bonate. But the greatest difference is shown in the case of their action on manganese sulphate; the peroxide throws down the brown precipitate of manganese dioxide, while percarbonate produces a small quantity of brown precipitate but mostly the light precipitate of manganese carbonate. On addition of sodium hydroxide to this precipitate in suspension, the dioxide is immediately formed. With a lead salt the same reactions occur.

From these reactions it would appear that the carbonate is formed, and this is oxidized slowly by the available oxygen contained in the solution as hydrogen peroxide. These salts were taken as perhaps the hardest to oxidize. The percarbonate readily oxidizes compounds such as ferrous and stannous salts. It will also liberate iodine from hydriodic acid solution.

Ordinarily, as an oxidizing agent sodium peroxide is to be preferred to potassium percarbonate. Moreover, the molecular weights are to be taken into account. The same amount of available oxygen is furnished by two and one-half times the amount of percarbonate as of peroxide.

In conclusion, potassium percarbonate can be produced from the pure carbonate, and is an oxidizing agent, but an oxidation reaction that cannot be caused by sodium peroxide remains to be found.

PITTSBURG, PA.

VOLUMETRIC METHODS FOR COPPER.

BY G. FERNEKES AND A. A. KOCH.

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IN LOOKING over the various volumetric methods for the determination of copper we found that a comparative study of the volumetric methods for this element had never been systematically taken up. We therefore decided to work over the principal methods for the purpose of ascertaining their scientific as well as their practical value. In each method the quantity of copper was varied, and the effect of interfering elements tried.

Carefully calibrated pipettes, measuring flasks and burettes were used. The copper sulphate for these experiments was prepared by C. A. F. Kahlbaum and was marked chemically pure. It, however, contained a trace of iron. With this copper sulphate several liters were prepared, so that 50 cc. contained approximately 0.1 gram copper. The solution was made slightly acid with sulphuric acid in order to prevent the precipitation of basic copper sulphate. Fifty cc. of this solution were diluted to 100 cc., 5 cc. nitric acid (sp. gr. 1.4) added, and the solution electrolyzed with a current of 0.3 ampere for six hours. The determinations gave the following results: Found: Cu, 0.0939, 0.0940, 0.0938. Average, 0.0939, which was taken as the exact amount of copper in 50 cc. of the copper sulphate solution.

POTASSIUM CYANIDE METHOD.

Since the method of Parks,[1] the originator of the potassium cyanide method, was published in 1851, numerous articles have appeared criticizing its accuracy. Liebig[2] showed that the quantity of ammonia employed seriously affected the titrations. Then Fresenius and Fleck[3] showed that ammonium salts had a deleterious effect upon the titrations. It was found that both ammonia and ammonium salts increase the quantity of potassium cyanide used. Steinbeck[4] claims that ammonium salts have only a very slight effect upon the titrations and that for practical purposes they are not worth considering. The same author shows that lead does not influence the results, and also gives some data showing the effect of zinc. In the latter instance it is, however, apparent that Steinbeck means to minimize the errors due to zinc, as Dulin[5] showed in a later paper that zinc, when present above 4 per cent., materially affects the titrations. The potassium cyanide method was very much improved by using sodium carbonate instead of ammonia for the purpose of neutralization. This variation was introduced by J. L. Davies,[6] and F. L. Merry, mentioned in the same article, employed tartaric acid to obtain the blue color and dissolve the precipitated copper carbonate. Finally, Fessenden[7] enumerates the errors of the potassium cyanide titration as usually carried out, and also critically discusses the method when sodium carbonate is used for neutralization. He claims excellent results by the latter variation of the method. As will be seen, we have in a great

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[1] *Mining Journal* (1851).

[2] *Ann. Chem.* (Liebig), **95**, 118 (1855); and Mohr: *Ibid.*, **94**, 143 (1855).

[3] *Z. anal. Chem.*, **8**, 15 (1869).

[4] *Ibid.*, **8**, 16 (1869).

[5] This Journal, **17**, 346 (1895).

[6] *Chem. News*, **58**, 131.

