of solid impurities.

Crude ammonium perchlorate is made by a large number of technical modifications of essentially the same process, and the degree of purity depends upon the particular process employed and upon the question of its purification by recrystallization. Varieties of crude ammonium perchlorate containing appreciable amounts of potassium perchlorate are particularly objectionable, but varieties having as high as 5 to 6 per cent of sodium perchlorate are profitably employed in the manufacture of perchloric acid. The natural tendency is to fail to concentrate the crude acid to a temperature of approximately 200° C. at atmospheric pressure in the preparation of 72 per cent acid for vacuum distillation. This is because appreciable decomposition of the hot acid results, a great portion of which decomposition takes place at 190° to 200° C. This decomposition can be almost completely eliminated by using large enough vessels in the concentration at ordinary pressures. Twenty-liter, round-bottom, Pyrex flasks serve well. Starting with such a flask of dilute (20 to 30 per cent) perchloric acid, at the point of concentration to 72 per cent acid the flask is approximately one-third full. Under these conditions the known tendency (*1*) of the concentrating acid to form lower hydrates which decompose, is offset by their reaction with the water vapor being expelled which counteracts their decomposition into chlorine and oxides of chlorine. Concentration to 72 per cent crude perchloric acid has the additional advantage that soluble impurities become less soluble to be removed later by chilling. In the distillation of even the crudest of perchloric acid, the process can be carried out until two-thirds of the starting material is distilled, and with more pure forms until 90 per cent of the starting product has distilled. This process of distillation which includes no ebullition makes it particularly suited to the freeing of perchloric acid from soluble solids because of the absence of spray from the distilling liquid.

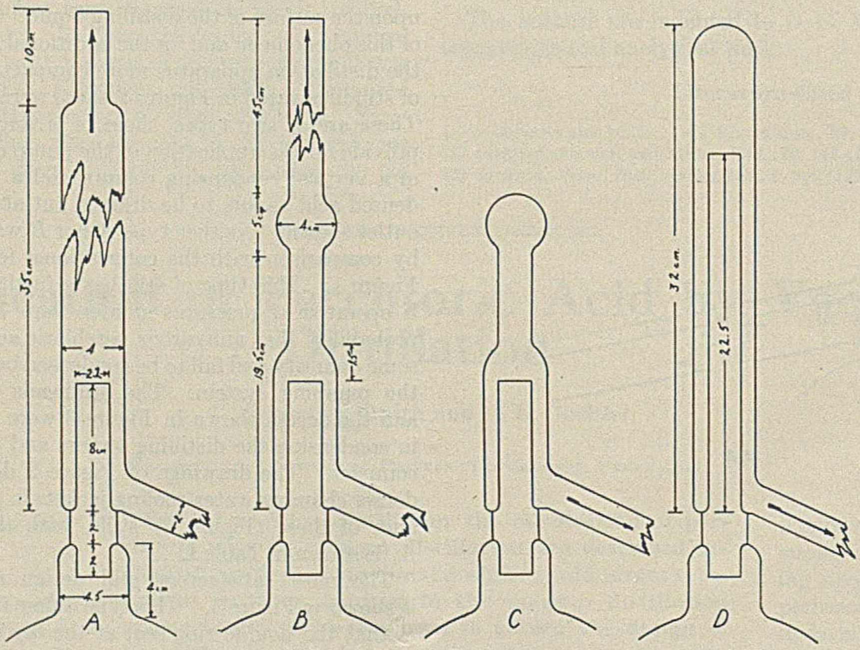

Figure 2—Types of Cold Target Stills

Variation in Acid Strength as Governed by Pressure of Distillation

The distillation of 73.60 per cent perchloric acid was carried out using the still design of Figure 3 at various pressures from 0.5 to 7.0 mm. The variation in the composition of the distillate and undistilled residue in the distilling flask was then examined by the determination of the density of the products obtained. The data obtained were of importance because of their bearing upon a process for the preparation of perchloric acid dihydrate by vacuum distillation. The method of determining the density of the various acids thus obtained will be given in a subsequent paper. The results of these determinations are given in Table II.

Table II—Variation in Acid Concentration Resulting from Distillation of 73.60 Per Cent Perchloric Acid at Pressures between 0.5 and 7 mm.

PRESSURE	DISTILLATE DENSITY 25°/4° C.	RESIDUE DENSITY 25°/4° C.	DIFFERENCE DENSITY	ACID IN RESIDUE-DISTILLATE
Mm.				%
0.5–1	1.71600	1.71621	0.00021	+0.15
2.0–2.5	1.71545	1.71520	0.00025	+0.18
4.0–4.5	1.71383	1.71416	0.00033	+0.23
6.5–7	1.71211	1.71190	0.00021	−0.15

An examination of this table shows that the maximum difference obtained in acid composition between distillate and residue between the range 0.5 to 7 mm. is 0.30 per cent. Thus by plotting the values obtained from the density of the acid of the distillate at various pressures of distillation as a function of the acid composition, it is observed that the pressure producing acid of the exact dihydrate composition is 5.7 mm. The plot of the data is shown in Figure 4. The

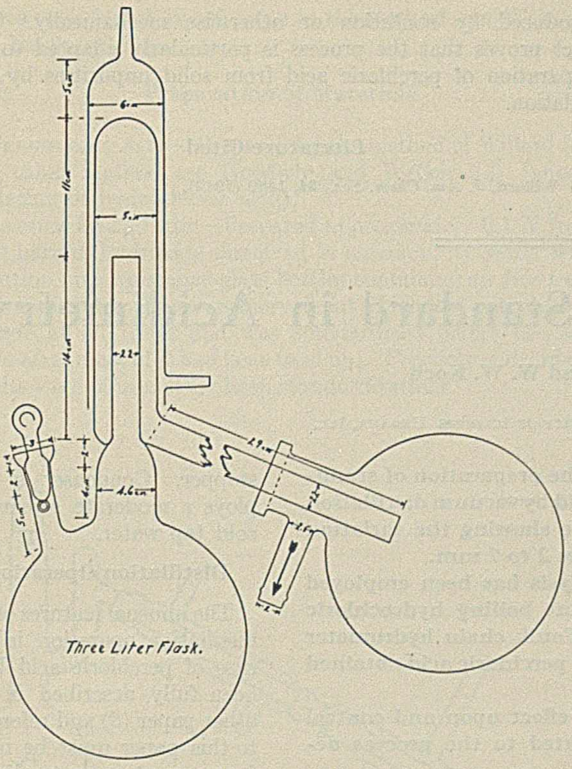

Figure 3—Design for Cold Target Still

density of the exact dihydrate was taken from unpublished data as 1.71282 at 25°/4° C.

Separation of Perchloric Acid from Sulfuric and Phosphoric Acids

The cheapest method of manufacture in the preparation of perchloric acid consists in the oxidation of ammonium perchlorate (*1*). By this process any ammonium sulfate or phosphate impurity in the raw materials would result in a contamination of perchloric acid produced, which would require the purification of the same by a distillation process capable of separating perchloric acid from sulfuric and phosphoric acids. The study was therefore made by this separation using the vacuum still of Figure 3, at varying pressures and with varying amounts of contaminating sulfuric and phosphoric acids.

The process in the case of both sulfuric and phosphoric acid was as follows: 71 to 72 per cent perchloric acid was adulterated with known quantities of sulfuric and phosphoric acids in separate determinations starting with 2 per cent by weight of the particular acid as impurity. The distillation was then carried out until a given portion of distillate was collected at a given pressure of distillation and the distillate set aside for further examination. The residue in the still, assuming the amount of contaminating acid carried over in the first operation was small, has a new ratio of contaminating acid which can be tested for complete separation by a further distillation. The second distillate is then set aside for analysis and the process continued. The extent of the contamination of the acid being distilled may then be taken as the mean of the starting and finishing concentrations.

The extent of the contamination of the distillate of perchloric acid by the sulfuric or phosphoric acid was determined in each case by its second distillation under the same conditions with an analysis of the total residue in the still for the contamination involved. The accuracy of this process depends upon the practically complete separation of the contaminant in one operation.

It would be predicted from a general knowledge of the variation in vapor pressure with the temperature that the separation of perchloric acid from both sulfuric acid and phosphoric acid would be more complete the lower the pressure of distillation. It would also be predicted that the sulfuric acid contamination would be the most difficult to remove. In the case of the mixed solutions of sulfuric and phosphoric acids with perchloric acid studied, the contamination was purposely made far more extensive than would ever be the case in the use of any serviceable stock of ammonium perchlorate for the manufacture of perchloric acid. The data resulting from the study of this purification are given in Table III.

Table III—Separation of Perchloric Acid from Sulfuric and Phosphoric Acids at Several Temperatures and Pressures

Perchloric acid used, 71–72%; volumes distilled, 500 to 3000 grams, per cent acid distilled, 50%

CONTAMINATING ACID		TEMPERATURE	PRESSURE
At start	In distillate		
%	*Gram*	*° C.*	*Mm.*
	Sulfuric acid		
0.2	0.0000	65–80	1
2–4	0.0039	105	10
4–5.73	0.0042	105	10
2–4.1	0.0013	75–85	1
4.1–6.2	0.0024	75–85	1
6.2–10.4	0.009	75–85	1
	Phosphoric acid		
3.5–12.8	None	75–85	1
12.8–19.9	None	75–85	1
19.9–36	Trace	75–85	1

The following conclusions can be drawn from the experiments listed in Table III.

For the separation of perchloric acid from sulfuric acid, if the contamination of the distillate is to be restricted to 0.001 per cent, the original impurity of sulfuric acid must not exceed 4 per cent and the pressure and temperature of the distillation must be as low as possible. The possible contamination is slowly increased by allowing the pressure to increase together with the temperature. The amount of sulfuric acid is not more than 0.004 per cent up to a concentration of 6 per cent of sulfuric acid in the product purified even under the most unfavorable conditions of temperature and pressure. The amount of sulfate in crude ammonium perchlorate is never great enough to require that the perchloric acid made from it be twice distilled *in vacuo* in order to completely free it from sulfuric acid.

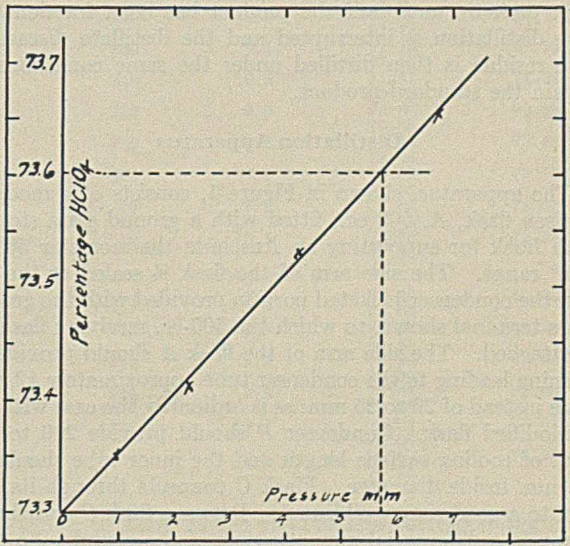

Figure 4—Plot of Data Used to Determine Exact Dihydrate Composition of Perchloric Acid

The separation of perchloric acid from phosphoric acid is not a problem even up to a contamination of 36 per cent if the temperature and pressure of the distillation is low, and probably the separation is equally good under the most unfavorable conditions. The data obtained in connection with the separation of perchloric acid from phosphoric acid prove that no contamination of the distillate resulted from spray produced by ebullition or otherwise mechanically. This fact proves that the process is particularly adapted to the separation of perchloric acid from solid impurities by distillation.

Literature Cited

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Perchloric Acid as a New Standard in Acidimetry[1]

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A still design to be used in the preparation of standard 73.60 per cent perchloric acid by vacuum distillation is described and a study made showing the variation in product within the pressures 2 to 7 mm.

An indirect method of analysis has been employed combining the use of constant boiling hydrochloric acid and a precision type of Foulk chain hydrometer in the analysis of 73.60 per cent perchloric acid obtained by this process.

Explanation is made of the effect upon and control of variables known to be related to the process described.

THE object of this paper is the description of a process for the preparation by vacuum distillation of perchloric acid to be used as a standard in acidimetry. The product obtained corresponds most closely to the dihydrate ($HClO_4 \cdot 2H_2O$, theory 73.603 per cent $HClO_4$). Within the limits of the pressure range used in this process, 2 to 7 mm. of mercury, the product obtained agrees with the composition of the true dihydrate as well as the analysis of the product can be determined, 73.60 ± 0.03 per cent, or an accuracy of one part in approximately 2500. It will be shown that the conditions of preparation are conveniently attained and easily duplicated.

Briefly the process is as follows: Perchloric acid of 72 per cent strength is distilled in a properly designed still at 2 to 7 mm. pressure until half the product has been fractionated. The distillation is interrupted and the distillate discarded. The residue is then distilled under the same conditions to obtain the standard product.

Distillation Apparatus

The apparatus, shown in Figure 1, consists of a modified Claisen flask, *A*, 500 cc., fitted with a ground glass stopper with hook for supporting an Anschütz thermometer 50° to 100° range. The side arm of the flask is sealed at the top and the condenser jacketed portion provided with the ground glass terminal shown, to which the 500-cc. receiving flask, *C*, is attached. The side arm of the flask *A* should provide an opening leading to the condenser tube approximately 12 mm. wide instead of 20 to 25 mm. as is ordinarily the case with the unmodified flask. Condenser *B* should provide 200 to 225 mm. of cooling surface length and the inner tube should be 10 mm. inside diameter. Flask *C* connects through its side arm to a good rotary oil pump. Between flask *C* and the oil pump is a differential mercury gage of the closed tube type reading pressures over a range of 0 to 20 mm. and should be accurate to ±0.5 mm. Between flask *C* and the oil pump is placed a soda-lime tube 25 to 35 mm. in diameter by 200 mm. long provided at each end with a 13 to 15 mm. adaptor. An air release inlet tube should be placed between the flask *C* and the soda-lime tube. Rubber tubing is used to make connections on the pump side of flask *C*. The ground glass union in the neck of flask *C* may be replaced by a rubber stopper. Condenser *B* employs a moderate stream of cold tap water.

Distillation Operation

The unusual features of the distillation operation in the case of perchloric acid have been fully described in another paper (*3*) and reference to this paper must be made for a correct understanding of this operation. The vacuum distillation of perchloric acid is not a hazardous operation. All pure perchloric acid of commerce is prepared by vacuum distillation. It is well to conduct the operation out of possible contact with wood or other inflammable material as fire may result in case of breakage. The distillation of perchloric acid under atmospheric pressure is accompanied by some decomposition to form chlorine, oxygen, and water. Such decomposition does not occur in the process described.

Table I—Boiling Point and Density of Various Perchloric Acid Solutions

$HClO_4$	B. P. 760 mm.	Density		$HClO_4$ Distillate
		15°/4° C.	25°/4° C.	
% by wt.	*° C.*			*% by wt.*
56.65	148.0	1.49	1.48	...
61.2	162.3	1.55	1.54	0.9
65.2	181.2	1.61	1.60	6.06
70.06	198.7	1.67	1.66	40.11
71.0	200.8	1.69	1.67	...
72.4	203.0	1.71	1.69	72.4

Selection of Perchloric Acid Used as Starting Material

Perchloric acid is usually purchased in the form of a 60 per cent solution. A solution of 72 per cent acid is more satisfactory and can now be obtained from the better supply houses. It may be made conveniently following the Willard (*8*) method of the oxidation of pure ammonium perchlorate with nitric and hydrochloric acid. Pure acid is preferred but relatively impure or "commercial" acid may be purchased and purified by distillation under reduced pressure. The distillation of constant boiling perchloric acid (the 72.4 per cent acid of Table I) may be carried out at atmospheric pressure but the loss by decomposition is appreciable. Acid less concentrated than 72 per cent may be converted to the constant boiling strength by boiling at 760 mm. until the temperature reaches 203° C. Decomposition begins at 60 per cent acidity and increases in amount as the reaction temperature increases. Two methods serve for its rough analysis, the determination of its density or its boiling point. Values for use in this connection are given in Table I. These

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[1] Received August 23, 1930.

values were found by reference to the work of van Wyk and van Emster (*9*,*1*).

Preparation of Materials

Perchloric Acid—Prepared by the method of Willard (*8*). For other method see Goodwin and Walker (*4*) (anodic oxidation of hydrochloric acid).

Barium Hydroxide—Prepared approximately 0.1 *N* from pure barium hydroxide dissolved in conductivity water with filtration into resistance glass bottles containing air free from carbon dioxide. It was preserved out of contact with carbon dioxide at all times and was standardized before use and again after most of it had been used up. Precisely concordant results were obtained for both standardizations.

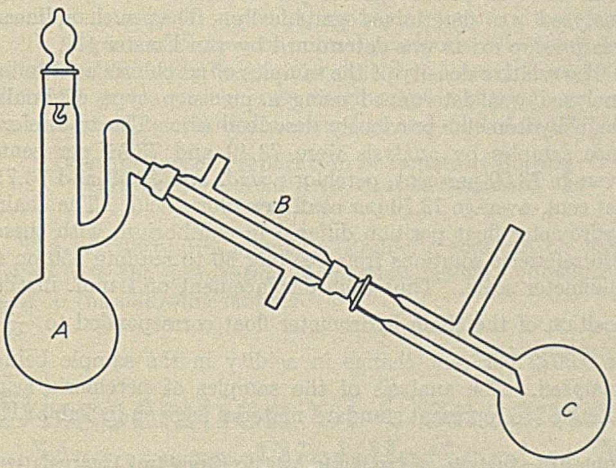

Figure 1—Distilling Apparatus

Standard Acid—Constant boiling hydrochloric acid was prepared following in every detail the directions of Foulk and Hollingsworth (*2*).

Indicator—The sodium salt of dibromothymolsulfonphthalein (bromothymol blue) was prepared as described by Lubs and Clark (*6*). The color change from yellow at a pH of 6.0 to blue at pH of 7.6 with green at the transition point, serves both in natural and in artificial light. Correction was made for the small amount of standard solution necessary for the end point color change.

Water—Conductivity water was used throughout.

Method of Analysis

Sampling—Both the constant boiling hydrochloric acid and the samples of perchloric acid were weighed in small 2-cc. glass bulbs having finely drawn capillary openings (miniature Dumas vapor density bulbs). These were filled by bending the capillary openings into a V shape, placing the open end within the sample to be taken contained in a small test tube, and warming the bulb to displace the air within by the acid of the sample. The sampling ampules were then cooled to room temperature and the capillary opening sealed by fusion with a fine blast flame. The difference between the weight of the sample tube and contents and the empty sampling tube, corrected for the weight of the fine capillary tube sealed off, gave the weight of the contents. The weight of the sample was not corrected for the weight of air over the sample which was somewhat different before and after sealing because of temperature effects. This correction was in all cases negligible for the reason that the sample tubes were nearly full in each case.

Weighing—All weighings were made using a Troemner balance accurate to ±0.02 mg. The weights used were calibrated by the Bureau of Standards and buoyancy corrections were applied.

Preparation and Titration of Samples—The filled sampling ampules, together with the capillary tube from the same, were added to a titration beaker. The sampling bulb and the capillary tube were broken and crushed under 100 to 150 cc. of water and a measured portion of the indicator solution added. The acid was then titrated with the standard barium hydroxide solution using weight burets (*7*). The weight of acid taken corresponded to from 100 to 200 grams of titrating solution. Both the standardization of the barium hydroxide solution against constant boiling hydrochloric acid and the titration of the unknown perchloric acid samples were carried out in exactly the same way.

Yield of Perchloric Acid as Function of Strength of Starting Material

In order to obtain data concerning the rate of concentration resulting from the vacuum distillation of various strengths of starting material, a fractional distillation of three different starting concentrations was made. The data are recorded in Table II.

Table II—Fractional Distillation of Perchloric Acid

1-5 to 7.5 mm. pressure; 2000 cc. still

Fraction	Weight *Grams*	Fraction Distilled *% by vol.*	$HClO_4$ %	Av. $HClO_4$ %
		70 PER CENT ACID		
1	190	9.0	51.03 51.07	51.05
2	290	12.0	66.72 66.75	66.74
3	300	11.0	72.49 72.52	72.51
4	230	9.0	73.03 73.08	73.06
5	220	8.6	73.02 72.98	73.00
6	225	8.8	73.31 73.35	73.33
7	113	4.4	73.09 73.09	73.09
Residue	932	36.5	73.65 73.65	73.65
		71 PER CENT ACID		
1	190	7.8	61.09 61.13	61.11
2	230	9.1	67.15 67.16	67.16
3	240	9.3	71.31 71.30	71.31
4	260	9.9	72.90 72.86	72.88
5	250	9.5	73.45 73.45	73.45
6	260	9.8	73.52 73.54	73.53
7	99	3.5	72.64 72.63	72.63
Residue	1070	40.5	73.55 73.55	73.55
		72 PER CENT ACID		
1	191	7.9	60.02 60.03	60.02
2	253	9.8	69.24 69.21	69.23
3	254	9.5	72.00 72.00	72.00
4	254	9.5	73.08 73.05	73.06
5	294	10.9	73.02 73.00	73.01
Residue	1417	52.5	73.59 73.54	73.57

As shown in Table II the yield of acid corresponding most closely to the dihydrate ($HClO_4 \cdot 2H_2O$) from 70, 71, and 72 per cent perchloric acid as starting material is 36.5, 40.5, and 52.5 per cent by volume, respectively. It is therefore advantageous to start with the 72 per cent acid in order to arrive at the best yield of the finished product. Concentration takes place rapidly in all cases up to the 73 per cent range after approximately 35 per cent by volume has been distilled. Less rapid concentration results after 73 per cent acid concentration is reached, but the yield from all three starting strengths is excellent for this type of preparation.

Factors Influencing Selection of 2 to 7 mm. as Pressure Range of Distillation Yielding Standard 73.60 Per Cent Perchloric Acid

The complex nature of the various possible dissociations of perchloric acid to form the different known hydrates during vacuum distillation over the pressure range 0 to 18 mm. has been fully discussed in another paper (*3*). From this work, which should be consulted for a proper understanding of the reactions involved, it is apparent that above 7 mm. pressure the distillate starting with 73.6 per cent acid strength contains the following hydrates of perchloric acid: $HClO_4.3H_2O$, $HClO_4.2H_2O$, and $HClO_4$ (anhydrous). Depending upon the ratio of the various hydrates formed, which in turn depends upon the pressure of distillation, it would be predicted that a distillate of varying composition would be obtained. The distillate obtained at 7 mm. pressure and below most nearly corresponds to 73.60 per cent perchloric acid (*3*).

Below 7 mm. pressure any variation in the acid concentration as a result of the formation of other hydrates than the dihydrate ($HClO_4.2H_2O$) is corrected for in the use of the still described in Figure 1. The side arm of the Claisen flask *A* provides a reflux chamber in which the other two forms $HClO_4.3H_2O$ and $HClO_4$ (anhydrous) are caused to combine and reflux into the distillation chamber. Variations in pressure below 7 mm. result in the formation of a distillate of such uniform composition, therefore, using the apparatus described, that the process conforms practically to the requirements leading to a method for the preparation of a new standard for acidimetry.

Determination of Lower Limit of Pressure Permissible in Process Employed

If the upper limit of pressure as indicated (*3*) is 7 mm. for all practical purposes, there remained the determination of the lower limit below which the distillation could not be carried out without appreciably affecting the acid concentration of the distillate. This was determined using the apparatus of Figure 1 with the 73.60 per cent perchloric acid and gradually decreasing pressures starting with 7 mm. The lower limit found by the analysis of the distillate at various pressures below 7 mm. was 2 mm. This is not a serious handicap since without the use of special equipment a pressure less than 2 mm. is hard to attain with the apparatus described. Furthermore the magnitude of the possible error is small as shown in the following manner:

The 73.6 per cent perchloric acid was distilled in an apparatus similar to that of Figure 1 except that all ground joints were eliminated by glass seals and a mercury vapor pump and liquid air trap used to increase the vacuum produced by the oil pump. Distillations were carried out using a pressure range of 0.02 to 0.1 mm. as determined using a McLeod gage.

Three hundred and twenty-three grams of acid were distilled and 150 grams of distillate obtained. A second portion of 360 grams of acid was distilled and 130 grams of distillate obtained. The two residues were then combined and 200 grams from these distilled. A distillate of 115 grams was thus obtained and the residue of 85 grams analyzed. It was found to be 73.8 per cent perchloric acid. The analyses of the preliminary residues showed that most of the concentration that has resulted took place in the early stages. The analyses of the distillates showed them to be correspondingly weak in acidity, 73.27 per cent. The temperature during these distillations varied between 60° and 70° C. There is, therefore, little danger of error due to distilling at too low pressure.

Preparation and Analysis of Constant Strength Perchloric Acid for Use as New Standard of Acidimetry

To test the application of the apparatus described and the pressure range determined, a series of acid samples were prepared in the apparatus described using approximately 72 per cent perchloric acid as starting material and various pressures between 2.2 and 7.0 mm. Most of these preparations were carried out at 3.5 to 5.0 mm. pressure since this range represents the mean between the two extreme pressures permissible; 300 to 400 cc. of 72 per cent perchloric acid were distilled and the samples taken from the second fraction after the original material had been half distilled.

The samples of standard perchloric acid were analyzed by an indirect method depending upon the determination of their relative density. Two reference samples, one greater and one lower in density, were then carefully analyzed as previously described. Assuming a linear relationship to exist between the density and percentage composition of samples intermediate in density between the two reference solutions, the percentage composition of the sample being analyzed was determined graphically. That such a linear relationship exists was determined by van Emster (*1*).

The relative density of the samples of perchloric acid to be analyzed was determined using a precision type of Foulk chain hydrometer previously described (*5*). The two reference samples by analysis were 73.49 and 73.51 per cent, average 73.50 per cent, perchloric acid, and 73.69 and 73.71 per cent, average 73.70 per cent, perchloric acid. The chain hydrometer float position differed in equilibrium with these two reference solutions from reading 60 to reading 150 on a millimeter scale. Thus each displacement of 1 mm. in the position of the chain hydrometer float corresponded to $\frac{0.20}{90}$ or 0.0022 per cent change in acidity in the sample being analyzed. The analysis of the samples of perchloric acid intended to represent standard material is given in Table III.

Table III—Analysis of Perchloric Acid by Graphical Interpolation of Relative Densities

Sample	Preparation Pressure *Mm. Hg*	Hydrometer Reading *Mm.*	Calcd. $HClO_4$ %
Ref. No. 1			73.50 (by analysis)
Ref. No. 2			73.70 (by analysis)
1	3.5-5.0	97	73.58
2	3.5-5.0	102	73.59
3	3.5-5.0	120	73.63
4	3.5-5.0	99	73.58
5	2.2	91	73.57
6	6.5-7.0	100	73.59
		Mean	73.59

By reference to this table it will be seen that if the pressure range 3.5 to 5.0 mm. is maintained, the average strength of the perchloric acid, obtained by distillation of approximately 72 per cent perchloric acid in the apparatus described, results in the preparation of perchloric acid of composition 73.60 per cent. This value is obtained if the distillate from the last 50 per cent of the distillation is taken. At pressures between 2 mm. and 7 mm. the variations in percentage composition of the perchloric acid obtained is inappreciable. It is at once apparent that slight variations in the pressure during distillation or slight inaccuracies in the reading of the pressure-recording device are of no appreciable influence upon the composition of the final product.

Specific Gravity of 73.60 Per Cent Perchloric Acid

Relative density measurements only were required for the purpose of this investigation. The determination of the specific gravity of 73.60 per cent perchloric acid gives 1.71282 at 25°/4° C. The ideal pressure for the distillation of 73.60 per cent perchloric acid has been shown to be 5.7 mm. (*3*).

Summary of Directions for Preparation of 73.60 Per Cent Perchloric Acid

Pure 72 per cent perchloric acid is distilled under a vacuum of 2 to 7 mm. in an apparatus described in Figure 1. When one-half of the product has been distilled the process is discontinued and the distillate set aside. A clean dry receiver is then used to collect the second fraction distilled under the same conditions. The pressure may vary between the limits given. A pressure of 5 to 6 mm. is best and most easily obtained. The rate of distillation is of no consequence and the temperature varies between 60° and 95° C. depending upon the rate of application of heat. The product obtained by this process varies ± 0.03 per cent in acid content and ± 0.0004 in specific gravity.

If the starting material is 71 per cent perchloric acid the conditions are the same except that 60 per cent is distilled and discarded. Starting with 70 per cent perchloric acid 65 per cent of the distillate is discarded.

Perchloric acid of this standard strength is slightly hygroscopic and fumes very faintly. It should be weighed with the usual precautions to prevent absorbing atmospheric moisture.

To prepare a solution of normal perchloric acid using the product obtained in the manner described a sample weighing 136.4201 grams (using brass weights and assuming average humidity and temperature) is weighed and diluted to 1000 cc.

Comparison of Preparation of Constant Boiling Hydrochloric Acid with That of Standard Perchloric Acid

The preparation of standard perchloric acid can be compared with the preparation of constant boiling hydrochloric acid in the following manner:

The pressure of distillation must be known in the case of hydrochloric acid and the use of a barometer is required. With perchloric acid the pressure may vary over the range 2 to 7 mm. and a very simple pressure-recording device may be used and the barometer eliminated. The preparation of constant boiling hydrochloric acid must be carefully controlled as regards the rate of distillation and prevention of bumping. The perchloric acid process does not vary with the rate of distillation which may be twice as great as in the former process, and the distillation is free from ebullition.

One cubic centimeter of 73.60 per cent perchloric acid (sp. gr. 1.71) equals 2 cc. of constant boiling hydrochloric acid in equivalents of acid contained. Since perchloric acid can be distilled by the process just described at twice as great a rate, and since 50 per cent of the starting product is obtained in comparison with 25 per cent for the hydrochloric acid, the yield of perchloric acid obtained in a given time as compared to hydrochloric acid may be as much as eight times as large.

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Dissociation of Concentrated Perchloric Acid during Vacuum Distillation at Moderately Low Pressures[1]

New Method for the Preparation of Anhydrous Perchloric Acid

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A study of the vacuum distillation of 73.3 to 73.6 per cent perchloric acid has been made over the pressure range 7 to 18 mm. and an apparatus described for the preparation of anhydrous perchloric acid in yields of 7 to 10 per cent of the weight of the starting product.

The anhydrous perchloric acid formed is shown to be more stable than that prepared by use of previously known processes.

The mechanism of the distillation described is explained, and this explanation found to be dependent upon the implied existence of a surface film of oxonium perchlorate (OH_3ClO_4).

THE following description has for its object the study of the nature of the process and products formed during the vacuum distillation of concentrated perchloric acid in the pressure range 8 to 18 mm. Perchloric acid of approximately the composition of the dihydrate ($HClO_4.2H_2O$, 73.6 per cent acidity) will be shown under the conditions named to undergo a set of dissociations formerly little known. An attempt to explain the mechanism of these dissociations will be made and the design of a special still particularly well adapted to such a study will be described. Under suitable conditions this process serves as a new method for the formation of anhydrous perchloric acid in somewhat small but satisfactory yields. The dissociation reactions involved are represented as follows:

$$4HClO_4{\cdot}2H_2O \longrightarrow 2HClO_4{\cdot}3H_2O + 2OH_3ClO_4 \quad (1)$$

$$2OH_3ClO_4 \longrightarrow HClO_4{\cdot}2H_2O + HClO_4\ (\text{anhyd.}) \quad (2)$$

The procedure employed constitutes the only distillation method known requiring no desiccating agent to accomplish this dehydration. A further distinctive feature consists in the minimum of hazard involved in the preparation of explosive anhydrous perchloric acid.

Historical Data

The first important study of anhydrous perchloric acid and its monohydrate was made by Roscoe (*2*). The existence of a constant boiling mixture with water (72.4 per cent at 760 mm., b. p. 203° C.) was shown. The anhydrous acid was prepared by the reaction between potassium perchlorate and 95 per cent sulfuric acid and by the distillation of constant boiling perchloric acid with 95 per cent sulfuric acid at 110° C. Perchloric acid monohydrate was prepared by dilution of the anhydrous acid with water or strong perchloric acid. This crystalline perchloric acid monohydrate at 100° C. gives a distillate of anhydrous acid and a residue corresponding to the composition of the dihydrate.

A more comprehensive research on the identification cryoscopically of the various hydrates of perchloric acid was made by van Wyk (*5*). The following hydrates were studied:

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[1] Received August 23, 1930. Presented before the Division of Physical and Inorganic Chemistry at the 79th Meeting of the American Chemical Society, Atlanta, Ga., April 7 to 11, 1930. A portion of a thesis presented by O. E. Goehler in partial fulfilment of the requirements for the degree of doctor of philosophy in the Graduate School of the University of Illinois.

Hydrate	Melting Point ° C.
$HClO_4$ (anhy.)	−112
$HClO_4 \cdot H_2O$	+ 50
$HClO_4 \cdot 2H_2O$	− 17.8
$2HClO_4 \cdot 5H_2O$	− 29.8
$HClO_4 \cdot 3H_2O$:	
Alpha	− 37
Beta	− 43.2
$2HClO_4 \cdot 7H_2O$	− 41.4

In the present discussion, for the sake of simplicity, any hydrate higher than the dihydrate will be designated as the trihydrate.

Special Properties Associated with Vacuum Distillation of Perchloric Acid

The vacuum distillation of concentrated (71 per cent) perchloric acid or of the approximate constant boiling composition (72.4 per cent at 760 mm.) up to the composition of the dihydrate (73.6 per cent) shows the distinctive features described in another paper (*3*). For a correct understanding of the present paper the former should be consulted. Under the conditions of vacuum distillation described below, the perchloric acid being distilled is not in simple equilibrium with the vapors formed. An attempt to explain the pronounced tendency of distilling perchloric to superheat is a secondary objective of the present work.

Preparation of Materials and Apparatus Design

Perchloric acid, 70 to 72 per cent, was purchased from the usual sources. The approximate dihydrate of perchloric acid (composition 73.6 per cent) was prepared by vacuum distillation of the former product discarding all but the last 35 per cent of the distillate.

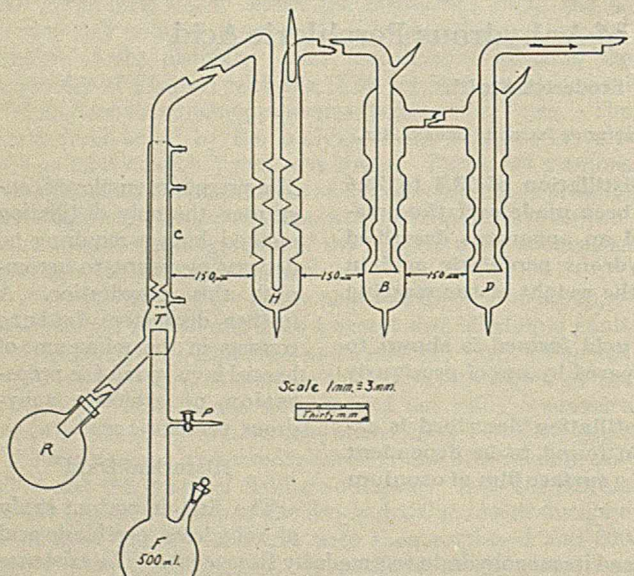

Figure 1—Distillation Apparatus

The distillation apparatus is shown in Figure 1 drawn to scale, and in Figure 2 set up ready for use. Distilling flask *F* is provided with receiver flask *R*, reflux condenser *C*, and reflux trap *T*, to by-pass condensate from *C* into *R*. A train of three joining liquid air traps (shown without Dewar flasks adjusted) are designated *H*, *B*, and *D*. Each liquid air trap is provided with sealed off intake and efflux tubes to provide for recovery of the products obtained. Liquid air trap *D* connects directly to a good rotary oil pump of generous capacity (a megavac pump) by means of rubber pressure tubing. A closed tube differential mercury manometer (not shown) is inserted in this portion of the line. This manometer had been previously checked for accuracy against a McLeod gage. Adjustments in the pressure of the distillation are made by opening stopcock *P* connected with a high-grade drying agent (anhydrone—granular anhydrous magnesium perchlorate). Thermometers for determining the temperature of the distilling liquid and vapors are supported by the stopper of flask *F* which is of the liquid seal type, moist with perchloric acid. Flask *R* is attached using a one hole rubber stopper. Flask *F* is heated by the use of a burner. Condenser *C* is cooled using tap water. No capillary air inlet to *F* is needed.

Distillation Operation

Flask *F* is charged with 250 to 350 grams of 73.4 to 73.6 per cent perchloric acid and the system evacuated to 2 to 5 mm. pressure. A 3 to 4 inch (7.6 to 10.2 cm.) flame from a Bunsen burner is then applied and at 75° to 85° C., depending upon the pressure, vapors of the dihydrate pass into condenser *C*, condense and reflux into *R*. When 15 to 20 cc. of distillate have been collected the operation is discontinued and the flask *R* emptied, dried, and replaced. The purpose of this preliminary operation is to prepare the distilling liquid for the treatment at the higher pressures and consequent greater degree of superheating. During the preliminary distillation, unless the acid is previously chilled, a slight degree of ebullition will result until dissolved gases are expelled. In this case some monohydrate may form in the vessels of the condenser. Some few trial runs are advisable to familiarize one with these operations.

The distillation is now carried out at pressures varying from 8 to 18 mm. within a 1-mm. maximum variation for any individual run. The pressure adjustment is easily made through use of a stopcock *P* if the oil pump has sufficient capacity. The traps *H*, *B*, and *D* are immersed in liquid air and the cooling water in *C* adjusted in rate of flow sufficient to cause a slight deposition of crystals of monohydrate (OH_3ClO_4) at its extreme upper end. These crystals must be maintained in the condenser during the whole distillation process. Perchloric acid dihydrate and trihydrate condense in *C* and reflux into *R* at the rate of 2 to 4 cc. per minute depending upon the degree of superheating. Anhydrous perchloric acid collects in the trap *H* (with a small amount of monohydrate), in trap *B*, and a few cubic centimeters in trap *D*. The yield of anhydrous perchloric acid is highest in the case of the greatest degree of superheating obtained at the higher pressure of distillation. A favored working range is between 12 and 15 mm.

The sampling and analyses necessary for following the various dissociations obtained are accomplished as follows: The distillation is discontinued and the pressure increased to atmospheric. The Dewar flasks containing the liquid air for traps *H*, *B*, and *D* (Figure 1) are removed and the frozen contents on the side walls allowed to melt and run to the bottom of the trap. The frost is then removed from the outside of the traps and the liquid air replaced over the level of the melted acid in the bottom of the trap until it is again frozen. The drawn-out extensions of the traps *H*, *B*, and *D* are then file-marked and broken open before the acid is melted within, and a tube containing a weighed portion of previously analyzed perchloric acid of 72 to 73 per cent acidity is placed in a position to mix with the anhydrous perchloric acid which quickly melts and runs into the absorbing acid.

By previously analyzing and weighing the absorbing acid followed by analysis of the solution obtained from the addition of the known weight of anhydrous acid, the strength of the absorbed acid can be calculated. The absorbing acid

Table I—Distillation of Perchloric Acid Dihydrate at 7 to 18 mm. Pressure in Preparation of Anhydrous Perchloric Acid

PRESSURE	CONCN. OF ACIDS IN FLASKS			TEMPERATURE OF DISTILLATION	AMOUNT DISTILLED	TOTAL DISTILLED	ANHYDROUS ACID	YIELD $HClO_4$ (ANHYDROUS)	
	Start, *F*	*R*	Residue, *F*						
Mm.	%	%	%	° *C.*	*Grams*	*Grams*	*Grams*	%	%
16–17	73.4	72.26	73.05	110–117	474.0	276.0	16.4	98	8.7
17.5–18	73.30	71.32	73.05	109–120	285.1	267.9	19.3	97	10.6
17–17.5	73.45	71.86	73.01	108–119	302.0	216.9	13.7	99	9.3
7–7.5	73.35	72.83	73.30	95–102	251.7	203.1	2.9	100	1.9
9–9.5	73.45	72.53	73.40	100–110	204.9	155.4	6.2	97	5.5

should be in sufficient quantity of such strength that the resulting acid concentration of the mixture shall not be greater than 77 or 78 per cent for the reason that above this strength the crystals of monohydrated perchloric acid are not soluble at room temperature. The sampling of the residue in flask *F* and receiver *R* is obviously easily accomplished. That the anhydrous acid obtained was not chlorine heptoxide (*1*), which would not be apparent by the method of analysis described, was proved by its greater chemical activity, freezing point, and other physical properties. Two representative preparations of anhydrous perchloric acid are recorded in Table I.

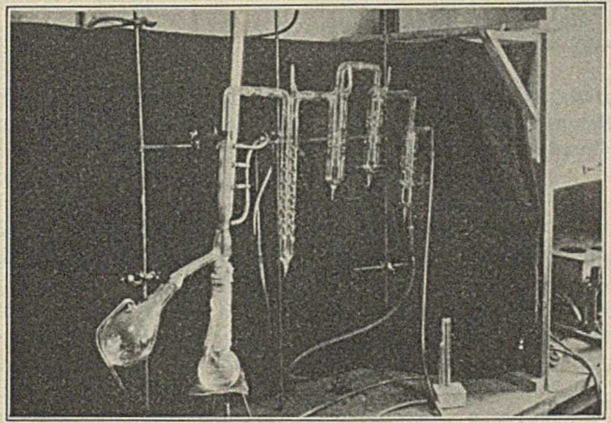

Figure 2—Set-up of Apparatus

From an examination of this table it is observed that the strength of the acid of the distillate has decreased as well as that of the residue left in flask *F*. Both of these results would be predicted to accompany Reaction 1 previously cited. A decrease in acidity for the residue in the distilling flask indicates that the dissociation of Reaction 1 takes place in great part in the liquid phase during the process of distillation. The dissociation of Reaction 2 resulting in the formation of anhydrous perchloric acid from the monohydrate is known to result at temperatures reached by the distillation under the pressures employed (*5*). The separation of the anhydrous acid in the vapor phase in the presence of higher concentrations of the dihydrate and trihydrate is due to the influx of dry air through the water condenser. The hydration of the anhydrous acid in contact with the higher hydrates of the vapor phase is thus prevented. That this reaction would result is shown by the formation of crystals of the monohydrate in the top of the water-cooled condenser. The rate of cooling in the water condenser is adjusted to maintain the conditions leading to the accumulation of the greatest yield of anhydrous acid. An even more completely anhydrous perchloric acid could be obtained if the cooling water of the water condenser were so adjusted as to result in the formation of the deposit of crystals of the monohydrate at a point further down in the condenser tube, but the yield of anhydrous acid would be lower.

The data of Table I show that a larger yield of anhydrous acid is obtained in the case of the higher pressures. However, experiments were made in which the air leak to the flask *R* remained at 8 to 8.5 mm., while the total pressure on the system was increased by means of a stopcock near the pump side of the system. The results show a slight increase in yield of anhydrous acid at the higher pressure but the data showed a decrease in yield as compared to the previously described adjustment of pressure (9–10 per cent yield dropped to 5–6 per cent working at 16–18 mm.).

Possible Explanation of Phenomenon of Superheating

Two characteristics of the dissociation Reactions 1 and 2 for which explanation is desirable are as follows: First, the explanation of the dehydration of perchloric acid accomplished without the presence of a drying agent. Second, the mechanism of the distillation operation accompanied by superheating to such an abnormal extent. It is possible that both these results are explained in the same manner.

The dissociation of perchloric acid dihydrate to form the trihydrate and monohydrate (Reaction 1) under ordinary conditions requires a drying agent of the efficiency of sulfuric acid. The dehydration of strong perchloric acid can be brought about by distillation in the presence of concentrated sulfuric acid with the formation of perchloric acid monohydrate (*1*). While hot concentrated perchloric acid is an efficient drying agent it would be contrary to ordinary experience that the higher hydrates of a given material should be capable of generating a lower hydrate of the same material.

Perchloric acid monohydrate has been shown (*4*) to be in reality of an oxonium structure. The formation of oxonium perchlorate according to the reaction

$$2HClO_4 \cdot 2H_2O = OH_3ClO_4 + HClO_4 \cdot 3H_2O$$

might account for a surface orientation of molecules of oxonium perchlorate which would account for the property of superheating. The retarded liberation of the vapors of the main product of the distillation $HClO_4 \cdot 2H_2O$ as well as the trihydrate of perchloric acid would seem by this mechanism to be explained. That this explanation is plausible is evident from the fact that monohydrated perchloric acid at 110° C. (approximately) is known to dissociate into the dihydrate and anhydrous perchloric acid.

As the oxonium perchlorate molecules dissociate at the surface of the distilling liquid, more assume their position to maintain the surface film and the superheated condition. The temperature of the vapors of the lower hydrates of perchloric acid forced through the surface film of oxonium perchlorate at the temperatures required (110° to 120° C.) do not react to hydrate the anhydrous perchloric acid in the vapors at this temperature.

That this is true is shown by the fact that when a permanent gas is admitted into these mixed vapors, the mean free path of the molecules is decreased to such an extent that the anhydrous acid molecules do not react as a whole with the lower hydrates at the lower temperatures of the condenser, nor do they come in contact with the lower hydrated condenser surface. The anhydrous acid does not condense on the first impact with a cold surface because the three liquid air traps, *A*, *B*, and *C*, are necessary to remove all the anhydrous acid from the air stream. All of the lower hydrates are removed by the water condenser which reflux into receiver *R*.

The anhydrous perchloric acid formed is more stable than this product is generally reputed to be. A sample stored under the prevailing outdoor temperatures of the late winter season did not explode for approximately two months. A sample could be stored at liquid air temperatures indefinitely without spontaneous decomposition, as shown by the fact that it does not form the usual accumulation of colored decomposition products which after sufficient accumulation bring about the explosion of the sample. A sample was stored in liquid air for 2 months with no decoloration and only exploded after subsequent exposure to room temperature for 4 weeks.

If samples of perchloric acid of greater strength than the dihydrate are desired, the monohydrate may be formed by the solution of the anhydrous acid to the point at which the product solidifies. This concentration of perchloric acid can be stored indefinitely without hazard. It must be kept in mind, however, that even though the process just described for the preparation of anhydrous perchloric acid is entirely without hazard if directions are followed closely, the handling of the product once formed may result in the most violent explosions if it is attempted to store it beyond the point of the formation of an amber color or in case it is allowed to come into contact with organic matter such as dry wood, paper, rubber, cork, cotton, etc.

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Oxonium Structure of Hydrated Perchloric Acid[1]

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Evidence has been supplied substantiating the oxonium structure of form of perchloric acid melting at 50° C., a conclusion previously demonstrated by others.

The exact melting point of oxonium perchlorate has been determined and found to be 49.905° + 0.005° C.

A new form of perchloric acid, oxonium perchlorate monohydrate, is postulated based upon the transition $HClO_4 \cdot 2H_2O = OH_3ClO_4 \cdot H_2O$. The alpha and beta forms of the trihydrate of perchloric acid previously known are likewise postulated to result from the transition $HClO_4 \cdot 3H_2O = OH_3ClO_4 \cdot 2H_2O$. The oxonium structure of all the known hydrates of perchloric acid is therefore indicated as a natural conclusion from the data shown.

The use of the data of this paper has been suggested for the construction of a density–acid concentration table, the analyses for which have been provided by physical rather than chemical means.

THE cryoscopic study of the system water–perchloric acid has been made by van Wyk (7) over the range H_2O–100 per cent $HClO_4$ with the investigation among other hydrates of the mono-, di-, and trihydrates. The melting point of the monohydrate was found to be 50° C. and of the dihydrate −17.8° C. Two forms of the trihydrate were found, the alpha form, m. p. −37° C., and the beta form, m. p. −43.2° C. In addition to these hydrates the two following forms were shown: $2HClO_4 \cdot 5H_2O$, m. p. −29.8° C., and $2HClO_4 \cdot 7H_2O$, m. p. −41.4° C. The freezing point of anhydrous perchloric acid has been found to be −112° C.

The great difference in the chemical and physical properties of anhydrous perchloric acid and its monohydrate has been explained on the assumption that the hydrate melting at 50° C. is in reality of the oxonium structure, OH_3ClO_4, rather than the simple monohydrated form of perchloric acid. This explanation of Hofmann has been studied experimentally by Volmer (6) who demonstrated that the x-ray lattices of the hydrate of perchloric acid m. p. 50° C. and ammonium perchlorate are practically identical. The Hofmann conclusion has, therefore, been rather satisfactorily substantiated and the Hantzsch theory of electrolytes likewise strengthened.

The object of the present investigation was originally the analysis of strong perchloric acid solutions by physical means through the more exact determination of the melting point of perchloric acid dihydrate and the simultaneous determination of its density. Since the relationship between the density and acidity of strong solutions of perchloric acid has been shown to be linear (7) the analysis in the region of the dihydrate could then be found with the density determination and a determination of the relationship, per cent acidity equals a function of the change in density. A second reference point in the density–percentage composition curve could then be established by determination of the physical constants of the monohydrate.[2]

The exact determination of the melting point of perchloric acid dihydrate was found to be complicated by the difficulty that a physical transformation (Reaction 2) apparently always takes place upon crystallization of a solution of perchloric acid of practically the correct acid composition 73.6 per cent $HClO_4$. The object of the present paper then became the use of this transition to further substantiate the oxonium structure of the hydrated perchloric acids other than the 50° melting form studied by Volmer. In thus strengthening the Hofmann conclusions as carried out in the x-ray studies of Volmer, it then became necessary to determine the exact melting point of oxonium perchlorate for the purpose of studying transition of Reaction 1. A secondary objective consisted in the explanation of the structure of the previously known alpha and beta forms of the trihydrate of perchloric acid (7) which is represented in Reaction 3.

$$OH_3ClO_4 \longrightarrow HClO_4 \cdot H_2O \qquad (1)$$
$$HClO_4 \cdot 2H_2O \longrightarrow OH_3ClO_4 \cdot H_2O \qquad (2)$$
$$HClO_4 \cdot 3H_2O \longrightarrow OH_3ClO_4 \cdot 2H_2O \qquad (3)$$

As a result of this investigation Reaction 1 was not found to take place. Reaction 2 was indicated and Reaction 3 was previously shown (7). It naturally follows that the two hydrates of the form $2HClO_4 \cdot 5H_2O$ and $2HClO_4 \cdot 7H_2O$ probably exist in the form $2OH_3ClO_4 \cdot 3H_2O$ and $2OH_3ClO_4 \cdot 5H_2O$. In other words the oxonium structure of hydrated perchloric acids in general is thus indicated.

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[1] Received August 23, 1930. Presented before the Division of Physical and Inorganic Chemistry at the 80th Meeting of the American Chemical Society, Cincinnati, Ohio, September 8 to 12, 1930.

[2] The exact chemical analysis of perchloric acid solutions is not practicable for the reason that a satisfactory reducing agent has not been found capable of forming hydrochloric acid which could then be compared with silver in the usual manner.

Transition of Crystalline Perchloric Acid Obtained at Freezing Point of Approximate 73.60 Per Cent Solution

The apparatus employed followed the design of Beckman (*1*) and of Kanolt (*4*) illustrated in Figure 1 drawn to the scale indicated. The large Dewar flask, *E*, served as the reservoir for a sulfuric acid–ice freezing mixture maintained at a temperature of −19° to −20° C. A partially evacuated Dewar, *D*, served as the jacket for the reaction chamber, *C*, containing the perchloric acid of the determination. Provision was made for the mechanical stirring of the freezing mixture using a platinum wire stirrer, *S*, moving with a period of 40 to 50 strokes per minute inserted through *B*. The freezing of the sample being examined was followed by use of a 10-junction thermocouple made in the conventional fashion from number 28 wire. The freezing mixture could be seeded out through *A* using a small capillary tube dipped in the acid used and frozen by brief immersion in liquid air. A stream of dry air was passed into tubes *A* and *B* to prevent contamination of the sample by atmospheric moisture. The whole cryoscopic bath was insulated from changes in temperature due to outside influences by use of wool felt coverings.

