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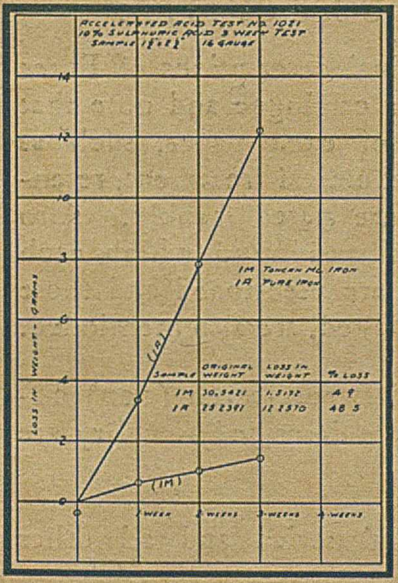

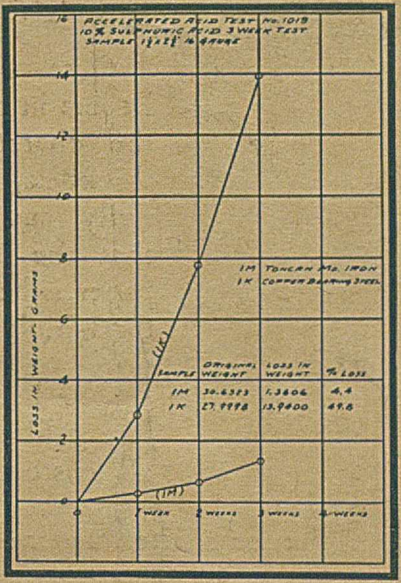

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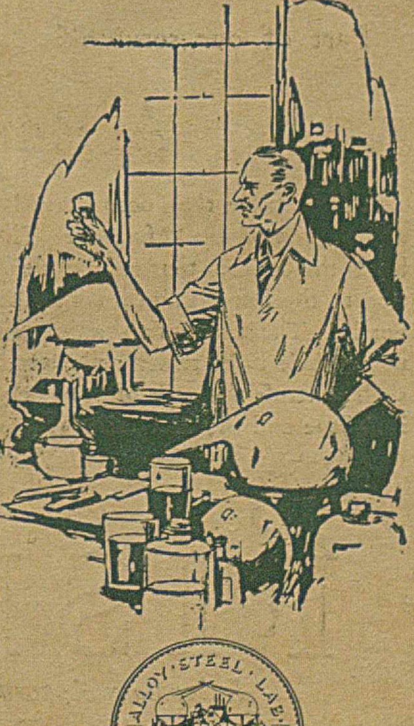

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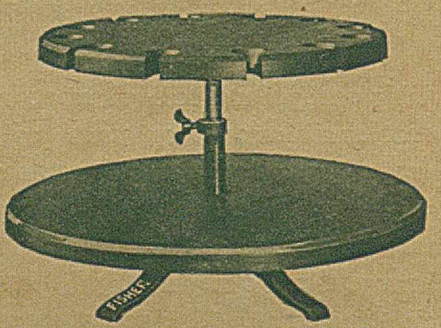

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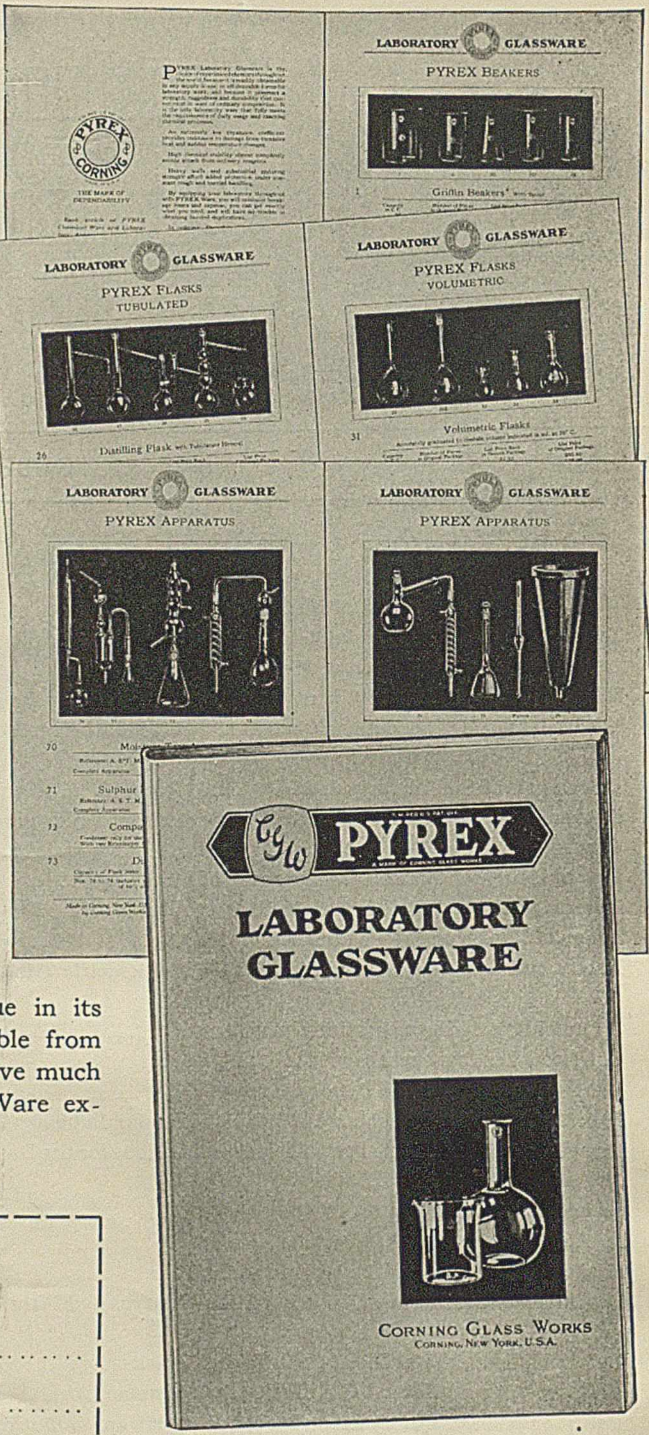
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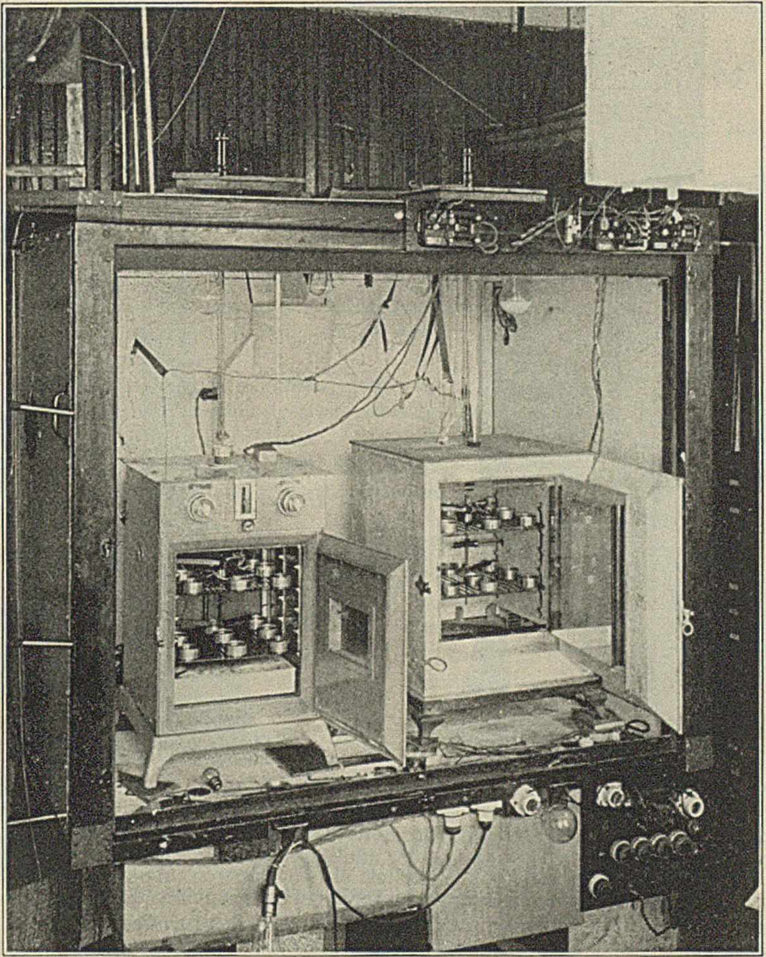

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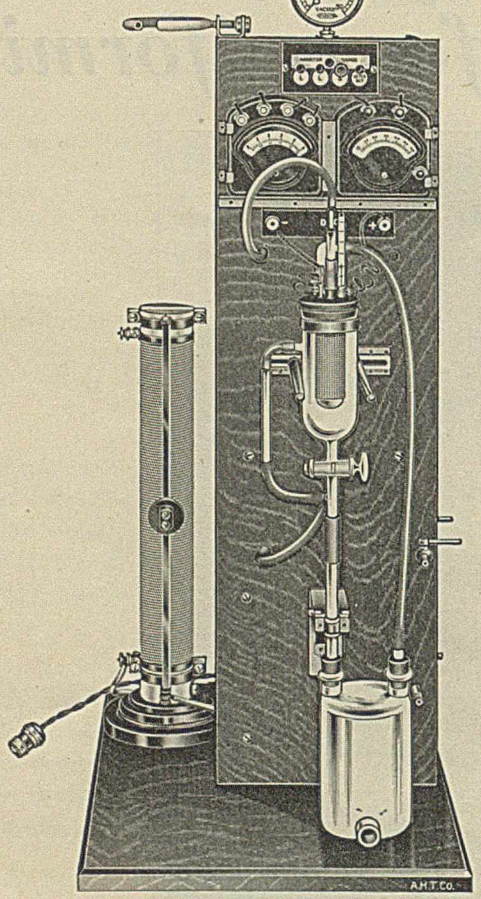

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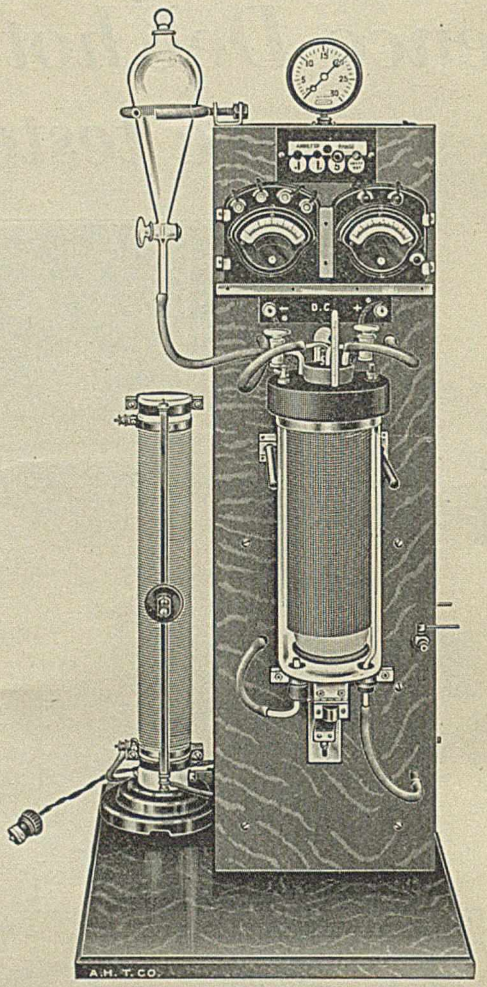

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Volumetric Determination of Manganese as Dioxide[1]

With Special Reference to Application of Potassium Bromate as Oxidizing Agent

I. M. Kolthoff and Ernest B. Sandell

University of Minnesota, School of Chemistry, Minneapolis, Minn.

The persulfate method for the oxidation of manganese to manganese dioxide has been studied and the factors which may affect the results have been investigated.

Instead of persulfate, the use of potassium bromate is recommended as an oxidizing agent. Reproducible results are obtained. The bromate method is suitable for manganese determinations in ores and can be applied to the determination of manganese in steel.

VARIOUS methods for the precipitation of manganese as dioxide and the volumetric determination of this compound have been proposed in the literature. From the practical point of view the most important procedures are those in which the precipitation of the dioxide takes place in acid medium; therefore, the writers have studied these more carefully. Oxidation in neutral or alkaline medium by means of bromine, hypobromite, chlorine, hypochlorite, or ferricyanide is unsatisfactory, in general, when iron is present, and even in the absence of iron results tend to be variable (*8*).

After a preliminary study of the methods in neutral or alkaline solution, the oxidation in acid medium was studied more in detail. In acid solution manganese is oxidized to the dioxide by boiling with ammonium or potassium persulfate. Von Knorre (*9*) has based a determination on this reaction. The precipitated manganese dioxide is collected by filtration, washed and dissolved in ferrous sulfate or hydrogen peroxide, and the excess peroxide is titrated with permanganate. The method does not give theoretical values; an empirical factor must be applied. The details of this method will be discussed in the experimental part of this paper. The method has been applied by Lüdert and others (*4*, *6*, *7*).

A method that has enjoyed considerably greater popularity than that of von Knorre is the familiar procedure based on the precipitation of manganese dioxide by long boiling with potassium chlorate in strong nitric acid solution. Beilstein and Jawein (*1*) first made use of this method of precipitation for a gravimetric determination of the element, Hampe (*5*) and others based a volumetric estimation on the same reaction. Hampe found that potassium bromate could be used in place of the chlorate but preferred the chlorate. As we shall see later, potassium bromate furnishes an excellent reagent for the oxidation of manganese to dioxide even in weakly acid medium.

Persulfate Method

The manganous salt used in the determinations to be described was manganous sulfate which had been purified by two precipitations with alcohol. It was tested for the presence of foreign cations and anions, and these were found to be absent. The solution was accurately standardized by weighing the manganese as anhydrous sulfate according to Blum (*2*). The average of several sulfur determinations (precipitation as barium sulfate) gave a result 0.2 per cent lower than the accepted value based on the weighing of anhydrous manganous sulfate. The precipitations of manganese dioxide were generally carried out in a volume of 50 cc. in the presence of sulfuric acid. From 3 to 5 grams of pure potassium persulfate were added to the solution and, after boiling for a sufficiently long time to effect complete precipitation, the manganese dioxide was filtered off and washed with hot water to remove all oxidizing agent. The manganese dioxide was determined iodometrically. If the solution from which manganese was precipitated contained iron, potassium fluoride was added before titrating to prevent the liberation of iodine by ferric iron, which is always adsorbed in small amounts by manganese dioxide. Obviously, the dioxide could have been dissolved in ferrous sulfate, hydrogen peroxide, or any other suitable reducing agent, and the excess of the latter titrated with potassium permanganate. The iodometric method was chosen merely for its greater rapidity and convenience.

Manganese in the absence of iron begins to precipitate before the boiling point is reached. The dioxide first separating is brown, but becomes nearly black after boiling for a few minutes, when precipitation is complete. During the oxidation a trace of permanganate is always formed. The filtrates from the manganese dioxide precipitations made either in the absence or presence of zinc (see Tables I and II) were usually found to contain manganese equivalent to 0.01–0.03 cc. of 0.1 N permanganate. In filtering through paper, permanganate is partially or completely reduced and the figures given are the amounts of permanganate formed by re-oxidizing with potassium persulfate in the presence of silver nitrate. When iron accompanies manganese, the formation of permanganate is much increased (approximately, tenfold) and varies according to the amounts of iron and manganese present. A high concentration of ferric iron and a low concentration of manganous salt favor the formation

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[1] Received May 18, 1929.

of permanganate. Varying the acidity from 0.4 *N* to 2 *N* did not seem to affect the reaction.

Table I—Oxidation of Manganese with Potassium Persulfate in the Absence of Zinc

No.	Mn Taken	Conditions	Mn Found	Error	Error
	Gram		*Gram*	*Gram*	*Per cent*
1	0.00671	10 cc. 4 *N* H_2SO_4; vol. = 50 cc.; boiled 5 min.	0.00638	−0.0033	−4.9
2	0.00671	10 cc. 4 *N* H_2SO_4; vol. = 50 cc.; boiled 5 min.	0.00652	−0.0019	−2.8
3	0.00671	10 cc. 4 *N* H_2SO_4; vol. = 50 cc.; boiled 5 min.	0.00628	−0.0043	−6.4
4	0.0266	10 cc. 4 *N* H_2SO_4; vol. = 50 cc.; boiled 5 min.	0.0256	−0.0010	−3.8
5	0.0671	Neutral soln.	0.0652	−0.0019	−2.8
6	0.0671	5 cc. 4 *N* H_2SO_4; boiled 5 min.	0.0646	−0.0025	−3.7
7	0.0671	5 cc. 4 *N* H_2SO_4; boiled 5 min.	0.0645	−0.0026	−3.9
8	0.0671	5 cc. 4 *N* H_2SO_4; boiled 5 min.	0.0645	−0.0026	−3.9
9	0.0671	5 cc. 4 *N* H_2SO_4; boiled 5 min.	0.0646	−0.0025	−3.7
10	0.0671	5 cc. 4 *N* H_2SO_4; boiled 5 min.	0.0649	−0.0022	−3.2
11	0.0671	10 cc. 4 *N* H_2SO_4	0.0645	−0.0026	−3.9

Table II—Oxidation of Manganese with Potassium Persulfate in Presence of Zinc Sulfate

No.	Mn Taken	Conditions	Mn Found	Error	Error
	Gram		*Gram*	*Gram*	*Per cent*
1	0.00671	10 cc. 4 *N* H_2SO_4; 3 g. $ZnSO_4.7H_2O$; boiled 5 min.	0.00646	−0.00025	−3.7
2	0.00671	10 cc. 4 *N* H_2SO_4; 3 g. $ZnSO_4.7H_2O$; boiled 5 min.	0.00635	−0.00036	−5.4
3	0.0266	10 cc. 4 *N* H_2SO_4; 3 g. $ZnSO_4.7H_2O$; boiled 5 min.	0.0258	−0.0008	−3.0
4	0.0671	10 cc. 4 *N* H_2SO_4; 3 g. $ZnSO_4.7H_2O$; boiled 5 min.	0.0651	−0.0020	−3.0
5	0.0671	Neutral soln.; boiled 5 min.	0.0655	−0.0016	−2.4
6	0.0671	Neutral soln.; boiled 5 min.	0.0656	−0.0015	−2.2
7	0.0671	Neutral soln.; boiled 5 min.	0.0654	−0.0017	−2.5
8	0.1330	10 cc. 4 *N* H_2SO_4	0.1315	−0.0015	−1.1

The presence of iron hinders the precipitation of manganese dioxide, but only seriously so when present in a ratio larger than 100 Fe to 1 Mn. When this ratio is not larger than 10 : 1, precipitation is complete within 10 minutes; when it is greater, the time of boiling must be correspondingly increased, and successive portions of persulfate must be added as the reagent decomposes rapidly in hot acid solution. It may be mentioned that the use of ammonium persulfate instead of potassium persulfate is somewhat dangerous, since after all the persulfate has decomposed the ammonium ions left in solution may reduce the manganese dioxide.

Discussion of Results—If the precipitation of manganese is made in the absence of zinc salts (Table I), there is a deviation from the theoretical of about −3.7 per cent for quantities of manganese ranging from 25 to 70 mg.

When a sufficient quantity of zinc ions (from 3 to 5 grams hydrated zinc sulfate) is present (Table II), results are higher but still are about 3 per cent below the theoretical. The influence of zinc is greater than von Knorre believed it to be. According to his statement, zinc increases the quantity of manganese found to such a slight degree as to be negligible.

In the presence of iron the values for manganese are about 2.4 per cent low, but are constant over a wide range of iron concentration (0.025 gram to 3.0 gram in 50 cc.). The results obtained by von Knorre are a little less than 1 per cent below the theoretical values. He states that in most cases the same empirical factor can be used in the presence and in the absence of iron. This is not true. From the results of sixteen determinations (Table III) the empirical factor is 1.024 times theoretical when iron is present with the manganese. The empirical factor (iron being present) according to work done in the Bureau of Standards (*3*, see also *1*) is 1.028 times the theoretical. Varying the acidity from 0.4 *N* to 2 *N* had no appreciable effect on the results.

Table III—Oxidation of Manganese with Potassium Persulfate in Presence of Iron as Nitrate or Sulfate

No.	Mn Taken	Fe Present	Conditions	Mn Found	Error	Error
	Gram	*Grams*		*Gram*	*Gram*	*Per cent*
1	0.00671	0.4	10 cc. 4 *N* H_2SO_4 in 50 cc. vol.; boiled 15 min.	0.00654	0.00017	−2.5
2	0.0266	1.4	10 cc. 4 *N* H_2SO_4 in 50 cc. vol.; boiled 15 min.	0.0258	−0.0008	−3.0
3	0.0671	0.025	10 cc. 4 *N* H_2SO_4 in 50 cc. vol.; boiled 15 min.	0.0655	−0.0016	−2.4
4	0.0671	0.12	10 cc. 4 *N* H_2SO_4 in 50 cc. vol.; boiled 15 min.	0.0657	−0.0014	−2.1
5	0.0671	0.12	10 cc. 4 *N* H_2SO_4 in 50 cc. vol.; boiled 15 min.	0.0352	−0.0019	−2.8
6	0.0671	0.12	10 cc. 4 *N* H_2SO_4 in 50 cc. vol.; boiled 15 min.	0.0654	−0.0017	−2.5
7	0.0671	0.12	10 cc. 4 *N* H_2SO_4 in 50 cc. vol.; boiled 15 min.	0.0654	−0.0017	−2.5
8	0.0671	0.4	10 cc. 4 *N* H_2SO_4 in 50 cc. vol.; boiled 15 min.	0.0657	−0.0014	−2.1
9	0.0671	0.6	10 cc. 4 *N* H_2SO_4 in 50 cc. vol.; boiled 15 min.	0.0655	−0.0016	−2.4
10	0.0671	1.2	10 cc. *N* H_2SO_4 in 50 cc. vol; boiled 15 min.	0.0658	−0.0013	−2.0
11	0.0671	2.4	10 cc. 4 *N* H_2SO_4 in 50 cc. vol.; boiled 15 min.	0.0650	−0.0021	−3.1
12	0.0671	2.4	10 cc. 4 *N* H_2SO_4 in 50 cc. vol.; boiled 15 min.	0.0659	−0.0012	−1.8
13	0.0671	3.0	10 cc. 4 *N* H_2SO_4 in 50 cc. vol.; boiled 15 min.	0.0656	−0.0015	−2.2
14	0.0671	0.12	5 cc. 4 *N* H_2SO_4	0.0652	−0.0019	−2.8
15	0.0671	0.12	15 cc. 4 *N* H_2SO_4	0.0653	−0.0018	−2.7
16	0.0671	0.12	25 cc. 4 *N* H_2SO_4	0.0654	−0.0017	−2.5

The presence of chromium (which during the precipitation of manganese is oxidized to chromic acid) does not lead to high results (Table IV). Small amounts of tungsten, molybdenum, and phosphoric acid may be present. However, when these occur in large quantities, results are seriously low on account of the incomplete precipitation of manganese, possibly due to the formation of complex trivalent compounds of manganese which are soluble. Cobalt, when it accompanies iron and manganese, does not lead to high results, even when present in large quantities. Von Knorre found the presence of cobalt to be disturbing, presumably on account of the co-precipitation of cobaltic oxide. Cobalt, when present with manganese in the absence of iron, has a tendency to give high results. The presence of chlorides in small amounts is not detrimental to the determination.

Recommended Procedure—To about 50 cc. of solution containing 20 to 100 mg. manganese, and at least an equal quantity of iron to maintain the constancy of the empirical factor, sufficient sulfuric acid is added to make the acid concentration 0.5 to 1 *N*. After adding 3 or 4 grams of potassium persulfate, the solution is heated to boiling and kept at the boiling point for 10 minutes. If much iron is present more persulfate is added and boiling continued for 10 or 15 minutes more. The mixture is then filtered; if the filtrate is turbid at first it is poured back on the filter. The precipitate is washed with hot water until all persulfate has been removed (test filtrate with potassium iodide and sulfuric acid). The filter paper containing the manganese dioxide is transferred to the flask in which the precipitation was made. The titration is made either iodometrically (with addition of fluoride) or with ferrous sulfate and potassium permanganate. Empirical factor = 1.024 times theoretical.

In the absence of iron add zinc sulfate. The empirical factor is then 1.030 times theoretical. It appears that the results in the absence of iron are not so reproducible as when it is present.

Table IV—Oxidation of Manganese with Potassium Persulfate in Presence of Iron and Other Elements

No.	Mn Taken	Fe Present	Addition	Conditions	Mn Found	Error	Error
	Gram	*Grams*			*Gram*	*Gram*	*Per cent*
1	0.0671	0.6	5 g. $ZnSO_4.7H_2O$	10 cc. 4 *N* H_2SO_4; 50 cc. vol.; boiled 5 min.	0.0656	−0.0015	−2.2
2	0.0671	...	1 g. $CuSO_4.5H_2O$	10 cc. 4 *N* H_2SO_4; 50 cc. vol.; boiled 5 min.	0.0658	−0.0013	−2.0
3	0.0671	...	1 g. $CuSO_4$ + 3 g. $ZnSO_4$	10 cc. 4 *N* H_2SO_4; 50 cc. vol.; boiled 4 min.	0.0666	−0.0005	−0.8
4	0.0671	...	0.1 g. chrome alum	10 cc. 4 *N* H_2SO_4; 50 cc. vol.; boiled 5 min.	0.0643	−0.0028	−4.2
5	0.0671	...	0.1 g. chrome alum + 3 g. $ZnSO_4$	10 cc. 4 *N* H_2SO_4; 50 cc. vol.; boiled 5 min.	0.0651	−0.0020	−3.0
6	0.0671	...	0.1 g. chrome alum + 3 g. $ZnSO_4$	10 cc. 4 *N* H_2SO_4; 50 cc. vol.; boiled 5 min.	0.0656	−0.0015	−2.2
7	0.0671	...	0.35 g. $CoSO_4.7H_2O$	10 cc. 4 *N* H_2SO_4; 50 cc. vol.; boiled 5 min.	0.0666	−0.0005	−0.7
8	0.0671	...	1.0 g. $CoSO_4.7H_2O$	10 cc. 4 *N* H_2SO_4; 50 cc. vol.; boiled 5 min.	0.0694	+0.0023	+3.4
9	0.0671	0.6	0.35 g. $CoSO_4.7H_2O$	10 cc. 4 *N* H_2SO_4; 50 cc. vol.; boiled 5 min.	0.0654	−0.0017	−2.5
10	0.0671	1.2	0.7 g. $CoSO_4.7H_2O$	10 cc. 4 *N* H_2SO_4; 50 cc. vol.; boiled 5 min.	0.0652	−0.0019	−2.8
11	0.0671	1.2	1.0 g. $CoSO_4.7H_2O$	10 cc. 4 *N* H_2SO_4; 50 cc. vol.; boiled 5 min.	0.0661	−0.0010	−1.5
12	0.0671	1.2	0.7 g. $CoSO_4.7H_2O$	20 cc. H_2SO_4; 50 cc. vol., boiled 10 min.	0.0659	−0.0012	−1.8
13	0.0671	0.5	1 g. $Ni(NO_3)_2.6H_2O$	10 cc. H_2SO_4; 50 cc. vol., boiled 10 min.	0.0656	−0.0015	−2.2
14	0.0671	0.6	0.18 g. H_3PO_4	5 cc. H_2SO_4; 50 cc. vol., boiled 10 min.	0.0651	−0.0020	−3.0
15	0.0671	0.6	0.02 g. H_3PO_4	10 cc. H_2SO_4; 50 cc. vol., boiled 10 min.	0.0656	−0.0015	−2.3
16	0.0671	0.6	0.02 g. H_3PO_4	10 cc. H_2SO_4; 50 cc. vol., boiled 10 min.	0.0657	−0.0014	−2.1
17	0.0671	0.6	0.01 g. H_3PO_4	10 cc. H_2SO_4; 50 cc. vol., boiled 10 min.	0.0660	−0.0011	−1.6
18	0.0671	0.6	0.01 g. H_3PO_4	10 cc. H_2SO_4; 50 cc. vol., boiled 10 min.	0.0661	−0.0010	−1.5
19	0.0671	0.6	0.05 g. Na_2WO_4	10 cc. H_2SO_4; 50 cc. vol., boiled 10 min.	0.0664	−0.0007	−1.0
20	0.0671	0.6	0.10 g. Na_2WO_4	10 cc. H_2SO_4; 50 cc. vol., boiled 10 min.	0.0655	−0.0016	−2.4
21	0.0671	0.6	0.10 g. Na_2WO_4	10 cc. H_2SO_4; 50 cc. vol., boiled 10 min.	0.0655	−0.0016	−2.4
22	0.0671	0.6	0.05 g. $(NH_4)_2MoO_4$	10 cc. H_2SO_4; 50 cc. vol., boiled 10 min.	0.0659	−0.0012	−1.8
23	0.0671	0.6	0.10 g. $(NH_4)_2MoO_4$	10 cc. H_2SO_4; 50 cc. vol., boiled 10 min.	0.0660	−0.0011	−1.6

Bromate Method

Contrary to the statements of Hampe (*5*), it was found that manganese could be oxidized completely to the dioxide by boiling for a short time with potassium bromate in dilute acid solution. The bromate used in this manner behaves in practically the same way as potassium persulfate in precipitating manganese dioxide, giving a precipitate of the same appearance and filterability. The reaction takes place in accordance with the following equation:

$$5Mn^{++} + 2(BrO_3)^- + 4H_2O \longrightarrow 5MnO_2 + Br_2 + 8H^+$$

As in the persulfate method, traces of permanganate are formed, the amount produced being increased when iron is present. The small error due to the formations of permanganate is obviated by the application of the empirical factor. The use of potassium bromate is preferable to that of potassium persulfate, as it is not easily decomposed by boiling in dilute acid solutions and, therefore, manganese can be precipitated with certainty in the presence of iron. With potassium persulfate the oxidation is effected with greater difficulty on account of the ready decomposability of this reagent, whereas with potassium bromate the results are easily reproducible.

The experimental results given in Tables V to VIII were obtained by titrating the manganese dioxide precipitate (produced by boiling with 1 to 2 grams of potassium bromate for 10 to 20 minutes in solutions usually 0.8 *N* with respect to sulfuric acid) iodometrically, as described under the persulfate procedure.

Table V—Oxidation of Manganese with Potassium Bromate in Absence of Zinc

No.	Mn Taken	Conditions	Mn Found	Error	Error
	Gram		*Gram*	*Gram*	*Per cent*
1	0.00671	10 cc. 4 *N* H_2SO_4; 50 cc. vol.	0.00635	−0.00036	−5.4
2	0.00671	10 cc. 4 *N* H_2SO_4; 50 cc. vol.	0.00638	−0.00033	−5.0
3	0.00671	10 cc. 4 *N* H_2SO_4; 50 cc. vol.	0.00636	−0.00035	−5.2
4	0.0266	10 cc. 4 *N* H_2SO_4; 50 cc. vol.	0.0256	−0.0010	−3.8
5	0.0266	10 cc. 4 *N* H_2SO_4; 50 cc. vol.	0.0257	−0.0009	−3.4
6	0.0671	10 cc. 4 *N* HNO_3; 50 cc. vol.	0.0649	−0.0022	−3.3
7	0.0671	10 cc. 4 *N* HNO_3; 50 cc. vol.	0.0649	−0.0022	−3.3
8	0.0671	10 cc. 4 *N* HNO_3; 50 cc. vol.	0.0651	−0.0020	−3.0
9	0.1330	10 cc. 4 *N* HNO_3; 50 cc. vol.	0.1282	−0.0048	−3.6

DISCUSSION OF RESULTS—The determination of manganese by oxidation with potassium bromate in the absence of zinc (Table V) and iron gives results which are about 3.4 per cent lower than the theoretical values for quantities of manganese from 25 to 130 mg. For small amounts the values obtained are still lower, being 5.2 per cent below the theoretical for 0.005 *N* solutions (= 7 mg. manganese in 50 cc. of solution). When sufficient zinc salt is present with the manganese (Table VI), the results are 2.0 per cent lower than theory demands, and this deviation remains sensibly constant for quantities of manganese ranging from 3 to 130 mg. Quantities of manganese as small as 2 to 3 mg. can be determined with an accuracy of about 1 per cent. Factor = 1.020 × theoretical titer.

Table VI—Oxidation of Manganese with Potassium Bromate in Presence of Zinc

No.	Mn Taken	Conditions	Mn Found	Error	Error	Deviation from Empirical Value
	Gram		*Gram*	*Gram*	*Per cent*	*Per cent*
1	0.00266	1 cc. 4 *N* H_2SO_4; 2 g. $ZnSO_4.7H_2O$; vol. = 10 cc.	0.00265	−0.00001	−0.4	
2	0.00266	1 cc. 4 *N* H_2SO_4; 2 g. $ZnSO_4.7H_2O$; vol. = 10 cc.	0.00264	−0.00002	−0.8	
3	0.00266	1 cc. 4 *N* H_2SO_4; 2 g. $ZnSO_4.7H_2O$; vol. = 10 cc.	0.00261	−0.00005	−2.0	
4	0.00266	1 cc. 4 *N* H_2SO_4; 2 g. $ZnSO_4.7H_2O$; vol. = 10 cc.	0.00265	−0.00001	−0.4	
5	0.00266	1 cc. 4 *N* H_2SO_4; 2 g. $ZnSO_4.7H_2O$; vol. = 10 cc.	0.00262	−0.00004	−1.5	
6	0.00266	5 cc. 4 *N* H_2SO_4; 2 g. $ZnSO_4$; vol. = 50 cc.	0.00260	−0.00006	−2.2	
7	0.00266	5 cc. 4 *N* H_2SO_4; 2 g. $ZnSO_4$; vol. = 50 cc.	0.00262	−0.00004	−1.5	
8	0.00671	10 cc. 4 *N* H_2SO_4; 3 g. $ZnSO_4$; vol. = 50 cc.	0.00648	−0 00023	−3.4	−1.4
9	0.00671	10 cc. 4 *N* H_2SO_4; 3 g. $ZnSO_4$; vol. = 50 cc.	0.00656	−0.00015	−2.2	−0.2
10	0.00671	10 cc. 4 *N* H_2SO_4; 3 g. $ZnSO_4$; vol. = 50 cc.	0.00654	−0.00017	−2.5	−0.5
11	0.0266	10 cc. 4 *N* H_2SO_4; 3 g. $ZnSO_4$; vol. = 50 cc.	0.0263	−0.0003	−1.1	+1.1
12	0.0266	10 cc. 4 *N* H_2SO_4; 3 g. $ZnSO_4$; vol. = 50 cc.	0.0260	−0.0006	−2.3	−0.3
13	0.0671	10 cc. 4 *N* H_2SO_4; 3 g. $ZnSO_4$; vol. = 50 cc.	0.0660	−0.0011	−1.6	+0.6
14	0.0671	10 cc. 4 *N* H_2SO_4; 3 g. $ZnSO_4$; vol. = 50 cc.	0.0657	−0.0014	−2.1	−0.1
15	0.1330	10 cc. 4 *N* H_2SO_4; 3 g. $ZnSO_4$; vol. = 50 cc.	0.1303	−0.0027	−2.0	+0.0
16	0.1330	10 cc. 4 *N* H_2SO_4; 3 g. $ZnSO_4$; vol. = 50 cc.	0.1311	−0.0019	−1.4	+0.6
				Average	−2.0	

In the presence of iron (Table VII) the method gives values for manganese which are 1.0 per cent low. The factor, therefore, is 1.010 × theoretical and this value holds for quantities of manganese from 30 to 150 mg. Varying the ratio of iron to manganese from 1 : 1 to 70 : 1 does not affect the result. When the amount of manganese is greater than that of iron, the results are more than 1 per cent below the theoretical. In these cases in which the ratio of iron to manganese is greater than 100 Fe : 1 Mn, the method becomes inconvenient, since the time of boiling required to precipitate manganese completely is half an hour or more. Increasing the acidity unduly tends to give lower results than indicated by the empirical factor. The average deviation from the empirical mean is 0.2 per cent; deviations of 0.5 per cent from the mean may occur.

Table VII—Oxidation of Manganese with Potassium Bromate in Presence of Iron as Nitrate

No.	Mn Taken	Fe Present	Conditions	Mn Found	Error	Error	Deviation from Empirical Value
	Gram	*Gram*		*Gram*	*Gram*	*Per cent*	*Per cent*
1	0.0298	0.7	10 cc. 4 *N* H_2SO_4; vol. = 50 cc.	0.0294	−0.0004	−1.3	−0.3
2	0.0298	2.1	10 cc. 4 *N* H_2SO_4; vol. = 50 cc.	0.0294	−0.0004	−1.3	−0.3
3	0.0755	0.7	50 cc. H_2SO_4; vol. = 200 cc.	0.0747	−0.0008	−1.1	−0.1
4	0.0755	0.03	10 cc. 4 *N* H_2SO_4; vol. = 50 cc.	0.0739	−0.0016	(−2.1)	−1.1
5	0.0755	0.03	10 cc. 4*N* H_2SO_4; vol. = 50 cc.	0.0745	−0.0010	−1.3	−0.3
6	0.0755	0.06	10 cc. 4 *N* H_2SO_4; vol. = 50 cc.	0.0744	−0.0011	−1.5	−0.5
7	0.0755	0.10	10 cc. 4 *N* H_2SO_4; vol. = 50 cc.	0.0747	−0.0008	−1.1	−0.1
8	0.0755	0.12	10 cc. 4 *N* H_7SO_4; vol. = 50 cc.	0.0745	−0.0010	−1.3	−0.3
9	0.0755	0.12	10 cc. 4 *N* H_2SO_4; vol. = 50 cc.	0.0748	−0.0007	−0.9	+0.1
10	0.0755	0.4	10 cc. 4 *N* H_2SO_4; vol. = 50 cc.	0.0746	−0.0009	−1.2	−0.2
11	0.0755	0.4	10 cc. 4 *N* H_2SO_4; vol. = 50 cc.	0.0749	−0.0006	−0.8	+0.2
12	0.0755	0.4	10 cc. 4 *N* H_2SO_4; vol. = 50 cc.	0.0749	−0.0006	−0.8	+0.2
13	0.0755	0.7	10 cc. 4 *N* H_2SO_4; vol. = 50 cc.	0.0751	−0.0004	−0.5	+0.5
14	0.0755	0.7	10 cc. 4 *N* H_2SO_4; vol. = 50 cc.	0.0746	−0.0009	−1.2	−0.2
15	0.0755	1.1	10 cc. 4 *N* H_2SO_4; vol. = 50 cc.	0.0750	−0.0005	−0.7	+0.3
16	0.0755	1.4	10 cc. 4 *N* H_2SO_4; vol. = 50 cc.	0.0749	−0.0006	−0.8	+0.2
17	0.0755	2.1	10 cc. 4 *N* H_2SO_4; vol. = 50 cc.	0.0747	−0.0008	−1.1	−0.1
18	0.1490	0.7	10 cc. 4 *N* H_2SO_4; vol. = 50 cc.	0.1480	−0.0010	−0.7	+0.3
19	0.1490	0.7	10 cc. 4 *N* H_2SO_4; vol. = 50 cc.	0.1480	−0.0010	−0.7	+0.3
20	0.0755	0.7	25 cc. H_2SO_4 in 50 cc.	0.0743	−0.0012	−1.6	−0.6
					Average	−1.0	

The presence of chromium (Table VIII) does not affect the determination. Molybdates, except in small amounts, give results that are too low, as in the persulfate method. Tungstates also lead to low results, but the influence of tungsten does not appear to be so great as that of molybdenum. Likewise, phosphoric acid interferes when present in considerable quantities; amounts equivalent to 1 cc. 2 *M* phosphoric acid may be present in 50 cc., the usual volume in which the determinations were carried out. Cobalt with iron and manganese does not give appreciably higher results, even when present to the extent of 70 mg. with 75 mg. of manganese. Small amounts of lead, nickel, and bismuth may be present. Chlorides will be oxidized by potassium bromate and will not interfere in the precipitation. Ammonium salts should not be present in any quantity. When vanadium is present, it is adsorbed to some extent by manganese dioxide and will therefore give a temporary end point if the dioxide is determined iodometrically. This may, of course, be prevented by dissolving the manganese dioxide in ferrous sulfate and titrating the excess of the latter with potassium permanganate.

RECOMMENDED PROCEDURE—The solution in which manganese is to be determined may contain from 20 to 150 mg. of the element in a volume of about 50 cc. Sufficient dilute sulfuric or nitric acid is added to make the solution 0.8 to 1 *N* with respect to acid. If iron is not present 3 to 5 grams of crystallized zinc sulfate are added. If only small amounts of iron are present it is best to add pure ferric nitrate or sulfate to make the amount of iron present in solution at least equal to the manganese. In this way the constancy of the empirical factor is assured and no zinc salt has to be added. The iron salt should be tested for the presence of manganese. One or 2 grams of potassium bromate are then added and the solution is heated to boiling. In the absence of iron the precipitation is complete within 5 minutes. If iron is present and its ratio to manganese is less than 10 Fe to 1 Mn, boiling for 10 minutes is sufficient. For more unfavorable ratios boiling should be continued for 15 to 20 minutes. When the amount of iron present is more than a hundred times greater than that of manganese, boiling must be continued for half an hour or more, and then, since the method becomes time-consuming, it is better to use the bismuthate method or the colorimetric procedure of Willard and Greathouse (*10*). If the volume of solution becomes much decreased on account of evaporation, water may be added. Filter the precipitate of manganese dioxide through ordinary filter paper. In some cases, the first portions of the filtrate will come through turbid; if these are refiltered no further trouble from this source will be experienced. Wash the precipitate thoroughly with hot water (6 to 8 portions of about 10 cc. each will usually suffice) to remove all the oxidizing agent, and transfer the filter paper containing the washed precipitate to the flask in which the precipitation was made. The manganese dioxide may be determined either iodometrically or by dissolving in ferrous sulfate or any other suitable reducing agent and titrating the excess of the latter with potassium permanganate. If the former procedure is to be followed add 50 to 75 cc. of water to the flask containing the dioxide, together with 5 cc. of 20 per cent solution of KF.-$2H_2O$, 5 cc. 4 *N* sulfuric acid, and sufficient (1 to 2 grams) potassium iodide. Titrate the liberated iodine with 0.1 *N* sodium thiosulfate. For quantities of manganese less than 20 mg. use 0.02 or 0.01 *N* sodium thiosulfate. Near the end point shake the flask well to make certain that all of the manganese dioxide has reacted and that no iodine remains in the filter paper.

