

illustrate these points are herewith given. Indefinite amounts of iron were used with each sample of copper. The solution of KMnO_4 (7 g. per l.) on determination gave Fe value of 1 cc. = 0.01207.

No.	Copper Gram	KMnO_4 Cc.	KMnO_4 Gram Cu per Cc.	Actual Ratio, K Cu : Fe	Copper Found Using Av. Actual Value of K Gram
1	0.0138	7.9	0.001972	0.1634	0.0139
2	0.0276	13.9	0.001985	0.1645	0.0276
3	0.0326	16.4	0.001987	0.1647	0.0326
4	0.0527	26.5	0.001988	0.1647	0.0526
5	0.0670	33.9	0.001977	0.1638	0.0674
6	0.0834	42.1	0.001982	0.1642	0.0836
7	0.0917	46.1	0.001988	0.1647	0.0916
8	0.1214	61.0	0.001990	0.1649	0.1212
9	0.1432	71.9	0.001992	0.1651	0.1428
10	0.1625	81.4	0.001996	0.1654	0.1617
11	0.1912	96.2	0.001988	0.1647	0.1911
12	0.2000	100.3	0.001992	0.1650	0.1994
Average =			0.001986	0.1646	

Hence, the actual copper value of the permanganate = $0.01207 \times 0.1646 = 0.001986$, thus the actual factor is 0.1646 and the theoretical 0.1626; the difference is probably due to the slight solubility of cuprous thiocyanate.

SOME OBSERVATIONS ON THE PROCEDURE

1—The strength of permanganate solution, 7 g. per l., as used above, was selected because 10 cc. closely equals 1 per cent copper on a 2-g. sample of ore. This is a very strong solution, about three times that usually used for the titration of iron, yet 1 cc. equals only 0.1 per cent copper; hence it is very easy to check to 0.02 per cent copper (on low-grade ores). Slight irregularities due to filter papers, etc., do not appreciably affect the results. However, the 5 cc. concentrated hydrochloric acid should not be added to the liquid being titrated until the end is nearly reached in order that enough manganese sulfate may be present to act as acceptor between the ferrous iron and the permanganate.

2—The precipitation of the cuprous thiocyanate from about a 2 per cent sulfuric acid solution (other acids having been removed by evaporation to sulfur trioxide fumes) has been found satisfactory. A solution containing 4 per cent sodium thiocyanate and 10 per cent sodium sulfite is used as precipitating agent (10 cc. of this usually suffices for most samples).

3—Unless the insoluble residue is very white it is advisable to remove it by filtration before precipitating the cuprous thiocyanate.

4—The solution containing the cuprous thiocyanate should be boiled to coagulate the precipitate. It may then be readily filtered on a coarse paper that has received two or three small washes of a "filler." This filler is made by agitating 1 g. of corn starch (cooking starch) with 1 l. of water. This is a mechanical filler and does not relieve one of the necessity of using a few drops of sulfuric acid in the hot water used to wash the precipitate to prevent formation of a hydrosol.

5—This starch filler has been found to insure very clear filtrates even when using coarse filter paper. The amount used has not been observed to consume any appreciable quantity of permanganate either by itself or by possible products of its hydrolysis under the conditions of the procedure.

6—The titration seems to be effected most accurately

in the solution volumes previously indicated. If larger amounts of copper are being titrated it would be better to use stronger permanganate.

SUMMARY

A modification of the usual permanganate method for copper is presented whereby (a) the theoretical ratio of copper to iron is reduced from 0.1897 to 0.1626; (b) the actual ratio factor is found to more closely approach the character of a linear coefficient; (c) the procedure seems in many cases to be more rapid and to give more accurate results.

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THE USE OF NICKEL CRUCIBLES FOR THE J. LAWRENCE SMITH FUSION IN DETERMINING SOIL POTASSIUM

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The scarcity and high price of platinum during the war led the writer to investigate the feasibility of substituting nickel crucibles for platinum ones in fusing soils by the J. Lawrence Smith method for total potassium. There would seem to be no theoretical reasons against the use of nickel for this purpose. Still, it is noticeable that wherever the Smith fusion method is described in the literature platinum crucibles are specified, and in view of this the writer did not feel justified in making the substitution without experimental proof of its adequacy.

Accordingly duplicate fusions were made on a number of soils, using a platinum crucible for one duplicate and a nickel crucible for the other. In all cases 0.5 g. of dry soil was taken and thoroughly mixed with 0.5 g. of ammonium chloride and 4 g. of calcium carbonate by grinding in an agate mortar. The mixtures were fused (after the usual preliminary heating to expel ammonia) for 45 min. at the highest heat obtainable with a good Bunsen burner. The subsequent operations were essentially as described by Ames and Gaither¹ and were carried out alike for all determinations. Porcelain dishes were used for the final evaporation with platinum solution. The potassium precipitates were collected on Gooch crucibles and dried in a water oven. The following table shows the weights of potassium chlorplatinate found by the two methods.

WEIGHTS OF K_2PtCl_6 FOUND BY FUSING SOILS IN PLATINUM AND IN NICKEL CRUCIBLES

SOIL No.	KIND OF CRUCIBLE	
	Platinum Gram	Nickel Gram
S-223	0.0142	0.0145
S-254	0.0080	0.0082
S-255	{ 0.0158	0.0178
	{ 0.0177	0.0175
S-258	0.0096	0.0098
S-259	0.0118	0.0118
S-260	0.0034	0.0032
S-262	0.0037	0.0038

DISCUSSION OF RESULTS

In only one case, *viz.*, Soil S-255, was there an appreciable difference in the weights found; and when the comparison was repeated on that soil, results were obtained which not only agreed between themselves, but also with the result previously obtained with the

¹ Ohio Agr. Expt. Station, *Bulletin* 261, 507.

nickel crucible. This indicates that the discrepancy at first observed was due to some undetected error in manipulation with the platinum crucible fusion, rather than to inadequacy of the nickel crucible.