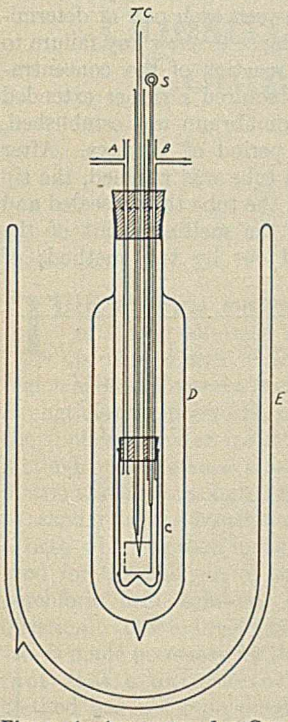

Figure 1—Apparatus for Crystallization of Perchloric Acid

The thermocouple was calibrated at the freezing point of very pure mercury using the value −38.87° C. The deviation from a standard thermocouple was found to be +0.00192 microvolts (*3*). A White single potentiometer was used for recording the temperature provided with a compensating resistance equal to that of the thermocouple. The standard cell used (1.0183 volts at 25° C.) was calibrated against a Bureau of Standards cell. The galvanometer was by Leeds and Northrup having a 5-second period, a sensitivity of 5 mm. per microvolt employing a critical damping of 72 ohms. The image from the galvanometer mirror was cast upon a wall at a distance of 18 feet giving a deflection of 13 mm. per microvolt.

The experimental procedure was as follows: Twenty cubic centimeters of perchloric acid varying in composition 72.3 to 73.8 per cent were placed in the freezing point tube, *C*, and the whole cooled by immersion in a carbon-dioxide-snow cooling chamber. After the acid was undercooled 1 to 2 degrees below its freezing point it was transferred to the vacuum chamber, *D*, immersed in the Dewar flask, *E*, containing the sulfuric acid–ice mixture at a temperature of 1 to 4 degrees above the freezing point of the perchloric acid being examined. The temperature of the well-stirred perchloric acid at this point was followed closely to observe the point of gradual rise in temperature, at which point it was seeded as previously described. The crystallization began at this point and a rise in temperature resulted which reached a variable high point, and instead of the temperature reaching a fixed maximum corresponding to the melting point of the dihydrate and remaining stationary for a fixed interval of time, it began to fall in a direction contrary to the direction of the bath temperature. At the point at which the last crystal disappeared in the solution, the temperature then mounted to the bath temperature. The time-temperature plot is shown in Figure 2.

The examination of Figure 2 representing the composite data for many duplicate determinations of a given sample shows the similarity in behavior in all cases. The general trend of the data shows that the crystal form first produced by the seeding of the undercooled perchloric acid undergoes a transition before the melting point of this form is reached at *B*. The transition takes place with the absorption of heat and is complete before the lower melting point is reached at some point lower than *A*. Reaction 2 above is, therefore, indicated with the stable form represented by the formula $OH_3ClO_4 \cdot H_2O$ (oxonium perchlorate monohydrate). That this form is obtained with the absorption of energy is in accordance with the explanation of the decomposition of perchloric acid of the same composition at approximately 18 mm. and 115° C. in the formation of anhydrous perchloric acid and previously shown (*2*). The dehydration of oxonium perchlorate monohydrate to form oxonium perchlorate according to this explanation was accompanied by the absorption of energy. Following the same explanation the beta form of perchloric acid trihydrate previously described (*7*) is to be correctly termed oxonium perchlorate dihydrate since the latter form results from the former with the consumption of energy. The repetition of the freezing point determination of various perchloric acid samples gave results of the same general type. These data are given in Table I.

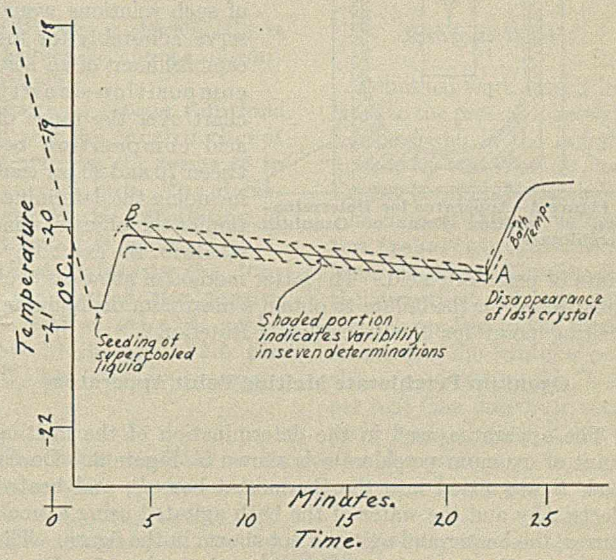

Figure 2—Time-Temperature Plot for Several Determinations

Table I—Maximum and Minimum Transition Temperatures for Various Strengths of Approximately 73 Per Cent Perchloric Acid

Perchloric Acid	Temperature of Transition	
	Maximum	Minimum
%	° C.	° C.
73.8	−19.11	−19.53
73.4	−19.97	−20.14
73.2	−17.85	−19.34
72.3	−19.40	−20.01

Determination of Melting Point of Oxonium Perchlorate

The determination of the melting point of oxonium perchlorate would serve a twofold purpose in connection with the present investigation. The possible transition of Reaction 1 above would be examined. Previous determination

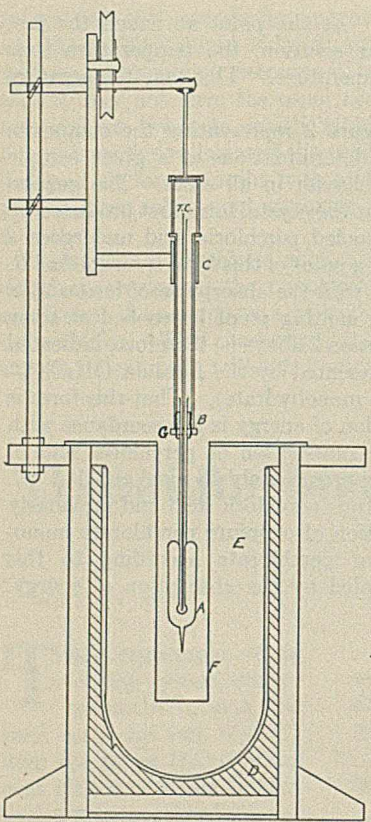

Figure 3—Apparatus for Determination of Melting Point of Oxonium Perchlorate

of the melting point of the 50° melting hydrate of perchloric acid indicated no transition and therefore the nonexistence of perchloric acid monohydrate ($HClO_4 \cdot H_2O$) as subsequently indicated by Volmer. Secondly, the determination of the maximum freezing point for perchloric acid–water system would establish the exact composition of perchloric acid by physical rather than chemical means. The solution of definite weights of oxonium perchlorate in known weights of water together with the determination of the density of such solutions would serve admirably for the establishment of an acid composition–density chart over the range of acid composition between 70 and 80 per cent including the determination of the physical constants for the exact dihydrate of perchloric acid. The latter method of attack is thus substituted for the failure to obtain a maximum or minimum melting point for the transition of Reaction 2.

Oxonium Perchlorate Melting Point Apparatus

The apparatus used in the determination of the melting point of oxonium perchlorate is shown in Figure 3. Dewar flask *E* was fitted into the thermostat box, *D*, and heated electrically and the water of the bath agitated using a small stirrer, the heater and agitator not shown in the figure. The reaction cell, *A*, was constructed on the order of a Dewar flask with very small bore for the entrance of the multiple thermocouple, *T.C.* The sample of acid of approximately the correct composition was added to cell *A* through the small opening at the bottom end and sealed for each observation. Cell *A* was agitated by use of the shaking device shown operating at approximately 300 revolutions per minute. The same temperature recording multiple thermocouple and White potentiometer previously described were used. The thermocouple was calibrated using thiophene-free benzene and the boiling point of water.

Preparation of Samples and Determination of Melting Point

Perchloric acid of approximately oxonium perchlorate composition was prepared from pure thrice-distilled perchloric acid of approximately 73.6 per cent composition prepared by the method of Smith and Koch (*5*) followed by the addition of anhydrous perchloric acid made by the method of Goehler and Smith (*2*). The crystalline perchloric acid thus obtained was melted and poured into the reaction chamber, *A*, Figure 3, which was then sealed for determination. If anhydrous perchloric acid is added to form a solution of greater acidity than that of oxonium perchlorate (OH_3ClO_4), the solution darkens upon storage due to decomposition. For this reason solutions less strong than that of the maximum melting point were prepared and subsequently concentrated by the addition of anhydrous perchloric acid. The anhydrous perchloric acid used for this operation was stored in liquid air to prevent its gradual decomposition and subsequent explosion. As the oxonium perchlorate composition was approached starting with less strong acid by addition of anhydrous perchloric acid, the crystalline acid was produced in larger and larger crystals until at the maximum melting point the entire tube consisted of a transparent mass of crystalline acid.

Four duplicate determinations of the melting point were carried out upon each tube. Between each pair of determinations 48 hours were allowed to elapse to show any failure to duplicate determinations. The reaction of the concentration of the acid in a given case required a rather extended period of time. To show that equilibrium was established, one sample was studied over a period of 16 days. After a given determination the sample tube was weighed, the tip broken off, anhydrous acid added, the tube then resealed and weighed. The determination of the melting point of the oxonium perchlorate was carried out by two methods of application of heat to bring about the melting. In one the bath temperature was maintained at 0.5° to 1.0° above the melting point of the sample and the sample allowed to melt as a result of this higher temperature employed. In the other case the bath temperature was gradually raised to a point equal to and slightly above the melting point of the sample. Both methods gave identical results. A graph of the temperature record for a typical run is shown in Figure 4. The results of the determination of the maximum melting point of a group of individual determinations for three different samples of material are given in Table II.

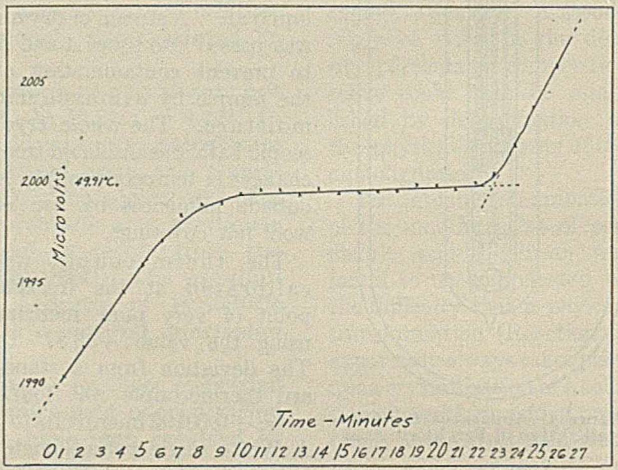

Figure 4—Temperature Record for Typical Runs in Determining Melting Point of Oxonium Perchlorate

Table II—Melting Point of Oxonium Perchlorate

Sample	Av. Max. Melting Point	Max. Deviation of Four Detns.
	° C.	° C.
1	49.903	0.017
2	49.906	0.023
3	49.910	0.019

Discussion of Results

The results show a satisfactory individual agreement as well as duplicate agreement. Results are expressed to thousandths of a degree although the thermocouple used does not exceed an accuracy of 0.005° C. The melting point of oxonium perchlorate is thus found to be 49.905° + 0.005° C. No evidence of the transition of Reaction 1 above was found. Perchloric acid monohydrate has not, therefore, been shown to exist and the oxonium structure of perchloric acid of this theoretical composition thus indicated.

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Oxonium Perchlorate as Reference Standard for Construction of Specific Gravity-Percentage Composition Table for Strong Perchloric Acid Solutions[1]

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Oxonium perchlorate (OH_3ClO_4, m. p. 49.905° C.) is used for the preparation of known strengths of concentrated perchloric acid solutions.

A determination of the density of strong solutions of perchloric acid is described and the construction of a density-acid composition chart over the range 65 to 75 per cent perchloric acid carried out. The determination of the constants used in the calculation of interpolated and extrapolated values is given.

The determination of reference points in the density-acid composition chart established the density of the dihydrate of perchloric acid at 25°/4° C. to be 1.71282. Constant boiling perchloric acid 72.4 per cent at 760 mm. and 203° C. has the approximate density 1.6964.

THE chemical analysis of strong solutions of perchloric acid in the region of 65 to 75 per cent acid strength is obtainable only by the application of an indirect method. A reference acidimetric standard is first used to standardize the solution of a base which is then in turn used for the analysis of the perchloric acid solution in question. This indirect analysis is made necessary by the fact that a satisfactory method has not been developed for the reduction of perchlorates to chlorides which could then be determined using silver. The preparation of an accurate density-percentage composition table within the range under question is desirable because concentrating dilute solutions of perchloric acid either at atmospheric pressure or under reduced pressure gives rise to acid within this range of percentage composition. Perchloric acid, when distilled at 760 mm., forms a constant boiling mixture with water which consists of 72.4 per cent acid. The formation of the approximate dihydrate of perchloric acid ($OH_3ClO_4 \cdot H_2O$) which has an acid composition of 73.60 per cent results from the vacuum distillation of perchloric acid of constant boiling strength (*2*, *5*, *6*, *7*).

The object of the present paper is the construction of a density-percentage composition table, the accuracy of which exceeds that of existing data, using a method which can be demonstrated to be superior to such data, and employing methods of chemical analysis only. The method of attack is wholly dependent upon the accuracy with which the melting point of the highest melting hydrate of perchloric acid can be determined (*2*) (OH_3ClO_4, m. p. 49.905° ± 0.005° C.). This product, by consulting the data of van Wyk (*8*) can easily be seen to serve better than any other known form of perchloric acid as a reference point in the analysis of strong perchloric acid following the cryoscopic method, and independent of chemical analysis.

Previous Work

Published work closely related to the present investigation is found in the investigations by van Wyk (*8*), van Emster (*1*), and Hantzsch (*3*). The data of these investigators (recalculated in some cases to gain uniformity for the purpose of easy comparison) as applied to the determination of the density of perchloric acid of strength 73.60 per cent (the dihydrate composition) is given in Table I. The values obtained as hereinafter described are included to conserve space.

Table I—Density of 73.60 Per Cent Perchloric Acid and Related Constants

Investigator	Density 25°/4° C.	Coefficient of Expansion Alpha	Coefficient of Expansion Range ° C.	n_D^{25}	$d\Delta/dC$
van Emster	1.70942	0.00121	15–30	.....	0.01351
van Wyk	1.7130	0.00121	20–50	.....	0.01390
Hantzsch	1.71299	.....		1.42064	0.01366
Present work	1.71282	0.00122	20–30	1.42052	0.01343

$$\text{Alpha} = \frac{d_1 - d_2}{t_2 - t_1}$$ (change in density per degree change in acid concentration).

Outline of Procedure

Samples of oxonium perchlorate (84.794 per cent $HClO_4$) are prepared by the method of Smith and Goehler and their exact composition and identity determined by the determination of their exact melting point (49.905° C.). Weighed portions of these samples of oxonium perchlorate are then diluted with weighed portions of pure water and a density determination made of the solutions thus prepared. The identity of the density thus found for solutions of the same acidity based upon the dilution of the individual preparations of oxonium perchlorate serves as an additional evaluation of the uniformity in composition of the high melting hydrates as determined by their melting point. Further dilution of the samples thus formed serves for the determination of other points on the density-acid composition curve. From

[1] Received August 23, 1930. A portion of a thesis presented by O. E. Goehler in partial fulfilment of the requirements for the degree of doctor of philosophy in the Graduate School of the University of Illinois.

the data thus accumulated the change in density per interval of change in acid composition is readily calculated and the agreement with a linear function thus examined. The analyses are, therefore, dependent only upon physical observations.

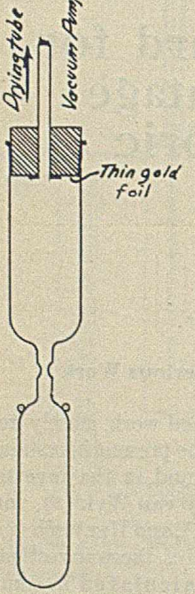

Figure 1—Reaction Tube

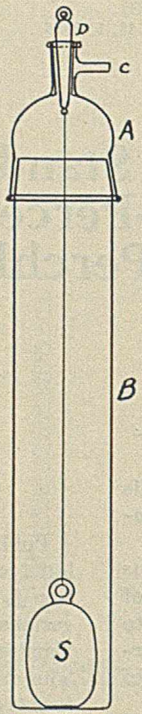

Figure 2—Densimeter Tube

Preparation of Solutions of Known Acid Composition

Oxonium perchlorate prepared as previously described (*2*), having the melting points 49.905° ± 0.005° C., was transferred to the lower portion of the reaction tube shown in Figure 1 in the following manner:

The melting point tube containing the oxonium perchlorate was placed in the upper portion of the reaction tube after the tip was broken to provide for the transfer of the contents. The stopper with a thin gold foil covering is inserted and the whole apparatus dried by evacuating a number of times and refilling with dry air. The whole reaction tube was then immersed in a water bath at 55° C. up to the height of the stopper and the contents of the melting point tube melted and allowed to collect in the lower part of the reaction tube. It was then fused at the constriction, and from the original weight of the tube and the two parts after the transfer of the oxonium perchlorate, the weight of the sample was obtained.

The weighed sample tube of oxonium perchlorate was file-marked at the neck, reweighed, and the tube opened. A weighed quantity of water was then added and the tube resealed. The composition of the resulting acid was then calculated and the density determined. The latter operations were repeated and a new acid concentration and density determined.

Determination of Density of Concentrated Perchloric Acid

The determination of the density of concentrated perchloric acid was carried out following the displacement method described in Bureau of Standards Bulletin 9 (*4*). The balance employed and the arrangement of the suspensions in the present work provided for an accuracy of ± 0.4 mg. Weights were calibrated and the vacuum corrections applied as well as corrections for atmospheric conditions, including psychrometer relative humidity, temperature, and barometric corrections.

The displacement sinker was made of Pyrex glass rod molded into shape, annealed 48 hours at 300° C. to minimize thermal hysteresis, and allowed to age for 10 days. The sinker was suspended by a platinum wire having a diameter of 0.0035 inch dull goldplated over the immersed portion to insure wetting by the perchloric acid and avoiding the phenomena associated with "sticking" which is thus best eliminated.

The densimeter tube is shown in Figure 2 and had two ground glass stoppers, *A* and *D*. Ground joint *A* provided for the introduction of the sinker and sample. Ground joint *D* supported the upper and lower suspensions and was protected against introduction of moist air by use of the side tube, *C*, through which a slow stream of dry air was passed during the period of time in which stopper *D* was disengaged.

The densimeter tube was maintained at a constant temperature with an accuracy of ± 0.01° C. using the large Dewar tube thermostat shown in Figure 3. The water of the thermostat bath was provided with mechanical stirrer, heating coil, and cooling coil, and its temperature was recorded by a Callender platinum resistance thermometer with compensating leads, using a specially designed Wheatstone bridge. The movement of the galvanometer by means of a system of lights and mirrors cast an image on a scale above the balance. By setting the Wheatstone bridge at the properly calculated setting for a given temperature, the bath temperature during measurement was closely controlled by use of a switchboard controlling the heating and cooling coils and stirrer of the thermostat. The platinum resistance thermometer was calibrated at the ice point, the freezing point of mercury, and the boiling point of water.

The volume of the sinkers employed was found to be as follows:

	No. 1	No. 2
Mass, grams	66.3081	21.5544
Volume:		
20° C.	28.5512	
25° C.	28.5528	9.6170
30° C.	28.5545	

Distilled water was used as the calibration liquid and the best values for its expansion with change in temperature. The calculation of the densities determined was made using the following formulation.

$$D\frac{t}{4} = \frac{(S - W) + (Z - Y)}{V_t}, \text{ where}$$

$D\frac{t}{4}$ = density of sample at temperature t
S = relative weight of sinker plus suspension
W = relative weight of sinker in liquid plus suspension
Z and Y = respective vacuum corrections for S and W
V_t = volume of sinker at temperature t

The results of series of determinations of points of reference to be used in the construction of a density–percentage composition chart for concentrated perchloric acid solutions are found in Table II.

Table II—Determinations of Points of Reference Used in Construction of Density–Percentage Composition Chart

Vacuum Wt. $HClO_4$	$HClO_4$	Vacuum Wt. Anhyd. $HClO_4$	Vacuum Wt. $HClO_4$ + H_2O	Resulting $HClO_4$	Density 25°/4° C.	$d\Delta/dC$[b]
Grams	%	*Grams*	*Grams*	%		
35.3531	84.794[a]	29.9774	41.0190	73.082	1.70583	.....
30.7492	84.794[a]	26.0735	35.6712	73.094	1.70608	.....
40.0530	73.082	29.2715	40.5097	72.257	1.69478	0.01341
40.3712	72.257	29.1710	41.6093	70.107	1.66582	0.01344
41.6093	70.107	29.1710	46.2831	63.027	1.57104	0.01358
35.4381	73.094	25.9031	36.5718	70.828	1.67552	0.01345

[a] Oxonium perchlorate (OH_3ClO_4), m. p. 49.905° ± 0.005° C.
[b] Change in density per degree change in acidity.

From an examination of this table it will be observed that the value for $d\Delta/dC$ (the change in density per unit change in per cent) within the experimental error shows the relationship to be linear over the 70–73 per cent acid concentration, an average value of 0.01343 being obtained. The agreement between the present work and the value obtained by van Emster (*1*) is better than that obtained

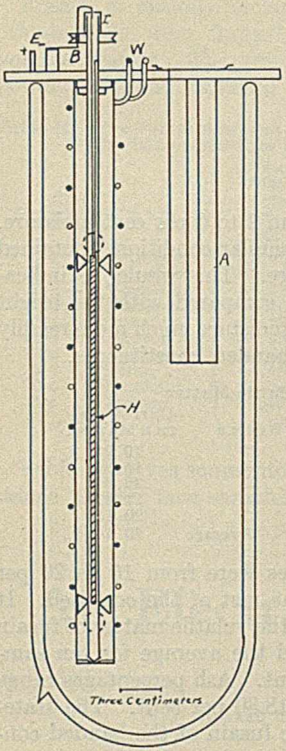

Figure 3—Dewar Tube

by comparison with van Wyk (*6*) or Hantzsch (*3*). The value $d\Delta/dC$, 0.01343, together with the data of Table II, gives for the density of 73.603 per cent $HClO_4$ (the $OH_3ClO_4 \cdot H_2O$ hydrate) the value 1.71282 with a probable accuracy of 5 units in the fifth place of decimals. Here the agreement is closer between the present work and that of van Wyk and Hantzsch. (Compare with Table I.) The determination of the coefficient of expansion resulted in a substantial agreement between the present work and previous observers (*8*, *1*, *3*). Between 63 and 70 per cent acid concentration the value for $d\Delta/dC$ increases slightly.

Construction of Density–Acid Composition Table for 65 to 75 Per Cent Perchloric Acid

The data of Table II serves for the construction of a table of values relating density and acid composition. The values obtained are included in Table III. Values given other than those for the exact multiple of 0.25 per cent in acid composition are the result of actual observation. The remainder are calculated. The values of the density experimental reference points are intended to be accurate to 5 units in the fifth decimal place and the acid composition to within ± 0.01 per cent. Values for the calculation are as follows: $d\Delta/dC = 0.01343$ between the limits 70 to 75 per cent acid composition, and $d\Delta/dC = 0.01351$ for the remainder. The calculated values for the density of Table III are thought to be accurate to the fourth decimal place.

Table III—Density and Percentage Composition of 65–75 Per Cent Perchloric Acid

$HClO_4$ %	Density 25°/4° C.	$HClO_4$ %	Density 25°/4° C.	$HClO_4$ %	Density 25°/4° C.	$HClO_4$ %	Density 25°/4° C.
63.027[a]	1.57104	....	.....	71.25	1.68099	...	.....
65.00	1.59665	68.25	1.64055	71.50	1.68434	74.25	1.72124
65.25	1.60002	68.50	1.64393	71.75	1.68774	74.50	1.77458
65.50	1.60340	68.75	1.64731	72.00	1.69106	74.75	1.72791
65.75	1.60678	69.00	1.65060	72.25	1.69442	75.00	1.73125
66.00	1.61016	69.25	1.65406	72.257[a]	1.69478	...	.....
66.25	1.61353	69.50	1.65744	72.50	1.69778	...	.....
66.50	1.61691	69.75	1.66082	72.75	1.70113	...	.....
66.75	1.62029	70.00	1.66420	73.00	1.70449	...	.....
67.00	1.62367	70.107[a]	1.66582	73.082[a]	1.70583	...	.....
67.25	1.62704	70.25	1.66756	73.094[a]	1.70608	...	.....
67.50	1.63042	70.50	1.67092	73.25	1.70785	...	.....
67.75	1.63380	70.75	1.67427	73.50	1.71120	...	.....
68.00	1.63718	70.828[a]	1.67552	73.75	1.71456	...	.....
...	.....	71.00	1.67763	74.00	1.71790	...	.....

[a] Values experimentally determined.
$d\Delta/dC$ 60–65% = 0.01351
65–75% = 0.01343

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An Improved Absorption Tube for Combustion Analysis[1]

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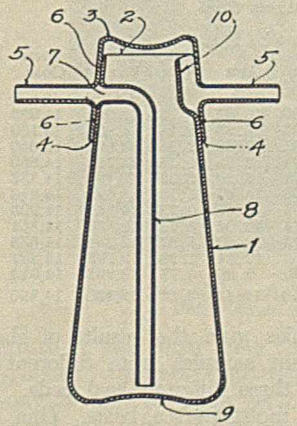
Since the advent of solid absorbents, such as Ascarite, for combustion analysis, many designs of absorption tubes have been proposed involving more and more advantages over their predecessors; yet none of them possessed at the same time all the refinements of manipulation combined with simplicity of design. To meet this need an apparatus, diagramed in the accompanying illustration, was devised.

The innovation consists in using an external instead of an internal stopper, allowing the cut-off of both openings without the use of return bends or other bypasses. This renders possible a simplification of design with the following advantages:

Minimal outside surface—easy to wipe to constant weight.
Minimal parts—one body, one stopper, one ground joint.
Minimal surface contour—low breakage.
Simple, positive operation—one turn of one stopper shutting inlet and outlet short off. (This was the particular point sought, so that for combustions in oxygen there would be no diffusion of air into the absorber during the operation of disconnecting.)
Minimal waste space—larger capacity completely utilized.
Stable standing.
Light weight.
Plain internal design—surface accessible to wiping.
Ground joint external—not contaminated in charging.
Simple construction—low cost.



Absorption Bottle for Solid Absorbents

Round glass body, 1, 2; external stopper, 3, 4; lateral tubes, 5; ground joint, 6; to tube attached to inner side of body neck, 7, 8; depressed channel communicating with the top interior, 10.

Absorbers of this type have been in satisfactory use in the laboratories of the Bakelite Corporation and at Columbia University, and have been readily made to order by the glass-blowing departments of Eimer and Amend and Columbia University.

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[1] Received October 13, 1930.

Fusain[1]

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FUSAIN, or mother-of-coal, is receiving more attention than formerly because of the various properties now being assigned to it. Certain studies in the laboratories at the University of Illinois have developed additional data which afford further information of value.

The bedding planes which are made of fusain are usually very thin but at times may be found in lenses 8 inches in thickness, although such deposits are exceptional. It is generally soft, friable, leaves soot marks on the fingers, and is more or less unconsolidated as compared with the rest of the coal in the bed. Because of the porous character of fusain in its normal state, it affords an easy passageway for infiltrating waters, and such waters, especially in the thicker bands, are very apt to deposit mineral matter from solution. In this way there will naturally result hard and dense layers quite in contrast to the soft friable layers that characterize most of the cleavage planes. These very thin layers are, therefore, usually the most friable and samples of such material can be removed in sufficient amount for analysis by use of care and a good brush.

It is not intended to discuss here the probable origin or method of formation of this material, but some information in that direction, as well as concerning its properties and chemical characteristics, may be gained by making the usual analysis and calculations for indicating the unit volatile and fixed carbon, as well as the unit B. t. u.

Mines were visited and lumps of freshly mined coal were selected containing fusain bands. Three or four lumps were selected from each mine. These samples were further sampled in the laboratory to obtain fusain samples free from other coal constituents, such as bright coal and dull coal. The lumps were broken along the bands of fusain and clean pieces selected, these pieces further broken down, and samples showing the presence of bright or dull coal discarded. Two kinds of fusain were noted during sampling operations, one a much harder variety than the other, and these two kinds were kept separate and are listed in the accompanying table as "soft" or "hard."

Table I—Proximate Analyses of Fusain from Moisture-Free Illinois Coal

Sample	County	Coal Bed	Volatile Matter	Fixed Carbon	Ash	Sulfur	Fuel Value	Unit Coal	Variety Fusain
			%	%	%	%	*B. t. u.*	*B. t. u.*	
7	Vermilion	6	23.95	59.20	16.85	5.73	12,080	14,980	Hard
8	Vermilion	7	26.95	54.25	18.90	8.18	11,800	15,100	Hard
9	Vermilion	6	20.75	71.45	7.80	2.58	13,600	15,050	Hard
10	Vermilion	6	13.78	79.24	6.98	1.56	13,710	14,860	Soft
22	Jackson	2	15.79	69.01	15.20	6.57	12,197	14,833	Soft
23	Jackson	2	13.00	80.33	6.67	1.78	13,794	14,913	Soft
25	Jackson	2	18.69	76.86	4.45	0.75	14,165	14,903	Soft
26	Jackson	2	15.22	71.74	13.04	4.75	12,560	14,851	Soft
29	Perry	6	21.04	65.34	13.62	5.97	12,291	14,635	Soft
30	Randolph	6	18.83	68.63	12.54	1.28	12,795	14,837	Hard
31	Jackson	6	18.30	71.80	9.90	0.77	13,295	14,912	Hard
Average			18.74	69.80	11.44	3.63	12,930	14,890	

The accompanying tables give the results of chemical analyses of eleven different samples from different parts of the state, taken from three different coal beds. These results are on a dry or moisture-free basis. One condition of fusain not given in the tables, but calling for reference, is the amount of moisture in the air-dry condition. Coals of the Illinois type when brought to the air-dry condition in the laboratory will contain from 2 to 6 per cent moisture, and the samples of fusain under similar conditions contained from 0.5 to 2.0 per cent moisture. This would be indicative of the porosity of fusain as compared with the bright and dull coal, since it gives up its moisture much more readily and completely than the other banded constituents.

Table II—Unit Volatile Matter

Sample	Unit Volatile Matter	Sample	Unit Volatile Matter
7	27.30	23	19.26
8	31.32	26	15.89
9	21.79	29	22.64
10	15.59	30	21.27
22	16.36	31	20.15
		Average	20.44

The volatile matter percentages were from 15 to 20 per cent lower than is general for the rest of the coal bed. It would appear from the data that the volatile matter of fusain is usually about 20 per cent, and the average for ten samples was found to be 20.44 per cent. Ash percentages range from a low of 4.45 to a high of 18.80 per cent. The statement is frequently made that the fusain of the banded constituents of coal contains more ash than the other bands, but this may not always be true as seen from the above. In fact, it would appear that fusain was originally a high grade low-ash material but, owing to infiltration of impurities because of its porous structure, the ash content was increased. Sulfur percentages follow rather closely the ash percentages—that is, a low-ash fusain is generally low in sulfur and, conversely, a high-ash fusain is generally high in sulfur.

The most striking feature to be noted here is the fairly consistent character of the material, and especially the uniformity of the unit B. t. u. values, considering that samples were taken from all parts of the state as well as from different beds. While the material is non-coking, it has too high and too consistent a volatile constituent to admit of its being the product of fire, as might be inferred from some designations applied to it. One of the striking characteristics of fusain is its absorption of water, and this has been referred to elsewhere as furnishing the mechanism for the slacking of bituminous coals (*2*).

Sinnat (*3*) has devised a method for determining the relative volume of absorption on the part of fusain for water and solutions, as compared with the coal substance with which it is associated. In some tests he found that fusain absorbed over 100 times as much as the coal in the same length of time. It is a well-recognized fact that fusain is unevenly distributed, hence we would expect an uneven absorption of water on the part of samples of coal from the same mine. It also indicates that underground waters will travel the most accessible fusain bands. The deposition of mineral salts which accompanies this process readily accounts for the high ash of some of the fusain bands.

The unit volatile matter, calculated by the method of Parr (*1*), gives the amount of volatile matter in the pure coal substance. The lowest value found is 15.59 and the highest 31.32, with an average of 20.44. However, the chief value of the unit volatile matter content lies in the fact that it would seem to refute completely the forest fire theory for the formation of fusain. The unit volatile matter would certainly be very much lower if fusain were formed because of forest fires sweeping over the coal-forming swamps.

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[1] Received August 2, 1930. Presented before the Division of Gas and Fuel Chemistry at the 80th Meeting of the American Chemical Society, Cincinnati, Ohio, September 8 to 12, 1930.

Fusain is entirely lacking in agglutinating power. No coke-buttons were formed during the determinations for volatile matter. The residue from the crucible is a fine powder with no evidence of any coking tendency.

Table III—Proximate Analyses of Moisture-Free Face Samples from the Same Mines as Fusain Samples of Table I

Sample	County	Coal Bed	Volatile Matter	Fixed Carbon	Ash	Sulfur	Fuel Value	Unit Coal
			%	%	%	%	*B. t. u.*	*B. t. u.*
7-*a*	Vermilion	6	40.90	54.45	4.65	2.21	13,555	14,297
8-*a*	Vermilion	7	41.64	49.59	8.77	3.46	12,904	14,310
9-*a*	Vermilion	6	39.35	53.40	7.25	1.70	13,390	14,189
22-*a*	Jackson	2	42.60	52.84	4.56	1.06	13,320	14,039
23-*a*	Jackson	2	33.28	48.58	18.14	3.25	11,577	14,705
25-*a*	Jackson	2	39.69	56.72	3.89	0.75	13,857	14,501
26-*a*	Jackson	2	43.62	52.54	3.84	1.94	13,649	14,295
29-*a*	Perry	6	44.48	44.80	10.72	2.62	12,427	14,231
30-*a*	Randolph	6	43.80	42.43	13.77	2.77	12,103	14,312
31-*a*	Jackson	6	41.49	47.56	10.95	1.06	12,672	14,405
Average			41.08	50.29	8.65	2.08	12,945	14,328

Table III gives some information concerning the coal substance proper, face samples of which were obtained in the usual manner when the fusain samples were taken. A striking difference is shown between the fusain and the total coal values for ash and sulfur. The unit coal B. t. u. values also are consistently higher for fusain. Other analyses of coals from the counties and beds given in this paper may be found in numerous publications of the Engineering Experiment Station, University of Illinois, and in Bulletin 56 of the Illinois State Geological Survey, Urbana, Ill.

The authors wish to emphasize the fact that these results, though meager, may point the way to other investigators and certainly shows the need for further fundamental study of the chemical properties of the various bands common to bituminous coal of the Illinois types—namely, vitrain, or bright coal (anthraxylon), dull coal (attritus), and fusain (mineral charcoal).

Literature Cited

(1) Parr, J. Ind. Eng. Chem., **14**, 921 (1922).
(2) Parr and Mitchell, *Ibid.*, **22**, 1211 (1930).
(3) Sinnat, *Trans. Inst. Mining Eng.*, **62**, 156 (1921).

An Electrically-Heated Melting Point Apparatus[1,2]

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THE apparatus shown in the accompanying illustrations has been used for a number of years with such satisfactory results that its general description seems worth while.

It consists essentially of an electrically-heated modified Thiele-Dennis melting point tube, *A*, a lead container, *B*, filled with sand to prevent damage by sulfuric acid in case of breakage, a lamp, *C*, and a rheostat, *D*, all suitably mounted for convenience and portability in the laboratory.

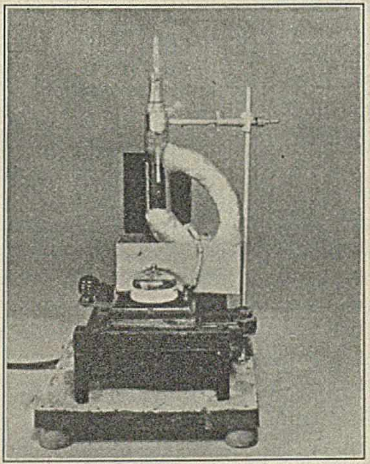

Figure 1—Melting Point Apparatus

The Thiele-Dennis tube is constructed of Pyrex glass and modified by having a smaller tube, *E*, which is closed at the lower end, sealed within the vertical portion, and extends 1 or 2 inches (25.44 or 50.8 cm.) below the point of attachment, *F*, of the side arm. This modified form thus constitutes a combination Roth-Thiele-Dennis apparatus. The side arm, *G*, is wound in the region of its lowest portion with asbestos-covered chromel heating element and insulated with asbestos. The asbestos covering and a portion of the vertical tube are painted with aluminum paint to reduce radiation to the minimum.

Employing a mixture of sulfuric acid and potassium bisulfate as the heating liquid makes it possible to reach a temperature of about 300° C., provided the absorption of moisture by the liquid is prevented by means of a calcium chloride tube at *H* when the apparatus is not in use. With the particular apparatus here illustrated and with a current of 1.4 amperes, about 6 minutes are required to raise the temperature in the inner tube from room temperature to 100° C., about 12 minutes from room temperature to 200° C., and about 25 minutes from room temperature to 300° C. Any desired range in temperature under 300° C., and the rapidity of change from one temperature to another are easily regulated by means of the adjustable rheostat. The melting of the substance itself is plainly observed with the aid of light coming through the small hole in *I* from the lamp *C*.

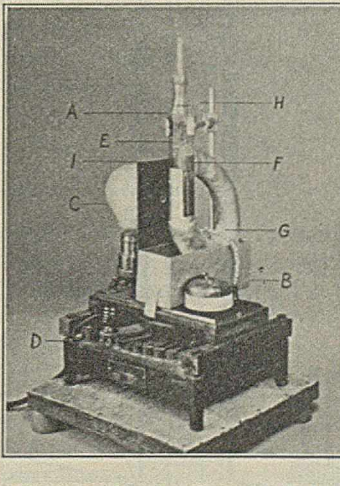

Figure 2—Another View of Melting Point Apparatus

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[1] Received October 7, 1930.

[2] Contribution No. 91 from Food Research Division.

Determination of Sulfur by Means of the Turbidimeter[1]

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REQUIREMENTS for sulfur determinations under widely varying conditions and in various and complex combinations seem to be on the increase. Not the least noticeable of these conditions is in connection with the work of the power plant where, for some of the determinations, convenience, speed, and a minimum or absence of chemical training are obvious conditions for arriving at the sulfur factor. On many accounts the sulfur photometer or turbidimeter lends itself in an attractive manner to this determination. Such an instrument has been in use for a number of years but the wider scope required for its functioning and the increasing demand for a high degree of accuracy, along with a greater facility of operation, has made it desirable to redesign the apparatus with these particular applications in view.

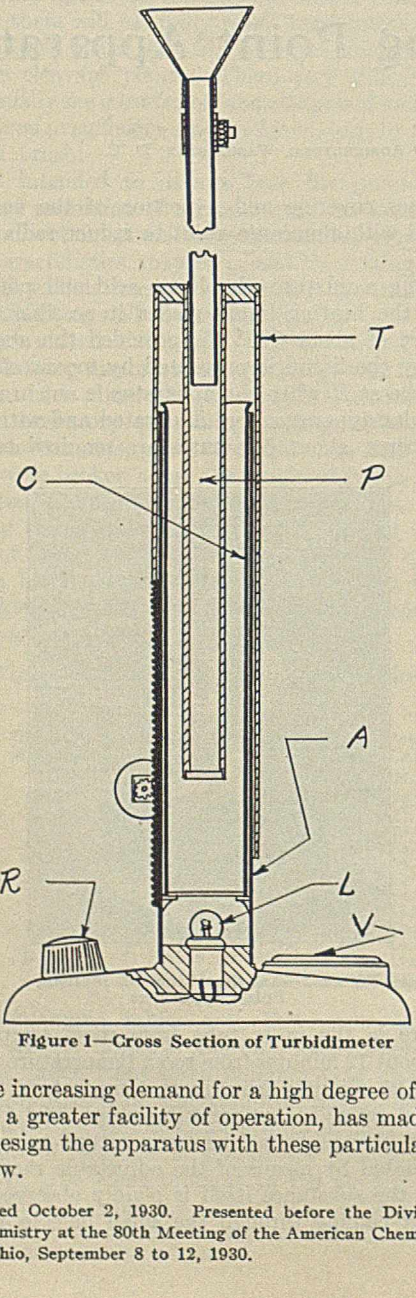

Figure 1—Cross Section of Turbidimeter

This extended use is especially notable in connection with the control of sulfates in boiler water, to conform to the A.S.M.E. standard, as a check on the development of embrittlement or cracking of the boiler plates.

Description of Apparatus

In Figure 1, the base supports all of the various parts. A light of about 2 candle power is mounted in the center with the current supplied from two or three dry cells. This current is passed through a voltmeter and also through a resistance, *R*, so that the light can be set at any standard voltage, where it can be retained throughout a test. *A* is a tube which serves as a standard for the other parts of the apparatus. It supports a stationary telescoping tube, *C*, with an optical glass bottom immediately above the light. This tube holds the turbid solution to be tested and also has a plunger tube, *P*, which is empty but which has an optical glass bottom and which may be moved up and down, toward or from the light, by the ratchet. The distance from the optical glass in the bottom of *P* to the optical glass bottom in *C* is measured in millimeters on the scale, *S*.

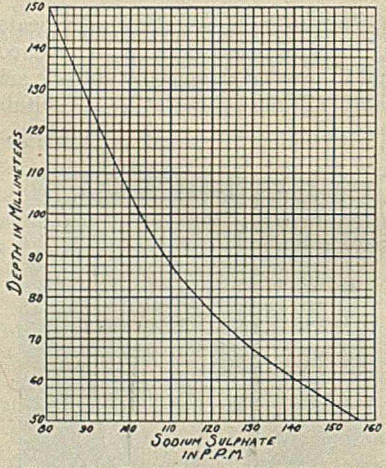

Figure 2—Turbidimetric Reading by Various Operators

The advantages of this arrangement are, that having made up the turbid solution to a standard amount, say 200 cc., the depth of turbidity for the conditions chosen is not disturbed by ripples on the surface of the liquid. Additions of more solution to secure greater depth are obviated. The optical glass is entirely submerged at all stages in the reading, and is moved up or down within the solution to secure the necessary depth and end point. Both tubes are of Bakelite or opaque glass and do not promote diffusion of the light. The eyepiece, located in a favorable position above the instrument, requires that the distance from the eye to the light be the same for all readings. The end point is taken as the complete disappearance of the red filament, which gives a far sharper end point than is possible between a lighter and darker spot of light where both consist of diffused light of varying intensities. By means of the resistance in the voltmeter it is possible to correct the variation in the strength of

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[1] Received October 2, 1930. Presented before the Division of Gas and Fuel Chemistry at the 80th Meeting of the American Chemical Society, Cincinnati, Ohio, September 8 to 12, 1930.

the battery so that a light of uniform candle power is always available.

It will be seen at once that the conditions thus secured correct many of the variables inherent in other forms of apparatus of this type. Indeed, the variation in eyes between different operators is reduced to a minimum, as may be seen from Table I. The solutions employed in this test were samples of boiler waters taken from the blow-off at the power plant. Four different persons made readings and the average of three readings for each person was taken. These people were taken at random and operators 3 and 4 were substantially without experience in this sort of work.

Table I—Turbidimetric Readings by Various Operators

SOLUTION	OPERATOR 1	OPERATOR 2	OPERATOR 3	OPERATOR 4
	Mm.	*Mm.*	*Mm.*	*Mm.*
1	126	127	129	132
2	91	84	85	85
3	66	65	65	67

Figure 2 is a curve developed by use of a standard solution of sodium sulfate, the readings being confirmed by a number of individuals. It should be remembered, however, that eyes vary, and especially so where the eye is focused on an object, as in this case, instead of observing the intensity of light on a given area. A person using glasses, therefore, will expect to obtain readings different from those obtained by one not using glasses. The variations, however, are uniform over the curve and the variation may be used as a constant or a new curve may be drawn to meet the specific conditions.

In Table II are given parallel determinations by use of the turbidimeter, as compared with the results by the ordinary gravimetric process. These results were also obtained on boiler waters with widely varying amounts of caustic and sodium carbonate.

Table II—Turbidimeter Results for Sulfates in Boiler Water

WATER NO.	TURBIDIMETRIC	GRAVIMETRIC
	P. p. m.	*P. p. m.*
17206	1770	1742
17299	1550	1582
17300	1482	1499
17318	808	812

It is believed that the sharpness of the end point and the good agreement obtainable by this instrument will make it of practical utility, especially in the power plant.

Application of a Bromine Method in Determination of Phenol and Cresols[1]

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With the increasing application of dephenolizing treatments to coke oven gas condensates in order that water supplies may not be contaminated by phenolic compounds, there is need for accuracy of method in determining the phenols content of the wastes before and after treatment.

While a method based on the combination of phenols with iodine has been considered more accurate than various bromine methods, data are presented which show that under certain prescribed conditions a bromine method yields the more accurate results.

WITHIN the last five years dephenolization of those coke oven liquors which eventually reach public water supply intakes, in order to eliminate so far as may be practicable the development of objectionable tastes following chlorination, has become a general practice.

To measure the efficiency of dephenolizing plants, the need exists for an accurate method of determining the phenols content of these wastes before and after dephenolization; the work to be described was prompted by the belief that existing methods are not sufficiently accurate.

The Skirrow (*12*) procedure for the estimation of phenols in gas liquors, the Rose and Sperr (*10*) modification of which is at present in general use, may be separated into two parts, first the removal of interfering substances, and second the combination of phenol and cresols with iodine, employing the method of Messenger and Vortmann (*7*). The procedure is subject to material errors, both in the removal of interfering substances and in the final determination of phenols. In this paper, only the determination of phenols is considered, preliminary purification being assumed.

Several bromine methods are also in use. For instance, U. S. Steel Corporation chemists (*14*) add bromine in excess, acidify, then dry and weigh the precipitate of bromine compounds of phenol and cresols. Williams (*13*) applies a bromine titration after preliminary purification. Shaw (*11*) has developed a method using a specialized preliminary distillation followed by a determination of the phenols in the distillate turbidimetrically with bromine.

Iodine Methods

Theoretically, phenol and *m*-cresol form triiodo compounds, while *o*-cresol and *p*-cresol form diiodo compounds. In the application of the Messenger-Vortmann method to mixtures all are conventionally calculated to phenol, C_6H_5OH, as triiodo compounds, according to the reaction:

$$C_6H_5OH + 6I + 3NaOH = C_6H_2I_3OH + 3NaI + 3H_2O$$

Thus, theoretically only two thirds of the *o*- and *p*-cresols present would be reported. Actually with these two cresols the proportion of iodine fixed is more than the requirement for the diiodo compounds and less than the requirement for the triiodo compounds.

The writer found that with *o*-cresol the iodine fixed was 118.8 per cent and with *p*-cresol 137.0 per cent of theory for the diiodo compound. Thus, only 79.2 per cent of the *o*-cresol and 91.3 per cent of the *p*-cresol present in a mixture would have been reported, applying the triiodo calculation.

Redman, Weith, and Brock (*9*) modified the Messenger-Vortmann method by substituting sodium bicarbonate for sodium hydrate and obtained results near to theory when working with phenol and the separate cresols. The writer, employing their method, also obtained results near to theory, phenol and *m*-cresol being calculated as triiodo compounds and *o*-cresol and *p*-cresol as diiodo compounds.

However, while this modification yields more accurate results than the Messenger-Vortmann method as employed by Skirrow, there still exists the error due to the unknown and no doubt varying proportions of phenol and the indi-

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[1] Received August 5, 1930.

vidual cresols present, when the method is applied to waste liquors.

It was also incidentally observed by the writer that the proportion of alkali recommended by Skirrow, 4 mols sodium hydroxide to 1 mol phenols (Messenger and Vortmann advised the use of at least 3 mols), does not yield maximum results for mixtures of phenol and cresols. It was found that higher results for *o*- and *p*-cresols, which were nearer to theory for the formation of triiodo compounds, were obtained by taking 6 mols of sodium hydroxide to 1 mol of cresol.

Bromine Methods

Koppeschaar (*5*) appears to have first applied bromine to the quantitative determination of phenol, using bromine water but later substituting a mixture of potassium and sodium bromides and bromates. He considered that the method was equally suitable for phenol or cresols, but was unable to investigate this point since he lacked pure cresols. In the bromide-bromate solution he used the equivalent of 2 grams of potassium bromate and 7.1 grams of potassium bromide per liter. (The present U. S. Pharmacopeia method for the assay of phenol calls for 3 grams of potassium bromate and 50 grams of potassium bromide per liter.) One hundred cubic centimeters of this solution were allowed to act on 0.1 gram of phenol for 15 minutes, then 10 cc. of potassium iodide, 125 grams per liter, and 5 cc. of concentrated hydrochloric acid solution were added.

Ditz and Cedivoda (*3*) noted that *o*- and *p*-cresols yield results differing from phenol and *m*-cresol, tending to form dibromo compounds in contrast to the tribromo compounds formed by phenol and *m*-cresol; they concluded also that while tribromophenol brom is completely reduced to tribromophenol by hydriodic acid, dibromo-*p*-cresol brom is only partially reduced; further that in the presence of a large excess of bromine *o*- and *p*-cresols may form tribromocresol broms.

Autenrieth and Beuttel (*1*) found that if bromine is added to *p*-cresol in only slight excess the precipitate is a mixture of dibromocresol brom and dibromocresol. With a large excess of bromine reacting for several days the precipitate was largely (about 88 per cent) converted into tribromophenol brom.

Lloyd (*6*) in a study of the bromine determination of phenol only, concluded that irregularities in results are due to the formation of varying amounts of tribromophenol brom and that this compound is not quantitatively converted into tribromophenol by hydriodic acid. He noted that the formation of tribromophenol brom was promoted by the presence of large excess of bromine and prolonged reaction, while its formation was repressed by the presence of a considerable concentration of acid and also of potassium bromide.

Pence (*8*) investigated a number of the factors affecting the bromine estimation of phenol and cresols. He found that prolonged reaction with a considerable excess of bromine gave higher results for *o*- and *p*-cresol than could be accounted for by the formation of either di- or tribromocresol broms and that reduction with potassium iodide was incomplete, higher results being obtained for *o*-cresol than for *p*-cresol. With *m*-cresol results were nearer theory for the formation of tribromocresol brom, followed by complete reduction to tribromocresol by potassium iodide, but high results were noted on prolonged standing with bromine.

Redman, Weith, and Brock (*9*) confirm the results of Pence and conclude that *o*- and *p*-cresol broms are not readily reduced by potassium iodide because the precipitate of these compounds condenses into dense particles which do not afford free access to the hydriodic acid. They state that with the bromine method the results are too dependent upon the dexterity and patience of the individual experimenters.

Kolthoff and Furman (*4*) conclude that phenol and *m*-cresol are accurately determined with bromine, while *o*- and *p*-cresol require somewhat more than two bromine atoms, the quantity of bromine taken up being dependent upon the amount in excess, the acid concentration, and the time of reaction.