Factors for manganese:
Zinc present and iron absent: 1 cc. 0.1 *N* $Na_2S_2O_3$ = 0.002747 × 1.02 = 0.002801 gram Mn
Iron present: 1 cc. 0.1 *N* $Na_2S_2O_3$ = 0.002747 × 1.010 = 0.002774 gram Mn

Table VIII—Oxidation of Manganese with Potassium Bromate in Presence of Iron and Other Elements

No.	Mn Taken	Fe	Addition	Conditions	Mn Found	Error	Error	Deviation from Empirical Value
	Gram	*Gram*			*Gram*	*Gram*	*Per cent*	*Per cent*
1	0.0755	0.7	0.05 g. Na_2WO_4	10 cc. 4 *N* H_2SO_4; vol. = 50 cc.	0.0746	−0.0009	−1.2	−0.2
2	0.0755	0.7	0.10 g. $(NH_4)_2MoO_4$	10 cc. 4 *N* H_2SO_4; vol. = 50 cc.	0.0739	−0.0016	−2.1	−1.1
3	0.0755	0.7	0.10 g. $(NH_4)_2MoO_4$	20 cc. 4 *N* H_2SO_4; vol. = 100 cc.	0.0741	−0.0014	−1.8	−0.8
4	0.0755	0.7	0.07 g. $(NH_4)_2MoO_4$	10 cc. 4 *N* H_2SO_4; vol. = 50 cc.	0.0741	−0.0014	−1.8	−0.8
5	0.0755	0.7	0.35 g. $CoSO_4.7H_2O$	10 cc. 4 *N* H_2SO_4; vol. = 50 cc.	0.0749	−0.0006	−0.8	+0.2
6	0.0755	0.7	0.35 g. $CoSO_4.7H_2O$	20 cc. 4 *N* H_2SO_4; vol. = 100 cc.	0.0749	−0.0006	−0.8	+0.2
7	0.0755	0.7	0.015 g. Cr^{III}	10 cc. 4 *N* H_2SO_4; vol. = 50 cc.	0.0744	−0.0011	−1.5	−0.5
8	0.0755	0.7	0.18 g. H_3PO_4	10 cc. 4 *N* H_2SO_4; vol. = 50 cc.	0.0747	−0.0008	−1.1	−0.1
9	0.0755	0.7	0.1 g. $Pb(NO_3)_2$; 0.1 g. $Bi(NO_3)_3$; 1.0 g. $Ni(NO_3)_2$	10 cc. 4 *N* H_2SO_4; vol. = 50 cc.	0.0744	−0.0011	−1.5	−0.5
10	0.0755	0.7	1 cc. 12 *N* HCl	10 cc. 4 *N* H_2SO_4; vol. = 50 cc.	0.0745	−0.0010	−1.3	−0.3
11	0.0755	0.7	4 cc. 16 *N* HNO_3	No H_2SO_4	0.0751	−0.0004	−0.5	+0.5

Applications of Bromate Method

The bromate method for manganese is especially applicable to the determination of large quantities of the element, and therefore the procedure described above may be advantageously applied to the analysis of manganese ores.

A sample of standard manganese ore, kindly furnished by the Mines Experiment Station of the University of Minnesota, was analyzed. A suitable amount of the ore (15 grams for an ore containing 10 per cent of manganese, at higher manganese content correspondingly less) was dissolved in hydrochloric acid with the addition of potassium chlorate according to the usual manner of getting manganese ores into solution. Without removing the excess hydrochloric acid, the sample was diluted to 500 cc. and 25-cc. portions were taken for the determination which was carried out as already described (with the addition of 1 gram ferric nitrate for the precipitation of the manganese). The following percentages of manganese were found:

	Per cent
Determination 1	24.24
Determination 2	24.18
Mines Experiment Station value	24.23

As has already been stated, the method is not suitable for small quantities of manganese in the presence of large amounts of iron. Therefore, to determine manganese in steel it is preferable to remove the iron, which can be done conveniently by addition of zinc oxide. The following procedure was adopted: A 2.0- to 2.5-gram sample of the steel was dissolved in nitric acid, and after solution was complete the liquid was transferred to a 250-cc. volumetric flask and diluted with water until the volume was 150–200 cc. An emulsion of pure zinc oxide was then carefully added to precipitate the iron, and the volume was made up to exactly 250 cc. After thorough mixing, the liquid was filtered and 50-cc. portions of the filtrate taken for analysis. These were treated with 5 cc. 4 *N* sulfuric acid and 1 gram potassium bromate and heated to boiling, and boiling was continued for 10 minutes. The precipitated manganese dioxide was determined iodometrically, the titrations being made with 0.01 *N* sodium thiosulfate. Since a trace of manganese is coprecipitated with the ferric hydroxide, the empirical factor was determined by taking 10 to 12 mg. manganese and 2 grams of iron (as manganese-free ferric nitrate) and treating these exactly as described above for steel. It was found that under the conditions described, 1 cc. of 0.01 *N* sodium thiosulfate was equivalent to 0.0002834 gram manganese whereas by direct titration 1 cc. 0.01 *N* thiosulfate is equivalent to 0.0002801 mg. The following results for manganese were obtained with Bureau of Standards steel samples:

No.	Steel	Bureau of Standards *Per cent*		Bromate Method *Per cent*
20a		0.661		0.662
				0.654
				0.662
			Av.	0.659
24	Vanadium	0.669		0.668
				0.668
			Av.	0.668
30a	Chrome vanadium	0.805		0.817
				0.803
				0.809
			Av.	0.810
32a	Chrome nickel	0.244		0.242
				0.244
			Av.	0.243

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Reaction between Lubricating Oils and Phosphorus Pentoxide[1]

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IN THE course of some experimental work on heat transfer being conducted at the North Central Station of the U. S. Bureau of Mines in coöperation with the University of Minnesota, it was found necessary to circulate nitrogen at room temperature continuously through a closed circuit by means of a Crowell's rotary blower in which vanes slide over the machined inner surface of a cylinder. The vanes fit closely into the cylinder, and it is essential that they be well lubricated. In order to eliminate any oxygen which might creep into the system, a by-pass chamber was constructed which contained yellow phosphorus.

Immediately after the use of yellow phosphorus was instituted, the pump caused considerable difficulty by heating up and sticking. It was dismantled and thoroughly cleaned, but it stuck again after about 15 minutes' operation. Upon dismantling again it was found that in this short time a thick gum similar to shellac in consistency and adhesiveness had formed on all friction surfaces. A qualitative test showed that this residue contained considerable phosphorus. It was apparent that the phosphorus pentoxide dust formed by the reaction of the phosphorus with the oxygen in the system had been carried over to the pump and had reacted with the oil to form this very sticky thick gum.

To verify this, qualitative tests were made by shaking up oil with phosphorus pentoxide. Three different standard lubricating oils and kerosene were tried. All gave thick sticky reddish brown gum at temperatures of 30° to 50° C. If water was added to the oil, the gum would dissolve and would not form again, even at 100° C., as long as sufficient water was present to form a separate phase.

The compound formed was probably due to the unsaturates which are present in all oils.

The author found it more convenient to eliminate the phosphorus by using hot copper for de-oxidation; cases might occur where it would not be possible to keep phosphorus pentoxide from coming in contact with lubricated friction surfaces. In such a case it would be quite essential to prevent the formation of the troublesome compound. It might be possible to do this by distilling the lubricating oil from a bath containing phosphorus pentoxide, thus eliminating most of the unsaturates. The experiments described above also indicate that it would be satisfactory to use an oil-water emulsion for lubrication if the mechanical details of the particular piece of equipment would permit.

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[1] Received July 3, 1929. Published by permission of the Director, U. S. Bureau of Mines. (Not subject to copyright.)

Quantitative Determination of Mercaptans in Naphtha[1]

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A method for the estimation of mercaptan based on titration with silver nitrate and ammonium thiocyanate is outlined. Alternatively, the mercaptans can be removed by silver nitrate and the sulfur determined by the usual lamp method.

Acidified cadmium chloride does not remove the mercaptans studied.

Mercury used for the removal of elementary sulfur as first recommended by Ormandy and Craven (*4*) and later altered by Faragher, Morrell, and Monroe (*3*) does not remove the mercaptans studied.

Glacial acetic acid and zinc used for the reduction of disulfides cause a partial decomposition of the mercaptans; hence the titration method cannot be used. The percentage of sulfur must be determined by some method, such as the lamp method, applied before the reduction and after the removal of the resulting mercaptans and other substances formed from the disulfides.

IN STUDYING the behavior of mercaptans in naphtha solutions, it was found advantageous to develop a method for the determination that would be rapid, fairly accurate, and applicable to small samples. Several methods are given in the literature. Youtz and Perkins (*7*) and Faragher, Morrell, and Monroe (*3*) outline methods based primarily on the use of the lamp method (*2*) for the estimation of sulfur. Wendt and Diggs (*6*) give a method for the determination of sulfur and mercaptans in naphtha, based on forming lead sulfide and converting it to lead sulfate which is weighed. Birch and Norris (*1*) use the iodometric method for studying the removal of mercaptans from a saturated hydrocarbon.

Birch and Norris (*1*) use silver nitrate for the separation and identification of mercaptans in petroleum distillates. In this paper it will be shown that mercaptans can be removed by silver nitrate and the percentage of sulfur remaining in the oil determined by the lamp method or that, alternatively, standard silver nitrate and standard ammonium thiocyanate solutions can be used for titration. Since hydrogen sulfide is often removed by acidified cadmium chloride (*3*) and mercury is frequently used (*3*) to remove elemental sulfur, the effect of both of these reagents on the percentage of mercaptans in naphtha was studied.

Materials

The mercaptans studied were ethyl, *n*-propyl, isopropyl, *n*-butyl, isobutyl, secondary butyl, *n*-amyl, isoamyl, pentathiol-2, and benzyl. All except ethyl, isobutyl, and isoamyl were prepared in this laboratory; the method of preparation will be published later. Ethyl, isobutyl, and isoamylmercaptans *n*-butyl and isoamyl disulfides, and *n*-butyl sulfide were purchased from the Eastman Kodak Company and were used as received. The naphtha used had the following physical properties:

Color	26+°
A. P. I. gravity at 60° F. (15.6° C.)	49.9°
Per cent sulfur (lamp method)	0.028
Initial boiling point	295° F. (146° C.)
End point	414° F. (213° C.)

Solutions

Naphtha. The mercaptans were weighed in sealed tubes and then broken in a known weight of naphtha.

Silver nitrate was approximately 0.05 *N* and the thiocyanate used was 0.03 to 0.05 *N*. The silver nitrate was standardized by precipitating silver chloride and weighing it.

Methods of Analysis

A known sample was thoroughly shaken with an excess of silver nitrate in a glass-stoppered Erlenmeyer flask. Two cubic centimeters of iron alum were added, followed by ammonium thiocyanate to an excess (to deep red color). This mixture was shaken thoroughly and the excess of thiocyanate removed by silver nitrate and then titrated to a permanent pink color. When the emulsion that is formed does not break readily, 5 cc. of ethyl alcohol are added just before the final titration.

Note—After an addition of the silver nitrate to a mercaptan solution, the silver mercaptides form small lumps which enclose some silver ion, and the results are high. These lumps must be shaken out entirely before the true consumption of silver nitrate can be found. This result can be accomplished by the use of a shaking machine with an excess of thiocyanate ion, but the thiocyanate ion itself may be held in the emulsion or scum formed and cause low results. Therefore, it is best to make several determinations of the net consumption of silver ion with the sample, and the last three of these should agree within the experimental error of reading the burets. Two readings are usually taken on each sample, one at a faint pink and the other, white; these readings should not vary more than 0.03 cc. Usually when there is no excess of silver ion or thiocyanate ion, the emulsion is absent and in its place is seen a scum over the surface of the solution in the flask.

The percentage of sulfur is calculated as follows:

$$\frac{\text{Cc. } AgNO_3 \times \text{normality } AgNO_3 \times 0.03206 \times 100}{\text{Weight of sample}} = \text{per cent of mercaptan sulfur}$$

If the lamp sulfur is to be used for residual sulfur, the sample is shaken with an excess of silver nitrate and the silver mercaptides formed are filtered off, washed thoroughly with water, and the sulfur in the solution determined.

Results

Table I shows that the percentage of a mercaptan can be determined with an average absolute error of 0.002 per cent or a relative error of 4 per cent. Unless great care is used, this value is high, owing to the difficulty of removing the excess silver nitrate that is held in the emulsion. The percentage of mercaptan sulfur (using *n*-propyl mercaptan) was found to be 0.0530 with a 25-cc. sample and 0.0541 with a 15-cc. sample. Other naphthas, which will be described in a later paper, were used with the same accuracy in the estimation of mercaptans.

Mercaptans can be removed by the use of silver nitrate and the residual sulfur estimated by the lamp method. The percentage of sulfur in the naphtha at the beginning was 0.028. Table I shows the percentage of sulfur added as isopropyl,

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[1] Received May 25, 1929. This paper contains results obtained in an investigation on "A Study of the Reactions of a Number of Selected Organic Sulfur Compounds," listed as Project No. 28 of the 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 and the Universal Oil Products Co. This fund is being administered by the Institute with the coöperation of the Central Petroleum Committee of the National Research Council.

[2] American Petroleum Institute Research Associate.

[3] Director, Project No. 28, American Petroleum Institute Research.

n-amyl, and *sec*-amyl mercaptan. After treatment with silver nitrate the average percentage of sulfur found in the naphtha used with isopropyl mercaptan was 0.027; with *n*-amyl mercaptan, 0.028; and with *sec*-amyl mercaptan, 0.029. In every solution tested, the naphtha was "doctor" sweet after removal of the mercaptan, no difference being found by varying the mercaptan or the naphtha.

Note—On reduction of the sample with zinc and glacial acetic acid and removal of the mercaptan by silver nitrate, a faint trace of mercaptan was found with aqueous doctor. This trace of disulfide must have been formed during the titration, since the original naphtha gave negative results by the same test, and may have been caused by a trace of the elemental sulfur used in sweetening the naphtha. Since the doctor test gives positive results with 0.001 per cent of mercaptan sulfur, the amount of disulfide formed in the solutions tested was of this order of magnitude.

Table I—Determination of Mercaptan Sulfur in Naphtha Solution by Titration

MERCAPTAN	SULFUR ADDED	SULFUR FOUND	MERCAPTAN	SULFUR ADDED	SULFUR FOUND
	Per cent	*Per cent*		*Per cent*	*Per cent*
Ethyl	0.0550	0.0574	*n*-Amyl	0.0501	0.0515
n-Propyl	0.0543	0.0541	Isoamyl	0.0487	0.0479
Isopropyl	0.0530	0.0538	sec-Amyl	0.0470	0.0483
n-Butyl	0.0477	0.0472	sec-Butyl	0.121	0.127
Isobutyl	0.0528	0.0501	Benzyl	0.1078	0.1067
sec-Butyl	0.0491	0.0514			

As has been previously stated (*3*) mercury has been used to remove elemental sulfur. The mercaptan solutions were shaken with mercury that had been washed with hydrochloric acid (*5*) and the percentage of mercaptan sulfur determined after this treatment. No mercaptan was removed, the analysis after the treatment showing a variation of ±0.0025 per cent from the original. Acidified cadmium chloride, recommended for the removal of hydrogen sulfide (*3*), was used as directed on these mercaptan solutions. No mercaptan was removed, the percentage of mercaptan sulfur determined after this treatment showing a variation of ±0.0029 per cent from the original. These tests show that the removal of sulfur by mercury and of hydrogen sulfide by acidified cadmium chloride does not affect the mercaptan content in the cases studied.

The ratio of silver nitrate to ammonium thiocyanate showed no alteration in the presence of a naphtha sample containing 10 mg. of sulfur as *n*-butyl disulfide, isoamyl disulfide, or isoamyl sulfide.

The reduction of a disulfide by glacial acetic acid and zinc to the corresponding mercaptan is accompanied by reactions that decompose the mercaptan. The titration of the mercaptan formed by silver nitrate in such solutions will give erroneous results. Thus a solution of *n*-butyl disulfide made to a strength of 0.0477 per cent of sulfur gave 0.0440 per cent of sulfur after 3 hours and 0.0392 per cent after $4^1/_2$ hours of digestion. Confirming this result, hydrogen sulfide was detected by the addition of hydrochloric acid to the zinc. Therefore, the determination of the sulfur in the naphtha after the removal of the mercaptan by some means is necessary.

Other reagents can be used for the removal of mercaptans from naphtha, and the results of such a study will be given in another paper. In the place of silver nitrate, salts of mercury can be used (*3*). Whether silver nitrate is applicable to all cases is questionable, since it may react with other sulfur compounds and may possibly not react with some mercaptans; but for the study of the removal of certain mercaptans from naphtha, it has proved to be very useful. Before extending the method to all mercaptans (or to a distillate), it should be tested with other mercaptans of different structure and length of carbon chain.

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(2) Bur. Mines, *Tech. Paper* **323-A**, Method 520.1.
(3) Faragher, Morrell, and Monroe, IND. ENG. CHEM., **19**, 1281 (1927).
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Relation between Physical Characteristics and Lubricating Values of Petroleum Oils[1]

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This paper is a preliminary report of the work done thus far in a projected experimental program of the Chemical Engineering Laboratory of the Pennsylvania State College. Certain well-known material has been included for the sake of outlining a complete basis on which to evaluate a lubricant.

Tests for physical characteristics are discussed in the light of their relation to lubrication. It is shown that some tests are satisfactory, others are non-essential, still others are inadequate and need to be changed, and certain new tests must be devised.

Paraffin wax is found to decrease Conradson carbon values. Temperature coefficients of viscosity are found to be changed by vacuum distillation. A plea is made for the establishment of a rational basis for evaluating lubricating oils.

THE properties of a petroleum oil most often considered when evaluating it as a lubricant are gravity, color, cold test, carbon residue, viscosity, viscosity-temperature coefficient, flash and fire, and lately evaporation. As pointed out by R. E. Wilson at the Institute of Chemistry in 1928, oiliness and resistance to oxidation should be included if satisfactory tests can be found for them. Owing to lack of specific knowledge of the constitution of petroleum, we are dependent on empirical tests and their relation to past experience for deciding which oil is the most suitable under any given conditions. This introductory paper is intended to bring out certain new ideas regarding the relation of the various tests to use and certain experimental results on a few of the properties so determined. Therefore, a brief discussion of each of the above-mentioned tests will not be out of place.

Gravity

The question of gravity can be dismissed in a few words. When considered with the other physical properties of an oil, it gives evidence of the nature of the crude from which the lubricant is made and probably what cut it is; but beyond this it must be recognized that gravity is no indication of lubricating value.

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[1] Presented before the Division of Petroleum Chemistry at the 77th Meeting of the American Chemical Society, Columbus, Ohio, April 29 to May 3, 1929.

Color

The color specification on oil is in the same category as gravity. As an indication of the thoroughness of some stages of refining it is of value, but it gives no indication of lubricating power. This is readily seen from the fact that a definite color can be secured by mixing a small amount of bright stock with gasoline, producing a mixture which is obviously unsuited for lubricating an internal-combustion engine. On the other hand, since the public has been educated to demand a "good color" in oils, the refiner is often forced to increase his operating expense to obtain a "good color" in a material already suitable as a lubricant.

Cold Test

The cold test is intended to give an indication of that temperature below which the oil will not flow readily and consequently lubrication is poor. However, the A. S. T. M. cold test does not tell the whole story. The question has been studied in detail by Wilkin, Oak, and Barnard (*12*). Some work was done along this line in this laboratory just prior to the publication of the above-mentioned article. A 1/4-inch (6-mm.) glass tube was immersed in the A. S. T. M. cold-test tube beside the standard thermometer. The tube was connected through a valve to a vacuum pump and pressure regulator so that a given suction could be applied at will. The temperature was then lowered in successive runs and the reading taken at the temperature at which air was sucked in continuously after a hole had been pulled in the oil. No screen was used on the end of the tube. The results for different immersions and for three different Pennsylvania oils are shown in Table I.

Table I—Cold Test Data

	A. S. T. M. Cold Test		Temperature for Tube Submerged: 1/4 in. (0.63 cm.)		1 in. (2.54 cm.)		2 in. (5.08 cm.)	
Oil	° *F.*	° *C.*	° *F.*	° *C.*	° *F.*	° *C.*	° *F.*	° *C.*
A	24	−4.4	32	0	20	− 6.7	10	−12.2
B	22	−5.6	28	−2.2	16	− 8.9	6	−14.4
C	18	−7.8	24	−4.4	14	−10.0	8	−13.3

It is evident from the table that there is a rough parallelism between the A. S. T. M. cold test and the actual point at which the flow ceases, but that the numerical values of the A. S. T. M. cold test mean little. For example, the values given for 2-inch immersion, which is not uncommon in present motors, show why it is possible to get circulation with Pennsylvania oil at temperatures below the cold test. These results together with those of Wilkin, Oak, and Barnard on the apparent viscosity of oils below the cold point, clearly show that oil inlets to the pump should be as large, as short, and as deeply submerged as practicable, and that screens or other filtering media should be located on the pressure lines with pressure relief by-passing to take care of possible clogging. No work has been done in this laboratory on oils from other crudes, but it is hoped that such a study will be included in the continued work mentioned by the above authors at the end of their article.

Carbon Residue

The carbon-forming tendency of an oil is generally measured by the Conradson carbon residue test. There have been many arguments pro and con regarding this test, but the writer believes that it has a real significance. The excellent work of Marley, Livingstone, and Gruse (*7*), as well as others, seems to offer conclusive proof of its suitability. Probably many of the arguments against it have been based on the fact that, in motors with well-fitted pistons and rings and without excessive splashing in the crankcase, high-carbon oils have deposited little carbon, the fallacy being due to the low oil movement past the rings. Where the oil consumption in normal operation can be traced to movement of oil into the combustion space, high-carbon oils show greater and harder deposits than low-carbon oils, the numerical ratio depending on the oil consumption.

Another prevalent misconception is that Pennsylvania oils give more carbon than others of about the same viscosity range owing to their wax content. In the course of preparing distillates for another purpose the question was investigated experimentally in this laboratory.

The oils used were distilled from Pennsylvania crude at temperatures below 350° F. (177° C.), using fire and a large excess of steam; and they contained varying quantities of wax, depending on the cut. In order to make this part of the work complete, a finished oil purchased from the service station was also tested, its wax content being varied by the addition of Parawax. Outside of dewaxing the distillates and adding wax to the commercial oil, no other treatment was given. A Conradson carbon test was made on the distillates as received from the still. They were then dewaxed using the solvent method with a mixture of ethylene chloride and methyl ethyl ketone, and the Conradson carbon was again determined at the end of this process. Similarly, the carbon values were determined for the commercial oil before and after the addition of increasing amounts of Parawax. Carbon tests were also made on the crude from which the distillates were produced and on Parawax alone. The results are shown in Tables II and III.

Table II—Effect of Wax Content on Carbon Residue

Parawax Added per 100 Parts Oil	Conradson Carbon
Parts	*Per cent*
0.0	0.48
6.3	0.39
12.2	0.38
22.7	0.34
33.4	0.35
59.1	0.28
64.8	0.19

Table III—Carbon Tests before and after Dewaxing

Sample	Gravity	Carbon before Dewaxing	Carbon after Dewaxing	Wax Removed per 100 Parts Dewaxed Oil
	° *A. P. I.*	*Per cent*	*Per cent*	*Parts*
E	29.7	0.50	0.60	14.0
M	30.7	0.37	0.49	10.4
Z	30.3	0.33	0.34	2.9
Z	30.3	0.33	0.40	9.3
C	29.8	0.20	0.28	8.3
A	33.4	0.16	0.24	22.0
B	32.1	0.05	0.05	9.1
N	33.0	0.03	0.03	14.0
Parawax		0.00		
Penna. crude	39.1	0.31		

The data of Table II are plotted in Figure 1.

Although it is difficult to secure close checks in determining carbon residue by the Conradson method, the figures in the second decimal place in the tables are significant as they were determined from several check runs. The tables clearly show that, in general, the removal of wax increases the Conradson carbon number of the dewaxed oil, and also that the wax itself forms no carbon in the test. The increase in carbon formation upon removal of the wax except in the low-residue oils can readily be explained on the basis that the hydrocarbons that are more volatile than wax give no carbon residue, while those that have the same or less volatility are the main carbon-forming constituents. On this basis the wax in the heavier cuts acts principally as a diluent. However, it has a further effect during the test, as shown in Figure 2. The line shown corresponds to simple dilution and is the graph of the equation

$$\frac{C_B}{C_A} = 1 + \frac{W}{100}$$

where C_A = carbon residue after adding wax
C_B = carbon residue of original oil
W = parts (by weight) of wax per 100 parts original oil

For the data in Table II,

C_A = carbon residue after dewaxing
C_B = carbon residue of original oil
W = parts (by weight) wax removed per 100 parts dewaxed oil

It will be noticed that all the points lie above the dilution curve except those corresponding to samples *B* and *N* in Table II, which showed such low carbon values that no precision could be obtained. The location of the points can be interpreted only to mean that the vaporization of the wax carries the heavier compounds off before they have a chance to crack down to carbon.

This explanation is consistent with the results of Marley, Livingstone, and Gruse (*7*) and also with those of Donaldson (*4*). The latter has shown that oils with a moderate volatility will distil off in a current of air leaving little residue. Those oils of less volatility are cracked before they can vaporize and deposit gum and carbon on the hot surface. These data, together with the above on carbon residue, show that, in the case of Pennsylvania oils at least, high carbon residue is not due to high wax content, but rather to the fact that these oils are less volatile than those in approximately the same viscosity range made from other crudes. The same fact has also been brought out by direct test, as shown by the results of the Cadillac Motor Company's evaporation test which has recently caused so much discussion among oil men (*9*).

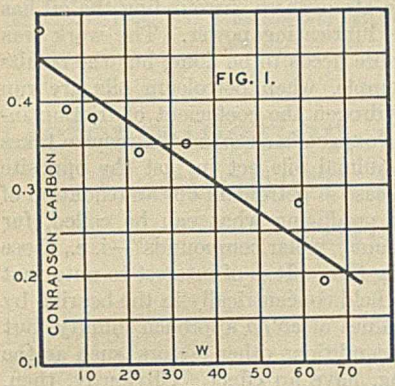


FIG. 1.

Volatility—Flash and Fire Tests

The question of volatility is thus drawn into the discussion entirely apart from its bearing on consumption in an internal-combustion engine. Recognition that a lubricating oil for automotive service must be relatively low in volatility is long standing. At present it is well known that fire and flash tests are not a true measure of the average volatility of an oil, since a small amount of relatively volatile component will materially lower the fire and flash without causing undue percentage loss by evaporation. A much more suitable test would be a vacuum distillation, such as the one described by Peterkin and Ferris (*10*) which would give a volatility curve similar to the Engler curve for gasoline, indicating in the case above, for instance, that a low flash and fire are to be expected from the shape of the low end of the curve, but that the average volatility as indicated by the middle and upper sections of the curve is nevertheless also low. This sort of a test requires more skill in control and somewhat more complicated apparatus, but the results are infinitely more valuable than those of flash and fire tests. On the other hand, the latter are very suitable in the refinery for control purposes where the product varies little from day to day and only small variations need to be checked. Flash and fire were originally applied to oils as they had been to lighter fractions to determine safe temperatures for their use. To this day, although there is no longer need of them, they are emphasized to the public as prime requisites in a lubricant. They indicate nothing as regards lubricating power and only serve to give inaccurate data on evaporation in certain cases, such as the one discussed above.

The Cadillac Motor Company's test was described and discussed by Earl E. Bown and others at the National Petroleum Association meeting in 1928 (*3*). The discussion in this article is very pertinent and the reader who is interested in volatility should consult this reference.

It is certain that in the distillation tests the final temperatures lie in the cracking range and therefore the results are dependent, not only on the volatility, but also on the rate of cracking. Certainly in a motor there is no need for oil to be exposed to any such temperatures as these except in the combustion chamber, where, as shown above in discussing carbon residue, moderate volatility is an asset. More work needs to be done in correlating the volatility test with block and road tests before definite conclusions can be reached. A word of warning, however, should be sounded in the meantime. There are many motors in use at the present time in which the oil temperature in the crankcase is low enough so that volatility is of no practical importance. The use of low-volatility oils in these motors will secure no better economy than can be had with more volatile oils; and an attempt to secure only low-volatile oil might seriously limit the available supply of lubricant.

Viscosity

The effect of viscosity on lubrication has been widely studied, and general agreement exists that, in the fluid-film region at least, which is the normal operating condition for a properly designed bearing, the modulus zN/p (*2, 13, 1, 8*) can be used to determine relative lubricating efficiencies. The interpretation of results must, of course, be conservative and applied with judgment. Within the range of experiments made to check this relation the agreement is very good.

Temperature-Viscosity Coefficient

The rate of change of viscosity with temperature—in other words, the temperature-viscosity coefficient—is probably of equal importance, since it measures the amount of thinning at high temperatures and of thickening at low. An oil with a high temperature-viscosity coefficient might be so thick at temperatures near the cold point as to prevent sufficient oil from being carried to the rubbing surfaces; and yet be so thin under operating conditions that the bearing would be running at zN/p values dangerously close to the critical point.

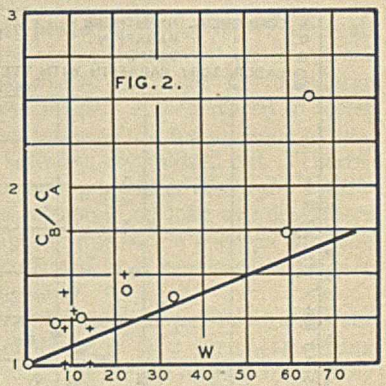


FIG. 2.

It is well known that, if the logarithm of the viscosity of a petroleum fraction is plotted against the logarithm of the temperature, the graph obtained is a straight line (*11*). Further, the higher the viscosity of a fraction the steeper the line. The slopes of the lines are obviously the temperature-viscosity coefficients of the respective fractions. If Wilson and Barnard's (*14*) suggestion of expressing the slope as the ratio of the viscosity at 100° F. (38° C.) to that at 210° F. (99° C.) is adopted, the coefficient can be specified in terms of quantities usually determined.

Little attention has been paid to this specification, though, probably owing to the general assumption that it is a characteristic of the crude and cannot be varied—in other words, that paraffin base crudes have the lowest temperature-viscosity coefficient, etc. This assumption is far from true, however. The following specifications of samples *N* and *Z* after dewaxing, and for a commercial Pennsylvania lubricating oil made from a similar crude, show that the coefficient can be changed by changing the refining methods:

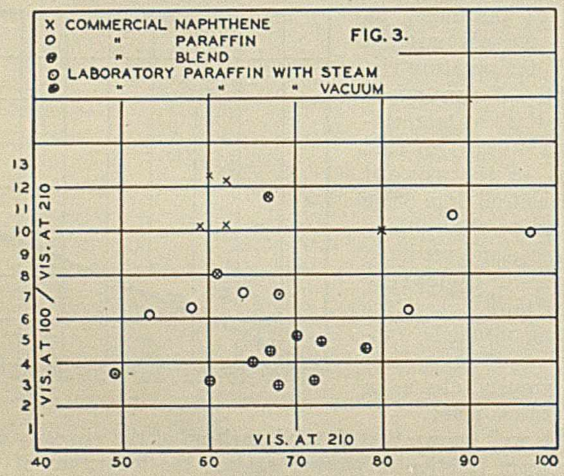
	SAMPLE "*N*"	SAMPLE "*Z*"	PENNSYLVANIA OIL
Gravity, °A. P. I.	33.0	30.3	29.8
Viscosity at 100° F. (38° C.), sec.	172	479	431
Viscosity at 210° F. (99° C.), sec.	49	68	64
Cold test, ° F.	24	24	22
Flash, ° F.	396	428	410
Fire, ° F.	454	491	480
Carbon residue, per cent	0.03	0.40	0.48

By using high-vacuum methods of preparing the distillates, on which further work is being done in this laboratory and which will be described in a later paper, oils with still flatter temperature-viscosity curve were made. The specifications of one of these oils are given below:

Gravity, °A. P. I.	29.5
Viscosity at 100° F. (38° C.), sec.	358
Viscosity at 210° F. (99° C.), sec.	78
Cold test, ° F.	24
Flash, ° F.	430
Fire, ° F.	485
Carbon residue, per cent	0.17

It should be noted that this vacuum-distilled oil has a viscosity at 210° F. (99° C.) higher than most oils now marketed for use in automobiles and yet has a relatively low viscosity at 100° F. (38° C.) as well as a low carbon residue for paraffin-base oils of this viscosity range. The oil is stable and does not change in properties when heated to the fire point.

The advantages of vacuum distillation for producing oils of low temperature-viscosity coefficients are emphasized by Figure 3. It will be noted that, in general, paraffin-base oils have lower coefficients than naphthene, that blends of the two have coefficients in an intermediate zone, and that vacuum-distilled paraffin oils have the lowest coefficients of all.



Oiliness and Resistance to Oxidation

As yet there are no completely satisfactory tests for "oiliness" or for resistance to oxidation. Considerable work has been done on trying to measure oiliness (*2*, *12*, *1*, *8*). The methods all consist in measuring the static coefficient of friction by one means or another or in locating the critical zN/p value. Wilson and Barnard (*13*) investigated the building up of an oil film in capillaries and pointed out that all film-forming substances do not lower the static coefficient of friction. In other words, it is not sufficient to form a plastic solid film (*15*), but the film must have the proper structure. Since Wilson and Barnard found that capillaries clogged more rapidly when oil was circulated through them than when they were simply immersed in the same amount of oil, it is evident that the film-forming constituents of an oil must be relatively small in amount and highly diluted with inactive component. Some work by Gilson (*5*) indicates that the structure of the film is dependent upon the nature of the bearing metals and that the atmosphere surrounding the oil has a great effect upon its lubricating power. The work was only preliminary and more needs to be done, but the results are startling. For example, when petroleum oils are run in an atmosphere of hydrogen the coefficient of friction increases, but when air or oxygen is supplied the reverse takes place. Vegetable and animal oils act in just the opposite way. Evidently in the case of petroleum oils an oxidation of some sort takes place, producing what can be called, for lack of a more exact name, "polar compounds"—i. e., those that form the lubricating film. It is of interest to note that since Gilson's shaft was held concentrically in the bearing by outside bearings, the values of zN/p approach infinity, but that, even under these conditions other factors, such as the materials of the bearing, have an effect. Obviously, then, resistance to oxidation should be great enough to prevent sludging of the oil but should allow the formation of the film-forming components.

A more exact measure of the rate at which these "polar compounds" form can be gained by using Langmuir's (*6*) water-spreading method. Some preliminary investigations in the laboratory have indicated that there are considerable differences between various commercial oils in this respect. This work is being continued and will also be reported later. Obviously, in the first few cases it is necessary to check the film-forming tendency with friction measurements. At the present time it appears that the best oil from this standpoint is one which forms the "polar compounds" at just the right rate to keep the bearings covered with plastic solid films.

Conclusion

It is hoped that the above discussion has emphasized the fact that the empirical tests now used for petroleum oils tell far from the whole story on performance—that certain of them are of little use and should be abandoned, that others should be retained, and that still others must be changed or new ones devised. In the author's opinion, those to be abandoned are gravity, color, flash, and fire; those to be retained, carbon residue, viscosity, and viscosity-temperature coefficient (remembering that the latter is a property not necessarily characteristic of the crude); and those to be changed or devised anew, cold test, evaporation, "oiliness," and resistance to oxidation. The last two classes should furnish a satisfactory basis for evaluating the lubricating qualities of an oil. The last class includes those tests on which further research should be carried out.

Any criticisms or suggestions as to changes in this basis for evaluating an oil will be gratefully received, since the mere establishment of a basis suitable to all will greatly advance the preparation of the best lubricant.

Acknowledgment

The writer wishes to acknowledge his indebtedness to the authors whose original papers have been freely cited throughout the discussion; to the Pennzoil Company for furnishing materials; to W. H. Zehrung, D. P. Barnard, W. H. McAdams, and H. C. Weber for suggestions on the presentation, and to the students in chemical engineering at this laboratory whose thesis work furnished much of the experimental data herein reported.

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Determination of True Sodium Content of Calcium Carbonate Intended for Use in J. Lawrence Smith Method for Alkalies[1]

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The usual method of testing reagent-grade calcium carbonate for its alkali salt content is to boil 4 grams of the salt with 50 cc. of water, filter, evaporate the extract to dryness, and ignite and weigh the residue remaining (*3*). It has long been recognized that this method is defective in principle, since it is generally impossible to extract small amounts of adsorbed alkali salts from insoluble precipitates by a simple washing process. Several experimenters have amply demonstrated this in the case of calcium carbonate in particular (*4*). Until recently, no suitable method of rapidly and accurately testing this chemical for alkali salts has been available. It appeared to the writer that the improved magnesium-uranyl acetate method for the direct determination of sodium (*1*) would provide a means for accurately determining the alkali content of this material, since by this method it is possible to determine small amounts of sodium in the presence of very large amounts of calcium, and the alkali content of reagent calcium carbonate consists almost wholly of sodium in some form, probably as the carbonate (*2*, *4*). Experiments were therefore instituted which resulted in the formulation of a suitable procedure for the accurate determination of sodium in this reagent. Test analyses were made on several representative samples of calcium carbonate from different sources by this new method, and the results were compared with those obtained by the extraction method as described in detail below.

Experimental Part

The extraction method used in these experiments was that described by Murray (*3*). In order to insure the absence of weighable residues from sources other than the calcium carbonate, blanks were run on the distilled water used and the extractions and evaporations were conducted in platinum vessels.

The magnesium-uranyl acetate method as modified for this purpose was as follows.

Procedure—Weigh out 2.000 grams of the calcium carbonate into a 150-cc. Erlenmeyer Pyrex flask. Dissolve the sample by cautious additions of dilute (1:1) hydrochloric acid introduced through a small funnel placed in the neck of the flask. Evaporate the solution just to dryness on a hot plate and dissolve the residue in 2 to 3 cc. of water. Then add 25 cc. of magnesium-uranyl acetate reagent and mix the two solutions thoroughly. Immerse the lower part of the flask in a large beaker containing water at 20° C. and stir the solution with a motor stirrer for 30 to 45 minutes. Filter off the resulting precipitate into a weighed Gooch crucible and wash with four or five 5-cc. portions of special wash liquid. Finally dry the crucible and precipitate in an air oven at 100–105° C. for 30 minutes. The weight of the precipitate multiplied by the factor 0.0153 gives the sodium content of the sample.

Preparation of Reagent—The reagent is prepared in two parts, which are mixed to obtain the final working reagent.

Solution A

Crystallized uranyl acetate	85 grams
Glacial acetic acid	60 grams
Distilled water	to 1000 cc.

Solution B

Crystallized magnesium acetate	500 grams
Glacial acetic acid	60 grams
Distilled water	to 1000 cc.

Each solution is separately heated to about 70° C. until all the salts are in solution, and then the two solutions are mixed at this temperature and allowed to cool to 20° C. The large vessel containing the mixed reagent is then placed in water at 20° C. and held at this temperature for an hour or two until the slight excess of salts has crystallized out. The reagent is finally filtered through a dry filter into a dry bottle. The reagent is permanent, although on long standing there may appear a slight precipitate due to the reaction with the sodium of the glass, in which case it is necessary to filter it before using it for an analysis.

Preparation of Special Wash Liquid—Precipitate the sodium from 1 to 2 cc. of dilute (1 to 2 per cent) sodium chloride solution with 50 cc. of the special reagent by shaking the two solutions together and wash the resulting precipitate of sodium-uranyl-magnesium triacetate with successive portions of 95 per cent alcohol. Suspend the washed precipitate in a large volume of 95 per cent alcohol and shake the mixture at frequent intervals for an hour. Finally filter the solution and use the filtrate for washing the sodium precipitates. The use of this special wash liquid is necessary in order to obtain exact results in washing very small precipitates. For technical control purposes sufficiently close results are obtainable if the precipitates are washed with ordinary 95 per cent alcohol.

General Remarks on Procedure—The excess of hydrochloric acid used in the solution of the sample must be nearly all removed by evaporation, since precipitation is not complete in the presence of free hydrochloric acid. On the other hand, care must be taken not to bake the residue and thus decompose the calcium chloride, since in that case it will not be possible to obtain a clear solution in water. A safer procedure is to finish the evaporation over a water bath. For extensive manipulative notes on the remainder of the method the reader is referred to the recent paper on the direct magnesium-uranyl acetate method for sodium (*1*). No difficulties will be encountered, however, if the details as given above are followed.

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[1] Received June 11, 1929.

Results

The average results obtained on several representative samples of reagent-grade calcium carbonate by both the old and new methods are shown in Table I. In each case the actual sodium in the extraction residue was determined by the new method in order to ascertain the actual amount of alkali extracted from the samples by boiling with distilled water.