[7] *Ibid.*, **61**, 253, 283.

measure duplicated and confirmed the results of the above investigators.

In our experiments, the copper sulphate solution was made ammoniacal with a large excess of ammonium hydroxide, the solution diluted to 100 cc. and tenth-normal potassium cyanide solution added until the blue color just disappeared. The quantities of copper sulphate used were 2 cc., 5 cc., 10 cc., 25 cc. and 50 cc., corresponding to 0.0038 gram, 0.0094 gram, 0.0188 gram, 0.0470 gram and 0.0939 gram copper. The quantities of ammonia (sp. gr. 0.905) used were 6 cc., 12 cc. and 18 cc. Further, the effect of ammonium salts and sodium carbonate was tried. In each case the number of cubic centimeters of potassium cyanide solution required to just dispel the blue color is the average of two titrations. The results are computed on the basis of three determinations, made at room temperature with 50 cc. copper sulphate and 6 cc. ammonium hydroxide. The average of these determinations gave 51.6 cc. potassium cyanide equivalent to 0.0939 gram copper or 1 cc. potassium cyanide equivalent to 0.00182 gram copper. The results obtained are as follows:

N/10 Potassium Cyanide.

1 cc. KCN = 0.00182 gram Cu.

Boiling Temp.

	NH_4OH added. cc.	Copper taken. Gram.	Copper found. Gram.	Diff.
1	6	0.0038	0.0037	—0.0001
2	12	0.0038	0.0050	+0.0012
3	18	0.0038	0.0066	+0.0028
4	6	0.0188	0.0164	—0.0024
5	12	0.0188	0.0193	+0.0004
6	18	0.0188	0.0212	+0.0024
7	6	0.0939	0.0896	—0.0043

17° C.

	NH_4OH added. cc.	Copper taken. Gram.	Copper found. Gram.	Diff.
1	6	0.0038	0.0049	+0.0011
2	12	0.0038	0.0070	+0.0032
3	18	0.0038	0.0084	+0.0046
4	6	0.0188	0.0200	+0.0012
5	12	0.0188	0.0223	+0.0035
6	18	0.0188	0.0227	+0.0039
7	6	0.0939	0.0939	0.0000
8	12	0.0939	0.0970	+0.0031
9	18	0.0939	0.0991	+0.0052

0° C.

	NH_4OH added. cc.	Copper taken. Gram.	Copper found. Gram.	Diff.
1	6	0.0038	0.0056	+0.0018
2	12	0.0038	0.0064	+0.0026
3	18	0.0038	0.0083	+0.0045
4	6	0.0188	0.0209	+0.0011
5	12	0.0188	0.0228	+0.0040
6	18	0.0188	0.0242	+0.0054
7	6	0.0939	0.0981	+0.0042

The results obtained in the above tables vary with the amount of copper in 100 cc. of solution, with the temperature, and with the amount of ammonia. Experiments carried out with a half-normal potassium cyanide solution, which corresponds more nearly to the strength used in practice, gave results which were in accordance with the above tables.

A series of experiments were now carried out for the purpose of determining the effect ammonium salts have upon the titration. Three salts were tried, *viz.*, ammonium chloride, ammonium sulphate and ammonium nitrate. In each case 5 grams of the salt were added before making the titration.

N/2 POTASSIUM CYANIDE.

1 cc. = 0.00673 gram Cu.

NH_4OH added. cc.	Copper taken. Gram.	Copper found. Gram.	Diff.
		NH_4Cl.	
6	0.0939	0.1051	+0.0112
		$(NH_4)_2SO_4$.	
6	0.0939	0.1110	+0.0171
		NH_4NO_3	
6	0.0939	0.1062	+0.0123

The three results given in the above table show that ammonium salts considerably increase the amount of potassium cyanide required to dispel the blue color.