Thus it appears that various reactions may take place upon the bromination of cresols and their subsequent reduction with hydriodic acid, and that their determination by the use of bromine has not met with much favor.

However, preliminary studies led the writer to the opinion that for the purpose of determining phenol and cresols in mixtures, such as for example, gas liquors and coke oven wastes, bromination offered possibilities of greater accuracy than the present iodine methods, and as a result of further experimental work a method was devised with which satisfactorily accurate results may be obtained.

In this work, the data of which is too extensive to be shown in full, the phenol used was a C. P. grade further purified by distillation, retaining the middle third. The cresols used were the "practical" grade of the Eastman Kodak Company, purified by distillation, retaining the middle third, redistilling this portion, and finally retaining the middle third. Some comparisons were also made with Kahlbaum's cresols, redistilling and retaining the middle third; no material differences were noted.

Experimental Data

CONCENTRATION OF ACID—Increase in concentration of hydrochloric acid in the range from 0.05 *N* to 0.25 *N* yielded progressively higher results for *o*- and *p*-cresol, *o*-cresol being the more affected. With higher concentrations the results were not materially higher and some liberation of iodine occurred by the acid alone acting upon potassium iodide. With phenol and *m*-cresol low results were noted with 0.05 *N* acid, maximum results with 0.1 *N*, the same results with 0.25 *N*, and low results with 1.25 *N*.

CONCENTRATION OF POTASSIUM IODIDE—Increase in concentration of potassium iodide in the range from 0.01 to 0.20 molar yielded progressively lower values for *o*-cresol. With *p*-cresol, *m*-cresol, and phenol no material differences were noted.

DURATION OF REDUCTION WITH POTASSIUM IODIDE—Increase in the time allowed for reduction with potassium iodide in the range from 2 minutes to 2 hours yielded progressively materially lower results for *o*-cresol. With *p*-cresol, *m*-cresol, and phenol only a slight progressive decrease in results was noted.

DURATION OF BROMINATION—Increasing the time allowed for the reaction with bromine in the range from 5 minutes to 4 hours yielded progressively much higher results for *o*- and *m*-cresol. A smaller progressive increase was noted for *p*-cresol and a still smaller increase for phenol.

EXCESS OF BROMINE—Raising the excess of bromine present, either by adding more potassium bromate or by taking smaller amounts of phenols, yielded progressively much higher results for *o*-cresol. With *p*-cresol, *m*-cresol, and phenol a much smaller increase in results was noted.

TEMPERATURE DURING BROMINATION—Increase of temperature in the bromine reaction in the range from 20° to 30° C. yielded materially higher results for *o*-cresol and *p*-cresol. With *m*-cresol and phenol no material change in results was noted.

VOLUME OF SOLUTION—Increase in volume of the solution containing phenols, in the range 25 to 250 cc., yielded progressively higher results for *o*- and *p*-cresols. With *m*-cresol a smaller increase was noted and with phenol a still smaller increase. Increase in volume to 700 cc. yielded much lower results in each case. It was observed that with a solution containing 0.025 gram of phenol or cresol in 200 cc., bromination produced a large volume of precipitate with phenol, a smaller amount with *m*-cresol, a very scanty precipitate with *p*-cresol, and no precipitate with *o*-cresol.

CONCENTRATION OF POTASSIUM BROMIDE—Increase in concentration of potassium bromide in the range 0.03 to 0.31 molar yielded a large progressive decrease in results for *o*-cresol, while with *p*-cresol a small progressive increase in results was noted. With *m*-cresol and phenol a small progressive decrease in results was noted. The results of variation in potassium bromide concentration are shown in Table I.

Table I—Effect of Potassium Bromide Concentration

Phenol or cresol taken, 0.0250 gram
Solution containing phenol or cresol, 200 cc.
$KBrO_3$ added, 25 cc. solution containing 3 grams in 1 liter
Acid added, 10 cc. 1:1 HCl
KBr added, 25 cc. solution containing 200 grams in 1 liter
Duration of bromine reaction, 1 hour; temperature, 25° C.
Duration of KI reduction, 30 minutes
$Na_2S_2O_3$, 0.9830 0.1 *N*; 25 cc. = 27.22 cc. $KBrO_3$ solution

KBr	PHENOL		*o*-CRESOL		*m*-CRESOL		*p*-CRESOL	
	$Na_2S_2O_3$	Wt. Phenol	$Na_2S_2O_3$	Wt. *o*-Cresol	$Na_2S_2O_3$	Wt. *m*-Cresol	$Na_2S_2O_3$	Wt. *p*-Cresol
Grams	*Cc.*	*Gram*	*Cc.*	*Gram*	*Cc.*	*Gram*	*Cc.*	*Gram*
0.75	16.52	0.02543	15.72	0.02780	14.52	0.02568	13.97	0.02470
1.50	16.32	0.02512	15.44	0.02730	14.42	0.02550	14.00	0.02475
3.00	16.24	0.02500	15.04	0.02659	14.12	0.02497	14.07	0.02488
6.25	16.22	0.02497	14.12	0.02497	14.02	0.02479	14.10	0.02493
10.00	16.20	0.02494	12.92	0.02285	13.92	0.02462	14.17	0.02506

In general, the results for phenol and *m*-cresol are not greatly affected by changes in the factors noted. *o*- and *p*-cresol are in general affected to a greater extent, *o*-cresol the more markedly with a tendency toward high results, *p*-cresol with a tendency toward low results. Thus, the problem is largely the adaptation of the various factors involved in the direction that lower results would be obtained for *o*-cresol and higher results for *p*-cresol.

Bromine Method for Phenol and Cresols

It was found possible to take advantage of the data obtained in this experimental work to devise a method which has been found to yield reasonably accurate results for phenol as well as for *m*-, *o*-, and *p*-cresol, singly or in mixture, as follows:

After carrying the sample through a suitable preliminary purification treatment, take an aliquot estimated to contain about 0.02 gram of phenol or cresols in terms of phenol and transfer to a 500-cc. glass stoppered flask. Add just enough distilled water to make the volume 200 cc. Add 25 cc. (measured) of potassium bromide solution containing 250 grams in one liter. Add 10 cc. of 1:1 hydrochloric acid solution and place in a water bath held at 25° C. Let stand until the temperature of the solution is 25° C. Add exactly 25 cc. of potassium bromate solution containing 3 grams in one liter. Mix well, then let stand at 25° C. (preferably within 1 degree, at most within 2 degrees) for exactly 60 minutes, shaking two or three times during this period. At the end of this time add 25 cc. of potassium iodide solution containing 200 grams in one liter, mix well, and let stand at 25° C. for exactly 30 minutes, shaking two or three times during this period.

Titrate the liberated iodine with 0.1 *N* sodium thiosulfate, adding starch solution near the end of the titration and disregarding any return of the blue starch-iodine color. Run a blank determination in the same manner.

The difference between the two titrations times 0.0015675 equals the weight of phenol and cresols in terms of phenol. The calculation is made according to the empirical reactions for cresols:

$$C_6H_4.CH_3OH + 8Br = C_6H.CH_3Br_3OBr + 4HBr \quad (1)$$

$$C_6H.CH_3Br_3OBr + 2HCl + 2KI = C_6H.CH_3Br_3OH + 2KCl + I_2 + HBr \quad (2)$$

The net result is 6 mols of bromine for 1 mol of cresol, a similar reaction taking place with phenol. While these reactions may go to practical completion with *m*-cresol, with *o*- and *p*-cresol it is probable that the first reaction only partially takes place, further that the tribromocresol broms which may be formed are incompletely reduced by hydriodic acid to tribromocresols, in which event high values would result. It is probable also that there is a considerable formation of dibromocresol broms with incomplete reduction to dibromocresols, with resulting low values when calculated as tri- compounds, and in addition there may be some conversion of tribromocresols into tribromophenol.

Table II—Results with Various Weights of Phenols

WEIGHTS TAKEN	WEIGHTS FOUND				
	Phenol	*o*-Cresol	*m*-Cresol	*p*-Cresol	**Composite**
Gram	*Gram*	*Gram*	*Gram*	*Gram*	***Gram***
0.0400	0.03947	0.03627	0.03947	0.03867	0.03816
0.03500	0.03463	0.03306	0.03459	0.03425	0.03420
0.03000	0.02980	0.02915	0.02972	0.02951	0.02984
0.02500	0.02496	0.02504	0.02482	0.02490	0.02492
0.02000	0.02000	0.02057	0.01986	0.02000	0.02010
0.01500	0.01500	0.01596	0.01494	0.01504	0.01514
0.01000	0.01006	0.01084	0.01000	0.09980	0.01008
0.00500	0.00504	0.00579	0.00495	0.00499	0.00518

Table III—Effect of Temperature

TEMP. OF SOLN.	WEIGHTS FOUND				
	Phenol	*o*-Cresol	*m*-Cresol	*p*-Cresol	Composite
° *C.*	*Gram*	*Gram*	*Gram*	*Gram*	*Gram*
20	0.02489	0.02417	0.02460	0.02426	0.02452
23					0.02473
25	0.02489	0.02492	0.02469	0.02487	0.02496
27					0.02509
30	0.02489	0.02584	0.02489	0.02540	0.02523

The method presented would seem to provide a balance of these conditions which yields nearly theoretical results.

The above method is accurate for phenol, *o*-, *m*-, and *p*-cresol when the weight present is about 0.022 gram. In the case of phenol, *m*-, and *p*-cresol, considerable variation from this weight does not materially affect the accuracy of the determination. However, with *o*-cresol extreme variations from this weight do materially affect the accuracy of the method. Thus, taking 0.022 gram of *o*-cresol, 100.16 per cent of theory was found; with 0.0261 gram, 97.17 per cent; with 0.0174 gram, 102.85 per cent.

With wastes such as gas liquors and coke oven wastes, while the proportion of *o*-cresol is uncertain and variable, it probably does not exceed one fourth of the total weight of phenol and cresols. On this basis, no appreciable error will be introduced if the indicated weight of phenols in terms of phenol is from 0.01 to 0.03 gram, equivalent to from 6.4 to 19.1 cc. of 0.1 *N* bromine fixed.

If the indicated amount of phenols is without this range, the determination should be repeated, using an aliquot which will fall within these limits.

If the concentration of phenols in the sample examined is so low that it is not practicable to have as much as 0.01 gram present in a volume of 200 cc., it is still possible to obtain results of considerable accuracy by increasing the concentration of potassium bromide. Thus, for weights of phenols of from 0.005 to 0.1 gram, 55 cc. of potassium bromide solution should be added.

Results noted with the method are shown in Table II, 1 cc. of 0.1 *N* bromine being calculated as equivalent to 0.0015675 gram phenol and 0.001801 gram cresol. The results under the heading "Composite" were obtained with a mixture of 4 parts of phenol, 2 parts of *o*-cresol, 1 part of *m*-cresol, and 1 part of *p*-cresol.

The effect of variation in temperature is shown in Table III, the weight taken in each case being 0.025 gram. There remains the error due to calculation of both cresols and phenol in terms of phenol. This may be eliminated if desired, by applying the method of Chapin (*2*) to estimate the proportion of phenol present in the mixture of phenol and cresols.

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Should a Change Be Made in Analytical Procedure for Evaluating Available Phosphoric Acid Content of Fertilizer Materials?[1]

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The rapidly changing fertilizer industry demands that a constant watch be kept on the methods of analysis used to evaluate the plant food content of materials offered.

Most of our present methods have been in use for many years. From time to time minor changes have been made in order that they will be suitable for a greater variety of work.

The present method of determining the available phosphoric acid has recently come into a prominent position due to the introduction of synthetic ammonia as a potential nitrogen-bearing fertilizer material. The use of ammonia either in the anhydrous or aqua form is dependent chiefly on the amount of this material that can be chemically combined with the superphosphate to which it is added. During recent experiments to study conditions accompanying the injection of ammonia into superphosphate, a number of difficulties were encountered with the present official method for determining the insoluble P_2O_5.

Table I—Insoluble P_2O_5 in Ammoniated Superphosphate

Ammonia content, 3.50 to 6.00%

Insoluble P_2O_5		Insoluble P_2O_5	
2-gram sample	1-gram sample	2-gram sample	1-gram sample
%	%	%	%
4.67	2.30	2.46	0.44
0.94	0.33	2.12	1.08
1.78	0.60	3.08	1.36
1.16	0.60	5.09	3.20
1.02	0.32	3.97	1.78
0.86	0.22	1.42	0.46
0.98	0.32	1.72	0.62
3.42	1.68		
3.84	1.60		

This method has been in use with little change for many years and it was with hesitancy, even after thorough painstaking analyses, that these variations were reported. The first of these irregularities was observed when we departed from the official procedure by using a 1-gram portion instead of 2. This deviation was made because it was at first thought that on the addition of ammonia too much dicalcium phosphate had been formed to be soluble in the 100 cc. of neutral ammonium citrate solution. With this deviation the insoluble P_2O_5 present was changed entirely as will be noted in Table I.

Table II—Effect on Insoluble P_2O_5 Results by Varying pH Value of Ammonium Citrate Solution

Ammonium Citrate Soln.	Insoluble P_2O_5	
	Ammoniated superphosphate	Superphosphate (not ammoniated)
pH	%	%
4.5	0.97	0.62
5.0	0.98	0.62
5.2	1.00	0.60
5.3	0.98	0.63
5.4	1.06	0.62
5.6	1.16	0.60
5.8	1.26	0.61
6.0	1.54	0.62
6.3	2.94	0.62
6.6	4.23	0.63
7.0	4.67	0.61
7.8	6.34	0.62
8.4	8.12	0.69
8.8	8.60	0.71
	WITH 1-GRAM PORTION	
7.0	2.30	0.60

After making a number of insoluble determinations on different samples containing varying amounts of ammonia, it became necessary to make up a new neutral ammonium citrate solution. The citrate solution was made up following the prescribed official procedure, using phenol red as the indicator. Following the preparation of the new batch of citrate solution several samples were run that had previously been run with the old citrate solution. The results of these differed very widely from those obtained with the old solution. With these variations it was believed that the difficulty lay in the citrate solution. Upon determining the true reaction of the first citrate solution it was found to have a pH value of 6.5, while the new citrate solution prepared last had a pH value of 7.0. This led to the belief that a slight variation in the pH value of the citrate solution may cause wide variations in the insoluble P_2O_5 results, in material to which ammonia has been added. A number of citrate solutions were then made up with pH values ranging from 4.5 to 8.8. Samples to which ammonia had been added to the extent of 5.76 per cent were then analyzed with

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each of these citrate solutions. Table II shows the results of this experiment. In addition to these figures a 1-gram portion was analyzed with the citrate solution having a pH value of 7.0. An insoluble P_2O_5 figure of 2.3 was obtained, while it will be noted that the 2-gram portion gave an insoluble P_2O_5 of 4.67 per cent. An experiment similar to that shown in the previous tabulation was made with a normal superphosphate—that is, one to which no ammonia had been added. The results of this experiment are also shown in this table.

It will be noted that the variations obtained with the normal superphosphate are within the limits of experimental error.

Another experiment to study the effect of varying the ratio of sample to citrate solution was then carried out, in a 65° C. bath for 30 minutes, on a 2-gram sample of normal superphosphate and on one which had been ammoniated 6.2 per cent. An ammonium citrate solution having a pH value of 7.0 was used. Table III gives the results of this experiment.

Table III—Effect on Insoluble P_2O_5 Results by Varying Amount of Citrate Solution

SUPERPHOSPHATE	AMMONIUM CITRATE					
	100 cc.	200 cc.	250 cc.	300 cc.	350 cc.	400 cc.
	%	%	%	%	%	%
Not ammoniated	0.83	0.78	0.74	0.69	0.66	0.64
	1.90	1.82	1.80	1.82	1.76	1.76
Ammoniated	5.46	2.54	2.01	1.64	1.80	1.49

It will be noted from these results that extreme variations are obtained with ammoniated goods, while the variations with a normal superphosphate are much less and scarcely more than that due to experimental error.

Another series of analyses was made to study the effect of the time of exposure of sample to citrate solution, on both the normal superphosphate and ammoniated superphosphate. In this series both a 1-gram portion and a 2-gram portion of sample were used. These results are shown in Table IV.

Table IV—Effect on Insoluble P_2O_5 Results by Varying Periods of Digestion

SUPERPHOSPHATE	2-GRAM SAMPLE			1-GRAM SAMPLE		
	1/2 hr.	1 hr.	1 1/2 hrs.	1/2 hr.	1 hr.	1 1/2 hrs.
	%	%	%	%	%	%
Not ammoniated	0.83	0.59	0.59	0.74	0.60	0.58
	1.90	1.74	1.74	1.84	1.80	1.76
Ammoniated	5.46	4.33	4.32	1.64	0.78	0.68

Difficulties with Official Method

The official method as it now stands seems to serve well in cases where ammonia has not been introduced, but from the data given in the preceding tabulations it is quite evident that this method will not serve without alteration in cases where ammonia has been introduced. Under the present status innumerable difficulties may be expected. For instance, let us picture for a moment conditions where a manufacturing department depends entirely on the laboratory to govern the compounding of its materials. Good practice demands that the laboratory follow the official method as closely as possible. Let us suppose that ammoniated superphosphate is to be used to compose a mixture. The analyst is required to weigh a 2-gram portion. The results of his analysis will be used to calculate the desired amount of the ammoniated superphosphate to be used. Let us suppose further that in compounding this mixture a 16 per cent available P_2O_5 will be used to give an 8 per cent available P_2O_5 in the finished product. When the sample of the finished material is submitted to the laboratory a 2-gram portion is again weighed. This means that there is the equivalent of only 1 gram of the ammoniated superphosphate taken in the analysis. Let us for a moment refer back to Table I and the first illustration given. This sample shows, with a 2-gram portion, 4.67 per cent insoluble P_2O_5, and with a 1-gram portion, 2.30 per cent insoluble P_2O_5, a difference of 2.37 per cent insoluble phosphoric acid. Such practice could not be tolerated very long. It would mean either reworking the material or sustaining a loss of 2.37 units of phosphoric acid. The same results in varying degrees will be found, depending upon the amount of ammoniated superphosphate used to compose the finished fertilizer mixture.

In addition to plant control difficulties, an unfair discrimination is made against the manufacturer of ammoniated superphosphate in favor of the dry mixer who uses it. The present official method specifies that the ammonium citrate solution shall be neutral, but further states that phenol red may be used as the indicator to determine the neutral point. This leaves it optional with the analyst where no standard indicator solutions are available, as to what the neutral point with phenol red may be. His choice of the neutral point may be anywhere between 6.8 and 8.4, although one would not expect extreme variations. As a matter of curiosity, samples of supposedly neutral ammonium citrate were obtained from a number of laboratories engaged in fertilizer work. The pH value was determined on each of these solutions and they were found to have a range from 6.1 to 7.1. Referring back to the insoluble determinations shown in Table II and visualizing material of this nature being compounded according to the results yielded with the citrate solution having a pH value of 6.1 and later being analyzed in a state control laboratory with a citrate solution having a pH value of 7.0, the results would have a great tendency to place the manufacturer offering such goods in a very bad position. Should it so happen that the pH value of the citrate solutions of the plant control laboratory and the state laboratory be reversed, the results would have a tendency to cause the factory management to make a change in their personnel. However, the results obtained with citrate solutions covering the pH range just mentioned, applied to unammoniated goods, would be satisfactory as shown in Table V.

Table V—Variations in Insoluble P_2O_5 Results with Change in pH Value of Citrate Solution

WEIGHT OF SAMPLE	CITRATE-INSOLUBLE P_2O_5 WHEN pH OF CITRATE SOLUTION IS:										NH_3
	7.0	6.7	6.5	6.2	5.7	5.4	5.0	4.6	4.2	3.5	
Grams	%	%	%	%	%	%	%	%	%	%	
	NORMAL SUPERPHOSPHATE—SLIGHT VARIATION										
2	0.19	0.18	0.16	0.16	0.17	0.16	0.17	0.16	0.16	0.16	None
1	0.18	0.18	0.18	0.17	0.16	0.20	0.17	0.18	0.16	0.16	
2	2.10	2.10	2.11	2.10	2.06	2.11	2.14	2.15	2.24	2.16	None
1	2.04	2.18	2.14	2.08	2.10	2.16	2.14	2.14	2.22	2.12	
	AMMONIATED SUPERPHOSPHATE—WIDE VARIATION										
2	6.66	6.49	6.19	4.52	3.09	2.64	1.89	1.77	1.29	0.72	5.78
1	4.12	4.12	3.60	1.62	0.84	0.66	0.58	0.58	0.56	0.44	
2	5.80	5.80	5.65	3.11	1.84	1.32	0.97	0.80	0.57	0.50	5.03
1	2.54	2.44	2.14	0.62	0.48	0.46	0.46	0.44	0.46	0.42	
2	6.36	6.20	6.12	4.65	3.33	2.76	2.50	2.03	1.41	0.87	5.76
1	4.24	4.26	3.80	2.00	1.16	0.72	0.56	0.58	0.52	0.40	
2	6.46	6.37	6.31	4.59	3.36	2.63	2.18	1.66	1.35	0.64	4.76
1	3.76	3.68	3.44	1.72	0.92	0.70	0.66	0.62	0.62	0.48	
2	5.32	5.26	4.98	3.54	2.07	1.35	1.00	0.66	0.48	0.25	6.21
1	3.48	3.34	3.20	0.98	0.38	0.32	0.30	0.32	0.27	0.26	

New Method Advocated

The main points at issue are: First, that the official method for the determination of insoluble P_2O_5 as it now stands is applicable in cases where ammonia has not been introduced, and the least that can be done is to pay a tribute to the authors who have contributed to such a method that has served well for so many years. We are now confronted with rapidly changing practices and materials, and it is very obvious that it may become necessary to devise an entirely new method to take care of this new product. By continuing with the present method, a hardship is being worked on the manufacturers of fertilizers and on the manufacturers of synthetic and by-product ammonia, as well as on the users of fertilizers. There is no doubt but that the injection of ammonia into fertilizer materials will remedy a number of difficulties with which the manufacturer and farmer have contended for a number of years. By this statement a reduction in the free acid content and an improvement in the storing and drilling qualities of fertilizer materials is meant.

By an injection of ammonia as such into superphosphate or superphosphate-bearing fertilizer materials, it is only with the greatest difficulty that the so-called reversion of the available phosphate is prevented. Numerous publications by various investigators lead to the belief that most of the available phosphoric acid under its present classification reverts to an insoluble form shortly after application to the soil. A number of investigators have also shown that phosphoric acid in that condition is still available as plant food. If these reports be true, and there is every reason to believe that they are, then it seems only reasonable and fair to both the manufacturer and the user that a thorough study be made as promptly as possible of the compounds formed in superphosphate during the injection of ammonia, with a view towards reclassifying and reinterpreting the term "available." Such an investigation involves a large number of pot and field tests and would necessarily have to be accompanied by a large amount of laboratory work. The writers understand that much of this work is now under way.

This seems to be one of the most important manufacturing problems with which the fertilizer industry is confronted today. Much benefit will result to all concerned if the maximum amount of this form of nitrogen can be used. It is essential that this question be very definitely worked out and as soon as possible, because the manufacturer must necessarily anticipate his processes of the future.

It is a duty of this organization to lay aside all precedent and carry on a well organized system of experiments, the results of which will answer the questions with which we are confronted.

Measurement of Abrasion Resistance

I—Paints, Varnishes, and Lacquers[1]

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A method of measuring the abrasion resistance of materials in the form of thin films has been devised. While designed primarily for the study of paint, lacquer, and varnish films, the method should be useful also in the study of a wide range of other materials. The method consists essentially in the following: Carborundum powder of uniform particle size is admitted at a constant rate to a directed stream of air under constant pressure and the resulting Carborundum-air blast is allowed to impinge upon a film of the test material mounted at a fixed angle. The weight of Carborundum required to wear through a unit thickness of material is taken as the abrasion resistance of the material. The development of this test has included an investigation of the variables pertaining both to the apparatus and to the material under test.

SINCE organic finishes such as paints and varnishes are often subject to abrading forces, it is desirable to evaluate them with respect to their resistance to abrasion. Several methods have been developed for this purpose, some of which have been described by Gardner (*1*). Among these, the Parlin method is representative of a type of test in which an abrading surface is moved at controlled pressure and speed over the organic film, and the abrasion value taken as the number of passes required to cut through the material. This method is open to criticism in that an appreciable frictional heating is produced at the interface of film and abrasive and, furthermore, that the abrading surface undergoes variation with use. On the other hand, Gardner's falling sand method, in which the abrasive falls by gravity through a long confining tube and impinges on the paint film, appeared more suitable in principle for the development of a precise test. The method to be described in the present paper has employed a modification of this principle in that air at carefully controlled pressure is used to drive the abrasive against the film under test.

The present abrasion test consists essentially in admitting a stream of Carborundum particles into a rapidly flowing air stream and allowing the uniform mixture of air and Carborundum to impinge against a film of known thickness of the material to be tested. The weight of Carborundum required to wear through the film is measured and arbitrarily defined as the abrasion value for a given thickness of the material. Obviously, in order to obtain reproducibility of measurement, it becomes necessary to hold the conditions of the test constant. With a view to making the method generally applicable, the variables that affect the abrasion value have been studied both as to their nature and relative magnitude.

Although the method is by no means restricted to the determination of relative abrasion resistance of paint films, the test has been developed using these as the test materials. It is well known that the properties of material of this type, especially when of oleoresinous origin, are much affected by temperature and humidity. It seemed necessary, therefore, to carry on this study under controlled air conditions. The effect of temperature and humidity of the air was investigated over a wide range of indoor variation, the air conditions ranging from 21.1° C. (70° F.) and 41 per cent relative humidity to 32.2° C. (90° F.) and 90 per cent relative humidity. The materials tested were: (1) three varnishes of differing oil lengths but of a common synthetic resin; (2) two series of lacquers each of a different resin in three different concen-

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trations; (3) a baked japan, a baked varnish, and a varnish enamel.

Apparatus and Procedure

The abrasion machine, which is shown together with pressure regulating devices in Figure 4, consists essentially of a box into the upper portion of which a nozzle confining the air-Carborundum stream is inserted. An adjustable table, upon which the sample to be tested is mounted, is brought into position against the lower end of the nozzle. For films over opaque base materials, illumination is effected from the front through a window in a door through which the sample is introduced. For films over transparent base, illumination is effected through a window in the rear. The Carborundum falls into a lower compartment of the box and a finely meshed screen allows the air to escape while retaining the Carborundum. For an actual determination, the test specimen is mounted in place, the air turned on, and when at equilibrium pressure, the Carborundum stream is started by removing a pinch clamp from the tube leading to the weighed container of Carborundum situated above the abrasion box. As soon as the blast of abrasive wears through the film revealing the underlying base uniformly over a small area about 2 mm. in diameter, the Carborundum stream is shut off and the loss in weight of the Carborundum container measured. The thickness of the film is determined at several points at the edge of the wear spot and the number of grams required to wear through unit film thickness calculated.

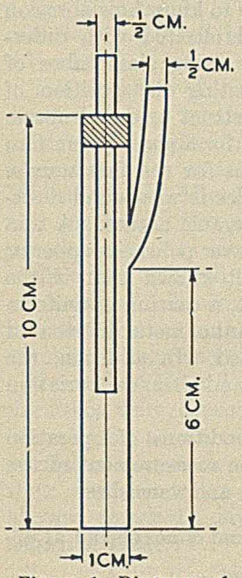


Figure 1—Diagram of Nozzle

In the present study, air at the desired temperature and humidity was obtained by compressing the air from the room, which was automatically conditioned. The heat generated by compression was dissipated by allowing the air to flow through a copper coil within a large water bath held at room temperature. The pressure of the air was then regulated by an adjustable T-outlet in a column of water. An equalizing reservoir was employed to smooth out minute fluctuations. Pressure as delivered to the abrasion machine was determined by means of a mercury manometer.

The heart of the instrument consists of the nozzle in which the air and Carborundum streams are intimately mixed. Many designs were tried and for the present development a nozzle shown in Figure 1 was employed.

This design combines simplicity of construction with ease of duplication, and it has made possible measurements of high precision. For ease of duplication of nozzles, a straight air tube was found essential, since any bends or kinks markedly affected the abrasion value obtained. In order to calibrate a new nozzle of this same design against a nozzle of known performance, it was necessary only to adjust the position of the inner air tube, by lowering or raising, with respect to the outer confining tube. The difference of diameters of the two tubes produces a flaring of the air stream with the result that the Carborundum which is introduced by gravity at any suitable point above the end of the inner tube is uniformly mixed with the air.

Variables Pertaining to Method

Since this study was conducted on paint films of various types, which unfortunately are variable in both physical and chemical behavior, it seemed desirable to segregate the variables that pertain to the method from those dependent on the material tested. Consequently, the various test variables are first discussed, and afterward the application of a standardized test to a variety of materials is shown.

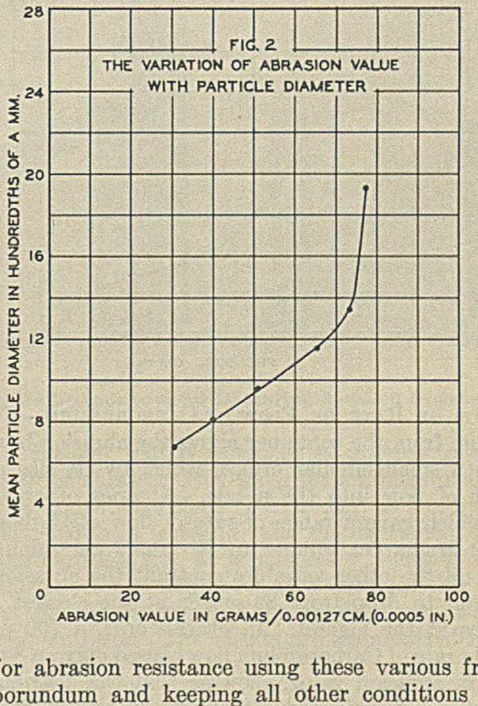
Effect of Position of Test Specimen on Abrasion Value—The position of the test specimen with respect to the end of the nozzle was varied both in distance from the end and in angle with respect to nozzle. The results are summarized in Table I.

Table I—Effect of Position of Test Material, Lacquer No. 18, on Abrasion Value

Distance from Nozzle	Angle to Perpendicular	Abrasion Value
Cm.	*Degrees*	*Grams*
0.0	45	31.8
0.5	45	35.8
1.0	45	44.5
0.0	30	22.2
0.0	45	31.5
0.0	60	50.1

The selection of a definite position is more or less arbitrary, so that in all subsequent experiments the test specimen was placed against the nozzle and at 45 degrees.

Effect of Particle Size—By means of standard A. S. T. M. sieves of 80, 100, 120, 140, 170, 200, and 230 mesh Carborundum was separated in a mechanical shaker into the various intermediate fractions. Sufficient time was allowed in the shaker to permit reasonably clean separation. A lacquer film of known composition and thickness was then tested for abrasion resistance using these various fractions of Carborundum and keeping all other conditions of test constant.



The results of this experiment are given in Table II.

Table II—Effect of Particle Size on Abrasion Value

Mesh Size	Mean Diameter of Particles	Abrasion Value
	Cm.	*Grams/0.0127 mm.*
80–100	0.0193	77.5
100–120	0.0134	73.3
120–140	0.0115	65.2
140–170	0.0097	51.0
170–200	0.0081	40.0
200–230	0.0068	30.7

The variation of abrasion value with particle size is graphically shown in Figure 2. For the small particles, the relation seems to be linear. For practical purposes, a given range of particle size must be selected, and since the smaller particles tend to give a more uniform wear spot the fraction between 170- to 200-mesh sieves was used in all succeeding experiments.

Effect of Air Pressure—In this experiment the effect of changes in air pressure alone was investigated. The results are given in Table III.

Table III—Effect of Air Pressure on Abrasion Value

Pressure *Cm. Hg*	Abrasion Value *Grams/0.0127 mm.*
2.8	246.5
3.85	151.8
5.0	99.6
6.0	79.0
6.9	66.9
7.8	56.5

Figure 3, graphically representing the values of Table III, shows how the abrasion value decreases as pressure increases. As higher pressures are approached, the rate of change of the abrasion value decreases. For this reason a pressure of about 6 cm. of mercury was selected as a standard condition. At this pressure the time required with the selected rate of flow of Carborundum was found convenient for all types of films tested.

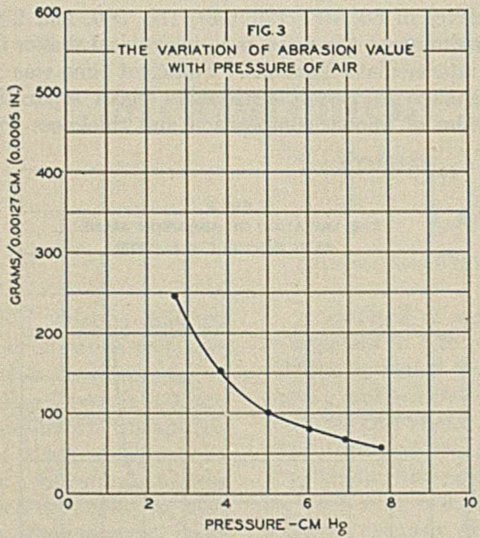


FIG. 3
THE VARIATION OF ABRASION VALUE WITH PRESSURE OF AIR

Effect of Rate of Flow of Carborundum—The Carborundum from the container above the abrasion box passes through a small circular orifice, which by its size controls the rate of flow into the nozzle. A series of orifices was tested which gave a range of rate of flow of Carborundum from 12 grams per minute to 86 grams per minute. On holding all the other variables constant the abrasion value was found to drop from 86 grams at the slowest rate to 80 grams at the highest. In other words, a 700 per cent change in rate of Carborundum flow caused only an 8 per cent change in abrasion value, showing that the distribution of the Carborundum in the air stream is almost insensitive to its rate of introduction. A rate of flow of about 24 grams per minute of 170- to 200-mesh Carborundum was selected as standard.

Effect of Source and Use of Carborundum on Abrasion Value—Two separate lots of Carborundum were screened and the 170- to 200-mesh fraction was used to determine the abrasion value of a given material. The same average value was obtained in the two sets of determinations, the difference being within the experimental error.

Various experiments indicated that, if so desired, the same Carborundum could be used safely for several determinations. A 5-pound (2.3-kg.) lot of Carborundum of 170 to 200 mesh was used repeatedly in the course of 200 wear determinations. On comparison of this used Carborundum with fresh material the same abrasion values were obtained on a given film. Furthermore, a screen analysis of the used and unused Carborundum showed no reduction in particle size, although a microscopic examination at a magnification of 170 × revealed slight chipping on some of the cutting edges.

Reproducibility of Abrasion Value with Duplicate Nozzles—It is of practical importance to know how abrasion values on any one material can be duplicated with different nozzles of the same design. By using glass tubes of approximately equal bore, and adjusting the position of the inner tube, it was possible to construct a second nozzle which gave an average abrasion value for a given japan film of 100.4 grams as against 100.2 grams for the first nozzle.

For purposes of calibration of nozzles it was found desirable to use a test film of other than organic nature. A thin electroplated coat of cadmium or zinc over polished copper or brass proved satisfactory. It is well known that if the conditions of plating are held constant, a coating of uniform thickness is obtained. The exact amount of metal distributed over the surface is readily determined. In addition, the material is not subject to the physical and chemical variation which organic films show with age.

In recapitulation, the following conditions of operation were shown to be well adapted for the measurement of the abrasion resistance of paints, lacquers, and varnishes:

Position of test specimen—flush against end of nozzle and at 45-degree inclination
Particle size of Carborundum—170 to 200 mesh
Air pressure—6 cm. of mercury
Rate of flow of Carborundum—24 grams per minute

Application of Test

It now became of interest to apply this standardized test to the evaluation of the abrasion resistance of various organic finishing materials. For this study a number of different varnishes and lacquers were formulated. The varnishes designated as V-15, V-16, and V-17 were of the compositions shown in Table IV.

Table IV—Composition of Varnishes

Component	V-15 *% by wt.*	V-16 *% by wt.*	V-17 *% by wt.*
Amberol resin	20.62	16.7	14.11
China wood oil	23.92	26.26	28.42
Linseed oil (bodied)	5.92	6.68	7.13
Lead acetate	0.15	0.165	0.18
Liquid cobalt	0.27	0.30	0.33
Mineral spirits	49.72	49.90	49.83
Total metal (ratio Pb:Co = 19:1)	0.086	0.095	0.103
Oil length, gal.	18	25	32

Six lacquers of the composition indicated in Table V were used.

Table V—Composition of Lacquers

Component	L-17 %[a]	L-18 %	L-19 %	L-20 %	L-21 %	L-22 %
1/2-sec. cotton, dry basis	60.5	45.4	36.4	60.5	45.4	36.4
Ester gum	30.4	45.4	54.5	..	..	..
Amberol gum	..	..	..	30.4	45.4	54.5
Dibutyl phthalate	9.1	9.1	9.1	9.1	9.1	9.1

[a] All per cents by weight.

In addition to these materials, a baked varnish, a baked black japan, and a varnish enamel were studied. The abrasion values for these materials as given in the succeeding tables represent the mean of two or more readings with the precision of the order given in a later separate discussion on the precision of the method.

All of the test specimens were prepared on best grade window glass by the spinning disc method and the films were allowed to dry in a horizontal position. Glass was selected as the base material because it is inert, relatively flat, and permits greater ease of observing end points. Furthermore, it was felt that the absolute abrasion value would be only slightly affected by this choice, since in the test, cohesion of the material primarily determines the values and adhesion plays only a small part. Only with extreme care was it possible to obtain thicknesses of good uniformity. In general, varnishes were better than the lacquers owing to their longer period of leveling. The uniformity of the lacquer films was definitely improved by the addition of slower evaporating solvents.

The thickness of the films was determined by means of an Ames dial gage reading to 0.0001 inch and permitting estimation of hundredths of a mil. The gage was checked against a Zeiss optimeter, Johannsen blocks, and a Pratt Whitney Super Micrometer, and showed excellent accuracy and precision. For use on compressible paint films, the practice of gently lowering the spindle of the gage on the surface was adhered to. An accuracy within ±0.02 mil was attained. However, an accuracy of 1 per cent is desirable in the thickness measurements when the precision of the abrasion measurement is considered.

Effect of Film Thickness on Abrasion Value—Since varnishes were expected to show a non-linear relationship between film thickness and abrasion value, the three different varnishes were each spun to three different thicknesses and their abrasion value measured. The sample panels were allowed to age 18 days after preparation. The results are shown in Table VI.

Table VI—Effect of Film Thickness on Abrasion Value of Varnishes

Material	V-15			V-16			V-17		
Thickness:									
Mil	0.37	0.62	1.03	0.44	0.53	1.13	0.49	0.78	0.96
Cm. × 10^{-3}	0.94	1.58	2.62	1.12	1.35	2.87	1.25	1.98	2.44
Abrasion value, grams	45.2	90.0	151.1	67.0	82.7	192.6	86.9	164.9	255.0

Table IV, which contains the varnish formulas, and Table VI show that as the oil length of the varnish increases the deviation from a linear relation becomes more pronounced. This indicates that such films at this age had not dried through uniformly. However, the short length varnish V-15 showed practically a linear relation. In general, then, varnishes ought to be compared for abrasion value at comparable levels of thickness.

Effect of Age—In order to enhance the effect of aging, panels coated with all the materials under test were maintained at 60° C. (140° F.) in an air oven for a period of 5 weeks and then compared for abrasion value with freshly prepared films. All the coatings were approximately 0.0127 mm. (0.5 mil) in thickness. Table VII shows the results of the aging test.

Table VII—Effect of Aging on Abrasion Value

Material	Abrasion Value, Grams/0.0127 mm. Unaged film[a]	Aged film
L-20	54.8	45.5
L-21	38.9	33.6
L-22	41.3	35.8
V-15	79.2	67.0
V-16	93.0	87.6
V-17	118.8	101.0

[a] The lacquer films were 2 days old and the varnish 6 days; both were maintained at 70° F. (21.1° C.) and 65 per cent relative humidity prior to test.

Just how much the normal aging of these films was accelerated as the result of maintenance at the elevated temperature is conjectural. For either type of material, it will be observed that the change in abrasion value was not large. It is apparent, however, that the abrasion test reveals the effect of aging.

Effect of Temperature and Humidity of Air on Abrasion Value—The various films employed in the present investigation were allowed in different experiments to come to equilibrium with the air and were maintained at four different conditions of temperature and humidity. The values obtained for abrasion resistance are given in Table VIII.

Table VIII—Effect of Temperature and Moisture on Abrasion Value

Material	70° F. (21.1° C.) 41% R. H. *G./0.0127 mm.*	70° F. (21.1° C.) 65% R. H. *G./0.0127 mm.*	90° F. (32.2° C.) 41% R. H. *G./0.0127 mm.*	90° F. (32.2° C.) 90% R. H. *G./0.0127 mm.*
L-17	53.5	44.3	49.0	49.7
L-18	45.3	37.8	36.6	40.0
L-19	30.0	24.8	25.6	30.1
L-20	54.3	55.8	44.6	48.3
L-21	38.7	38.9	33.1	35.5
L-22	41.7	41.3	34.7	36.7
V-15	61.0	79.2	76.9	98.2
V-16	69.0	93.0	88.1	118.8
V-17	106.0	118.8	119.0	172.2
Baked varnish	88.0	78.6	82.5	95.6
Varnish enamel	61.4	58.2	62.5	81.6
Baked japan	77.4	66.4	66.4	68.8

It has been shown by Lowry and Kohman (*2*) that the quantity of water absorbed by rubber and paper from the atmosphere is approximately constant at various temperatures provided the relative humidity is held constant. It was assumed that the same relationship held true for paint films and a means was thereby afforded of separating the effect due to temperature changes from those due to changes in moisture of the film.

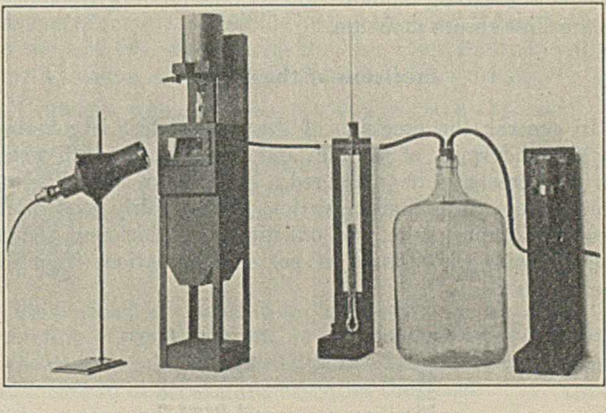


Figure 4—Apparatus for Measuring Abrasion Resistance

It was thought that it would be of interest to correlate the values for abrasion with those for hardness of the films under the above conditions of humidity and temperature. The Pfund hardness tester (*3*) was the instrument used for measuring hardness and, as is customary, the load required to give a diameter of impression of 3 units (in this case 0.3 mm.) on the vernier scale of the eyepiece was arbitrarily defined as hardness. The results are summarized in Table IX.

Table IX—Effect of Moisture and Temperature on Pfund Hardness

Material	70° F. (21.1° C.) 41% R. H. *G./0.3 mm.*	70° F. (21.1° C.) 65% R. H. *G./0.3 mm.*	90° F. (32.2° C.) 41% R. H. *G./0.3 mm.*	90° F. (32.2° C.) 90% R. H. *G./0.3 mm.*
L-17	1050	825	940	500
L-18	1185	850	1200	500
L-19	1000	900	900	500
V-15	500	380	200	2
V-16	285	235	80	10
V-17	150	40	20	4
Baked varnish	1500	1370	1360	900
Varnish enamel	425	265	235	12

The amberol lacquer series (L-20–L-22) showed cracking of the film when tested at the 70° F. and 41 per cent humidity condition and was therefore omitted.

Inspection of Tables VIII and IX leads to some interesting observations on the behavior of the materials with change in temperature and moisture content of the films.

EFFECT OF TEMPERATURE—(*a*) The temperature coefficient of abrasion is greater for the varnishes than for the lacquers. At 41 per cent relative humidity, a change from 70° F. to 90° F. causes the varnishes to increase in abrasion resistance, while the lacquers, the japan, and the baked varnish decrease over the same range of temperature. The varnish enamel shows no temperature coefficient.

(*b*) All of the materials soften with increase in temperature, the change being greatest in the case of the varnishes.

EFFECT OF MOISTURE—(*a*) The abrasion values for the varnishes increase markedly with increase in moisture content of the films, the change becoming more pronounced with increasing oil lengths. For example, the longest oil varnish tested, V-17, displays an increase in abrasion value of 45 per cent at 32.2° C. (90° F.) over the range of humidities investigated.

(*b*) The amberol lacquers show only a slight increase in abrasion resistance with increase in humidity, while the ester gum lacquers, the japan, and the baked varnish appear to pass through a minimum abrasion value in the neighborhood of 65 per cent relative humidity.

(*c*) The hardness for all the materials decreases definitely as the films take up moisture.

(*d*) The spread of hardness values for the varnishes is greater at the lower humidities, the values tending to converge as the films absorb moisture.

Precision of the Method

In general, the precision of the present test is governed by the uniformity of the film and the accuracy with which its thickness can be measured. A series of 116 different abrasion determinations on various films of fairly good thickness uniformity gave, on omitting the thickness factor, the following distribution of per cent deviations from the mean value:

No. of Detns.	Deviation Limits %
46	0.0 to 0.5
24	0.5 to 1.0
28	1.0 to 2.0
16	2.0 to 3.0
2	3.0 to 4.0

The average per cent deviation of these determinations was 0.99.

To illustrate how the precision of the abrasion determinations depends on the smoothness of the film surface, a series of lacquers that exhibited an orange peel surface, when re-spun with a slow evaporating solvent to eliminate orange peel effect, gave the reduction of the average per cent deviation from the mean value from 6.2 to 0.6 per cent.

Investigation showed that the method of illumination—i. e., whether from the rear or from the front—has very little effect upon the attainable precision. The choice of a relatively large bare area, 2 mm. in diameter, for the end point, rather than the first appearance of tiny pinholes was influenced by the fact that the larger area is more representative of the film as a whole. The high order of precision which was obtained in the application of the test justifies this choice of end point. It was found that the time difference between the first pinhole and the end point selected, increased as the total time required for the test increased.

Discussion

The method of measuring abrasion resistance described in the present paper should provide a useful tool of high precision in research on the formulation of paint materials. Since this method concerns itself primarily with cohesional characteristics of materials it may be used to study the influence of composition on those qualities related to cohesion. A more definite interpretation of the fundamental significance of this test should be obtained in the study now under way in which it is sought to correlate abrasion and hardness with tensile strength and elongation.

The direct application of the test to paint films with a view to correlating the abrasion values as measured with service performance still requires considerable study, since abrading forces in service produce wear degradations in a variety of ways. A direct application of the test in the form described may be in the evaluation of the relative abrasion resistance of paint, lacquer, and varnish films when used in the airplane industry. No question of significance need arise in this application, since the air speeds in service and in the test are comparable and it has been shown that relative concentration of abrading particles is negligible when distributed randomly. Quite likely, by a suitable choice of air pressures, particle sizes, and particle concentrations, other typical forms of wear action by forces of abrasion can be made to simulate service conditions, in that manner simplifying the problem of interpretation of the test for practical purposes.

As mentioned previously in this paper, the test is not restricted to the evaluation of abrasion resistance of paint materials. For instance, it has been found that various electroplated metals, chromium, zinc, and cadmium, gave a wide range of values for abrasion resistance with a high degree of duplicability. It seems likely that this method may serve as an effective means of investigation of the wearing quality of electrodeposits.

Literature Cited

(1) Gardner, H. A., "Physical and Chemical Examination of Paints, Varnishes, Lacquers and Colours," 4th ed., Institute of Paint and Varnish Research, 1927.

(2) Lowry, H. H., and Kohman, G. T., *J. Phys. Chem.*, **31**, 23–57 (1927).

(3) Pfund, A. H., *Proc. Am. Soc. Testing Materials*, **25**, 393 (1925).

Alcohol Replacing Gasoline in Brazil—Among the methods used in Brazil to encourage the use of alcohol motor fuel instead of gasoline is a 50 per cent reduction in tariff fines in the City of Maceio to motorists using the fuel, according to a statement by the Department of Commerce.

The alcohol fuel is a domestic Brazilian product made from sugar waste and is being marketed in competition with imported gasoline, a considerable part of which comes from the United States. The retail price of gasoline during the third quarter of the year in Rio de Janeiro ranged from 40 to 45 cents, according to the department.

In the Pernambuco area of Brazil gasoline sales have been greatly reduced in recent months and importations have correspondingly decreased. United States exports of gasoline to Brazil during the first nine months of 1930 exceeded 1,000,000 barrels, which was nearly equal the amount of the corresponding period of 1929. Exports during the month of October, however, were slightly more than 14,000 barrels as compared with more than 120,000 barrels in the same month of a year ago.

Whether alcohol motor fuel will be able to maintain itself as a satisfactory substitute for gasoline cannot be settled until the public has learned its effect on motors and carburetors, whether it is more economical and whether it develops satisfactory power.

The Iodide Method for Copper[1]

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In the presence of much arsenic the usual iodide method for copper gives high results. By increasing the pH of the solution during the titration the action of arsenic acid on potassium iodide is retarded, but so is the action of copper. Maximum pH values at which cupric ion is completely reduced by iodide ion have been determined. These pH values vary with different acids because of the formation of insoluble or slightly ionized compounds of copper. The maximum pH value at which arsenic acid liberates iodine from potassium iodide solutions has been determined.

General equations for the calculation of the electrode potentials of solutions of arsenic and arsenious acids and of solutions of iodine and iodide have been developed. The theoretical maximum pH value at which arsenic acid liberates iodine from potassium iodide solution has been calculated and shown to agree substantially with the value obtained by experiment.

A solution containing copper, arsenic acid, and potassium biphthalate may be adjusted to a pH value at which all of the copper but none of the arsenic will react with iodide.

The action of ferric iron on potassium iodide may be completely suppressed, in the absence of manganese, by the addition of ammonium bifluoride.

A very short and accurate method for determining copper in ores, slags, mattes, etc., has been developed from the above considerations.

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A COMPREHENSIVE survey of the literature pertaining to the iodide method for copper disclosed the following facts:

When a solution of cupric ion is treated with an excess of potassium iodide, the following reaction takes place:

$$2Cu^{++} + 4I^- = 2CuI + I_2$$

The liberated iodine may be reduced to iodide ion by the action of standard sodium thiosulfate solution and the quantity of copper calculated, providing that the reaction proceeds quantitatively to the right, no other substance which oxidizes iodide ion to iodine is present, and no substance which reduces free iodine to iodide ion is present.

Ferric iron will liberate iodine, and, as it is almost always present in copper ores, provision must be made for removing it or rendering it inactive. In Low's iodide method (*14*) iron is separated from copper by means of aluminum. In Mott's short iodide method (*15*) it is changed to ferric fluoride, which has no effect on potassium iodide on account of the very slight dissociation of this substance.

Arsenic in its trivalent form reduces free iodine, and in strongly acid solutions pentavalent arsenic liberates iodine from potassium iodide. No provision for removing arsenic is made in either of the above methods. Low in his method states that arsenic is without effect.

The following questions were selected for more detailed study:

(1) Under what conditions do arsenic and antimony liberate iodine from iodides?

(2) What hydrogen-ion concentration is best for the reaction between cupric ion and iodide ion, and how may this optimum concentration be obtained?