From the data shown in the table it is obvious that the extraction method gives neither true nor comparative results for the alkali content of reagent-grade calcium carbonate. The minute amounts of sodium found in the residue obtained by evaporating the water extract demonstrate clearly the futility of attempting to remove and determine adsorbed alkali salts by a washing process. The residues obtained by extraction consist chiefly of calcium carbonate dissolved by the relatively large volume of water used in the method.

The results also show that there is a considerable variation in the sodium content of the samples of reagent-grade calcium carbonate from different sources, although the usual method of testing the material would not indicate this variation.

Table I—Comparative Results in Determination of Sodium in Samples of Reagent Calcium Carbonate by Extraction Method and by Magnesium-Uranyl Acetate Method

SAMPLE	ALKALI CONTENT LABEL STATEMENT	SODIUM CONTENT NEW METHOD	SODIUM CONTENT CALCD. TO CARBONATE	ALKALI CONTENT EXTRACTION METHOD	SODIUM ACTUALLY PRESENT IN EXTRACTION RESIDUE[a]
	Per cent	*Per cent*	*Per cent*	*Per cent*	*Per cent*
Standard stock material	None	0.13	0.30	0.02	0.002
Standard stock material	0.05	0.12	0.28	0.02	0.003
Specially prepared lot	Low	0.02	0.05	0.04	0.001
Standard stock material	0.01	0.008	0.018	0.01	<0.001
Selected lot from standard stock material	0.053	0.006	0.014	0.01	<0.001

[a] Expressed in percentage of sample taken.

It was found, also, that the magnesium-uranyl acetate method gave results for the sodium content of this chemical in a shorter time than the usual extraction procedure.

In conclusion, it may be stated that this new method for determining small amounts of sodium is applicable to a wide range of chemicals intended for reagent purposes, especially those of the alkali and alkaline earth groups, and even of many of the heavy metals as well. In many of these cases the method as outlined above is quite suitable, but in some other cases certain modifications are necessary. Investigations in regard to these modifications are being pursued and it is intended to publish the findings later.

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Calculation of the Compounds in Portland Cement[1]

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The bases for a calculation of the compounds present in Portland cement from chemical analyses are presented. Arithmetical and diagrammatical methods are given for such a calculation. The compounds considered are $4CaO.Al_2O_3.Fe_2O_3$, $3CaO.Al_2O_3$, $2CaO.SiO_2$, $3CaO.SiO_2$, uncombined MgO, uncombined CaO, and $CaSO_4$. Other components than those included in these compounds are not at present considered as their forms of combination are not known.

SYSTEMS containing combinations of the components CaO, MgO, Al_2O_3, Fe_2O_3, and SiO_2 have been studied and reported by this and other laboratories (*3, 5, 7, 8, 10, 11*). It has been found that when these components are intimately mixed in proportions similar to those found in Portland cements, and burned to equilibrium, the following compounds are formed: $4CaO.Al_2O_3.Fe_2O_3$, $3CaO.Al_2O_3$, $2CaO.SiO_2$, $3CaO.SiO_2$, and MgO.

Note—In a former publication (*6*) it was reported that MgO enters into solid solution with $4CaO.Al_2O_3.Fe_2O_3$, the end member of the series being $4CaO.2MgO.Al_2O_3.Fe_2O_3$. Magnesia in excess of that required for the above combination was found to remain as uncombined MgO. More recent information obtained in this laboratory indicates that the amount of the solid solution is much smaller than had previously been reported. Although there is no reasonable doubt that a large part of the magnesia remains uncombined, the exact nature and degree of the reaction by which the $4CaO.Al_2O_3.Fe_2O_3$ is changed in color and pleochroism in the presence of a small amount of magnesia has not been determined. This problem is under further investigation. At present the magnesia may be considered as remaining essentially uncombined, and the iron compound as existing essentially in the form of $4CaO.Al_2O_3.Fe_2O_3$.

In addition to the five components listed above, commercial Portland cements contain small amounts of other materials in variable quantity. These may include soda, potash, titania, manganese oxides, phosphates, and perhaps still other materials. The total amount of these lesser components, however, probably does not often exceed 2 per cent.

The manner of combination of these lesser components is not known. It is possible that some of them, as perhaps the alkalies, may have a significant influence on the relative amounts of the major compounds that are formed, but since the manner of their combination is not yet known, the effects of their presence cannot now be evaluated. Consequently, it is not possible at present to consider those components in the calculation of cement constitution.

It is assumed that the compounds of Portland cement are essentially the same as those of the pure five-component system given above when the components are present in the proportions found in commercial cements. The general correctness of this assumption has been confirmed by information obtained from cooling curves (*4*), from microscopic examinations (*1*) and from x-ray diffraction photographs (*1*).

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Manner of Reaction

The manner in which the components react determines the relative amounts of the resulting compounds. Information obtained at this laboratory leads to the following generalizations:

(1) The ferric oxide reacts with alumina and lime to form $4CaO.Al_2O_3.Fe_2O_3$. (See note.)

(2) The magnesia remains essentially in the form of uncombined MgO.

(3) The alumina remaining from combination as $4CaO.Al_2O_3.Fe_2O_3$ reacts with lime to form $3CaO.Al_2O_3$.

(4) The lime remaining from the above combinations reacts with the silica. The compound $2CaO.SiO_2$ is formed, and any CaO then uncombined reacts with the $2CaO.SiO_2$ to form $3CaO.SiO_2$. If CaO remains after converting all of the $2CaO.SiO_2$ to $3CaO.SiO_2$, it will be present as uncombined CaO.

The formation of the compounds as described assumes that a condition of equilibrium has been reached during the progress of the reactions in the kiln. A small amount of uncombined CaO may remain in the clinker, however, indicating (if the composition is such that the CaO would be completely combined at equilibrium) that the reactions are not altogether complete. This departure from complete combination is not usually of sufficient magnitude to produce a change in the nature of the compounds formed, but it does produce a change in the relative amounts of the compounds produced. For that reason it is important that free CaO in the cement be determined (*9*) and that the amount present be taken into consideration in the calculation of the constitution. If this is not done, an error of usually small but uncertain magnitude may be introduced.

The "insoluble residue" obtained in a cement analysis is composed of quartz, titania, and several other materials. The amount of the residue is usually very small, about 0.2 per cent. Because of the low quantity of this material and the variable and uncertain nature of its composition, it seems inexpedient to attempt to introduce a correction factor for it. In unusual cases where the amount of the residue is high, it may be desirable to analyze it to ascertain if an appreciable quantity of silica has remained as free quartz. If the residue is found to contain an appreciable amount of silica, then the silica content of the residue should be deducted from the total SiO_2 to obtain the value of the SiO_2 taking part in the reactions.

The "ignition loss" consists essentially of moisture and carbon dioxide that have been taken up by the cement following the burning operation. In calculating the constitution, this value is accordingly set down without further change.

By means of the information given above, the relative amounts of the compounds present in Portland cement or clinker may be calculated from the chemical analyses. It is essential in any case to consider the SO_3 content and calculate that to $CaSO_4$.

Accuracy of Computations

The accuracy of the computations depends on the correctness of both the postulations and the analytical values. The postulations as given represent the best available information, but are subject to revision and extension as has been pointed out. The general correctness of the analytical values will vary with the conditions of test and the personal factor. In any case it is not recommended that analyses be considered as accurate beyond the first decimal place.

An examination of the factors given below will show that errors of analysis often are magnified in the computations for compound composition. Thus a plus error (other values remaining fixed) of 0.2 per cent CaO or uncombined CaO (expressed as percentage of the cement) will increase the computed $3CaO.SiO_2$ about 0.8 per cent and decrease the computed $2CaO.SiO_2$ about 0.6 per cent. A plus error of 0.2 per cent Fe_2O_3 will increase the computed $4CaO.Al_2O_3.Fe_2O_3$ about 0.6 per cent, decrease the $3CaO.Al_2O_3$ about 0.3 per cent, decrease the $3CaO.SiO_2$ about 0.3 per cent, and increase the $2CaO.SiO_2$ about 0.2 per cent. A plus error of 0.2 per cent Al_2O_3 will increase the computed $3CaO.Al_2O_3$ about 0.5 per cent, decrease the $3CaO.SiO_2$ about 1.3 per cent, and increase the $2CaO.SiO_2$ about 1.0 per cent. A plus error of 0.2 per cent SiO_2 will decrease the computed $3CaO.SiO_2$ about 1.5 per cent and increase the $2CaO.SiO_2$, 1.3 per cent. For these reasons only analytical data that are believed to be reliable should be employed for the computation of compound composition, and an expression of the compounds $4CaO.Al_2O_3.Fe_2O_3$, $3CaO.Al_2O_3$, $3CaO.SiO_2$, and $2CaO.SiO_2$ should not be given to a closer approximation than the nearest whole number.

Method of Calculation

Each per cent of SO_3 enters into combination with 0.70 per cent CaO to form 1.70 per cent $CaSO_4$:

$$\frac{CaO}{SO_3} = \frac{56.07}{80.065} = 0.70 \text{ per cent CaO} \ldots\ldots\ldots\ldots (c_1)$$

Each per cent of Fe_2O_3 enters into combination with 0.64 per cent Al_2O_3:

$$\frac{Al_2O_3}{Fe_2O_3} = \frac{101.92}{159.68} = 0.64 \text{ per cent } Al_2O_3 \ldots\ldots\ldots\ldots (a_1)$$

and with 1.40 per cent CaO:

$$\frac{4CaO}{Fe_2O_3} = \frac{224.28}{159.68} = 1.40 \text{ per cent CaO} \ldots\ldots\ldots\ldots (c_2)$$

to form 3.04 per cent $4CaO.Al_2O_3.Fe_2O_3$.

The total MgO is recorded as uncombined MgO.

The total Al_2O_3 minus (a_1) gives the Al_2O_3 (a_2) available for combination as $3CaO.Al_2O_3$. Each per cent of (a_2) will enter into combination with 1.65 per cent CaO to form 2.65 per cent $3CaO.Al_2O_3$:

$$\frac{3CaO}{Al_2O_3} = \frac{168.21}{101.92} = 1.65 \text{ per cent CaO} \ldots\ldots\ldots\ldots (c_3)$$

The amount of CaO available for combination with SiO_2 is obtained by subtracting from the total CaO the sum of the uncombined CaO, the CaO (c_1) combined as $CaSO_4$, the CaO (c_2) combined as $4CaO.Al_2O_3.Fe_2O_3$, and the CaO (c_3) combined as $3CaO.Al_2O_3$:

$$\text{Total CaO} - (\text{uncombined CaO} + c_1 + c_2 + c_3) = \text{CaO available to combine with } SiO_2 \ldots\ldots (c)$$

The total SiO_2 (s), unless corrected for silica in the "insoluble residue," is calculated first to combine with CaO to form $2CaO.SiO_2$. Each per cent of SiO_2 (s) will combine with CaO to form 2.87 per cent $2CaO.SiO_2$:

$$\frac{2CaO.SiO_2}{SiO_2} = \frac{172.20}{60.06} = 2.87 \text{ per cent } 2CaO.SiO_2$$

This first approximation to the value of $2CaO.SiO_2$ is subtracted from the SiO_2 (s) + CaO (c), which gives the CaO (c_4) available to combine with $2CaO.SiO_2$ to form $3CaO.SiO_2$.

Each per cent of CaO (c_4) combines with $2CaO.SiO_2$ to form 4.07 per cent $3CaO.SiO_2$:

$$\frac{3CaO.SiO_2}{CaO} = \frac{228.27}{56.07} = 4.07 \text{ per cent } 3CaO.SiO_2$$

The $3CaO.SiO_2$ subtracted from the total SiO_2 (s) + CaO (c) gives the true amount of $2CaO.SiO_2$ present.

If the computed $3CaO.SiO_2$ is greater than $s + c$, no $2CaO.SiO_2$ is present. In that case each per cent of SiO_2 (s) combines with CaO to form 3.80 per cent $3CaO.SiO_2$:

$$\frac{3CaO.SiO_2}{SiO_2} = \frac{228.27}{60.06} = 3.80 \text{ per cent } 3CaO.SiO_2$$

This amount of $3CaO.SiO_2$ subtracted from SiO_2 (s) + CaO (c) gives the percentage of uncombined CaO. The above

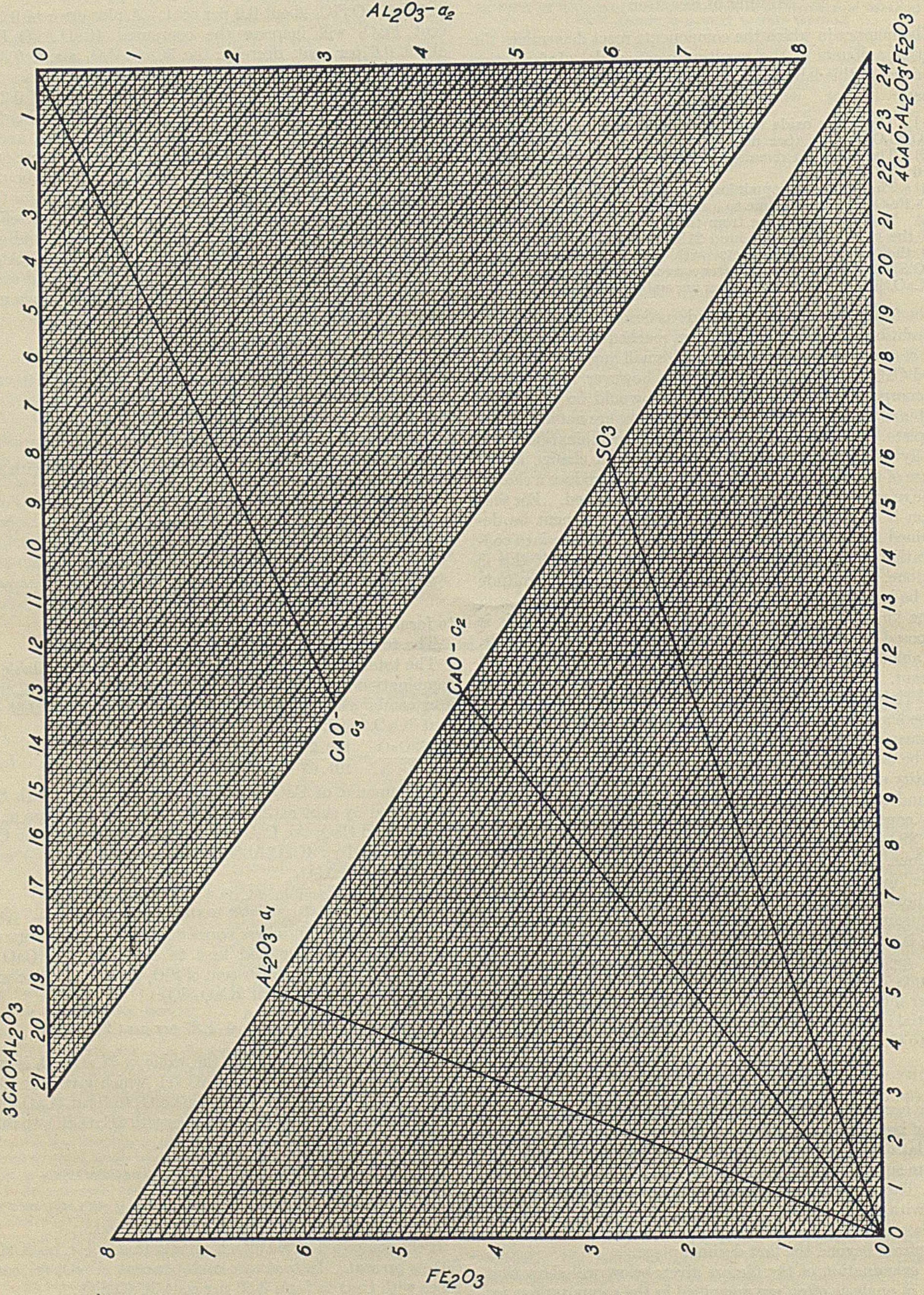

Figure 1

condition can obtain only when the lime is in excess of that which can go into combination at equilibrium, and the uncombined CaO has not been determined and deducted as previously described.

Application of the Method

A diagrammatic method for obtaining these relations has been found useful in computing the amounts of the compounds from chemical analyses. Such a method has not the precision

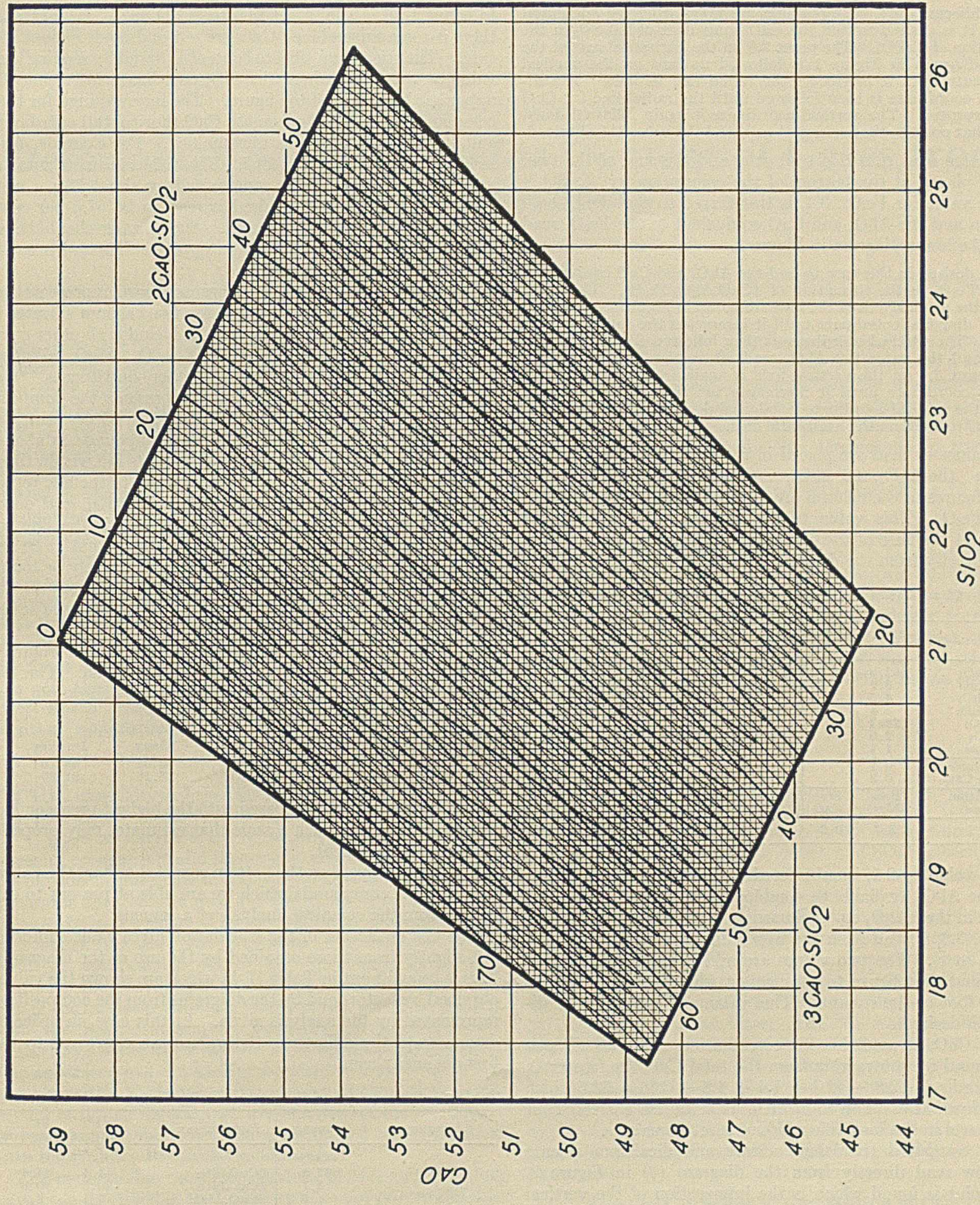

Figure 2

of the mathematical factors, but the values read are probably within the accuracy of the analytical procedures and the method has the advantage of speed and simplicity.

In Figures 1 and 2 the relations expressed in the factors given above are plotted in a convenient form. As an illustration of the use of the diagrams and the factors, an analysis of a commercial cement and the computation of compounds are presented. A chart (Table I) will be found an aid in the proper recording of the significant figures. The analytical data are given on the chart, together with the values as read from the diagrams. A few abbreviations appear on the chart: C_4AF for $4CaO.Al_2O_3.Fe_2O_3$, C_3A for $3CaO.Al_2O_3$, C_3S for $3CaO.SiO_2$, and C_2S for $2CaO.SiO_2$.

The values for ignition loss, 1.1, and magnesia, 3.7, are transferred to the lower horizontal row, wherein are placed the compounds of the cement.

The value for free CaO, 0.3, is transferred to the "free CaO" column opposite CaO, and brought down to the lower row compounds.

The value for SO_3, 2.0, is transferred to the "SO_3 eq." column, and the CaO equivalent read from the lower diagram in Figure 1.

In this case only, both readings are taken from the horizontal axis. It is desired to find the CaO equivalent of 2.0 SO_3 in the formation of $CaSO_4$. The point 2.0 on the horizontal axis of the lower diagram in Figure 1 is followed upward on the vertical coördinate until it intercepts the radial line for SO_3. The diagonal coördinate is then followed until the radial line for CaO is intercepted. The vertical coördinate is again followed down from that point to the horizontal axis, and the value 1.4 obtained.

The value read, 1.4, is placed at c_1 and the sum of the two, 3.4, is placed at the bottom of the column under "$CaSO_4$."

The value for Fe_2O_3, 3.4, is transferred to the "Fe_2O_3 eq." column and the Al_2O_3 and CaO equivalent to the Fe_2O_3 read from the lower diagram in Figure 1.

It is desired in this case to find the Al_2O_3 and CaO equivalents of 3.4 Fe_2O_3 in the formation of $4CaO.Al_2O_3.Fe_2O_3$. The point 3.4 on the vertical axis of the lower diagram in Figure 1 is followed on the diagonal coördinate until it intercepts the radial line for Al_2O_3. The vertical coördinate is then followed down from that point and the value 2.2 Al_2O_3 read off on the horizontal axis. The point 3.4 on the vertical axis is again followed on the diagonal coördinate until it intercepts the radial line for CaO. Again the vertical coördinate is followed downward and the value 4.8 CaO read off on the horizontal axis.

The values as read are placed in the column at their proper places: the Al_2O_3, 2.2, at a_1; and the CaO, 4.8, at c_2. The three figures in the column are now added to give the $4CaO.Al_2O_3.Fe_2O_3$. This value to the nearest whole number is placed at the base of the column. The amount also may be read directly from the diagram if desired.

Table I—Chart Used for Recording Significant Data in Computation of Compounds

COMPONENTS	ANALYSIS	FREE CaO	SO_3 EQ.	Fe_2O_3 EQ.	Al_2O_3 EQ.	c AND s	C_2S
CaO	62.8	0.3	c_1 1.4	c_2 4.8	c_3 3.8	c 52.5	
MgO	3.7						
Al_2O_3	4.5			a_1 2.2	a_2 2.3		
Fe_2O_3	3.4			3.4			
SiO_2	22.3					s 22.3	
SO_3	2.0		2.0				
Loss	1.1						
Insoluble	0.1						
Free CaO	0.3						
Ignition loss	Free MgO	Free CaO	$CaSO_4$	C_4AF	C_3A	C_3S	C_2S
1.1	3.7	0.3	3.4	10	6	44	31

The value a_1, 2.2, is subtracted from Al_2O_3, 4.5, to give a_2, 2.3, the Al_2O_3 available to combine as $3CaO.Al_2O_3$, which is placed in the "Al_2O_3 eq." column at a_2. The CaO equivalent of this, 3.8, is read from the upper diagram of Figure 1 and placed at c_3. The two values are added to give the $3CaO.Al_2O_3$ and that figure to the nearest whole number brought to the foot of the column. This value also may be read directly if desired.

The CaO, c, available for combination with the silica is now found by subtracting from the total CaO the free CaO, c_1, c_2, and c_3: $62.8 - (0.3 + 1.4 + 4.8 + 3.8) = 52.5$ which is set down at c. The total SiO_2, 22.3 (unless corrected for the quartz in the insoluble residue) is set down at s.

The computed tricalcium silicate and dicalcium silicate are now read directly from the diagram (*2*) in Figure 2. The point is found which is the intersection of the vertical coördinate representing SiO_2 (s) and the horizontal coördinate representing the CaO (c) available for combination with the silica. The $3CaO.SiO_2$ corresponding to this point, 44 per cent, is read to the nearest whole number on the diagonal coördinate that is parallel to the lower right base line, as indicated. The $2CaO.SiO_2$, 31 per cent, is read on the diagonal coördinate that is parallel to the upper left base line, as indicated. These values are set down in the lower row of compounds under C_3S and C_2S, respectively.

In the event that the point represented by the intersection of the coördinates for CaO and SiO_2 lies to the left of the diagram, there is present an excess of lime above that required to convert all of the $2CaO.SiO_2$ to $3CaO.SiO_2$. In that case there is some uncombined CaO present and no dicalcium silicate. The tricalcium silicate content is found by reading that value at the point where the SiO_2 coördinate intersects the upper left boundary of the figure. The lime required for that compound is then read off on the CaO (horizontal) coördinate and the remaining lime is uncombined. For example, consider that $c = 59.0$ and $s = 20.5$. The SiO_2 coördinate cuts the upper boundary at a point represented by about 78 per cent $3CaO.SiO_2$. The CaO required is read to be 57.5 per cent. The free CaO is then 1.5 per cent. Such a value should be recorded in the "free CaO" column opposite SiO_2 and brought to the lower row of compounds.

The upper right boundary curve as drawn represents the compositions at which the sum of the two calcium silicates is 80 per cent. The remaining material includes all other compounds—as $3CaO.Al_2O_3$, $4CaO.Al_2O_3.Fe_2O_3$, MgO, alkalies, free CaO if present, $CaSO_4$, and any other constituents. The lower left boundary curve as drawn represents the compositions at which the sum of the two silicates is 65 per cent, the remaining 35 per cent being the other compounds as above. It is probable that most commercial cements fall within these limits, but the diagram may be extended up to the line representing 100 per cent $2CaO.SiO_2$ plus $3CaO.SiO_2$, and down as far as desired. The upper left boundary is the line for zero $2CaO.SiO_2$ and the lower right boundary is cut at 20 per cent $3CaO.SiO_2$ since Portland cements will scarcely be found with less than that amount of the tribasic silicate. If desired, however, the diagram may be extended to the lower right to zero $3CaO.SiO_2$.

The data necessary to construct the diagrams in Figure 1 are obtainable from the factors previously given. The following locations of the external angles of the diagram in Figure 2 will define the position of that figure.

	LEFT	TOP	RIGHT	BOTTOM
CaO	48.64	58.95	53.81	44.70
SiO_2	17.36	21.05	26.19	21.30

The diagrams must be prepared with the highest precision and should be drawn to such a scale that estimates may properly be made to 1 per cent.

There now appear on the bottom row of the chart the values for all of the compounds which we are able at present to calculate from the chemical analysis of a cement.

The use of factors in the calculation gives values differing but slightly from those obtained by the use of the diagrams. This is brought out in Table II, in which are shown the values obtained by factors and by the diagrams from the composition represented by the analysis given. In this case, in order to demonstrate the difference, the values are expressed to the first decimal place.

Table II—Comparison of Computations by Factors and by Diagram

COMPONENTS	ANALYSIS	COMPOUNDS	BY FACTORS	BY DIAGRAM
	Per cent		*Per cent*	*Per cent*
CaO	62.8	$3CaO.SiO_2$	44.4	44.4
MgO	3.7	$2CaO.SiO_2$	30.5	30.6
Al_2O_3	4.5	$3CaO.Al_2O_3$	6.1	6.1
Fe_2O_3	3.4	$4CaO.Al_2O_3.Fe_2O_3$	10.3	10.4
SiO_2	22.3	Free MgO	3.7	3.7
SO_3	2.0	Free CaO	0.3	0.3
Ignition loss	1.1	$CaSO_4$	3.4	3.4
Insoluble[a]	0.1	Ignition loss	1.1	1.1
Free CaO[a]	0.3			
Total	99.8		99.8	100.0

[a] Not included in total.

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Determination of the Sulfur Content of Gases from Boiler Furnaces[1,2]

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The form and the quantity in which sulfur exists in the products of combustion are important in connection with their action on the refractories of the furnace, the metal of preheaters, economizers, and steel stacks, and with the acids and gases emitted from the stack. The equilibrium equation shows that at furnace temperatures the sulfur will be present as SO_2 and that SO_3 will be formed as the gases cool.

Apparatus and methods are described for sampling the gases after they have passed the boiler tubes and from the furnace; these are designed to reduce the possibility of catalytic action between the points of sampling and analyses. At the lower temperatures an iron pipe with glass lining is used, and at furnace temperatures a copper glass-lined water-cooled sampler. A suction pump draws the gases at a constant rate of 0.1 cubic foot per minute through the apparatus which absorbs the sulfur gases, after which they pass through a flowmeter. The absorption apparatus for the SO_3 and SO_2 determination consists of one bottle with a fine-grained dry alundum thimble which retains the droplets of H_2SO_4 and a second bottle with a coarser alundum thimble immersed in a NaOH solution containing some H_2O_2 which absorbs the SO_2. Water is run through the glass tubing into the first thimble and bottle and the SO_3 determined by titrating with NaOH.

The second bottle is titrated with standard acid to determine the SO_2.

Results of tests to determine the accuracy of this method are given. When only the total sulfur is required, the first bottle is omitted; if the gases contain soot and tar which would clog the alundum thimble, the impinger principle is utilized, there being two impinger bottles in series. The composition of the gases by Orsat is also determined and from these data and the coal analysis the ratio of the sulfur in the gases to that in the coal can be computed.

....

The importance of the effect of the small concentrations of sulfur dioxide and sulfur trioxide in boiler-furnace gases on the life of the refractories, on the external corrosion of economizers and preheaters, and on the pollution of the outside air has made it desirable to have a small portable apparatus that can be used for the rapid determination of these gases in the range of concentration in which they exist in a boiler furnace. The apparatus here described is the result of work carried out by the Pittsburgh Experiment Station of the United States Bureau of Mines in an investigation of the service conditions of refractories, conducted jointly with the Special Research Committee on Boiler-Furnace Refractories of the American Society of Mechanical Engineers. The apparatus was checked for accuracy and made up into a test kit at the Engineering Experiment Station of the University of Illinois for use in an investigation of the prevention of corrosion by flue gases, being conducted in coöperation with the Utilities Research Commission.

The methods for the determination of SO_2 and SO_3 that have been described in the literature have not proved suitable for analysis of boiler-furnace gases. Their deficiencies have existed in one or more of the following features: (1) Iodometric or other reductimetric methods are excluded because of the existence of reducing agents in the gases besides SO_2; (2) the condensation of H_2SO_4 even at temperatures as high as 200° C. prevents the collection of the gas for subsequent analysis; and (3) the rapid oxidation of SO_2 by the oxygen present in the gas prevents scrubbing the gas by water or any solution before the separation of SO_2 and SO_3 has been made. A simple portable apparatus that can be assembled in the average power-plant laboratory is essential.

Hawley (*2*) has shown that, although SO_3 combines with water vapor to form a fog which will pass through water or a solution of alkali without being completely absorbed, it may be separated from the gases by a filter. Nestell and Anderson (*3*) used Hawley's method for the separation of SO_3 and SO_2 by employing a paper filter. The SO_2 was then absorbed and oxidized by an excess of a standard solution of Na_2CO_3 containing H_2O_2. The SO_3 collected was determined by titration with standard alkali and the SO_2 was determined from the excess Na_2CO_3 by titration with standard acid. The application of these principles has led to the development of a simple and rugged portable apparatus suitable for power-plant work.

Reactions of Sulfur in Combustion of Coal

Sulfur occurs in coal in amounts ranging from 0.5 to 7 per cent. When coal is burned on a grate or in powdered form, a certain percentage of sulfur, usually low, remains in the ash and the remainder unites with the oxygen and passes out of the furnace with the gases. Sulfur dioxide may be assumed to be the primary product of the combustion, and the presence of SO_3 is due to oxidation of SO_2 at temperatures lower than those of combustion.

The reaction of SO_2 with oxygen is very slow except in the presence of catalysts. In boiler furnaces the ash particles carried by the gases, as well as surfaces with which the gases

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[2] Published by permission of the Director, U. S. Bureau of Mines, and the Director of the Engineering Experiment Station, University of Illinois. (Not subject to copyright.)

come in contact, should act as catalysts. The ratio of the partial pressures of SO_3 and SO_2 is expressed by

$$\frac{p_{SO_3}}{p_{SO_2}} = K\sqrt{p_{O_2}}$$

when K is a constant that depends on the temperature. Bodenstein and Pohl (*1*) have shown that K has a value of 31.3 at 982° F. and 0.013 at 2732° F. If the oxygen content of the combustion gases is 5 per cent by volume, the maximum SO_3:SO_2 ratios in the presence of an efficient catalyst would be 7 at 982° F. and 0.003 at 2732° F.

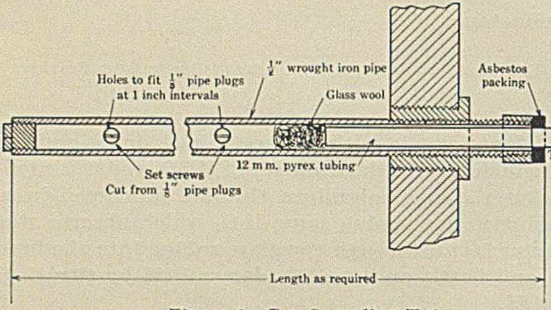

Figure 1—Gas-Sampling Tube

When the gases are sampled in the furnace it is sufficient, therefore, to determine the total sulfur and compute it as equivalent SO_2; beyond the boiler tubes, where a knowledge of the SO_3 and SO_2 is necessary, the gases should be cooled quickly and possibility of catalytic action avoided.

Description of Apparatus and Method

The apparatus required is (1) a sampling tube, (2) an absorption system, (3) a gas meter, (4) a source of reduced pressure, (5) an Orsat apparatus, and (6) connecting glass tubing.

SAMPLING TUBE—Figure 1 shows the sampling tube used to collect the gases in the economizer and preheater where the temperature of the gases does not exceed 900° F. (482° C.). A $^1/_2$-inch (1.3-cm.) iron pipe long enough to reach half-way across the setting at the point of sampling is closed at one end by a plug or cap and has holes fitted with $^1/_8$-inch (3-mm.) pipe plugs at 12-inch intervals along its length. A sample may be drawn from any one point by removing a pipe plug, and the average composition of the stream is computed from the average of the several samples. A 12-mm. Pyrex tube inserted through a cap at the outer end extends several inches inside the setting. Moistened asbestos paper is packed around the glass to prevent air from passing into the pipe. A tuft of glass wool placed before the end of the glass tube in the iron pipe filters out any dust carried by the gas.

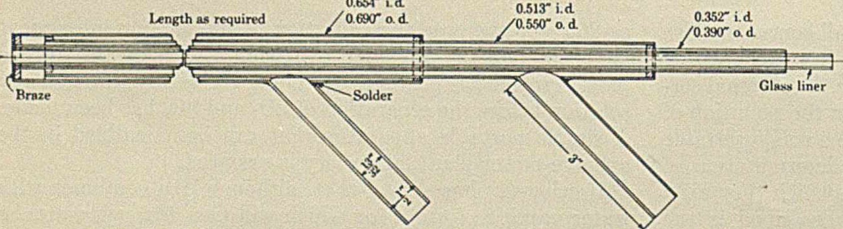

Figure 2—Water-Cooled Sampler with Glass Liner for Sampling SO_2 from Furnace Gases

Figure 2 shows a water-cooled sampler which may be used where the temperature is as high as 3000° F. (1649° C.). It is made of thin copper tubing in lengths to suit. The cooling water passes to the end of the sampler and then back to the outlet. A water pressure of at least 75 pounds per square inch (5.3 kg. per sq. cm.) is necessary to insure sufficient flow when the tube extends 6 feet into the gases and where the temperature exceeds 2600° F. (1427° C.). A glass tube extends through the center of the sampler to the end so that the gases do not come in contact with the metal. An average value of the gas stream can be obtained by inserting the sampler to definite positions, or the gas-absorption apparatus may be mounted on a movable support so that it can be moved across the stream of gas during the period of sampling. The sampler should be slightly inclined so that any condensation will flow toward the absorption bottles.

ABSORPTION APPARATUS FOR SO_2 AND SO_3—Figure 3 shows diagrammatically the apparatus for the determination of SO_2 and SO_3 and its relation to the other apparatus. Figure 4 is a photograph of the apparatus assembled in a portable cabinet; an Orsat apparatus is mounted on the back of the cabinet. *A* and *B* are 500-cc. wide-neck bottles. The alundum thimbles are carried by inverted Gooch funnels; that of bottle *A* is cemented to the funnel by a high-melting de Khotinsky cement; the thimble and funnel of bottle *B* are held together by a short length of rubber tubing.

The gases from the sampler which have been cooled below the dew point of H_2SO_4 pass through the dry, fine-grain alundum thimble, which retains the droplets of acid. The second bottle, *B*, contains a standard NaOH solution and some H_2O_2; 50 cc. of 0.2 normal base with 10 cc. of 3 per cent H_2O_2 are usually sufficient. The coarse alundum thimble serves as an efficient bubbler and the SO_2 is absorbed. After the sample has been collected about $^1/_4$ cubic foot (7 liters) of air is drawn through to remove any SO_2 from the first bottle.

The volume of SO_3 in the sample is found by washing out the glass sampling tube and the first alundum thimble and titrating the resultant solution with standard alkali. The washing is accomplished by passing water through the alundum tube while the suction pump is running. A 3-way cock in the glass tubing just beyond the sampler permits this to be done without dismantling the set-up. The volume of SO_2 collected in bottle *B* is found by titrating the excess NaOH with standard acid, using methyl orange or the new methyl red–methylene blue indicator.

A rate of flow of 0.1 cubic foot (2.8 liters) per minute has been found satisfactory; the rate is measured by the capillary orifice meter, and is kept constant by adjusting the relief valve ahead of the suction pump. The volume of gases drawn is computed from the average rate of flow and the time of sampling. A wet meter may be added as a check or for greater accuracy if desired, but the inherent inaccuracies in sampling the gases because of stratification and variations in rates of flow of the gas stream make the orifice flowmeter accurate enough.

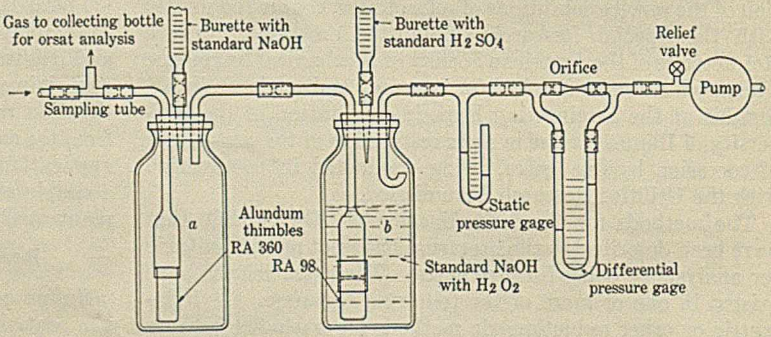
Gas to collecting bottle for orsat analysis
Burette with standard NaOH
Burette with standard H2 SO4
Relief valve
Orifice
Pump
Sampling tube
a
b
Alundum thimbles
RA 360
RA 98
Static pressure gage
Standard NaOH with H2 O2
Differential pressure gage

Figure 3—Apparatus for Determination of SO_2 and SO_3 in Flue Gases

A continuous sample of the gases is collected during the period of each sampling and is analyzed by the Orsat.

ACCURACY OF METHOD—The accuracy of the apparatus and method as described was determined by the analysis of gas-air mixtures which contained known amounts of SO_2 and SO_3. The former was generated from $NaHSO_3$ and H_2SO_4 and was stored and measured in a mercury-sealed gas buret. A measured volume of SO_2 was mixed with air and passed through a tube which contained a weighed amount of analyzed H_2SO_4 and which was heated electrically to about 450° F. (232° C.) This SO_2–SO_3–air mixture was drawn through the apparatus. The titrations were then carried out just as in the ordinary procedure. Table I gives the results of the tests.

Table I—Analysis of Synthetic Mixtures

VOLUME OF SO_2 TAKEN	VOLUME OF SO_2 FOUND	RECOVERY	WEIGHT OF SO_3 TAKEN	WEIGHT OF SO_3 FOUND	RECOVERY
Cc.	*Cc.*	*Per cent*	*Gram*	*Gram*	*Per cent*
86.3	84.5	98.0	0.1092	0.1072	98.4
88.0	84.0	95.4	0.1046	0.1055	100.8
88.8	89.1	100.2	0.1184	0.1196	101.0
88.3	89.9	101.7	0.1110	0.1063	96,0
88.0	86.9	98.8	0.1180	0.1092	99.8
Average		98.9			99.2

Table II—Theoretical Maximum Amounts of SO_2 in Flue Gases

CONSTITUENT			COAL A			COAL B
Moisture			2.90			11.35
Ultimate analysis, dry coal:						
Carbon			79.86			57.36
Hydrogen			5.02			5.41
Oxygen			4.27			18.02
Nitrogen			1.86			1.05
Sulfur			1.18			4.76
Ash			7.81			13.40
			100.00			100.00
Excess air, per cent	20	60	100	20	60	100
Dry flue-gas analysis, per cent by volume:						
CO_2	15.1	11.2	9.0	14.8	11.0	8.8
SO_2	0.08	0.06	0.05	0.45	0.34	0.27
Weight of SO_2 per cubic foot of dry gas, at standard conditions, grams	0.0681	0.0507	0.0404	0.3750	0.2795	0.2280

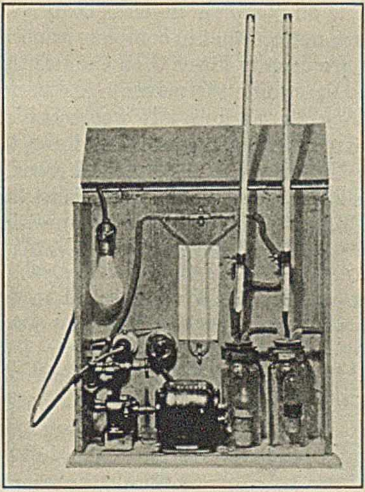

Figure 4—Assembly of Apparatus for Determination of SO_2 and SO_3

DETERMINATION OF TOTAL SULFUR IN GASES AS SO_2—A simpler apparatus and procedure can be employed if it is not desired to determine SO_2 and SO_3 separately, and a determination of the total sulfur is sufficient. One method is to use the assembly in Figure 3 but omit bottle *A*. The thimble immersed in the NaOH solution in bottle *B* is depended upon to break up the gas bubbles so that the fine SO_3 mist will be absorbed. The procedure is similar to that previously described.