The variation introduced by J. L. Davies[1] was now tried. The copper sulphate solution was treated with a slight excess of sodium carbonate, and titrated with potassium cyanide. The precipitated basic copper carbonate gradually disappeared, the solution turned intensely blue and on further addition of potassium cyanide became colorless, the end-point being very distinct. The number of cubic centimeters of potassium cyanide used in three determinations with varying amounts of copper are as follows: (1) 50 cc. $CuSO_4$ solution required 24.03 cc. KCN;

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[1] *Chem. News*, 58, 131.

(2) 25 cc. $CuSO_4$ solution required 7.01 cc. KCN; (3) 5 cc. $CuSO_4$ solution required 1.40 cc. KCN.

The results show that when one-half and one-tenth the amount of copper was contained in the solution, only one-half and one-tenth the number of cubic centimeters of potassium cyanide were used. From the good agreement obtained in the above determinations it appears that the addition of a cubic centimeter of ammonia, after neutralization with sodium carbonate, as suggested by Sutton,[1] is unnecessary. Furthermore an excess of sodium carbonate did not influence the results.

The effect of lead, cadmium, arsenic, antimony and tin salts was tried. Lead salts did not influence the titrations, while cadmium salts seemed to increase the quantity of potassium cyanide used in proportion to the quantity of cadmium salt added. Arsenic, antimony and tin salts in the reduced condition seriously changed the results, but in the oxidized state were without influence on the titrations. The error introduced by using zinc to precipitate the copper from its solutions can be entirely avoided by using aluminum, which we have found does not affect the results.

Our results show, that the quantity of potassium cyanide required to make a titration for copper, decreases with an increase of temperature, but increases with an increase of ammonia or ammonium salts. Further the quantity of potassium cyanide used varies with the quantity of copper in 100 cc. of solution, when ammonia is used for neutralization instead of sodium carbonate. In performing these experiments it was noticed that the quantity of potassium cyanide required to just dispel the blue color, varied with the speed with which the titration was performed, but no definite tests were made as to the extent of this variation. The percentage errors resulting from these differences may be very great when small quantities of copper are to be determined, as is the case with tailings and slags, where the copper is titrated hot after precipitating the iron with ammonia.

That this may really be the case, is shown by the results obtained on a symposium of copper and copper matte, initiated by Dr. A. R. Ledoux[2] of New York City. Six chemists reported results by the cyanide method ranging from 54.80–50.55 per cent.,

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[1] Sutton's "Volumetric Analysis," 7th ed., p. 179.

[2] *Trans. A. I. M. E.*, **25**, 250, 1000; Dewey: This Journal, **18**, 814.

all but one being lower than the lowest electrolytic determination. It is, however, probable that good results can be obtained, if the copper in the unknown is titrated under the same conditions as when the potassium cyanide solution is standardized; that is, temperature, dilution, ammonia, ammonium salts, and the time required to perform the titration and standardization must be the same. Otherwise it is better to use sodium carbonate for neutralization instead of ammonia, and then perform the titration with standard potassium cyanide solution.

POTASSIUM IODIDE METHOD.[1]

The solution of copper sulphate was put into an Erlenmeyer flask, any free mineral acid neutralized with ammonia, then made slightly acid with acetic acid, 3 grams potassium iodide added, and the free iodine liberated according to the reaction

$$2Cu(C_2H_3O_2)_2 + 4KI = Cu_2I_2 + 4K(C_2H_3O_2) + 2I,$$

titrated with approximately tenth-normal sodium thiosulphate and starch solution. The sodium thiosulphate solution was standardized with twice resublimed iodine and the copper value for tenth-normal thiosulphate computed. The starch solution was made in the ordinary way and kept in well-stoppered sterilized bottles.[2] In all the experiments given below the dilution was 100 cc.

Low[3] claims that in order to obtain the right amount of copper it is necessary to add at least 3 grams potassium iodide. We have carried out a series of determinations to see if with smaller quantities of copper less potassium iodide could be used, to liberate the equivalent quantity of iodine. Two cc. copper sulphate solution equivalent to 0.0038 gram copper were made up to 100 cc., 2 cc. of acetic acid (80 per cent.) and 0.5 gram potassium iodide added. This solution was allowed to stand ten minutes and frequently shaken. One drop of sodium thiosulphate solution was found sufficient to dispel the blue color. The same experiment was repeated and the solution allowed to stand twelve hours. Again one drop of sodium thiosulphate solution was sufficient to dispel the blue color. In the next two experiments the same quantities of copper sulphate, potassium iodide and acetic acid were used. This solution was shaken frequently for

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[1] Low : This Journal, **18**, 457 ; **24**, 1082 ; *Eng. Min. J.*, 1896, p. 124.