(3) Is it necessary to remove iron, and if not what is the best method for preventing its action on iodides?

Effect of Arsenic on Iodide Method for Copper

Experiments were made to find out whether or not arsenic affects either Low's or Mott's method. The results are given in Table I. In each case 50 cc. of copper sulfate solution containing 0.2 gram of copper were carefully measured with a pipet, and acetic acid and ammonium bifluoride were added in the proportions noted. To some of the samples arsenic acid solution was added. Then 3 grams of potassium iodide were put into each, and the liberated iodine titrated with standard thiosulfate solution. Each result is the mean of two or more titrations. Evidently pentavalent arsenic does have an effect upon either the long or the short iodide method. In the last two experiments the blue color returned within 2 or 3 minutes after the end point had been reached.

Table I—Effect of Arsenic on Low's and Mott's Method

COPPER TAKEN	16 *N* ACETIC ACID	AMMONIUM BI-FLUORIDE	POTASSIUM IODIDE	ARSENIC	COPPER FOUND
Gram	*Cc.*	*Grams*	*Grams*	*Gram*	*Gram*
0.2000	10	...	3	...	0.2000
0.2000	5	...	3	...	0.2000
0.2000	5	...	3	0.1	0.2010
0.2000	5	...	3	0.2	0.2015
0.2000	2	2	3	0.2	0.2015

More detailed information than could be found in the literature (*1, 3, 6–8, 11, 12, 16–22*) was desired on the reaction between arsenic acid and iodide ion and a series of experiments to determine the extent of this reaction at various hydrogen-ion concentrations was undertaken.

Solutions containing a constant amount of arsenic acid at different hydrogen-ion concentrations were prepared. A measured quantity of potassium iodide solution was added to each, and at the end of 5 minutes the liberated iodine was determined by titration with dilute thiosulfate. The results are given in Table II and Figure 1.

Table II—Reaction between Arsenic Acid and Iodide Ion at Various pH Concentrations

ARSENIC TAKEN	pH OF SOLUTION	THIOSULFATE	ARSENIC REDUCED
Gram		*Cc.*	%
0.0230	2.51	1.55	0.219
0.0230	2.61	1.30	0.184
0.0230	2.85	1.14	0.161
0.0230	2.93	1.01	0.143
0.0230	3.12	0.90	0.127
0.0230	3.33	0.70	0.099
0.0230	3.64	0.50	0.072
0.0230	4.77	None	None

In all of the titrations 10 cc. of arsenic acid in potassium biphthalate buffer solution were treated with 3 cc. of potassium iodide solution containing 2 grams of potassium iodide. After 5 minutes 1 cc. of starch solution was added, and the liberated iodine titrated with dilute thiosulfate solution, 1 cc. of which was equivalent to 0.00003 gram of arsenic. The duration of the titration was 1 minute. By means of the quinhydrone electrode the hydrogen-ion concentration was determined on another portion of each arsenic-

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[1] Received September 12, 1930. A thesis submitted for the degree of master of science in chemistry at the Michigan College of Mining and Technology.

phthalate solution before the addition of potassium iodide.

Another set of solutions was prepared in which phosphate buffers were substituted for phthalate solutions. These were titrated as before, and the curve obtained from plotting the results was practically the same as that given in Figure 1.

The reaction may be written

$$H_3AsO_4 + 2HI = H_3AsO_3 + I_2 + H_2O$$

or, assuming the existence of the triiodide ion

$$H_3AsO_4 + 3HI = H_3AsO_3 + HI_3 + H_2O$$

In addition to the hydrogen-ion concentration, the iodine and iodide concentrations, the temperature, and the time all affect the amount of iodine liberated by a given weight of arsenic. Table II and Figure 1 show only the trend. It should be noted that under the usual conditions of acidity prevailing in the final solution when copper is being determined by the iodide method, any arsenic present will not start to react until most of the iodine has been titrated.

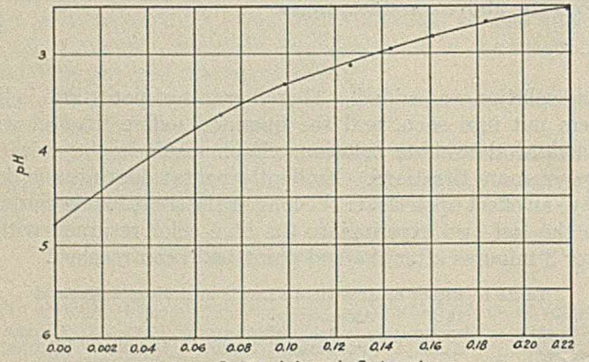

Figure 1—Liberation of Iodine at Various pH Concentrations

As the titration is usually performed rather rapidly, any arsenic present will not have a chance to react with iodide ion for a long enough time to reach equilibrium. A reaction period of 5 minutes was arbitrarily chosen for the experiments listed in Table II. This period was thought to represent the usual length of time during which arsenic would have a chance to react while a titration was being performed. The concentration of potassium iodide in all of these experiments with arsenic was greater than it would ordinarily be in a copper titration. Nevertheless, it appears that at the usual acidities and concentrations occurring in the iodide method, arsenic, if present, is a distinct menace to the accuracy of the copper determination.

Similar buffer solutions were prepared from antimony, and the results of titration were plotted as before. The curve obtained was practically the same as that given for arsenic in Figure 1.

Another series of experiments was carried out in the following manner: Ten cubic centimeters of arsenious acid solution containing sodium carbonate, potassium biphthalate, and a little starch were treated with a solution of iodine in potassium iodide until the blue starch-iodine color just appeared. One drop of arsenious acid solution was added, which discharged the color. Dilute sulfuric acid was added 1 cc. at a time to the colorless solutions and pH determined after each addition until the blue color reappeared. Duplicate determinations gave pH 3.65 and pH 3.50 as the points at which the blue first became apparent.

These experimental results are in substantial agreement with the results predicted theoretically by the oxidation-reduction potentials of the iodine-iodide and the arsenic-arsenious couples, as is shown below.

Oxidation-Reduction Potentials of Arsenic-Arsenious Solutions

The reaction of arsenic acid acting as an oxidizing agent or of arsenious acid acting as a reducing agent may be formulated thus:

$$HAsO_4^{--} + 2e + 4H^+ \rightleftharpoons H_3AsO_3 + H_2O$$

The ionization constants for the third step in the ionization of arsenic acid and for the first step in the ionization of arsenious acid are practically the same (*2*, *5*, *9*, *24*, *25*) and therefore they need not be considered in the treatment which follows.

The equilibrium state may be formulated thus:

$$\frac{(HAsO_4^{--})\,(e)^2\,(H^+)^4}{(H_3AsO_3)} = K \qquad (1)$$

from which

$$e = \sqrt{\frac{K(H_3AsO_3)}{(H^+)^4\,(HAsO_4^{--})}}$$

substitution of this value of (*e*) in the general electrode equation (*4*)

$$E = \frac{RT}{F}\ln(e_m) - \frac{RT}{F}\ln(e_s) \qquad (2)$$

in which (e_m) and (e_s) represent the electron concentrations in the metallic electrode and the solution gives:

$$E = \frac{RT}{F}\ln(e_m) - \frac{RT}{F}\ln\sqrt{\frac{K(H_3AsO_3)}{(H^+)^4\,(HAsO^{4--})}} \qquad (3)$$

Rearrangement and combination of constants gives

$$E = C + \frac{2RT}{F}\ln(H^+) - \frac{RT}{2F}\ln\frac{(H_3AsO_3)}{(HAsO_4^{--})} \qquad (4)$$

It is convenient to have the expression in terms of the total concentrations of arsenic and arsenious acid present instead of in terms of the ion concentrations. In solution the total reductant, *Sr*, may be assumed to equal the concentration of arsenious acid, and the total oxidant, *So*, may be assumed to be given by the sum of the concentrations of the various ions and unionized substances containing pentavalent arsenic.

$$So = (HAsO_4^{--}) + (H_2AsO_4^-) + (H_3AsO_4) \qquad (5)$$

The equilibrium equations for the first and second steps in the ionization of arsenic acid are

$$\frac{(H_2AsO_4^-)\,(H^+)}{(H_3AsO_4)} = Ko_1$$
$$\frac{(HAsO_4^{--})\,(H^+)}{(H_2AsO_4^-)} = Ko_2 \qquad (6)$$

Substitution of values obtained from these equations in Equation 5 gives

$$So = (HAsO_4^{--}) + \frac{(HAsO_4^{--})\,(H^+)}{Ko_2} + \frac{(HAsO_4^{--})\,(H^+)^2}{Ko_1\,Ko_2} \qquad (7)$$

from which

$$(HAsO_4^{--}) = So\,\frac{Ko_1\,Ko_2}{Ko_1\,Ko_2 + Ko_1\,(H^+) + (H^+)^2}$$

Substitution of this value of ($HAsO_4^{--}$) and of *Sr* for (H_3AsO_3) in Equation 4 gives

$$E = C + \frac{2RT}{F}\ln(H^+) - \frac{RT}{F}\ln\frac{Sr}{So} - \frac{RT}{F}\ln\frac{Ko_1\,Ko_2 + Ko_1\,(H^+) + (H^+)^2}{Ko_1\,Ko_2} \qquad (8)$$

At 25° C. $\frac{RT}{F}$ ln is equal to

$$\frac{1.9885 \times 298 \times 2.3026}{23074} \log = 0.059 \log$$

Ko_1 is about 5×10^{-3} (*23*) and Ko_2 is about 4×10^{-5} (*2*) depending upon the concentration of the arsenic acid.

Substituting these values in Equation 8 and remembering that $-\log (H^+) = pH$ we get

$$E = C - 0.118\ pH - 0.0295 \log \frac{Sr}{So} - 0.0295 \log \frac{2 \times 10^{-7} + 4 \times 10^{-5} (H^+) + (H^+)^2}{2 \times 10^{-7}} \quad (9)$$

Equation 9 is the general equation for the electrode potential, E, of any solution containing arsenic and arsenious acids.

Washburn and Strachan (*23*) found that, when the activities of arsenic acid, arsenious acid, and hydrogen ion are all equal to unity, E equals 0.574 volt. Substitution of these values in Equation 9 gives

$$0.574 = C - 0.197 \text{ or } C = 0.771 \quad (10)$$

The complete general equation is therefore

$$E = 0.771 - 0.118\ pH - 0.0295 \log \frac{Sr}{So} - 0.0295 \log \frac{2 \times 10^{-7} + 4 \times 10^{-5} (H^+) + (H^+)^2}{2 \times 10^{-7}} \quad (11)$$

which may be used to calculate the potential of any mixture of arsenic and arsenious acids at any hydrogen-ion concentration. An alternate method of calculating the value of C follows.

When equilibrium is reached in the reaction between arsenic acid and iodide, the equation may be written

$$HAsO_4^{--} + 3I^- + 4H^+ \rightleftharpoons H_3AsO_3 + I_3^- + H_2O$$

and the following relationship holds

$$\frac{(HAsO_4^{--})\ (I^-)^3\ (H^+)^4}{(H_3AsO_3)\ (I_3^-)} = K \quad (12)$$

This may be combined with Equation 6 to give

$$\frac{(H_3AsO_4)\ (I^-)^3\ (H^+)^2}{(H_3AsO_3)\ (I_3^-)} = K^1 \quad (13)$$

Washburn and Strachan calculated the value of K^1 from seven equilibrium experiments and found an average at 25° C. of 5.54×10^{-2}. They also found that in the following equilibrium K has a value of 1.3×10^{-3} at 25° C.

$$\frac{(I^-)\ (I_2)}{(I_3^-)} = K = 1.3 \times 10^{-3}$$

or

$$(I_3^-) = \frac{(I^-)\ (I_2)}{1.3 \times 10^{-3}} \quad (14)$$

Substitution of these values in Equation 13 gives

$$\frac{(H_3AsO_4)\ (I^-)^2\ (H^+)^2}{(H_3AsO_3)\ (I_2)} = 42.6 \quad (15)$$

The average value of Ko_1 in Washburn and Strachan's experiments was 5.6×10^{-3}. When this value and that of Ko_2 given previously are substituted in Equation 6,

$$(H_3AsO_4) = \frac{(HAsO_4^{--})\ (H^+)^2}{2.25 \times 10^{-7}}$$

Substitution of this value in Equation 15 gives

$$\frac{(HAsO_4^{--})\ (I^-)^2\ (H^+)^4}{(H_3AsO_3)\ (I_2)} = 9.6 \times 10^{-6} \quad (16)$$

The general electrode equation for the arsenic-arsenious couple, Equation 3, may be put in the following form:

$$E_{As} = C + 0.0295 \log \frac{(HAsO_4^{--})\ (H^+)^4}{(H_3AsO_3)}$$

The equation for the iodine-iodide couple, as will be shown later, is

$$E_I = 0.6211 - 0.0295 \log \frac{(I^-)^2}{(I_2)}$$

At equilibrium $E_{As} = E_I$ and

$$C + 0.0295 \log \frac{(HAsO_4^{--})\ (H^+)^4}{(H_3AsO_3)} = 0.6211 - 0.0295 \log\ (I^-)^2$$

$$0.6211 - C = 0.0295 \log \frac{(HAsO_4^{--})\ (I^-)^2\ (H^+)^4}{(H_3AsO_3)\ (I_2)}$$

$$= 0.0295 \log 9.6 \times 10^{-6}$$

from which $C = 0.769$

Table III contains values of E calculated from Equation 11 at different hydrogen-ion concentrations when $\frac{Sr}{So}$ has the values given in columns 2, 3, and 4, respectively.

Table III—Calculated Values of E under Different Conditions

pH	$E\ \frac{Sr}{So} = 1$	$E\ \frac{Sr}{So} = \frac{1}{1000}$	$E\ \frac{Sr}{So} = \frac{1}{10,000}$
0	0.574	0.663	0.692
0.5	0.544	0.633	0.662
1.0	0.515	0.603	0.633
1.5	0.485	0.573	0.603
2.0	0.456	0.544	0.574
2.5	0.425	0.514	0.543
3.0	0.394	0.482	0.512
3.5	0.353	0.441	0.471
4.0	0.298	0.387	0.416
4.5	0.241	0.330	0.359
5.0	0.181	0.270	0.299
6.0	0.062	0.151	0.180

Oxidation-Reduction Potentials of Iodine-Iodide Solutions

The reduction of triiodide ion to iodide ion may be formulated

$$I_3^- + 2e \rightleftharpoons 3I^-$$

The equilibrium state may be formulated thus

$$\frac{(I_3^-)\ (e)^2}{(I^-)^3} = K$$

or

$$(e) = \sqrt{\frac{(I^-)^3\ K}{(I_3^-)}} \quad (17)$$

Substitution of this value of (e) in the general electrode equation (2) gives

$$E = C - 0.059 \log \sqrt{\frac{(I^-)^3\ K}{(I_3^-)}} \quad (18)$$

from which, by rearranging and combining constants,

$$E = C' - 0.0885 \log (I^-) + 0.0295 \log (I_3^-) \quad (19)$$

The equilibrium between free iodine, iodide ion, and triiodide ion may be formulated thus

$$\frac{(I_2)\ (I^-)}{(I_3^-)} = K \quad (20)$$

Substituting the value of (I_3^-) obtained from this equation in the electrode equation (19) and combining terms,

$$E = C'' - 0.059 \log (I^-) + 0.0295 \log (I_2) \quad (21)$$

This is the equation relating E with the activities of iodide ion and iodine in any solution. Jones and Kaplan (*10*) have found that, when the iodide ion has unit activity and the iodine concentration (I_2) is a constant and equal to the solubility (0.00132 molar at 25° C.), the normal potential e_o is 0.5362 against the hydrogen electrode. The following equation represents their findings for the saturated I_2 electrode:

$$E = 0.5362 - 0.059 \log (I^-) \qquad (22)$$

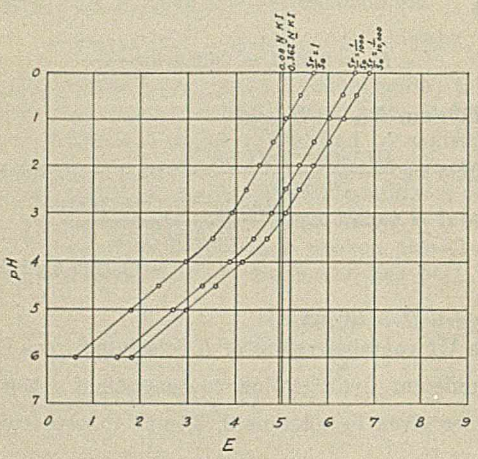

Figure 2—Values of E under Various Conditions

When the activity of the iodide ion is unity and the solution has an iodine concentration of 1.32×10^{-3} gram-mols per liter, the general equation (21), derived above, takes the following form, assuming that the activity coefficient of the free iodine is one:

$$E = C'' + 0.0295 \log 1.32 \times 10^{-3} = 0.5362 \qquad (23)$$

from which $C'' = 0.6211$. The following equation represents the relationship between E and the activities of both iodide ion and iodine:

$$E = 0.6211 - 0.059 \log (I^-) + 0.0295 \log (I_2) \qquad (24)$$

Values of E for several concentrations of iodide and iodine have been calculated in the following manner: Taking for the concentration of free iodine the smallest amount detectable with starch—i. e., 2.5×10^{-5} gram-mols per liter (*13*)—and again assuming that its activity coefficient is one, the equation becomes

$$E = 0.6211 - 0.059 \log (I^-) + 0.0295 \log 2.5 \times 10^{-5}$$

or

$$E = 0.4851 - 0.059 \log (I^-) \qquad (25)$$

When a solution contains 3 grams of potassium iodide in 50 cc., it is 0.362 normal. Using Jones and Kaplan's constants and Bronsted's equation to solve for the activity coefficient, f, gives

$$\log f = -0.373 \sqrt{0.362} + 0.125 \times 0.362 = -0.1789 \qquad (26)$$

from which $f = 0.66$.

The E value of a solution 0.362 normal with respect to potassium iodide and containing just enough free iodine to give a visible color with starch is given by the following equation:

$$E = 0.4851 - 0.059 \log 0.362 - 0.059 \log 0.66 \qquad (27)$$

from which $E = 0.522$ volts. Similarly the E value of a solution containing 2 grams of potassium iodide in 15 cc. is $E = 0.5045$.

These values do not change with changes in the hydrogen-ion concentration. In Figure 2 are plotted the results tabulated in Table III, together with the oxidation-reduction curves, in this case straight lines, for the iodine-iodide solutions mentioned above.

When conditions are such that a point on the curve for arsenic lies to the right of the curve for iodine, there is a tendency for free iodine to be liberated. At pH 2.85 a solution which is 0.36 normal with respect to potassium iodide is in equilibrium with a solution which contains practically all of its arsenic in the pentavalent state only when there is a detectable quantity of free iodine in the solution. When stronger solutions of potassium iodide are present, the pH at equilibrium must be correspondingly greater.

It seems advisable, therefore, from a theoretical standpoint to keep the pH of the solution at 3.5 or above during the titration of copper when arsenic is present in order to prevent the liberation of iodine by arsenic.

Effect of Hydrogen-Ion Concentration on Reaction between Cupric Ion and Iodide Ion

A series of titrations was carried out to determine the effect of ammonium acetate on the reaction between cupric ion and iodide ion. The results are given in Table IV.

Table IV—Effect of Ammonium Acetate on Reaction

COPPER TAKEN	16 N ACETIC ACID	15 N AMMONIUM HYDROXIDE	POTASSIUM IODIDE	COPPER FOUND
Gram	*Cc.*	*Cc.*	*Grams*	*Gram*
0.2000	..	...	3	0.2000
0.2000	5	1	3	0.2003
0.2000	5	2	3	0.2003
0.2000	5	3	3	0.2000 slow
0.2000	10	5	3	0.1995 very slow

In the fourth titration the end point was slow in appearing. The blue color would reappear after having been discharged. The same difficulty was experienced to a much greater extent in the fifth titration, the time required for this titration being about 20 minutes. This behavior was due to the decreased speed of reaction between cupric ion and iodide ion which in turn was probably caused by the lower hydrogen-ion concentration and the decrease in activity of the cupric ion, both of which were brought about by the large amount of acetate ion present. The results show that although a small amount of ammonium acetate does no harm, large amounts should be avoided.

It was next decided to determine whether or not copper could be titrated at a low enough hydrogen-ion concentration to preclude the effects due to arsenic. Buffer solutions containing copper at constant concentration, salts at constant concentration, and varying hydrogen-ion concentration, were prepared and after addition of potassium iodide, were titrated. The results are given in Table V and Figure 3.

Table V—Titration of Copper in Various Buffer Solutions

TARTRATE		CITRATE		PHOSPHATE		ACETATE		PHTHALATE	
pH	% Cu	pH	% Cu	pH	% Cu	pH	% Cu	pH	% Cu
2.08	100	2.14	100	3.21	100	4.27	100	5.50	100
2.36	100	2.44	100	3.64	100	4.45	100	5.70	100
2.51	79[a]	2.81	98.3[a]	3.80	90[a]	4.63	99.4	5.83	98.0
2.64	71[a]	2.96	96.5[a]	3.84	89[a]	4.71	94.8	5.96	96.0
2.86	60[a]	3.15	93.4[a]	3.74	79[a]	4.78	92.1	6.24	91.5
3.16	50[a]	3.33	85.6[a]			4.95	85.1	6.23	87.0[a]
3.47	34[a]	3.52	70.8[a]			5.15	79.0[a]	6.28	83.0[a]
		3.73	57.8[a]			5.15	66.0[a]	6.32	77.5[a]
		3.96	45.6[a]			5.15	63.0[a]	6.34	73.1[a]
		4.48	20.5[a]					6.45	65.9[a]
								6.76	39.0[a]

[a] Precipitates.

Each of the solutions listed in Table V was 0.0375 molar in acid concentration and 0.015733 molar in copper sulfate. The same technic was employed in mixing the various solutions. After mixing, the pH was determined on a portion of the solution by means of the quinhydrone electrode. In a large number of the solutions, precipitates formed and the low percentage of copper found by titration was due at least partially to them. At first attempts were made to titrate the copper in the precipitates by allowing them plenty of time to dissolve after the titration had been started. This plan was changed later to the less representative but more practical plan of allowing the precipitates to settle and pipetting off the clear liquid for titration. The latter method gives practically the same results on account of the very slow solubility of the precipitates. Five cubic centimeters of the clear solution were pipetted off into a small beaker. Two cubic centimeters of potassium iodide solution, containing 1 gram of potassium iodide, were added and the solution was titrated with dilute thiosulfate solution in the usual manner. The per cent of copper titrated under these conditions was calculated and plotted against the pH of the solution.

From an inspection of Figure 3 it appears that the amount of copper which enters into reaction with potassium iodide depends upon the nature of the acid present as well as upon the hydrogen-ion concentration. This is due in some cases, noted above, to the formation of insoluble copper salts, but in those cases where no precipitates appeared the explanation is not so apparent. The assumption of the formation of unionized or slightly ionized copper compounds is one way out of the difficulty. This also accounts for the effect of ammonium acetate in the usual method. (As the amount of acetate ion increases, the amount of undissociated cupric acetate increases and the amount of cupric ion decreases, thereby slowing up the reaction between cupric ion and potassium iodide.)

From an inspection of Table V and Figure 3 it is apparent that phthalic acid is better than acetic for the iodide determination when arsenic is present.

Fluoride-Phthalate-Iodide Method for Copper

A method for the determination of copper in ores, mattes, slags, etc., containing arsenic or antimony, has been developed in which potassium biphthalate is used to buffer the solution. Ammonium bifluoride is added to inhibit the reaction between ferric iron and iodide. That it really has such an effect is shown by the results of several titrations given in Table VI.

Table VI—Effect of Iron in Presence of Fluoride

Copper Taken	Iron	Ammonium Bifluoride	16 N Acetic Acid	Copper Found
Gram	*Gram*	*Grams*	*Cc.*	*Gram*
0.2000	0.02	1	5	0.2000
0.2000	0.10	1	5	0.2000
0.2000	0.20	2	5	0.1999
0.2000	0.30	2	5	0.2002

Treat a suitable sample of ore, slag, etc., with nitric acid until all copper is in solution. Boil down to about 5 cc., add 30 cc. of water, and boil to assure complete solution of soluble matter and also to expel oxides of nitrogen. Filter and wash the residue well with hot dilute nitric acid. If the residue is small in amount or light-colored, filtration may be omitted. Concentrate the solution by boiling to about 30 cc., cool, add ammonium hydroxide until the iron is all precipitated and the solution smells faintly of ammonia. Avoid adding an excess. Add 2 grams, weighed, of ammonium bifluoride, shake, add 1 gram, weighed, of potassium biphthalate, shake, add 3 grams, weighed, of potassium iodide, shake. Titrate at once with thiosulfate, approaching the end point slowly. When near the end point, add sufficient starch solution. After the blue color has been completely discharged, it should not return within 30 minutes at least.

If the copper is not all taken into solution by nitric acid, some other method must be employed, in which case 10 cc. of bromine water should be added with the 30 cc. of water above to assure complete oxidation of arsenic and antimony, and the boiling continued until all of the free bromine has been expelled. When a mixture containing pentavalent arsenic or antimony and free sulfur is taken to fumes of sulfuric acid, the sulfur acts in much the same manner as organic matter would and reduces the arsenic and antimony to the trivalent state.

Addition of potassium biphthalate to the approximately neutral solution fixes the pH at about 4. Here copper will react with potassium iodide but pentavalent arsenic and antimony will not.

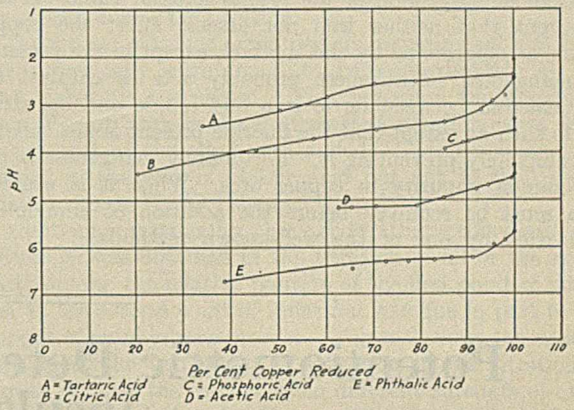

Figure 3—Titration of Copper in Various Buffer Solutions

In the presence of large amounts of iron or aluminum more ammonium bifluoride must be added. Aluminum forms an insoluble fluoride which, when present in large amounts, occludes some copper and slows up the titration. Approximately 1 gram of ammonium bifluoride should be added for each 0.1 gram of iron or aluminum, but the accuracy of the method decreases as the amount of iron increases. A quick return of the blue color may be due to insufficient ammonium bifluoride.

Table VII—Effect of Impurities on Method

Impurity		pH at E. P.	Copper Found
		IRON	
Gram			*Gram*
Fe			
0.1		4.3	0.1998
0.1		4.0	0.2001
0.1		4.1	0.2001
		ARSENIC	
As			
0.1		4.3	0.1997
0.1		3.9	0.2002
	IRON AND ARSENIC TOGETHER		
Fe	As		
0.1	0.1	4.10	0.2002
0.2	0.2	3.82	0.2000
0.2	0.4	3.95	0.2002
0.1	0.1	3.90	0.2000
	MANGANESE ALONE AND WITH IRON		
Fe	Mn		
...	0.1	4.16	0.2007
...	0.1	4.10	0.2000
...	0.1	4.51	0.1993
...	0.1	4.10	0.2000
0.1	0.1	4.10	0.2020
0.1	0.1	4.13	0.2020
0.1	0.1	4.06	0.2021
0.1	0.01	4.10	0.2007
0.2	0.1	4.50	0.2060

An excess of ammonium hydroxide should be avoided, as it lowers the hydrogen-ion concentration and decreases the rate of reaction between copper and potassium iodide. A quick return of the blue color after it has been completely discharged may be due to insufficient acidity.

Oxides of nitrogen and free bromine, if present in the solution when potassium iodide is added, will cause results to run high and may cause a return of the blue after the end point has been reached.

The precipitate of ferric hydroxide should dissolve completely when shaken with ammonium bifluoride. If it does not, either too much ammonium hydroxide or too little ammonium bifluoride was added.

The results given in Table VII were obtained by treating a copper sulfate solution of 0.2 gram of copper containing the indicated impurities by the above method. The pH values of the solutions at the end point were determined by means of the quinhydrone electrode.

From an inspection of the results given in Table VII it is apparent that neither iron nor arsenic affect the copper value, as determined by this method, except in the presence of manganese. Manganese probably acts as catalyst for the reaction between ferric iron and iodide and speeds it up to such an extent that the fluoride present is not capable of completely preventing it. Fortunately manganese is not a common impurity in copper ores. When it is present, iron must be removed before the addition of ammonium hydroxide by one of the well-known methods.

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Potentiometric Determination of Acidity in Insulating Oils[1]

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The estimation of acidity in oils employing the alkali blue procedure has been found to give more satisfactory results than the A. S. T. M. procedure. In the latter method, methyl alcohol should not be substituted for ethyl alcohol.

Electrometric titrations have been carried out on type organic acids successfully.

The silver–silver chloride electrode can be used satisfactorily in routine determination of acidity. The most important disadvantage of the electrometric procedure is the time required. It is recommended that a preliminary approximate titration be carried out.

IN THE past the determination of acidity in oils has been accomplished generally by a procedure similar to that outlined in the A. S. T. M. Tentative Standards 1929, page 397. Recently Seltz and McKinney (*5*) described a quinhydrone-potentiometric method employing amyl alcohol as a solvent, lithium chloride as the conducting salt, and a boundary of agar-agar containing lithium chloride to separate the reference electrode from the solution under investigation. Later, Seltz and Silverman (*6*) eliminated the agar-agar boundary and substituted the silver–silver chloride electrode as the reference electrode. A comprehensive survey of the past work on potentiometric titration may be had by reference to a paper by Furman (*2*).

The following paper deals with the comparison of the electrometric method and several other procedures, employing indicators in which known acids were dissolved in a transformer oil. Many factors influencing the electrometric titration have also been experimentally studied.

Apparatus

The diagrammatic arrangement of the electrometric apparatus may be obtained by reference to the previously mentioned paper by Seltz and McKinney. The potentiometer was a Biddle high resistance instrument, accurate to 0.1 millivolt, used with an external galvanometer. The buret was 5 cc. in capacity and graduated to 0.02 cc. and was permanently connected to the source of alkali. All precaution was taken to exclude carbon dioxide. The solution was stirred with compressed tank nitrogen except when a volatile acid was titrated. In this case, the solution was stirred mechanically, or approximately nine-tenths of the alkali was added and the remainder of the titration carried out with nitrogen stirring. When using the agar-agar boundary, the reference solution was *n*-butyl alcohol saturated with respect to potassium chloride and benzoic acid. The solvent was *n*-butyl alcohol saturated with potassium chloride. The alkali was 0.05 *N* and was standardized potentiometrically against B. S. benzoic acid. It was prepared by dissolving C. P. stick potassium hydroxide in *n*-butyl alcohol and the insoluble carbonate removed by filtration. The quinhydrone was crystallized from *n*-butyl alcohol and melted sharply at 170° C.

Experiments

Known acids were dissolved in oil with subsequent determination of neutralization number in order to compare the results obtained employing four different procedures—namely, A. S. T. M. using methyl alcohol as a solvent, A. S. T. M. using ethyl alcohol as a solvent, alkali blue, and electrometric. The latter method was carried out with the two previously described reference electrodes (*5*, *6*). The concentration

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[1] Received September 4, 1930.

of acids was chosen at random and in the case of the higher concentration of stearic acid in oil, a supersaturated solution was obtained. On long standing, stearic acid crystals separated and a more dilute solution was prepared. In each procedure, except the electrometric, the blank on the solvent was obtained by titration to a definite shade, and the solvent then added to the oil sample, whereupon the titration was carried out as near as possible to the same shade. In the case of the A. S. T. M. procedure using methyl alcohol, the point was difficult to obtain. A faint pink color is soon obtained in the alcohol-water phase which does not appear to increase in depth until the end point recorded in the table was reached. Since the color change should be observed in the alcohol–water phase, care should be taken to allow the phases to separate even though working with an almost colorless oil. Table I is a tabulation of neutralization numbers obtained by titrating oil samples employing different methods.

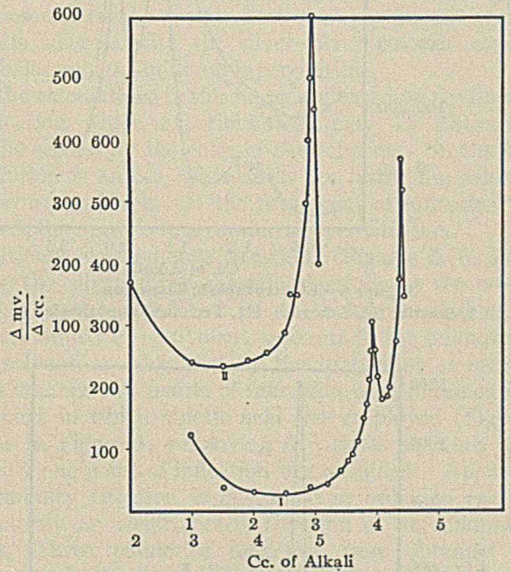

Figure 1—Electrometric Titration

I, Stearic acid; II, Abietic acid

Table I—Neutralization Numbers of Acids Dissolved in Transformer Oil

Method	Benzoic	Acetic	Stearic (I)	Stearic (II)	Cyclohexane Carboxylic	Naphthenic	Rosin Technical
CH_3OH, 50 cc. H_2O, 50 cc. Phenolphthalein (1%), 1 cc.	2.23	0.50	0.26	0.64	2.14	0.99	0.92
C_2H_5OH, 50 cc. H_2O, 50 cc. Phenolphthalein, 1 cc.	2.29	0.52	0.37	0.91	2.15	1.03	0.97
CH_3OH, 75 cc. Benzene, 75 cc. Alkali blue, 2 cc.	2.29	0.51	0.42	1.00	2.18	1.02	0.97
Water, 100 cc. Phenolphthalein, 1 cc.		0.47					
Electrometric[a] *n*-Butyl, 125 cc. Saturated KCl Quinhydrone, 0.05 gram	2.31	0.49	0.42	0.99	2.17	1.05	1.11

[a] Oil samples were rather concentrated. Experiments have been carried out whereby neutralization number was lowered to 0.1 by addition of neutral oil. Total oil sample then weighed 20 grams.

As may be seen from the table, serious differences may arise when such acids as stearic or abietic are present. In calculating the neutralization numbers, the strength of alkali was determined by titrating a weighed amount of benzoic acid using the four different methods when no oil was present. Table II contains the results of titrating stearic acid when no oil was present. Thus 0.005 gram of stearic acid was contained in one gram of oil sample (stearic acid II). A much larger amount was titrated in the absence of the oil and in Table II the number of the milligrams of potassium hydroxide equivalent to the 0.005 gram of stearic acid was calculated by proportion.

Table II—Titration of Stearic Acid in Absence of Oil

Method	Potassium Hydroxide Equivalent to 0.005 Gram Stearic Acid
	Mg.
CH_3OH and H_2O	0.95
C_2H_5OH and H_2O	0.95
CH_3OH and benzene	0.99
Electrometric	1.00

The discrepancies encountered with an acid of the stearic acid type practically disappear when the oil is absent. The difficulty is probably connected with the fact that two phases are present during the titration.

The results obtained when titrating stearic acid and rosin electrometrically were found to be approximately 10 per cent higher than expected. This suggested the possibility of an obscure peak in the electrometric titration curve when 90 per cent of the alkali was added. This possibility was verified in the case of stearic acid but not in the case of abietic acids, as Figure 1 shows.

Additional investigations have shown that a curve with two inflections was obtained in the titration of all of the acids. Furthermore, the relative position of the first point of inflection to the second point of inflection was due in part to the amount of quinhydrone present. Figure 2 shows the relative position of the two points of inflection in the titration of aliquot parts of the solvent when different amounts of quinhydrone were employed. However, there appears to be no stoichiometric relation between the amount of quinhydrone when calculated as a monobasic acid and the additional amount of alkali required. The experiment in which 0.01 gram of quinhydrone was used was repeated several times, and the result given represents an average value. A saturated solution was not employed due to the relatively large solubility of quinhydrone in butyl alcohol.

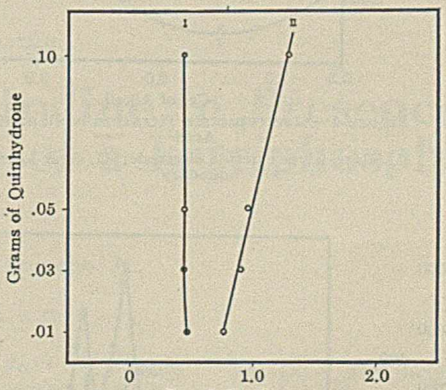

Figure 2—Relation of Amount of Quinhydrone to End Point of Titration

I, First point of inflection; II, Second point of inflection

It has been suggested that small amounts of oxygen in the compressed tank nitrogen may account for the second point of inflection. MacInnes and Jones (*3*) stirred their solutions mechanically in the presence of air and obtained two points of inflection which are attributed to quinhydrone as a weak acid. Rabinowitsch and Kargin (*4*) relate the phenomenon to the presence of carbon dioxide in the solution. Clarke and Wooten (*1*) failed to obtain two points of inflection in the absence of oxygen although these authors observed "marked irregularities on the alkaline side of the equivalence point." Our results are similar to those of MacInnes and Jones, although no attempt was made to eliminate the oxygen from the compressed tank nitrogen. It is probable that with

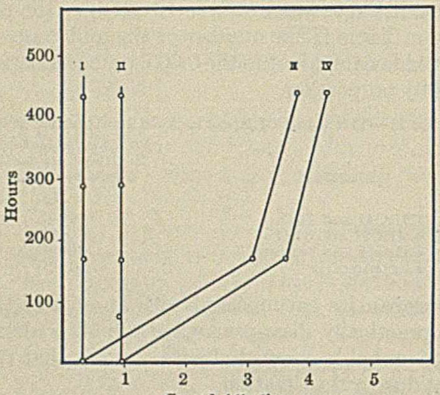

Figure 3—Relation of Time of Standing to Acidity of Solvent

I, First point of Inflection in dark; II, Second point of inflection in dark; III, First point of inflection in diffused daylight; IV, Second point of inflection in diffused daylight

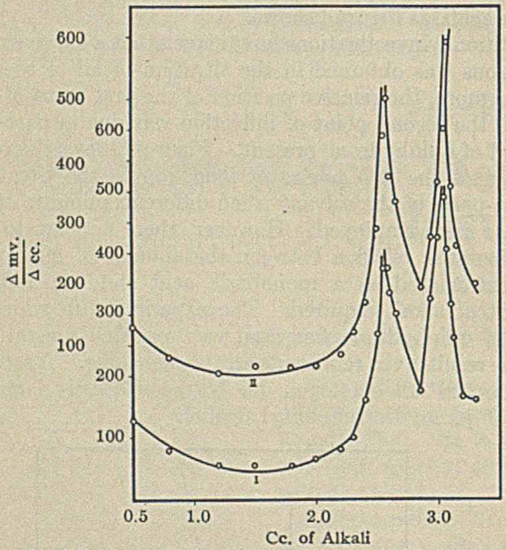

Figure 4—Electrometric Titration of Benzoic Acid

I, Silver–silver chloride electrode; II, Agar-agar boundary

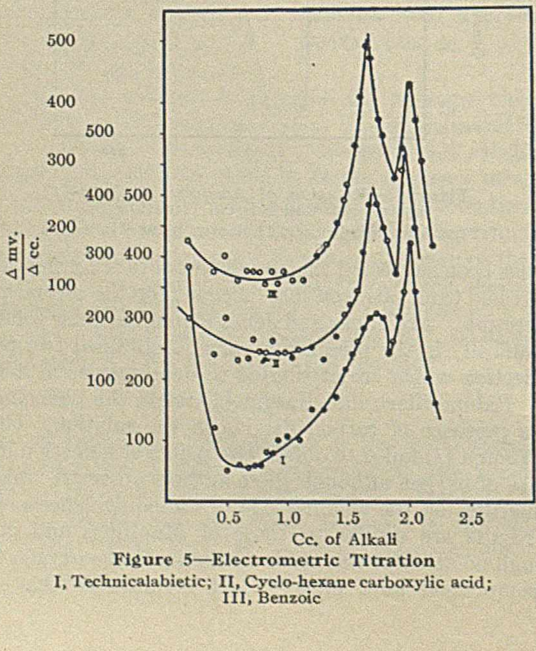

Figure 5—Electrometric Titration

I, Technicalabietic; II, Cyclo-hexane carboxylic acid; III, Benzoic

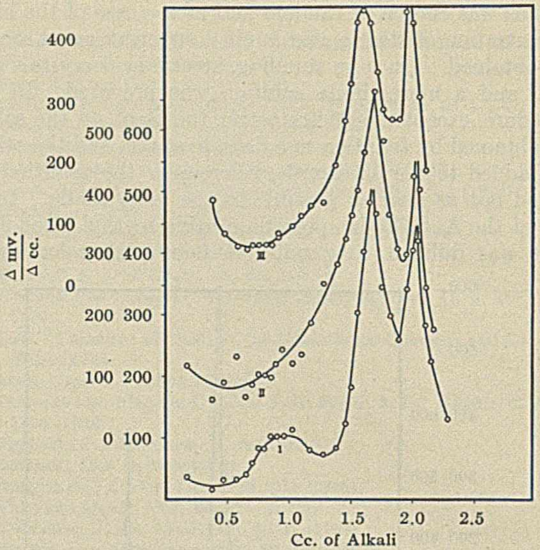

Figure 6—Electrometric Titration

I, Stearic; II, Salicylic; III, Technical naphthenic

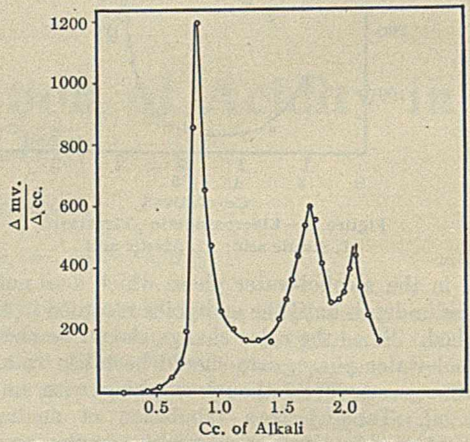

Figure 7—Electrometric Titration of Hydrochloric Acid in Butyl Alcohol

smaller amounts of quinhydrone than used in our experiments the two points of inflection would tend to merge and appear as one.

The variation in the acidity of the solvent was found to be mainly associated with the time of standing in the light, the time of reflux—i. e., in the preparation of the saturated solution—and the method used in dissolving the quinhydrone. Figure 3 represents the change in the acidity of the solvent when it was exposed to daylight and when it was stored in a dark bottle. If the saturated solution of potassium chloride in butyl alcohol is at an elevated temperature when the quinhydrone is added, the solution turns dark with an increase in the acidity of the solvent. A low and constant blank can be obtained by refluxing for $^1/_2$ hour, adding the quinhydrone when the solution is at room temperature, and storing the solution in a dark bottle.

The use of the silver–silver chloride electrode as a reference electrode (*6*) to replace the agar-agar boundary has been tried with success in this laboratory. A piece of silver sheet, 1-cm. square, was soldered with silver solder to a platinum wire 3 cm. in length. To the other end of the platinum wire, a piece of copper wire was soldered to serve as a lead to the potentiometer. A piece of glass tubing containing the copper wire was fused to the intervening platinum wire. The silver sheet was then covered with silver chloride by merely dipping it into the fused salt. In this manner the time of preparation of the reference electrode is greatly reduced (*6*). The silver–silver chloride electrode was placed in the solution to be titrated together with the agar-agar electrode. The connections were changed after each addition of the alkali and the resulting points of inflection agreed very well. Apparently there is no diffusion of the benzoic acid from the reference electrode into the unknown acid sample when the agar-agar plug is correctly made (Figure 4). An off-balance of roughly 2 millivolts on the potentiometer can be observed when employing the agar-agar electrode whereas with the silver–silver chloride electrode, an off-balance of 0.5 millivolt is perceptible.

All the calculations in this paper are based on the first point of inflection which experimentally may be distinguished from the second by the color of the solution. In the former the solution is amber, whereas in the latter the solution is dark brown to black. If the first point of inflection is not obtained, the result is in error due to over-titration.

Additional electrometric titrations (Figures 5, 6, 7), employing the silver–silver chloride electrode as the reference electrode, were carried out in which known acid oil samples were added in equivalent amounts to the unknown acid in the solvent as calculated by the first point of inflection. In this manner two points of inflection were obtained in the experiment in which abietic acid was employed (Figure 5), whereas in Figure 1, employing five times as much abietic acid, only one point of inflection was obtained. Apparently, a preliminary titration is necessary in order to carry out satisfactorily an electrometric titration of an unknown oil sample. Three points of inflection were obtained when titrating hydrochloric acid. It is quite probable that the unknown acid in the solvent is not hydrochloric. Benzoic and salicylic acids behaved as a single acid. The question arises as to the use of the second point of inflection in the calculation of neutralization numbers. As applied to the acids used in these experiments, the authors prefer the first point of inflection from the standpoint of time consumed and of agreement of duplicate experiments. Obviously, dibasic acids and a mixture of acids of widely different strengths as well as the relative quantities of the acids present in the mixture have a bearing on the problem.

It is interesting to compare the order of the acids as determined by the potential of the cell at the halfway point of titration. The well-known relation between the ionization constant and the hydrogen-ion concentration in water at the halfway point of titration should enable one to arrange the acids in order of their strength. The solvent in our experiments was butyl alcohol, the single potential of the silver–silver chloride electrode in butyl alcohol is unknown, and the effect of the acid or acids in the solvent is unknown. However, the relative position of one acid to another should remain unchanged. The e. m. f. at the halfway point of titration when graphically obtained is approximate, since few points are ordinarily taken in that region of the curve. Table III contains these data.

Table III—Order of Acids as Determined by E. M. F. at Halfway Filtration Point

ACID	E. M. F. at HALFWAY POINT	K_a IN WATER
Hydrochloric	340	
Salicylic	120	1×10^{-3}
Benzoic	65	6×10^{-5}
Cyclohexane carboxylic acid	40	
Technical naphthenic	40	
Stearic	25	
Abietic	20	

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Oxidation of Ferrous Iron by Iodine in Presence of Phosphate and Non-Existence of a Ferriphosphate Complex[1]

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The reaction $Fe^{++} + {}^1/_2 I_2$ aq. $\longrightarrow Fe^{+++} + I^-$ goes to completion in the presence of phosphate and of a moderate concentration of acid. This reaction, even in solutions almost neutral, is too slow to be of analytical significance.

The reason for the completion of the reaction is probably the decrease in the ratio Fe^{+++} to Fe^{++} brought about by the addition of the phosphate.

Probably no complex ion is formed between ferric iron and phosphate, but only a weak electrolyte whose composition probably ranges from $FePO_4$ in solutions containing little phosphate, to $Fe(H_2PO_4)_3$ in solutions containing an excess of phosphate.

In 1926 Bonner and Yost (*1*) published a method for the determination of ferrous iron using sodium hypochlorite as the oxidizing agent. This method in brief is as follows: Ferrous iron, on being added to a solution containing disodium phosphate and sodium hypochlorite, is immediately oxidized to ferric iron and precipitated as a phosphate. Addition of iodide to this mixture results in the liberation of iodine and in the formation of a certain amount of iodate. Addition of acid dissolves the ferric phosphate, presumably with the formation of a complex ion (*7*). Any iodate present is at the same time reduced to iodine by the iodide. The liberated iodine is then titrated with thiosulfate. The reactions involved are:

$$2Fe^{++} + ClO^- + 2H^+ \longrightarrow 2Fe^{+++} + Cl^- + H_2O \quad (1)$$

$$3I^- + 4ClO^- + 2H^+ \longrightarrow IO_3^- + 4Cl^- + H_2O \quad (2)$$

The fundamental idea on which this method is based is that the ferric iron, converted by the phosphate into a fairly stable complex, is thus removed from the scene of the reaction. There will therefore be no reverse reaction of ferric iron with iodide, which ordinarily prevents the titration of

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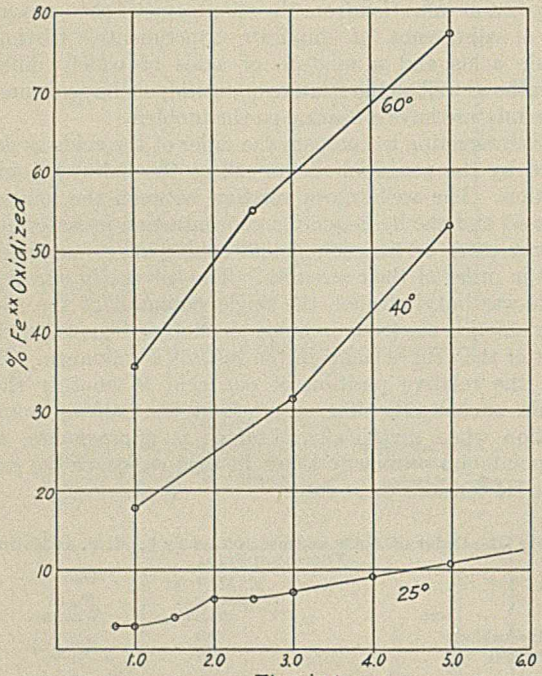

Figure 1—Rate of Oxidation of Iron by Iodine

ferrous iron with iodine. The idea of the complex was based upon the work of Wineland and Ensgraber (*7*) already referred to.

H. W. Foote (*3*) has suggested that the above method be further simplified, either by direct titration of the ferrous iron by iodine in the presence of phosphate, or by adding an excess of iodine solution also in the presence of phosphate, and titrating back with thiosulfate. That these proposed modifications were not practicable was known to Bonner and Yost at the time they wrote their paper. Nevertheless, acting on Foote's suggestion, we have made a more careful examination of the reactions involved.

Rate of Oxidation of Iron by Iodine

We first determined the rate of the oxidation of ferrous iron by iodine in the presence of phosphate, the solutions being 0.1 *N* in sulfuric acid. In this way we were able to show that the reaction actually goes to completion. The procedure adopted was to mix together, in glass-stoppered flasks, 15 cc. of 0.1 *N* ferrous sulfate solution; 15 cc. of 0.3 *N* disodium phosphate solution; 25 cc. of 0.1 *N* iodine solution; 50 cc. of water. The mixed solutions were always 0.1 *N* in sulfuric acid which was added with the ferrous sulfate solution. These flasks were kept in a thermostat at the desired temperature. At definite intervals a flask was removed and the excess iodine titrated with thiosulfate. A large number of these determinations was made, and the results are readily reproducible. Figure 1 shows that the reaction is very slow at 25° C., being in fact less than 50 per cent complete in 24 hours. At 40° C. the reaction is complete in about 15 hours, and at 60° C. in about 9 hours. We have no explanation for the curious hump in the 25° C. curve.

The data on which the curves of Figure 1 are based are given in detail in Table I. Each titration given is the mean of at least two determinations. The precision of the experiments at 40° and 60° C. is of course much less than that of experiments at 25° C. due to the higher vapor pressure of the iodine causing some loss from the solutions.