Trouble caused by clogging of the thimble has been experienced with this method when the gases contain soot and tar. Figure 5 shows an alternative method which utilizes the impinger principle and has the advantage of having a lower pressure drop. Two impinger bottles are used in series so that the second bottle will absorb the sulfur gases when the first becomes sufficiently saturated to pass them. The efficiency of absorption by this method has been checked by putting a third bottle in series and also by using iodine as an indicator.

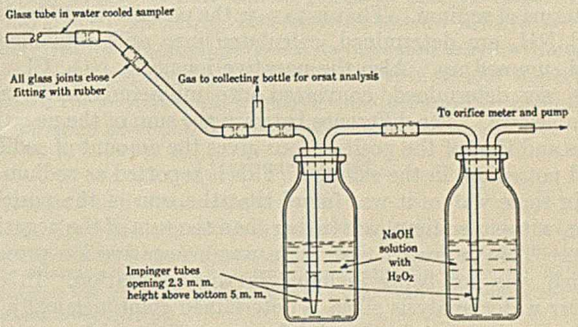
Glass tube in water cooled sampler
All glass joints close fitting with rubber
Gas to collecting bottle for orsat analysis
To orifice meter and pump
NaOH solution with H_2O_2
Impinger tubes opening 2.3 m. m. height above bottom 5 m. m.

Figure 5—Arrangement of Apparatus for Determination of SO_2 Content of Furnace Gases

Comparison of Sulfur in Gas with That in Coal Burner

The volume of sulfur gases per unit volume of flue gas will vary with the excess air. Sherman and Rice (*4*) have suggested a comparison of the ratio of sulfur to carbon in the gas; if the weight of sulfur is computed in grams per cubic foot of flue gas at 32° F. and standard pressure, the weight of carbon per cubic foot is given by

$$\text{Wt. C} = 15.2\ (CO_2 + CO)$$

where CO_2 and CO are the volumes of these gases per cubic foot of the sample from the Orsat analysis. The fraction of the total sulfur in the coal which appears in the flue gas may then be computed as follows:

$$\text{Fraction of S in gas} = \frac{\text{Ratio S:C in gas}}{\text{Ratio S:C in coal}}$$

Table II gives the theoretical amounts of SO_2 when burning two coals with different percentages of excess air.

Acknowledgment

The work of the Bureau of Mines was done at the Pittsburgh Experiment Station under the direction of P. Nicholls, supervising engineer of the Fuels Section. Acknowledgment is made of the advice and assistance of R. A. Sherman, fuel engineer, and W. A. Selvig, associate chemist. The work at the Engineering Experiment Station of the University of Illinois was under the direction of Professor D. B. Keyes of the Department of Chemical Engineering.

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Spain Looks to Promotion of Chemical Industry

The Spanish Government is giving special attention to the promotion of its chemical industry. The Minister of Public Works recently stated that 400,000 kilowatts of electric energy would be necessary to produce Spain's annual requirements of 80,000 tons of nitrates. The Council of Energy is in charge of this project, which will cover a period of years. Eventually Spain hopes to produce nitrates as cheaply as Germany.

Occurrence of Silicates in Natural Waters[1]

O. W. Rees

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THE method for boiler water analysis as used by the Illinois State Water Survey provides that sodium and potassium be determined by difference and reported in terms of sodium. That is to say, the positive ions Ca, Mg, and NH_4 are determined, calculated into milli-equivalents, and summed up. Also the negative ions SO_4, NO_3, Cl, and CO_3 are determined, converted into milli-equivalents, and summed up. The difference between the sum of the negative ions and that of the positive ions gives the amount of sodium and potassium in the sample. This is reported as sodium.

In some waters it was found that the sum of the positive ions, without sodium, was higher than the sum of the negative ions. This indicated that there was a negative ion present which was not being included in the calculation. In our boiler water analysis silica is determined colorimetrically by the use of ammonium molybdate reagent, which was suggested first by Winkler (*1*) and later modified by Neave (not published). This method determines only soluble silica, so it was thought that probably this should be reported as the silicate ion and included with the negative ions instead of reporting it as SiO_2 as is now done. This method of calculation has been tried in cases where the negative ions were low and has been found to give good results. By this method of calculation sodium has been shown in the analysis, whereas it was not shown by the old method.

In general, the sum of the hypothetical combinations is lower than the total residue obtained by evaporation. The calculation of silica as silicate and inclusion in the hypothetical combinations seems to help this difference.

The boiler water analyses in Table I illustrate the points.

Table I—Boiler Water Analyses

(Figures in milli-equivalents)

Sample 60,206

WITHOUT SiO_3		WITH SiO_3	
Positive ions:			
Ca = 2.658		Ca = 2.658	
Mg = 1.895		Mg = 1.895	
NH_4 = 0.003		NH_4 = 0.003	
Total =	4.556	Total =	4.556
Negative ions:			
SO_4 = 0.608		SO_4 = 0.608	
NO_3 = 0.171		NO_3 = 0.171	
Cl = 0.113		Cl = 0.113	
CO_3 = 3.400		CO_3 = 3.400	
		SiO_3 = 0.398	
Total =	4.292	Total =	4.690
Negatives − positives	−0.264	Negatives − positives	0.134

Sample 63,413

WITHOUT SiO_3		WITH SiO_3	
Positive ions:			
Ca = 3.317		Ca = 3.317	
Mg = 4.086		Mg = 4.086	
NH_4 = 0.006		NH_4 = 0.006	
Total =	7.409	Total =	7.409
Negative ions:			
SO_4 = 0.792		SO_4 = 0.792	
NO_3 = 0.000		NO_3 = 0.000	
Cl = 0.226		Cl = 0.226	
CO_3 = 6.000		CO_3 = 6.000	
		SiO_3 = 0.431	
Total =	7.018	Total =	7.449
Negatives − positives	−0.391	Negatives − positives	0.040

The effect of including SiO_3 in the hypothetical combinations of these two analyses is shown in Table II.

Table II—Hypothetical Combinations with and without SiO_3

Sample 60,206

	WITHOUT SiO_3 *P. p. m.*	WITH SiO_3 *P. p. m.*
Sodium nitrate, $NaNO_3$	...	11.4
Ammonium nitrate, NH_4NO_3	0.2	0.2
Magnesium nitrate, $Mg(NO_3)_2$	12.8	2.5
Magnesium chloride, $MgCl_2$	5.5	5.4
Magnesium sulfate, $MgSO_4$	37.7	36.6
Magnesium carbonate, $MgCO_3$	39.0	48.1
Calcium carbonate, $CaCO_3$	129.0	113.1
Calcium silicate, $CaSiO_3$	...	23.2
Silica, SiO_2	12.0	...
Iron oxide, Fe_2O_3	0.0	0.0
Magnesium oxide, MnO	0.0	0.0
Total hypotheticals	236.2	240.5
Residue (by evaporation)	278.0	278.0

Sample 63,413

	WITHOUT SiO_3 *P. p. m.*	WITH SiO_3 *P. p. m.*
Sodium chloride, NaCl	...	2.3
Ammonium chloride, NH_4Cl	0.3	0.3
Magnesium chloride, $MgCl_2$	10.8	8.6
Magnesium sulfate, $MgSO_4$	48.9	47.7
Magnesium carbonate, $MgCO_3$	123.8	131.3
Calcium carbonate, $CaCO_3$	161.4	144.4
Calcium silicate, $CaSiO_3$	...	25.0
Silica, SiO_2	13.0	...
Iron oxide, Fe_2O_3	0.7	0.7
Manganese oxide, MnO	0.0	0.0
Total hypotheticals	358.9	360.3
Residue (by evaporation)	373.0	373.0

It will be noted that the difference in the sums of the hypothetical combinations is small. However, the sums are increased slightly. (In calculating boiler analyses where the positive ions, without sodium, are higher than the negatives, the percentage error is determined and distributed among all the ions.)

As further proof that silicates are present as such in water and should be included with the negative ions, some calculations were made on complete mineral analyses. For several years it has been noticed that in complete mineral analyses the negative ions are usually lower than the positive ions. It is the practice to determine the percentage error and distribute this error among all the ions. It was thought that the inclusion of silicate as a negative ion might lower this percentage error. Table III bears this out. In all cases, however, the inclusion of silica as the silicate ion made the sum of the negative ions higher than the sum of the positive ions. This is just the reverse of the situation when silicate is not included.

Table III—Error between Positive and Negative Ions

SAMPLE	WITHOUT SiO_3 *Per cent*	WITH SiO_3 *Per cent*
63,154	2.71	0.18
63,279	3.86	0.17
63,280	2.85	0.90
63,282	1.62	2.07
63,293	1.36	0.91
62,780	1.09	0.61
63,008	2.85	2.81
62,779	0.82	0.83

Further calculations were made in which the value for sodium was arrived at by difference and compared with the actual value as determined by the chloroplatinate method. In one case silicate was not included as a negative ion and in the other case it was included. It will be noted in Table IV that where silicate is omitted the values for sodium are low, while the inclusion of silicate gives values which check more closely the determined values.

Table V gives a comparison between the residue (by evaporation) of these mineral analyses and the hypothetical combinations in which silica is included in one case as silicate ion and in the other as SiO_2. This table indicates that calculating silica as silicate alters the hypotheticals very little.

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[1] Presented before the Division of Water, Sewage, and Sanitation Chemistry at the 77th Meeting of the American Chemical Society, Columbus, Ohio, April 29 to May 3, 1929.

Table IV—Comparison of Calculated and Determined Values for Sodium

SAMPLE	DETD.	BY DIFFERENCE Without SiO_3	With SiO_3
	P. p. m.	*P. p. m.*	*P. p. m.*
63,154	56.6	45.2	57.3
63,279	18.7	5.9	19.3
63,280	20.3	10.5	23.4
63,282	43.8	36.6	53.4
63,293	59.9	51.1	65.9
62,780	83.7	77.4	87.3
63,008	11.1	1.0	21.5
62,779	107.9	103.6	112.4

Table V—Comparison of Values for Residue and Sum of Hypothetical Combinations

SAMPLE	RESIDUE (BY EVAPORATION)	SUM OF HYPOTHETICAL COMBINATIONS Silica as SiO_2	Silica as SiO_3
	P. p. m.	*P. p. m.*	*P. p. m.*
63,154	566	556.3	555.9
63,279	381	377.2	368.1
63,280	352	377.2	378.5
63,282	558	569.5	566.9
63,293	877	827.3	825.8
62,780	822	741.2	740.6
63,008	409	426.3	425.9
62,779	684	666.5	666.4

In soft waters of comparatively low mineral content, more commonly in surface waters, we have often found that our boiler water analysis shows the presence of no sodium. Repeated checks on the determinations made have shown them to be correct and only by the inclusion of silica as the silicate ion is the presence of sodium shown. In one case the inclusion of silica as the silicate ion made the analysis show the presence of 3 p. p. m. of sodium. (Of course this figure represents sodium and potassium combined.) By actual determination 6 p. p. m. of sodium and potassium combined were shown to be present.

In harder waters of comparatively high mineral content, and in waters where the silica is quite small in amount, the inclusion of the silicate ion is probably not so important. While, strictly speaking, we believe it should always be included, yet for practical purposes its inclusion may be limited. We suggest that where the silicate amounts to half the error between the positive and negative ions it should be included. Otherwise it need not be included.

Literature Cited

(1) Winkler, *Z. anal. Chem.*, **54**, 365 (1914).

Note—The silica determinations for the boiler water analyses of Samples 60,206 and 63,413 were made colorimetrically. The silica determinations in the mineral analyses were all made gravimetrically except No. 63,282. This sample had a rather high turbidity, so a colorimetric determination was made on a filtered sample.

The analyses used in the above tables were picked at random from the files of the State Water Survey. All samples were collected in bottles of resistant glass and analyses were made soon after collection. See Collins and Riffenburg, IND. ENG. CHEM., **15**, 48 (1923).

Determination of Silica in the Presence of Fluorspar[1]

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THE determination of silica in the presence of fluorspar has always been accomplished either by difficult and complex analytical procedures or by rapid arbitrary control methods of doubtful precision. The method is usually one of the following types: fusion with alkali carbonate followed by extraction with water and treatment of the filtrate with either ammonium carbonate–zinc oxide or mercury–ammonium carbonate; fusion with lead oxide; extraction of the ore with acetic acid. Stadeler (*3*) studied five methods for the determination of silica in the presence of fluorine and found only one, that of Berzelius, to give reliable results if the fluorine content was above one per cent. The method of Berzelius, however, is long and tedious, even though accurate. The present study was undertaken to determine whether a more simple method could be found for the determination of silica in the presence of fluorspar.

Jannasch and Weber (*1*) in 1899 reported that there was no loss of silica when a silicate containing a fluoride was fused with boric oxide over an oxygen blast lamp. The fluorine was expelled as boron trifluoride. Meulen (*2*) in 1923 proved that calcium fluoride could be decomposed by sulfuric acid in the presence of boric acid without etching glass. This was confirmed in the following experiments. The hydrofluoric acid liberated by the acid treatment immediately reacts with the boric acid to form boron trifluoride, which does not attack glass. In all the experiments performed, Pyrex beakers were used and in no case was there the slightest evidence of etching from repeated determinations in the same beakers. The fluorspar was decomposed with an acid in the presence of an excess of boric acid. Hydrochloric, sulfuric, and perchloric acids were each separately used for the decomposition. Preliminary results showed that the perchloric-boric acid decomposition gave the most satisfactory results. That the perchloric acid was more satisfactory was due to the fact that calcium perchlorate is very soluble and can be more easily removed from the residue than calcium sulfate.

The following procedure was used in all of the subsequent determinations of silica: A 0.5-gram sample of the finely ground fluorspar was treated with 15 ml. of 20 per cent perchloric acid saturated with boric acid at 50° C. The ore was digested with this solution in a Pyrex beaker until fumes of perchloric acid had come off for 4 to 5 minutes. A few milliliters of water were then added, and the fuming repeated for 4 to 5 minutes. The residue was then diluted to 50–75 ml., the solution heated, and the silica and insoluble material filtered off. The filter paper was washed first with a dilute solution of perchloric acid and finally with hot water until free of calcium salts as shown by tests with ammonium oxalate. The filter paper containing the silica was ashed in a platinum crucible, two drops of concentrated sulfuric acid added, and the residue ignited to constant weight. The silica in the residue was determined in the usual manner by volatilization with hydrofluoric acid. An examination of the residue with a microscope before volatilization with hydrofluoric acid showed that there was no undecomposed calcium fluoride.

A sample of C. P. calcium fluoride which was analyzed for silica and found free of this substance was used in making the following tests. A very pure specimen of quartz was used as a source of the silica. The analysis of the quartz showed that it contained 99.92 per cent silica.

Constant weights of the powdered calcium fluoride were mixed with varying amounts of pulverized quartz and the silica was determined by decomposition with the perchloric-

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[1] Presented before the Division of Industrial and Engineering Chemistry at the 77th Meeting of the American Chemical Society, Columbus, Ohio, April 29 to May 3, 1929.

boric acid mixture. These results show that the silica content of a calcium fluoride–quartz mixture can be determined very accurately. Tests were made on mixtures containing 0.5 gram of calcium fluoride and from 0.01 to 0.1 gram of quartz. The method is no doubt applicable to samples containing larger amounts of quartz. The results are listed in Table I.

Table I—Determination of Silica in Fluorspar-Quartz Mixture

(Weight of CaF_2, 0.5000 gram)

SiO_2 Contained	SiO_2 Detd.	Error	SiO_2 Contained	SiO_2 Detd.	Error
Gram	*Gram*	*Gram*	*Gram*	*Gram*	*Gram*
0.0100	0.0102	+0.0002	0.0498	0.0495	−0.0003
0.0100	0.0099	−0.0001	0.0498	0.0494	−0.0004
0.0199	0.0196	−0.0003	0.0511	0.0511	0.0000
0.0200	0.0198	−0.0002	0.0527	0.0527	0.0000
0.0200	0.0199	−0.0001	0.0987	0.0988	+0.0001
0.0217	0.0217	0.0000	0.0987	0.0987	0.0000
0.0349	0.0347	−0.0002	0.0998	0.0994	−0.0004
0.0350	0.0347	−0.0003	0.0998	0.0994	−0.0004
0.0475	0.0477	+0.0002			

A synthetic sample containing 12.60 per cent silica was prepared from a sample of fluorspar and quartz. The results of a series of analyses on this sample are given in Table II.

In order to test further the accuracy of the perchloric-boric method, a Bureau of Standards sample of fluorspar No. 79 was obtained. The silica content as determined by the Bureau of Standards was 1.89 per cent with a maximum deviation of ±0.15 per cent. The results of a series of determinations made in this laboratory using the perchloric-boric acid method of decomposition was 1.87 per cent silica, the maximum deviation in results being ±0.05 per cent.

Table II—Determination of Silica in Synthetic Sample

(Weight of sample, 0.5000 gram)

SiO_2 Contained	SiO_2 Found	Deviation	SiO_2
Gram	*Gram*	*Gram*	*Per cent*
0.0630	0.0626	−0.0004	12.52
0.0630	0.0630	0.0000	12.60
0.0630	0.0629	−0.0001	12.58
0.0630	0.0634	+0.0004	12.68

Tests were also made to determine whether perchloric acid could be used alone for decomposition without losing silica. The analysis of synthetic samples and the Bureau of Standards sample for silica gave low results.

Conclusions

(1) Fluorspar can be decomposed by treatment with a mixture of perchloric and boric acids without an appreciable loss of silica.

(2) The method is rapid and is capable of a high degree of precision.

(3) Decomposition of the fluorspar with perchloric acid alone gives low results.

Literature Cited

(1) Jannasch and Weber, *Ber.*, **32**, 1670 (1899).
(2) Meulen, *Chem. Weekblad*, **20**, 59 (1923).
(3) Stadeler, *Stahl Eisen*, **47**, 662 (1927).

Determination of Total Carbon in Soils[1]

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THE great diversity of the soil carbon compounds introduces certain difficulties into the determination of total carbon that are not encountered in ordinary analyses. The wet combustion method (*3*) commonly employed has two major disadvantages—an elaborate train to remove the large quantities of sulfur dioxide and sulfur trioxide fumes, and the inconvenience of handling boiling sulfuric acid. Further, there is the possibility that inert portions of the organic matter may not be completely oxidized by this method, especially in heavy soils, because of the relatively low temperature of the reaction, approximately 400° C. The difficulty of destroying the carbon that often collects on the sides of the flask in Kjeldahl digestions points strongly to the possibility of such an error.

These objections are not found in the dry combustion method described by Salter (*1*). It seemed to give promise of being a more convenient method and at the same time of yielding more accurate results than the wet combustion method, and therefore an investigation of its suitability for making a large number of total carbon determinations in soils was undertaken.

The great "dilution" of the soil organic matter by inert mineral material suggested the possibility of dispensing with the usual two-unit furnace for organic work and of inserting the loaded boat immediately into the hot unit containing the copper spiral, thus avoiding the loss of time occasioned by heating the charge gradually. The mineral portion of the soil, usually exceeding 95 per cent, is relied on to retard volatilization sufficiently to permit complete oxidation. If the volatile compounds are driven off too rapidly to be fully oxidized, the results will be low and the method unsatisfactory. No reference was found in the literature concerning this point, and therefore it was thought necessary to give it some attention.

Samples whose carbon content had been determined by the wet combustion method were available. It was assumed that, should the dry combustion figures check with the above and in addition be consistently reproducible, the method could be called satisfactory.

Preliminary work indicated that the dry combustion results were too low, as is shown in Table I. In addition to the possibility of too rapid volatilization, it seemed likely that the oxygen might not readily penetrate through the charge to react with the more inert carbon compounds. Both of these difficulties should be overcome by a suitable oxidizing agent in the bottom of the boat. Manganese dioxide was chosen because of its infusibility and the high temperature at which it releases oxygen, 570° C.

Table I—Comparison of Methods

(Grams of CO_2)

Soil	Dry Combustion with MnO_2	Dry Combustion without MnO_2	Wet Combustion
	Gram	*Gram*	*Gram*
234	0.0840	....	0.0820
236	0.0545	....	0.0528
238	0.0550	....	0.0536
244	0.0505	....	0.0526
250	0.0510[a]	....	0.0480[a]
251	0.0518	....	0.0500
256	0.0420	....	0.0439
267	0.0525	0.0500	0.0535
249	0.0530[a]	....	0.0490[a]
270	0.0985	0.0930	0.0980
273	0.0630	0.0590	0.0635
276	0.0990	0.0950	0.0993

[a] Difference exceeds experimental error.

With this modification the agreement between the two methods is good, in general, as indicated in Table I. The dif-

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[1] Received April 5, 1929.

ferences exceed the limits of experimental error in two cases, Samples 250 and 249. It is thought that in these cases the wet method failed to oxidize the carbon completely, as was previously suggested. Table II shows the increased amounts of carbon dioxide obtained when manganese dioxide was used. As would be expected, the difference increases with increasing carbon content. Sample 7 is a calcareous subsoil, low in organic carbon, and it is seen that with this sample the same results were secured without manganese dioxide as with it.

Table II—Effect of MnO_2 Using Dry Combustion Method
(Grams of CO_2)

SOIL	WITH MnO_2 *Gram*	WITHOUT MnO_2 *Gram*	DIFFERENCE *Gram*
276	0.0992	0.0950	0.0042
458	0.0124	0.0114	0.0010
Clyde 1	0.2510	0.2415	0.0095
273	0.0630	0.0590	0.0040
267	0.0525	0.0500	0.0025
417	0.0682	0.0640	0.0042
7	0.2150	0.2150	0.0000

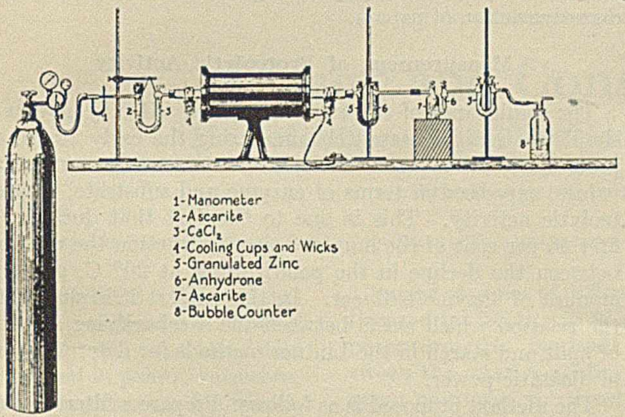

Figure 1—Combustion Train

While experimental error is estimated at ±0.0005, the value ±0.0003 more nearly approximates the variations found in running one hundred samples in duplicate. This smaller error only slightly exceeds balance errors, for with a 100-gram load sensitivity scarcely exceeds 0.0001. This figure is doubled on subtracting two readings. Moreover, account must be taken of errors of weighing and transferring the charge.

Sample 276 was determined on fifteen different days, it being used as a "standard" to check the apparatus. The values obtained with this sample all fell within the limits 0.0990 ± 0.0005, as given in Table I; other samples gave equally good agreement when redetermined. It is believed that the above evidence is sufficient to justify the statement that complete oxidation is obtained with this modified dry combustion method.

The details and precautions necessary in making this determination are evident to anyone familiar with dry combustion work. With a 2-gram charge about 0.25 gram of manganese dioxide was found satisfactory unless the carbon dioxide released exceeded 0.1500 gram, in which case the charge was reduced to 1 gram. Larger amounts of manganese dioxide tended to cause minute explosions, scattering material over the interior of the tube. This resulted in erratic blanks and seemed to reduce the efficiency of the copper as a catalyst. The temperature must be sufficient to decompose calcium and magnesium carbonates, approximately 950° C. The train must provide for removal of such compounds as nitrogen peroxide, sulfur dioxide, and sulfur trioxide, in addition to considerable water. Anhydrone (*2*) was found a desirable substitute for phosphorus pentoxide in removing water vapor from the train because of its ease of handling.

The time allowed for a combustion was 10 minutes. Table III shows that practically all the carbon dioxide was expelled in 5 minutes, so the 10-minute period chosen should be quite safe. The rapid flow of oxygen used, 10 to 15 liters per hour, and the presence of manganese dioxide probably account for the short reaction time.

Figure 1 shows the set-up of the combustion train used in this study.

Table III—Effect of Time of Combustion Using Modified Dry Combustion Method
(Grams of CO_2)

SOIL	5 MINUTES *Gram*	10 MINUTES *Gram*	15 MINUTES *Gram*
270	0.0985	0.0985	0.0985
276	0.0990	0.0990	0.0990
Clyde 1	0.2490	0.2510	0.2510
7	0.2140	0.2150	0.2150

Literature Cited

(1) Salter, J. IND. ENG. CHEM., **8**, 637 (1916).
(2) Smith, *Ibid.*, **19**, 411 (1927).
(3) Waynick, *Ibid.*, **11**, 634 (1919).

Action of Papain on the Polarization of Gelatin[1]

A New Method of Measuring Proteolytic Activity

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WHEN a gelatin solution is cooled, its polarization remains practically constant until the temperature reaches 35° C. (*4*). From there downward the levo-rotation rapidly increases. When warmed, the reverse change takes place. Thus, in the table below it is shown that the polarization changed from −13.4° V. at 20° C. to −7.3° V. at 35° C. Recent work by Kraemer (*2*) and by Kraemer and Fanselow (*3*) has revealed the extraordinary sensitiveness of the polarization of chilled gelatin to temperature and to pH, and Fanselow (*1*) has shown the remarkable influence of electrolytes.

The mutarotation of gelatin is rapidly lowered by proteolytic enzymes. Papain, pepsin, pancreatin, and the proteolytic enzyme of malt are all active.

The work described herein was done to develop, if possible, a method for the determination of proteolytic power, through the measurement of the rate of decline of the mutarotation of gelatin. The enzyme papain was used throughout. It was found necessary to control the pH and after the action of the enzyme to refrigerate the solution long enough for the mutarotation to assume the highest practicable value when the solution was warmed to the temperature selected for the readings. It was also necessary to wait for some time after warming to the selected temperature to allow time for the readings to become constant. The temperature arbitrarily chosen was 20° C.

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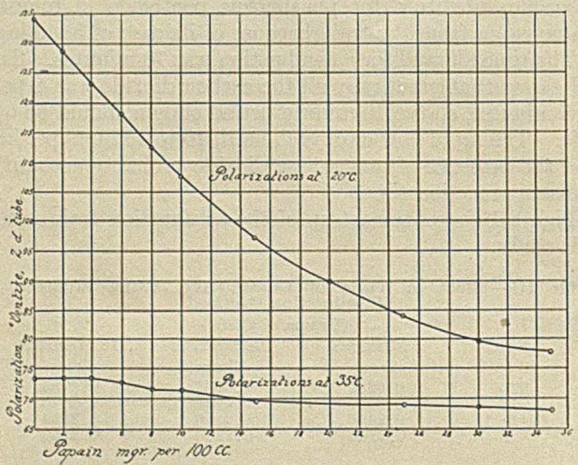
[1] Presented before the Division of Sugar Chemistry at the 77th Meeting of the American Chemical Society, Columbus, Ohio, April 29 to May 3, 1929.

Changes in Polarization of Gelatin during Digestion

The following experiment was made to show the changes in polarization of gelatin during digestion with papain:

A commercial food gelatin containing 10.4 per cent moisture and 1.15 per cent ash was used. This was a blend of the second extraction of gelatin from pigskin. This gelatin was produced by an acid cook, the skins having been acidified to the proper pH with hydrochloric acid. Its solution showed no turbidity at 4.8 pH, but gave marked clouding at pH 6.8.

A gelatin solution was made containing 2 grams of air-dry gelatin per 100 cc. Its pH was 4.7. The papain solution contained 1 gram per liter and polarized at −0.35° V. in a 2-dc. tube. Eleven flasks of gelatin solution were prepared, each containing 50 cc. of the above gelatin solution and 10 cc. of Walpole's acetate buffer of 4.8 pH (8 cc. of 1 *N* acetic acid and 12 cc. of 1 *N* sodium acetate, diluted to 100 cc.). They were warmed to 45° C. in a thermostat. A series of flasks was then prepared containing varying amounts of the above papain solution and sufficient water to bring the volume of each to 40 cc. These solutions were also heated to 45° C. in the thermostat.



The gelatin solutions were poured one by one into the papain-containing solutions, time of mixing being noted. The flasks were then stoppered and the solutions heated at 45° C. for an hour. They were then cooled sharply in ice water and refrigerated overnight at about 5° C. They were then warmed to 20° C. in a bath kept at 20° C., let stand for at least 1 hour at 20° C., and polarized at 20° C. and at 35° C. in a jacketed tube. A portion of the control solution, which contained no papain, was placed in a 2-dc. polariscope tube as soon as it cooled after removal from the thermostat, and refrigerated with the others. The tube was placed in the water bath at 20° C. for an hour and then polarized at 20° C. Destruction of jelly power by papain took place during the early part of the destruction of the mutarotation, and no difficulty was experienced in pouring the solutions digested with papain into the polariscope tube, even those containing but 2 and 4 mg. of papain, respectively. These solutions were, however, somewhat more viscous than the others.

The polarizations given below are corrected for the slight rotations due to the papain.

The polarizations at 20° C. decreased from −13.4° V. to −7.75° V. as the papain was increased to 35 mg. The relation between the polarization declines at 20° C. and the papain present was linear to the point at which about 40 per cent of the mutarotation was destroyed by the enzyme. The polarization at 35° C. declined but slightly—from −7.3 to −6.8.

The mutarotation of the gelatin control was 6.1° V. Heating the gelatin with 35 mg. of papain destroyed over four-fifths of the mutarotation, the final value observed then being but 0.95° V.

Changes in Polarization at 20° and 35° C. of Gelatin Solutions Heated for 1 Hour at 45° C. with Papain at 4.8 pH

Papain	Polarizations At 20° C.	Polarizations At 35° C.	Mutarotation
Mg. per 100 cc.	*° V.*	*° V.*	*° V.*
0	−13.4	−7.3	6.1
2	−12.85	−7.3	5.55
4	−12.3	−7.3	5.0
6	−11.8	−7.25	4.55
8	−11.25	−7.15	4.10
10	−10.75	−7.15	3.60
15	− 9.7	−6.95	2.85
20	− 9.0	−6.95	2.05
25	− 8.4	−6.90	1.5
30	− 7.95	−6.85	1.1
35	− 7.75	−6.80	0.95

These regular declines of the rotations of gelatin at 20° and 35° C. may reasonably be regarded as measures of the digestive action of papain.

Measurement of Proteolytic Activity

The significance of the work is twofold. It may give us a simple method of accurately measuring the early stages of proteolytic action. It also may enable us to assign numerical values, expressed in terms of enzyme and substrate, to proteolytic activity. This is due to the fact that during the first 40 per cent of the mutarotation destruction the relation between the decline in the polarizations at 20° C. and the amount of enzyme is linear. In this respect it is similar to the relation which exists between the saccharifying enzyme of malt and starch in the Lintner methods for determination of diastatic power.

The method proposed is as follows: Prepare a filtered solution of a commercial food gelatin containing 2 grams per 100 cc., using preferably a gelatin made from acid-conditioned stock showing no turbidity near pH 4.8 and having a pH of about 4.8. For each test prepare two solutions, one consisting of 50 cc. of the above solution of gelatin and 10 cc. of Walpole's acetate buffer of 4.8 pH, the other consisting of 40 cc. of a mixture of the papain solution and water. Warm both solutions to 45° C. in a water bath at 45° C. Then pour the gelatin solution into the enzyme solution, note the time, stopper the flask containing the mixed solutions, and digest at 45° C. for an hour, or other time selected. (If this time is much longer than an hour the solution should be preserved by shaking with a few drops of toluene.) Cool sharply, preferably in ice water, refrigerate for 16 hours at about 5° C., warm to 20° C. in a water bath at 20° C., let stand for at least 1 hour at this temperature, and polarize. Correct for the optical activity of the papain solution. The result is the 20-degree polarization of the partly digested gelatin.

To determine the percentage of gelatin digested the polarization of the original gelatin solution is required, and also that of the gelatin solution when digestion is practically complete. These two determinations, which may be determined once for all on a given lot of gelatin, should be made as follows.

Polarization of Gelatin at 20° C.—Prepare a check lot, using no papain, heating the gelatin, buffer solution, and water in the manner above described. After cooling put a sample of the solution in a polariscope tube, chill, refrigerate for 16 hours at about 5° C., warm to 20° C., keep at 20° C. for an hour, and polarize at 20° C.

Polarization of Digested Gelatin at 20° C.—Prepare two solutions of gelatin and buffer, and papain and water as described above, using sufficient of an active papain solution to lower the 20° C. polarization to a value that is nearly constant. Papain solution equal to about 50 mg. of an active papain is sufficient. Mix, incubate, chill, refrigerate, warm to 20° C., let stand, and polarize at 20° C. Correct for the polarization due to the papain solution.

Calculate the percentage of gelatin digested. If over 40 per cent is digested, the determination must be repeated using less papain or a shorter time.

Compute the proteolytic activity by the following formula:

$$P = \frac{W}{w\,t}$$

where P = proteolytic power
W = weight of air dry gelatin digested
w = weight of papain
t = time in hours

Examples. The polarization of the original gelatin solution at 20° C. under the conditions described was −13.3 ° V., that of the digested gelatin was −6.7° V. The polarization due to the papain solution used for digesting the gelatin was −0.5° V. Thus, the polarization of the digested gelatin corrected for that of the papain was −6.2° V.

The results obtained in the assay of five samples of papain were as follows:

Sample	Papain Used	Polarization at 20° C.	Fall in 20° C. Polarization	Gelatin Digested	Proteolytic Power
	Mg.	° *V.*	° *V.*	*Per cent*	
1	5	−11.0	2.3	32.4	65
2	5	−11.75	1.55	22.0	44
3	5	−12.05	1.25	17.6	35
4	5	−12.15	1.15	16.2	32
7	5	11.2	2.1	29.5	59

Literature Cited

(1) Fanselow, Colloid Symposium Monograph, Vol. VI, p. 237.
(2) Kraemer, *Ibid.*, Vol. IV, p. 102.
(3) Kraemer and Fanselow, *J. Phys. Chem.*, **27**, 1169 (1925).
(4) Smith, *J. Am. Chem. Soc.*, **41**, 135 (1918).

Nature and Constitution of Shellac

II—Potentiometric Titrations in 95 Per Cent Ethyl Alcohol[1]

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Varied samples of different grades of shellac have been titrated for acidity in 95 per cent ethyl alcohol using a potentiometric method. A comparison is made between the relative acidity of shellac in this solvent with some common spirit-soluble acids and other soluble gums. This work shows that the total acidity of the varied solutions can be determined with a high degree of accuracy. Shellac gives solutions whose acidity is comparable with that of the weak organic acids, and it is but slightly more acidic than the other spirit-soluble gums. The possibilities of using this method as a guide in studies of such problems as the livering of paints is mentioned.

ALTHOUGH several substances showing acid characteristics are used in paints, varnishes, and lacquers, our knowledge of the effects of different hydrogen-ion concentrations upon the properties of protective coating compositions is very limited. Certainly resins and some oils should give measurable hydrogen-ion concentrations in those compositions containing ionizing solvents such as the alcohols. Furthermore, it is possible that their behavior in these compositions may have some analogy to the conditions that may exist in poorer conducting systems. A comparison of the ionizing property of shellac with other spirit-soluble resins and some organic acids, as presented in this paper, therefore seems highly desirable. This information may prove to be of considerable assistance in the investigation of such problems as the livering of paints and varnishes, where the nature of the acids, and not the total acidity, appears to be the important factor when basic substances such as the metal oxides are incorporated in the protective coating (*3, 6, 7*).

In such investigations the potentiometric method for titrating acidity would appear to possess some advantages. For example, one can distinguish between strong mineral acids and weak organic acids by the shape of the titration curves. This method can also be used when the depth of color of the solutions prohibits the use of indicators. The feasibility of employing such methods in non-aqueous solvents has already been demonstrated (*1, 10, 11*). For example, Seltz and McKinney have titrated benzoic and stearic acids and the acidity of three turbine oils in amyl alcohol with quinhydrone electrodes.

Chemical Nature of Resin Acids

The acid character of natural resins is usually assumed to be caused by the presence in these materials of a group of substances known as the resin acids. In considering the chemical nature of these acids, it is of interest to remember that shellac is an insect product whereas the other resins are of botanical origin. It would appear from what is known of their chemistry that the essential constituents comprising the shellac molecules are aliphatic compounds while many of the other resins are readily reduced by zinc dust to aromatic hydrocarbons (*2, 4, 8*). Nagel and Körchen (*8*) consider resins such as amber, copal, and some of the rosins to contain extremely weak acids in comparison with shellac, which they believe has a pronounced acid character. They attribute this supposed difference in acidity either to marked differences in the ratio of number of carbon atoms to carboxyl groups in their molecules or to the existence of phenol groups in place of carboxyl groups in the resin acids in gums other than shellac. Their conclusions are based upon their success in preparing a methyl derivative of shellac both by Fischer's method of esterification with 3 per cent hydrogen chloride as catalyst and by the interaction of shellac with diazomethane. The methyl derivative so prepared had practically a zero acid value. They also observed the slight corrosion effects of alcohol solutions of shellac upon several metals.

Choice of Solvent

For this potentiometric work we had the choice of several solvents (*3*). However, 95 per cent ethyl alcohol was chosen for the following reasons: It is one of the best, and the most commonly used solvent (either pure or when denatured with

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[1] Presented before the Division of Paint and Varnish Chemistry at the 77th Meeting of the American Chemical Society, Columbus, Ohio, April 29 to May 3, 1929. This article is contribution No. 2 from the Shellac Research Bureau. For the first article of this series see Ind. Eng. Chem., **21**, 226 (1929).

[2] Research fellow, Shellac Research Bureau.

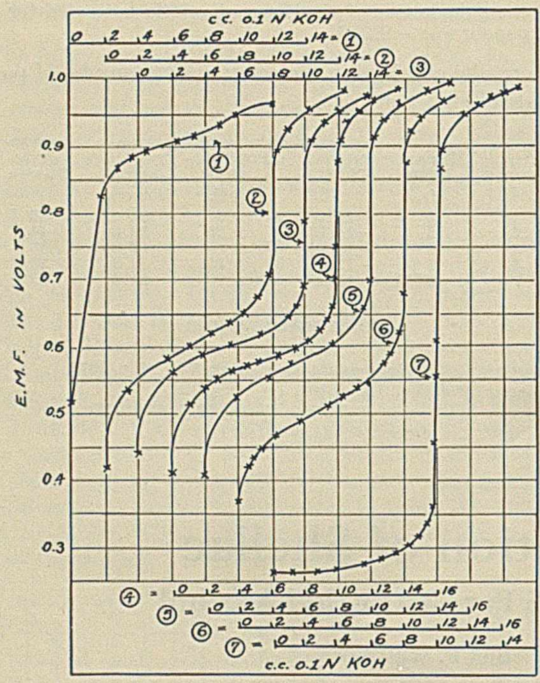

Figure 1—Pure Organic Acids

1—Carbolic acid (phenol)
2—Glutaric acid
3—Lauric acid
4—Benzoic acid
5—Cinnamic acid
6—Malic acid
7—Sulfuric acid

methanol) for shellac. As a solvent it is in many respects very similar to water. A fair degree of constancy of composition can be obtained by a simple distillation, and it may be readily obtained in quantity. Hence the technic (with some modifications) and the results obtained should show a fairly close analogy to the best known liquid systems, water solutions, while at the same time the method employed with this solvent should be applicable to others of a similar type.

Apparatus and Materials Used

The apparatus consisted of the usual potentiometric set-up consisting of potentiometer, lamp and scale galvanometer, and reference and indicating electrodes in a titration vessel. The potentiometer (Leeds and Northrup) had a range of 0 to 1.61 volts and an accuracy of 0.5 millivolt with resistances less than 10,000 ohms. The galvanometer had a sensitivity of 40 megohms and a period of 3 seconds. The indicating electrode was a hydrogen electrode with the Hildebrand type of electrode vessel. This electrode was chosen because of its accuracy in measuring alkaline solutions. The reference electrode was a calomel half-cell containing a saturated solution of lithium chloride in 95 per cent alcohol—i. e., Hg/Hg_2Cl_2–LiCl 95% C_2H_5OH //. This cell gives a constant voltage and has a high conductivity. Because of the slight solubility of potassium chloride in ethyl alcohol, such cells were found to give too low a conductivity for accurate readings of the galvanometer. The titration vessel consisted of a 100-cc. beaker tightly fitted with a rubber stopper carrying the above hydrogen and calomel cells, a buret, and hydrogen gas outlet. The outlet was sealed from air by dipping into 95 per cent alcohol. The alkali used for titrating was a 0.1 *N* solution of potassium hydroxide in 95 per cent alcohol.