Although, as shown, correct results are obtained by using a nickel crucible, it cannot be claimed that nickel is as satisfactory as platinum. The nickel crucibles are decidedly attacked by the fusion mixture, so that the life of a crucible is rather short. The inner surface of the crucible soon becomes rough and pitted, making it somewhat difficult to remove the mass cleanly. The fused mass is always colored green by dissolved nickel, and it does not slake and disintegrate as well as those from platinum crucibles. But,

as also mentioned by Ames and Gaither,¹ poor slaking does not affect the final result.

SUMMARY

It is found that the same result for soil potassium is obtained whether the soil is fused in a platinum or a nickel crucible.

Nickel crucibles are attacked by the J. Lawrence Smith fusion mixture and are therefore not as satisfactory as platinum crucibles.

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¹ *Loc. cit.*

ADDRESSES AND CONTRIBUTED ARTICLES

CHEMICALS RECEIVED BY THE BUREAU OF CHEMISTRY DURING THE WAR¹

By H. E. Buc

For a good many years the Bureau of Chemistry has been regularly examining all the stock chemicals purchased. Without going into a detailed account of this work, initiated by Dr. L. F. Kebler and carried on under his charge, it may be said that during the period of half a dozen years preceding the war the chemical reagents on the market, mostly of American make, were quite generally of excellent quality. During the first year of the war, according to our records, there was no marked change. Since that time, however, the Bureau has had considerable difficulty in procuring good chemicals belonging to certain classes, and we have been occasionally disappointed with chemicals belonging to types that generally come quite pure.

The writer's experience covers a period of four years, 1915-1919. During that time about 1300 samples were examined. Of these about 150 shipments were found to be more or less unsatisfactory. During a similar preceding period of four years, 1911-1915, during which a like number of chemicals were tested, only about 50 were unsatisfactory. Too much importance should not be attached to the proportion of 150 to 50 as the kinds of chemicals tested were not exactly parallel. On the other hand, in the latter period, in addition to the above 150, a number of tests were made of samples submitted by dealers. When these were found unsatisfactory, the agents or manufacturers were so informed, thus diminishing the number of shipments of unsatisfactory chemicals. It should also be added that the shortcomings of the chemicals tested in the war period were more serious than those recorded in the pre-war period.

A more detailed comparison between the two periods is hardly necessary. The main purpose of this paper is to point out the present situation in regard to ordinary reagents, as shown by the examinations made in the Bureau of Chemistry. For the purpose of this discussion the chemicals may be divided into several classes which differ widely in quality.

LIQUID INORGANIC CHEMICALS—Hydrochloric, sulfuric, nitric, and phosphoric acids, and ammonia, generally have met our requirements.

LIQUID ORGANIC CHEMICALS—The ordinary alcohol, ether, acetone chloroform, carbon tetrachloride, carbon disulfide, and glycerin have been found satisfactory for practically all chemical purposes. On evaporating large quantities of ether the penetrating odor of formaldehyde is often perceived in the last portions. However, attempts to identify formaldehyde

by means of morphine were futile. All samples of carbon tetrachloride examined contained carbon disulfides.

Other liquid organic reagents have been of less excellent quality.

Good methyl alcohol is obtainable, but not without at least traces of acetone. Amyl alcohol of good quality is not to be had. Not only does it contain appreciable amounts of pyridine but the boiling range is very wide. This is also true of amyl acetate. Pure benzene seems to be non-existent. Thiophene and carbon disulfide are always present, and quite often the boiling range points to the presence of homologs.

"Absolute" organic chemicals (free from water, etc.) are generally unobtainable. This is true of acetic acid, methyl alcohol and ethyl acetate, which are occasionally desired in absolute or nearly absolute condition. We prepare our own absolute ethyl alcohol (not less than 99.8 per cent), having started to make it ourselves long before the war, owing to the fact that we were unable to procure a dependable grade.

In the case of absolute ether, for the most part the products sent to us are good. Occasionally we are obliged to reject samples which show turbidity when treated with sodium. Our experience with the preparation of this product, which at one time we did ourselves, indicates the necessity of thoroughly washing out the alcohol in the preliminary stage. A heavy test for aldehyde seems always to accompany the turbidity obtained with sodium.

Acetic acid (99.9 per cent) complying with the dichromate test requirement is now unobtainable; but even before the war this grade was not easy to get. The best grade which we can obtain at present, and that from only one firm, is labeled 99.5 per cent, but is actually a little higher. Samples that have reached us from other firms rarely go above 99.0 per cent.

ALKALI SALTS—This embraces a number of common and important reagents. For the most part they are of good quality, but certainly not dependably so. We have on record sodium chloride with quite a little magnesium present, and ammonium chloride leaving a high residue on ignition.

"Anhydrous" alkali carbonates seldom have less than 8 to 12 per cent of water. Sodium and potassium hydroxides, particularly the latter, at one time gave us considerable trouble. The quality coming in now is fair, except for too strong a test for chlorides. Incidentally, it should be said that the strength of these chemicals is higher than is commonly supposed. Sodium hydroxide comes about 97 per cent potassium hydroxide, hardly ever falls below 86 per cent and occasionally goes above 90 per cent. Potassium permanganate, long a source of worry to our purchasing office, now comes in good quality, in spite of a rather novel appearance and color. Occasionally, however, it bears more than traces of chloride.

¹ Presented before the Division of Industrial and Engineering Chemistry at the Philadelphia Meeting of the American Chemical Society, September 2 to 6, 1919.