Willard and Hall (*6*) have shown that small amounts of ferrous iron in the presence of phosphate and in solutions approximately neutral are almost immediately oxidized by iodine. Therefore we also determined the rate of the reaction at various other acid concentrations. Using aurine indicator to obtain neutral solution, as suggested by Willard and Hall, we made rate measurements at 25° C. on solutions of pH approximately 6.5, 2.5, and 1.5. At pH 6.5, and using solutions about 0.03 *N* in ferrous iron, the reaction is complete in about 6.5 hours. At pH 2.5 about 75 per cent of the iron has been oxidized in 18 hours. At pH 1.5, the rate is about the same as at pH 1.0, where most of our measurements were made.

Table I—Rate of Oxidation of Iron by Iodine

25° C.; THIOSULFATE EQUIVALENT, 23.70 CC.			40° C.; THIOSULFATE EQUIVALENT, 24.1 CC.			60° C.; THIOSULFATE EQUIVALENT, 24.1 CC.		
Time	Thiosulfate	Fe^{++} Oxidized	Time	Thiosulfate	Fe^{++} Oxidized	Time	Thiosulfate	Fe^{++} Oxidized
Hours	*Cc.*	%	*Hours*	*Cc.*	%	*Hours*	*Cc.*	%
0.00	37.45	0.00	0.00	33.65	0.0	0.0	33.65	0.0
0.75	36.81	2.74	1.00	29.3 ± 0.3	17.8	1.0	25.1 ± 0.1	35.5
1.00	36.80	2.74	3.00	26.0 ± 0.2	31.5	2.5	20.3 ± 0.3	55.0
1.50	36.47	4.13	5.00	20.8 ± 0.2	53.1	5.0	15.1 ± 0.3	77.0
2.00	35.89	6.60						
2.50	35.95	6.34						
3.00	35.76	7.11						
4.00	25.28	9.14						
5.00	34.90	10.78						
20.50	30.01	31.40						
24.00	29.12	35.18						

Using only 5 mg. of ferrous iron, we were able to corroborate the statement of Willard and Hall, referred to above. It is interesting to note that we were able to carry out this oxidation in the absence of phosphate, the ferric iron in this case being precipitated as the hydroxide instead of as a phosphate. In the absence of phosphate, however, the results were erratic and usually low. These neutral solutions either with or without phosphate are very sensitive to atmospheric oxidation, and air must be rigorously excluded.

Theoretical Considerations

Since this reaction goes actually though slowly to completion, and if the formation of a ferriphosphate complex might be assumed, the explanation seems almost obvious. The two reactions whose rates are involved are evidently:

$$Fe^{+++} + H_2PO_4^- \longrightarrow \text{complex} \qquad (3)$$

$$Fe^{++} + \tfrac{1}{2} I_2 \text{ aq.} \longrightarrow Fe^{+++} + I^- \qquad (4)$$

Reaction 3 must be rapid, as is evidenced by the work of Bonner and Yost (*1*). Reaction 4 is probably rather slow and the equilibrium is known to be established quite slowly.

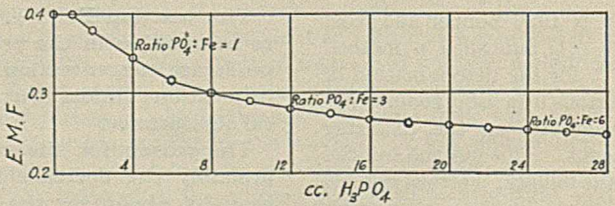

Figure 2—Potentiometric Titration of Ferric-Ferrous Solution with Phosphoric Acid

At equilibrium and in the absence of phosphate, only a small part of the iron has been oxidized. The reason that Reaction 4 goes to completion as written must be that the concentration ratio Fe^{+++} to Fe^{++} in the presence of phosphate and a low H$^+$ concentration is smaller than the equilibrium ratio of Fe^{+++} to Fe^{++} in the same reaction, phosphate being absent. This latter equilibrium ratio is readily determined, and is known to be approximately 10^{-3} (*2*). In order to show what the ratio Fe^{+++} to Fe^{++} is in a solution containing phosphate, the following experiments were performed:

A solution was made up containing 25 cc. of 0.05 *M* ferrous sulfate solution, 0.5 cc. of 0.05 *M* ferric sulfate solution, 0.5 cc. of 0.1 *N* sulfuric acid solution, and 25 cc. of water. The ratio Fe^{+++} to Fe^{++} in this solution was 0.02 or $10^{-1.70}$. The measured e. m. f. of this solution at 25° C. against a normal calomel electrode was 0.359 volt. An entirely similar solution was then made up, excepting only that the 25 cc. of water were replaced by 25 cc. of a 0.3 molal solution of disodium phosphate. This solution gave an e. m. f. against the same calomel electrode at 25° C. of 0.255 volt. From these measurements, by means of the relationship

$$E = E_o + 0.059 \log Fe^{+++}/Fe^{++}$$

we calculate that the ratio Fe^{+++} to Fe^{++} is now $10^{-3.45}$. The addition of the phosphate has therefore greatly decreased the concentration of Fe^{+++} in the solution, and has decreased the ratio Fe^{+++} to Fe^{++} to a value markedly less than the equilibrium ratio of Reaction 4. This seems to substantiate our previous statement that the reason this reaction goes to completion must be the decreased ratio Fe^{+++} to Fe^{++}. This may be brought about by the formation of a ferriphosphate complex. This conclusion is made the more plausible by the fact that while the reaction is completed in solutions 0.1 *N* in sulfuric acid, the reaction is not completed in solutions approximately 3 *N* in acid. In other words, at acid concentrations such that this hypothetical complex cannot form, equilibrium is established with but little Fe^{+++} present. If one carries out this oxidation in solutions nearly neutral, the progress of the reaction is accompanied by the formation of a white precipitate, presumably a ferric phosphate. This precipitate, filtered out and washed, dissolves slowly in 3 *N* sulfuric acid to a colorless solution. Addition of iodide to this solution liberates, at once, an abundance of iodine, showing that at such an acid concentration, the reaction cannot go to completion.

Non-Existence of Ferriphosphate Complex

The fact that the oxidation of ferrous iron by iodine fails to proceed in the presence of 3 *N* acid seems to indicate that any complex which may be formed is not a very stable one. The evidence for the existence of such a complex seems to be furnished entirely by the work of Wineland and Ensgraber (*7*) who assign to it the formula $Fe(PO_4)_2^{---}$. If any complex is formed, even of moderate stability, it should be possible to determine both its presence and its composition by means of a potentiometric titration of a ferric-ferrous solution with phosphoric acid (*4*). Such a titration has been carried out and its graph is given in Figure 2. For purposes of comparison, the graphs obtained by titrating (*a*) silver nitrate with potassium cyanide and (*b*) silver nitrate with ammonia, Figure 3, are inserted. As is readily seen, the iron-phosphate graph shows no indication of any complex as stable as the silver ammonia complex. From coördination considerations, the most likely complexes should be $Fe(HPO_4)_3^{---}$ or $Fe(H_2PO_4)_6^{---}$. No indication is given of either of these. The existence of any ferriphosphate complex must, therefore, be called in question and the behavior of ferric solutions containing phosphate attributed to the formation of a weak electrolyte. Since, as the graph shows, the rapid change in the Fe^{+++} to Fe^{++} ratio has ceased when the ratio of phosphate to ferric iron has become about 3, we may conclude that the ultimate composition of the weak electrolyte approximates $Fe(H_2PO_4)_3$. However, the addition of a small amount of phosphoric acid removes most of the color from a ferric solution. Thus, in the titrations just cited, the greater part of the color disappeared with the addition of the first cubic centimeter of phosphoric acid. Ten cubic centimeters of 0.1 *N* ferric chloride solution are almost completely decolorized by 0.5 cc. of 85 per cent phosphoric acid. These observations suggest that some compound richer in iron than is the primary phosphate is present in the solutions which contain little phosphoric acid. In the second case cited, the ratio of phosphate to iron is 1, suggesting the formula $FePO_4$.

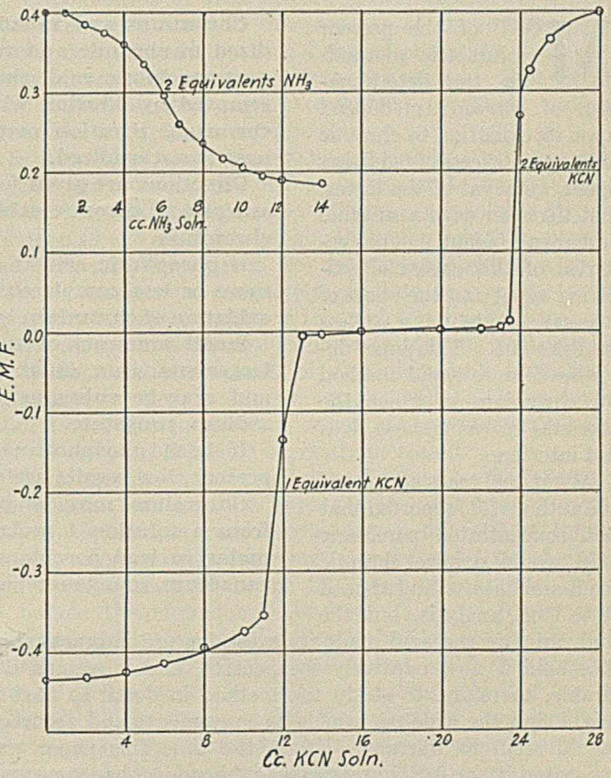

Figure 3—Titration of Silver Nitrate

The white precipitate referred to above, which forms during the oxidation of ferrous iron by iodine in nearly neutral solutions containing phosphate, contains as an average of 4 analyses, 26.8 per cent iron. These analyses were made by the method of permanganate titration, following reduction with stannous chloride (*5*). Similar analyses made of the product called by Wineland and Ensgraber "alkali free ferriphosphoric acid" gave 26.6 per cent iron. As the compound $Fe_2(HPO_4)_3$ contains 28.0 per cent iron, it is probable that each of these substances is the secondary ferric phosphate.

Acknowledgment

A part of this work has been done by the senior author in the Gates Chemical Laboratory of the California Institute of Technology. He wishes here to express his appreciation of all the many courtesies shown him.

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Determination of Chromium and Vanadium in Ores and Alloys after Oxidation with Perchloric Acid[1]

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Chromium and vanadium may be completely oxidized to chromic and vanadic acid by boiling 70 per cent perchloric acid, the oxidizing action of which is removed by dilution with water, after which any of the usual titration methods may be used. Manganese is not oxidized.

Directions are given for applying this process to the analysis of chromic oxide, chromite, steel, and ferrochromium.

If phosphoric acid is added, manganese is oxidized more or less completely to a manganic salt, but the oxidation of chromium is hindered.

Small amounts of tungsten do not interfere but larger amounts must be removed before oxidation and may be subsequently added to the solution as sodium tungstate.

If both phosphotungstic acid and vanadium are present, low results are obtained.

Chromium may be precipitated as lead chromate from a solution 1 molar in perchloric acid and 0.04 molar in lead perchlorate and thus separated from vanadium, manganese, and iron.

MOST of the present volumetric methods for the determination of chromium depend upon its oxidation to chromic acid by an excess of oxidizing agent, removal of the latter, and titration with a suitable reducing agent. The removal of this excess of oxidizing agent and the effect of manganese are more or less troublesome. This paper describes a more rapid method for chromium in which the presence of manganese does not interfere.

About ten years ago one of the authors (*11*) reported that hot, concentrated perchloric acid would oxidize chromic oxide and its salts, and applied it to steel analysis, but the high price of the acid made its extensive use impracticable. The acid is now relatively inexpensive, and it seemed desirable, therefore, to study the method in detail so that it might find the wide use which its convenience and accuracy would seem to warrant. Up to the time this paper was presented (*1*), no further reference to this subject had appeared. Since that time Lichtin (*6*) has suggested the use of perchloric acid in the analysis of chrome alum and its liquors. He erroneously assumed that chloric acid was an intermediate product in the oxidation process. James (*3*) has given brief directions for its use in the analysis of chromium iron alloys. No analyses, however, were given to show the accuracy of his procedures, some of which are known to be inaccurate.

Perchloric acid, like sulfuric, in dilute solution is very stable and not affected by any of the ordinary reducing agents. Upon boiling it loses water until it reaches a concentration of 70 to 72 per cent, and this acid distils at about 203° C., accompanied by some decomposition, thus:

$$4HCl_4 = 2Cl_2 + 7O_2 + 2H_2O$$

Oxides of chlorine are not formed.

This oxygen is available for oxidation and under these conditions the acid is a powerful oxidizing agent. To remove its oxidizing power, all that is required is dilution with water. The free chlorine present is readily removed by boiling or blowing air through the solution. Nearly all metals and non-metals are readily attacked by the hot, concentrated acid. Manganese, however, is not oxidized beyond the bivalent state except when considerable phosphoric acid is present. In this respect it differs from other oxidizing agents for chromium. Even chromite and chromic oxide, which are quite inert towards other acids, are completely oxidized. The method is very rapid. Moreover, since concentrated perchloric acid is an excellent dehydrating agent for silica (*12*), the latter may be determined after titration of the chromium with no extra trouble. It is not, however, satisfactory for removing tungstic acid (*12*).

In spite of the properties mentioned above, 70 to 72 per cent perchloric acid is perfectly stable and non-oxidizing at ordinary temperatures, but obviously should be kept out of contact with organic matter. It is non-explosive and no trouble has been experienced with violent reactions, even when used by students.

Commercial perchloric acid, free from ammonium, chromium, and vanadium, is entirely satisfactory for the determination of the latter elements and is much cheaper than the C. P. acid.

Standardization of Dichromate

C. P. potassium dichromate, unless specially purified, is not a safe primary standard. It may even contain a slight excess of chromic acid. The material used in this work was the best obtainable, but it was tested in two ways—against U. S. Bureau of Standards arsenious oxide, which gave a value of 100.06 per cent dichromate, and against ferrous sulfate which had been titrated against permanganate standardized against Bureau of Standards sodium oxalate, which gave 100.16 per cent. The arsenite method (*9*) was more accurate because only one titration was involved and because dilution and acidity were without effect. The dichromate must not be added to the alkaline arsenite solution or too much arsenite will be used. One gram of dried potassium dichromate was dissolved in 25 cc. of water and acidified with 6 to 8 cc. of sulfuric acid (sp. gr. 1.5). To this solution was added 1.02 grams of dried arsenious oxide dissolved in 25 cc. of water and 3 grams of sodium hydroxide crystals. Reduction of dichromate was complete in a minute or two. Fifty cubic centimeters of hydrochloric acid (sp. gr. 1.1) were added and the excess arsenite titrated with 0.02 *N* bromate which had been standardized against arsenious oxide using approximately the same concentration of hydrochloric acid. Change in acidity, volume of solution, and concentration of substances have a negligible effect on the ratio of arsenite to dichromate, but a certain minimum concentration of hydrochloric acid must be present in the bromate titration, the end point of which may be determined electrometrically (*17*) or by the use of methyl orange indicator, if the color of the solution is not too deep. The excess of arsenite may also be titrated with permanga-

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nate, using a trace of iodine as catalyst, with or without erioglaucine A as indicator (*5*).

Standardization of Ferrous Sulfate

It has been shown by Eppley and Vosburgh (*1*) that the result of a dichromate–ferrous sulfate titration is influenced by acidity, volume of solution, and concentration of dichromate. Their results show variations of more than 0.5 per cent when these factors are varied. The following experiments confirm their results: In solutions 3.4 molar with respect to sulfuric acid, 25 cc. of 0.1 N dichromate in a volume of 150 cc. required 25.43 cc. of ferrous sulfate when titrated electrometrically, and when the volume was doubled, 25.35 cc. Portions of 50 cc. with the same acidity required, in volumes of 100 cc. and 600 cc., 51.96 cc. and 50.66 cc., respectively, of another ferrous sulfate solution. The presence of ferric or perchlorate ion has no effect on the location of the end point. It is obvious, therefore, that it is essential to standardize the ferrous sulfate under the same conditions of acidity and volume prevailing in the analysis, using, preferably, about the same amount of titrating solution.

If it is desired to use diphenylbenzidine as indicator (*15*), the acidity must be reduced by the addition of sodium acetate sufficient to react with all free sulfuric or perchloric acid. This was shown by titrating 25-cc. portions of 0.1 N dichromate under different conditions. In all cases the solution had a volume of 150 cc. and contained 15 cc. of phosphoric acid (sp. gr. 1.37). In one case it was titrated directly, using diphenylbenzidine as indicator, and required 25.51 cc. of ferrous sulfate. In two parallel experiments the solution contained 20 cc. of 70 per cent perchloric acid, was treated with 32 grams of sodium acetate trihydrate, and the value, 25.41 cc., was obtained both electrometrically and by the indicator method.

To work out the conditions necessary to obtain satisfactory chromium determinations, synthetic mixtures of iron and chromium were prepared using ingot iron and the tested potassium dichromate. The oxidation was carried out in a beaker 20 cm. in height and of 350 cc. capacity. This extra-tall beaker, ordinarily unnecessary, was used to avoid any possible loss, either by spraying from the gases evolved or from the occasional bumping of the dilute perchloric acid. The concentrated acid boils quietly.

Amount of Perchloric Acid Required—If too little acid was used, solid ferric perchlorate separated even in the boiling acid and the results were low. For 1 gram of iron, 20 cc. of 70 per cent acid were satisfactory, for 2 grams, 25 cc., and for 5 grams, 60 cc. Less is likely to cause incomplete oxidation of chromium, especially if the sample is dissolved directly in the hot acid, some of which is thus used up.

Time of Boiling for Complete Oxidation—The oxidation is the critical part of the process. After the acid has concentrated to dense fumes, 20 minutes of gentle boiling is sufficient, unless some reducing material, such as carbon, is present. Oxidation starts rather suddenly and the change in color due to the formation of red chromic acid is usually quite evident. Ten or fifteen minutes more is sufficient to complete the oxidation. The beaker must be kept covered, and should be at least 11 or 12 cm. high, the 500-cc. tall form with lip being satisfactory. A Soxhlet flask of this capacity is still better and prevents any possibility of mechanical loss by bumping or spraying. A conical flask is not so good because the depth of liquid is not great enough. Most of the acid condenses and runs down in oily drops on the sides of the vessel and on the cover glass. This appearance is an excellent sign that the acid is sufficiently concentrated to have its maximum oxidizing power. Much time is saved by dissolving the sample directly in the concentrated acid, if possible, taking care not to heat too strongly at first. When the solution must be evaporated to fumes, especial care is needed to prevent mechanical loss.

If the concentrated acid solution is allowed to stand overnight before titration, some oxygen is apparently lost and results are slightly low.

Time of Boiling to Remove Chlorine—Three minutes was found sufficient. The solution must, of course, first be diluted to at least double its volume. The chlorine may also be removed by bubbling air through the solution.

Interference of Ammonium Salts—Slightly low results were always obtained in the presence of ammonium salts. The error amounted to about 1 mg. of chromium in 50 mg. when 1 gram of ammonium nitrate was added. It is therefore important that when commercial perchloric acid is used, it be free from ammonium salts.

Action of Other Substances—Halides, nitrate, and acetate are volatilized. Sulfate in moderate amount does not interfere except that most sulfates are insoluble in perchloric acid and cause bumping. Reducing agents in general and even graphitic carbon are entirely oxidized in a short time. Vanadium is completely oxidized to vanadic acid. Tungsten in large amounts is incompletely oxidized by perchloric acid, and if already oxidized to tungstic acid, carries down appreciable amounts of chromium and vanadium. Phosphate in considerable amount, as will be shown later, tends to prevent complete oxidation of chromium unless the quantity of perchloric acid is greatly increased.

The results shown in Table I were obtained by the following procedure: The requisite amounts of ingot iron and potassium dichromate were weighed into a tall, 400-cc. lipped beaker. Five cubic centimeters of water and 1 cc. of nitric acid were added, and enough hydroxylamine hydrochloride to reduce the chromium. At least 25 cc. of 70 per cent perchloric acid were added, followed by the desired amount of ingot iron. The solution was boiled until the appearance of dense white fumes of perchloric acid and for 15 to 20 minutes longer to complete the oxidation. An equal volume of water was added to the somewhat cooled solution, which was boiled to expel chlorine, diluted, cooled, and titrated electrometrically with ferrous sulfate standardized at the time it was used, against dichromate under the same conditions of volume and acidity.

Table I—Determination of Chromium and Vanadium in Synthetic Mixtures of Iron and Chromium after Oxidation with Perchloric Acid

WEIGHT OF SAMPLE	CHROMIUM ADDED	CHROMIUM FOUND
Grams	%	%
5	0.274	0.273
5	0.264	0.263
2	0.708	0.707
2	0.666	0.664
1.5	0.879	0.876
1.5	1.020	1.020
0.4	14.23	14.21
0.4	14.48	14.48
0.35	77.47	77.43
0.35	76.53	76.52

Procedure for Chromium and Vanadium Steels Containing Little or No Tungsten

Place samples of 0.5 to 2 grams, depending on the chromium content, in a 500-cc. tall-form lipped beaker, or better still in a 500-cc. Soxhlet flask, and add 20 to 25 cc. (depending on the size of the sample) of 70 per cent perchloric acid, commercial or c. p. Cover the vessel and warm until all the metal has dissolved, taking care not to let the action become too violent. Most steels will dissolve in less than 5 minutes. Boil the solution 15 to 20 minutes, noting the change in color if much chromium is present, and continuing the boiling at least 10 minutes longer. The perchloric acid should condense and run down the sides of the beaker or flask. Cool somewhat, add an equal volume of water, and boil 3 minutes to expel chlorine. After cooling, the solution is diluted to a suitable volume and is ready for titration as described later.

Cast iron or alloys high in carbon should be dissolved in dilute perchloric acid, either with or without nitric acid, and evaporated to fumes; the action of the hot concentrated acid is too violent. If it is necessary to use 4- or 5-gram samples, add 50 or 60 cc. of acid. This is desirable in cast iron or steel very low in chromium. Boiling for 1 or 2 hours may be necessary to oxidize all the graphite, and further addition of perchloric acid may become necessary.

Procedure for Ferrochromium

An alloy of this type requires different treatment, because when boiled with 70 per cent perchloric acid, the chromium trioxide formed, which is fairly insoluble even in the hot acid, tends to coat the particles of ferrochromium and prevent further oxidation. Weigh 0.2 gram of the powdered alloy into a 500-cc. tall lipped beaker or Soxhlet flask. Add 20 cc. of hydrochloric acid, sp. gr. 1.18, and heat for 15 minutes. Add 15 cc. of 70 per cent perchloric acid and boil 30 minutes after all hydrochloric acid is expelled. Cool somewhat, add a few cubic centimeters of water to dissolve the chromium trioxide, and reoxidize by boiling 15 minutes after the water is expelled. Add a few cubic centimeters of water and look for any undissolved particles of metal. If any are present, another oxidation may dissolve them. Otherwise pour off most of the solution, add a few cubic centimeters of 70 per cent perchloric acid to the residue, and boil till solution is complete. Add the main decanted liquid, evaporate off the water, and reoxidize for 5 minutes. Dilute and boil off chlorine.

Table II shows the results obtained with steels and ferrochromium.

Table II—Determination of Chromium and Vanadium in Steel and Ferrochromium after Oxidation with Perchloric Acid

Wt. of Sample	Chromium Present	Chromium Found $FeSO_4$ indicator	Chromium Found $FeSO_4$ electrometric	Arsenite Permanganate (*5*)	Vanadium Present	Vanadium Found (*5*)
Grams	%	%	%		%	%
		Cast Iron, B. S. 82				
5	0.24	0.240	0.240			
5	0.24	0.239	0.240			
5	0.24	0.240				
		Cr-Ni Steel, B. S. 32b				
2	0.638	0.637	0.637			
2	0.638	0.636	0.638			
		Cr-Mo Steel, B. S. 72				
1.5	0.911	0.908	0.909			
1.5	0.911	0.910	0.909			
		Stainless Steel, B. S. 73				
0.4	13.93	13.89	13.90	13.88		
0.4	13.93	13.92	13.89	13.88		
0.4	13.93	13.92	13.91			
		Ferrochromium, B. S. 64				
0.15	67.9	67.80	67.78			
	67.9	67.79	67.81			
		Cr-V Steel, B. S. 30a				
2.0	1.02			1.005	0.21	0.21
2.0	1.02			1.010	0.21	0.21
2.0	1.02			1.010	0.21	0.21

Procedure for Chromic Oxide and Chromite

Chromic oxide, which is not attacked by the usual acids, is readily oxidized to chromic acid by boiling 70 per cent perchloric acid, a 0.15-gram sample requiring 15 minutes. Chromite is more resistant; if ground to pass a 200-mesh sieve it requires 60–90 minutes. Storer (*7, 10*) suggested the use of concentrated nitric acid and sodium chlorate for this purpose. Gröger (*2*) used it successfully for chromic oxide, but both he and others found that it did not completely dissolve chromite.

Pure chromic oxide was prepared by precipitating mercurous chromate from chromic acid solution and igniting it in hydrogen.

Weigh a 0.5-gram sample into a tall, 500-cc. lipped beaker, or better still, Soxhlet flask. Add 20 cc. of 70 per cent perchloric acid and boil 30 to 60 minutes. Cool somewhat, then add a few cubic centimeters of water to dissolve the chromium trioxide which coats the particles. If any unattacked ore remains, evaporate off the water and boil the concentrated acid again for 20 or 30 minutes. If this treatment does not decompose all the ore, pour off most of the solution, add to the residue 10 cc. of perchloric acid, and boil until the ore is dissolved. Add the main decanted solution, evaporate off the water, oxidize 5 minutes, dilute, and boil off the chlorine. The solution is diluted to a suitable volume and when cool, is ready for titration.

The results obtained by this procedure, using samples of chromite and pure chromic oxide, are shown in Table III.

Table III—Determination of Chromium in Chromic Oxide and Chromite after Oxidation with Perchloric Acid

Chromic Oxide Present		Chromic Oxide Found (Electrometric)
Gram		*Gram*
	CHROMIC OXIDE	
0.1423		0.1424
0.1401		0.1401
0.1409		0.1408
0.1423		0.1422
0.1471		0.1471
	CHROMITE	
%		%
57.49[a]		57.48
57.49		57.47

[a] Decomposed by perchloric acid, oxidized by persulfate.

Titration of Chromic Acid

After the chromium has been oxidized as already described, it may be titrated by any of the usual methods.

(1) Excess of standard ferrous sulfate is added and the excess is titrated back by means of standard permanganate, allowing 1 minute for the end point if vanadium is present. This method is so well known as to need no description. The color due to ferric perchlorate is so slight that there is no advantage in adding phosphoric acid. In the absence of vanadium, the end point is made much sharper by adding 0.5 cc. of a 0.1 per cent solution of erioglaucine A, better known as alphazurine (Schultz 506) as recommended by Knop (*4*). The change from green to red after the addition of an excess of 0.03 cc. of 0.1 *N* permanganate in 300 cc. is very distinct even in the presence of the chromic salt. The color lasts only a few seconds.

(2) Excess of standard arsenite is added, which is then back-titrated with permanganate in the presence of hydrochloric acid and a trace of iodide as catalyst, as described by Kolthoff and Sandell (*5*). If vanadium is absent, alphazurine as indicator improves the end point. In testing this method 2-gram samples were used, phosphoric acid was not really necessary, and vanadium was determined in the same solution by titration with ferrous sulfate using diphenylbenzidine as indicator, following the directions of the authors. Good results were obtained. The amount of acetate to be added is discussed in connection with the next method.

(3) The chromic acid (and vanadic acid, too, if present) is titrated directly with standard ferrous sulfate either electrometrically in a strongly acid solution, or by the use of diphenylbenzidine as indicator in a solution containing phosphoric acid and sufficient sodium acetate to react with all the perchloric acid present, according to the method of Willard and Young (*15*). The procedure is as follows: After boiling off the chlorine, cool, dilute the perchloric acid solution to 200 to 400 cc., add 15 cc. of phosphoric acid (sp. gr. 1.37) and, stirring constantly, a weight of sodium acetate trihydrate equivalent to the excess of perchloric acid used in dissolving the steel. One gram of iron was found to require about 5.4 cc. of 70 per cent perchloric acid

for conversion into ferric perchlorate, and 1 cc. of this acid contains 1.17 grams of perchloric acid, equivalent to 1.58 grams of crystallized sodium acetate. Thus, if 20 cc. of acid are added, the excess will require about 23 grams of acetate. If the steel was first dissolved in nitric acid, the excess of perchloric acid will be a little greater. The proper amount of acetate has been added when more would form a permanent white precipitate of ferric phosphate. If this occurs, add dilute sulfuric acid, with constant stirring, until the solution clears. Unless the acidity is reduced in this way, the color change at the end point will be slow. Add 0.6 to 0.8 cc. of 0.1 per cent diphenylbenzidine solution (in phosphoric or acetic acid), and allow 5 minutes, but not more than 10, for the purple color to develop. It will appear brownish until most of the chromic acid is reduced. If no color appears, add a few drops of dilute sulfuric acid. Titrate with ferrous sulfate to a clear green, approaching the end point carefully. Add a correction of 0.04 cc. of 0.1 *N* ferrous sulfate for each 0.5 cc. of indicator.

For the electrometric method add 25 to 30 cc. of sulfuric acid (sp. gr. 1.5) and titrate chromic plus vanadic acids with ferrous sulfate. If much vanadium is present, a much sharper end point is obtained by cooling the solution to 5° C.

Whichever method is used, it has already been shown that the ferrous sulfate should be standardized in the same way and under the same conditions of volume and acidity at about the time it is used.

Titration of Vanadium

This may be determined by any of the usual methods, a list of which is given in references (*15*) and (*5*).

Silica has been dehydrated by the boiling perchloric acid and after the titration it may be filtered off and determined (*12*).

These different methods were used in obtaining the concordant results shown in Table II.

Steels Containing Tungsten

When present in considerable amount, tungsten is only slowly and incompletely oxidized by hot 70 per cent perchloric acid. The tungstic acid formed seems to protect some of the metal. Dilute acid dissolves the steel, leaving tungsten powder, which is incompletely oxidized by the concentrated acid. The steel was, therefore, dissolved in hydrochloric acid, the tungsten oxidized by boiling with nitric acid in the usual way, and the solution evaporated with 25 cc. of 70 per cent perchloric acid. The concentrated acid was boiled 20 minutes to oxidize the chromium which was titrated with ferrous sulfate. The steel contained 4.10 per cent chromium, 14.80 per cent tungsten, and no vanadium. The amount of chromium found was about 1 mg. too low.

The precipitate of tungstic acid was filtered off and dissolved in hot, dilute sodium hydroxide. It contained about 1 mg. of chromium, mostly as chromate, and accounted completely for the low results. The chromic acid is noticeably adsorbed by it. The precipitate takes on a deeper orange color. This effect was further shown by mixing sodium tungstate and chromate solutions, adding perchloric acid, evaporating, and boiling. The amount of chromium in the precipitate was always 1 or 2 mg. When vanadium was present, about the same proportion of it was found in the tungstic acid. Several days' leaching of the precipitate with dilute sulfuric acid failed to remove any of these metals. Moreover, the amount of ferric oxide in the precipitate was much greater. One-gram samples of Bureau of Standards Steel 50 containing 17.56 per cent tungsten, 3.61 per cent chromium, and 0.76 per cent vanadium, were treated as above. The precipitate of tungstic acid contained 6.4 mg. of iron, 1.4 mg. of chromium, and 0.3 mg. of vanadium as oxides. When corrected for these impurities, 17.63 per cent of tungsten was obtained. In a steel containing 5.8 per cent of tungsten it was difficult to obtain a clear filtrate, but even with cinchonine the value obtained was only 5.60 per cent. The procedure recommended by James (*3*) is, therefore, unsatisfactory. All the silica was contained in these precipitates.

It seemed worth while to try to prevent the interference of tungsten by converting it into the soluble phosphotungstic acid. Certain difficulties were encountered, however. Phosphoric acid tends to prevent complete oxidation of chromium by perchloric acid, as shown in Table IV. Dichromate was added and reduced by hydroxylamine hydrochloride. Each result is the average of two or more experiments.

Table IV—Effect of Phosphoric Acid on Oxidation of Chromium by Perchloric Acid

EIGHTY-FIVE PER CENT PHOSPHORIC ACID	SEVENTY PER CENT PERCHLORIC ACID	TIME OF OXIDATION	CHROMIUM PRESENT	ERROR CHROMIUM
Cc.	*Cc.*	*Minutes*	*Mg.*	*Mg.*
5	20	15	100	−4
5	20	30	100	−7
15	20	15	100	−40
15	20	30	100	−50
5	25	20	50	−1.3
5	30	20	50	−1.0
5	35	20	50	−0.8
5	25	20	25	−0.5
5	32	25	25	−0.3
5	40	25	25	−0.3
5	30	25	25	−0.2
5	35	25	25	−0.1

Effect of Manganese

It is well known that trivalent manganese is stabilized by phosphoric acid. It was found that by boiling the correct mixture of perchloric and phosphoric acids, manganese could be quantitatively oxidized to a manganic salt and titrated by ferrous sulfate. If, therefore, chromium is oxidized in the presence of considerable phosphoric acid as described above, the manganic salt must be reduced before the chromic acid is titrated, and dilute hydrochloric acid is suitable for this purpose. One-gram samples of steel to which manganese sulfate was added were boiled 25 minutes with 3 cc. of 85 per cent phosphoric acid and 35 cc. of 70 per cent perchloric acid. The solutions were diluted to 150 cc., the stated amounts of 2.3 *N* hydrochloric acid (one part of concentrated acid and four of water) added, and after boiling 5 minutes any manganic salt present was titrated electrometrically with ferrous sulfate. The results are shown in Table V.

Table V—Effect of Hydrochloric Acid (2.3 *N*) on Manganic Phosphate

MANGANESE PRESENT	MANGANESE FOUND AFTER ADDITION OF HCl					
	0	1 cc.	2 cc.	3 cc.	5 cc.	10 cc.
Mg.	*Mg.*	*Mg.*	*Mg.*	*Mg.*	*Mg.*	*Mg.*
11.3	5.1	3.3	1.0	0	0	0
51	18.0				0.3	0
101	40.6					0.2

In all cases there was insufficient phosphoric acid for complete oxidation. Ten cubic centimeters of 2.3 *N* hydrochloric acid are sufficient to reduce considerable amounts of manganese, and it was found that it would not reduce any of the chromium when 50 mg. of it and 2 grams of iron were present. Even 25 cc. caused only a slight reduction.

These results show that if even 5 cc. of 85 per cent phosphoric acid are present, the amount of perchloric acid must be greatly increased even with small amounts of chromium, and that with larger amounts, even this does not entirely eliminate the error.

It was found that 10 cc. of 85 per cent phosphoric acid were required to keep in solution 0.2 gram of tungsten when boiled with 30 cc. of perchloric acid. With 5 cc., a heavy cream-colored precipitate formed which persisted on dilution, but this amount of phosphoric acid was sufficient for 0.1 gram of tungsten, the slight precipitate dissolving on dilution.

Three cubic centimeters were sufficient for 0.05 gram. In the presence of 1 and 2 grams of iron, however, 5 cc. are sufficient for 0.1 and 0.15 gram of tungsten, respectively. Using 3 cc. of phosphoric acid under the same conditions, a precipitate forms but dissolves when 10 cc. more are added after dilution, and the solution boiled. Table VI shows the results obtained by oxidizing chromium under varying conditions, using in all cases 3 cc. of 85 per cent phosphoric acid and 35 cc. of 70 per cent perchloric acid. After dilution, 10 cc. more of the former were added. Each of the errors shown is the average of several experiments.

Table VI—Effect of Phosphotungstic Acid on Oxidation of Chromium by Perchloric Acid

IRON	TUNGSTEN	CHROMIUM	ERROR CHROMIUM
Grams	*Grams*	*Mg.*	*Mg.*
1	0.1	12	−0.07
1	0.1	50	−0.20
1	0.2	50	−0.25
2	0.2	50	−0.07
0.75	0.2	50	−0.35
2[a]	0.2	50	+0.03

[a] No phosphoric acid added after oxidation. Solution cleared on dilution.

By using the conditions of the last experiment in Table VI, adding extra iron, dissolving the steel in a mixture of phosphoric, nitric, and hydrochloric acids, and reducing the manganic salt by hydrochloric acid, the right value was obtained for a steel containing 18.7 per cent tungsten and 3.13 per cent chromium. In another experiment using the conditions of the next to the last analysis in Table VI, the result was 3.08 per cent. This error of 0.5 mg. of chromium persisted in all cases where 10 cc. of phosphoric and of dilute hydrochloric acid were added after the oxidation, and was probably due to some reducing material in the acid. One gram of steel containing 15 per cent of tungsten required no extra phosphoric acid to keep it in solution.

Effect of Vanadium

If vanadium is present, low results for chromium are always obtained, so that the above method is of somewhat limited applicability. In the presence of phosphotungstic acid, Willard and Young (*15*) have shown that vanadic acid forms a complex which is only partially reduced by ferrous sulfate. Attempts to break up this complex by boiling with perchloric acid or by adding fluoride were without effect.

To show the magnitude of this error, varying amounts of vanadium as sodium vanadate were added to 1 gram of a steel containing 4.10 per cent chromium, which was treated as described above for chrome-tungsten steel. Assuming that all the chromium was titrated, the errors in vanadium, with 2, 10, and 30 mg. of the latter present, and 0.2 gram of tungsten, were −1.7, −3.9, and −5.0 mg., respectively. With 0.1 gram of tungsten, the corresponding errors were −1.5, −2.1, and −3.6 mg. of vanadium.

Method Not Involving Phosphoric Acid

Willard and Young (*15*) have shown that a large amount of tungstic acid, as sodium tungstate, may be added without precipitation to an acid solution containing sufficient ferric salt. This dissolved tungstic acid does not interfere in the electrometric titration of chromic and vanadic acids. In applying this to a chrome-vanadium-tungsten steel, from which tungsten had been removed in the usual way and the chromium and vanadium in the filtrate oxidized by perchloric acid, it was noticed that if the tungstic acid was dissolved off the filter by hot 4 per cent sodium hydroxide and added to the oxidized filtrate containing sufficient iron, the results were always low by 0.5 mg. of chromium, even if the tungstate solution had been oxidized by peroxide or persulfate. This was proved to be due to organic matter introduced by the filter paper, no matter whether the sodium hydroxide was hot, cold, or fairly dilute. Sodium carbonate solution did not cause this error but it was impossible to oxidize all the chromium in the residue. It seemed essential, therefore, to fuse the tungstic oxide with sodium carbonate, the air acting as oxidizing agent. Although more troublesome, this method has been shown to eliminate all errors.

Procedure for Chromium or Chromium and Vanadium in Tungsten Steels

A sample of 1 to 1.5 gram is usually convenient. Place it in a 150- or 250-cc. beaker, and add 10 cc. of water and 30 cc. of hydrochloric acid (sp. gr. 1.18). Heat until the steel is completely decomposed and to the hot solution add cautiously from a pipet 8 to 10 cc. of nitric acid (sp. gr. 1.42), without removing the cover glass. Boil gently with occasional swirling until all dark metallic particles have been oxidized to yellow tungstic acid, and evaporate to 20 cc. If necessary, add 10 cc. of hydrochloric acid and 3 cc. of nitric, and boil down again to 20 cc. Dilute to 75 cc., boil a few minutes to dissolve all salts, filter into a 500-cc. Soxhlet flask, or, less satisfactorily, into a tall 500-cc. lipped beaker, and wash with hot, 2 per cent hydrochloric acid. Remove the flask or beaker and wash out the acid with 1 per cent ammonium nitrate solution, taking care that these washings are discarded because ammonium salts prevent complete oxidation of chromium.

To the filtrate add 1 gram of iron as ferric chloride or nitrate, but not sulfate; if a 1.5-gram sample was used, add only 0.5 gram of iron. Add 25 cc. of 70 per cent perchloric acid (or more if a larger sample was taken) and evaporate to fumes of the acid.

In the meantime, ignite the tungstic acid precipitate in an open platinum or iron crucible and fuse it for 5 minutes with 1.5 grams of sodium carbonate with free access of air. Or fuse with sodium peroxide in an iron crucible free from chromium, dissolve in water, and boil to remove peroxide.

Boil the main perchloric acid solution in the covered flask or beaker 20 minutes after the appearance of dense fumes of the acid. Dilute with an equal volume of water, boil 3 minutes to expel chlorine, and while still hot, pour into it with constant stirring the sodium tungstate solution together with the small amount of ferric oxide which it contains. A clear solution will result.

Determination of Chromium

If only chromium is to be determined, add to the cool solution excess of standard ferrous sulfate and titrate back with permanganate as previously described. No phosphoric acid is needed. The arsenite method of Kolthoff and Sandell may also be used. The ferrous sulfate must be standardized under the same conditions of acidity and volume.

Determination of Vanadium

Vanadium may be determined in the same solution after destroying the excess of permanganate by a drop of arsenite (*5*), but the vanadic acid must be titrated electrometrically with ferrous sulfate, because, as has already been pointed out, tungsten prevents the formation of color with diphenylbenzidine.

The excess of permanganate may be conveniently destroyed by adding 1 or 2 cc. of 0.1 *M* sodium azide (*16*) and boiling for a moment, or at room temperature by adding more azide and letting stand a short time.

Boiling with a little dilute hydrochloric acid is also effective.

Determination of Chromium and Vanadium

To the perchloric acid solution, add 25 cc. of sulfuric acid (sp. gr. 1.5), cool, and titrate chromic and vanadic acids electrometrically with ferrous sulfate. If much vanadium is present, cool the solution to 5° C.

The tungstic acid in solution begins to precipitate after several hours.

Indicator Method for Chromium and Vanadium

This differs from the method just described in the removal of tungstic acid to prevent its interference with the indicator. Proceed as already described including the filtration and washing of the tungstic acid precipitate. Use paper pulp. The oxidation of chromium in the filtrate is carried out in the same way, except that no iron is added, and the titration is carried out as directed. If no color develops, it is probable that tungstic acid was not completely removed or too much acetate was added.

The small amounts of chromium and vanadium in the tungstic acid are determined colorimetrically after fusion in an open crucible with 1 or 2 grams of sodium carbonate (*15*). The melt is dissolved in water and filtered. If it is colorless, no chromium is present. If it is yellow, estimate the chromium by matching the color in a beaker with an alkaline solution of equal volume to which standard dichromate is added. Then acidify the solution with phosphoric acid and estimate the vanadium colorimetrically by the method of Willard and Young. If chromium is present, add to the vanadium standard an equivalent amount of dichromate.

One-gram samples of Bureau of Standards Steel 50 containing 17.56 per cent tungsten, 3.61 per cent chromium, and 0.756 per cent vanadium, were treated as described, the chromium being titrated by the ferrous sulfate–permanganate method, without any indicator. The values obtained were 3.61, 3.61, 3.60, 3.62, and 3.60 per cent. In the first experiment, 10 cc. of 85 per cent phosphoric acid were added before the permanganate titration, but the end point was sharper without it. The value for vanadium in one sample was found to be 0.753 per cent by adding 20 cc. of 0.1 *M* sodium azide to reduce the excess of permanganate, letting stand 20 minutes at room temperature, and titrating vanadic acid electrometrically with ferrous sulfate.

It should be noted that perchloric acid is an excellent solvent for many alloys which dissolve with difficulty in other acids.

Separation of Chromium as Lead Chromate from Perchloric Acid Solution

It has been shown by Willard and Kassner (*8*, *14*) that lead chromate is completely insoluble in 1 *M* perchloric acid which is 0.01 *M* in lead perchlorate, and practically insoluble in 5 *M* acid if twice as much lead is present. It would thus appear quite feasible to separate chromium from vanadium, manganese, and other metals by precipitation as lead chromate after oxidation by perchloric acid as described above. The results of experiments along this line showed that such a method was possible if proper conditions were maintained.

Lead perchlorate was prepared by evaporating lead nitrate with a slight excess of perchloric acid as described by Willard and Kassner (*13*), but no attempt was made to free it from acid. A salt prepared from litharge seemed to contain some reducing material. The solution was diluted to 0.5 molar.

Lead chromate was completely precipitated in a short time from a solution containing considerable iron, 1 *M* perchloric acid and 0.04 *M* lead perchlorate. These were adopted as standard conditions. Such a solution contains in 200 cc., 16 cc. of 0.5 *M* lead solution and 17 cc. of 70 per cent perchloric acid. Extra lead must be added if much chromium is precipitated, 100 mg. of chromium requiring 4 cc. of 0.5 *M* solution.

A solution oxidized by boiling perchloric acid always contains, after dilution, small amounts of chloride which interfere slightly with complete precipitation of lead chromate. The addition of a few drops of silver perchlorate, prepared from the nitrate in the same way as the lead salt, removed this source of error. It was sometimes necessary to neutralize part of the free acid, and ammonia was found best for this purpose because sodium hydroxide usually contains chloride and sometimes reducing substances. The procedure followed, after the perchloric acid solution had been boiled to remove chlorine, was to neutralize part of the acid if necessary, add a slight excess of silver perchlorate, heat just to boiling, add the proper amount of lead perchlorate, and cool to room temperature, stirring occasionally. If filtered hot, some chromate remained in solution. The precipitate was very dense and crystalline. It was filtered on a Gooch crucible, washed with cold water, transferred to a beaker, excess of standard arsenite added, then 50 cc. of hydrochloric acid (sp. gr. 1.09), after which the excess of arsenite was titrated with bromate. The lead chromate could also be dissolved in saturated sodium chloride solution containing 1 cc. of concentrated hydrochloric acid per 100 cc., and titrated with ferrous sulfate. If 1 gram of the steel is dissolved in 20 cc. of 70 per cent perchloric acid and diluted to 175 or 200 cc., the acidity will be about right.

Good results were obtained when about 80 mg. of chromium were present, but with 30 mg. there was an error of −0.2 to 0.3 mg., the cause of which is yet unexplained. Vanadium was determined in the filtrate by titration with ferrous perchlorate to avoid precipitation of lead sulfate, and the results were good when all the chromium had been precipitated. In a solution containing tungstic acid held in solution by ferric perchlorate, 0.6 to 0.8 mg. of chromium remained in solution. Further work is in progress to obviate the difficulties mentioned. Table VII shows the results obtained under proper conditions.

Table VII—Separation of Chromium as Lead Chromate

WEIGHT OF SAMPLE	CHROMIUM PRESENT	CHROMIUM FOUND	VANADIUM PRESENT	VANADIUM FOUND
Grams	%	%	*Mg.*	*Mg.*
	Cr-Ni Steel, B. S. 32b			
2.2	0.638	0.635		
2.2	0.638	0.630		
	Stainless Steel, B. S. 73			
0.6	13.93	13.89		
0.6	13.93	13.88		
	Synthetic Mixture			
Grams Fe	*Mg.*	*Mg.*		
3	83.15	83.15	32.7	32.5
3	83.55	83.60	32.7	32.5

Manganese can be determined in the filtrate from lead chromate by methods not applicable in presence of chromium.

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Determination of pH of Ammonia Latex[1]

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The pH of latex has been determined at various concentrations of ammonia (1) by the use of indicators, and (2) by the application of the glass electrode. The two curves thus obtained were comparable but not identical.

It is shown that the glass electrode gives results reproducible with a high degree of accuracy up to pH 9.5 and a fair degree of accuracy up to pH 11.0. Above pH 11.0 it is necessary to calibrate each electrode. An ordinary galvanometer allowed measurement of the e. m. f. to 1 millivolt. The assymetry of the glass was so small as to be negligible.

THIS paper covers the work done so far in these laboratories on the development of an accurate and rapid method for determining the pH of latex.

From a practical viewpoint one of the most troublesome features of the direct use of a hydrogen electrode is the deposition of a film of rubber on the platinum, which by increasing the internal resistance of the cell, so reduces the sensitivity of the null point instrument that after a few determinations the apparatus must become inoperative. A more serious objection to this electrode is the uncertainty attached to measurements made in solutions containing proteins.

The glass electrode, however, is believed to be very satisfactory. Although no comprehensive theory of its mechanism has yet been formulated, it has been used successfully under conditions where the hydrogen electrode and indicators would be useless (*4, 3*). In this paper a method of making and using a modified Haber cell is described, and the results of measurements of the pH values of normal latexes are compared with those previously obtained by means of indicators.

Colorimetric Method

The successful use of indicators depends upon the preparation of a clear serum. This was done by mixing about 50 cc. of latex with 0.5 gram of carbon black, then filtering 20 cc. of the mixture under a pressure of 15 lbs./sq. in. (1.0563 kg./sq. cm.). Probably by causing a partial coagulation of the rubber particles the carbon black increased the rate of filtration without appreciably altering the pH of the serum, though even under the most favorable circumstances not more than 2 or 3 cc. of serum could be obtained in an hour. The filter was made by pouring a mixture of Cellite and water on a filter paper in a small Buchner funnel, washing it with water several times by suction, and finally drying it at 100° C. The funnel was closed with a rubber stopper kept tight by two metal plates bolted together, and air-pressure was applied through a tube in the stopper. It was necessary to use pressure instead of suction to minimize loss of ammonia by vaporization, but the ammonia content of the filtrate was always less than would be expected when calculated from the results of titration of the latex on the assumption that all the ammonia is in the serum. The difference could be partly accounted for by adsorption of ammonia on the carbon black, but it is no doubt also due to adsorption of ammonia on the rubber particles.

The example of data given in Table I obtained by titration of latex and the serum prepared from it by pressure filtration shows that this use of carbon black in pH measurement might be expected to give low results. That no corresponding difference of pH was found may be ascribed to the inadequacy of the colorimetric method to measure small changes of hydrogen-ion activity.

The pH of the serum was determined by the familiar comparator method, about 2 cc. being required for each determination. It is claimed that an accuracy of about ±0.1 can be obtained by means of indicators, but when they are used with latex serum a more liberal allowance for error must be made.

Most of the available indicators for use in alkaline solution are unsatisfactory on account of their small color change, and the presence of proteins in the solution under examination is known frequently to cause large error. That the measurements were sometimes unreliable was proved when two indicators covering the same pH range did not agree even approximately, and a partial discharge of the color of the indicator often occurred, probably because of adsorption on colloidal matter. Owing to the difficulty in obtaining reliable results it was decided that an electrometric method must be used. The experimental results obtained with indicators and latex serum are shown graphically in Figure 1.

Table I—Titration of Latex and Serum by Pressure Filtration (33.1% solids)

NH_3 in Latex	Calcd. NH_3 in Serum	Obsd. NH_3 No carbon black	Carbon black
%	%	%	%
1.46	2.18	1.93	1.75
2.18	3.26	2.70	2.53

The Glass Electrode

MacInnes and Dole (*6*) who have recently studied the effect of variation in the composition of the glass on its suitability as an electrode, recommend a soda-lime glass of composition disilicon oxide, 72 per cent; calcium oxide, 6 per cent; and sodium oxide, 22 per cent (Number 015, supplied by the Corning Glass Company, Corning, N. Y.). This glass has been used to make bulbs for the electrodes in the following way: Electrodes 1, 2, and 3 were made by drawing out at one end a tube of soft laboratory glass, diameter 13 mm., to a diameter about 5 mm. A piece of the special glass was fused in the narrow end of this tube and blown into the form of a small bulb, strong enough to withstand the pressure of 2 or 3 inches (5.08 or 7.62 cm.) of 0.1 *N* hydrochloric acid, yet so thin that the resistance was surprisingly low and screening was unnecessary. An ordinary Leeds and Northrup galvanometer was sensitive enough to allow measurement of the e. m. f. within 1 millivolt, which corresponds to an accuracy of about ±0.02 pH. The open end of the tube was coated with paraffin, then filled with 0.1 *N* hydrochloric acid, and closed by a rubber stopper to prevent evaporation when not in use. Figure 2 shows the wiring of the arrangement with a diagrammatic representation of the glass electrode and the calomel half cell. Instead of having the rest of the electrode within the bulb it was combined with a 0.1 *N* hydrochloric acid calomel electrode, the side tube of which was lowered into the acid in the bulb when a measurement of e. m. f. was to be made.