Preparation of Hydrogen Electrodes

It was found that Popoff's method for preparing the hydrogen electrodes (*9*) gave the best results. The gold plating of the electrode before deposition of platinum black was not necessary. Electrodes were first cleaned by electrolyzing as anode in concentrated hydrochloric acid. They were then washed with distilled water and coated with platinum black as cathode in a 3 per cent platinic chloride solution containing $^1/_{40}$ per cent lead acetate, washed with distilled water, electrolyzed in dilute sodium hydroxide, and then in 10 per cent sulfuric acid solution. After washing with distilled water, they were allowed to stand for a few minutes in 95 per cent alcohol before use.

Equilibrium with the hydrogen electrodes could not be successfully obtained unless air was excluded by using the closed titration vessel described. With this method initial equilibrium was obtained in 5 to 10 minutes. However, during the titration equilibrium was obtained after each new addition of alkali within 3 minutes with the pure organic acids and within 5 to 7 minutes with the acids of the resins. This difference is undoubtedly due to the difference in the viscosities of the two types of solutions.

Procedure

In order more readily to compare the relative acidity of the different solutions by means of the shape of the titration curves, solutions of equivalent total titratable hydrogen-ion concentrations are desired. For this reason dry weights of each of the substances were taken such that each titration would require 10 cc. of 0.1 *N* alkali; instead of taking 1-gram samples of the resins as is customary. In the case of the pure monobasic acids this is equal to 0.001 mol; with the dibasic acids, one-half of that weight. The samples were dissolved in 25 cc. of 95 per cent ethyl alcohol, which had been redistilled from a fairly concentrated solution of potassium hydroxide containing a small amount of silver nitrate. The beaker containing the solution was then tightly stoppered

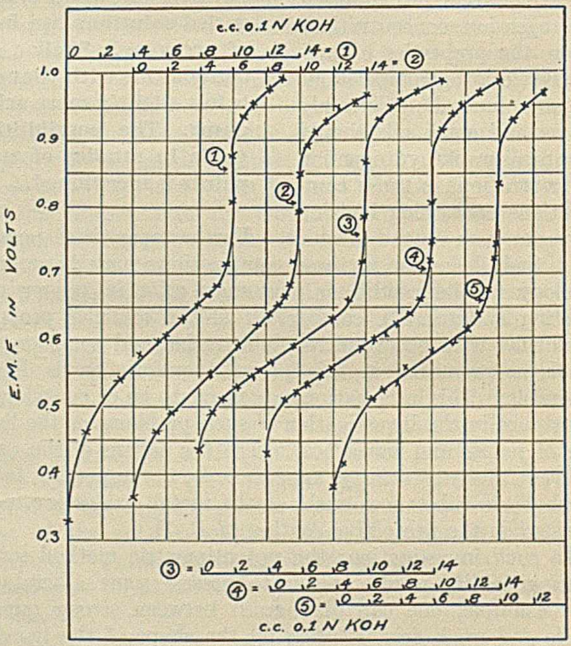

Figure 2—Shellac

	Acid Value
1—Wax-free bleached shellac	117.6
2—Dry bleached shellac	85.7
3—Seed-lac	70.6
4—T. N. Pure orange shellac	67.5
5—U.S.S.A. T. N. orange shellac	73.3

Note—Samples 3, 4, and 5 were analyzed by J. W. Paisley, O. M. Olsen, and F. S. White, of the Chemists' Committee of the U.S.S.I.A., for iodine value and alcohol-insoluble with following results:

	I. V.	A. I.
Seed-lac	15.2	4.86
T. N. Pure	18.0	3.12
U.S.S.A. T. N.	25.1	3.98

as described, and hydrogen gas run through the titration vessel for 10 minutes. The hydrogen electrode was then inserted and the gas bubbled at a rate of one bubble per second. Increments of 1 to 2 cc. of alkali were added. Constancy in voltage was awaited before recording readings. The alkali had been previously standardized against weighed amounts of pure benzoic acid.

Summary and Discussion of Results

The data are presented in graphical form in Figures 1 to 3. This work clearly shows that it is possible to titrate the acidity of shellac and spirit-soluble resin solutions potentiometrically in 95 per cent ethyl alcohol. In all cases except the weakly acidic phenol, sharp changes in the slope of the titration curves take place when sufficient alkali has been added to neutralize the acidity. This shows that the total acidity of these solutions can be determined with a high degree of accuracy. It indicates that substances like shellac, and the resins studied, behave as acids of low molecular weight, even though we are led to believe, from other considerations, that they give colloidal solutions in such solvents as alcohol. This seems to be especially the case with gum mastic, where even to the eye the solutions are clearly suspensions. It is possible, with substances of high molecular weight such as we are studying, that what we have is charged colloidal particles resulting from ionization process as the anions of our solutions. On the other hand, we might be dealing in some cases with practically neutral particles which are capable of adsorbing large numbers of hydroxyl ions like fuller's earth, thereby disturbing the equilibrium of water in the solvent

$$H_2O \rightleftharpoons H^+ + OH^-$$

so that the solution becomes acidic. If this adsorption is such that it is not readily displaced at low concentrations, what we actually titrate is the acidity of the resulting solution and not that caused by the ionization of the colloidal particles. The problem is further complicated from a theoretical point of view in that hydrolysis may occur in certain cases even with 0.1-normal caustic.

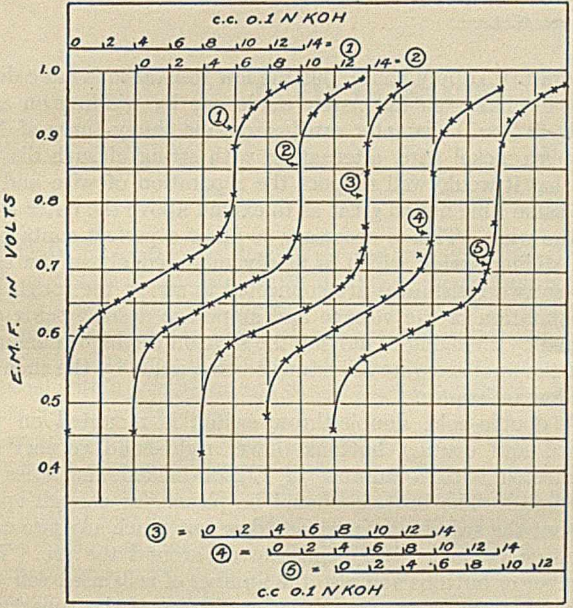

Figure 3—Spirit-Soluble Resins

	Acid Value
1—Sandarach	112.0
2—Mastic (suspension)	57.5
3—Rosin (colophony)	153.6
4—Kauri (soluble portion)	112.0
5—Manila copal	123.2

However, it is quite probable that the paint and varnish chemist is frequently more interested in the relative acidity of varied solutions than in the actual acidity of the substances comprising these solutions. From this viewpoint it can be seen that shellac and resin solutions resemble those of the pure weak organic acids. The curves for these substances in many respects closely resemble those of the four acids, glutaric, benzoic, lauric, and cinnamic. Seed-lac solutions most closely resemble lauric and cinnamic acids. The bleached shellacs, where a slight partial hydrolysis of the resin may have taken place in their manufacture, show closer analogy to the dibasic glutaric acid. However, the actual differences in these particular curves are not so great that we are in position to draw definite conclusions with regard to the constitution of the different shellac particles in alcohol.

On the other hand, there is little doubt that the differences in acidity between shellac solutions and those of the other resins are not so great as Nagel and Körchen have been led to believe. In fact, if the acidity is caused by the presence of resin acids in the solutions, shellac would contain acids that are but slightly more acidic in solution than manila copal, kauri, or rosin.

Since the neutralization points (the mid-points of the vertical part of the curves) of the shellac and resin curves occur at voltages considerably higher than the mineral acid, sulfuric acid, there should be little question but that this acid, and other mineral acids of a similar strength, can be determined in the same solution with the resinous substances. Such a titration curve should have two distinct vertical portions equivalent to each of the two types of acids being titrated. On the other hand, we would not expect to be able to distinguish between mixtures of the varied resins in this solvent when in the same solution because of the close proximity of the various end points as shown (*5*).

When we consider the mass law equation for the ionization of an acid as HA,

$$(H^+) = \frac{(HA)}{(A^-)} Ka$$

where the parentheses represent concentration and Ka is the equilibrium constant, we can see that when Ka is small, as in the cases of weak acids such as studied here, it is a more important factor in the determination of the magnitude of the hydrogen-ion concentration than is the concentration of the acid or the acid value of a resin. With weak acids the value of Ka is to an extent a measure of the strength of an acid solution. Unfortunately, not knowing the values for the liquid junction potentials between the calomel cell and the solutions studied, we cannot express the hydrogen-ion concentrations in absolute values or calculate accurately Ka from the hydrogen-ion concentrations by Nernst's equation

$$E = Eo - 0.059 \log (H^+)$$

In this equation E is the voltage observed if the liquid junction voltages are so small that they can be neglected, and Eo is a constant for each different cell combination used. Until the liquid junction potentials have been shown to be very small or of constant value for the entire range of hydrogen-ion concentration, it is not permissible to consider them part of Eo. However, until detailed study of cell combinations in non-aqueous solvents has been undertaken, it can be seen that this method may be used as a valuable guide in determining relative hydrogen-ion concentrations. Since the hydrogen ion has been found to be the active constituent in many reactions of acids in aqueous solution, it is not unreasonable to conclude that this method may have some application to the study of the stability and flocculation of protective coating compositions in seeking a control and a knowledge of the cause of livering difficulties.

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A Combination Electrochemical Switchboard[1]

W. Faitoute Munn

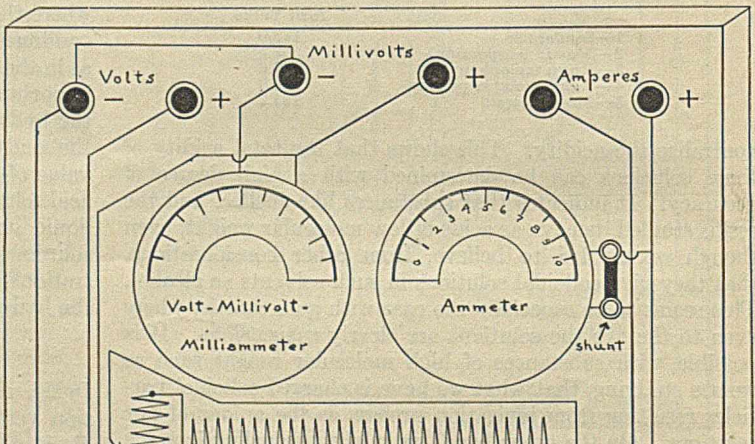
318 White St., Orange, N. J.

A NEW compact electrochemical switchboard has been designed which is very useful in a number of fields of work. It may be used for the deposition of metals, either for the plating or deposition of one metal or for the separation of two or more elements by means of voltage control. It may be used for pyrometry measurements by employing the millivolt connections and standardizing the thermocouple used against a known series of temperatures and drawing a graph to be used for all future readings. It may be used for low-voltage testing of primary batteries, ampere readings, either on plating baths or on outside separate circuits, or for millivolt readings. This apparatus has been thoroughly tested, has been in use for a number of years, and can be relied upon to give very satisfactory results.

The apparatus is mounted on a piece of $^1/_2$-inch (1.3-cm.) slate, 2 feet (60 cm.) square. There are two meters—an ammeter having a full-scale deflection of 10 amperes and a millivolt meter having a full-scale deflection of 75 millivolts. The millivolt meter is wired for voltmeter use by connecting in series with the millivolt terminal connections a coil of No. 40 Tarnac, double silk-insulated wire or other low-temperature-coefficient alloy wire, the amount being found by experiment and checked by comparing with an accurate standard voltmeter so that the full-scale deflection will give a reading of 7.5 volts. This reading takes the place of the 75-millivolt reading. This resistance is shown in the drawing as "V.R." A milliampere reading on the same meter is obtained by making up a small shunt resistance. ("M.A.Shunt" in the drawing) and corrected by checking against a standard milliammeter so that the full-scale deflection will read 750 milliamperes. These calibrations should first be only roughly approximated and wired and mounted according to the drawing and finally corrected after all the wiring has been completed. This precaution is very necessary as the wires used in connecting up the board give sufficient resistance to affect the calibration of the meters very appreciably if such calibration took place before the connections on the board were made. All wiring should be done with heavy copper insulated wire, nothing smaller than No. 14 B. & S. being used, and all joints and connections should be carefully soldered, using resin, and not zinc salts or other compounds, for the flux.

There are two resistances—a high resistance, about 100 ohms, and a low resistance. The high-resistance unit may be purchased at a laboratory supply house, but the low resistance is more difficult to obtain, so the writer made one by winding on a 1-inch (2.5-cm.) diameter cardboard tube thirty turns of No. 18 pure nickel wire, alternating with string of such diameter that it would well support the separation of wire and at the same time not so great as to extend above the outer level of the wire. This is necessary to allow a perfect contact of the sliding spring which is finally mounted above the coil. These two resistances are connected in series, the rough approximation of the voltage and amperage desired being obtained by changing or moving the slide on the high resistance and the final accurate adjustment being made by the slide on the low resistance.

A double-pole, double-throw switch is mounted on the board and contact buttons (lower right-hand corner) are connected with a number of Edison-Lelande batteries or dry cells. The buttons should be placed far enough apart so that the switch contact blade does not touch any two consecutive buttons when being moved around the arc. The number of buttons and also the number of cells used will depend upon the voltage required by the user of the apparatus.



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[1] Received June 1, 1929.

If everything is now completed and the deposition of copper, for example, is required, the platinum cathode and anode which are suspended in the solution to be electrolyzed are connected to the minus and plus terminals, respectively, shown in the lower left-hand corner of the board. The double-pole switch is now thrown to the right, thus showing a volt reading across the bath terminals or electrodes, same being indicated on the left-hand meter. The current will be registered on the right-hand meter. If the ampere reading is less than 0.5 its accuracy will be doubtful, so to obtain an exact ampere reading the double-pole switch is thrown to the left, whereby the left-hand meter will register the fraction of an ampere in milliamperes. The bath may then be adjusted as to current flow desired by moving either, or both, of the variable resistances. The voltage across the bath may now be found at any time by simply throwing the switch handle to the right. If the voltage is not correct, it may be changed by cutting in, or out, the number of cells on hand, by means of the switch and buttons on the lower right corner of the board.

Outside volt readings on any low-voltage circuit may be obtained on the left meter by connecting the battery in question to the two upper left-hand terminals and throwing the handle of the double pole switch to the right. Outside ampere readings on any circuit may be obtained on the right meter by connecting the battery circuit in series with the two upper right-hand terminals. Outside millivolt readings or pyrometer readings may be obtained on the left meter by connecting the thermocouple to the two upper, central terminals.

As soon as the worker is acquainted with the design of the apparatus described above, he will find it very useful and rapid, and it will save more time, labor, and equipment in a short time than the entire cost of construction involves.

Corrosion Testing Apparatus[1]

D. F. Othmer

Eastman Kodak Co., Rochester, N. Y.

This apparatus was devised for the testing of the rate of corrosion of various volatile liquids on a large number of samples of various metals. It was desired to test the materials with boiling acids of various concentrations and with various volatile impurities. It was necessary to find a material with a minimum rate of corrosion throughout a wide range of concentration.

The apparatus consists of a balloon flask heated electrically to boil the liquid and supply vapors to a glass column packed with beads or small glass Raschig rings[2] supported by a glass bulb pierced with holes and resting on indentations in the neck of the column as shown. A condenser with calcium chloride tube is superimposed as shown. The lower end of the column is drawn to a tip and has two small holes blown in the side just above this neck. Vapors enter these lateral openings and liquid runs down the tube wall and is discharged through the tip without priming. The lower end of the condenser is finished in the same way.

The pieces of metal to be tested are inserted at various heights and are continually in contact with the vapors ascending and the hot clean wash descending the column. If a pure substance or an azeotropic mixture, such as nitric or hydrochloric acid and water, is boiled in the flask, the concentration of liquid throughout the column will be constant and samples at different heights will have the same wash. If a mixture of other than constant boiling point is boiled in the flask, the concentrations of wash at different heights will vary, but in different columns of the same length they will be the same at the same height. These concentrations may be measured by sampling at liquid outlet tubes at various heights (not shown on the drawing), but when only a comparative ratio between rates of corrosion on different metals is desired, this is not necessary and the samples are merely inserted at the same heights.

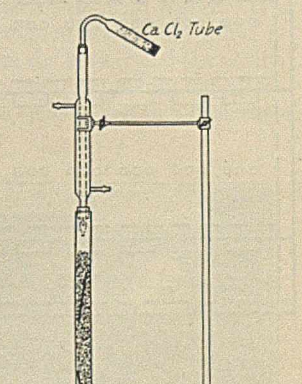
Two of these columns of the same dimensions were set up above boiling dilute hydrochloric acid of 16.25 per cent HCl. Identical samples of sheet nickel were inserted in each of the columns 25 cm. and 125 cm. from the bottom of the packing. The columns were packed to a height of 50 cm. above the top of the upper sample and surmounted with condensers. A wash of about 30 cc. a minute was obtained in each column. The test was run for 18 hours, at the end of which time the samples at the bottom were found to have lost 0.92 and 1.09 per cent, respectively, while those in the middle lost 0.011 and 0.007 per cent, respectively. No analysis was made of the acid strength in the column, but these data and the vapor composition curve of hydrochloric acid and water (*1*) indicate considerable difference in the acid strength at the two heights.

The advantages of this method of determining the rate of solution are several:

(1) The pieces to be tested are in contact with saturated vapor and boiling liquid at all times.

(2) Metallic salts settle in the pot, and the wash liquid is always clean and uncontaminated with the accumulations of the products of corrosion (as it would usually be in plant apparatus).

(3) Because of these advantages, the rate of corrosion may be studied under more nearly reproducible conditions, and comparative tests on different materials have a greater value in determining relative usefulness.



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Mexican Textile Industry Showing Improvement

The depression in the Mexican textile industry, which prevailed throughout 1928, showed no signs of abatement during the first six months of 1929, but since that time the position of the industry has improved considerably, according to information received in the Textile Division, Department of Commerce.

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[1] Received April 12, 1929.

[2] Available in various sizes from the Technical Glass Co., Rochester, N. Y.

Electrolytic Board for the Determination of Lead[1]

With Comments on Procedure for Lead in Low-Grade Tailings of Southeast Missouri Lead District

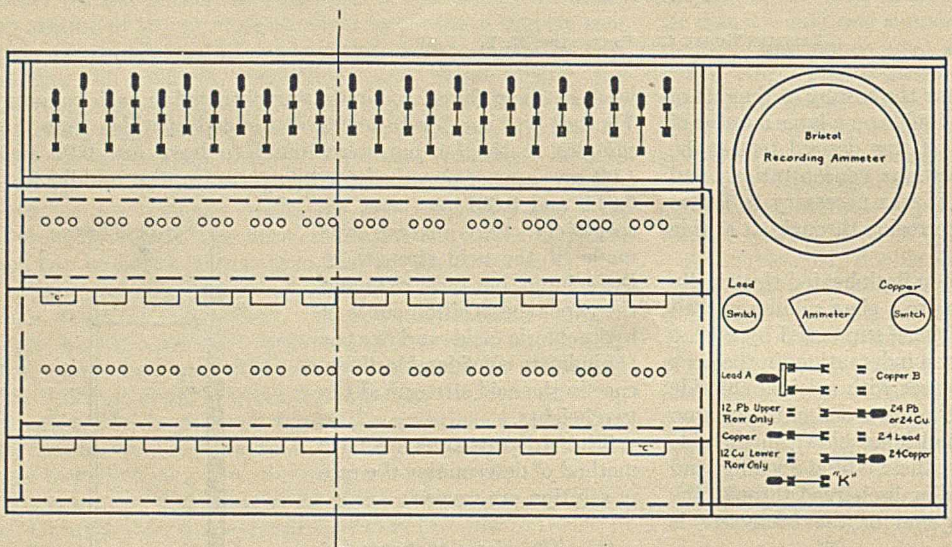
O. W. Holmes and D. P. Morgan

Missouri School of Mines and Metallurgy and U. S. Bureau of Mines, Mississippi Valley Experiment Station, Rolla, Mo.

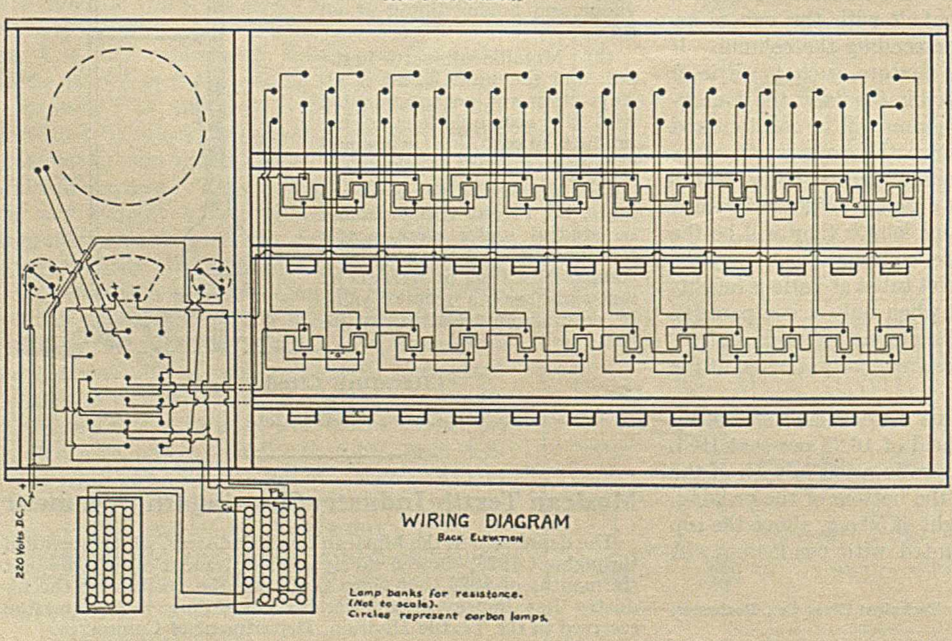
Recent improvements in the practice of milling lead ores of the southeast Missouri lead mining district have resulted in the production of low-grade mill tailings. The tenor of the lead in the tailings is often between 0.05 and 0.25 per cent. In view of the fact that large tonnages are handled daily and that further improvements are under way, it is imperative that the lead content of these tailings be accurately determined. For this purpose an electrolytic board, which speeds up the electrolytic determination of lead in low-grade mill tailings, has been devised at the Mississippi Valley Experiment Station of the United States Bureau of Mines, in coöperation with the Missouri School of Mines and Metallurgy, as a result of several years' work in coöperation with large lead-mining companies.

Apparatus

The apparatus is a modification of the Guess-Haultain cabinet, and is so arranged that 24 leads, or 24 coppers, or 12 leads and 12 coppers may be run simultaneously. The cabinet is shown in detail in the figure. It has two rows of 12 cells each, one above the other, and any cell may be removed from the circuit without disturbing the others. Stationary anodes and cathodes are used. The anode is made of sand-blasted corrugated sheet platinum, and its dimensions are 6 by 3 cm. Each cell contains two platinum-foil cathodes, 8.4 by 0.3 cm. The electrode holders are made of aluminum, and extend horizontally from the surface of the cabinet. When the electrodes are in place, a 150-ml. beaker of regular form with lip, containing the electrolyte, may be put in place and the movable beaker-rest pulled out.



FRONT ELEVATION
Doors "d" and "e" Removed



WIRING DIAGRAM
Back Elevation

Lamp banks for resistance.
(Not to scale).
Circles represent carbon lamps.

When it is desired to remove an anode while a series of determinations is being made, the removal is accomplished in the following manner: The beaker support is slipped back into the cabinet, the knife switch corresponding to the cell is closed, and, simultaneously, the beaker containing the electrolyte is lowered and removed. The anode may then be removed and treated in the usual manner.

The cabinet contains, as an integral part, a recording ammeter of 0 to 5 amperes capacity for overnight determinations of copper. Another small ammeter with a range of 0 to 6 amperes is incorporated in the apparatus for lead work.

By means of conveniently arranged switches a line current of 220 volts, d. c., may be thrown into any series of cells and the amperage recorded on the desired ammeter. The

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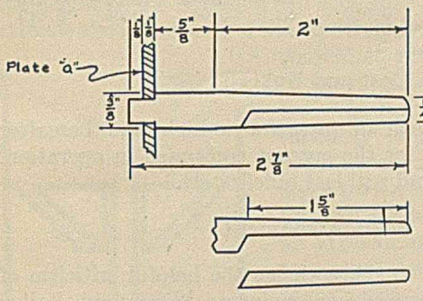
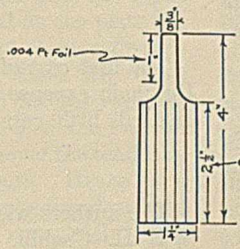
[1] Received June 7, 1929. This paper represents work done under a coöperative agreement between the U. S. Bureau of Mines and the Missouri School of Mines and Metallurgy. Published by permission of the Director, U. S. Bureau of Mines. (Not subject to copyright.)

amperage may be adjusted by means of a variable resistance, using either a rheostat or a bank of carbon lamps.

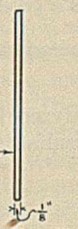
The aluminum electrode holders were originally 7.3 by 0.97 cm. at the base, tapering to 0.64 cm. at the end. These were cast in a carbon block mold, and later the base was machined to 0.64 cm. The electrode holders are riveted to aluminum plates for connection at the back of the cabinet face. They were cut lengthwise through the middle to a depth of 4.1 cm. and then cut from the side until one of the pieces fell away. When in service the pieces are held together by gum rubber tubing slipped over them; they make a clamp that holds the electrodes firmly when inserted in the slit. The wires are protected from fumes by placing them behind the cabinet face.



Detail of Electrode Holder



Pt Anode



Pt Cathode

The apparatus is a modification of those used in the southeast Missouri lead belt. It incorporates new ideas and details, which simplify the manipulation.

Method

In this method it is convenient to weigh one or more "factor weights" of the sample, depending upon the lead content. When the lead content of the sample does not exceed 2 per cent, two or more factor weights are used; when it is from 2 to 7 per cent, one factor weight is used. If the sample contains over 7 per cent lead, the molybdate method is recommended. The theoretical factor used for converting lead dioxide to lead is 0.866.

Weigh the desired amount of sample into a 150-ml. beaker. Add 25 ml. of nitric acid (sp. gr. 1.42), and heat until the evolution of brown fumes has ceased. Wash down the sides of the beaker with water and add 15 to 20 ml. of a solution of ammonium nitrate, made by dissolving 454 grams of the chemically pure salt in 2 liters of distilled water. Dilute the electrolyte to about 145 ml. Electrolyze for 2 hours at a temperature of 70° to 80° C., with a current density of 2 amperes and a potential of 3.5 volts.

General Discussion

When interfering elements are absent, electrolysis may extend overnight at 0.2 ampere.

When the lead content of the electrolyte is less than 0.010 gram, 25 ml. of a solution of lead nitrate, containing the equivalent of 0.0048 gram of lead dioxide per milliliter, should be added before electrolysis, in order to increase the lead content to the point where maximum deposition is obtainable. Experiment has shown that the results are more satisfactory when the electrolyte contains the equivalent of 0.012 to 0.080 gram of lead dioxide.

Precautions

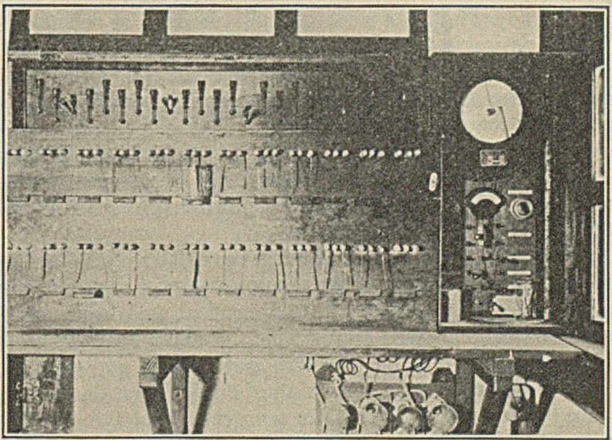
This method cannot be used with a high degree of accuracy when the electrolyte contains more than 0.03 gram of manganese. The quantity of manganese may be regulated by reducing the size of the sample. The detrimental effect of manganese will then be overcome by the presence of the given amount of free nitric acid in the electrolyte. In no case should the concentration of free nitric acid in the electrolyte exceed 15 per cent by volume. The presence of manganese in a sample prevents electrolysis at low current density for a long period of time. The manganese would deposit with the lead.

Copper, iron, and zinc do not interfere with the deposition of lead. Antimony and bismuth, when present, would probably have to be combated in the same manner as manganese—that is, by reducing the size of the sample taken for analysis; no recent experience has been encountered with antimony and bismuth. Arsenic must be removed before electrolysis.

The acidity of the electrolyte has a very important effect upon the deposition of the lead dioxide. Experience has shown that 15 per cent by volume of nitric acid (sp. gr. 1.42) is necessary for the best results. Erratic results are obtained when the acid concentration varies far from this value.

Before electrolysis the anodes are cleaned by immersion in a dilute solution of nitric and oxalic acids. They are then brushed with a camel's-hair brush, rinsed with distilled water, ignited to constant weight in the flame of a Fisher burner, cooled in a desiccator, and weighed.

After electrolysis is complete, the anode is detached and immediately immersed in a beaker of distilled water. It is dipped consecutively into two beakers containing ethyl alcohol. The anode is removed from the beaker and the alcohol burned off, keeping the anode in motion to prevent the alteration of the deposit. The anode is then cooled in a desiccator and weighed.



Electrolytic Board

Accuracy

It has been found that this method of electrolytic recovery of the lead in mill tailings is the best for mill practice when the time element is standardized; but research has to be done to determine its absolute accuracy. Because of the simplified procedure and the small number of steps necessary the electrolytic method is much to be desired over others. In fact, it is possible to accomplish more determinations with a high degree of accuracy in less time than when any other method is employed.

It is desirable to keep the following points in mind in order that the highest degree of accuracy may be obtained:

(1) The size of the sample taken depends not only on the lead content of the ore but on the manganese, antimony or bismuth content as well.

(2) Maximum recovery is not possible when the lead content of the solution is below 0.012 gram PbO_2.

(3) Low results are obtained when the solution contains more than 0.070 gram of lead, because the deposit flakes off.

(4) Manganese is deposited very readily from solutions when a low current density is employed.

(5) Practically complete deposition of lead from pure solutions is obtained by using low current densities for long periods of time.

(6) Current densities of 2 to 3 amperes for 2 hours is sufficient for low-grade materials; electrolysis for 2 hours is a good standard.

(7) The electrodes should be sand-blasted occasionally to facilitate the adherence of the deposit.

A number of mill-tailing samples were analyzed by this method by two different laboratories and the results shown in the table were obtained:

Copper

The apparatus as given for lead determinations is also adapted to, and suitable for, the determination of copper. The method employed is the standard procedure for electrolytic copper. The apparatus is not the type generally employed for such work, but highly accurate results are obtainable by overnight deposition.

SAMPLE	LAB. 1	LAB. 2	DIFF.	SAMPLE	LAB. 1	LAB. 2	DIFF.
	Per cent	*Per cent*	*Per cent*		*Per cent*	*Per cent*	*Per cent*
1	0.08	0.075	0.005	8	0.30	0.31	0.010
2	0.10	0.095	0.005	9	0.30	0.29	0.010
3	0.10	0.098	0.002	10	0.09	0.08	0.010
4	0.70	0.700	...	11	0.04	0.05	0.010
5	0.52	0.52	...	12	0.045	0.06	0.015
6	0.44	0.45	0.010	13	0.04	0.05	0.010
7	0.40	0.39	0.010				

Cost and Upkeep

The first cost of such an apparatus is high, but thereafter the main expense is for the current consumed in operation. It needs little care and will last indefinitely.

Acknowledgment

The authors wish to acknowledge the helpful criticism of Will H. Coghill, supervising engineer, Mississippi Valley Station of the United States Bureau of Mines, W. T. Schrenk, head of the Chemistry Department of the Missouri School of Mines and Metallurgy, and J. B. Clemmer, junior metallurgist, Mississippi Valley Station of the United States Bureau of Mines, Rolla, Mo.

Laboratory Rectifying Columns with Non-Siphoning Bubbling-Cap Plates[1]

Johannes H. Brunn[2]

BUREAU OF STANDARDS, WASHINGTON, D. C.

IN ORDER to obtain, in the laboratory, an efficient fractional distillation of a complex mixture such as petroleum, it is desirable to carry out the distillation at a low speed, using a high reflux ratio, and with intermittent additions of liquid to the still pot. If ultimate separation of the compounds is intended, it is furthermore advisable to start with large quantities of material. For these reasons the distillation usually extends over a comparatively long period of time and the need of a still with the following properties is apparent.

It should be possible to shut down the still without allowing the liquid on the plates of the column to drain back into the still pot on cooling, as thereby fractions that are already separated would be allowed to mix again. The intermittent addition of cold liquid to the still pot during a distillation should not tend to start siphoning of liquid down the column owing to the sudden decrease in temperature of the still pot. In continuous industrial stills this is prevented by preheating and carefully adding the liquid to the still pot at a continuous, uniform rate. Preheating is often undesirable for laboratory separations, however, and for the higher petroleum fractions it would increase the possibilities of cracking. For these reasons rectifying columns with non-siphoning bubbling-cap plates have been developed and are shown in the accompanying figures.

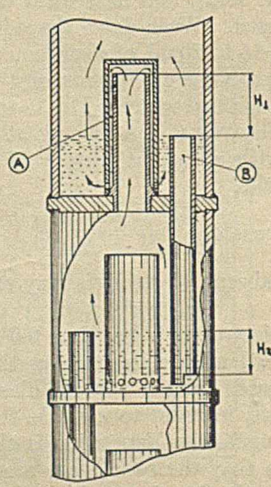


Figure 1

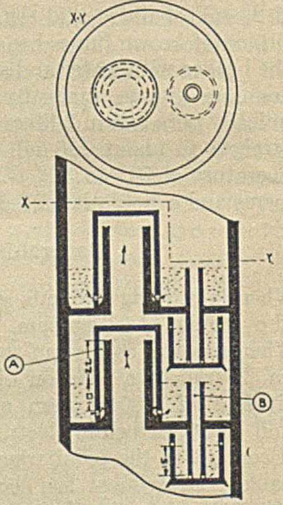


Figure 2

In Figure 1 the ascending vapor normally follows the path of the arrows, passing up through the "vapor-riser" in the center of the plate, then down along the inside wall of the bubbling cap. Near the bottom of the cap the vapor is forced out through a series of small holes. The liquid is thoroughly agitated by the stream of fine bubbles passing through it. When condensed liquid fills the plate above a

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[1] Received March 8, 1929. Publication approved by the Director of the Bureau of Standards of the U. S. Department of Commerce. This paper describes rectifying columns which have been developed in connection with an investigation on "The Separation, Identification, and Determination of the Chemical Constituents of Commercial Petroleum Fractions," listed as Project No. 6 of the American Petroleum Institute. 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] American Petroleum Institute research associate at the U. S. Bureau of Standards.

certain level, it overflows through *B*. In order to maintain an even distribution of the vapor through the holes in the bubbling cap, this must be coaxial with the vapor inlet tube. A simple method of accomplishing this is to ream the bottom of the bubbling cap to fit the tapered portion of the vapor inlet tube (or a loose tapered ring) as shown in Figure 1.

The siphoning of liquid through *A* is prevented by making the height of the bubbling cap such that the vapor inlet tube extends above the level of the liquid on the plate by an amount somewhat greater than the depth of the liquid seal on the plate below. In Figure 1 H_1 is made considerably larger than H_2. This provides a path for the vapor to pass downward in the column through *B* whenever the tendency to siphon occurs. Hence in a column of this type the plates will always remain completely filled with liquid.

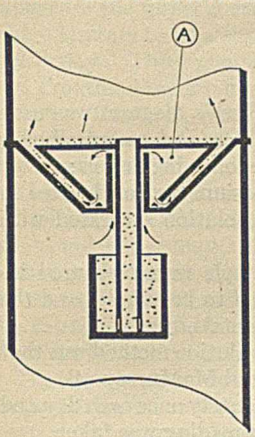

Figure 3

The design shown in Figure 2 is based upon the same principle as that in Figure 1, the difference being the fact that the liquid seal is kept separated from the plate below. Whenever vapor passes downward through the seal, a small amount of liquid is removed from the seal. The dimensions must therefore be properly adjusted so that, after this loss, the amount of liquid remaining is large enough to prevent any vapor from passing upward through *B*.

Figure 3 shows a combined reflux drain and bubbling-cap plate which is non-siphoning. This design differs from those of Figures 1 and 2 in that, when the tendency to siphon occurs, the vapor passes downward, not through the liquid seal, but through the bubbling cap itself. This has been accomplished by making the capacity of *A* larger than the volume of all the liquid on the corresponding plate when in operation. The liquid on the plate will at first be sucked into the large bubbling-cap, *A*, which will be only partly filled. The vapor can then bubble backward through this liquid without emptying the plate.

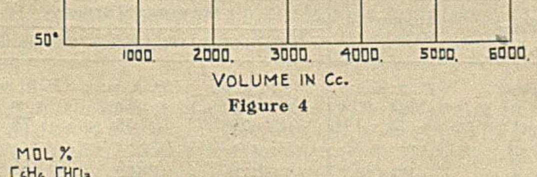

Figure 4

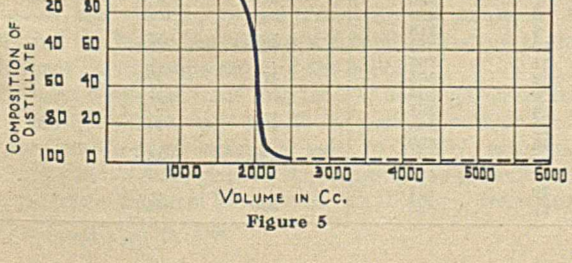

Figure 5

A plate column of this particular design has not been built, but it should work satisfactorily for laboratory separations in which a relatively low rate of distillation is employed. If high rates of distillation were employed, the space within which the bubbles rise through the liquid might have to be increased.

A twenty-plate rectifying column of the type described in Figure 1 has been built and found to work very satisfactorily. In order to test the heating system and auxiliary apparatus of this still, it was charged with a mixture of 2 liters of chloroform and 4 liters of benzene, and a distillation was carried out. The results of this run are shown in Figures 4 and 5. Figure 4 shows the temperature-volume curve for the distillation and Figure 5 shows the composition of the distillate in mol per cent plotted against the volume of each fraction. About 1500 cc. of the chloroform came over at a concentration of about 98 mol per cent. As indicated by the dotted line in Figure 5, the distillation was discontinued when 2500 cc. of distillate were obtained.

Figure 6 shows a non-siphoning bubbling-cap column that has been developed for rectifying stills constructed of glass. Its operation is based on the same principle as the metal still shown in Figure 2. A column consisting of two plates of this design has been made with an outside diameter of 35 mm. and found to work satisfactorily. For columns of smaller diameters, however, this type has the disadvantage that the return of liquid through *B* does not take place so readily as it should and the column tends to "flood" except when low rates of distillation are employed. It is evident that the dimensions of the drain tube *B* and the cup below are limited by the same relations as described in connection with Figure 2.

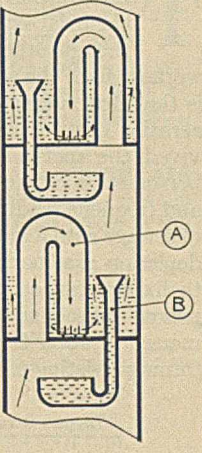

Figure 6

A glass rectifying column that is entirely free from the objections mentioned above is shown in Figure 7. This type is also simpler to make, as the "vapor-riser" is simply flanged at one end and then sealed directly into the column. The bubbling cap is loose and is provided with six narrow slits for the purpose of breaking up the bubbles. The reflux drain, *B*, is located outside the column and can be made large enough to take care of practically any rate of reflux which may be desired. The diameter of a column of this type is not subject to any limitation as to size, and the column should therefore work satisfactorily even with a "hold up" of only a few tenths of a cubic centimeter, or less, per plate. A rectifying still adapted to vacuum distillation and consisting of ten plates of the type shown in Figure 7 has been made and found to function satisfactorily.

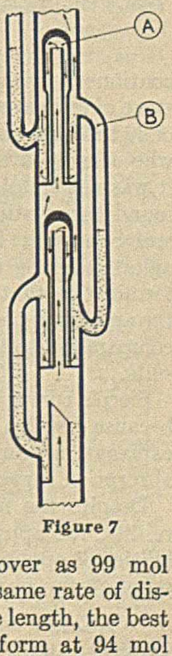

Figure 7

In a test distillation at atmospheric pressure of a mixture of 50 mol per cent chloroform + 50 mol per cent benzene, all but the last 50 cc. of the chloroform distilled over as 99 mol per cent. Using the same mixture and the same rate of distillation in a "jack-chain" column of the same length, the best efficiency obtained at any time was chloroform at 94 mol per cent.

Comparison of the Dilution and Absorption Methods for the Determination of Biochemical Oxygen Demand[1]

G. E. Symons with A. M. Buswell

State Water Survey, Urbana, Ill.