[2] Treadwell: Kurze's "Lehrb. Analyt. Chem.," B. II., 2te. auf., p. 452.

[3] This Journal, **18**, 457.

ten minutes, then diluted to 100 cc. and titrated. The quantity of tenth-normal thiosulphate used was 0.35 cc. = 0.0022 gram copper and 0.37 cc. = 0.0024 gram copper. The same experiment repeated without the addition of acetic acid required 0.30 cc. tenth-normal thiosulphate = 0.0019 gram copper.

We next varied the quantity of potassium iodide. Two cc. copper sulphate solution and 1.5 grams potassium iodide were diluted to 100 cc., and titrated without the addition of acetic acid. The amount of sodium thiosulphate required was 0.47 cc. = 0.0030 gram copper. The same experiment with the addition of acetic acid and allowing the solution to stand five minutes required 0.55 cc. thiosulphate solution = 0.0035 gram copper. In all the above tests the blue color reappeared upon standing; another drop of thiosulphate solution would again dispel the blue color, but the blue color would continue to return until the equivalent quantity of iodine had been liberated. Using 2 cc. copper sulphate = 0.0038 gram copper, 2 grams potassium iodide and 2 cc. acetic acid, two determinations gave 0.60 cc. and 0.58 cc. tenth-normal thiosulphate = 0.0038 gram copper. In these two cases the solution remained colorless for some time upon standing.

Experiments were now performed with varying quantities of copper sulphate, using 2.5 grams of potassium iodide. The results are as follows:

	Copper taken. Gram.	Copper found. Gram.	Diff.
1	0.0939	0.0936	—0.0003
2	0.0939	0.0938	—0.0001
3	0.0939	0.0937	—0.0002
4	0.0939	0.0941	+0.0002
5	0.0939	0.0940	+0.0001
6	0.0470	0.0470	0.0000
7	0.0470	0.0473	+0.0003
8	0.0188	0.0188	0.0000
9	0.0188	0.0190	+0.0002
10	0.0188	0.0186	—0.0002
11	0.0188	0.0187	—0.0001
12	0.0038	0.0038	0.0000
13	0.0038	0.0038	0.0000
14	0.0038	0.0038	0.0000
15	0.0038	0.0037	—0.0001

In Nos. 4 to 9, 5 cc. acetic acid were added. In No. 14 the potassium iodide was added before making up the solution to 100 cc. In No. 15 the acetic acid was omitted.

Experiments showed that arsenic, antimony and tin salts in the oxidized form, when added to the copper sulphate solution, do not affect the titrations. In the case of arsenic, two tests on 10 cc. copper sulphate = 0.0188 gram copper, and 0.5 gram sodium arsenate, gave 0.0187 gram and 0.0188 gram copper respectively. Similar results were obtained for antimony and tin. The effect of lead, bismuth, cadmium, zinc and aluminum salts was tried, and found to be without influence upon the titrations. In the case of lead and bismuth it was somewhat difficult to tell the end-point of the reaction.

Our results show that an excess of acetic acid does not influence the titrations. In order to correctly determine the amount of copper in a solution of 100 cc. containing 0.0038 gram copper, at least 1.5-2 grams potassium iodide must be added, and for a solution containing 0.0939 gram copper per 100 cc., 2.5 grams potassium iodide are sufficient to liberate the equivalent quantity of iodine.