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It was thought that as this bulb might consist partly of glass from the supporting tube it would be unsatisfactory, and the bulbs of electrodes 1-A, 2-A, 3-A, 4-A, and 5-A were blown from tubes of the special glass. However, the data given below show that except in strongly alkaline solution, electrode 3 is in good agreement with the others.

Calibration of Electrodes—Sorensen's glycine sodium chloride–sodium hydroxide standards were used (pH values at 25° C. obtained by slight interpolation of those given by Clark, *1*).

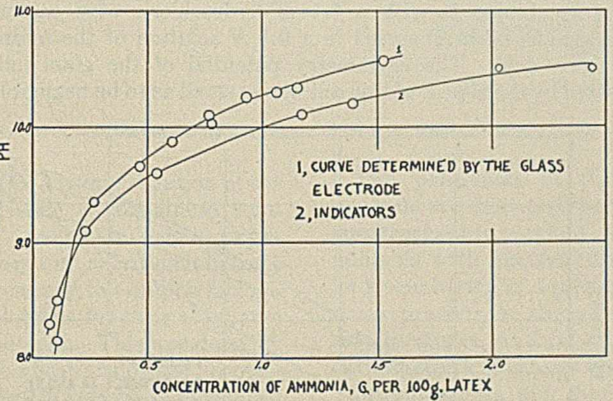

Figure 1—Relation between Concentration of Ammonia and pH

Materials—Fifty per cent sodium hydroxide solution allowed to stand in a Pyrex tube till the carbonate settled. Portion of clear solution diluted with boiled distilled water and adjusted to 0.1 N. Stored in a paraffined Pyrex bottle.

Thirty-six per cent hydrochloric acid solution diluted and adjusted to 0.1 N with anhydrous sodium carbonate.

Potassium chloride, sodium chloride, and glycine. Best obtainable materials recrystallized several times.

All rubber stoppers were boiled in sodium hydroxide solution, hydrochloric acid, then water.

Buffer standards of pH greater than 11 kept in paraffined Pyrex bottles.

The slide wire, S (maximum scale reading 1000), used as a potentiometer, was proved to have a uniform resistance, and the voltmeter was calibrated with a standard Weston cell. The slide wire setting was varied to give voltmeter readings at intervals of 0.1 volt, and assuming a uniform voltage drop in the slide wire, the actual voltage was calculated in each case from the reading of the null point for the Weston cell. To determine the e. m. f. of the glass electrode cell the null point was first obtained, and then the slide wire was set to show a voltage of 0.5, corresponding to an actual voltage of 0.5810 when corrected by the calibration curve of the voltmeter. The e. m. f. was calculated from the readings of the slide wire at the null point and at 0.5810 volt.

By the use of the resistance box, R, the e. m. f. range could be varied.

Table II—E. M. F. of Cell with Buffer Standards

(Electrode 3)

pH of Buffer Standard (Soln. X)	Slide Wire Reading at Null Point[a]	E. M. F. of Cell
		Volt
8.43	561	0.3812
8.77	593	0.4030
9.54	681	0.4628
10.30	751	0.5103
11.12	814	0.5531
11.89	876	0.5953
12.45	915	0.6218
12.74	931	0.6325

[a] Slide wire reading at 0.581 volt 855 throughout.

Calculation of E. M. F.—The arrangement is:

$$\text{Hg} \mid \text{HgCl, KCl (satd.)} \parallel \text{soln. } X \mid \text{glass} \mid 0.1\ N\ \text{HCl, HgCl} \mid \text{Hg}$$

Assuming the glass surface reversible to the hydrogen-ion activity, this combination will be equal in potential to the sum of the two cells.

(A) Hg | HgCl, KCl (satd.) ||soln. X | H_2
(B) Hg | HgCl, 0.1 N HCl | H_2

The potential of (A) at 25° C. is

$$E = 0.2458 + 0.05915\ \text{pH}_x\ (2)$$

and of (B), 0.3989 (*5*). The relation between the e. m. f. and the pH of solution X is, therefore, at 25° C.:

$$E = -0.1531 + 0.05915\ \text{pH}_x$$

Table III—Comparison of Observed with Calculated Values of E. M. F. of Cell 1

(Electrode 3)

pH of Soln. X	E Theoretical	E Observed	Deviation
			Millivolts
8.43	0.3455	0.3812	35.7
8.77	0.3656	0.4030	37.4
9.54	0.4112	0.4628	51.6
10.30	0.4561	0.5103	54.2
11.12	0.5064	0.5531	46.7
11.89	0.5502	0.5953	45.1
12.45	0.5833	0.6218	38.5
12.74	0.6004	0.6325	32.1

The values given in Table III are not shown graphically but were used to obtain the curve in Figure 1.

Determination of pH of Normal Latex—The results given in Table IV were obtained with latex X-167 (total solids 37.9 per cent, ammonia 0.84 per cent). The ammonia content was varied by adding small quantities of a 24 per cent aqueous solution of ammonia to about 500 cc. of latex, and it was determined in each case by titrating against 0.1 N hydrochloric acid 1 or 2 grams diluted with water to 300 cc.

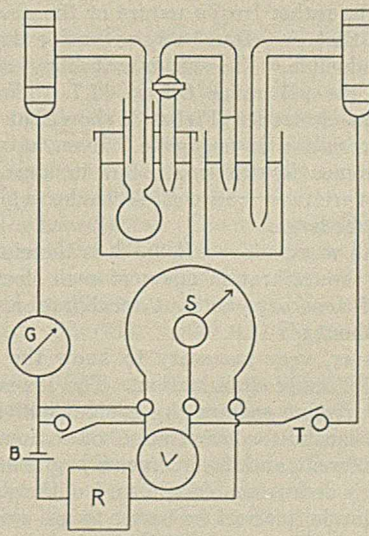

Figure 2—Wiring of Cell and Potentiometer

These results are plotted as a smooth curve in Figure 1. It will be noticed that the "blown" latex returned to very nearly the same pH when ammonia was added to it, showing that the removal of ammonia is probably a reversible process.

It was impossible to prevent the deposition of a film of rubber on the glass bulb. This did not seem to affect the e. m. f., but it greatly reduced the sensitivity of the galvanometer. The bulb was, therefore, washed in ammonia solution, and the rubber film could be removed by means of a small brush. Since it was necessary to clean the electrode in this way after each determination, the Haber form is better than the more fragile type devised by MacInnes and Dole (a very thin membrane sealed on the end of a supporting tube).

Table IV—pH of Latex *X*-167
(Electrode 3)

NH_3 per 100 Grams of Latex	Slide Wire Reading at Null Point[a]	E. M. F.	pH from Calibration Curve
Gram			
LATEX BLOWN AND STIRRED FOR 2 HOURS			
0.11	524	0.356	8.15[b]
0.27	660	0.448	9.35
0.47	691	0.470	9.66
0.61	711	0.483	9.87
0.77	731	0.497	10.10
LATEX AS RECEIVED			
0.78	725	0.493	10.03
0.93	746	0.507	10.26
1.06	751	0.510	10.30
1.15	753	0.512	10.34
1.53	771	0.524	10.57

[a] Slide wire reading at 0.581 volt 855.
[b] pH value obtained by extrapolation.

The reversibility of the electrode after use with latex was checked against some of the original buffers. The results of this test appear in Table V.

Table V—Stability of Electrode 3

pH of Buffer Standard	E. M. F. of Cell after Use with Latex	Previous E. M. F.	Change
			Millivolts
9.54	0.4600	0.4628	− 2.8
10.30	0.5096	0.5103	− 0.7
11.12	0.5402	0.5531	−12.9
11.89	0.5953	0.5953	0

It was known that the standard of pH 11.12 had probably changed, and neglecting the result with this solution the reversibility of the electrode is apparently fairly satisfactory.

Reproducibility of Electrodes

Owing to the rather fragile nature of the glass electrodes it is desirable that as well as being reversible they should be readily reproducible. The reproducibility has been examined over the pH range 8.4 to 12.7. The calibration curves of a few electrodes (Figure 3) show that up to about pH 9.5 the variation is negligible. Even at pH 11.0 the greatest difference is still small, but in strongly alkaline solution the variations between electrodes which agree at lower pH may be large.

For accurate work above pH 9.5 it is therefore necessary to determine the calibration curve of each electrode, but a fair degree of accuracy, without recalibration, can be expected up to about pH 11.0.

It is, however, very necessary to know the composition of the solution under examination. The lowest curve obtained with glycine–sodium hydroxide buffer standards with a small constant concentration of sodium chloride is remarkably different, and the divergence begins at a lower pH.

Owing to this depression of the e. m. f. of the glass electrode by sodium chloride it would be better to use gylcine–sodium hydroxide buffer mixtures for calibration instead of Sorensen's standards, but as the effect is large only at high pH, and Sorensen's standards of greatest alkalinity have only a small concentration of this salt, the error introduced by their use is probably small. It would be best to calibrate the electrodes with glycine–sodium hydroxide mixtures for the pH range 8.0 to 11.0, and with sodium hydroxide solutions of known pH for values above 11.0.

It is the experience of the authors that up to pH 10.0 or 11.0 most of the electrodes differed only slightly and there is little difficulty in obtaining reliable results, but beyond pH 11.0 careful calibration of the electrode immediately before use is essential.

It is also necessary to allow the electrodes to reach equilibrium. Immediately after filling them with acid the e. m. f. is always high, and an equilibrium value is reached in about 24 hours; the bulbs were therefore filled with acid and immersed in water for a day or two before they were used.

Asymmetry Potential of the Glass

The potential in the glass bulb of electrode 3 was measured by combining it with a 0.1 *N* hydrochloric acid calomel electrode, both immersed in a 0.1 *N* solution of the hydrochloric acid. The asymmetry potential of the glass indicated by the e. m. f. of this cell was so small as to be negligible.

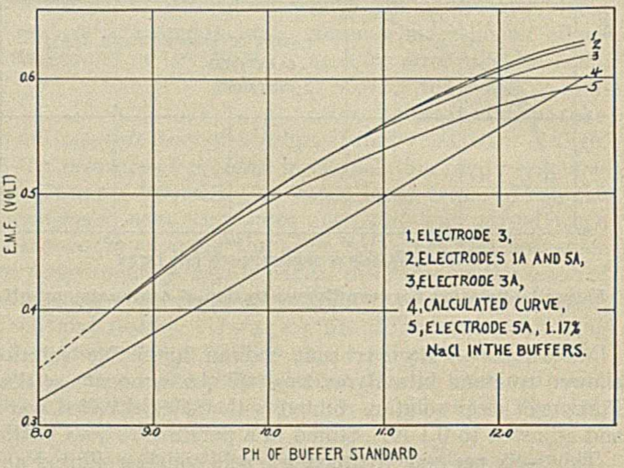

Figure 3—Calibration Curves of Glass Electrodes

Discussion of Results

In the absence of a generally accepted theory it is impossible at the present time to decide whether the pH values determined by the glass electrode are strictly in accordance with those that would be obtained by a hydrogen electrode were it applicable to latex. Hughes (*3*) suggests that the glass membrane acts as a sodium acid silicate buffer which keeps the hydrogen-ion concentration within the glass phase constant. This buffer action begins to become less effective at about pH 9, which is the value at which MacInnes and Dole find deviations begin from the hydrogen electrode. These authors state that when the base present is tetramethylammonium hydroxide there is only a very small deviation even at pH 13. Hughes ascribes the difference in action of the various hydroxides as probably due to greater power of penetrating the glass. Thus potassium hydroxide has less penetrating power than sodium hydroxide owing to the larger potassium ion, and it might be expected that tetramethylammonium hydroxide would have still less penetrating power owing to the large $N(CH_3)_4$ complex.

This leads to the view that the composition of the buffers used in calibrating the electrode should be as far as possible similar to the composition of the solution of which the pH is to be determined. However, in the absence of any data on the relative effects of sodium and ammonium ions on the potential of the glass electrode, the pH values recorded here can be considered provisionally as probably not very far from the true ones.

The two curves in Figure 1 are not strictly comparable as they refer to different latexes, but it is known that the pH values determined by the glass electrode are always higher than corresponding values obtained by means of indicators. The lowest parts of the curves do not differ so much, and in this region the indicators are more satisfactory, chiefly because their color change for a given increase of hydrogen-ion activity is greater. The increasing divergence between the curves at higher ammonia concentrations might be accounted for partly by loss of ammonia from the serum during filtering. The curves become much flatter at about 0.3 per cent ammonia; this is probably due to acidic substances in the latex.

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Spectrographic Determination of Aluminum in Biological Ashes[1]

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The principles of the spectrographic method of analysis are discussed and a critical study made of the spectrographic method of qualitative and quantitative analysis with special reference to effects on accuracy and sensitivity of individual radicals and radical mixtures present in the aluminum-containing salts and salt mixtures, and relative merits of the arc and condensed spark methods of excitation.

Modifications are developed of the spectrographic method of quantitative analysis involving both arc and condensed spark methods of excitation.

Tests have been made of the effects of volatility of aluminum compounds on the spectral excitability of the aluminum they contain.

Aluminum has been determined in a number of biological materials using spectrographic technics developed in this investigation.

IN AN investigation of the role of aluminum compounds in animal physiology and nutrition it became necessary to examine biological ashes for their aluminum contents. This was done by modifications of the spectrographic method as developed by Hartley (*2*), de Gramont (*1*), Meggers (*4*), and others. This method is based on the existence of correlations between low concentrations or quantities of an element in a spectral source (flame, arc, or spark) and the numbers and intensities of certain of its spectral lines especially its *raies ultimes*. It is quite generally recognized that such correlations are materially affected by a number of details in the spectrographic technic so that they can be used for quantitative estimations only when obtained under controlled conditions. However, the literature is lacking in specificity on the extent to which control is necessary. Statements exist to the effect that methods of excitation, time of exposure, and plates used are among the items which effect *raies ultimes* in a spectrogram and must, therefore, be controlled in making quantitative estimations by the spectrographic method. But very little is known concerning the effects on *raies ultimes* of the containing materials and the anions attached to the element determined at the time of excitation, both of which may vary considerably and are more or less beyond control of the operator in estimating aluminum contents of biological ashes by the spectrographic method. The purpose of the experiments here recorded was to ascertain whether these two items, the aluminum-containing material and the anions or negative radicals attached to the aluminum at the time of excitation, possessed effects specific of the containing materials or attached anions, or effects which could be correlated with their properties like alkalinity, acidity, volatility, etc., or whether they possessed no effects whatever on *raies ultimes*, in which case their number and intensities will be due entirely to the concentration of the element which they represent. Publication of these results seems warranted since they may have application in other spectrographic work.

Spectrographic Equipment

SPECTROGRAPH—The spectrograph used was Hilger's E-1. This is a quartz prism spectrograph of the Littrow type which disperses the spectrum from 1930 to 8000 Å. over a distance of 30 inches, any 10-inch section of which may be photographed on a 4 by 10 inch (10.16 by 25.4 cm.) plate. Ordinarily the desired portion of the spectrum is not longer than 10 inches, which can be covered in one exposure. The desired portion is obviously that which contains the persistent lines of the element under investigation, which in this case is aluminum. Its most persistent lines are 3944 Å. and 3961.5 Å. with a less persistent pair of lines at 3082 Å. and 3092 Å. On Meggers' authority, obtained by the authors' communication with him, the line 3092 Å. is of no value in this work on account of a nitrogen line of the same wave length.

SPARK HOOK-UP—The electrical hook-up for producing the high tension spark consisted of a 1.0-kilowatt step-up transformer, ratio 1:200, a variable resistance in series with the primary, a 0.02-microfarad condenser across the secondary, and a self-induction coil in series with the secondary. The variable resistance reduced the primary voltage—i. e., the house current from 118 to 90 volts—which voltage prevented overloading the transformer. The self-induction coil, consisting of 250 turns of No. 20 gage insulated wire on a cardboard tube 5.5 cm. in diameter, served to smooth out the spark discharge and in that way diminished the intensity of the air lines which otherwise would have been present in the spectrum.

ARC HOOK-UP—The arc was produced by a 220-volt direct current with a 30.9-ohm resistance in the circuit. This resistance had a carrying capacity of $4^1/_2$ amperes. While a direct current supply of 150 volts is sufficient to maintain an arc between any metallic electrodes, it is highly desirable to use voltages higher than this on account of the fact that arcs between electrodes of material possessing good thermal conductivity tend to extinguish easily.

ELECTRODES AND ELECTRODE HOLDERS—The electrodes used exclusively throughout this work were special aluminum-free copper rods 5 mm. in diameter, supplied as electrodes for this purpose by Hilger. For the spark procedure they were held in a Hilger F 449 adjustable holder in which they were adjusted vertically with respect to one another so that the gap between their points was 7 to 8 mm. The upper electrode was pointed by about a 45-degree taper and the lower

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[1] Received October 16, 1930.

electrode was drilled to a depth of 4 mm. with a $^9/_{64}$-inch (0.356-cm.) drill. The resulting hole has a capacity for 20 to 30 mg. of ash material which is considerably more than that used up by the spark in one minute.

In the arc procedure the electrodes were held vertically in a Gaertner arc electrode holder provided with rack and pinion which allowed simultaneous adjustment of the electrodes for striking the arc, followed by simultaneous separation, thereby maintaining stationary the center of the gap. An arc 2 cm. long was necessary to eliminate the continuous spectrum of the incandescent electrode tips. The lower electrode was drilled in the same manner as for the spark, while the upper electrode was left unpointed. Since the positive pole of an arc is the hotter, presumably because of bombardment by electrons from the cathode, better results are obtained by making the lower electrode, which contains the sample, the positive pole.

PLATES AND DEVELOPER—The selection of the photographic plates will obviously vary with the region to be photographed, the source of light, the exposure, and the width of slit. The work in this investigation was confined to the short visible and near ultra-violet region of the spectrum for which Eastman 33 and 36 plates were found satisfactory. The choice between these two plates depended mainly on the width of slit used, the 33 plate being preferred and used for a 0.05-mm. slit, and the 36 plate for a 0.03-mm. slit. In the case of either plate the exposure was 60 seconds for the spark and 15 seconds for the arc.

The plates were developed in a lantern slide formula of elon-hydroquinone selected for its strong contrast effects.

Spectrographic Technic

The spectrograph is first adjusted for the visible portion of the spectrum by the required rotation and focus of the prism. The slit is then opened to the width of about 1 mm., and its middle portion exposed by means of the Hartmann diaphragm. Then the light source, arc or spark, is adjusted laterally and vertically at a distance of about 30 cm. from the slit so that the electrode tips can be seen in the center of the lens field of the spectrograph, after which the slit is closed to a width of about 0.03 mm. and the cylindrical quartz lens interposed between the light source and slit, and adjusted so as to focus the light as sharply as possible on the slit.

In all experiments the Hartmann diaphragm was used. This sliding diaphragm has three apertures which allow the use of three successive portions of the same slit for photography of three comparison spectra without liability of lateral displacement of the spectral lines. The image in passing through the optical system of the spectrograph becomes inverted. Therefore, all spectra were made in 1, 2, 3 order from bottom to top on the diaphragm to give 1, 2, 3 order from top to bottom on the plate. The 1, 2, 3 order on the plate consisted of: (1) control spectrum of cleaned electrodes, (2) spectrum of sample, and (3) addition of element in question as a means of locating the lines, in this case the lines of aluminum.

The electrodes for the spark technic are easily cleaned with 10 to 15 per cent hydrochloric acid. The upper electrode can be used throughout a series of exposures without removing and can be cleaned in position by immersing in the acid and rinsing with a stream of distilled water from a wash bottle. The lower electrode must be removed for cleaning, which must be very thorough for each succeeding spectrogram. The same general procedure was followed for cleaning the arc electrodes, except that a more reactive acid must be used because the higher temperature of the arc tends to fuse the tips of the electrodes so that they may occlude some of the aluminum contained in the previous sample. Cold 25 per cent nitric acid was used for cleaning the arc electrodes, care being taken to confine the more vigorous reaction to the tips. After such cleaning the lower electrode was redrilled, an operation which not only served to reshape it but also to cut away any contaminating material not removed by the cleaning acid.

Experiments

Arc and spark spectrograms were prepared of a series of salts and salt mixtures containing aluminum in concentration from 0 to 1000 p. p. m. The individual salts used for this purpose were: sodium acid sulfate, sodium sulfate, monobasic sodium phosphate, tribasic sodium phosphate, and sodium chloride.

The mixtures used were:

Mixture 1—Tricalcium phosphate, 2 parts; orthopotassium phosphate, 3 parts; sodium sulfate, 1 part; magnesium sulfate, 1 part.

Mixture 2—Orthopotassium phosphate, 1 part; potassium sulfate, 1 part; tribasic sodium phosphate, 1 part.

Mixture 3—Tricalcium phosphate, 1 part; magnesium sulfate ($MgSO_4.7H_2O$), 1 part.

In preparing the several series of aluminum concentrations in the above salts and salt mixtures, the calculated volume of an aluminum ammonium sulfate, $Al_2(SO_4)_3(NH_4)_2SO_4.24H_2O$, solution containing 0.01 to 0.1 per cent of the element aluminum was in each case added and mixed into the required weight of the salt or salt mixture contained in a 50-cc. Pyrex beaker. For example, in preparing a concentration of 5 p. p. m. of aluminum in any of the above salts, 1.0 cc. of a 0.01 per cent solution of aluminum in the form of the aluminum ammonium sulfate was added and mixed into 2 grams of the salt contained in a 50-cc. Pyrex beaker. The material was then dried at 110° C. Just previous to spectral excitation the material was pulverized and mixed again by means of a cleaned copper electrode.

The single salts represent the anions as variables and in combination with a common cation—viz., sodium. Mixture 1 was composed to represent a biological ash. Its composition approximates that of biological ashes. Mixture 2 is intended to show the effects of cations of the first group of the periodic system, the members of which have low ionization potentials. Mixture 3 represents cations of the second group of the periodic system. These have somewhat higher ionization potentials than those of the first group.

Spectrograms were prepared of these mixtures by the technic already described. The results are given in Table I, in which the conventions used denote the following line intensities:

Completely invisible by lens........................	−
Questionably visible by lens or of same intensity as electrode control................................	±?
Visible by the aid of the lens........................	±
Visible to naked eye as a light line (without the aid of the lens)..	+
Visible to naked eye as a heavy line (without the aid of the lens)..	++
Sufficiently heavy to cause a fogged line.............	+++

A study of Table I shows that in practical use correlations between aluminum concentrations and aluminum lines are unaffected by the radicals which constitute the aluminum-containing materials.

As has already been stated for the above aluminum-containing salt mixtures, the aluminum, in the form of very dilute solutions of aluminum ammonium sulfate containing 0.01 and 0.1 per cent of the element aluminum, was added and mixed into a weighed quantity of the salt mixture which was then evaporated to dryness at 110° C. previous to arcking or

Table I—Effect of Anions on Correlation between Spectral Effects and Aluminum Concentration in Sodium Salts

SALT	ALUMINUM CONCENTRATION		ARC			SPARK		
	Ash basis	Fresh[a] tissue basis	3082 Å.	3944 Å.	3961.5 Å.	3082 Å.	3944 Å.	3961.5 Å.
	P. p. m.							
NaHSO₄	Control		−	−	−	−	−	−
	25	0.25	±?	+	+	−	+	+
	50	0.5	±	++	++	−	+	+
	100	1.0	±	+	+	−	+	+
	200	2.0	+	++	++	±	+	+
	500	5.0	+	++	++	+	++	++
Na_2SO_4	Control		−	−	−	−	−	−
	25	0.25	−	±	+	−	±	+
	50	0.5	−	+	+	−	+	+
	100	1.0	±	+	+	−	±	+
	200	2.0	−	−	−	−	±	+
	500	5.0	+	++	++	±	+	+
NaH_2PO_4	Control		±?	+	+	−	−	±
	25	0.25	−	±	+	−	±	+
	50	0.5	±?	+	+	−	±	±
	100	1.0	±?	+	+	−	+	+
	200	2.0	±?	±	+	−	+	+
	500	5.0	±?	+	+	+	+	++
Na_3PO_4	Control		−	−	−	−	−	−
	25	0.25	−	±	+	−	−	−
	50	0.5	±	+	+	−	±	+
	100	1.0	±	+	+	−	±	+
	200	2.0	±	+	+	−	±	+
	500	5.0	±	++	++	−	−	±
NaCl	Control		−	−	−	−	−	−
	25	0.25	−	−	±	−	±	+
	50	0.5	±	+	+	±	+	+
	100	1.0	±	+	+	+	+	+
	200	2.0	±	++	++	+	++	++
	500	5.0	±	++	++	+	++	++
Mixture 1	Control		−	−	±	−	−	±?
	5	0.05	−	−	±	−	−	±
	10	0.1	−	−	±	−	±	±
	20	0.2	−	−	±	−	±	+
	50	0.5	−	±	+	−	±	+
	100	1.0	−	+	+	−	+	+
	200	2.0	−	+	+	±?	+	+
	500	5.0	±?	+	++	±?	+	+
	1000	10.0	±	+	++	±	+	++
Mixture 2	Control		−	−	−	−	−	±?
	5	0.05	−	−	±	−	−	±
	10	0.1	−	−	±	−	−	+
	20	0.2	−	±?	+	−	−	+
	50	0.5	−	±	+	−	−	+
	100	1.0	−	+	+	−	−	+
	200	2.0	−	+	+	±?	+	+
	500	5.0	−	+	+	±	+	+
	1000	10.0	±	+	+	±	+	+
Mixture 3	Control		−	−	±?	−	−	±?
	5	0.05	−	−	±	−	−	±
	10	0.1	−	±?	+	−	−	±
	20	0.2	−	±?	+	−	−	+
	50	0.5	−	±	+	−	−	+
	100	1.0	±	+	+	−	−	+
	200	2.0	±	+	+	±?	±	+
	500	5.0	+	+	+	±	+	+
	1000	10.0	++	++	++	±	+	+

[a] Fresh tissue containing about 1 per cent ash.

sparking. Accordingly, the aluminum itself must have existed in the form of a salt of the predominating anion in the mixtures. Since these anions showed no effect on the relationship or correlation between aluminum concentration in the spectral source and spectral results—i. e., aluminum lines—it may also be concluded that the anion attached to aluminum itself has no effect on this relationship. However, in order to confirm this conclusion, arc and spark spectra were prepared of 1.0, 0.1, 0.01, and 0.001 mg. of aluminum introduced into the spectral sources (the arc and the spark) as chlorides in one series, as oxides in another series, and as phosphates in a third series. Correlations in the resulting spectrograms were then compared. The experimental procedure in this comparative study was as follows:

ALUMINUM CHLORIDE SPECTROGRAMS—A series of aluminum chloride solutions were prepared containing, respectively, 1.0, 0.1, 0.01, and 0.001 mg. of the element aluminum per 0.05 cc. (one drop) of solution. Arc and spark spectrograms were prepared of the residues of one drop of each of these solutions. The one-drop residues were obtained in the cup of the lower electrode by introducing one drop of the solution into the cup and then evaporating its water content by holding the electrode vertically in one hand and playing a small flame of a micro burner along the side of the electrode by means of the other hand until evaporation became visible. The flaming was always stopped before the upper portion of the electrode became too hot to be held in the bare hand. In that manner an evaporating temperature higher than 70° or 75° C. was avoided. At such temperatures the drop evaporated to apparent dryness in less than 2 minutes and presumably without any decomposition of aluminum chloride. The spectrograms of the one-drop residues prepared in this manner are recorded in Table II in which they are identified as aluminum chloride spectrograms.

ALUMINUM OXIDE SPECTROGRAMS—The above aluminum chloride solutions were used as sources of aluminum in preparing arc and spark spectrograms of the corresponding or same quantities of aluminum in form of the oxide. The experimental technic was the same as that followed in preparing the above aluminum chloride spectrograms except that one drop of concentrated ammonia was added to each of the several one-drop residues of the aluminum chloride solutions just before these residues reached complete dryness in the holes of the lower electrodes. The evaporation was then continued and completed with the necessary precautions to prevent spattering, after which the upper end of the electrode was heated nearly to a dull redness in order to render the residue chloride-free, in which condition it was then excited. The spectrograms of these residues are recorded and identified in Table II as aluminum oxide spectrograms.

ALUMINUM PHOSPHATE SPECTROGRAMS—In preparing arc and spark spectrograms of the same quantities of aluminum in the form of the phosphate, the source of aluminum was an aluminum phosphate solution in 7 to 8 per cent phosphoric acid which contained 1.0 mg. of aluminum per 0.05 cc. (one drop) of solution. From this solution dilutions were made containing, respectively, 0.1, 0.01, and 0.001 mg. of aluminum per 0.05 cc. of solution. Water was used in making these dilutions so that the original 7 to 8 per cent phosphoric acid was diluted correspondingly. One-drop residues of these solutions were prepared in the cup of the lower electrode in the same manner as that followed in the case of the chloride solutions except that the residues from the original undiluted solution, that containing 1.0 mg. of aluminum per 0.05 cc. of undiluted 7 to 8 per cent phosphoric acid, were heated nearly but cautiously to dull redness previous to excitation. The spectrograms of these residues are recorded and identified in Table II as the aluminum phosphate spectrograms.

Table II—Effect of Form of Combination of Aluminum on Correlation between Spectral Effects and Aluminum Concentration

SAMPLE	3082 Å.			3944 Å.			3961.5 Å.		
ARC	$AlCl_3$	Al_2O_3	$AlPO_4$	$AlCl_3$	Al_2O_3	$AlPO_4$	$AlCl_3$	Al_2O_3	$AlPO_4$
Mg.									
0.001	±?	±?	±?	±	+	+	+	±	+
0.01	±?	±	+	+	+	+	+	+	+
0.1	+	+	+	++	++	++	++	++	++
1.0	++	++	++	++	++	++	++	++	++
SPARK									
0.001	+	+	+	+	+	+	+	+	+
0.01	+	+	+	+	+	+	+	+	+
0.1	+	+	+	++	++	++	++	++	++
1.0	++	++	++	++	++	++	++	++	++

An inspection of Table II shows that chlorides, oxides, and phosphates of aluminum produce equivalent correlations between aluminum lines and quantities of the element aluminum in the spectral source excited by either the arc or the spark. The results in these tables, therefore, warrant the conclusion that the negative radical attached to aluminum in the spectral source at the time of excitation does not affect the correlations between the quantities and presumably also the concentrations of aluminum in the spectral source, and the aluminum lines in the resulting spectrograms. Accordingly, the numbers and intensities of the aluminum *raies ultimes* are due entirely to the quantity or concentration of aluminum in the spectral source and independent of the radicals attached to the aluminum.

The view has been expressed that the excitability of the aluminum spectrum may vary with the volatility of the aluminum compound in the spectral source—that is, with the volatility of chemical form or combination in which aluminum is excited, whether excitation be by the arc or by the condensed spark. Accordingly, the aluminum spectrum will be very readily and completely excited when the aluminum is present in the spectral source in the form of a volatile compound like aluminum chloride, and will escape excitation more or less entirely when the aluminum is present in the spectral source in form of a relatively non-volatile compound like aluminum phosphate. However, the results in Table II also show that volatility of the form in which aluminum occurs in the spectral source does not affect or determine the sensitiveness of the spectrographic method for detecting the presence or absence of small amounts of aluminum either by the arc or spark methods of excitation. In connection with these tests it is a well known fact that hydrated aluminum chloride when heated to dryness yields the non-volatile oxide of aluminum.

The sensitivity of the method is demonstrated by the extremely small quantities of aluminum detected by either the arc or the spark as shown by the data in Table II, and by the extremely low concentrations of aluminum which are detected in the salt mixtures. In these materials 5 p. p. m. of aluminum were sufficient to produce the aluminum line 3961.5 Å. This concentration is equal to 0.05 p. p. m. of aluminum of fresh biological tissue of which the ash is 1 per cent. An ash content of 1 per cent has been assumed in computing p. p. m. of aluminum on the basis of fresh tissues. The data contained in the above tables show both from the standpoint of sensitivity and quantitative correlations that the arc and spark agree very well over the range investigated.

Determination of Aluminum in Biological Material

In ascertaining the presence or absence of an element so common in its occurrence as aluminum, more than ordinary cleanliness was exercised. Such cleanliness was practiced throughout the entire procedure, including the isolation or the dissection of the biological sample. Materials such as potatoes were thoroughly washed in distilled water and peeled twice with a nickel-plated knife which had been washed in distilled water. The potato was washed between peelings and again before placing in the cleaned silica dish for ashing.

Equally extreme precautions were exercised in the collection of rat organs. The thorax and abdomen were skinned from a mid-line incision, using care to keep hair and foreign material from the exposed abdomen and thorax. The abdomen and thorax were then opened with nickel-plated instruments previously cleaned in distilled water. The organs were removed with clean instruments and washed in a stream of distilled water before being placed in the clean silica dishes.

Eggs were washed in distilled water and dried with filter paper before breaking into clean Pyrex beakers. The samples represent homogeneous mixtures of white and yolk obtained by whipping the egg in the beaker with a glass rod.

Isolation or dissection of the material for analysis was followed immediately by its ashing, which served the purpose of concentrating the sample by removal of the organic matter. All samples were ashed by a technic which was essentially the same as that described by McCollum, Rask, and Becker (*3*). The material was ashed in silica dishes supported on silica or nichrome triangles over Bunsen flames. In all cases the material was ashed in the shortest possible time in a room with little disturbance to avoid as completely as possible contamination by dust.

It was impossible to obtain carbon-free ashes from animal tissues. An attempt was made to burn the carbon completely by passing a stream of oxygen through a specially bent silica tube into the ash mixture at different stages of the ashing process, the ashing being carried out in silica crucibles or beakers of about 50 cc. capacity. The oxygen was previously purified by passing through a wash train of concentrated sulfuric acid. It was found that the combustion could not be controlled in such a procedure and this experiment resulted in a fusion of the ash to the silica dish. Even though the carbon was completely burned, the procedure had to be abandoned on account of the fusion.

The ash was therefore subjected to the spectrographic technic as already described. Both arc and spark spectrograms were prepared of most ashes, so that results obtained by each method of excitation could be compared with the results obtained by the other method of excitation.

Table III—Spectral Effects with Aluminum Concentrations in Various Biological Materials

MATERIAL	ARC			SPARK		
	3944 Å.	3961.5 Å.	Aluminum concentration in fresh tissue	3944 Å.	3961.5 Å.	Aluminum concentration in fresh tissue
			P. p. m.			*P. p. m.*
Rat[a]	+	+	0.5 to 1.0	−	±	0.05
	+	+	0.5 to 1.0	−	±?	0.05
	+	+	0.5 to 1.0	−	±?	0.05
	+	+	0.5 to 1.0	−	±?	0.05
	+	+	0.5 to 1.0	−	±?	0.05
	+	+	0.5 to 1.0	−	±	0.05
	±	+	0.5	−	±?	0.05
	±	+	0.5	−	±?	0.05
	±	+	0.5	−	±?	0.05
	±	+	0.5	−	±?	0.05
	±	+	0.5	−	±?	0.05
	±	+	0.5	−	±?	0.05
	−	−	0.05	−	−	0
Egg	±	+	0.5	−	±?	0.05
	−	±	0.2	−	±?	0.05
	−	+	0.5	−	±?	0.05
	−	+	0.5	−	±?	0.05
	−	+	0.5	−	±?	0.05
	±	+	0.5	−	±?	0.05
	−	−	0.05	−	−	0
Thyroid	+	+	2.0			
	+	+	2.0			
	+	+	2.0			
Potato	−	−	0.05	−	±	0.05
	−	±?	0.05	−	±	0.05
	−	−	0.05	−	±	0.05
	−	±?	0.05	−	−	0
	−	±?	0.05	−	−	0
	−	±?	0.05	−	−	0
	−	±?	0.05	−	−	0
	−	±?	0.05	−	−	0
	−	±?	0.05	−	±	0.05
Carrot	−	±?	0.05	−	±	0.05
Nut	−	±	0.05	−	−	0

[a] Each rat is represented by its liver, kidneys, spleen, and testes or ovaries.

Table III contains the results of the spectrographic determinations of aluminum in biological materials. The arc and spark lines are recorded separately and in terms of the conventions defined above. The lines obtained by each method of excitation have been translated into the parts of aluminum per million of fresh tissue which they represent according to the respective arc and spark standard spectrograms given in the last three parts of Table I.

Rat viscera as listed in Table III consist of the combined liver, kidneys, spleen, and testes or ovaries of one adult and apparently healthy rat raised on stock diet. The arc method of excitation shows 0.5 to 1.0 p. p. m. of aluminum in the viscera of six rats; not more than 0.5 p. p. m. of aluminum in the viscera of six other rats and less than 0.05 p. p. m. of aluminum in the viscera of one rat. The spark method of excitation resulted in only a faint image of one single line, 3961.5 Å., in each of these same thirteen sets of rat viscera. This weak spectral effect represents, according to the spark standards, only 0.05 p. p. m. of aluminum. Such a difference between the results of the arc and spark methods of excitation is inconsistent with the results of these two methods of excitation obtained on the aluminum standards listed in the second section of Table I. As shown by this data, the arc and spark methods of excitation produce lines equivalent to one another in each of the aluminum standards containing the same concentration of aluminum over the range from 0 to 1000 p. p. m. of aluminum and the same variations in aluminum lines with variations in aluminum concentrations over this range, indicating that no differences exist between the arc and spark methods of excitation either in sensitivity or in correlations with aluminum concentrations. However, the lower concentrations of aluminum indicated in rat viscera by the spark method of excitation suggest that this method of excitation is for some reason not applicable to the ashes of rat viscera, or rather to the ashes of rat viscera in the condition in which they were excited.

The egg samples represent individual whole eggs, exclusive of shell, obtained from different markets on different days. The arc method of excitation shows a concentration of not more than 0.5 p. p. m. of aluminum in five of the egg ashes listed in Table III, a concentration of approximately 0.2 p. p. m. of aluminum in one of the two remaining egg ashes, and less than 0.05 of aluminum in the other. The spark method shows a concentration of aluminum of less than 0.05 p. p. m. in all seven of these same egg ashes. Accordingly, the spark method of excitation also shows lower concentrations of aluminum in egg ashes than does the arc method, although the differences between the two methods of excitation are not quite so large in the case of egg ashes as in the case of the ashes of rat viscera.

The ten potatoes listed in Table III are samples of medium-sized potatoes purchased on different days from five or six different markets. The one carrot listed in the table was a sample of a medium-sized apparently healthy carrot prepared as previously described. The walnut listed in the table represented the meats of four apparently healthy English walnuts prepared with the same precautions. All of these twelve samples show practically the same concentrations of aluminum by both the arc and spark methods of excitation. These concentrations are less than 0.05 p. p. m. in nine of the ten potatoes, and approximately 0.05 p. p. m. in one potato, the carrot, and the walnut.

The main purpose of the data in Table III was to ascertain the width and the abundance of the distribution of aluminum in biological matter. For such purposes these data may seem limited, due to the limited number of materials examined. However, the variety and the character of the materials are such as to warrant the conclusion that the concentrations of aluminum in biological matter must invariably be very low.

Tha nature of the spectrographic method of analysis is such that error seems possible only in one direction, that of producing aluminum lines when little or no aluminum is present in the sample, in which case aluminum lines will be due to aluminum from outside sources such as atmospheric dust introduced during the ashing process. Such errors are, to say the least, highly probable, due to the wide spread occurrence of aluminum and to the small amount ncesssary to produce aluminum *raies ultimes*. On the other hand, it is inconceivable that aluminum actually present will ever fail to produce aluminum lines when excitation is properly done. If it is assumed that errors in the spectrographic detection or estimation of aluminum will invariably be one-sided in the above manner, then the lowest concentrations reported in Table III will be the more nearly correct ones. The writers are inclined to this view as a result of 2 years' experience with spectrographic methods of quantitative analysis.

No complete or otherwise satisfactory explanation is available for the above observed inconsistencies in the relation between the performances of the arc and spark methods of excitation. The lower concentrations of aluminum indicated in rat viscera by the spark may have been due to unburned carbon which was always present in their ashes, since potato ashes, on which the two methods agree more nearly, were practically free from carbon. Carbon was also, of course, completely absent from the aluminum standards in which the two methods gave identical results. Carbon particles might tend to occlude any aluminum present which would be liberated by burning of the carbon at the high temperature of the arc. Apparently, therefore, the spark method of excitation is not applicable to ashes containing unburned carbon, whereas the arc method is. Further experimental work is required to explain these inconsistencies.

Aluminum in Chemically Pure Reagents

In connection with this study arc spectrograms were prepared of a number of c. p. labeled inorganic salts. The salts were selected from unopened bottles which gave no declaration of aluminum on the label. Salts whose labels declared the presence of aluminum were specifically excluded from the test. The results are recorded in Table IV and show that in the case of such highly purified products as chemically pure reagents detectable amounts of aluminum may occur in a large percentage of the samples, in this case about 50 per cent.

Table IV—Aluminum *raies ultimes* Produced by C. P. Labeled Reagents

SAMPLE	ARC	
	3944 Å.	3961.5 Å.
Lithium sulfate	−	±
Sodium sulfate	−	±
Sodium thiosulfate	−	−
Sodium iodide	−	±
Potassium nitrate	−	−
Potassium sulfate	−	−
Potassium chloride	±	+
Cupric chloride	+	+
Magnesium chloride	−	−
Calcium phosphate	−	±?
Barium carbonate	−	±?
Manganous sulfate	−	±?
Manganous chloride	−	+
Ferric phosphate	−	+
Ferrous ammonium sulfate	−	−
Ferrous chloride	−	±?
Nickel chloride	+	+

Conclusions

The spectrographic method of analysis is capable of detecting the presence of 5 p. p. m. of aluminum in all of the several kinds of salts and salt mixtures on which the sensitivity of the spectrographic method was tested.

The spectrographic method of analysis will determine quantitatively, with an error of ±25 per cent, concentrations of aluminum ranging from 0.5 to 1000 p. p. m. in inorganic materials, including biological ashes.

The arc and the condensed spark methods of excitation appear to be equally satisfactory when applied to the several salts and salt mixtures used in this investigation as aluminum-containing materials. These two methods of excitation also appear to be equivalent to one another for determining aluminum in certain biological ashes, but in other biological ashes, especially those containing unburnt carbon, the arc method seems more sensitive and the spark less so. The presence of carbon seems to reduce the sensitiveness of the spark method of excitation but not the sensitivity of the arc method, so that the spark is not so satisfactory in its applicability to biological ashes containing unburnt carbon, as the arc.

There is no noticeable relationship between the volatility of the form in which aluminum occurs in the spectral source and the sensitivity of its spectrographic detection either by the arc or the condensed spark methods of excitation.

Chemical composition of aluminum-containing salts and salt mixtures does not affect correlations between aluminum concentrations and spectral effects. That is, these correlations are independent of the composition of the aluminum-containing salts or salt mixtures.

About one-half of the C. P. labeled reagents examined contained traces of aluminum detectable by the spectrographic method.

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A Mill for Small Samples[1]

W. H. Cook, E. P. Griffing, and C. L. Alsberg

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The elaborate system of microanalysis developed by organic chemists for the analysis of homogeneous material has been largely inapplicable to biological solid materials, owing to the difficulty of grinding and sampling a micro-quantity of such material without loss of substance or moisture. The authors were confronted with the problem of analyzing individual wheat leaves, necessitating the use of semi-microchemical methods, and the preparation of this material for analysis required a grinder capable of reducing small quantities of substance without loss. The grinding of such material is extremely difficult because of its fibrous nature.

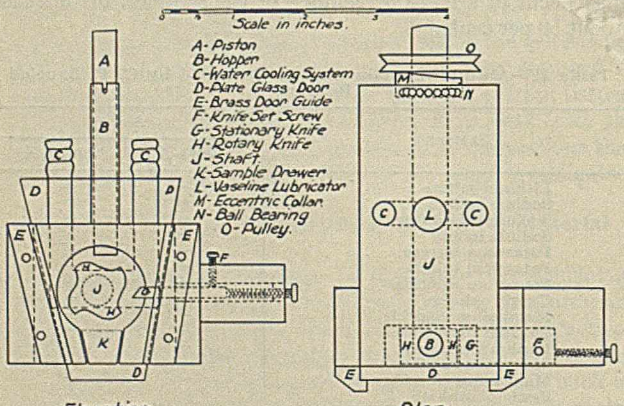

Figure 1—Micro-Grinding Mill

For this purpose a mill was designed on the general cutting principle of the Wiley laboratory mill (*2*), but many modifications in construction were necessary because of the greatly reduced size. A rapid shearing effect is obtained by the action of a hard tooled steel knife with four blades keyed to a shaft, cutting against one blade of tooled steel placed in the wall of the grinding chamber. The rotating knife also serves to keep the material in motion, and when it has been ground sufficiently, aids in its discharge through a screen in the bottom of the chamber.

Dimensions

The main body of the mill, as diagramed in Figure 1 and pictured in Figure 2, consists of a cast-iron block 2 inches square and 4 inches long, $3^1/_2$ inches of which are occupied by the bearing for the half-inch shaft. The front half inch forms the grinding chamber which is $1^1/_4$ inches in diameter, and the rotating knife, *H*, keyed to the shaft, *J*, occupies about three-quarters of its capacity. The length of the rotating blades from the center of the shaft is ${}^1/_2$ inch. The stationary blade, *G*, is attached to the wall of the chamber in such a manner as to allow different clearances between the blades, or to take up wear from sharpening. A brass tube, *B*, ${}^7/_{16}$ inch in diameter leads into the top of the grinding chamber for introducing the material, and is closed during grinding by means of a solid brass piston, *A*, which is pinned to prevent its dropping on the knife during grinding. The bottom of the chamber is formed by a copper drawer, *K*, which acts as a receptacle for the ground material. The top of the drawer consists of a piece of mesh of the desired size, ${}^8/_{16}$ by ${}^{11}/_{16}$ inch in dimension. The sides of the drawer slant to a narrower base to prevent the drawer from dropping out, and a snug fit to the main frame keeps the ground material from sifting out during grinding. The front face of this drawer is open to permit removal of the sample and is closed during operation by the plate glass front of the grinding chamber. This glass door fits tightly by being ground to fit brass guides fastened to the main frame, and allows easy access to the grinding chamber for cleaning, as well as permitting one to see the grinding operation. Around the shaft at the opposite end from the grinding chamber is a ball bearing to take out sideplay and prevent wearing due to the high speed of the mill. The rest of the shaft between the

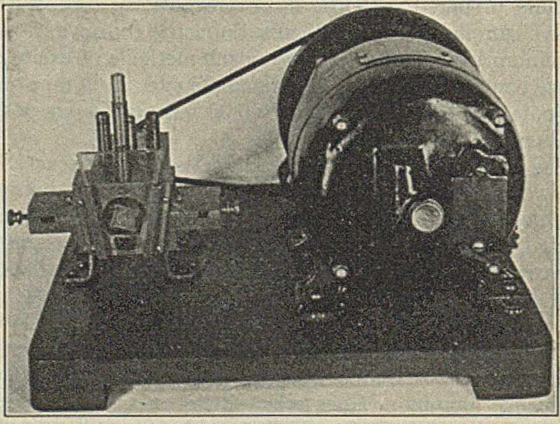

Figure 2—Mill for Small Samples

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[1] Received November 7, 1930.

ball bearing and grinding chamber is surrounded by babbitt metal. It is lubricated by vaseline through a hole in the center of the bearing and is driven by a 1-inch pulley attached to the end opposite the grinding chamber.

Operation

One of the difficulties encountered in early trials was that of keeping the material in motion. The small size of the rotating knife made it necessary to drive the mill at the rate of 5600 r. p. m. to give sufficient surface speed to keep the material agitated. A plug of metal (not shown in Figure 1) to fill in the angle between the wall of the grinding chamber and the stationary blade helped to prevent the material from gathering at that point. The use of more than the one stationary blade in the wall of the chamber in order to increase the cutting speed of the mill is impossible due to the tendency of the material being ground to gather on the top of the blade. A slightly eccentric collar was placed on the shaft at the pulley end to furnish enough vibration to ensure that the finely ground material would pass through the sieve.

Since a temperature increase during grinding might be detrimental to the material by causing moisture loss, etc., the mill was provided with a water-cooling system surrounding the shaft. So far it has been unnecessary to use it, as the large bulk of iron in the main body of the mill tends to take up and conduct away the small amount of heat developed.

A second experimental mill made with a smaller body did need a water-cooling system to prevent overheating. A nickel-plated brass face was used for that portion containing the grinding chamber.

This grinding mill has been found very satisfactory for grinding small samples of material difficult to grind. In grinding wheat kernels it is necessary to break them up in a mortar to prevent them from tearing the copper mesh by hitting it too suddenly. It is better to cut leaves, also, into rather small pieces convenient for loading. The capacity of the mill is about five to eight kernels of wheat or several wheat leaves at one charge, and the operation can be performed practically without loss of material, with proper precautions, so that a representative sample may be obtained for microanalysis. It is rapid in operation. At an operating speed of 5600 r. p. m. and a clearance of $^1/_{2000}$ inch between the rotating and stationary blades, a single charge of material is reduced to pass an 80-mesh sieve in from 3 to 4 minutes. The simplicity and accessibility of the grinding chamber permits thorough and rapid cleaning between samples. The homogeneity of ground wheat leaves or kernels has been demonstrated by more than 200 analyses for total nitrogen content, successive 20-mg. samples having been found to check within a few hundredths of 1 per cent of nitrogen. Analyses were made according to the ter Meulen and Heslinga hydrogen method (*1*).

The Arthur H. Thomas Company of Philadelphia has designed and is about to place on the market a micro-grinding mill involving the main principles of construction of the mill described in this article.

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Determination of Aluminum in Ferrochromium and Chromium Metal[1]

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In the following method iron is separated by means of cupferron while chromium is oxidized by evaporating the solution with perchloric acid, and aluminum is separated by precipitation with ammonia.

Two and one-half grams of the sample are transferred to a 250-cc. covered beaker and treated with 15 cc. of hydrochloric acid (sp. gr. 1.19). If the aluminum content is less than 0.1 per cent it is necessary to work on a 10-gram sample. This is accomplished by dissolving four 2.5-gram portions of the sample and subsequently combining the four aluminum hydroxide precipitates, obtained as described below, by filtering on a single 9-cm. paper and washing with a 2 per cent ammonium chloride solution. The solution is warmed to about 60° C. until all action has ceased, when 3 cc. of Perhydrol (30 per cent hydrogen peroxide) are added and the liquid boiled down to a sirup. Thirty cubic centimeters of hydrochloric acid (1 to 1) are introduced, the solution heated until all salts have dissolved, diluted with water to 50 cc. and filtered on a 9-cm. paper containing some ashless paper pulp into a 400-cc. beaker, and reserved. The paper and residue are washed 18 to 20 times with hot water and ignited in a 30-cc. platinum crucible. Five drops of sulfuric acid (1 to 1) and 2 cc. of hydrofluoric acid (48 per cent) are introduced and the silica is volatilized by evaporating the solution to the complete expulsion of the acids.