THE dilution method for the determination of biochemical oxygen demand is most widely used at present though other methods have been proposed by various workers since the test was introduced. One of these methods is that first suggested by Adeney (*1*) in 1908, known as the aeration or direct absorption method. Sierp (*7*) recently revived the method and suggested it "to reduce the cumbersomeness of the dilution method and afford quick, direct, and frequent readings." Adeney incubated a known volume of sewage with a known volume of air and followed the oxygen depletion gasometrically. Magnesium hydroxide was added to fix the carbon dioxide. Several forms of apparatus appeared subsequently, the simplest a partly filled bottle immersed in water to prevent re-aeration and the more complex forms consisting of mechanical shaking apparatus to allow for continuous agitation. Under the latter conditions the first stage of oxidation was completed in from 10 to 14 days instead of 20 to 28 days as found by other methods. Besides Adeney, who concluded that while the aeration method was accurate it was not suitable for routine work, Rideal and Burgess (*5*) found the existing apparatus unsatisfactory due to leakage, and Sand and Troutman (*6*) believed that the amount of agitation given a sample is an important factor in the determination that should not be overlooked. They also found the apparatus poor and unsuccessful. Calvert (*3*) states that comparative tests show that the method yields divergent results.

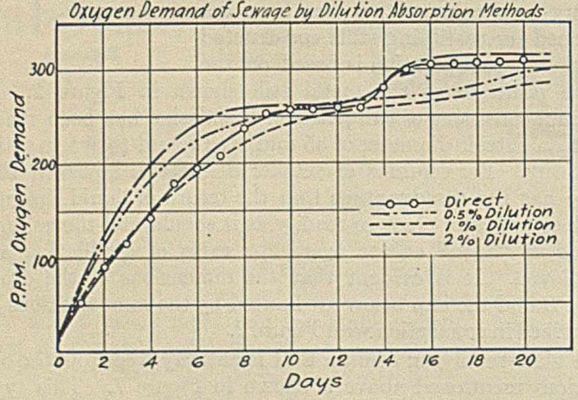

Figure 1—Oxygen Demand of Sewage by Dilution and Absorption Methods

Sierp's curves do not show a nitrification period, probably because distilled water was used for dilution purposes. This explanation cannot be used, however, in regard to the direct absorption curve.

Despite the reported difficulties and apparent divergent results, the apparatus and method appeared to have possibilities of application to the study of the oxygen demand of pure substances which is being carried on in this laboratory.

Procedure

An apparatus built according to Sierp's diagram was used for the comparison of the two methods and essentially his procedure was followed, except in the following details:

(1) The concentration of the potassium hydroxide used in the leveling bulb was a 10 per cent solution saturated with sodium chloride.

(2) Four hundred milliliters of sample were measured instead of weighed because it was found to be simpler and the error involved is well within experimental error.

(3) The dilution water used in the dilution method was that recommended by Greenfield, Elder, and McMurray (*4*).

(4) The apparatus was shaken vigorously once each day and allowed to stand 30 minutes before a reading was taken.

(5) Incubation was at 20° C.

(6) The oxygen demand was calculated by the formula:

$$\text{P. p. m.} = 0.004379 \times R \times P$$

where R = reading in cubic centimeters

P = barometric pressure, in millimeters

$$0.004379 = \text{factor}\left(\frac{273}{293} \times 2.5 \times 1.429 \times \frac{1}{760}\right)$$

1.429 = weight in milligrams of 1 cc. of oxygen at 0° C.

2.5 = factor to calculate 400 cc. to 1 liter

$\frac{273}{293}$ = factor to reduce temperature to 0° C.

$\frac{1}{760}$ = factor to reduce pressure to standard conditions

Two experiments were made comparing the direct method with 0.5, 1, and 2 per cent dilutions of raw sewage. Biochemical oxygen demand tests by the dilution method were made according to standard methods (*2*).

Discussion

The experiments show little difference in the results as obtained by the two methods. The data of the first experiment are listed in Table I. The data of the second experiment are plotted in Figure 1.

Table I—Biochemical Oxygen Demand of Sewage by the Direct Absorption and Dilution Methods

TIME	DIRECT METHOD	DILUTION METHOD		
		5% dilution	1% dilution	2% dilution
Days	*P. p. m.*	*P. p. m.*	*P. p. m.*	*P. p. m.*
0	21	0	0	0
1	78	70	56	78
2	...	...	...	...
3	...	...	...	...
4	171	123	170	182
5	186	184	195	202
6	222	...	...	...
7	272	269	215	227
8	298	...	...	...
9	318	...	...	...
10	350	430	265	287
11	365	...	...	...
12	365	476	395	363
13	365	...	...	...
14	381	...	...	...
15	389	492	445	390
16	390	...	...	...
17	403	524	465	...
18	410	...	...	...
19	431	...	...	...
20	438	560	510	...

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[1] Presented before the Division of Water, Sewage, and Sanitation Chemistry at the 77th Meeting of the American Chemical Society, Columbus, Ohio, April 29 to May 3, 1929.

In the first experiment the B. O. D. as obtained by the dilution method is somewhat higher, while in the second experiment the reverse is true but to a lesser degree. The trend of the curves is the same up to the point of second-stage oxidation where apparently the reactions do not follow the same course. (Table I, and 1 and 2 per cent dilution curves in Figure 1.) The two methods agree, however, as well as do the three dilutions in the dilution method. All the points obtained by the direct method do not lie exactly on the curve. There appears to be a slight rest period between the fifth and eighth day. These points off the curve might be due, as Sand and Troutman point out, to the amount of agitation given the sample. However, the extremely anomalous results frequently obtained by the dilution method are absent in the direct process.

The buffered dilution water effects the same condition as the removal of carbon dioxide in the direct method, since the pH would not change. Thus the course of the reactions is probably similar so that the final results are approximately the same. The second or nitrification stage occurred after the thirteenth day by both methods in one experiment and after the tenth day in the other.

The condition of decreasing oxygen concentration which frequently hampers the dilution method is absent in the direct method. On the contrary, there is an increase in concentration of oxygen in the sample. Apparently this has little effect on the biological processes. That oxidation was not complete in 20 days is shown by the fact that the liquid contained only 30 p. p. m. of oxygen at the twentieth day, when according to Henry's law of solubilities it should have contained about 40 p. p. m. if the gas above was pure oxygen, which it was shown to be by analysis.

Conclusions

The direct process does away with the large number of subsamples necessary in the dilution method. The condition of decreasing oxygen concentration is absent. Anomalous results are not obtained by the two methods, when a buffered dilution water is used in the latter. Daily direct readings are easily obtainable but hourly changes are not noticeable. Both methods show two-stage oxidation. The amount of agitation given the direct-process apparatus apparently causes some slight variation in readings. The direct process has the advantage over the dilution method in the matter of time and technic necessary to obtain the data. Care must be taken to keep the apparatus at constant temperature when readings are taken.

It is suggested that the direct process can conveniently and profitably be used in the study of pure substances, sewage sludge, and trade wastes where high dilutions necessary in the dilution method introduce large error.

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(1) Adeney, Fifth Rept., Royal Sewage Commission, 1908, App. VI.
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(3) Calvert, *J. Soc. Chem. Ind.*, **32**, 265 (1913).
(4) Greenfield, Elder, and McMurray, Ind. Eng. Chem., **18**, 1276 (1926).
(5) Rideal and Burgess, *Analyst*, **34**, 139 (1909).
(6) Sand and Troutman, *J. Soc. Chem. Ind.*, **31**, 1166 (1912).
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Stabilized Starch Indicator[1]

M. Starr Nichols

Water and Sewage Division, State Laboratory of Hygiene, Madison, Wis.

IN THE determination of dissolved oxygen in waters by the Winkler method a sensitive stable starch solution is one of the first prerequisites.

Soluble starch is used by many workers, but in the writer's experience the color produced by iodine varies from the true blue color to that of violet. Invariably when the violet color obtains the sensitiveness is somewhat reduced.

A good commercial grade of potato starch has fulfilled the requirements as far as sensitivity and color are concerned, but there still remains the lack of stability. Bacteria, yeasts, and fungi thrive in the prepared solution. The Standard Methods of the American Public Health Association (1925) prescribe the following procedure for the preparation of this reagent:

> Mix a small amount of clean starch with cold water to form a thin paste and stir the mixture into 150 to 200 times its weight of boiling water. Boil a few minutes, then sterilize. It may be preserved by adding a few drops of chloroform.

This method makes a satisfactory starch reagent, but unless one adds the chloroform and maintains an excess in the bottom of the bottle the reagent will spoil; moreover, there is a tendency toward separation of the colloid.

Recently there has come into limited use a starch solution made in accordance with the above method and preserved by the addition of common salt to nearly saturation. Growths will not take place in the reagent, but the salt seems to cause precipitation of the colloid. In this semi-precipitated state. the sensitivity is lowered somewhat because of the slow reactivity of the flocculated colloid. Salicylic acid has been used for the preservation of foods of various kinds and a simple trial proved that it would serve as a preservative for this solution. The starch indicator reagent is prepared as follows:

> To 50 grams of potato starch add about 250 cc. of cold water and mix to form a thin paste; then pour it gradually with constant stirring into 20 liters of boiling tap or distilled water. Boil for 15 minutes with constant stirring. Allow to cool somewhat and add 25 grams of salicylic acid. Stir until the preservative is dissolved. The colloid remains in dispersion well; the reagent keeps nearly indefinitely even though exposed to air, and is very sensitive.

As this reagent is made only about one-half as strong as the solution recommended in Standard Methods, the writer has found it advantageous to use about 2 cc. for a 200-cc. volume titration.

Treadwell and Hall (*1*) have pointed out that starch paste requires the presence of an alkali iodide to suppress the dissociation of the blue iodide-starch color; they showed (*2*) the effect of this added iodide on the sensitivity. They showed that it required four and one-half times as much *N*/100 iodine to produce the first permanent blue color in 200 cc. of distilled water as is required if 1 gram of potassium iodide is added to the water before the iodine is introduced.

The accompanying table gives the sensitivity of the stabilized starch solution 2 months old.

---

[1] Received April 25, 1929.

Sensitivity of Starch Reagent
(2 cc. used)

Water	Depressant Salt Used	N/800 Iodine to First Permanent Blue Color
Cc.	*Grams*	*Cc.*
200[a]	KI 0.40	0.4
200	KI 1.0	0.4
200	KI 5.0	0.2
200	NaCl 0.5	1.9
200	NaCl 1.0	1.8
200	NaCl 5.0	1.6
200	KBr 5.0	3.2
200	No salt present	3.6

[a] 0.25 cc. of concd. H_2SO_4 added, which is approximately the amount present in the Winkler titration.

It will be noted that if the amount of potassium iodide present equals that present in the Winkler titration, only 0.02 cc. of a N/40 iodine solution would be required to produce the first permanent blue color or an equal quantity of N/40 thiosulfate solution to discharge the last trace of blue color. This is easily within the limits of experimental error.

Literature Cited

(1) Treadwell and Hall, "Analytical Chemistry," Vol. I, p. 299 (1914).
(2) *Ibid.*, Vol. II, p. 653.

An Analysis of a Peat Profile[1,2]

Reinhardt Thiessen and R. C. Johnson[3]

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Since coal was formed in a similar manner as peat is being formed today and at one time was in the peat stage, a better knowledge of the nature and chemistry of peat should add to a better knowledge of the nature and chemistry of coal.

Peat formation is largely a microbiological problem, and may be considered under three phases: in the air, partly submerged, and completely submerged. All classes of plants and every plant product must be considered. The microbiological reactions in the first phase are aerobic; and fungi, actinomyces, bacteria, burrowing insects, Crustacea, and other lower forms of life are instrumental in reducing the plant substances into a more or less decayed and macerated state. The second stage is transitional and only bacteria and some actinomyces remain active. In this shallow zone much living plant matter, mostly lignin and cellulose, in the form of roots, is added. In the third and permanent stage anaerobic bacteria only function. It has been demonstrated that bacteria exist and are active at all depths.

Theoretically, therefore, changes should occur in a peat deposit after its deposition. To answer this, analyses of samples from a peat profile were made with respect to relative amounts and nature of the major components such as water-soluble matter, ether-soluble matter, humins, lignin, cellulose, and insoluble residues consisting mostly of spore, pollen, and cuticle matter.

This offered at the same time a relation of the various components and the changes they have undergone during the period of their existence. Since the inception of the deposit dates from a time soon after the last ice age, considerable time must have elapsed, with proportionally less time for the successive younger layers until the present.

The analyses given in the tables and figures show that lignin and cellulose decrease with the depth of the deposit and hence with age, and the humins increase with the depth and hence with age. There was, therefore, a progressive humification with age. Because too many unknown factors enter into the time changes, on account of large mixtures of the original contributory plant products, no solution is offered by these analyses as to whether lignin is the chief contributor, or whether both lignin and cellulose contribute in more equal proportions.

The different floras that prevailed successively during the deposition of the peat mass caused different and specific types of peat to be laid down; successive layers give chemically different types of peat and these are reflected in the curves as fluctuations.

....

IT IS generally agreed that coal is of plant origin and was formed in a manner similar to that in which peat is being formed today. A thorough study of peat from its inception to the more mature stages at its greatest depth becomes essential to the understanding of the constitution of coal and its formation. With this objective a study was undertaken of the transformation of plant substances into peat and the composition of a deposit in profile from top to bottom with respect to its major components, their nature, their changes, and their relations. By such a study it is hoped to discover more definitely what plant substances contributed to coal and what are now their chemical and physical natures.

A work of this kind includes the study and consideration of every compound and product of all plants. The chemistry of plant substances is remarkably well known. Only one chief and important constituent, lignin, defies solution. This is unfortunate, as it is the most important contributor to peat and coal. The study also involves the chemistry of decay, the action of fungi, bacteria, actinomyces, burrowing insects, and other lower organisms. During the last ten years much has also been learned of the chemistry of decay (*4*); much, however, is yet to be learned. With these available data the composition of peat can in some measure be postulated; yet many questions and problems remain unanswered.

The Bog

The peat on which these studies were carried out was obtained from a wooded swamp in Manitowoc County, Wis., known as Hawk Island Swamp. This is a typical wooded swamp of which there are a considerable number, formed by uneven deposits of gravel after the retreat of the last ice age. It is of considerable area and is covered with

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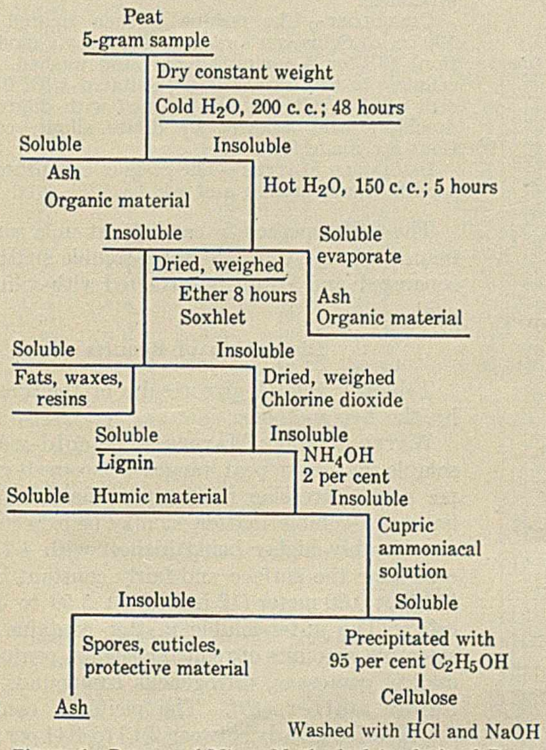
[1] Presented before the Division of Gas and Fuel Chemistry at the 77th Meeting of the American Chemical Society, Columbus, Ohio, April 29 to May 3, 1929.

[2] Published by permission of the Director, U. S. Bureau of Mines and of the Carnegie Institute of Technology and the Mining Advisory Board. (Not subject to copyright.)

[3] Formerly research fellow, Carnegie Institute of Technology.

a dense growth of white cedars, *Thuja occidentales*, interspersed with some tamaracks, birches, black ash, and spruces. In its original primeval condition few or no herbaceous plants and shrubs grew on the surface owing to the dense overgrowth; but mosses, lichens, and liverwort grew in great profusion. It is therefore a typical wooded swamp. The depth of the peat deposit is 1.52 to 3.65 meters (5 to 12 feet); where the samples were taken it is 3.04 meters (10 feet) deep.



Peat
5-gram sample
Dry constant weight
Cold H_2O, 200 c. c.; 48 hours
Soluble
Insoluble
Ash
Organic material
Hot H_2O, 150 c. c.; 5 hours
Insoluble
Soluble
evaporate
Dried, weighed
Ether 8 hours
Soxhlet
Ash
Organic material
Soluble
Insoluble
Fats, waxes, resins
Dried, weighed
Chlorine dioxide
Soluble
Insoluble
Lignin
NH_4OH
2 per cent
Soluble
Humic material
Insoluble
Cupric ammoniacal solution
Insoluble
Soluble
Spores, cuticles, protective material
Precipitated with 95 per cent C_2H_5OH
Cellulose
Ash
Washed with HCl and NaOH

Figure 1—Bureau of Mines Method of Analysis of Peat

Large samples were taken from top to bottom in the form of columns 0.61 meter (24 inches) in length and about 0.51 by 0.51 meter (20 by 20 inches) square; these were shipped to the laboratory at Pittsburgh. The natural condition of the peat mass was thus preserved and every phase of peat formation could be studied without having disturbed the original characteristics.

The surface layer consists of semi-decayed logs, twigs, and branches, and fragments thereof in every conceivable size, together with the residue of the surface flora, and in every stage of decomposition and maceration. Slightly beneath the surface is a shallow zone penetrated with a dense mass of roots and rootlets of the plants now growing on it. The next 1.22 meters (4 feet) are composed of a woody peat derived from material such as is now found on the surface. At the lower horizon of the woody peat it becomes increasingly mingled with moss residues, which rapidly develop into a typical moss-peat about 0.30 meter (12 inches) in depth. The next 0.91 to 1.52 meters (3 to 5 feet) consist of a reed-sedge-grass peat, the products of a marsh stage. The last 0.30 meter (12 inches) of peat at the bottom consists chiefly of a highly macerated mass, the product of an open-water stage. The entire deposit is, however, sublayered owing to slight differences in plant societies and degree of decay and maceration.

Agents of Decay

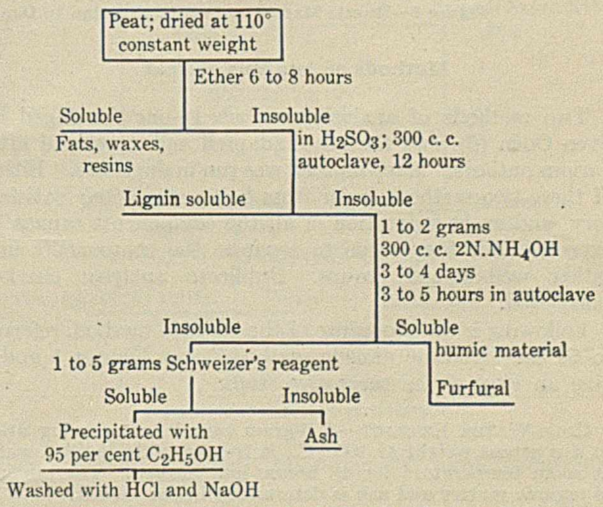
Peat formation is largely a problem of microbiology. It may roughly be divided into three stages: (1) in the air with free access of air; (2) completely submerged under water and débris and deprived of free access of air; and (3) a stage between these two under more or less fluctuating conditions. The most important changes and eliminations during the transformation of plant substances into peat occur in the first stage, while the plant substances are still exposed to free access of air. Immediately after the plant products or plant parts have separated from the parent plants, or after the death of the whole plant itself, they are attacked by fungi, actinomyces, bacteria, insects, and other lower organisms. These, together with the dynamic agencies of the atmosphere, reduce the plant substances to a semi-decayed, more or less disintegrated mass. As the mass is more and more covered with subsequent débris, the activity of the microörganisms changes through elimination of the more strictly aerobic forms, until finally faculative aerobic bacteria remain. This is also the shallow zone permeated with the root of the flora of the swamp. Finally, when the débris is completely submerged and the permanent deposit is established, all organisms except anaerobic bacteria have ceased to function.

Bacteria in Peat

It has now been satisfactorily proved that bacteria exist in peat and are functioning to all depths of the deposit. A large number of inoculations have been made from the top to the bottom of several peat deposits, and it is rare that cultures are not obtained. These cultures are being propagated on wood in the form of sawdust and shavings, on cellulose, and on other plant materials contained in flasks and bottles with proper mineral culture solutions; they are still active after 7 to 19 months. Available nitrogen is essential for their activities.

From these observations it may be deduced that further changes, generally termed "humifications," are going on in the formed deposit, but this had as yet not actually been demonstrated.

To prove definitely the further influence of bacteria on peat after its deposition, and the further humification, analyses were made from top to bottom with respect to its major components—namely, water-soluble matter, ether-soluble material, humins, lignin, cellulose, and certain insoluble constituents. From the large samples shipped from the field small lumps were selected at 3-inch (7.6-cm.) intervals for the first 2 feet (6.1 meters) and at 6-inch (15-cm.) intervals for the remainder of the depth, and dried at 105° C. From this series 5-gram samples were selected.



Peat; dried at 110° constant weight
Ether 6 to 8 hours
Soluble
Insoluble
Fats, waxes, resins
in H_2SO_3; 300 c. c. autoclave, 12 hours
Lignin soluble
Insoluble
1 to 2 grams
300 c. c. 2N.NH_4OH
3 to 4 days
3 to 5 hours in autoclave
Insoluble
Soluble
humic material
1 to 5 grams Schweizer's reagent
Furfural
Soluble
Insoluble
Precipitated with 95 per cent C_2H_5OH
Ash
Washed with HCl and NaOH

Figure 2—Sven Oden's Method of Analysis of Peat

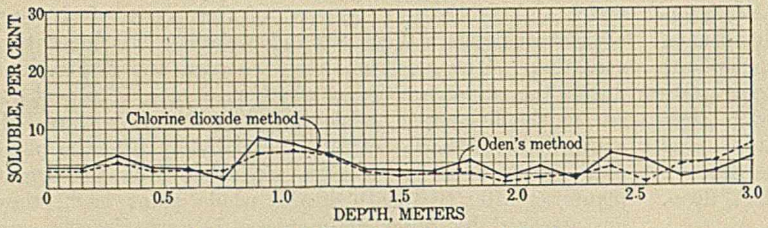


Figure 3—Ether-Soluble Material in Peat

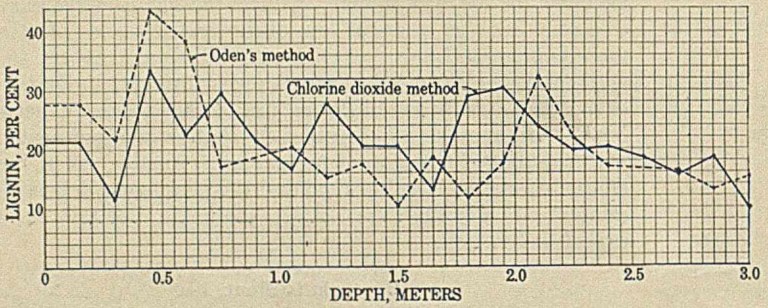


Figure 4—Lignin Content of Peat in Relation to Depth

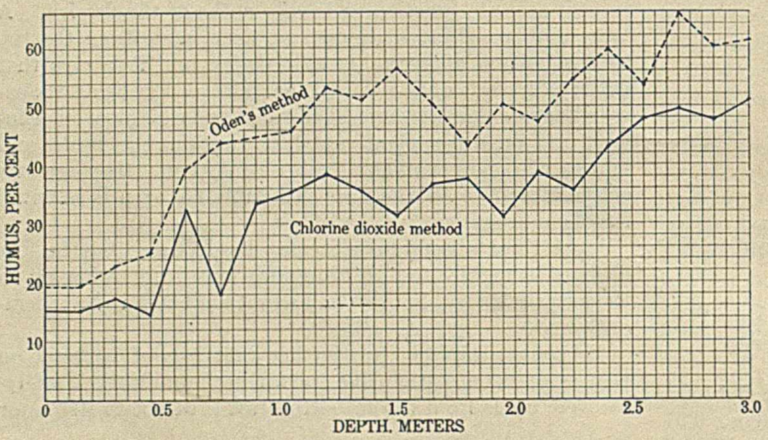


Figure 5—Humic Matter in Peat in Relation to Depth

Methods of Analysis of Peat

Two methods of analysis were used—one developed by Sven Odén (*6*), and the other adapted and developed after various authors. Each method was run in duplicate. Either of these two methods is far from being completely satisfactory, and exact separation of all the components cannot be expected, but they serve to separate the components into rather well-defined groups. Duplicate analyses checked fairly well.

Following is the procedure of the adopted method, referred to as the "chlorine dioxide method," and Figures 1 and 2 give an idea of the successive steps:

COLD-WATER EXTRACT—A 5-gram sample, after being dried to a constant weight at 105° C., is treated with distilled water at room temperature for 48 hours, and filtered. The amount of organic matter and ash is determined in the filtrate.

HOT-WATER EXTRACT—The residue of the cold-water extract is refluxed 3 hours with 150 cc. of distilled water, filtered, and the ash and organic matter determined in the filtrate.

ETHER EXTRACT—The residue of the hot-water extract is refluxed 8 hours in a Soxhlet with ether; the residue is dried and weighed and the extract determined by difference.

LIGNIN DETERMINATION—The residue of the ether extract is then treated with 200 cc. of approximately 1.5 *N* chlorine dioxide solution at room temperature for 48 hours, filtered, and washed until free from chlorine. This is repeated until the chlorine dioxide solution is no longer colored. The residue is dried and weighed and the difference calculated as lignin content. The ash is determined in the filtrate and corrections made.

HUMIC MATTER—The dried and weighed residue of the lignin extract is now treated 5 days with 2 *N* solution of ammonium hydroxide followed by heating to 110° C. for 3 hours under 15 pounds (1 atmosphere) pressure in an autoclave. It is then filtered through a Gooch crucible, washed, dried, and weighed; the humic matter is determined by difference.

CELLULOSE—The residue is then treated with 100 cc. of Schweizer's reagent (Dawson's modification) (*7*) for 5 hours, filtered, and washed. The cellulose in the filtrate is precipitated with 95 per cent alcohol, filtered, and washed with dilute hydrochloric acid followed by dilute alkali; corrections are made for ash.

INSOLUBLE MATTER—The residue constitutes insoluble organic matter and ash.

The Odén method is carried out in a similar manner except that no water-soluble matter is separated and lignin is extracted with sulfurous acid.

Discussion of Results

Tables I and II give results of the analyses by the two methods.

WATER-SOLUBLE MATTER—The cold-water-soluble matter in peat ranges between 1 and 3 per cent, increasing from top to bottom. The hot-water-soluble matter, as may be expected, is considerably higher being highest with 4.25 per cent near the surface and fairly constant below the first 0.30 meter (12 inches) at 3.50 to 4 per cent. The water-soluble matter contains considerable amounts of reducing sugars, pentosans, methyl pentosans, nitrogenous compounds, and humic matter (*10*). The pentosan contents fluctuate irregularly between 2.13 to 4.44 per cent. The total reducing sugars irregularly increase from 3.65 per cent at the top to 13.88 per cent at the 2.44-meter (8-foot) level. This increase is yet to be explained.

ETHER-SOLUBLE MATTER—The ether-soluble matter, as seen in the tables and in Figure 3, remains fairly constant from top to near the bottom, fluctuating irregularly between approximately 2 and 6.6 per cent and becoming higher in the last 0.30 meter (12 inches). The ether-soluble matter contains chiefly fats, waxes, and resins. The color of the extract varies from brown at the top to greenish brown at the bottom. They are soluble in a hot ether or alcohol-benzene mixture, but are insoluble in the cold liquor.

The crude ether-soluble matter may be separated into a benzene-soluble brown fraction and an ether-soluble green wax. In solution this purified wax has a green color much resembling alcoholic solution of chlorophyll. On cooling and evaporation it crystallizes out in a green mass which, on drying on a water bath, assumes a dark green color. It has a melting point of 83° to 84° C. and a saponification value of 216; its acid number is 63.79 and its ester number is 152.21. Though this wax resembles the montan waxes in general, it more closely resembles a wax isolated from Irish peat (*1*), except that its saponification number is higher.

LIGNIN CONTENT—The greatest importance and interest is centered around the lignin, cellulose, and humin contents. The relation of the relative amounts of these three components gives an index of the changes, generally termed "humification," going on in the deposit as time advances. This group also involves the much debated question as to the origin of humins; one school maintains that lignin alone, or primarily (*2*), is the source of humin; another maintains that lignin and cellulose contribute in more equal proportions (*5*). Not many years ago cellulose alone was considered; evidence now points in the direction that cellulose contributes only indirectly and then in small amounts (*8*).

Table I—Analysis of Peat by Chlorine Dioxide Method

Depth		Hot-Water Soluble[a]	Ether-Soluble[b]	ClO_2–3%[c]	NH_4OH[d]	Schweizer's[e]	Insoluble[f]
Inches	*Meters*	%	%	%	%	%	%
3	0.076	..	1.8	36.50	9.9	24.97	4.1
6	0.15	..	3.77	21.30	15.15	38.85	8.46
9	0.23	2.48	3.83	18.12	14.60	38.81	12.93
12	0.30	..	5.28	11.50	17.30	33.02	12.77
15	0.38	..	..	...	...	...	...
18	0.45	..	3.56	33.4	14.67	22.33	9.46
21	0.53	4.25	3.45	41.3	15.53	14.46	10.41
24	0.61	..	1.39	22.3	32.10	7.35	23.71
30	0.76	..	1.34	29.6	18.00	9.58	30.54
36	0.91	3.55	8.57	21.3	33.2	9.21	18.30
42	1.06	5.80	7.25	16.4	35.4	2.50	13.56
48	1.22	3.08	4.66	27.7	38.54	6.85	14.36
54	1.37	..	2.96	20.3	35.78	5.01	19.52
60	1.52	4.46	2.92	20.16	31.02	20.39	15.36
66	1.67	..	2.53	12.61	36.58	23.03	19.21
72	1.83	2.3	4.28	28.81	37.71	7.24	23.71
78	1.98	..	1.66	30.2	31.12	10.12	20.19
84	2.13	1.3	3.47	23.95	38.6	4.03	24.05
90	2.28	..	1.84	19.43	35.91	2.17	...
96	2.44	0.9	5.67	20.15	42.86	0.88	21.50
102	2.59	..	4.12	18.28	47.96	0.43	23.35
108	2.74	..	1.53	15.75	49.50	1.03	18.26
114	2.89	..	2.21	18.25	47.8	...	19.36
120	3.04	..	4.45	10.00	51.05	...	20.40

[a] Hexosans, pentosans, humins, starches, gums, organic nitrogen, and amines.
[b] Fats, waxes, and resins.
[c] Lignin and pentosans.
[d] Humic matter.
[e] Cellulose.
[f] Spores and cuticles.

Table II—Analysis of Peat by Odén's Method

Depth		Ether-Soluble[a]	H_2SO_3[b]	NH_4OH[c]	Schweizer's[d] Cupric Ammoniacal Soln.	Insoluble[e]
Inches	*Meters*	%	%	%	%	%
3	0.08	2.89	42.3	7.01	44.73	2.0
6	0.15	3.01	27.3	19.62	38.51	10.62
9	0.23	3.22	23.6	21.83	37.15	15.23
12	0.30	4.13	21.7	22.84	40.53	12.07
15	0.38	2.95	52.6	12.2	23.3	9.03
18	0.45	2.80	43.4	25.02	11.27	18.31
21	0.53	3.88	34.8	30.84	9.03	21.05
24	0.61	2.88	38.3	39.16	11.63	18.53
30	0.76	2.80	16.7	43.93	7.18	...
36	0.91	5.96	...	...	...	...
42	1.06	4.2	20.32	45.87	5.01	23.35
48	1.22	3.68	15.12	53.2	3.58	25.20
54	1.37	2.69	17.52	51.78	18.23	9.37
60	1.52	1.95	10.28	56.38	22.08	10.82
66	1.67	2.2	18.63	50.21	10.36	15.64
72	1.83	2.1	11.7	43.98	...	20.18
78	1.98	0.84	17.56	50.2	4.83	10.36
84	2.13	1.51	34.20	47.29	1.08	15.30
90	2.28	1.67	21.81	54.6	2.01	20.35
96	2.44	3.17	17.36	59.8	0.00	18.43
102	2.59	0.61	...	53.7	0.00	21.06
108	2.74	3.5	16.28	65.80	2.16	23.46
114	2.89	4.2	13.06	60.28	...	26.32
120	3.04	6.6	15.20	61.03	0.00	28.35

[a] Fats, waxes, and resins.
[b] Lignin.
[c] Humic matter.
[d] Cellulose.
[e] Spores and cuticles.

As may be expected, because the surface layer contains much sound woody matter, chiefly in the form of roots and semi-rotten stem fragments, the lignin content in the uppermost layer of peat is high. As shown in Tables I and II and Figure 4, the lignin rapidly drops from a relatively high percentage, 36 to 44 per cent at the surface, to a low point, between 10 and 12 per cent, just below the middle of the deposit in the moss-peat zone; at the 1.83-meter (6-foot) level in the horizon of the grass-sedge-reed peat the lignin content again suddenly rises to a high point of more than 30 per cent, owing to a high state of preservation of this zone; it then decreases to less than 10 per cent at the bottom.

Alkali-Soluble Matter—The alkali-soluble matter comprises essentially the humins. These are the most important and interesting components, as they constitute the main contributors to coal.

As shown by Tables I and II and Figure 5, the curves of the humic contents are definitely related in reverse order to that of the lignin curves. It starts with a low figure (between 8 and 10 per cent) in the surface layer, and gradually rises to the bottom of the woody peat zone with over 50 per cent, taking a slight downward turn in the moss-peat zone, again taking an upward turn in the grass-sedge-reed peat, and gradually rising to a high point of above 60 per cent at the bottom.

It should be remembered that the curves of the data obtained by Odén's method include the water-soluble humins as well as certain hexosans and pentosans; therefore they are relatively higher (*3*).

The humic material, as separated from peat with 2 *N* ammonium hydroxide, is far from being a unit substance; in fact, it is a heterogeneous substance and can be separated into a number of fractions, as follows: (1) a water-soluble fraction called fulvic acid; (2) a hot-alcohol-soluble fraction called hymatomelanic acid; and (3) an insoluble fraction, the humic acid proper. The last fraction may again be separated into a sodium carbonate–soluble and a sodium carbonate–insoluble fraction. The sodium carbonate–soluble fraction, precipitated with hydrochloric acid, is further separable with pyridine into a soluble and insoluble fraction. The hot-alcohol fraction, or hymatomelanic acid, on cooling separates out into a wax with a melting point of 79° C. after filtering and desiccating the filtrate. A resin acid is dissolved out with ether.

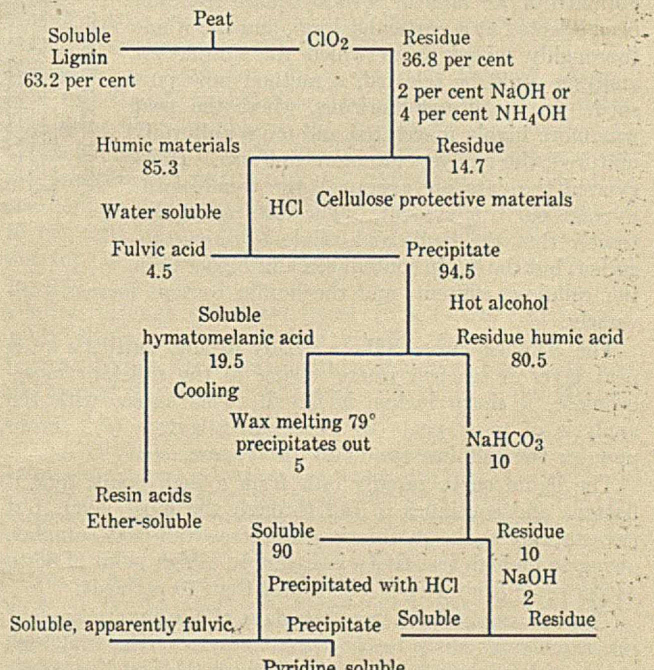


Figure 6—Separation of Humins

The complete procedure, beginning with peat, is outlined in flow sheet of Figure 6.

Cellulose Content—As in the lignin content, and for the same reason, the cellulose content is high in the surface layer, being more than 40 per cent. From this it rapidly falls to a low figure of 2 to 10 per cent in the lower horizon of the woody peat. In the moss-peat layer the cellulose again rises to over 20 per cent to the cellulose-resistant mosses. It is still high in the better preserved grass-reed peat layer, in which it falls to none or merely a trace. Tables I and II and Figure 7 give results of analyses.

Comparison of Lignin, Cellulose, and Humin Curves

If we had to deal with peat derived from decomposing wood alone, it would be simple to establish a clear relation between the three components, lignin, cellulose, and humins; unfortunately, we have a large number of other plant substances to consider, such as the remains of leaf tissues, bark, fungi, algae, liverworts, mosses, and lichens, whose tissues are quite different in chemical composition from that of wood. But it is safe to say that wood is the largest contributor and there should be some harmony in the data found. As will be noted, data obtained in the first foot of the material are erratic. This is due to a faulty selection of samples for analysis. More uniform results would have been obtained if an area of several square feet had been selected at a particular level, and the whole thoroughly mixed, from which the sample for analysis could be selected, a method now pursued. In the deeper horizons, where the peat was more highly macerated and more uniformly matured, the analyses are more uniform. However, if the data are averaged, the trend of the average curve is evident. The data show distinctly that the lignin and cellulose decrease together, but the lignin content remains higher than the cellulose content, and the humin content increases inversely.

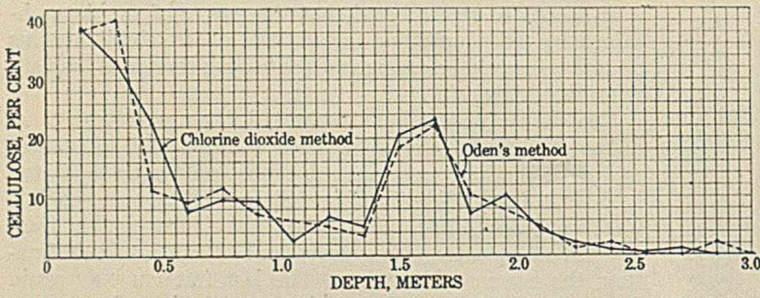


Figure 7—Cellulose Content of Peat in Relation to Depth

The cellulose curves take a steady decline until the moss peat layer is reached where, owing to the resistant moss-cellulose, a sharp incline is noted. This agrees with the analysis of moss peats by other investigators (*9*). From now on the cellulose gradually disappears.

The lignin curve rapidly falls from a high point, then it flattens and continues to fall through the moss layer, but rises rapidly again on entering the grass-reed-peat complex, owing to its high resistivity in lignin, to a high point of 36 to 44 per cent; from here it falls to less than 10 per cent.

The curves obtained from the data of the humin content rise rapidly inversely to the lignin content. The first high points of the humin curves coincide with the first low points of the lignin curves, but not with the cellulose curves; the first high points of the humin curves approximately coincide with the high cellulose point in the moss-peat zone.

The questions now naturally arise—what becomes of the lignin and cellulose and what is the source of the increasing humins? Unfortunately, as already indicated, the analyses give no definite clues, because of the many and varied substances that have contributed. Both lignin and cellulose decrease in general toward the deeper strata and the humin increases proportionately. It can therefore be argued that both are contributors. Experiments on decomposing wood have shown that the cellulose in it disappears, decomposing mainly into water and carbon dioxide, while the lignin is transformed into the so-called humins. Cellulose, when subjected to the action of microörganisms, does not form humins directly. The bodies of the organisms, however, formed synthetically during the decomposition of cellulose, give rise to humin in definite proportions (*8*). From such experiments and others it is assumed that the humins are derived primarily from the lignin in woody tissues.

The steady increase in the insoluble matter, consisting chiefly of spore, pollen, and cuticle matter, is explained by the fact that these components are very resistant to all kinds of reactions, and will therefore concentrate and remain undecomposed and accumulate as the other materials gradually decompose more and more and are totally lost to the deposit. Tables I and II and Figure 8 give results of determinations.

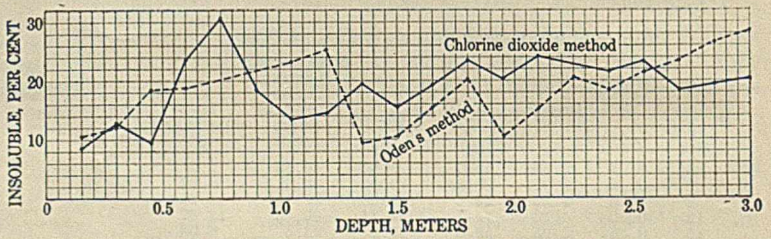


Figure 8—Insoluble Material in Peat in Relation to Depth

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(8) Waksman, *Proc. Intern. Soc. Soil Sci.*, **2**, 293 (1926).

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Wider Use for Inferior Wood

An annual saving of 113,000 acres of standing timber would result if the 33,000 carloads of non-utilized wood developed in North Carolina each year should be put to proper use, the committee on wood utilization, Department of Commerce, announced. In its report on a survey conducted in North Carolina, the committee urges sawmills to establish by-products industries involving the utilization of sawdust in the manufacture of pulp, paper, wood chemicals, and similar products.

The committee has already completed a similar survey in Virginia and another is in progress in Maryland. The investigation in each case covers only such waste-wood items as are not being put to profitable use, even for fuel.

The bulletin on the North Carolina survey discusses in detail the recognized methods for reducing wood waste, and also brings out important points in connection with the utilization of wood waste unavoidably produced. It gives a detailed account of this wood waste in North Carolina, enumerates the names of the mills by counties, and, in each instance, gives an accurate description of the number of carloads of wood waste available at every plant and the kind of wood, both as to species and type of waste.

The "Survey of Non-Utilized Wood in North Carolina" may be obtained from the Superintendent of Documents, Government Printing Office, Washington, D. C., at 20 cents per copy.

Analytical Reactions of Tetraethyl Lead[1]

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Analytical methods have been described for the determination of tetraethyl lead and related compounds in concentrated preparations, and of tetraethyl lead in dilute solution in gasoline.

The limits of accuracy of these methods, and their applicability, under different conditions, have been discussed.

THE wide distribution of motor gasoline containing tetraethyl lead has stimulated interest in the analytical methods that can be applied to organic lead compounds. Except for the publications of Krause and his co-workers several years ago (*9*) and the more recent article by Gilman (*8*), practically no methods of analysis applicable to concentrated organic lead preparations have been published. On the other hand, several methods of analysis of gasoline for tetraethyl lead have been suggested in the literature (*1, 2, 4, 5, 7, 10*) which, from the authors' experience, are somewhat lacking in both convenience and accuracy. Since the methods suggested by Krause and by Gilman are of only limited applicability, it may be of interest to present in detail and discuss the methods which have been developed in this laboratory and employed for several years.

The methods as described herein apply particularly to tetraethyl lead and other ethyl lead compounds. Their applicability to other alkyl lead compounds will be considered in the discussion.

For the physical and chemical properties of organic lead compounds on which the analytical methods are based, the reader is referred to a review of the subject by one of the authors (*3*).

Experimental Methods

METHOD 1. TOTAL LEAD IN CONCENTRATED PREPARATIONS—

Caution—Concentrated preparations of organic lead compounds are highly poisonous. They should be handled under a hood equipped with vigorous suction, and care should be employed to prevent contact with the hands.

(*a*) *Gravimetric.*

Reactions: $PbEt_4 \longrightarrow PbBr_2 \longrightarrow PbCrO_4$

To about 25 cc. of carbon tetrachloride in a 500-cc. Erlenmeyer flask add about 1 cc. of tetraethyl lead or its concentrated solution, weighed in a Lunge pipet (*6*). Keep the Erlenmeyer flask ice cold, and add slowly and with constant shaking an excess (5 to 10 cc.) of a 30 per cent solution of bromine in carbon tetrachloride.

Evaporate on a steam bath the carbon tetrachloride from the solid lead bromide. To the dry lead bromide add a mixture of 30 cc. of concentrated ammonia (sp. gr. 0.90) and 50 cc. of 50 per cent acetic acid, washing down the sides of the flask. Boil until the precipitate is completely dissolved and any remaining carbon tetrachloride removed. Filter from any insoluble matter and wash the flask out well with hot water into a beaker. Dilute the filtrate and washings to 450 cc. and heat to boiling on a hot plate. Now add slowly and with constant stirring 40 cc. of a 5 per cent solution of potassium dichromate. Stir for 5 minutes while the solution is boiling, then remove from the hot plate and keep in a warm place for one hour. Collect the precipitate on a weighed and ignited Gooch crucible and wash well with hot water. Dry in a crucible air bath, or in an oven at 105° C. and weigh as $PbCrO_4$.

(*b*) *Volumetric.*

Reactions: $PbEt_4 \longrightarrow PbBr_2 \longrightarrow PbMoO_4$

Prepare the ammonium acetate solution of lead as in section (*a*), boil it down to 150 cc., and titrate hot with a standard molybdate solution, until a yellow coloration is obtained with tannic acid used as outside indicator. The molybdate solution is standardized against a known weight of lead or lead chloride (*11*). The indicator used is a 0.5 per cent freshly prepared solution of tannic acid. Care must be taken always to use the same amount of indicator (2 drops) and solution (4 drops). A blank is run on the same amount of water and ammonium acetate, and the amount of molybdate solution used to give a distinct coloration (about 0.3 cc.) is subtracted from the result of the titration.

METHOD 2. TOTAL ORGANIC LEAD IN DILUTE SOLUTION (IN GASOLINE)—(*a*) *Gravimetric.* Measure with a pipet 100 cc. of gasoline containing tetraethyl lead in a 400-cc. beaker. Add slowly a solution of 30 per cent bromine in carbon tetrachloride, until the permanent brown-red color of bromine is obtained.[2] Filter promptly through asbestos in a dry Gooch crucible—or preferably through a fritted Jena glass filter crucible of No. 2 porosity—and wash with petroleum ether. Put the crucible back in the beaker where the precipitation was made and add about 3 cc. of nitric acid (sp. gr. 1.40) in the crucible. Add a warm solution of 10 per cent nitric acid in quantity just sufficient to cover the top of the crucible, bring to boiling, remove the crucible, and boil down to about 3 cc. Dilute and filter the solution through soft filter paper (if a Gooch crucible was used), rinsing the beaker and crucible with warm water. Just neutralize the filtrate with ammonium hydroxide and add 5 cc. of 50 per cent acetic acid. Continue as per Method 1 (*a*).

Note 1—Gasolines containing a high percentage of unsaturated compounds absorb bromine vigorously with evolution of heat. In such cases it is highly advisable to dilute the sample with about 100 cc. of a volatile petroleum fraction fairly free from unsaturated compounds (cracked stock), to add the bromine slowly, and to keep the beaker in ice. When this precaution is not taken, the results are apt to be low. Suitable diluents are, for instance, fighting grade aviation gasoline, petroleum ether, and ligroin.

Note 2—Some gasolines, when treated with bromine, give a tarry liquid insoluble in gasoline. In such cases the precipitated lead bromide should be washed with special care with petroleum ether, in order to remove the tar thoroughly before dissolving the lead bromide in nitric acid.

(*b*) *Volumetric.* Prepare the ammonium acetate solution as in Method 2 (*a*), boil down to 150 cc., and titrate hot with a standard molybdate solution as in Method 1 (*b*).

Note 1—The molybdate solution may be made to contain 2.380 grams of commercial C. P. salt, in which case 1 cc. of this solution used on an original 100-cc. sample of gasoline corresponds to 0.1 cc. of tetraethyl lead (sp. gr. 1.65) per gallon of gasoline.

Note 2—In some cases the lead nitrate which begins to precipitate when the solution is concentrated to 3 cc. volume is contaminated by a small amount of organic matter. It is then advisable to evaporate to dryness and treat with fuming nitric acid, repeating the operation until a clean white residue of lead nitrate is obtained.

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[1] **Received May 2, 1929.**

[2] This method of separating the lead from the gasoline was worked out independently in several laboratories during the early part of the research work on tetraethyl lead.

METHOD 3. TETRAETHYL LEAD IN CONCENTRATED PREPARATIONS—

Reaction. $Pb(C_2H_5)_4 + I_2 = Pb(C_2H_5)_3I + C_2H_5I$

Solutions. 0.1 *N* iodine containing 50 grams of C. P. potassium iodide per liter; 0.1 *N* sodium thiosulfate; starch solution; C. P. benzene.

Apparatus. 250-cc. glass-stoppered flasks; weighing pipet (see *Note 4*); weighing burets or accurate volumetric apparatus.

Procedure. Weigh accurately 0.5 cc. of pure tetraethyl lead, or 1 cc. or less of its concentrated solution, and add it to 50 cc. of C. P. benzene in a 250-cc. glass-stoppered flask. Add at once 0.1 *N* iodine solution in amount equal to 2 to 5 cc. above the theoretical. (For tetraethyl lead the weight of the sample multiplied by 15 gives very nearly the correct volume of 0.1 *N* iodine; for a solution its approximate concentration must be determined by a trial titration.) Shake vigorously for 2 to 3 minutes and titrate the excess iodine with 0.1 *N* sodium thiosulfate, using starch solution as indicator and shaking vigorously meanwhile.

The number of cubic centimeters of 0.1 *N* iodine required times 0.01617 equals the weight of tetraethyl lead in the sample.

Note 1—In order to obtain accurate results, it is important that the procedure be followed in all its details, especially in regard to the amount of benzene and the concentration of potassium iodide in the iodine solution.

Note 2—When titrating with sodium thiosulfate part of the iodine is in the aqueous potassium iodide layer and part in the benzene. The titration can be run rapidly until the blue color of the iodine-starch in the water layer disappears. This will reappear on shaking, and the titration is then completed by adding the thiosulfate drop by drop, shaking well between additions.

Note 3—If the excess iodine is less than 2 cc., the results are usually low and the analysis should be repeated. More than 5 cc. excess can usually be added safely, but 2 to 5 cc. is best. If a yellow precipitate (of lead iodide) appears, the analysis should be rejected.

Note 4—For a convenient type of pipet devised primarily for this use, see Reference (*6*).

METHOD 4. MIXTURES OF TETRAETHYL LEAD AND DILEAD HEXAETHYL—Such mixtures are usually obtained in the preparation of alkyl lead compounds by the Grignard reaction. If no other substance is present, the specific gravity will indicate the composition of the mixture, the specific gravity of the two compounds being approximately 1.65 and 1.94, respectively. More accurate information will, however, be obtained by analysis. Both substances react with iodine:

$$Pb(C_2H_5)_4 + 2\,I = Pb(C_2H_5)_3I + C_2H_5I$$
$$Pb_2(C_2H_5)_6 + 2\,I = 2\,Pb(C_2H_5)_3I$$

The total lead present can be determined by Method 1.

From the results of the iodine titration and the determination of total lead, performed as per Methods 1 and 3, the amounts of tetraethyl lead and dilead hexaethyl can readily be calculated.

METHOD 5. TRIETHYL LEAD SALTS, WITH OR WITHOUT TETRAETHYL LEAD PRESENT—The triethyl lead salts are extracted with aqueous ammonia in which they are more soluble than in organic solvents.

Procedure. Dilute about 5 cc. of the concentrated preparation with 20 cc. of petroleum ether, and shake it with two successive portions of 20 cc. of a concentrated aqueous ammonia solution. Boil most of the ammonia off gently, acidify the remaining solution with nitric acid, boil down to about 3 cc., and analyze for lead as per Method 2 (*a*) or 2 (*b*).

METHOD 6. TETRAETHYL LEAD AND TRIETHYL LEAD SALTS—Extract the preparation with ammonia as per Method 5 to obtain the triethyl lead compounds. Treat the residue as per Method 1 to obtain the tetraethyl lead.

Discussion

ACCURACY—According to the experience of the authors, Method 1 is as accurate as ordinary analytical methods in inorganic chemistry—i. e., 0.3 to 0.1 per cent depending on the skill and care applied. In Method 2 the accuracy depends somewhat on the concentration of lead present, and on the nature of the solvent. (Gasolines containing large amounts of unsaturated compounds tend to give a tarry precipitate, which cannot always be transferred quantitatively.) However, the accuracy of routine analysis is better than 1 per cent for quantities of 0.75 to 3.0 cc. of tetraethyl lead per gallon of gasoline (0.02 to 0.08 per cent by volume, 0.04 to 0.16 per cent by weight), which seems to be sufficient for all practical purposes.

Method 3 appears to be good to at least 0.3 per cent when pure preparations are handled and when the procedure is followed accurately. The accuracy of Method 4 is somewhat uncertain, because no alkyl compound of the type Pb_2R_6 has ever been isolated in the pure state. Comparison with other properties (density, stability) seems to indicate that the method is quite reliable.

Methods 5 and 6 will give results accurate to within 1 to 2 per cent on the triethyl lead salts. The accuracy appears to be limited more by the instability of the compounds involved than by any shortcomings of the method.

APPLICABILITY—As stated in the introduction, the methods have been developed primarily for the analysis of tetraethyl lead and accompanying impurities. The aryl lead compounds are much more stable than the alkyl compounds, and the methods given here would have to be modified somewhat to apply in their case (*8*).

Methods 1 and 2 have been applied successfully to several alkyl lead compounds beside ethyl. Methods 3 and 4 would probably also be applicable in their case, but the authors have had no experience with them.

Methods 5 and 6 will determine with certainty the presence of as little as 1 per cent of a triethyl lead salt in tetraethyl lead.

Methods 1 and 2 appear to be applicable to practically all organic solvents, with the exception of those that would react too violently or too completely with bromine. Methods 3 and 4 are obviously applicable only in the absence of substances which react with iodine in the conditions specified. The conditions of concentrations and the amount of reagent are of such importance from the standpoint of accuracy that the method would probably not be applicable to dilute solutions in the presence of unknown substances.

Acknowledgment

The authors wish to acknowledge the assistance of several members of the laboratory staff, particularly O. R. Dorion, in carrying out experimental work.

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Determination of Inert Gas Content of Gas Mixtures by Means of Calcium as an Absorbent[1]

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An apparatus is described which permits the analysis of various gas mixtures for the noble gases by a method involving absorption of all common gases and the measurement of change of pressure at constant volume.

Samples of air, nitrogen, hydrogen, and oxygen have been analyzed. Results are reproducible to within 0.002 or 0.003 per cent. Sources of error and possible improvements in the apparatus are discussed.

NITROGEN used in experimental work at the Fixed Nitrogen Research Laboratory is frequently a commercial product prepared by the fractional distillation of liquid air. Nitrogen thus prepared generally contains small amounts of the noble gases. Recently it has become necessary to determine quantitatively the aggregate amount of these impurities in the nitrogen and in its mixtures with hydrogen. An analytical method has been devised which employs certain well-known chemical reactions of metallic calcium but which embodies apparatus and technic not previously described. This method assures rapid analyses, capable of measuring 0.01 per cent of inert gas.

Chemistry of the Reaction

In 1898 Moissan first prepared calcium in sufficient quantities for a careful study of its physical and chemical properties (*6*). This finely divided crystalline metal he found to react vigorously with both nitrogen and hydrogen to form the nitride and hydride, respectively. He also observed that the dissociation pressures of these compounds were "immeasurably" small at dull red heat.

These observations were qualitatively verified by Arndt (*1*). He, however, reported that the metal begins to volatilize at about 700° C. (Pilling (*8*) has calculated the vapor pressure of calcium at 700° C. to be 0.19 mm. of mercury), whereas the melting point is about 800° C., and that the absorption of the gases begins at approximately the temperature of volatilization. After absorption of the gases, analysis with a Plücker spectrum tube showed the absence of nitrogen but indicated a residual pressure of hydrogen.

The findings of Sieverts (*11*) gave full qualitative support to the results of earlier investigators as to end products, but his conclusions as to reaction conditions have not been confirmed by more recent investigators. He attributed the variable activity of calcium samples to differences in crystal size. Ruff and Hartmann (*9*) have shown that this variation is due to foreign metals alloyed in varying amounts with the calcium samples.

Kraus and Hurd (*4*) studied equilibria in systems involving calcium, hydrogen, and nitrogen, and in this connection measured the dissociation pressures of calcium hydride and of calcium nitride. At 734° C. they found the dissociation pressure of pure calcium hydride (CaH_2) to be 4.2 mm. of mercury. At 792° C. the pressure had risen to 15.2 mm. The dissociation products, however, appear to be hydrogen and a subhydride of calcium, for hydrogen heated with an excess of calcium at 870° C. is apparently completely absorbed. These findings are in general agreement with the work of Moldenhauer and Roll-Hansen (*7*) and more recently that of Ephraim and Michel (*2*), who reported a subhydride of calcium with a high dissociation temperature. The smoothness of the rapid reaction between the metal and hydrogen is attributed to the great solubility of the subhydride in the metal.

The dissociation pressure of calcium nitride is given by Kraus and Hurd as 0.3×10^{-3} mm. of mercury at 958° C., the lowest temperature at which experimental measurements were made. Whatever the exact mechanism of the reactions of calcium with hydrogen and nitrogen, it is certain that almost complete absorption takes place. Moreover, as was first pointed out by Soddy (*13*), most of the other common gases likewise react with hot calcium to form compounds with extremely low dissociation pressures. Soddy used this property of calcium to obtain high vacua in glass containers. At the present time it is being employed on a large scale by the incandescent lamp industry for removing foreign gases from argon-filled lamps. It appears from the literature (*5*) that hot calcium with water vapor reacts to form the oxide and hydride; carbon monoxide and carbon dioxide give the oxide and free carbon or calcium carbide depending upon the temperature; hydrogen sulfide gives sulfide and hydride, while sulfur dioxide yields sulfide and oxide. Methane, ethylene, and other hydrocarbons give the hydride and free carbon or the carbide; halogens react giving the corresponding halides; and the halogen acids give the halides and hydride.

Sieverts and Brandt (*12*) seem to have been the first to employ the activity of hot calcium for purposes of gas analysis. Their method yields data reproducible to not less than 0.1 per cent. For example, they found dried air to contain 1.06 per cent argon, whereas the present accepted value is 0.94 per cent (*3*). The essential fact is that their method was based on change in pressure caused by the absorption by hot calcium of all save the noble gases. Measurement of change in pressure at constant volume and temperature is likewise the basis for the analytical procedure about to be described.

Apparatus

The apparatus under discussion has been kept as simple as possible commensurate with its ability to measure 0.01 per cent of inert gas. In the accompanying diagram *A* indicates the reaction chamber blown from a section of 3-inch (7.6-cm.) Pyrex tubing. At one end it is drawn out to a neck fitted with a ground-glass stopper, *N*, through which are sealed tungsten leads, *M*. *B* is a quartz shield tube to protect the glass walls of the container, and is held in position by two aluminum collars, *EE*. The collars and the tube were placed in *A* before *A* was drawn down. *C* is a smaller quartz tube of a size that will pass through the neck of *A*. It is wound with nichrome ribbon, *D*, the two ends of which are coupled to copper leads, *L*. *K* indicates calcium metal shavings. Two brass collars, *PP*, serve to hold the nichrome ribbon and also to center the tube *C* in the larger tube *B*. The current necessary to heat the calcium is adjusted by the variable resistance, *O*, and is led in through the tungsten leads, *M*, sealed through the Pyrex stopper *N*. The leads *L* are thick enough to withstand a certain amount of stress involved in pushing and pulling the tube *C* in and out of *A* and *B*. To assist further in this, two slender hooked brass rods (not shown) are used. At

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[1] Received July 9, 1929.

the other end, the container *A* is drawn down and sealed to a 3-way stopcock *F*. One outlet of *F* connects through a spiral glass tube and a second 3-way stopcock, *G*, with a McLeod gage, *H*, and a closed-end manometer, *I*. The second outlet of *F* is connected with a third 3-way stopcock, *J*, which communicates with a vacuum pump and with the source of the sample to be analyzed.

Procedure

When an analysis is to be made, all parts of the apparatus should be completely evacuated before the sample is introduced. If, however, a pump capable of giving a high vacuum is not available, analyses can be made just as accurately by means of a pump that will reduce the pressure to a few millimeters. In this case the procedure is to evacuate the entire apparatus as far as possible by opening *F* and *J* to the pump. At intervals *F* is turned to communicate through *G* with the gage and manometer. In this way the latter are evacuated without difficulty, since their capacity is small compared with that of *A*. When the pressure in the apparatus is reduced to the limit of the pump, *J* is opened to the sample and *A* filled to atmospheric pressure. By turning *F* open to *G* momentarily and again bringing *A* to atmospheric pressure by reopening *F* to *J*, the pressure in the system as a whole will be approximately atmospheric when *F* is again opened to *G*. If the refilling and evacuating are repeated several times, the residual air in the apparatus will be negligibly small. In case the gas to be analyzed is available only in small amounts. the apparatus may be flushed out with nitrogen and the pressure exerted by the residual nitrogen at the time the sample is taken into the apparatus subtracted from the pressure exerted by the sample. The pure nitrogen will, of course, be completely absorbed by calcium. If desired, the calcium may be heated and the residual nitrogen removed in that way before the sample is drawn in.

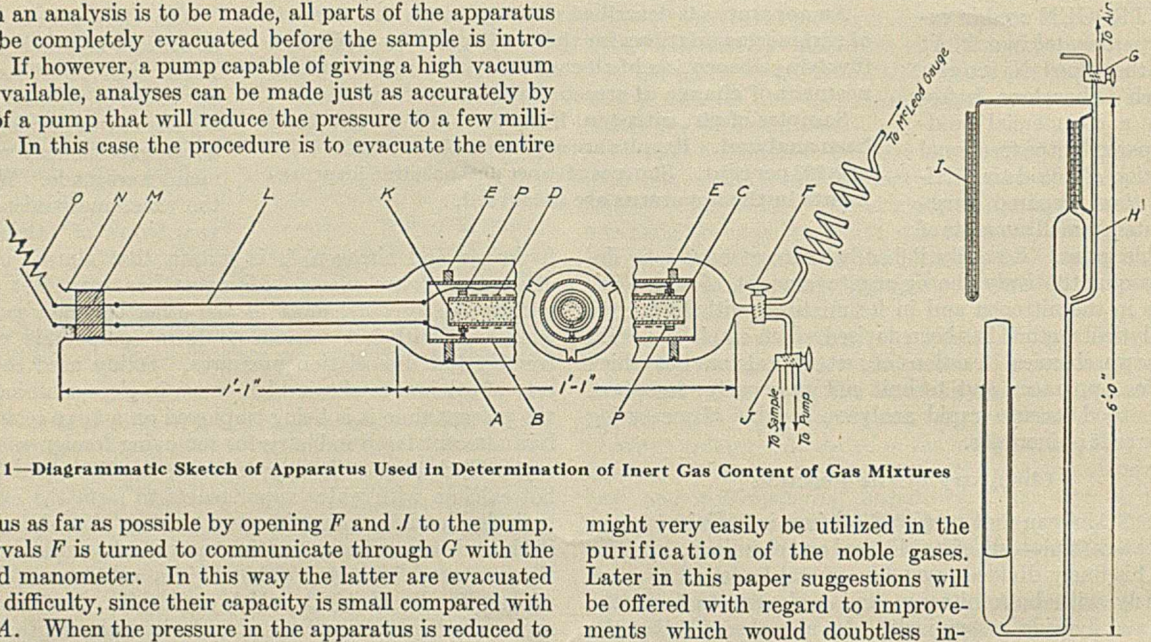

Figure 1—Diagrammatic Sketch of Apparatus Used in Determination of Inert Gas Content of Gas Mixtures

The capacity of *A* is approximately 1500 cc., while the capacity of the McLeod gage, manometer, and connecting tube is about 150 cc. The tube *C* holds only 10 or 15 grams of calcium shavings, and to avoid the necessity of recharging the tube with calcium each time, the pressure of the sample is kept down to 7 or 8 cm., or less. In this way also the final pressure, which is due to inert gases present, may be fixed at the most convenient value for reading on the McLeod gage.

In the apparatus as used, two extra tungsten leads (not shown in the diagram) were sealed through the stopper *N* in order to make use of a thermocouple for temperature regulation. This is unnecessary, since visual control is sufficient. When the nichrome ribbon glows at a red heat, the calcium is sufficiently hot to react efficiently and quickly.

After the reaction of the calcium with the gas begins, the pressure decreases very rapidly and the reaction is complete in 10 or 15 minutes. The calcium is reheated and cooled several times until no further reduction of pressure is noted. Nitrogen is apparently completely absorbed during a single heating. In the analyses, the results for which are given in this paper, no attempt was made to bring the final temperature back to exactly the initial value. The pressure was read on the McLeod gage as soon as the outside surface of *A* felt cool to the touch. Undoubtedly the interior of *B* was still many degrees warmer than the exterior of *A*, but the effect of the heat was not appreciable in the reading of the gage because of the small fraction of the total volume of gas which was at this higher temperature.

A modification of the apparatus as it has been described might very easily be utilized in the purification of the noble gases. Later in this paper suggestions will be offered with regard to improvements which would doubtless increase the accuracy of the measurements.

Experiment Results

Analyses were made of various gas mixtures. All samples were dried by passing through a drying tube filled with phosphorus pentoxide. The results are summarized in the accompanying table.

Analysis of Gas Mixtures

MATERIAL ANALYZED	ORIGINAL PRESSURE	FINAL PRESSURE	RESIDUAL GAS
	Mm.	*Mm.*	*Per cent*
Air	55.5	0.524	0.944
	60.2	0.567	0.942
Nitrogen	65.5	0.050	0.077
	49.0	0.038	0.078
	62.4	0.048	0.077
	64.6	0.049	0.076
Hydrogen	68.1	0.004	0.006
	43.0	0.004	0.009
Oxygen	31.9	0.031	0.097
	43.2	0.042	0.097

The nitrogen samples were taken from a cylinder filled by a commercial firm which obtains nitrogen of a high degree of purity by fractional distillation of liquid air.

Hydrogen gas generated by electrolysis of sodium hydroxide in cells of commercial type furnished the hydrogen samples. The constant final pressures obtained even with samples of widely varying size is of interest and will be discussed in another place.

The oxygen gas was taken from two cylinders provided through the courtesy of a local firm, one sample being taken from each cylinder. This gas was also prepared by fractional distillation of liquid air and contains a somewhat higher percentage of rare gases than does nitrogen. This might be expected from a comparison of the boiling points of oxygen, argon, and nitrogen.

Discussion of Sources of Error and Suggested Improvement in Apparatus

Very probably the largest source of error in the apparatus as described in this paper lies in the reading of the mercury manometer. It is doubtful if the differences in level can be read with an accuracy greater than ±0.2 mm. unless a good grade cathetometer is employed. It is suggested that the initial pressure be read with a McLeod gage registering to 0.5 atmosphere. Such a gage can be read with an accuracy exceeding 0.1 mm.

Characteristics inherent in the McLeod gage introduce an error in the precise reading of small pressures. For example, variations in the bore of the capillary may exist. The personal error also enters with the reading of the differences in level of the mercury columns. A discussion of these characteristics is given in the book by Dushman entitled "High Vacuum."

The McLeod gage, the empty portion of the mercury manometer, and the connecting glass tube were not heated at any time in the making of the analysis, although these parts could easily be heated without any modification of the apparatus. The following quotation from Soddy (*13*) emphasizes the necessity of this in order to bring about greater accuracy:

> The value of calcium as a means of producing the highest vacuum depends on its power to absorb almost instantly the gases condensed on the glass walls as soon as the latter are expelled by heating. As is well known, the real difficulty in the production of high vacua depends not as much on the removal of all the original air, which is comparatively easily and quickly accomplished even with a pump, but on the effective removal of the gases which are condensed on the glass walls of the vessel being exhausted, and which tend to recondense in the pump when driven out of the vessel, and to introduce a kind of steady vapor pressure until they have all been removed.

It may be explained that Soddy excluded the noble gases from the vessels which he wished to evacuate by means of calcium. Adsorbed gases may be one explanation of the constant final pressure obtained in the case of hydrogen analyses. This explanation is given weight by the findings of Sherwood (*10*), who observed a continuous deterioration of vacuum with time in glass. In the light of the findings of Kraus and Hurd (*4*) it is doubtful if unabsorbed hydrogen in the presence of excess of calcium would account for this residual pressure. The spectroscope could be used in establishing the facts in this case.

Temperature variation, at the times of the initial and final pressure readings, introduces a small error which could be eliminated by the use of a removable water jacket. There is also a small error introduced through the change in volume of the apparatus caused by the shifting of the mercury columns when the sample is absorbed by the calcium. This factor is reduced to a negligible value in the apparatus here described because of the comparatively great volume of the chamber *A*. Sieverts and Brandt (*12*) found it necessary to calculate a correction for this factor in their work because of the small size of their gas samples.

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Determination of Total Moisture in Carbon Blacks[1]

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IN THE course of an extended research on various grades of carbon black, determinations of total moisture were made by an adaptation of an old method. The method used was similar to one described by Allen and Jacobs (*1*) for measuring water in tar. The chief difference in the present method is that small amounts of moisture in carbon blacks must be weighed, whereas the larger amounts in tar could be measured. The difficulties in weighing the evolved moisture are described in the ensuing method of determination.

Five grams of carbon black were placed in a 500-cc. round-bottom flask with 25 to 35 cc. of dry xylene and 200 cc. of dry mineral oil. A short air condenser led to the bottom of a 25-cc. distilling flask, which in turn was connected to two or more calcium chloride tubes. The flask containing the sample was heated to 150–175° C. in an oil bath, a stream of dry nitrogen being passed through the apparatus. The water and xylene were distilled into the small distilling flask and thence, by warming in a water bath, into the calcium chloride tubes, the current of nitrogen being continued. It required but a few minutes to remove the water from the xylene, indicated by the disappearance of cloudiness, and the calcium chloride tubes were then connected directly to the nitrogen line and the gas was passed through until the tubes reached constant weight. Xylene is not adsorbed by calcium chloride and nitrogen does not remove water from it at room temperature during the time required for the experiment. The increase in weight of the calcium chloride tubes is the amount of water in the sample of carbon black. The amount of water thus determined is considerably higher than the 105° C. oven loss in 5 hours, and indicates that most of the moisture is of the "bound" or "capillary" type.

A comparison of the moisture as determined by the xylene method and the 105° C. oven is shown in the table:

BLACK	TOTAL H_2O	105° C. LOSS	BLACK	TOTAL H_2O	105° C. LOSS
	%	%		%	%
Micronex No. 1	5.75	1.42	High-temperature black[b]	0.87	0.30
Micronex No. 2	5.96	1.85	Acetylene black No. 1	3.19	0.07
Micronex No. 3	5.20	1.56	Acetylene black No. 2	3.67	0.07
Heated Micronex (950° C.)[a]	0.98	0.00	Goodwin	1.50	0.33
Cabot No. 1	4.88	1.79	Thermatomic (Special)	1.25	0.10
Cabot No. 3	3.54	1.66	Lampblack	6.75	3.26
Cabot No. 2	5.41	1.57	Super-Spectra	1.07	0.10
			Zinc oxide[c]	0.75	0.02

[a] Heated 10 minutes at 950° C. in a closed crucible.
[b] Made at 1500° C.
[c] Added for comparison.

The relationship of this "bound" moisture to any physical property of a rubber mix containing the black could not be shown. It is probable that other characteristics of the black, such as adsorptive capacity, particle size, etc., are more effective in causing variations than the amount of moisture. Nevertheless the large amount of water in blacks as compared with that in other pigments, such as zinc oxide, is indicative of their relative adsorptive capacities.

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[1] Received June 13, 1929.

Analyses of Some Natural Gasoline Gases before and after Treatment[1]

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ALTHOUGH the natural gasoline industry has been in existence a good many years, it has been only the last year or two that real efforts have been made to determine the exact composition of the gases from which the gasoline has been obtained, together with the composition of the residue gases. The usual tests, such as combustion analyses, gravity, absorption in oils, etc., and the different field tests have a certain value but their limitations are well known. The results differ quite widely when made on gases of varying composition and with the variations commonly used in making the tests they leave considerable uncertainty as to the design of a plant and what may be expected in practice. A knowledge of the exact composition of the gases to be treated is desirable when designing a plant, and after a plant has been installed analyses of the raw and treated gases will furnish much valuable information as to proper operating conditions.

The rapidly increasing demand for the propane and butane fractions will also make analyses of this kind valuable, since the usual tests throw very little light on the individual hydrocarbons. Only a small percentage of the propane usually present in natural gas is removed by the absorption plant at the present time, while from 30 to 50 per cent of the butane may be taken out. With a demand for these products there is no doubt but that in the future the design of plants and operating conditions will be materially altered in such a way as to obtain more of these products, which until now have been undesirable. As a matter of fact, it may not be long before plants will be designed for the purpose of obtaining these two products while any natural gasoline recovered will be considered as a by-product.

Analytical Data

The following data on three natural gasoline plants using mineral seal absorption oil were selected as representing three rather different gases so far as gasoline content is concerned, and it is believed indicate about what may be expected from plants operating on such gases at the present time. Combustion analyses of the gases are also given for the sake of comparison and, as would be expected, the percentages of the constituents calculated in this way are quite different from those actually present in the gases.

It will be noted that the residues obtained from fractionation and combustion methods, which should be identical, are not in very close agreement, while the calculated heating values are fairly satisfactory in this respect. Any strictly additive property should be the same whether calculated from fractionation or combustion analyses, and heating values and gravities are very nearly additive. In each case the percentages of methane and ethane increase in the treated gases, while the higher hydrocarbons decrease, and this is probably true generally in absorption plants.

The actual composition of each raw gas shows a rather regular decrease as we pass from the methane to the higher hydrocarbons, but this is not true in all natural gases, as some have been examined that show more hexane than pentane present. This point was checked up rather carefully and is believed to be correct. In work done at the University of Kansas heptane is the highest hydrocarbon that has been determined in natural gases, but traces of octane have been detected.

It will be noted that in each case the gasoline not absorbed, which may be considered as the pentane fraction left in the residue gas, amounts to about 0.2 per cent, or slightly less than 0.1 gallon per thousand feet of gas. This seems to be about the limit of absorbability in practice, though no doubt it could be diminished by using larger quantities of absorbing oil. Residue gases have been examined that contained as much as 0.9 per cent of pentane, which shows a very poor recovery.

Analyses of Some Natural Gasoline Gases

(All results calculated air-free)

Constituent	Gas A		Gas B		Gas C	
	Raw	Treated	Raw	Treated	Raw	Treated
FRACTIONATION ANALYSES						
	Per cent	*Per cent*	*Per cent*	*Per cent*	*Per cent*	*Per cent*
CH_4	85.8	86.1	65.8	70.2	41.4	46.1
C_2H_6	6.5	7.4	10.5	11.1	24.4	28.7
C_3H_8	3.6	3.0	7.6	6.4	16.7	15.5
C_4H_{10}	1.2	0.9	3.6	1.9	6.8	4.3
C_5H_{12}	0.5	0.2	1.6+	0.2+	4.9	0.2
C_6H_{14}	Trace	...	1.0	Trace	1.2	Trace
C_7H_{16}	...	...	Trace	...	0.1	...
CO_2	0.3	0.2	0.7	0.5	0.7	0.7
Residue	2.1	2.2	9.1	9.7	3.8	4.5
B. t. u.	1131	1113	1270	1138	1755	1509
	Lbs. per 1000 ft.		*Lbs. per 1000 ft.*		*Lbs. per 1000 ft.*	
C_3H_8	4.19	3.49	8.85	7.45	19.43	18.03
C_4H_8	1.84	1.38	5.52	2.92	10.44	6.60
	Gallons per 1000 ft.		*Gallons per 1000 ft.*		*Gallons per 1000 ft.*	
C_5H_{12}	0.183	0.073	0.584	0.088	1.79	0.078
C_6H_{14}	...	...	0.41	Trace	0.494	Trace
C_7H_{16}	...	...	Trace	...	0.043	...
COMBUSTION ANALYSES						
	Per cent	*Per cent*	*Per cent*	*Per cent*	*Per cent*	*Per cent*
CH_4	78.05	78.80	43.45	58.40	...	20.97
C_2H_6	19.58	18.64	46.50	31.60	88.10	74.20
C_3H_8	...	...	...	...	7.96	...
CO_2	0.26	0.23	0.69	0.44	0.76	0.74
Residue	2.11	2.33	9.36	9.56	3.18	4.09
B. t. u.	1133	1117	1259	1148	1765	1519
SALABLE GASOLINE RECOVERED						
Gallons per 1000 ft. (about)	0.1		0.9		2.2	
Shrinkage, per cent (about)	1		6		14	

The quantitative connection between the volume of the raw gas and the residue gas is not very certain from the data usually obtained; however, where there is a considerable residue in a gas it may be assumed that this is only slightly affected in the absorbing process. With this assumption it has calculated in a number of cases that the total gas absorbed will be slightly more than twice the pentane and higher hydrocarbons actually absorbed. This value checks fairly well with the measured volumes when it has been possible to obtain such data.

Methods of Analysis

Details of the method used in the analyses would require considerable space, but in a general way the published meth-

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[1] Received April 16, 1929. Presented before the Division of Petroleum Chemistry at the 77th Meeting of the American Chemical Society, Columbus, Ohio, April 29 to May 3, 1929.

ods, with numerous modifications, were followed. The gases were fractionated by means of liquid air at different temperatures and as much of the work was a check on modifications of the apparatus and manipulation as well as on the gases, the fractions were analyzed by combustion methods. To eliminate variations in molecular volumes and any absorption of carbon dioxide after combustion, the higher fractions were calculated from the combustion data by combining the carbon dioxide and contraction and using this combined value with the oxygen consumed. This involves no additional manipulation, since there are no residues in these higher fractions. Three or four fractionations gave a rather pure product, but in practically all cases the combustion analyses indicated the presence of two hydrocarbons. For some reason the propane fraction seemed to be the easiest to obtain in a fairly pure condition.

Detection and Determination of Carbon Disulfide and Sulfur in Fluids[1]

A Colorimetric Method

J. A. Pierce[2]

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THE practice of adulterating pressed oil with pulp-extracted oil has resulted in the presentation, from time to time, of qualitative methods for the detection of traces of carbon disulfide in the product. The literature has also brought up the problem of determining the presence of free sulfur in those pulp oils that have been so thoroughly refined that carbon disulfide is absent.

Most of the recognized tests for carbon disulfide are not reactive with free sulfur. In 1926 Saccardi (*6*), for instance, presented his lead plaster method for the detection of carbon disulfide and claimed it to be sensitive to 1 part in 1,160,000 of carbon disulfide in olive oil. Conzoneri (*1*) objected to it on the grounds that it was useless in those oils that had been so super-refined that no carbon disulfide was present. Saccardi's description of his own technic is evidence that it is useless in detecting free sulfur. Its general application is therefore limited. The method of Fachini (*2*) was tried out in the author's laboratory and found to give the cherry-red color with any olive oil, either virgin or extracted.

Other methods have been presented which are sensitive either to carbon disulfide or to sulfur, and which are credited with giving very satisfactory results, but their technic is too involved and too much time is consumed in arriving at a result. Thus, the Milliau test (*4*) is stated as being sensitive to 0.05 per cent of carbon disulfide, but it has the disadvantage of requiring the use of a sealed tube and several hours of manipulation. Again, the thallo-acetylacetone method of Kurowski, discussed by Utz (*7*), is also tedious, and has been found sensitive to only 1 per cent with certainty. Such processes have no place in the commercial laboratory where rapid work is imperative.

One method of detecting carbon disulfide readily is that which results in the precipitation of easily identified crystals of metallic xanthates. This is official in the U. S. Pharmacopeia X for testing carbon tetrachloride for carbon disulfide. Even this method may require 3 hours of waiting. A study of the literature in regard to the xanthate test fails to disclose any authoritative claim for great sensitiveness, and Milliau (*5*) vigorously disapproves of it on this ground. Evidently its popularity is largely dependent upon its simplicity.

The purpose of this paper is to present what the writer believes is an original method for the detection of carbon disulfide, which combines extreme sensitiveness with ease of manipulation and speed. The test can be carried out in less than 5 minutes, and is sensitive at least to 1 part of carbon disulfide in 30,000 parts of oil or other inert liquid. The work has been carried on chiefly with olive oil, but exhaustive tests were also made with carbon tetrachloride, chloroform, and ether. Results have been so uniformly satisfactory that its use is recommended in all liquids in which carbon disulfide is likely to be found with the exception of those that are opaque, very highly colored, or are themselves reactive with the reagent. As an instance of the last case, the reagent reacts with carbon tetrachloride with the formation of a transient port-wine color, but the test easily identifies the presence of carbon disulfide by the formation of a precipitate not found when carbon disulfide is absent.

The Reagent

In 1905 Von Nagy Ilosva (*8*) presented his paper on the determination of the triple bond in organic compounds, with special reference to acetylene. During the course of an experiment with allylene the present writer discovered, quite accidently, that Von Nagy Ilosva's reagent gave a characteristic reaction with carbon disulfide, and became so interested in the peculiar characteristics of the Ilosva solution that work was undertaken which resulted in this paper.

Von Nagy Ilosva's directions for making his reagent are as follows: Dissolve 1 gram of copper sulfate (nitrate or chloride) in a small amount of water in a 50-cc. graduated flask. Add 4 cc. of strong ammonium hydroxide, and then 3 grams of hydroxylamine hydrochloride. The latter completely decolorizes the copper solution. Then add water to the mark and shake the flask. The resulting reagent is that used in our work. It must be kept in the dark and should not be used when it is much more than a week old. Deterioration is shown by a blue color which sometimes appears with startling suddenness.

Materials

The chemicals used in the preparation of the reagent, as well as the chloroform, were of analyzed quality. Oils were obtained from a reputable importer, had passed standard tests for purity, and were further tested for carbon disulfide by the xanthate method with negative results. The history and origin of these oils were known.

Method of Determination

The oil to be examined is diluted one-half with pure chloroform to reduce its viscosity and to increase the specific gravity of the solution to the extent that the reagent may float on the top after shaking. Five cubic centimeters of the oil solution

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[1] Received June 14, 1929.

[2] Fellow, The Johns Hopkins University.

are placed in a test tube, 2 cc. of the reagent are added, the tube is stoppered and tilted back and forth for half a minute or so, and then placed aside for observation. Violent shaking is to be avoided as being unnecessary and also conducive to the formation of a slowly separating emulsion.

Experimental Work

The reagent, shaken with pure carbon disulfide, instantly reacts with the formation of an opaque, chocolate-colored aqueous solution. In a minute the solution clears, and a heavy, slimy precipitate of the same color floats at the interface of the two phases. This is the typical reaction.

Oils, diluted one-half with chloroform and treated with exactly determined concentrations of carbon disulfide, were tested as above. Work started with 1 per cent of carbon disulfide, and further tests were made with solutions stepped down to 0.0033 per cent of carbon disulfide. The characteristic reaction was evident in all cases, the only difference being the depth of the color of the first formed solution and the amount of the subsequent precipitation. As the work proceeded it became obvious that an operator familiar with the color effects obtained could determine with almost quantitative precision the amount of carbon disulfide present. The limit was not reached even at 0.0033 per cent, but it was decided that, for the purpose intended, no greater delicacy was necessary.

Experiments were carried on with carbon disulfide-free oil which had been shaken with precipitated sulfur and then carefully filtered through paper. The dissolved sulfur instantly reacted with the test solution, forming a dense, deep, black precipitate with a metallic luster. There was no preliminary coloring of the solution. These experiments were positive even when the known sulfur content was extremely small.

Experiments were made on oils containing both carbon disulfide and free sulfur. Differentiation between the two is not easy with the unaided eye, but microscopic examination shows the presence of a brown and of a black precipitate, both clearly distinguishable.