The residue is fused with 2 grams of sodium carbonate and the melt dissolved in 25 cc. of hot sulfuric acid (1 to 4). If four 2.5-gram portions are taken for analysis the residues may be combined and only one fusion made, increasing, of course, the weight of sodium carbonate used to 8 grams. The solution is boiled to expel carbon dioxide, approximately 2 grams of ammonium chloride and a very faint excess of dilute filtered ammonium hydroxide (1 to 3) are then introduced, and the solution is boiled for no longer than 1 or 2 minutes. The precipitate is filtered on a 9-cm. paper containing some ashless paper pulp and washed thoroughly with hot 2 per cent ammonium chloride solution. The paper holding the precipitate is transferred to the 400-cc. beaker containing the main solution and macerated to a pulp by means of a glass rod. The liquid is then heated just short of boiling for about 5 minutes to insure the complete solution of the precipitate.

The solution (which should have a volume of about 100 cc. and an acidity of approximately 15 per cent) is cooled to approximately 15° C. and the iron precipitated by the addition of a slight excess of a freshly prepared, cold 6 per cent solution of cupferron (ammonium nitrosophenylhydroxylamine, $C_6H_5(NO)ONH_4$), while all aluminum and chromium will remain in solution. A brownish red, partly amorphous, partly crystalline, precipitate separates out. As soon as a drop of the reagent causes the formation of a transient snow-white crystalline precipitate, all of the iron is down. The

[1] Received October 16, 1930.

solution is filtered on an 11-cm. paper containing some ashless paper pulp, the paper and precipitate washed well with cold 5 per cent hydrochloric acid, and discarded.

The filtrate and washings are collected in a 600-cc. beaker and boiled down to a volume of about 50 cc. Fifty cubic centimeters of nitric acid (sp. gr. 1.42) are introduced and the boiling continued until the volume has been reduced to approximately 10 cc. Twenty cubic centimeters of nitric acid (sp. gr. 1.42) and 30 cc. of perchloric acid (60 per cent) are added, the solution evaporated to strong fumes of perchloric acid, and heated for an additional 30 minutes to insure the complete oxidation of the chromium to chromic acid. One hundred cubic centimeters of water are introduced, the solution is warmed, filtered on a 9-cm. paper, and the silica washed with warm water. The filtrate and washings, which should not exceed 175 cc., are collected in a 400-cc. beaker.

The solution is nearly neutralized with filtered ammonium hydroxide (1 to 3) and heated to boiling. Approximately 5 grams of ammonium chloride and some ashless paper pulp are added and the solution treated with dilute ammonium hydroxide (1 to 3) drop by drop until the color just changes to a distinct yellow. The solution is boiled for no longer than 1 or 2 minutes and immediately filtered on a 9-cm. paper. The paper and precipitate are washed thoroughly with hot 2 per cent ammonium chloride solution, transferred to a 150-cc. beaker and treated with 15 cc. of hydrochloric acid (1 to 2). The solution is heated to boiling for several minutes, diluted with warm water to 100 cc., and treated with a brisk stream of hydrogen sulfide for 15 minutes to precipitate platinum. Any precipitate that forms is filtered on a 9-cm. paper, washed 10 to 12 times with hydrogen sulfide water containing 1 per cent hydrochloric acid, and discarded.

The filtrate contained in a 400-cc. beaker is boiled to expel hydrogen sulfide, 5 cc. of perchloric acid (60 per cent) are added, and the solution is evaporated to strong fumes of perchloric acid and heated for an additional 15 minutes. One hundred cubic centimeters of warm water are added and the solution is nearly neutralized with filtered ammonium hydroxide (1 to 3) and heated to boiling. Approximately 2 grams of ammonium chloride, some ashless paper pulp, and several drops of an 0.2 per cent alcoholic solution of methyl red are introduced and the solution treated with dilute filtered ammonium hydroxide (1 to 3) drop by drop until the color just changes to a distinct yellow. The solution is boiled for no longer than 1 or 2 minutes and immediately filtered on a 9-cm. paper. The paper and precipitate are washed thoroughly with hot 2 per cent ammonium chloride solution.

The precipitate is ignited in a weighed platinum crucible first at a low temperature and finally over a blast lamp for 5 minutes or in an electric furnace at 1150° C. for 15 minutes. The crucible covered with a closely fitting lid is allowed to stand in a desiccator until cool and then rapidly weighed. A second heating of equal duration is advisable, especially as it permits more rapid weighing and consequently more accurate results. Ignited alumina is very hygroscopic, and absorbs within the first 10 minutes' exposure to the air a large proportion of the total water which it will take up in 24 hours. A well-fitting crucible cover is quite efficient in preventing the adsorption of moisture by the alumina while the crucible is in the desiccator or on the balance pan.

Elimination of Phosphorus

The precipitate obtained as described will contain part or all of the phosphorus in the alloy (depending upon the aluminum content) but rarely contains chromium; should it be colored, indicating the presence of chromium sesquioxide, it is fused with 1 to 2 grams of sodium carbonate. The melt is dissolved in the least necessary amount of hot water and the chromium determined colorimetrically. A small amount of sodium peroxide is added and the liquid is boiled for a few minutes and cooled. The chromate solution is transferred to a Camp comparison tube. The volume should now be about 15 cc. To the other comparison tube there is added from a 10-cc. buret an amount of standard potassium chromate solution (1 cc. = 0.00050 gram Cr.) which contains slightly less chromium than the sample, and sufficient water to make their volumes exactly equal. After having mixed each, the intensity of the two solutions is compared. The color of the sample should be slightly more intense than that of the standard. An additional small amount of the standard chromate solution is added to the tube containing the standard, and an equal amount of water to the tube holding the sample. After having mixed the contents of the tubes the intensities of the colors are again compared. These operations are repeated until an exact match is obtained. The number of cubic centimeters of the chromate solution used, multiplied by 0.00050, multiplied by 1.4615, gives the weight of chromium sesquioxide to be deducted.

After having determined the chromium colorimetrically, the solution from the sodium carbonate fusion is transferred to a 300-cc. Erlenmeyer flask and made acid with an excess of 2 cc. of nitric acid (sp. gr. 1.42). The solution is heated to boiling to expel carbon dioxide and the chromium reduced to the trivalent state by the addition of a sufficient amount of sulfurous acid, and by boiling. The liquid is cooled to 40° C., approximately 5 grams of ammonium nitrate, 0.05 gram of ferrous sulfate (free from phosphorus), and 40 cc. of molybdate solution added, and the phosphorus precipitated as ammonium phosphomolybdate by 5 minutes of vigorous shaking. The precipitate is allowed to settle and the phosphorus is determined by either the alkalimetric or the molybdenum reduction (Emmerton) method. The weight of phosphorus found, multiplied by 2.2887, is the weight of phosphorus pentoxide to be deducted from the weight of the alumina precipitate.

The weight of the alumina precipitate, less the weights of chromic oxide and phosphorus pentoxide found, is multiplied by 52.94 and divided by the weight of sample taken to give the percentage of aluminum in the alloy.

A blank should be run on all the reagents used and any aluminum found deducted from the result obtained as above described.

Experimental Proof of Accuracy of Method

In order to test the accuracy of the method a number of experiments were carried out. The procedure consisted in salting several samples of the Bureau of Standards standard sample 64 of high carbon ferrochromium[2] with varying amounts of pure aluminum chloride. The accurately measured aliquot portions of the standard solution of pure aluminum chloride were added to the weighed samples of ferrochromium, which were then dissolved and otherwise treated as given in the description of the method. The results obtained are shown in the table.

Experiments to Test Accuracy of Method

Experiment	Ferrochromium Taken	Aluminum Added	Aluminum Found	Aluminum Recovered[a]	Error
	Grams	*Gram*	*Gram*	*Gram*	*Gram*
1	5	Nil	0.00105		
2	5	Nil	0.00100		
3	10	Nil	0.00220		
			Av. 0.021%		
4	5	0.00228	0.00339	0.00234	+0.00006
5	5	0.0039	0.00498	0.00393	+0.00003

[a] After correcting for 0.021 per cent Al in alloy.

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[2] The Bureau of Standards obtained a result of 0.020 per cent aluminum, and Electro Metallurgical Co., 0.022 per cent, when this standard was made.

Determination of Zirconium in Plain Carbon and Alloy Steels[1]

Thos. R. Cunningham and R. J. Price

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ZIRCONIUM is separated from the elements enumerated below as $ZrHPO_4$, which is converted to ZrP_2O_7 on ignition. A determination may be completed on steels free from tungsten, tin, tantalum, or columbium in not over 2 hours. The exact determination of very small percentages of zirconiun in the presence of varying amounts of one or more of the elements titanium, aluminum, tungsten, molybdenum, chromium, vanadium, uranium, cobalt, nickel, copper, tin, arsenic, manganese, tantalum, columbium, and silicon, all of which are found in one type or another of plain carbon or alloy steel, is a somewhat difficult analytical problem. The method herein described is designed to be applicable to any commercial steel.

From 5 to 10 grams of the drillings are transferred to a 500-cc. covered beaker and dissolved in 40 to 60 cc. of hydrochloric acid (sp. gr. 1.19). When all action appears to have ceased from 8 to 15 cc. of Perhydrol (30 per cent hydrogen peroxide) are introduced to oxidize the iron, to break up any separated carbides, to oxidize tungsten, and to peroxidize the titanium. If the steel contains tungsten, a yellow precipitate of tungstic acid will be noticed at this point, in which case the procedure must be modified as described below. Titanium is not precipitated as phosphate when in the sexivalent state. The solution is diluted with warm water to 350 cc., treated with 8 to 10 grams of diammonium phosphate dissolved in 50 cc. of water, and stirred vigorously for several minutes. Some ashless paper pulp is introduced, and after allowing the solution to stand for one-half hour at a temperature of approximately 70° C. it is filtered on an 11-cm. paper. The precipitate and paper are washed 15 to 20 times with 2 per cent hydrochloric acid, ignited in porcelain at a low temperature to burn off the paper, and transferred to a 30-cc. platinum crucible. Two cubic centimeters of sulfuric acid (1 to 1) and 5 cc. of hydrofluoric acid (48 per cent) are added and the solution is evaporated to strong fumes of sulfur trioxide.

The sulfuric acid solution is transferred to a 150-cc. beaker, the crucible being rinsed with 5 cc. of hydrochloric acid (sp. gr. 1.19) and a little water, and added to the beaker. The solution is diluted with warm water to 75 cc., treated with 3 grams of diammonium phosphate dissolved in 25 cc. of water, stirred vigorously, and allowed to stand for one-half hour at a temperature of approximately 70° C. The solution is filtered on a 9-cm. paper containing some ashless paper pulp and the precipitate of $Zr\ (HPO_4)_2$ and paper washed 15 to 20 times with 2 per cent hydrochloric acid. The precipitate is ignited in platinum first at a low temperature to burn off the paper, and finally at 1000° C., cooled in a desiccator, and weighed. The weight of ZrP_2O_7 is multiplied by 34.23 and divided by the weight of sample taken to give the percentage of zirconium in the sample. For extreme accuracy the precipitate of ZrP_2O_7, which may be contaminated with small amounts of $Ti_2P_2O_9$, is fused with several grams of potassium pyrosulfate and the fusion dissolved in 40 cc. of 10 per cent sulfuric acid containing 5 cc. of 3 per cent hydrogen peroxide. The titanium is then determined by the hydrogen peroxide colorimetric method and the calculated weight of $Ti_2P_2O_9$ deducted from the weight of the precipitate of ZrP_2O_7. The weight of $Ti_2P_2O_9$ is obtained by multiplying the weight of titanium found by 3.16.

The ignited and weighed residue may not correspond exactly to the composition of ZrP_2O_7 (*1*) but it is believed to be very close to it, since the results obtained by the above described procedure agree almost exactly with those obtained by the cupferron method. By the latter procedure the zirconium is weighed as zirconium dioxide. This method should not be applied to the determination of large amounts of zirconium because the precipitate of $Zr(HPO_4)_2$ is somewhat gelatinous, which makes it rather difficult or almost impossible to wash out the excess of the precipitant completely.

In the case of chromium steels that do not dissolve completely in the hydrochloric acid–Perhydrol treatment, the ignited residue, instead of being treated with sulfuric acid and hydrofluoric acid to remove silica, is treated with 5 cc. of hydrofluoric acid (48 per cent), 3 cc. of nitric acid (sp. gr. 1.42), and 3 cc. of perchloric acid (60 per cent), and the solution evaporated to strong fumes of perchloric acid. The perchloric acid serves to break up chromium carbide and to oxidize the chromium to chromic acid which does no harm.

In the case of tungsten steels, after adding the Perhydrol, the solution should be boiled for about 5 minutes before diluting with warm water to 350 cc. and treating with the diammonium phosphate solution. After allowing the solution to stand for one-half hour at a temperature of about 70° C., it is filtered on an 11-cm. paper and the paper and precipitate washed well with 2 per cent hydrochloric acid, ignited in porcelain at a low temperature, and transferred to a 30- or 50-cc. platinum crucible. The residue is fused with about 10 grams of sodium carbonate and the melt is dissolved in hot water in a 250-cc. beaker. Some ashless paper pulp is added and the precipitate of sodium zirconate is filtered on a 9-cm. paper and washed thoroughly with 2 per cent ammonium nitrate solution to remove all sodium tungstate and sodium salts. The precipitate of sodium zirconate is ignited in the same platnium crucible previously used and fused with 1 to 2 grams of potassium pyrosulfate. The fusion is dissolved in 75 cc. of hot 5 per cent hydrochloric acid containing 5 cc. of 3 per cent hydrogen peroxide, and the zirconium precipitated with diammonium phosphate as previously described. The precipitate is allowed to stand one-half hour at a temperature of about 70° C., filtered on a 9-cm. paper, washed well with hot 2 per cent hydrochloric acid, and ignited in a weighed platinum crucible. The precipitate is treated with a few drops of sulfuric acid (1 to 1) and several centimeters of pure hydrofluoric acid (48 per cent), and any silica is expelled by evaporating the solution to the complete expulsion of the sulfuric acid. The crucible is heated at 1000° C., cooled in a desiccator, and weighed. The weight of ZrP_2O_7 is multiplied by 34.23 and divided by the weight of sample taken to give the percentage of zirconium in the sample.

Should the steel be known to contain tin, tantalum, or columbium, the phosphate precipitate is filtered, washed thoroughly with 2 per cent hydrochloric acid, ignited in porcelain, transferred to a platinum crucible, and in the case of tin, fused with sodium carbonate, or transferred to a

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[1] Received October 16, 1930.

nickel crucible if tantalum or columbium are present and fused with several grams of potassium hydroxide. The melt is dissolved in water and the determination completed as described for tungsten steels.

Experimental Proof of Accuracy of Method

A number of experiments were carried out to obtain dependable data concerning the accuracy of the method. It is a well-known fact that unless hydrogen peroxide is added to peroxidize the titanium, it will be carried down with the zirconium phosphate precipitate, and for this reason alone, when extreme accuracy is desired, the final zirconium phosphate precipitate should be tested for titanium. The procedure consisted in salting a number of samples of plain carbon steels, a sample of Cr-W-V steel, and stainless steel of the 18 chromium–8 nickel variety known to be free of zirconium, with varying amounts of pure zirconium chloride. Five-, ten-, and twenty-gram samples, respectively, were used. The accurately measured aliquot portions of the standard solution of pure zirconium chloride were added to the weighed samples of steel, which were then dissolved and otherwise treated as given in the description of the method. The results obtained are given in the table.

Experiments to Test Accuracy of Method

Experiment	Kind of Steel	Steel Taken	Zirconium Added	Zirconium Found	Error
		Grams	*Gram*	*Gram*	*Gram*
1	Plain C	20	0.00101	0.00095	−0.00006
2	Plain C	20	0.00101	0.00102	+0.00001
3	Plain C	5	0.0025	0.0025	.....
4	Plain C	5	0.0025	0.0025	.....
5	Cr-W-V[a]	10	0.0006	0.00058	−0.00002
6	18 Cr-8 Ni	5	0.00133	0.00132	−0.00001

[a] Bureau of Standards standard sample 50A of high-speed steel. Two 5-gram portions were taken and the precipitates combined after making the sodium carbonate fusion to separate the tungsten.

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Rapid Colorimetric Method for Determination of Molybdenum in Plain Carbon and Alloy Steels[1]

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An accurate colorimetric method for the determination of molybdenum in the presence of nickel, chromium, tungsten, and other elements, is given. It is best adapted to steels containing a maximum of 1 per cent molybdenum. However, good results have been obtained when the molybdenum content was as high as 2.5 per cent.

One-half gram or one gram of the sample (if the molybdenum is 0.10 per cent or less) is transferred to a 150-cc. covered beaker and treated with 25 cc. of sulfuric acid (1 to 4) at a temperature of approximately 60° C. When all action appears to have ceased, 3 cc. of Perhydrol (30 per cent hydrogen peroxide) are introduced and the liquid is boiled for several minutes. The solution is then filtered on a 9-cm. paper to remove carbon and the residue washed with water and discarded. The filtrate and washings are collected in a 250-cc. beaker and boiled down to a small volume to decompose completely the excess of Perhydrol. The Perhydrol destroys the hydrocarbons and partially reduces the molybdenum to a lower state; part of the molybdenum is oxidized by the air. In the case of plain carbon or alloy steels, or steels containing tungsten, the above filtering operation is omitted. One gram of tartaric or citric acid is added (to tungsten steels only) and the solution made slightly alkaline with 10 per cent sodium hydroxide and then acid with an excess of 10 cc. of sulfuric acid (1 to 1). The tartaric or citric acid serves to hold up the tungsten. If only a small amount of tungsten is present this treatment may be omitted.

The cold solution is transferred to a 250-cc. separatory funnel provided with a glass stopper, diluted to a volume of 100 cc. with cold water, and treated with 10 cc. of 5 per cent potassium thiocyanate solution. The stoppered flask and contents are shaken vigorously for several minutes, then treated with from 5 to 10 cc. of stannous chloride solution and again shaken vigorously for several minutes. The stannous chloride reduces the iron from the ferric to the ferrous condition and the molybdenum from the sexivalent to the quinquevalent or quadrivalent state. The potassium thiocyanate reacts with the reduced molybdenum to form a complex potassium-molybdenum thiocyanate, which imparts an amber to reddish brown color to the solution, depending upon its intensity.

The solution is cooled to approximately room temperature, 50 cc. of ether added, and the separatory funnel stoppered and shaken vigorously for 30 seconds and then allowed to stand until the liquid has separated into two distinct layers. The lower or acid layer, which will contain the greater part of any iron, chromium, nickel, or tungsten, is drawn off and discarded, and the upper or ethereal layer, which will contain practically all of the molybdenum, is then drawn off into a 50-cc. Camp comparison tube. The tube is stoppered with a soft cork to prevent evaporation of the ether and its contents are mixed thoroughly by manipulating the tube in the usual manner. After standing for several minutes it is ready for comparison with the standard.

Preparation of Standard for Comparison

With a little practice it is not difficult to estimate approximately the percentage of molybdenum in the sample. Twenty-five cubic centimeters of 8 per cent ferric sulfate solution are transferred to a 250-cc. separatory funnel and the standard molybdenum solution added from a buret. The solution is diluted with cold water to approximately 100 cc. and the development of the molybdenum color and extraction are completed as previously described. It is advisable to allow the molybdenum solution to stand in the comparison tube for several minutes before comparing with the standard, as the intensity of the color sometimes changes at first but remains stable thereafter for 7 days and even longer if kept in the dark when not in use.

The percentage of molybdenum in the sample is then determined by comparing the intensity of the color of the ethereal solution of potassium–molybdenum thiocyanate with that of the standard. The darker of the two solutions, the sample and the standard, is diluted carefully with ether

[1] Received October 16, 1930.

and mixed thoroughly until they match exactly. The amount of molybdenum per cubic centimeter in the standard is then figured and the calculation of the percentage of molybdenum in the sample is obtained by multiplying the weight of molybdenum in each cubic centimeter by the number of cubic centimeters, dividing by the weight of sample taken, and multiplying by 100. The following example illustrates the calculations involved: In comparing the standard with the sample, 15 cc. of the standard molybdenum solution (1 cc. = 0.0002 gram Mo) were used and diluted to 44 cc. with ether. Therefore,

$$15 \times 0.0002 = 0.0030 \text{ gram Mo}$$

$$\text{or } \frac{0.0030}{44} = 0.000068 \text{ gram Mo per cc.}$$

The sample was diluted to 36 cc.; hence,

$$36 \times 0.000068 = 0.00245 \text{ gram Mo in the 1-gram sample,}$$
or 0.245 per cent Mo

Solutions Required

STANDARD MOLYBDENUM SOLUTION—1 cc. = 0.0002 gram molybdenum. This solution is prepared by dissolving 0.430 gram of pure sodium molybdate in one liter of water containing 10 cc. of sulfuric acid (1 to 1), and mixing thoroughly. One hundred cubic centimeters of this solution are measured carefully by means of an accurately calibrated pipet into a 250-cc. beaker, 12 cc. of sulfuric acid (1 to 1) are added, and the solution is put through a Jones zinc reductor into 35 cc. of ferric phosphate solution and titrated with a standard solution of 0.05 *N* potassium permanganate (1 cc. = 0.0016 gram Mo).

A blank determination is run on the reductor and the solution of ferric phosphate (this usually amounts to about 0.2 cc.) by passing 100 cc. of 6 per cent sulfuric acid and 150 cc. of water (same amount as used in the analysis) through the reductor in exactly the same way as the molybdenum solution, and titrating the liquid with permanganate. The amount of 0.05 *N* potassium permanganate required to impart a pink tint to the liquid constitutes the blank to be deducted from the buret reading when standardizing the molybdenum solution.

FERRIC SULFATE SOLUTION (8 per cent)—Eighty grams of pure ferric sulfate are dissolved in one liter of 20 per cent sulfuric acid. The presence of iron is essential in the preparation of the standard since it has been determined by experiment that the ethereal solution of potassium-molybdenum thiocyanate is more comparable and also more stable than when it is omitted. The iron appears to have a catalytic effect.

STANNOUS CHLORIDE SOLUTION—Three hundred and fifty grams of stannous chloride are added to 200 cc. of hydrochloric acid (1 to 1) in a 500-cc. Erlenmeyer flask, the liquid boiled gently until the salt has almost dissolved, transferred to a liter bottle, and diluted with freshly boiled water to 1000 cc. A few pieces of metallic tin are introduced to prevent oxidation.

FERRIC PHOSPHATE SOLUTION—Twenty-five grams of ferric sulfate are dissolved in 950 cc. of water containing 40 cc. of phosphoric acid (sp. gr. 1.72) and 10 cc. of sulfuric acid (sp. gr. 1.84).

The accuracy of the method is indicated by the tabulated results obtained on several samples of steel and on Bureau of Standards standard sample 61 of ferrovanadium by the volumetric and colorimetric methods.

Experiments to Test Accuracy of Method

SAMPLE	WEIGHT OF SAMPLE	MOLYBDENUM FOUND Volumetric method	MOLYBDENUM FOUND Colorimetric method
	Gram	%	%
Steel 1	0.6000	0.26	0.27
Steel 1	0.6000		0.27
Steel 1	0.6000		0.27
Steel 2	0.2500	0.33	0.34
Steel 2	0.5000		0.34
Steel 2	0.7500		0.33
Steel 2	1.000		0.33
Ferrovanadium standard 61[a]	0.5000	0.72	0.73

[a] The Bureau of Standards obtained a result of 0.72 per cent Mo by weighing as lead molybdate, and Electro Metallurgical Co., 0.72 per cent by the volumetric method when this standard was made in 1924.

The volumetric determinations were made on a 2-gram sample, the molybdenum being separated from the iron and vanadium with hydrogen sulfide by the present standard methods before passage of the sulfate solution through the Jones reductor.

Time Required for Analysis

	Minutes
Weighing of sample	½
Soln. of sample and boiling almost to fumes of sulfur trioxide	8
Cooling and making ether separation	10
Comparison with standard	2

The above time may be reduced after one has become accustomed to the method. It has been found that the intensity of the color remains stable for at least a week. Therefore, by making up a sufficient number of fresh standards the beginning of each week, say within a range of 0.02 per cent, it will only be necessary to dilute the unknown until the colors match. Of course the standards should all be diluted to the same volume. This will aid in reducing the time taken for making the comparison.

Lots of Bromine in the Ocean

Although practically all of the bromine produced in the United States has been obtained from salt brine deposits located in different states, the outstanding potential source of this chemical material is the sea, according to the United States Bureau of Mines. The rapidly increasing use of this material in motor fuel has attracted attention to the bromine content of the ocean. Bromine occurs in sea water to the extent of 60 to 70 p. p. m., except where fresh water from rivers may cause local dilution near the coast. Since the area of the oceans is 139,295,000 square miles—almost two and one-half times the area of the land—and since the depth averages 3 miles, sea water represents a virtually inexhaustible source of supply of any chemicals that can be commercially extracted therefrom. Experiments have demonstrated that this bromine actually is available, and the importance of this discovery is evidenced by the fact that only 1 cubic mile of sea water would supply for 392 years all the requirements of a plant producing 100,000 pounds of bromine per month.

Owing to the corrosive nature of the element it enters commerce largely in the form of its salt. Bromine is also sold as "mining salt," a mixture of sodium bromate and bromide. Solidified bromine has been used for laboratory work. Diatomaceous earth, formed with a suitable binder and burned into coherent sticks, is saturated with the liquid. These porous sticks absorb 50 to 75 per cent of bromine by weight.

Previous to about 1922 bromine was used principally in the form of sodium potassium or ammonium bromide in photography and for medicinal purposes. The photographic trade usually buys ammonium bromide of U. S. P. grade. "Mining salt" was formerly used in some quantity in the extraction of gold from its ores, but this use has apparently greatly declined. Bromine is used in the production of certain dyes, and liquid bromine as well as many of its compounds is employed in analytical chemistry. During the war some hand grenades and gas bombs were loaded with bromine or with organic bromine compounds.

The principal outlet for bromine at present, however, is as ethylene dibromide used in tetraethyl lead and antiknock compounds.

The world's bromine has come chiefly from Germany and the United States, being produced in the United States as early as 1846.

Problems in Estimation of Unsaturated Hydrocarbons in Gases

III—Some Factors in Bromination with Potassium Bromide–Bromate Mixture[1,2]

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It has been shown that aluminum chloride and certain other metallic salts prevent the quantitative titration of ethylene by the bromide-bromate method. It has further been established that oxygen prevents the quantitative titration of acetylene by the bromide-bromate method.

A standard procedure is developed by which ethylene and acetylene and some of their higher homologs are titrated quantitatively by bromide-bromate solution. This procedure is applied to the analysis of synthetic mixtures of gaseous olefins and acetylenes with encouraging results.

It is suggested that oxygen may be one of the principal causes of the irregularities found in halogen titrations of the acetylenes by other methods.

Propine and butine-1 are prepared and their boiling points determined in a vacuum-jacketed spiral column.

The estimation of the unsaturated content of petroleum fractions by halogenation methods has been found to be subject to disconcerting variations. Further, the addition of the halogens to the acetylenes is incomplete. The causes for these variations have remained obscure. Two excellent reviews of this subject have recently been given (*9*, *12*), and the present paper deals with an experimental investigation of the factors affecting the completeness of the titration of unsaturated hydrocarbons by bromine, using the bromide-bromate method of Francis (*11*, *1*, *2*).

Experimental

Since this research dealt mainly with gaseous hydrocarbons, it was necessary to develop a special procedure for the titrations. The equipment required was a stout-walled reaction bottle fitted with a stopcock, described below, a machine to shake the reaction bottles set in a vertical position at a rate of 250 strokes per minute with a 4.5-cm. stroke, gas burets, Hempel gas pipets, 2 Geissler burets, and 1 Mohr buret fitted with a rubber tube 40 cm. long. The materials used were potassium bromide–bromate solution (approximately 0.5 *N*), sodium thiosulfate solution (about 0.1 *N*), 10 per cent sulfuric acid, bromine in potassium bromide solution, 33 per cent potassium hydroxide solution, potassium pyrogallate solution, and saturated potassium iodide solution.

The reaction bottle is a modification of the type used by Dobrjanski (*7*), and consists of a 300-cc. glass-stoppered bottle with a capillary stopcock sealed through the stopper. A short connecting tube of larger bore is sealed to the stopcock for attaching the apparatus to burets.

The general procedure for the titration of gaseous olefins is as follows: The bromide-bromate solution is measured into the reaction bottle which is then stoppered and evacuated by a water pump. A measured volume of the gas is drawn in without breaking the residual vacuum. Then dilute sulfuric acid is admitted slowly from the Mohr buret. Although the bromide-bromate solution is stable in neutral solution, it decomposes when acidified, liberating bromine. An equivalent quantity of acid is necessary to liberate the bromine as is shown by the following equation:

$$KBrO_3 + 5KBr + 3H_2SO_4 = 3K_2SO_4 + 3Br_2 + 3H_2O$$

Hence, by slow addition of the acid, the bromine is liberated slowly, and the rate can be so controlled that the bromine is taken up by the unsaturated compounds as fast as it is generated. In this manner, the concentration of the halogen is kept low so that substitution reactions are practically avoided. After the reaction is completed, saturated potassium iodide solution and considerable water are added. The vacuum is broken and the stopper removed. Then the iodine formed is titrated with standard thiosulfate solution. The mols of bromine absorbed by one mol of gas can easily be calculated.

After a large number of preliminary tests had been made on the olefins and acetylenes, the important fact was discovered that oxygen prevents the quantitative titration of acetylenes and probably of some diolefins. Accordingly, a procedure has been adopted which excludes oxygen as far as possible from the reaction flask.

Standard Procedure

The bromide-bromate solution required for the experiment is measured from the buret into the reaction bottle. The volume used should be only about 2 cc. in excess of the equivalent quantity, which must be determined by trial experiments or from a priori information about the approximate composition of the sample. The bottle is then evacuated by a water pump until the solution boils. If the tap water is not considerably cooler than room temperature, it may be necessary to heat the bottle with warm water. The gas sample is measured in a buret, is washed twice with potassium pyrogallate solution in a Hempel pipet (shaking one-half minute each time), and is then drawn into the buret and measured. The connecting tube of the evacuated bottle is filled with water to prevent the addition of air. It is then connected to the buret and the washed sample drawn into the bottle. The connecting tube is again filled with water and attached to the Mohr buret containing 10 per cent sulfuric acid. The rubber tube is about 40 cm. long to permit vigorous shaking of the bottle while it is attached to the buret. One cubic centimeter of the acid is added every half minute, the bottle being shaken vigorously between the additions. A volume of acid equal to the volume of bromide-bromate

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[1] Received September 4, 1930. This paper contains results obtained in an investigation of the "Relative Rates of Reaction of the Olefins," listed as Project No. 19 of American Petroleum Institute Research. Financial assistance in this work has been received from a research fund of the American Petroleum Institute donated by John D. Rockefeller. This fund is being administered by the Institute with the coöperation of the Central Petroleum Committee of the National Research Council.

[2] Contribution No. 65 from the Research Laboratory of Organic Chemistry, Massachusetts Institute of Technology.

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[4] Junior research fellows, Project No.19.

mixture taken is added, which is about a 200 per cent excess. When all the acid has been added, the buret is disconnected and the acid in the connecting tube is nearly all drawn in, care being taken that no air is admitted. The bottle is then shaken by the machine for 1 to 1¼ hours to complete the reaction. At the end of this time the bottle is removed and 3 to 5 cc. of saturated potassium iodide solution added; 20 cc. of water are also added before the vacuum is broken, the bottle is opened, and the solution diluted to from 100 to 150 cc. The iodine liberated is titrated to a colorless solution with standard thiosulfate solution. The total volume of unsaturated gas in a separate portion is determined by finding the fraction that is absorbed by bromine in potassium bromide solution.

Only a slight modification of this method is necessary for the titration of liquid or solid samples. The sample is sealed in a thin-walled glass capsule (*4*), weighed, and placed in the reaction bottle. After evacuating, the capsule is broken by shaking the bottle, the sulfuric acid is added, and the remainder of the analysis carried out as above.

Substances

Paraffins—Samples of gases compressed into small steel bottles were purchased. The degree of purity claimed for them was: methane, 92 per cent; ethane, 99 per cent; isobutane, 99 per cent; and normal butane, 99 per cent (*10*).

Olefins—The methods by which the olefins were prepared have already been described (*3*, *5*).

Diolefins—*Propadiene* (*allene*), b. p. −32.8° to −31.3° C., was prepared by slowly dropping 2, 3-dibromopropene (Eastman Kodak Company) into boiling alcohol and zinc dust (*13*).

1, 3-Butadiene (*erythrene*), b. p. −2° to −1° C., was prepared by reducing erythrene tetrabromide with zinc dust in boiling alcohol solution. As Thiele has pointed out (*19*), it is necessary to add the tetrabromide slowly to the alcohol in order to obtain good yields. This requirement was met by placing the crystals in a test tube under the drip from a reflux condenser fitted to the flask, and under these conditions the yield of butadiene was 80 per cent of the theoretical. The erythrene tetrabromide, which had been prepared from cracked gases and recrystallized, was obtained through the kindness of V. Schneider.

Acetylenes—Ordinary acetylene from a tank of the compressed gas was washed with water, with concentrated potassium hydroxide, with concentrated sulfuric acid, and was then stored over water. The sample gradually became contaminated with air.

Methylacetylene, b. p. −20° to −18° C. (compare −27.5° C., International Critical Tables, *14*), was prepared by slowly adding methyl iodide to sodium acetylide in liquid ammonia (*13*). The liquefied product was fractionated through a vacuum-jacketed spiral column.

Ethylacetylene was prepared in a similar manner, using ethyl iodide in place of methyl iodide, b. p. 6.8° to 8.5° C., (compare Picon's figure, 8° C., *18*). The value 18.5° C. given in the International Critical Tables (*17*) seems to be too high.

Samples of 1-heptine, 1-octine, 2-octine, and 4-nonine, were kindly supplied by R. L. Wakeman, who will describe their preparation elsewhere.

Cyclic Hydrocarbons—*Cyclopropane* (*trimethylene*) was prepared by dropping trimethylene bromide (Kahlbaum) into boiling isoamyl alcohol and zinc dust (*20*). The evolved gas was bubbled through 10 per cent potassium permanganate to remove olefins, liquefied, and fractionated. However, the product was not pure, probably because the permanganate treatment was not thorough enough. About 20 per cent by volume dissolved quickly in bromine water, and the remainder slowly; b. p. −28° to −27° C. (compare the value −34.4° C. given in the International Critical Tables, *15*).

The values obtained in various experiments are collected in Table I.

Table I—Results of Experiments with Various Substances

Substance	Procedure	Shaking Period	No. of Expts.	Mols Br_2 per 1 Mol Substance
		Hours		
	PARAFFINS[a]			
Methane	Standard	2½	1	0.01
Ethane	Standard	1⅓	1	0.00
Butane	Standard	1¼	1	0.02
Isobutane	Standard	1¼	1	0.07

[a] In this series the gases were not shaken with pyrogallate solution, but were washed with bromine in potassium bromide solution to remove any unsaturated compounds that were present.

Substance	Procedure	No. of Expts.	Mols Br_2 per 1 Mol Substance
	OLEFINS		
Ethylene	Standard	4	1.01
	With 7 × 10^{-3} mols O_2	2	0.95
	With 5 × 10^{-3} mols $AlCl_3$	1	0.16
	With 5 × 10^{-3} mols $Al_2(SO_4)_3$	2	0.46
	With 5 × 10^{-3} mols $Al_2(C_4H_4O_6)_3$	1	0.47
	With 5 × 10^{-3} mols $NiCl_2$	1	0.15
	With 5 × 10^{-3} mols $NiSO_4$	2	0.46
	With 5 × 10^{-3} mols HCl	1	1.02
Propene	Standard	1	1.01
	With 5 × 10^{-3} mols $Al_2(SO_4)_3$	1	1.00
1-Butene	Standard	1	1.07
	With 5 × 10^{-3} mols $AlCl_3$	1	1.04
2-Butene	With 5 × 10^{-3} mols $Al_2(SO_4)_3$	1	0.98
Isobutene	Standard	1	1.01
Isopropylethene	Standard	1	1.06
	DIOLEFINS		
Propadiene (allene)	Standard	1	1.94
1,3-Butadiene (erythrene)	Standard	1	2.00
	ACETYLENES[b]		
Acetylene (25.6% mixture in air)	Standard	1	1.89
Acetylene (25.6% mixture in air)	Standard (except not washed by pyrogallate)	1	1.47
Acetylene (1.48 × 10^{-3} mols)	1.36 × 10^{-3} mols O_2 added	1	1.64
Acetylene (1.42 × 10^{-3} mols)	3.23 × 10^{-3} mols O_2 added	1	1.49
Methyl acetylene	Standard	2	1.97
Ethyl acetylene	Standard	2	2.02
1-Heptine	Standard	1	2.01
1-Octine	Standard	2	1.74
2-Octine	Standard	1	2.05
4-Nonine	Standard	1	1.75
	CYCLIC HYDROCARBONS[c]		
Cyclopropane (trimethylene)	Standard	1	0.17
	With air present	1	0.16

[b] Numerous preliminary experiments carried out before the role of oxygen was recognized indicated that aluminum, nickel, and mercuric salts aided the quantitative titration of acetylene, but since these same salts prevent the quantitative titration of ethylene they were not further investigated.

[c] About 20 per cent of this sample dissolved rapidly in a solution of bromine and potassium bromide, the remainder very slowly, hence it must have contained some olefin (see preparation above).

Mixtures

A synthetic mixture (Experiment 3, Table II) containing 18.4 per cent of acetylene and 19.6 per cent of ethylene in air was titrated by the standard procedure (first washing with pyrogallate solution to remove oxygen). A 98.0-cc. sample (3.88 × 10^{-3} mols) containing 38 per cent (1.47 × 10^{-3} mols) of unsaturated gases, as shown by absorption in bromine water, reacted with 2.15 × 10^{-3} mols of bromine. From these figures the composition of the gas is easily calculated:

$$\% \text{ acetylene} = \frac{(2.15 - 1.47)}{3.88} \times 100 = 17.6\% \text{ (compare } 18.4\% \text{ actual)}$$

$$\% \text{ ethylene} = \frac{[(2 \times 1.47) - 2.15]}{3.88} \times 100 = 20.4\% \text{ (compare } 19.6\% \text{ actual)}$$

These results are in fair agreement with the actual composition of the sample. As pointed out below, the pyrogallate solution absorbs some of the unsaturated gases and more of the acetylenes than of the olefins. The collected results of the tests on synthetic mixtures are shown in Table II.

Table II—Analysis of Synthetic Mixtures by Standard Procedure

EXPERIMENT	MIXTURE	OLEFIN		ACETYLENE	
		Found	Actual	Found	Actual
		Mol %	*Mol %*	*Mol %*	*Mol %*
1	Ethylene, acetylene	64.0	62.5	25.7	28.1
2	Ethylene, acetylene	63.5	62.5	27.1	28.1
3	Ethylene, acetylene	20.4	19.6	17.6	18.4
4	Ethylene, acetylene	21.4	19.4	15.2	17.0
5	2-Butene, methyl acetylene	33.2	37.1	66.8	62.9

Dobrjanski (*7*) has used a similar method with success for the determination of erythrene in its mixtures with butenes, but his procedure is considerably more complicated.

Since acetylene is known to be more soluble in water than some of the gaseous olefins, being 8.6 times as soluble as ethylene at 25° to 30° C. (*17*), several semi-quantitative tests were carried out on the relative solubilities in pyrogallate reagent. Ethylene, propene, and 1-butene were absorbed at a rate of approximately 0.1 cc. per minute of contact when 100 cc. of gas were shaken well in a Hempel pipet filled with the reagent which was comparatively free from the olefins. On the other hand, acetylene was absorbed at a rate of 0.8 to 0.9 cc. per minute of contact under similar conditions.

Discussion

The most important facts which have been made clear by these experiments are that oxygen prevents the titration of acetylenes and that the titrations are largely quantitative in its absence. What may be a similar effect has been observed by Verhoogen (*21*) in brominations of the stereoisomers of α,β-dichlorethylene. She found that the fraction of the bromine disappearing after 23 hours varied with the gas in contact as follows: air, 0.14; nitrogen, 0.99; carbon dioxide, 0.998; and oxygen, 0.03.

It is possible that the explanation of these phenomena is that the intermediate dibromoethylenes absorb oxygen to give, after intramolecular rearrangement, bromacetyl bromides. Demole (*6*) showed that 1,1-dibromoethylene absorbs oxygen and Verhoogen (*21*) showed that the trans-form of α,β-dichlorethylene was greatly changed on standing 23 hours with oxygen. The resulting liquid fumed strongly in air, liberating hydrogen chloride and ketones. If this explanation is correct, it should be possible by careful measurements to detect the actual absorption of oxygen, and also to identify the products. On the other hand we may be dealing here with negative catalysis. Verhoogen concluded that in her experiments cited above, the rates of bromine addition were different.

The products from the bromination of the acetylenes in the absence of oxygen were heavy colorless liquids which sometimes crystallized. If, as seems probable, they are the corresponding tetrabromides, a way is open for the preparation of numerous tetrabromides which formerly have been difficult to synthesize.

The influence of oxygen in titrations by the Hanus and other methods will bear investigation. Thus Faragher, Gruse, and Garner (*8*) found that 1-heptine adds, from the Hanus reagent, only halogen corresponding to one double bond, whereas in our experiments both bonds were apparently saturated (see Table I).

Now that the disturbing influence of oxygen in these titrations has been made clear, the use of the bromide-bromate method for estimating unsaturated hydrocarbons can probably be considerably extended.

The error caused by the solubility of acetylene in aqueous solutions is serious. When in Experiment 1 of the acetylene section of Table I a correction is made for the solubility of the acetylene in the pyrogallate solution, the value 1.98 mols of bromine per mol of acetylene actually admitted to the reaction flask is obtained. Thus, it is obvious that for more accurate determinations of the unsaturated hydrocarbons in mixtures, it will be necessary either to use some other method for removing the oxygen, or to determine experimentally corrections for the solubilities of the gases present in the mixture.

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Quantitative Determination of Pyrethrin I[1]

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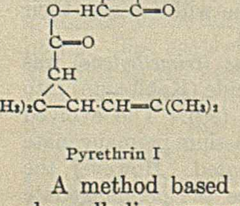
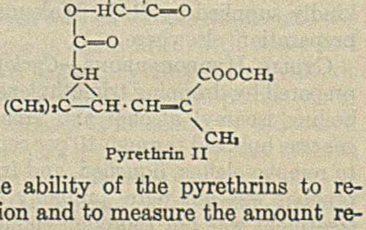
The classical researches of Staudinger and Ruzicka (*4*) established the constitution of the toxic principles present in pyrethrum flowers. They gave to the two active constituents the names pyrethrin I and pyrethrin II, and assigned to them the formulas given herewith.

Two methods for the quantitative determination of these constituents have been investigated by the author. It is the purpose of this paper to discuss the results which were obtained, and to report a series of experiments relating to the determination of these constituents in kerosene extract of pyrethrum flowers.



Pyrethrin I



Pyrethrin II

A method based on the ability of the pyrethrins to reduce alkaline copper solution and to measure the amount re-

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duced by comparison with a standard dextrose solution has been described by Gnadinger and Corl (*1*).

The acid method, originally published by Staudinger and Harder (*3*), has been simplified by Tattersfield, Hobson, and Gimingham (*5, 6*). Their short acid method for pyrethrin I is a determination which requires but a small sample and can be carried out in a short time. Briefly, 10 or 20 grams of flowers are extracted with petroleum ether in a Soxhlet extractor, the extract is hydrolyzed with alcoholic soda, is made acid and steam-distilled. The distillate is titrated with 0.02 *N* caustic soda.

Pyrethrin I has been shown to be more toxic to insects than pyrethrin II. Tattersfield, Hobson, and Gimingham found pyrethrin II to be but one-tenth the toxic strength of pyrethrin I, but in a more recent paper (*2*), Gnadinger and Corl maintain it is about 80 per cent as toxic. Inasmuch as the ratio of pyrethrin I to pyrethrin II is fairly constant, a method for the determination of pyrethrin I in flowers or an extract gives a good index of its toxic strength, regardless of the relative toxicity of the two constituents.

Sample 1, a sample of 1928 Dalmatian flowers, was run by both the short acid and the copper reduction methods with results that gave a good comparison between these two. The short acid method gave 0.31 per cent pyrethrin I, while the copper reduction method showed 0.75 per cent total pyrethrins.

The short acid method has been applied to a group of Dalmatian and California flowers, with the results given in Table I.

Table I—Analysis of Pyrethrum Flowers

SAMPLE	DESCRIPTION	PYRETHRIN I
		%
1	1928 Dalmatian, closed	0.31
36	1928 Dalmatian, closed	0.24
31	1928 Dalmatian, closed	0.23
61	1929 Dalmatian, closed	0.21
56	1929 California, open	0.20
63	Stems from sample 56	0.021

Experimental Work

Both these methods have been described only for samples of flower, stems, stalks, etc. A method for determining these constituents in a kerosene extract would be of value as a control test in the preparation of such extracts as are often used in commercial insect sprays. The short acid method was selected as the one best suited for developing into a control method.

No sample of pure pyrethrins or of an extract containing a known concentration of them was available to serve as a standard for experimental work, so a sample of concentrated kerosene extract was run several times by the method described for the flowers. A 5-cc. sample was used, along with 45 cc. of low boiling petroleum ether. A dilute extract was prepared by adding nineteen parts of kerosene to one part of concentrated extract, and this sample was run by the various methods described below. Table II shows the results on the original and dilute samples. For purposes of comparison, the results on the dilute sample have been calculated back to the original sample.

Table II—Pyrethrin I Content of Concentrated Extract

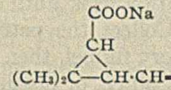
METHOD	PYRETHRIN I
	Grams/liter
Original	3.6, 4.6, 4.8, 4.8, 5.4, 6.2 (av. 4.9)
Dilute samples:	
Original	1.8
Superheated steam	4.7, 5.1
Vacuum distillation	5.0, 5.1
Hydrolysis (2 extractions)	4.6, 4.9
Hydrolysis (3 extractions)	5.0

It will be noted that when the short acid method was applied directly to this dilute extract, using a 100-cc. sample, less than one-half the pyrethrin I is determined. This is probably due to the large volume of kerosene present in the distillation flask since 100 cc. more distillate collected gave but a small additional titration. A small volume of kerosene does not seem to affect the distillation.

The method which makes use of superheated steam is one in which 90 to 95 per cent of the kerosene is distilled, after hydrolysis of the pyrethrins, at a temperature of about 200° C. in a current of superheated steam. The results obtained were in good agreement with results from other methods, but no further work has been done on this one because the hydrolysis method gave equally good results, and is simpler.

In the vacuum distillation method, the same amount of kerosene was distilled at a pressure of from 2 to 3 mm. This method was not further developed on account of mechanical difficulties which render it unsatisfactory as a control method.

The hydrolysis method is based on the saponification of pyrethrin I to form the sodium salt of chrysanthemum monocarboxylic acid.



This removes the pyrethrin I from the kerosene layer, which may then be discarded. In order to keep the volume low and avoid transferring to a separatory funnel, the kerosene solution is extracted with two successive portions of alcoholic soda, and these extracts, along with a few cubic centimeters of kerosene, are then combined. Two extractions were found sufficient for complete removal of the pyrethrin I. When acid is added, the sodium salt breaks up, and the monocarboxylic acid is steam-distilled and titrated in the manner described by Tattersfield and Hobson (*6*).

Good checks were obtained using this method. Different operators running the same sample obtained results checking within 10 per cent of the total pyrethrin I, and an experienced operator can check himself within 5 per cent. Table III shows the results of a series of experiments in which ground Dalmatian flowers were steeped with kerosene at approximately 40° C. for 24 hours, after which the flowers were drained (but not dried), and analyses were run on both the wet flowers and the extract. The kerosene content of the wet flowers was about 30 per cent.

Table III—Comparison of Spent Flowers with Extracts

SAMPLE	PYRETHRIN I	
	Wet flowers	Extract
	%	%
37	0.067	0.064
40	0.040	0.041
42	0.018	0.024
44	0.015	0.012
46	0.008	0.009
64[a]	...	0.030

[a] Sample 64 was a mix of equal parts of samples 40 and 42.

The method which has been used to determine pyrethrin I in kerosene extracts follows. The presence of any ester of the type which is often used for an odorant will cause high results, hence this method is applicable only to extracts which are known to contain no foreign material. For the same reason it is not suitable for use in the qualitative determination of pyrethrins in an unknown extract.

Method

SOLUTION REQUIRED—Sodium hydroxide in methanol, approximately 1 *N*. Fiftieth normal sodium hydroxide, 0.02 *N*. The strength of this solution should be checked occasionally. Sulfuric acid, 1 *N*. Petroleum ether, maximum boiling point 60° C.

APPARATUS—For refluxing the sample and subsequent distillation, use a long-necked flask of 100 cc. capacity. The author used an ordinary distillation flask on which the side arm had been sealed.

Procedure—Measure 100 cc. of extract into a long-necked flask of the type described above. (A smaller sample may be used if more than 0.05 per cent pyrethrin I is known to be present.) Add 5 cc. alcoholic soda solution and reflux for $1\frac{1}{2}$ to 2 hours, the bulb of the flask being immersed in a beaker of hot water. Shake occasionally. Remove from the beaker and pour off as much kerosene as can be decanted without disturbing the alcohol layer into another similar flask which contains a second 5 cc. portion of alcoholic soda. Reflux as before, and when completed, pour off the kerosene layer, rejecting it. A few cubic centimeters of kerosene will remain in each flask. Add to the second flask 11 cc. 1 *N* sulfuric acid, shake, and transfer to the first flask. Rinse the second flask with two 25-cc. portions of petroleum ether, and after transferring these washings to the first flask, confirm its acidity with phenolphthalein. Distil in a current of steam, using a long condenser cooled with ice water. Do not apply a flame to the distillation flask until all the petroleum ether has been distilled. Collect the petroleum ether and 50 cc. of water in a separatory funnel, then continue the distillation until an additional 50 cc. of distillate has been collected. Keep the volume low in the distillation flask, but do not allow it to go dry.

The titration is carried out in an Erlenmeyer flask to which has been added about 20 cc. carbon dioxide-free water, a few cubic centimeters of ethyl alcohol, and 1 cc. of phenolphthalein indicator. Add to this enough 0.02 *N* sodium hydroxide to give a definite pink color, usually one to two drops will be sufficient. Shake the contents of the separatory funnel vigorously and add the water layer to the second 50 cc. of distillate. Wash the petroleum ether layer with about 20 cc. of water, then add it to the titration flask. Titrate to a definite pink, shaking well and allowing the layers to separate after each addition. Extract the combined distillates with a second 50-cc. portion of petroleum ether, and add this to the titration flask. Continue the addition of caustic until the pink color is the same as it was originally. A blank determination should be run, using 100 cc. of kerosene, and the proper deduction should be made from each determination. This will usually be about 0.3 cc.

Calculations—From the molecular weight of 330, we get the relation, 1 cc. 0.02 *N* caustic = 0.0066 gram pyrethrin I.

Summary

The copper reduction and the short acid methods for determining active constituents in pyrethrum flowers are compared, and several samples of Dalmatian and California flowers run by the short acid method.

A series of experiments on the adaptation of the short acid method to a kerosene extract of pyrethrum are discussed.

A method for the quantitative estimation of pyrethrin I in a kerosene extract is described, along with a table showing pyrethrin I content of spent flowers and the extracts from these flowers.

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(2) Gnadinger and Corl, *Ibid.*, **52**, 3300 (1930).
(3) Staudinger and Harder, *Ann. acad. sci. Fennicae*, [A] **29**, No. 18 (1927).
(4) Staudinger and Ruzicka, *Helv. Chim. Acta*, **7**, 177, 450 (1924).
(5) Tattersfield and Hobson, *J. Agr. Sci.*, **19**, 433 (1929).
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A Modified Balance for Approximate and Quick Weighing[1]

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Many cases arise when the time required to make a weighing must be kept at a minimum either because the weighings are approximate and large expenditure of time is unwarranted or because many things of the same kind are to be weighed. The economics of mass production demand that as little time as possible be spent upon each weighing. There is a very simple and inexpensive method for accomplishing this by modifying an ordinary beam balance as shown in Figure 1. A spring, *S*, is mounted directly under the beam, *H*, in which two adjustable studs, *A*, are inserted. These studs barely make contact with the spring, *S*, in the balanced condition. For example, the distance between the hardened ends of the studs and the spring may be 0.01 inch (0.25 mm.). The index, *B*, is lengthened and its position read by a scale, *C*. In making a weighing the scale pan, *G*, is depressed to the stop, *E*, and then is released quickly and carefully. If the weights on the two scale pans are equal the index will be deflected on its first swing to a point that may be marked zero on the scale, but if the weight on the scale pan, *F*, is slightly more than that on *G*, the index will not travel to that point. The distance traveled depends upon the difference in the weights on the pans. The modification described is best suited for comparing one article with another which is intended to be of the same weight and which is to be trimmed or adjusted to a given weight within certain tolerances. In such a case the standard article ("weigh-by") may be placed upon the pan *F*, and others, placed on pan *G*, be compared with this.

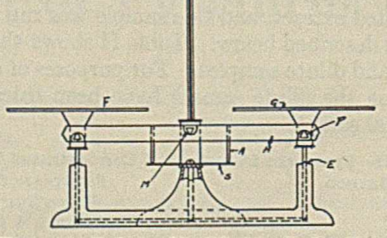

Figure 1—Balance Modified for Indicating Offweight on First Deflection

The scale *C* may be put in units of weight, of length, or of volume. For example, for comparison and control of pieces cut from ribbon or tubed stock, the scale *C* may be graduated in centimeters, indicating the length which must be cut from, or added to the piece in order to make its weight within tolerance limits equal to the weight of the standard. For

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[1] Received September 20, 1930. Presented before the Division of Rubber Chemistry at the 80th Meeting of the American Chemical Society, Cincinnati, Ohio, September 8 to 12, 1930.

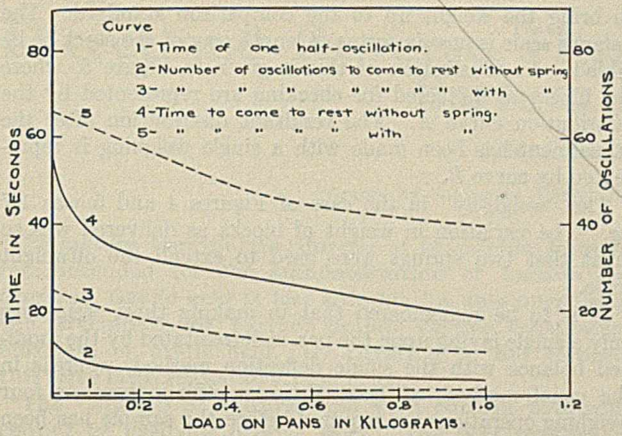

Figure 2—Time and Number of Oscillations before Coming to Rest

general purposes, the scale *C* graduated in terms of grams is more useful. It may even be graduated in terms of spoonfuls in case the materials being weighed are being meted out by approximate volumes, or it may indicate the number of cuts of a given size that are required to reduce the weight to within specified tolerances.

In a balance so equipped, it was found that an article could be laid upon the pan, the beam deflected, and the scale indicating the underweight or overweight read off in 2 seconds. By the ordinary method of weighing, this process consumed at least $2^1/_2$ seconds when the balances are read on the go—that is, when the state of balance was merely judged as to overweight or underweight by noting several deflections of the balance. An experienced operator can do this with fair accuracy at high speed. However, when the weight is obtained in 2 seconds, by the modified balance, exact information as to overweight and underweight is at hand, while when obtained by the ordinary method just mentioned, the overweight or underweight is only guessed at, so that at least one other trial on the balance is necessitated. This increases the time for one adjustment to at least 5 seconds.

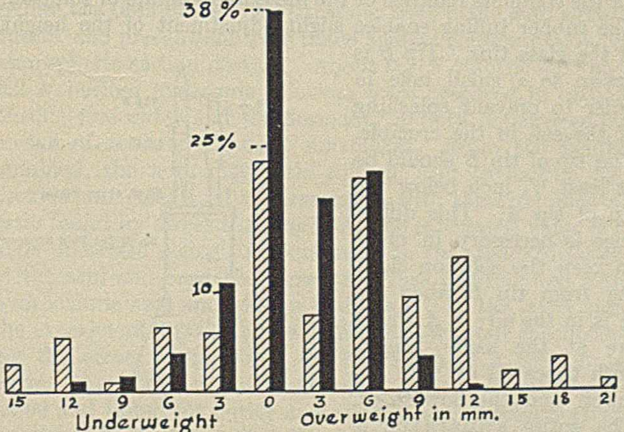

Figure 3—Distribution of Weight among Rubber Blocks before and after Adjustment with Balance

It was modified to indicate offweight quickly.

Figure 2 shows how certain characteristics of a balance change when it is equipped with a spring for quick weighing. From these curves a comparison may be made for different modes of weighing. In the method now discussed for the new balance, a weighing is made on the first half-oscillation of the index. The time (approximately 1 second) of the first half-oscillation is constant over a large range of loads (curve 1). When the condition of the balances is merely guessed at, one must observe theoretically at least $1^1/_2$ oscillations—making the time required approximately 3 seconds, but a much longer time is involved in actual practice, as just indicated.

Comparison with Unmodified Balance

To compare a balance modified for quick weighing with one unmodified and used in the ordinary way by estimation of the state of balance, a number of strips of rubber used in a routine process in the factory were weighed and adjusted by the two methods. The results are indicated in Figure 3, where the distribution of the samples according to weight is indicated by full columns for the balance equipped with the spring and used in the first deflection manner and by light columns for the customary method. Overweight and underweight are indicated on the abscissa in terms of centimeters of length. By the new method the number of products which are exact is over 50 per cent greater than the number by the usual method. In general, the distribution is changed in a very favorable manner—that is, the number showing small over- or underweight is generally much larger by the new method. The number which lie in the region of large underweight and large overweight are very much greater by the customary method than by the first deflection method with the modified balance. Further striking data are shown in Figure 4. In this case the distribution according to weight of rubber blocks as received is shown by curve *A*. After weighing and trimming by the usual method the distribution for several thousand blocks is represented by curve *B*. When the modified balance is used in the first deflection manner, curve *C* is obtained. The number of blocks weighing within 1 per cent of the standards has been greatly increased in the last case. There are practically no blocks differing by as much as 2 per cent from the standard. These weighings were made by one who had had much experience with these blocks in the factory. She had had no experience with the new method of weighing.

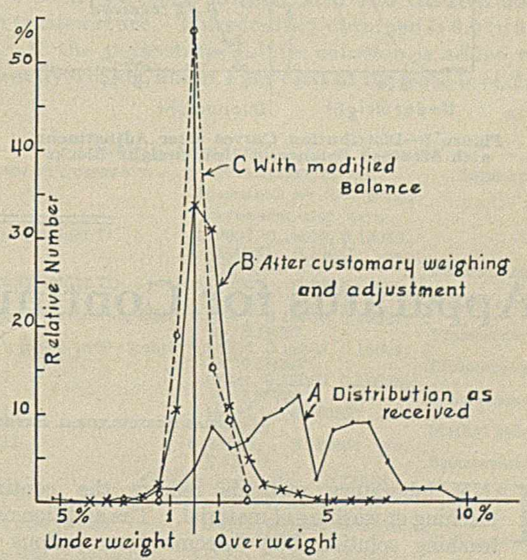

Figure 4—Distribution Curves for Overweighted Blocks before and after Adjustment with Ordinary and Modified Balances

When the things to be checked by weighing have a cross section not favorable for adjustment by cutting off given lengths, then another method is to make certain that the blocks of material as delivered for checking are on an average slightly underweight. Then for adjustment, some small quantity of the material of standard shape may be added

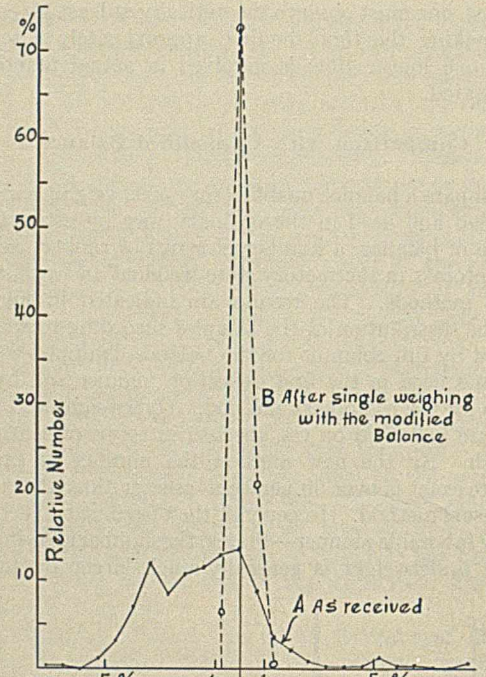

Figure 5—Distribution Curves after Adjustment with Modified Balance of Underweight Blocks

to bring the weight up to the comparison standard. The balance scale is now in terms of length, say of the stock to be added. An illustration of this is given in Figure 5, where the blocks as delivered for checking are represented by the distribution curve *A*. The resultant distribution after the adjustment has been made with a single weighing is represented by curve *B*.

The "weigh-by" in the case of Figures 4 and 5 was 1.7 kg. The variation in weight of blocks as delivered was so great that two springs were used to extend the offweight scale.

It is to be remembered that in making these weighings only a single laying upon the pan is necessitated by the modified balance with the single deflection method, whereas in the usual method, at least two, sometimes three or four weighing operations are required before the sample has been brought within limits. Not only is the distribution curve more favorable with the former method from the standpoint of elimination of waste, but it also consumes considerably less time. To make the weighings represented in Figure 4 required at least 10 per cent less time using the modified balance in the first deflection manner than when the customary method is employed. On another occasion 6 blocks per minute were adjusted by the new as compared with 5.04 by the customary method, or 19 per cent faster. If a comparison be made on the basis of the time required to bring about the same distribution, a much greater difference is brought out.

Apparatus for Continuous Leaching with Suction[1]

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MANY laboratory methods require the continued leaching or washing of material. The addition of the leaching solution may become very tedious and time-consuming if a wash bottle or aspirator bottle be used. Schollenberger and Dreibelbis (*1*) describe an apparatus for continuous leaching. It is not, however, adopted to use with suction, and hence is unsuited to many laboratory operations. For example, in the determination of the base exchange capacity of a soil, as conducted in this laboratory, 10 grams of soil in a 35-cc. Gooch crucible are leached with 250 ml. of a neutral, normal solution of ammonium acetate. The excess ammonium acetate is then washed out with 95 per cent alcohol until the leachate gives no test with Nessler's solution. Suction is applied in order to reduce the time required for leaching and washing. Many soils leach very slowly, and without some self-operating apparatus a great deal of time may be lost in adding the leaching solution. For this reason, a number of different arrangements of apparatus were tried and the one described below finally selected. This has been found very satisfactory. The sizes and dimensions of the materials used are those adapted to the work described above. They may, of course, be varied at will to meet the requirements of other work.

The diagram gives all the essential characteristics of the apparatus. A few points should, however, be noted. The glass tubes are flush with the bottom of the stopper allowing for the complete removal of the measured volume of solution. The rubber tubing enables slight adjustment of the height of the glass tips. Tip *B* is drawn to a small hole in order to prevent splashing of the soil in the crucible. The tip of tip *B* should be at least $^1/_4$ inch below the tip of tip *A*. This difference is necessary in order to keep the solution flowing from tip *B* when tip *A* is in the air; if *A* and *B* are at the same height, both tubes fill up with solution and the flow stops. The entire apparatus is inverted after filling with the solution, and supported by a wooden support, with the bottom of both tips within and below the edge of the crucible.

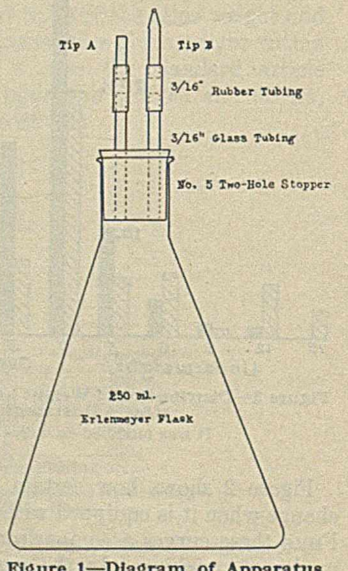

Figure 1—Diagram of Apparatus

Literature Cited

(1) Schollenberger and Dreibelbis, *Soil Science*, **30**, 165 (1930).

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[1] Received October 11, 1930. Technical Article 127 of the Texas Agricultural Experiment Station.

Direct and Reverse Titration of Sulfuric Acid with Barium Hydroxide[1]

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Potassium biphthalate (Bureau of Standards) is to be recommended for the standardization of barium hydroxide. Oxalic acid is less suitable for this purpose as the precipitate of barium oxalate carries down some bioxalate or oxalic acid. By titrating in hot solution this error is decreased to 0.1 per cent.

The titration of sulfuric acid with barium hydroxide cannot be used for precise work. The best results are obtained if the titration is performed at room temperature and if, after the first color change, the mixture is boiled and more base added until the color of the indicator persists for 15 to 30 seconds. After continued boiling for 5 minutes, the solution is cooled and the titration finished at room temperature. The accuracy obtained is 0.1 to 0.2 per cent. In the titration of a hot solution of sulfuric acid there is a greater occlusion of barium hydroxide.

In the precipitation of sulfuric acid with barium chloride, a small part of the acid is occluded. In precipitation at room temperature the occlusion is larger than at higher temperature.

The titration of barium hydroxide with sulfuric acid leads to erroneous results. A part of the base is occluded and a part adsorbed by the precipitate. The adsorbed base can be removed by boiling the mixture with a small excess of sulfuric acid; the error by occlusion is still about 1 per cent. The best results are obtained if the barium hydroxide is added to an excess of potassium sulfate at room temperature. The mixture is titrated at room temperature and, after the color change, boiled for 5 minutes with a small excess of sulfuric acid and titrated back at room temperature. The accuracy obtained is 0.0 to 0.2 per cent. If the potassium sulfate solution is added to the barium hydroxide, about 1 per cent of the base is occluded.

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IT IS a well-known fact that barium sulfate precipitated from a sulfate or barium solution has a tendency to carry down other ions present in the solution. In the titration of sulfuric acid with barium hydroxide or in the reverse procedure, the possibility exists that either sulfuric acid or barium hydroxide may be co-precipitated. No accurate data on the accuracy of this titration are to be found in the literature. E. von Drather (*2*) concluded from rough experiments that in the titration of 0.2 *N* barium hydroxide with 0.2 *N* sulfuric acid, about 2 to 3 per cent too little base was found.

A special study of the deviations found in the titration of sulfuric acid with barium hydroxide and in the reverse procedure has been made. All titrations were made with weight burets, and precautions were taken against contamination by atmospheric carbon dioxide. About 0.2 *N* sulfuric acid and 0.2 *N* barium hydroxide solutions were prepared in carbon dioxide-free water and the normality of both determined by means of various standard substances. From the figures obtained, the normality ratio sulfuric acid to barium hydroxide was calculated and compared with the experimental ratio found by direct titration. As the calculated value is a little uncertain owing to errors made in the standardization of the acid and base, the same procedure was followed with hydrochloric acid and sodium hydroxide. In the latter case the experimental ratio can be determined without encountering the errors arising from the formation of a precipitate during the titration. Pure standard substances were prepared and tested for purity according to the directions given by one of the authors (*3*). The results have been corrected for the titration error, which was determined in an experimental way (for details compare Kolthoff, *3*). The results are given in Table I. The experimental and the calculated ratios agree within 0.02 to 0.03 per cent.

Calculated ratio of normality : sodium hydroxide to hydrochloric

$$\text{acid} = \frac{0.18914}{0.18084} = 1.0460$$

Ratio found: 1.0462, 1.0462, 1.0463 (bromocresol green)
Ratio found: 1.0464, 1.0464 (phenolphthalein)
Average: 1.0463

Table I—Standardization of Reagents

STANDARD SUBSTANCE	NORMALITY FOUND *Equivalents per 1000 grams*	INDICATOR
	HYDROCHLORIC ACID	
Na_2CO_3 (product I)	0.18091, 0.18079, 0.18082, 0.18087, 0.18087; av. 0.18085	Bromocresol green
Na_2CO_3 (product II)	0.18083, 0.18085; av. 0.18084	Methyl orange
$KHCO_3$ (recryst. from H_2O)	0.18092, 0.18086, 0.18084; av. 0.18087	Bromocresol green
$KHCO_3$ (pptd. with alcohol)	0.18084, 0.18083, 0.18084; av. 0.18084	Bromocresol green
Borax I	0.18081, 0.18080, 0.18085; av. 0.18082	Bromocresol green
Borax I	0.18082, 0.18082; av. 0.18082	Methyl red
Borax II	0.18083, 0.18085; av. 0.18084	Bromocresol green
	Average normality: 0.18084	
	SODIUM HYDROXIDE	
Benzoic acid (B. S.)	0.18912, 0.18913, 0.18910; av. 0.18912	Phenolphthalein
Benzoic acid (Kahlbaum)	0.18918, 0.18913, 0.18911; av. 0.18914	Phenolphthalein
Oxalic acid	0.18917, 0.18915, 0.18918; av. 0.18917	Phenolphthalein
Oxalic acid (+$MgCl_2$)	(0.18935, 0.1894)	Bromocresol green
Potassium biphthalate	0.18909, 0.18912, 0.18915; av. 0.18912	Phenolphthalein
	Average normality: 0.18914	
	BARIUM HYDROXIDE	
Benzoic acid (B. S.)	0.19229, 0.19231, 0.19231, 0.19233; av. 0.19231	
Potassium biphthalate (*a*)	0.19221, 0.19222	
Potassium biphthalate (*b*)	0.19232, 0.19233, 0.19234; av. 0.19233	
Oxalic acid (*c*)	0.19300, 0.19305	
Oxalic acid (*d*)	0.19248, 0.19250, 0.19256	
	Average normality: 0.19232	

The sulfuric acid was standardized against the various standard substances used for the hydrochloric acid solution, an average normality of 0.20493 (equivalents per 1000 grams) being found. A few words may be said about the standardization of barium hydroxide with potassium biphthalate and oxalic acid, respectively. In a titration of an oxalic acid solution with barium hydroxide, the barium oxalate precipitating during the procedure carries down some oxalic acid or bioxalate. If the mixture is heated to boiling after the first color change of phenolphthalein, then cooled to room temperature and the titration continued until the color becomes pink again, the deviation is still 0.35 per cent from the theoretical value. By direct titration at room temperature Bruhns (*1*) found an error of 0.24 per cent, whereas

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[1] Received September 26, 1930.

Schmitt (*4*) found a deviation of 0.3 per cent. According to the latter the titration of a hot solution of oxalic acid gives theoretical results. This statement was not confirmed in the present work, a deviation of 0.1 per cent from the theoretical value being found, if a hot solution of oxalic acid was titrated with barium hydroxide. Therefore, for work of high precision oxalic acid cannot be recommended for the standardization of barium hydroxide. Potassium biphthalate, on the other hand, is very useful, and gives theoretical results if a 0.05 *N* solution is titrated at a temperature of 40° to 50° C. At room temperature some barium phthalate may crystallize out at the end of the titration and carry down a trace of barium hydroxide. The error, however, is very small, amounting to about 0.05 per cent. In Table I the results of the standardization of barium hydroxide with benzoic acid, potassium biphthalate, and oxalic acid, respectively, are also reported. The titration of potassium biphthalate (*a*) was carried out at room temperature, the results given under (*b*) were obtained at 40° to 50° C., and the results reported for oxalic acid (*c*) were found by titrating at room temperature until a temporary end point was reached. The mixture was heated to boiling, cooled with protection of a soda-lime tube, and the titration finished with barium hydroxide (error 0.35 per cent). In experiment (*d*) the boiling solution of oxalic acid was titrated with barium hydroxide. After the end point had been reached, the color of the indicator did not change if the mixture was heated to boiling and cooled to room temperature.

Titration of Sulfuric Acid with Barium Hydroxide

The titration of sulfuric acid with barium hydroxide is given in Table II.

Calculated ratio of normality : sulfuric acid to barium hydroxide

$$= \frac{0.20493}{0.19223} = 1.0660$$

Table II—Titration of Sulfuric Acid with Barium Hydroxide

Calculated normality ratio $H_2SO_4 : Ba(OH)_2$, 1.066

Experiment	Addition	Temp.	No. of Titrations	Normality Ratio H_2SO_4: $Ba(OH)_2$ Found	Av. Deviation from Mean	Av. Deviation from True Ratio
		° *C.*			%	%
1	......	Room	4	1.067	0.1	+0.1
2*a*	......	100	3	1.072	0.2	+0.6
2*b*	......	100	3	1.070	0.1	+0.4
3*a*	0.5 *N* $BaCl_2$ added in excess to H_2SO_4 at room temp.	Room	2	1.057	0.0	−0.85
3*b*	0.5 *N* $BaCl_2$ added in excess to H_2SO_4 at room temp.	Room	2	1.057	0.05	−0.85
3*c*	0.5 *N* $BaCl_2$ added in excess to H_2SO_4 at 100° C.	100	2	1.062	0.0	−0.4
4	H_2SO_4 added to excess $BaCl_2$ at 100° C.	Room	2	1.062	0.1	−0.4
5	$Ba(NO_3)_2$ added to H_2SO_4 at 100° C.	Room	2	1.062	0.0	−0.4

Explanatory Remarks

Experiment 1. The end point obtained in the cold was not permanent. Therefore, the liquid was heated to boiling and barium hydroxide added until the mixture was slightly alkaline; the boiling was continued for 5 minutes and the titration then finished at room temperature.

Experiment 2*a*. Barium hydroxide was added rapidly to the hot sulfuric acid solution. When the end point had been reached (first tinge of pink) the mixture was boiled for 5 minutes; the pink color of phenolphthalein faded only slightly during the boiling. The titration was finished at room temperature.

Experiment 2*b*. In this case barium hydroxide was added very slowly to the hot sulfuric acid. End point obtained as in Experiment 2*a*.

Experiment 3*a*. Twenty per cent excess neutral 0.5 *N* barium chloride solution was added drop by drop to the sulfuric acid, and the titration made immediately after the precipitation; after the first color change the mixture was boiled for 5 minutes and the titration finished at room temperature.

Experiment 3*b*. After the precipitation of barium sulfate with barium chloride, the liquid was heated to boiling and kept at 100° C. for an hour, and titrated after standing overnight; the titration was made as in Experiment 3*a*.

Experiment 3*c*. Hot barium chloride was added drop by drop to hot sulfuric acid. Titration with barium hydroxide was made in hot solution; near the end point the liquid was boiled for a few minutes. The final end point was obtained at room temperature. If the precipitate was allowed to stand an hour at 100° C. and then titrated in the cold after standing overnight, practically the same results were obtained.

Experiment 4. Titration was made in hot solution; the final end point was obtained after cooling.

Experiment 5. The mixture was titrated after cooling to room temperature, the final end point obtained after boiling the liquid and cooling.

Titration of Barium Hydroxide with Sulfuric Acid

The titration of barium hydroxide with sulfuric acid is given in Table III.

Table III—Titration of Barium Hydroxide with Sulfuric Acid

Calculated normality ratio $H_2SO_4 : Ba(OH)_2$, 1.066

Experiment	Addition	Temp.	No. of Titrations	Normality Ratio	Av. Deviation from Mean	Av. Deviation from True Ratio
		° *C.*			%	%
1*a*	......	Room	3	1.084	0.3	+1.7
1*b*	......	Room	2	1.076	0.15	+0.95
2*a*	......	100	2	1.082	0.1	+1.5
2*b*	......	100	3	1.075	0.1	+0.85
3*a*	$Ba(OH)_2$ added to excess K_2SO_4 at room temperature	Room	2	1.070	0.0	+0.4
3*b*	$Ba(OH)_2$ added to excess K_2SO_4 at room temperature	Room	3	1.064	0.2	−0.2
4*a*	$Ba(OH)_2$ added to excess K_2SO_4 at 100° C.	Room	3	1.083	0.3	+1.6
4*b*	$Ba(OH)_2$ added to excess K_2SO_4 at 100° C.	Room	3	1.066	0.1	0.0
5*a*	Excess K_2SO_4 added to $Ba(OH)_2$ at room temperature	Room	2	1.083	0.1	+1.6
5*b*	Excess K_2SO_4 added to $Ba(OH)_2$ at room temperature	Room	3	1.078	0.3	+1.1

Explanatory Remarks

Experiment 1*a*. The average normality ratio was obtained by taking the first color change in the cold as the end point. When the mixture was boiled the liquid became alkaline owing to slow liberation of co-precipitated barium hydroxide. Thus, in a particular titration the ratio found by taking the end point as the first disappearance of the pink color of phenolphthalein at room temperature was 1.087; after boiling 5 minutes, cooling, and adding acid to restore neutrality, the ratio became 1.085, and after another 5-minute period of boiling, 1.083, etc.

Experiment 1*b*. When the end point had been reached in the cold, about 1 gram of the standard sulfuric acid was added in excess and the mixture boiled for 10 minutes, then cooled, and the acid back-titrated with barium hydroxide.

Experiment 2*a*. After the color change in hot solution, the liquid was kept at the boiling point for 10 minutes, then cooled, and the titration finished at room temperature. The amount of barium hydroxide liberated by boiling for 10 minutes corresponded to about one drop of 0.2 *N* sulfuric acid.

Experiment 2*b*. After the color change at 100° C., about 1 gram of sulfuric acid was added in excess and the mixture boiled for 10 minutes; after cooling to room temperature the titration was finished with barium hydroxide.

Experiment 3*a*. The barium hydroxide was added drop by drop to 50 cc. of 0.5 *N* potassium sulfate solution and the mixture then titrated with sulfuric acid. Since the end point obtained in the cold was not permanent, the mixture was kept at 100° C. for 5 minutes, then cooled, and the titration finished at room temperature with sulfuric acid. The ratio thus obtained is given in Table III. After boiling the neutralized mixture for nearly an hour, the ratio 1.066 was obtained—nearly the theoretical value.

Experiment 3*b*. Barium hydroxide was added at room temperature to potassium sulfate as in Experiment 3*a*, but when a temporary end point had been obtained in the cold by titration with sulfuric acid, 1 gram of acid was added in excess and the liquid boiled for 10 minutes; the titration was finished as always at room temperature.

Experiment 4*a*. Fifty cc. of 0.2 N potassium sulfate were used. The barium hydroxide was added slowly and with constant shaking of the hot potassium sulfate solution. After cooling, the first end point obtained with sulfuric acid gave the ratio recorded in Table III. On boiling the mixture, barium hydroxide was slowly liberated. Thus, by boiling for 45 minutes and adding sulfuric acid whenever the liquid became alkaline, the value of the ratio finally obtained was 1.071.

Experiment 4*b*. As in Experiment 4*a*, but when the end point had been reached at room temperature, a gram of 0.2 N sulfuric acid was added in excess and the mixture boiled 10 minutes; the titration was then finished in the cold with barium hydroxide.

Experiment 5*a*. Fifty cc. of 0.5 N potassium sulfate at room temperature were slowly added to the cold barium hydroxide solution and the mixture titrated cold with sulfuric acid.

Experiment 5*b*. Same conditions as Experiment 5*a*, but when the end point was reached in the cold a slight excess of 0.2 N sulfuric acid was added and the mixture boiled for 10 minutes; the titration was finished, after cooling, with barium hydroxide.

Discussion of Results

TITRATION OF SULFURIC ACID WITH BARIUM HYDROXIDE—Under no conditions are highly accurate results obtained; moreover, they are not so well reproducible as in ordinary acidimetric titrations where no precipitate is formed. Therefore, the titration is not suitable for work of precision. The best results are obtained if the acid is titrated at room temperature with barium hydroxide using phenolphthalein, phenol red, or methyl red as an indicator. After the first color change, the mixture is heated to boiling, more base is added until the color persists for 15 to 30 seconds. The boiling is continued for 5 minutes and the titration finished after cooling to room temperature (protection with soda-lime tube). It seems that a trace of barium hydroxide can be carried down by the barium sulfate (see Experiment 1, Table II); accuracy 0.1 to 0.2 per cent. For most practical work, these results are satisfactory.

If a hot solution of sulfuric acid is titrated, the deviation is much larger, amounting to about 0.6 per cent (Experiments 2*a* and 2*b*, Table II). Unexpectedly it is found that this error is due to co-precipitation of barium hydroxide with the barium sulfate although an acid solution is titrated. If the base is run in with great speed, a local excess is formed; better results may be expected if the barium hydroxide is added drop by drop with continuous shaking of the flask. That this is really the case is shown by Experiment 2*b*, though the deviation is still 0.4 per cent.

If the sulfuric acid is precipitated at room temperature with an excess of barium chloride, a co-precipitation of sulfuric acid takes place. The error is about 0.9 per cent (Experiment 3*a*). It was expected that heating the mixture after precipitation at room temperature might decrease the deviation as a result of growth of the small particles of the barium sulfate to larger crystals. However, as shown by Experiment 3*c*, Table II, heating had no effect.

If a hot solution of sulfuric acid is precipitated with a warm solution of barium chloride, the error due to occlusion is smaller though it still amounts to about 0.4 per cent.

It seems that two factors are responsible for the deviating results: adsorption and occlusion. Occluded sulfuric acid or barium hydroxide cannot be removed by boiling or by treatment with excess of base or of acid. The adsorbed acid can be removed fairly rapidly by boiling the mixture near the equivalence point for 5 minutes. By experiment, it could be shown that freshly precipitated barium sulfate adsorbs sulfuric acid. An excess of a hot solution of barium chloride was added to a warm solution of sulfuric acid. After 5 minutes' standing the mixture was filtered, and the precipitate washed with water until the reaction of the filtrate was neutral. The total filtrate was titrated with barium hydroxide. The ratio found was 1.037, thus indicating an adsorption of about 3 per cent sulfuric acid by the precipitate.

TITRATION OF BARIUM HYDROXIDE WITH SULFURIC ACID—In the titration of a cold or hot solution of barium hydroxide with sulfuric acid a strong co-precipitation of the base by the precipitate occurs, the error amounting to about 2 per cent (Experiment 1*a*, Table III). This adsorbed base is only slowly removed by boiling the mixture near the equivalence point. It is better to add a small excess of sulfuric acid, boil for 5 minutes, and titrate back. The error then is still about 0.8 to 1 per cent and is caused by an occlusion of barium hydroxide by the precipitate (Experiment 1*b*).

From the Experiments 3*a* to 4*b* (Table III) it may be inferred that if barium hydroxide is added to an excess of neutral potassium sulfate solution, an adsorption of the base by the precipitate takes place. This adsorbed base can be removed by boiling the mixture near the equivalence point for a few minutes with a small excess of sulfuric acid. After back titration at room temperature the error is 0.0 to 0.2 per cent. By boiling the mixture near the equivalence point without adding an excess of acid, the adsorbed base is very slowly removed.

If the potassium sulfate solution is added to the barium hydroxide, an adsorption and occlusion of the base takes place. The error by occlusion is about 1 per cent.

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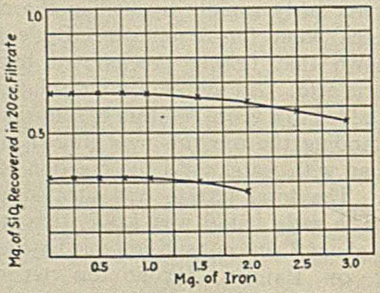
NOTES AND CORRESPONDENCE

Colorimetric Determination of Silica

Editor of Industrial and Engineering Chemistry:

In a recent issue [IND. ENG. CHEM., Anal. Ed., 2, 276 (1930)] Thayer has made an exhaustive criticism of the well-known Diénert and Wandenbulcke [*Compt. rend.*, 176, 1478 (1923)] method for the estimation of silica in natural waters. He has shown that in the presence of phosphate and iron the yellow color, which develops on adding ammonium molybdate and sulfuric acid to a dilute solution of silica, is considerably enhanced. In the case of sea water and many other natural waters, where phosphorus and iron are present only in minute amounts, the method of Diénert and Wandenbulcke can be used without modification. But where the waters contain considerable amounts of these elements, it is necessary to precipitate the phosphate and the iron and determine the silica in the filtrate. Thayer has shown that phosphate can be precipitated satisfactorily as calcium triphosphate at a weakly alkaline reaction but that in the presence of iron, in amounts of 25 mg. and more per liter, part of the silica is precipitated along with the phosphate and iron (Table IX). He has found, however, that iron can be precipitated in acetic acid solution as ferric phosphate without loss of silica, and the excess of phosphate then precipitated as calcium triphosphate.

In Thayer's paper there occurs the paragraph (p. 281): "After the writer had developed this method, his attention was called to the work of King, who determined silica in animal tissue by the Diénert and Wandenbulcke method after removing the phosphates with magnesia mixture. When no iron is present King's method should give quite satisfactory results, for there is little choice between the use of magnesium and calcium chloride. King states that the iron is precipitated along with the phosphate. He does not cite data to show that there is no loss of silica from his solutions at the same time. The experiments cited above, however, make it seem highly probable that part of the silica is precipitated as ferric silicate during the precipitation of phosphate in King's procedure."



Effect of Iron on Recovery of Silica in Magnesia Precipitation of Phosphate from Silicate Solution

Thayer ignores the fact that I cited four analyses of lung and liver tissue where the results of the colorimetric estimations agreed very closely with those obtained by the ordinary macro-gravimetric method. It would seem that this close agreement of the results of the colorimetric method with those of the established method of gravimetric analysis of silica, is adequate experimental proof that there was no loss of silica during the precipitation of the phosphate and the iron which, of course, is invariably present in small amounts in animal tissue.

According to the reliable figures of Forbes and Swift [*J. Biol. Chem.*, **67**, 517 (1926)], who made a great number of careful analyses of a large variety of animal tissues, the largest amount of iron found in any tissue was 0.0188 per cent in the case of beef kidney with a moisture content of 78.67 per cent. This is equivalent to 0.088 per cent iron on the dry weight, or 0.88 mg. iron per gram of dry tissue.

King's method for the estimation of silica [*J. Biol. Chem.*, **80**, 25 (1928)] called for the use of 0.2 to 1.0 gram of dry tissue (0.25 gram was usually used), which was ashed, and the solution of the ash made to 30 cc. before adding the magnesia mixture. If, therefore, iron in quantities up to 0.88 mg. in 30 cc. of a silica phosphate solution is precipitated along with the phosphate on addition of magnesia mixture without loss of silica, it would seem highly improbable "that part of the silica is precipitated as ferric silicate during the precipitation of phosphate in King's procedure."

The following experiment shows that silica is not precipitated under these conditions unless more than 1 mg. of iron is present in the 30 cc. of solution. Since there is only a fraction of this amount of iron present in the amount of tissue used, there would seem to be no danger of loss of silica under the conditions specified in the method.

(1) Test solutions were prepared containing 1 mg. of silicon dioxide, 2 mg. of phosphorus (as $NH_4H_2PO_4$), and variable amounts of iron from 0 to 2 mg. (as $FeCl_3$), in 26 cc. To each were added 2 cc. of magnesia mixture and 2 cc. of 2.5 *N* ammonium hydroxide. After the mixtures had stood 5 minutes they were centrifuged clear and 20-cc. portions of each taken for the determination.

(2) Test solutions, consisting of 0.5 mg. of silicon dioxide, 1 mg. of phosphorus, different amounts of iron, and 1 cc. each of magnesia mixture and 2.5 *N* ammonium hydroxide, were made to 30 cc., filtered after 5 minutes, and colorimetric determinations made on 20 cc. of the filtrate.

The results obtained are illustrated in the accompanying graph. The presence of iron in quantities up to 1 mg. did not interfere with the recovery of the silica. Above that amount there was a partial precipitation of the silica which increased with larger quantities of iron.

EARL J. KING

DEPARTMENT OF MEDICAL RESEARCH
UNIVERSITY OF TORONTO
TORONTO, CANADA
September 22, 1930

....

Editor of Industrial and Engineering Chemistry:

I regret that Mr. King apparently thinks I have implied a doubt as to the validity of his experimental data concerning the determination of silica in animal tissues, for it was hardly my intention so to do. It is obvious, I believe, from the comparison of colorimetric and gravimetric analyses cited by King in his original paper [*J. Biol. Chem.*, **80**, 25 (1928)], that his method of precipitating phosphates with magnesia mixture makes possible the satisfactory determination of silica in animal tissues, a point to which I will return later.

Neither was it my intention to reject the method as entirely unworthy of further attempts to develop it. Indeed, as compared with my calcium chloride solution, magnesia mixture has the advantage of being a standard reagent; and King's method, if it will work under all conditions, has the advantage of carrying out the precipitation of both iron and phosphates in one operation. It is with reference to the last point that I did, and still do, consider the method inadequately tested, as I shall try to point out.

Let us examine the results of the two experiments King cites in his letter with respect to the most extreme conditions which they represent. Experiment 2 shows that 1 (0.67?) mg. of iron in the presence of 0.67 mg. of phosphorus did not interfere with the determination of silica up to 0.33 mg. in 20 cc. of solution. Assuming that the iron will be precipitated as ferric phosphate or ferric silicate, there were present in the experimental solutions five equivalent weights of iron, six of phosphorus, and one of silica. In other words there was a slight excess of phosphorus over iron, and six times as much phosphate as silicate. The same ratio of constituents was used in both experiments; therefore the experiments give no information regarding the precipitation of silica as iron silicate when the proportion of phosphorus to silica is smaller. They do show that when the amount of iron is increased, there is a loss of silica. I believe that the worker who wishes to use the method would do well to assure himself more fully in regard to the influence of the ratio of phosphorus to silica and iron on the determination of silica.

It may safely be assumed, however, that there will be an excess of phosphorus over iron when animal tissue is the object of study, for the human body (if it be considered a fair example of mammalian bodies) contains, according to Lotka ["Elements of Physical Biology," p. 197], an average of 1.14 per cent phosphorus as against 0.01 per cent iron. Although the ratio is reduced to 0.4 per cent phosphorus [Forbes and Keith, Ohio Agr. Exptl. Sta., *Tech. Bull.* 5, 141 (1914)] to nearly 0.02 per cent iron [Forbes and Swift, *J. Biol. Chem.*, **67**, 517 (1926)] in the case of beef kidney, there is still about 35 times as much phosphorus as iron.

LEWIS A. THAYER

DEPARTMENT OF BOTANY
STANFORD UNIVERSITY, CALIF.
October 22, 1930

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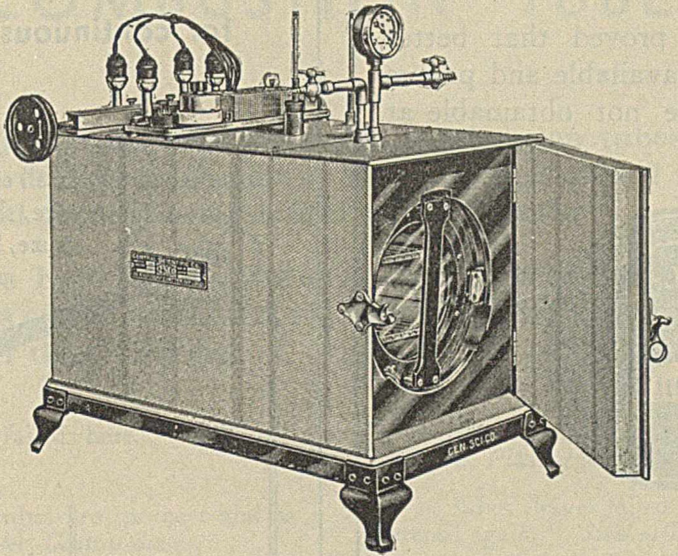

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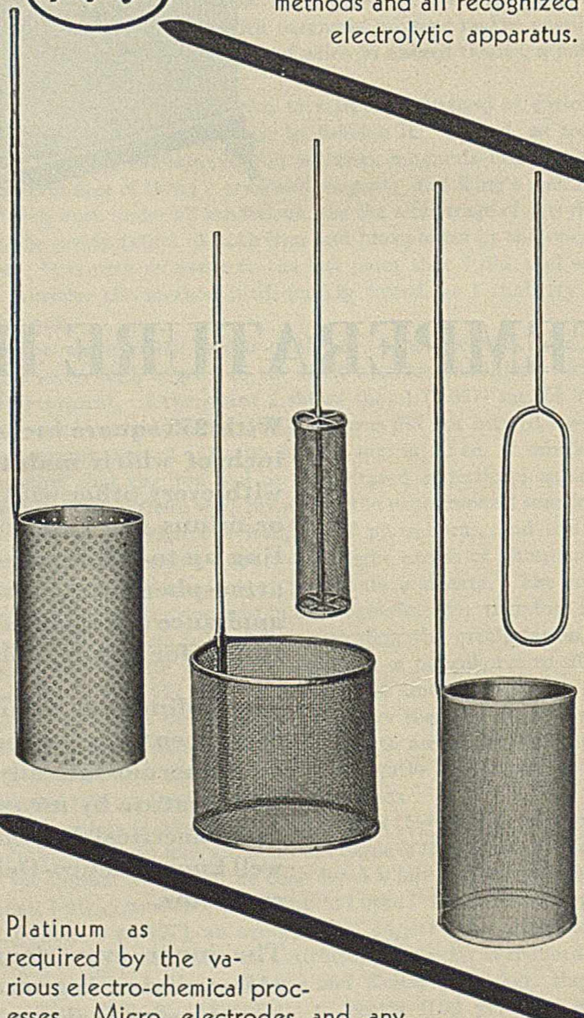

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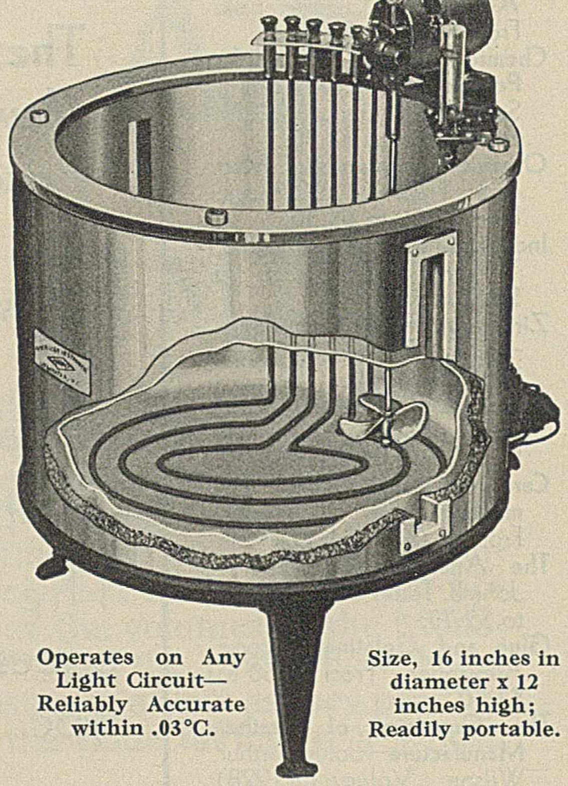

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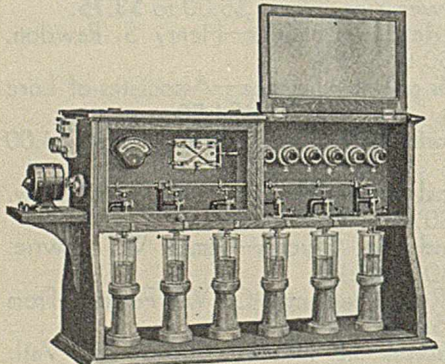

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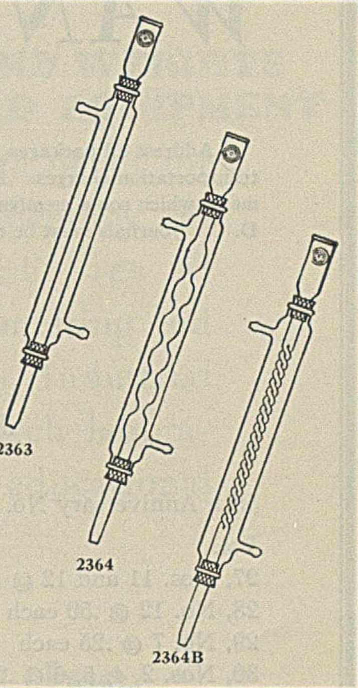
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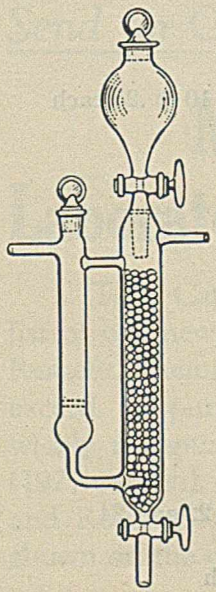

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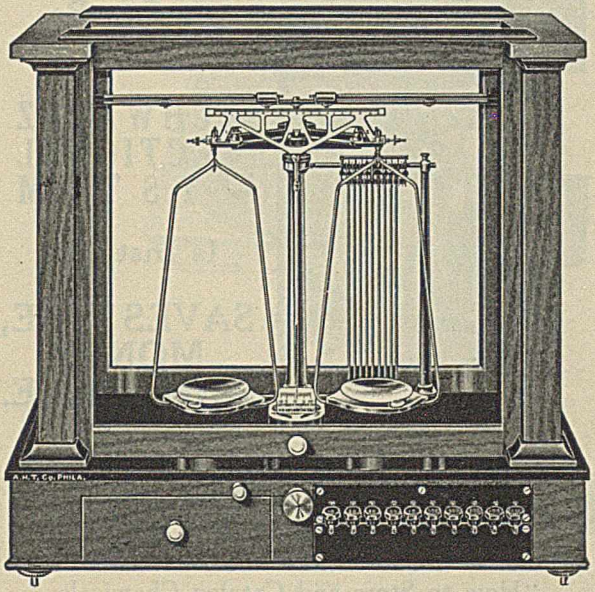

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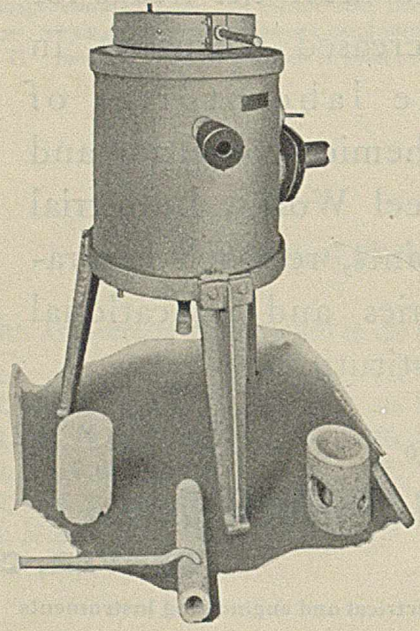

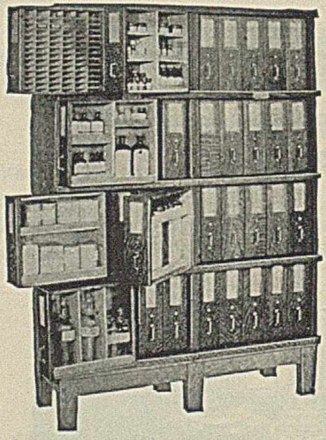

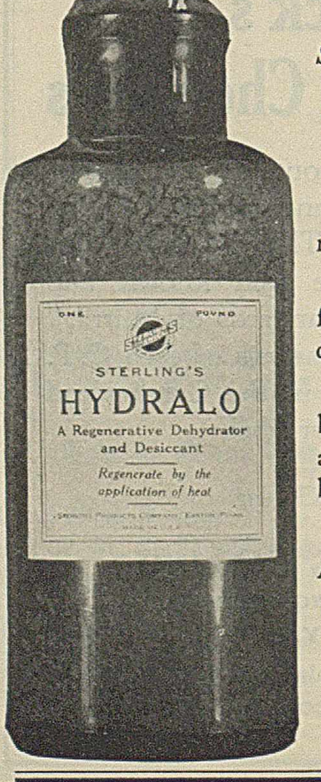
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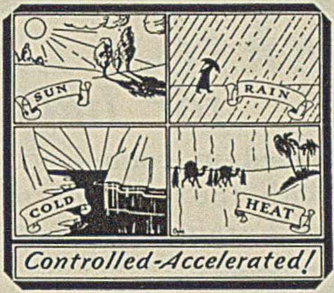
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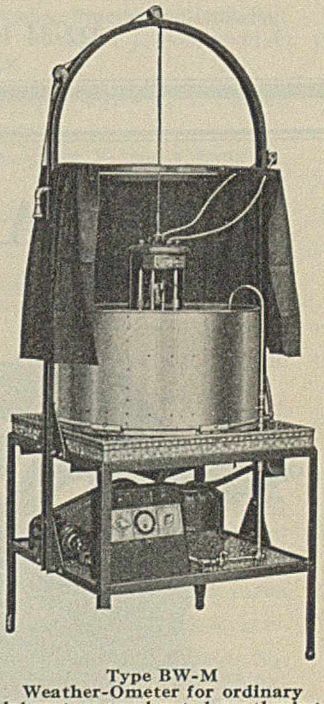

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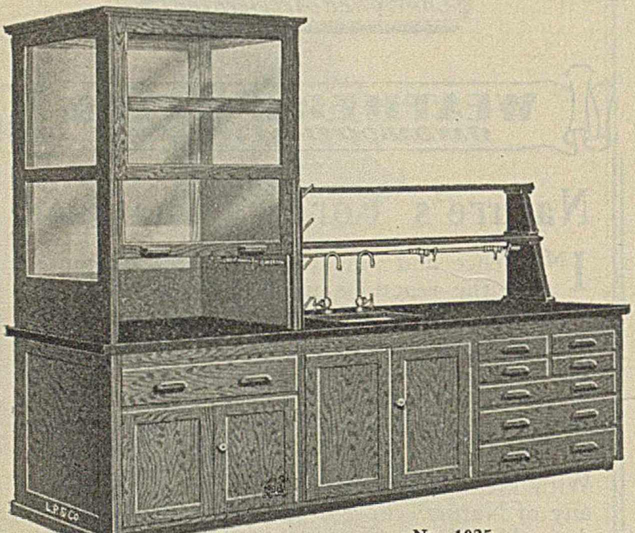

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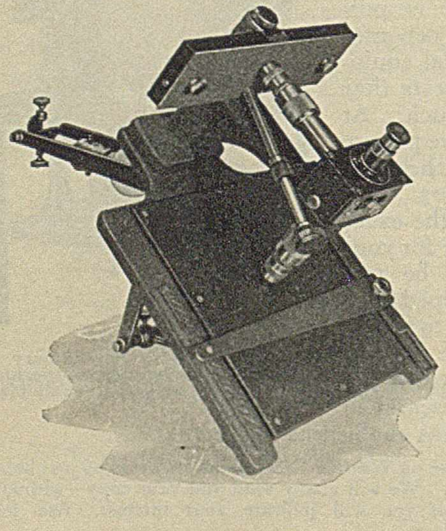

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