An effort was made to determine the identity of these two precipitates. That formed when free sulfur reacts with the solution is cuprous sulfide. The brown precipitate formed as the result of reaction between carbon disulfide and the reagent is believed to be a mixture of cuprous sulfide and a substance described by Mellor (*3*) as being the resultant of the reaction between carbon disulfide and hydroxylamine. Mellor's substance is described by him as being at first yellow, then orange, and then precipitating sulfur. The aqueous filtrate from the resultants of the reaction between carbon disulfide and the reagent was found by the writer to give these same color effects. Continued washing of the precipitate left behind a black substance reacting for cuprous sulfide. It is therefore assumed that the brown precipitate is a mixture of black cuprous sulfide and the yellow or orange material such as Mellor describes.

Acknowledgment

The writer wishes to thank E. Emmet Reid, of The Johns Hopkins University, for helpful advice, and the Pompeian Corporation, of Baltimore, for having supplied the oils with which the tests were made.

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The Segregation of Analyzed Samples[1]

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IN THE preparation for analysis of samples consisting of two or more solids it is essential that the various components be mixed to uniformity. It is equally important that such samples show no tendency to segregate under normal conditions of storage and transportation. Many investigations concerning proper procedure in sampling for analysis are recorded, but no study was found dealing with the question of segregation. This paper presents the results of such an investigation with particular reference to samples prepared for student use.

Coarsely ground mixtures of two or more solid materials differing in density will segregate upon jarring which results from transportation or storage under conditions subject to vibration. The magnitude of the segregation may be considered as inversely proportional to the degree of subdivision and directly proportional to the differences in density of the mixed materials. Since the differences in density cannot be changed in any particular case, the degree of subdivision represents the controlling variable.

The proportion of the total weight of a given solid constituting its surface is inversely proportional to the square of the particle diameter. The resistance to segregation may be considered as the result of intermolecular surface attraction. Accordingly anti-segregation properties may be developed by decreasing the particle size. Since surface increase varies inversely as the square of the diameter of the particle size, the tendency to segregate may be lessened with materials quite variable in density by grinding to smaller size.

Apparatus

A cylindrical section of thin brass tubing 4 inches (10 cm.) in length and of approximately 1-inch (2.5-cm.) bore was sawed into six equal parts. Five parts were provided with collars made from $^{1}/_{4}$-inch (6-mm.) sections of another brass tube of bore just sufficient to permit the insertion of the sections of the first tube. The larger sections were soldered to the smaller, leaving half their width protruding. The sixth section was then soldered to a disk of sheet brass to serve as the bottom cell and the five sections with collars were placed together to form a column. A second removable disk of sheet brass served as a cover. The six cells were clamped together by means of three brass rods riveted to the outside edge of the base and passed through holes in the cover, which was fastened down by means of thumb screws. The six sections assembled are shown at *A*, Figure 1.

The remainder of the jarring machine (Figure 1) consisted of two circular wooden pulleys, *B*, provided with metal bushings fitting over a $^{3}/_{8}$-inch (9-mm.) vertical shaft. The shaft was mounted in a heavy metal base, and the two pulley wheels were separated by a metal runway, *C*, made from a 1-inch (2.5-cm.) section of a tube 4 inches (10 cm.) in diameter machined to contain two 12-mm. vertical offsets and a gradual rise between and fastened firmly to the bottom pulley. On the bottom side of the upper pulley were two small wheels supporting it on the runway. The sample containers were fastened to the opposite side directly above. The bottom pulley was turned by means of a belt and motor with reducing shaft and its revolutions were counted and recorded automatically. The top pulley was prevented from revolving but a short distance by means of a horizontal bar fastened to the shaft, *D*, against one of the uprights. The turning of the bottom pulley raised the upper pulley through a distance of approximately 12 mm. and allowed it to fall twice during each revolution and approximately 200 times per minute. Besides the resulting vertical jar, there was an equal-numbered, but much less intense, horizontal jar due to the partial turning of the upper pulley as the result of a frictional torque between the two.

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[1] Presented before the division of Chemical Education of the 77th Meeting of the American Chemical Society, Columbus, Ohio, April 29 to May 3, 1929.

The remainder of the apparatus, *E*, consisted of a familiar carriage for two small ball-mill jars for the preparation of the samples. The jarring apparatus and the carriage were operated by one motor. A powdered sample of iron ore, when jarred by falling through the distance of $^{1}/_{2}$ inch (1.3 cm.) a million times, settled down to such an extent as to fill but slightly more than four of the six sections of the tower. Other powders settled varying amounts, usually three-fourths to two sections, the contents of each full section would always have to be forced out when the tower sections were separated after jarring a million times. The machine required approximately 90 hours' operation for this number of falls, and in all cases at least this period was employed.

Effect of Degree of Subdivision

MIXTURE OF ARSENIC TRIOXIDE AND POTASSIUM SULFATE—The case of two mixtures found to segregate upon test will be given first. A mixture of arsenic trioxide and potassium sulfate was ground in the ball mill for a period of time thought to be adequate to guarantee uniformity and to produce a sufficient fineness of division. No directions being available for this case, the degree of subdivison before and after grinding was not tested and its actual uniformity not questioned.

The analyses of the separate sections and related data are given in Table I.

Table I—Segregation of a Mixture of Arsenic Trioxide and Potassium Sulfate

SECTION	WT. MATERIAL	As_2O_3	ERROR	As_2O_3 THEORY	As_2O_3 FOUND	ERROR
	Grams	%	%	*Grams*	*Grams*	*Gram*
1	4.52	21.39	−11.88	1.50	0.97	−0.53
2	15.68	35.15	+1.87	5.22	5.51	+0.29
3	12.93	34.18	+0.91	4.30	4.42	+0.12
4	13.99	33.43	+0.16	4.65	4.68	+0.03
5	13.72	33.60	+0.33	4.56	4.61	+0.05
6	14.08	33.36	+0.09	4.68	4.70	+0.02
Total	74.92				24.89	

As_2O_3 in original mixture, 33.27 per cent.
As_2O_3 calculated from sectional analyses, 33.21 per cent.
Densities: As_2O_3 = 3.9; K_2SO_4 = 2.66.

The original sample was uniform, as shown by the duplication of results obtained on individual samples.

MIXTURE OF MERCURIC OXIDE AND POTASSIUM SULFATE—The second example illustrating segregation was a mixture of approximately 22 per cent mercuric oxide and 78 per cent potassium sulfate. The data are given in Table II.

Table II shows that the segregation is greatly diminished but is distinctly apparent in the two top sections. The difference in sections 2, 3, and 4 is hardly greater than the experimental error involved. Sections 5 and 6 showed no differences over the original composition.

Table II—Segregation of a Mixture of Mercuric Oxide and Potassium Sulfate

SECTION	WT. MATERIAL	HgO	ERROR	HgO THEORY	HgO FOUND	ERROR
	Grams	%	%	*Grams*	*Grams*	*Gram*
1	2.47	20.85	0.65	0.548	0.515	−0.033
2	16.08	22.31	0.11	3.569	3.586	+0.017
3	15.48	22.34	0.14	3.436	3.457	+0.021
4	15.05	22.30	0.10	3.341	3.356	+0.015
5	14.30	22.23	0.03	3.115	3.119	+0.004
6	16.07	22.20	0.00	3.568	3.568	0.000

HgO in originial mixture, 22.20 per cent.
HgO calculated from section analyses, 22.16 per cent.
Densities: HgO = 11.0; K_2SO_4 = 2.66.

Since the densities of arsenic trioxide and mercuric oxide are at great variance—3.9 and 11.0, respectively—the results found were decidedly the reverse of those predicted. One difference consisted in the fineness of division. In the case of the second mixture all passed a 100-mesh sieve and 10 per cent passed through a 200-mesh sieve, whereas 94 per cent of the mixture containing arsenic trioxide passed a 100-mesh and 74 per cent a 200-mesh screen (*1*). The degree of subdivision alone is not, therefore, the only controlling factor.

Effect of Surface Energy

Surface energy might be considered as a contributing factor. According to Dundon (*2*) the surface energy of a series of substances is roughly proportional to their density and inversely proportional to their molecular weight. In the case of the two mixtures studied, since one common component (K_2SO_4) is present, the respective surface energies of the other components (As_2O_3 and HgO) may be compared. Since their molecular weights are practically the same, resistance to segregation would be predicted in greater degree for the more dense material—the mercuric oxide. The facts are in agreement with the assumptions. If surface energy in reality does play a part, the effect is obtained with materials comparatively large (approximately 15 to 25 μ) in particle size. Surface energy increases to be demonstrated by determination of increase in solubility of small over large particles require subdivision to smaller dimensions (0.1 to 0.5 μ).

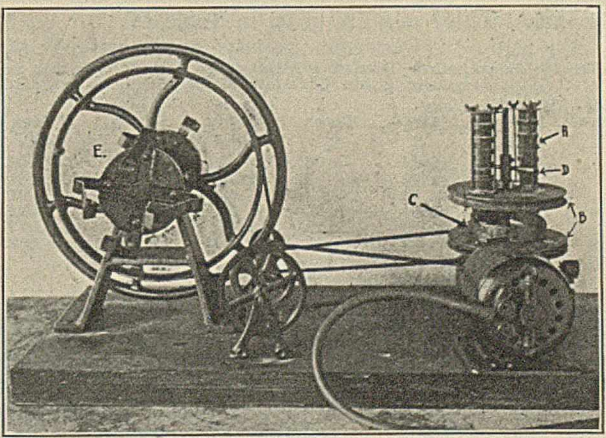

Figure 1

If surface energy is related to the property of resistance to segregation, a further decrease in particle size resulting in an increase in surface energy should give a non-segregating mixture in the case of the materials studied. Accordingly a portion of the first mixture was ground until 99.8 per cent passed a 200-mesh sieve. The data for the jar segregation of this mixture are given in Table III.

Table III—Segregation of a Mixture of Arsenic Trioxide and Potassium Sulfate Ground to Pass 200-Mesh Sieve

Section	Wt. Material	As_2O_3	Error	As_2O_3 Theory	As_2O_3 Found	Error
	Grams	%	%	*Grams*	*Grams*	*Gram*
1	5.208	37.59	+4.32	1.733	1.958	+0.179
2	6.526	30.71	−2.56	2.171	2.004	−0.167
3	10.872	33.21	−0.06	3.617	3.611	−0.006
4	10.097	33.25	−0.02	3.359	3.357	−0.002
5	10.834	33.31	+0.04	3.604	3.609	+0.005
6	10.080	33.22	−0.05	3.358	3.352	−0.006

As_2O_3 in original mixture, 33.27 per cent.
As_2O_3 calculated, 33.36 per cent.
Densities: $As_2O_3 = 3.9$; $K_2SO_4 = 2.66$.

It will be observed that segregation occurred in sections 1 and 2. The segregation was the reverse of the usual process, since the heavier component, arsenic trioxide, concentrated in section 1 and the potassium sulfate settled to section 2. The reason for this behavior was observed from the fact that the upper 10 per cent of the material being jarred had sufficient freedom of movement to form pills of the size of shotgun shell shot which were hard and well polished. The powder in the top section of the sample holder was behaving somewhat like a liquid showing the effects of surface tension. The surface energy effects were best manifest by the proportion of 37.6 per cent As_2O_3 to 52.4 per cent K_2SO_4. Resistance to segregation was none the less demonstrated for the lower 80 per cent of the sample as shown by the analyses, which are in agreement with the surface energy hypothesis already given. The formation of the pill aggregates in this test strengthened the assumption that surface energy relationships are involved.

The fact that arsenious oxide sublimes unchanged and mercuric oxide dissociates when heated was thought to have a possible influence on the segregation relationships. Since in addition there is almost a threefold difference in density, a mixture of these two compounds was ground together until all would pass through a 200-mesh sieve and tested. The data for this case are given in Table IV.

Table IV—Segregation Test of a Mixture of Arsenic Trioxide and Mercuric Oxide Ground to 200 Mesh

Section	Wt. Material	As_2O_3	Error	As_2O_3 Theory	As_2O_3 Found	Error
	Grams	%	%	*Grams*	*Grams*	*Gram*
1	17.122	44.74	−0.05	7.669	7.660	−0.009
2	24.027	44.84	+0.05	10.762	10.774	+0.012
3	26.130	44.82	+0.03	11.704	11.711	+0.007
4	24.727	44.84	+0.05	11.075	11.087	+0.013
5	24.989	44.88	+0.09	11.193	11.215	+0.022
6	25.801	45.02	+0.23	11.556	11.616	+0.050

As_2O_3 in original mixture, 44.79 per cent.
As_2O_3 calculated, 44.86 per cent.

From Table IV it will be seen that no segregation resulted.

A mixture of approximately 92 per cent mercuric oxide and 8 per cent magnesium carbonate was likewise tested in the segregation machine and upon analysis of the top and bottom portions the following figures were obtained for HgO: top 91.91, bottom 91.89 per cent. The original materials were mixed in about equal parts by volume.

Two samples of iron ores—one Zenith iron ore low in silica and high in ferric oxide and another iron ore high in silica and correspondingly low in ferric oxide—were likewise segregated in the usual manner after being ground to pass a 200-mesh sieve. The top and bottom sections were then analyzed, with the results given in Table V.

Table V—Jar Segregation Analysis of Iron Ores

Iron Ore	Original Analysis		Segregation Analyses			
			Top		Bottom	
	Fe	SiO_2	Fe	SiO_2	Fe	SiO_2
	%	%	%	%	%	%
Zenith	66.70	2.51	66.46	2.47	66.87	2.47
Commodore	56.15	9.83	55.98	9.78	56.13	9.77

It will be seen that, as nearly as the analysis can be relied upon, there was no segregation of silica from the heavier ferric oxide in these two samples.

Effect of Artificial Increase of Density

Since in all the cases thus far tested using samples of great variation in density ground to pass a 200-mesh sieve there was shown to be no segregation upon jarring, it was thought proper to attempt to segregate such a sample by artificially increasing the density of one component. This would show two things in case no segregation was observed—(1) that natural density variations in materials could not provide segregation properties in opposition to the surface energy relationships, and (2) that an extended exposure to jarring is not likely to alter the effects.

Table VI—Effect of Electromagnet in Increasing Apparent Difference in Density of Magnetic Iron Oxide in Its Mixture with Magnesium Oxide

Section	Wt. Material	Fe_3O_4	Error	Fe_3O_4 Theory	Fe_3O_4 Found	Error
	Grams	%	%	*Grams*	*Grams*	*Gram*
1	5.859	78.35	+0.03	4.588	4.594	+0.006
2	17.111	78.58	+0.26	13.401	13.447	+0.046
3	15.933	78.21	−0.13	12.479	12.461	−0.018
4	14.003	78.61	+0.29	10.967	11.008	+0.041
5	16.977	78.58	+0.26	13.296	13.340	+0.044
6	16.783	78.37	+0.05	13.144	13.156	+0.012

Fe_3O_4 in original mixture, 78.32.
Fe_3O_4 calculated, 78.37 per cent.

Accordingly a mixture of magnetic oxide of iron and "light" magnesium oxide was mixed in the ball mill and after being ground to pass 200 mesh was placed in the segregation machine. The six-section tower (*A*, Figure 1) was then used as the solenoid of an efficient electromagnet in such a way that half of the six sections were protruding and half acting as the core of the magnet. The electromagnet was provided with a soft iron core and tested under the effect of the same activating current as that used during the tests and was found capable of picking up a one-pound piece of iron. That the downward pull on the Fe_3O_4 of the sample was appreciable was observed by suspending an iron bar partially within the empty core of the electromagnet. The sample was jarred by being allowed to fall together with the magnet for the usual million falls through the usual distance. A second sample not provided with a magnet was jarred at the same time, but the analysis of this portion did not prove necessary. The results of the test are reported in Table VI.

The data of Table VI show that within the experimental limit of accuracy no segregation results in the case of a magnetically augmented difference in the apparent density of magnetic iron oxide when mixed with magnesium oxide. The proportionate increase in apparent density is unknown, but it must have been appreciable. Mixtures of iron dust with powdered non-magnetic metals, such as iron-tungsten mixtures, were not tested under the influence of a magnetic field because such mixtures are not met in practice.

Conclusions

From the work described above it is concluded that, when mixtures of materials of different density are mixed to uniformity following grinding to pass a 200-mesh sieve, they cannot be segregated by jarring or by the influence of vibrational storage conditions no matter what the actual differences in density. It is believed that the selection of materials tested is sufficiently representative to warrant the conclusion that no mixture of materials will exhibit such a tendency to segregate and that the tests were sufficiently severe to apply in addition no limitation to the time under which the segregation influence is applied.

In case of referee analyses of supposedly identical samples, if different analysts fail to agree the fault cannot be placed, as it frequently is, on the segregation of samples, provided they are ground to pass a 200-mesh sieve.

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Solubility of Benzidine Sulfate and Benzidine Hydrochloride in Hydrochloric Acid Solutions[1]

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Solubility of Benzidine Sulfate

In the course of an investigation requiring the quantitative determination of sulfate it was found that the usual barium sulfate method was not entirely satisfactory owing to the formation of mix-crystals with other constituents present. Accordingly an attempt was made to adapt the well-known benzidine sulfate method. As the precipitation of the sulfate had to be made from solutions of decided acidity, it was necessary to know to what extent the solubility of the benzidine sulfate is affected by changes in acid concentration. No solubility data were found in the literature, however, apart from those given by Bisson and Christie (*1*) on the solubility of benzidine sulfate in pure water at various temperatures.

Accordingly determinations were made of the solubility in hydrochloric acid solutions of various concentrations. The solubilities were determined directly by agitating a known weight of the salt with a known weight of the acid solution (about 50 grams) in a glass-stoppered flask immersed in a thermostat at 25° C. until equilibrium had been attained.

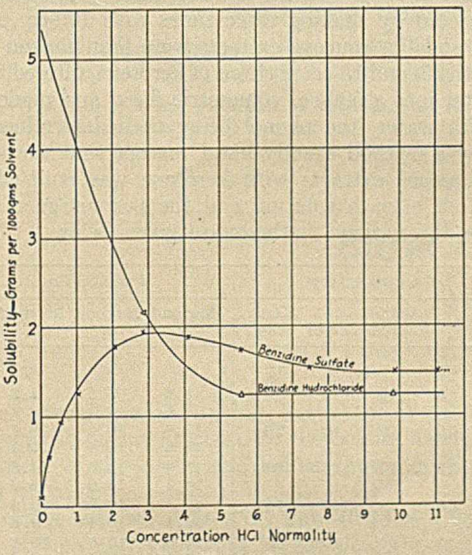

Figure 1

Preliminary experiments showed that attainment of equilibrium required about 36 hours; twice this time was allowed. The residue was then filtered off on a sintered glass crucible, washed with acid solution of the same concentration as that used, dried, and weighed. A portion of the filtrate was titrated with standard sodium hydroxide solution. The benzidine sulfate used was prepared by adding a slight excess of sulfuric acid solution to a solution of Kahlbaum's benzidine "for analysis," filtering, washing free from excess acid, and drying to constant weight at 110° C.

The results are shown in Table I and Figure 1.

Solubility of Benzidine Hydrochloride

As these data show, the solubility of benzidine sulfate in hydrochloric acid solution increases very rapidly with increasing acidity. It passes through a maximum at a concentration of about 3.5 normal and then decreases. It was thought that this effect might indicate that the solubility limit of the benzidine hydrochloride presumably formed by interaction of the acid with the sulfate had been reached. On this point also data were lacking and determinations were made of the solubility of benzidine hydrochloride in hydrochloric acid solutions. The results are given in Table II and Figure 1. It will be noted that the solubility of benzidine hydrochloride in 3.5 *N* hydrochloric acid is actually less than the solubility of the sulfate.

Table I—Solubility of Benzidine Sulfate in Hydrochloric Acid Solutions

Concn. HCl in Filtrate *N*	Solubility *G. per 1000 g. soln.*	Concn. HCl in Filtrate *N*	Solubility *G. per 1000 g. soln.*
0.000	0.098 (*1*)		
0.239	0.537	4.139	1.885
	0.548		1.889
	Av. 0.542		Av. 1.887
0.530	0.943	5.622	1.771
	0.941		1.778
	Av. 0.942		Av. 1.774
1.009	1.252	7.601	1.551
	1.254		1.536
	Av. 1.253		Av. 1.544
2.074	1.789	9.942	1.496
	1.792		1.501
	Av. 1.790		Av. 1.499
2.825	1.921	11.099	1.488
	1.939		1.493
	Av. 1.930		Av. 1.490

Table II—Solubility of Benzidine Hydrochloride in Hydrochloric Acid Solutions

Concn. HCl in Filtrate *N*	Solubility *G. per 1000 g. soln.*
0.000	5.346
2.884	2.114
	2.225
	Av. 2.172
5.607	1.244
	1.248
	Av. 1.246
9.870	1.226
	1.221
	Av. 1.224

Conclusions

From these results it is obvious that in applying the benzidine sulfate method in the determination of sulfate, accuracy can be attained only if the acid concentration is kept very low, and it should be pointed out that even under these conditions there may be a considerable error due to solubility of the precipitate.

Literature Cited

(1) Bisson and Christie, J. Ind. Eng. Chem., 12, 485 (1920).

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[1] Received June 20, 1929.

Large Metal Soxhlet Extractor

Editor of Industrial & Engineering Chemistry:

I am reminded of the large metal Soxhlet extractor that I had made about thirty years ago which was essentially like that shown on page 140 of the Analytical Edition for July 15, with the exception that the siphon tube was made of block tin. The advantage of this feature was that it could be bent down to accommodate larger or smaller quantities of materials to be extracted and hence lesser amounts of solvents were needed.

B. M. Pilhashy

San Francisco, Calif.
July 31, 1929

Determination of Phenol in Presence of Salicylates[1]

E. H. Hamilton and C. M. Smith

Food, Drug, and Insecticide Administration, U. S. Department of Agriculture, Washington, D. C.

SINCE the passage of the Federal Caustic Poison Act it has become necessary to ascertain the percentage of phenol (carbolic acid) in many coal-tar insecticides and disinfectants. For this determination the Insecticide Control laboratory of the Food, Drug, and Insecticide Administration employs a method devised by Chapin (*2*) for use with saponified cresol solutions.

Briefly this method is as follows: The product is dissolved in water and made to a known volume. Aliquots of the solution are placed in each of two test tubes and treated with Millon's reagent. A pink solution develops if phenol is present. Then formaldehyde is added to the solution in one of the test tubes and this changes the color to yellow. A pair of test tubes containing a standard aqueous solution of phenol are treated similarly. The amount of phenol in the unknown is determined by adding successive known quantities of the red standard solution to the yellow unknown solution and equal quantities of the yellow standard solution to the red unknown solution, comparing the colors after each addition, until the color of the two unknown solutions becomes the same. The proportion of phenol present in the unknown is then calculated from the number of cubic centimeters of the standard solution used.

This method has given satisfactory results except with products containing salicylates, for, as Chapin (*1*) has pointed out, salicylates give the same color changes as phenol. Some insecticides, especially mineral oil solutions of phenols, often contain oil of wintergreen or oil of birch as a perfume, and both these essential oils consist largely of methyl salicylate. The first two products of this nature analyzed showed 12.5 and 11.3 per cent phenol by Chapin's original method using sodium hydroxide, 9.1 and 9.2 per cent when the sodium hydroxide was omitted, and 8.3 and 8.7 per cent by a procedure (suggested by E. L. Griffin of this laboratory) depending on saponification of the methyl salicylate, separation of the salicylic acid from the tar acids by means of a sodium bicarbonate solution, and estimation of the phenol by Chapin's method.

The last procedure was presumed to give the correct results, but because it is rather long and tedious, and also because the omission of sodium hydroxide from Chapin's method resulted in fairly comparable values, it was decided to investigate the possibility that the kerosene originally in the product, or added to it, might be counted on to retain the methyl salicylate while the water used might extract the phenol. For this purpose it was desirable to know the partition coefficient of phenol between kerosene and water. As there appeared to be no information on this subject in the literature, the partition coefficient was determined as follows: A stock solution was prepared from C. P. phenol and water to contain approximately 4 grams of phenol per 100 cc., and from this solutions of one-half and one-fourth its strength were prepared. A 25-cc. portion of each solution was shaken with an equal quantity of kerosene and the mixture allowed to separate into two layers. The aqueous layer was drawn off, filtered through a wet filter to remove any residual kerosene, and the amount of phenol remaining determined by titration of an aliquot with a standard bromide-bromate solution. The results are given in the following table.

No attempt was made to approach equilibrium from the other direction because of the low solubility of phenol in kerosene. The results indicate that conditions are favorable for extraction of phenol from kerosene by means of water.

INITIAL SOLUTION	WATER LAYER	KEROSENE LAYER (BY DIFF.)	PARTITION COEFFICIENT
Grams per 100 cc.	*Grams per 100 cc.*	*Grams per 100 cc.*	
4.05	3.20	0.85	3.8
2.02	1.62	0.40	4.0
1.01	0.81	0.20	4.0

Five kerosene solutions containing known proportions by weight of phenol, oil of birch, and para-cresol were then prepared. A commercial grade of birch oil and chemically pure phenol (congealing point 38.8° C.) were used. The para-cresol, of which a technical grade boiling at 202° C. and containing 0.2 per cent phenol was used, was added to increase the solubility of the phenol. The results given later prove that, even though this cresol aids in dissolving phenol in kerosene, it does not retard the extraction of the phenol by water. The phenol in these preparations was, for purposes of comparison, determined by four methods, as follows: A, directly by Chapin's method for unsaponified cresol solutions; B, directly by Chapin's method for saponified cresol solutions; C, by a method in which 50 cc. of kerosene were added to 10 cc. of each solution, after which the phenol was extracted by shaking three times with 100-cc. portions of water and the aqueous extracts were then shaken successively with 25- and 15-cc. portions of kerosene, filtered through a wet filter into a 500-cc. volumetric flask, and made to the mark with water, the phenol being then determined as in B; D, by a method exactly like C except that the washing of the aqueous extracts with kerosene was omitted. The composition of each solution and the percentage of phenol found by the various methods are given below.

SOLN.	COMPOSITION				PHENOL FOUND			
	Phenol	Oil of birch	*p*-Cresol	Kerosene	Method A	Method B	Method C	Method D
	%	%	%	%	%	%	%	%
1	5	10	5	80	8.6	5.5	4.9	5.2
					8.6	5.5		5.1
2	10	10	10	70	13.6	10.6	10.1	10.0
					13.6	10.1	10.1	10.1
3	15	10	15	60	18.1	15.0	14.8	14.8
					18.1	15.0	15.0	14.8
4	10	5	10	75	12.1	10.4	9.9	10.2
					12.1	10.4	9.8	10.2
5	10	20	10	60	16.6	10.6	10.1	10.2
					16.4	10.6	10.2	10.2

It is evident that method A gives results which are very much too high, owing to the saponification of some of the methyl salicylate by the sodium hydroxide used. Method B gives results which, while quite close to the amount of phenol actually present in the solutions, tend to be slightly high. Methods C and D both give results agreeing with the theoretical within the limit of error of the methods on pure phenol solutions. As Method D is simpler than Method C in that the washing of the aqueous extract with kerosene is omitted and thereby the formation of troublesome emulsions avoided, it is preferable. It also offers a considerable saving of time and labor over the sodium bicarbonate extraction method.

Literature Cited

(1) Chapin, J. Ind. Eng. Chem., **12**, 771 (1920).
(2) Chapin, U. S. Dept. Agr., *Bull.* **1308** (1924).

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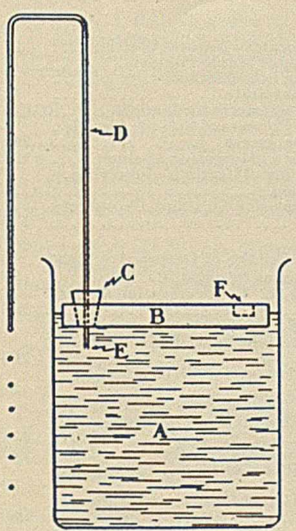
[1] Received July 29, 1929.

Device for Maintaining a Constant Rate of Flow of Liquids[1]

John D. Sullivan

Southwest Experiment Station, U. S. Bureau of Mines, Tucson, Ariz.

DURING the course of leaching experiments that were being performed at the Southwest Experiment Station of the U. S. Bureau of Mines in coöperation with the Department of Mining and Metallurgy, University of Arizona, it became necessary to devise means of maintaining a constant rate of supply of leaching solution. The ores were being leached by the open-drainage principle and required a supply of leaching liquor that would keep the mass saturated and at the same time not cause a flooding of the surface.



A simple apparatus was developed which met all the requirements. It is especially valuable if a drop-by-drop rather than a continuous flow is desired. The construction of the apparatus is very simple, and the figure showing it is practically self-explanatory. *A* is a beaker, jar, crock, or other containing vessel of whatever size needed; *B* is a piece of wood cut in a circular form of diameter slightly less than that of the container, *A*; *C* is a cork which fits into a hole bored in the float, *B*; *D*, a piece of glass tubing bent so as to act as a siphon, passes through cork *C* and down into the solution in *A*. The size of the bore of *D* depends upon the size of drop desired. The siphon can be raised or lowered by moving the glass in *C* so that any desired solution head may be maintained. If a very slow drip is desired, the end of the tube, *E*, may be constricted. The constriction is at the end that is under solution rather than the outside end because otherwise the crystallization of salts might seal off the end. When a small container is used and the weight of *D* is so great that *B* is tilted from the horizontal, lead or other heavy material may be placed on the side opposite *C*. For this purpose a hole, *F*, may be bored part way through the float on the side opposite the cork and the amount of lead shot required to balance may be added.

Once the desired rate of flow or drop is obtained by choosing a tube of the proper bore and by manipulating *D* to secure the required hydrostatic head, this rate can be maintained indefinitely. As the solution level drops, the float drops the same distance and the same hydrostatic head is maintained; likewise the same hydrostatic head is maintained when solution is added to the container. When the temperature changes, the viscosity of the solution changes, and the rate of siphoning is thereby influenced, but under ordinary room or laboratory conditions the temperature variations are not great enough to have much effect.

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[1] Received July 3, 1929. Published by permission of the Director, U. S. Bureau of Mines. (Not subject to copyright.)

Buret Clamp and Holder[1]

Marion Hollingsworth

The Ohio State University, Columbus, Ohio

THE convenience of having bottles of standard solutions with burets attached to the bottles has led to the development of the clamp and holder shown in the accompanying drawing.

The part *A* is of wood 11 × 27 mm. (0.43 × 1.06 inches) in cross section and somewhat longer than the scale on the buret which it is designed to support. The edges are slightly beveled towards the front so that *A* will remain rigid in the holder.

The block *B* is of spring brass and wood. The cross section of the brass is 7 × 11 mm. (0.25 × 0.43 inch) and it is bent as shown in the detail drawing. The whole is made to slide easily on *A* and yet is held at any position quite securely by the spring being reëntrant at *C*. The block *D* is similar to *B* but is fastened firmly to the end of *A*. All brass jaws are covered with rubber tubing.

The holder is of wood 25 mm. (1 inch) thick. It must be long enough to carry the clamp past the sides of the bottle and wide enough to fit over the neck. It has been found better to make the neck opening quite large and then line it with cork to the proper size. One 6-mm. (0.25-inch) bolt with wing nut is sufficient to hold both holder and clamp in position. However, the holder is more rigid during adjustments if a small dowel pin is inserted in the end back of the bottle neck.

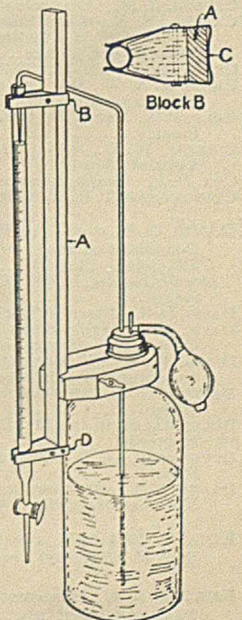
The advantages of this clamp and holder are:

(1) The entire buret scale is always free.

(2) The buret may be removed or inserted with one hand.

(3) The clamp may be used either end up, and when made long the buret may be placed in any elevation relative to the bottle—opposite, above, or below.

(4) The buret is held so rigid that the upper end of the supply tube may be drawn to small bore and the end inserted through a grooved cork, set opposite the zero mark on the buret. This gives zero adjustment when the buret is filled and the pressure within the bottle is released.



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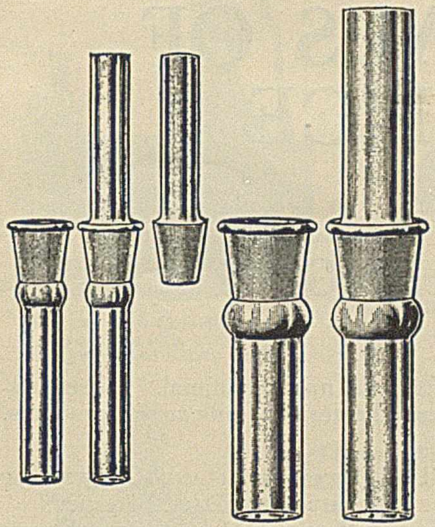
[1] Received February 26, 1929.



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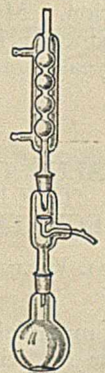

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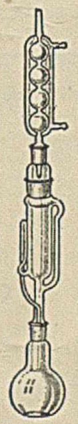

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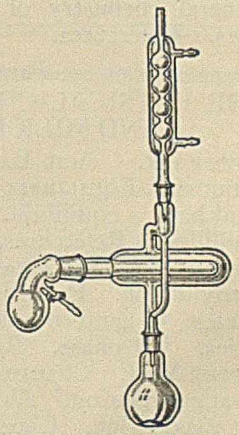

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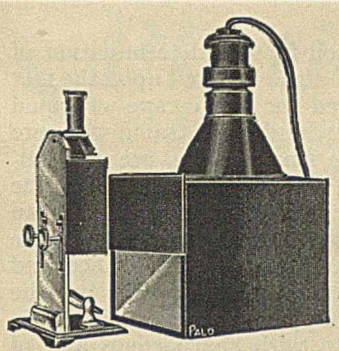

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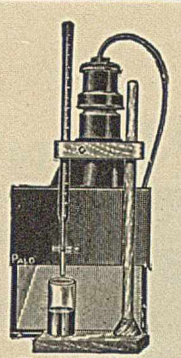

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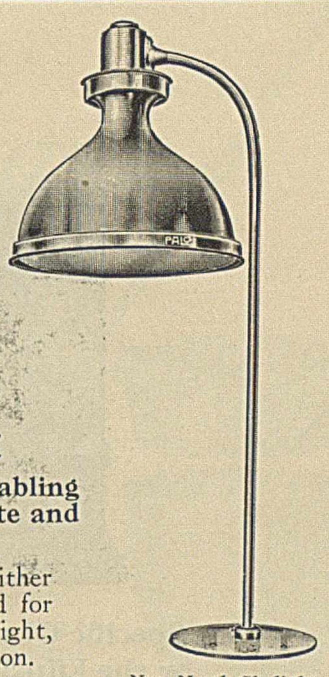

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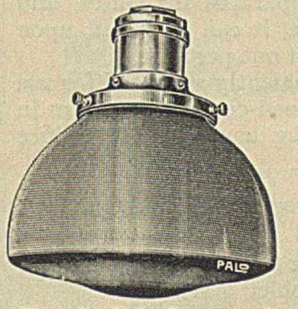

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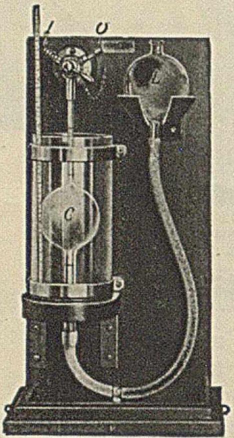

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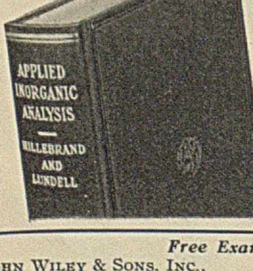

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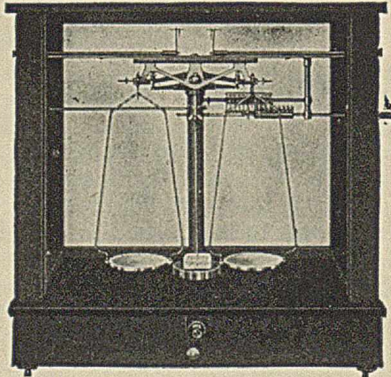

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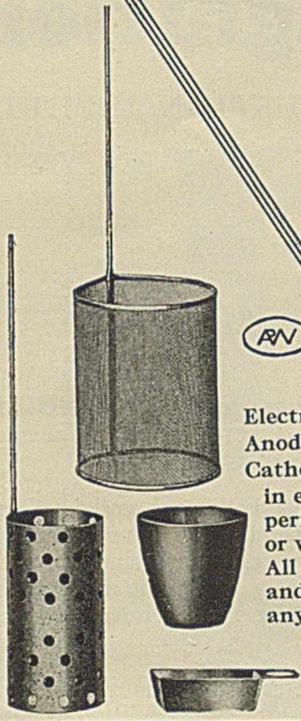

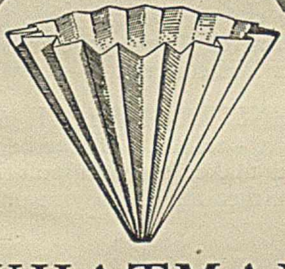

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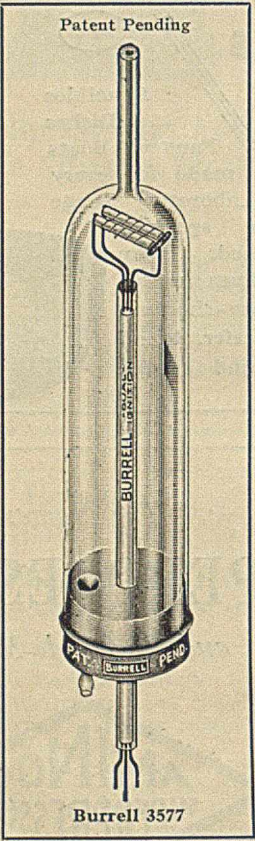

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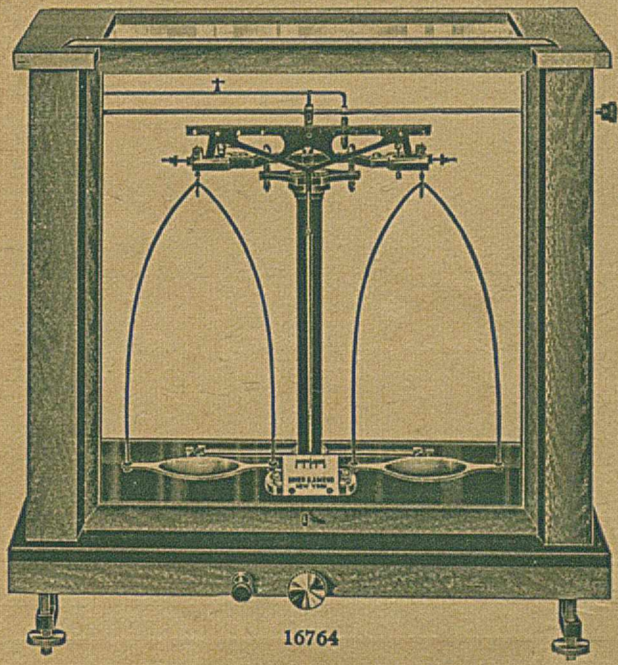

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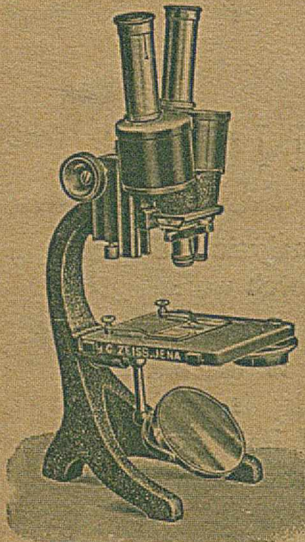

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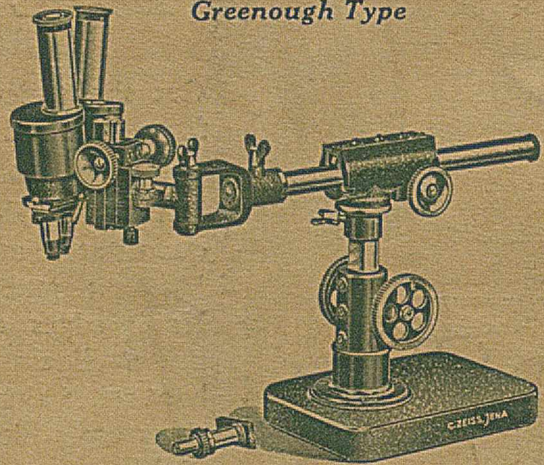

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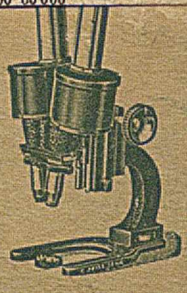

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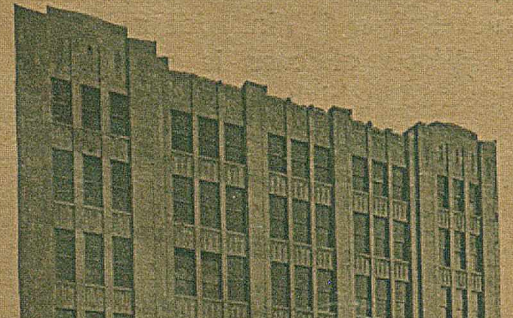

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