FERROCYANIDE METHOD.[1]

In this method, the copper sulphate solution, slightly acid with sulphuric acid, was titrated hot with a standard solution of potassium ferrocyanide. The reaction

$$2CuSO_4 + K_4Fe(CN)_6 = Cu_2Fe(CN)_6 + 2K_2SO_4$$

is complete when a drop of the solution brought into contact with a drop of dilute ferric chloride solution on a white porcelain plate gives a blue coloration. The end-point in this reaction, using ferric chloride as an indicator, is indistinct. Near the end-point of the reaction a dirty dark spot is obtained with ferric chloride, which on further addition of potassium ferrocyanide becomes blue. This dirty coloration is evidently due to the brown precipitated cupric ferrocyanide.

At room temperature the precipitate of cupric ferrocyanide is very finely divided, but upon boiling becomes flocculent and settles more rapidly. For the results given below the titrations were performed hot, but it was never possible to free the solution entirely from the fine granular precipitate, and the above-mentioned dirty coloration invariably appeared. The copper value of 1 cc. of the potassium ferrocyanide solution was 0.00427 gram copper. The results were computed from this value.

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[1] Matteo Spica: *Staz. Sperim. Agric. ital.*, **26**, 593 (1894); *Chem. Centrbl.*, **65**, 815 (1894).

	Copper taken. Gram.	Copper found. Gram.	Diff.
1	0.0929	0.0931	+0.0002
2	0.0929	0.0927	—0.0002
3	0.0465	0.0453	—0.0012
4	0.0465	0.0452	—0.0013
5	0.0093	0.0088	—0.0005
6	0.0093	0.0092	—0.0001

The following elements are precipitated under similar conditions, by means of potassium ferrocyanide: silver, lead, cadmium, mercury, bismuth, zinc, manganese, nickel, cobalt and iron. It is therefore evident, that this method can only be used with a pure solution of copper.

CUPROUS THIOCYANATE, METHOD OF RIVOT.[1]

Fifty cc. of the copper sulphate solution, slightly acidified with sulphuric acid, were saturated with sulphur dioxide, ammonium thiocyanate added until in slight excess, the solution stirred and the precipitate allowed to settle several hours. Pure white cuprous thiocyanate settled out. The cuprous thiocyanate was then filtered through a previously dried and weighed Gooch crucible, washed until free from ammonium thiocyanate, the crucible with the precipitate dried at 110° C. and again weighed; the difference in the two weighings gave the weight of cuprous thiocyanate. The following are the results:

	$Cu_2(CNS)_2$. Gram.	Copper taken. Gram.	Copper found. Gram.	Diff.
1	0.1800	0.0939	0.0941	+0.0002
2	0.1798	0.0939	0.0939	0.0000
3	0.1798	0.0939	0.0939	0.0000
4	0.0362	0.0188	0.0188	0.0001
5	0.0360	0.0188	0.0188	0.0000

The results obtained with a pure copper sulphate solution show a very close agreement with the theoretical, for both the larger and smaller amounts of copper.

VOLHARD'S METHOD.[2]

In this method the copper is precipitated by a standard potassium thiocyanate solution under the same conditions as described under the method of Rivot. The excess of potassium thiocyanate is titrated by means of a standard silver nitrate solution, using

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[1] *C. R.*, **38**, 868; also R. G. Van Name: *Z. anorg. Chem.*, **26**, 230; Busse: *Z. anal. Chem.*, **17**, 53; **30**, 122; Treadwell: Kurze's "Lehrb. Analyt. Chem.," 2te. auf., B. II, p. 126.

[2] *Ann. Chem. Pharm.*, **190**, 251 (1877); *Z. anal. Chem.*, **18**, 285 (1879).

iron alum as an indicator. The assumption is, that no other element excepting silver is precipitated by potassium thiocyanate in acid solution. Chlorides must not be present, but this condition is fulfilled in the course of an ordinary copper assay. A tenth-normal silver nitrate solution was employed, and the potassium thiocyanate solution was standardized against the silver nitrate solution. The results in the table below were obtained with a copper sulphate solution. One cc. potassium thiocyanate was equivalent to 0.006299 gram copper.

	Copper taken. Gram.	Copper found. Gram.	Diff.
1	0.0929	0.0926	—0.0003
2	0.0929	0.0925	—0.0004
3	0.0465	0.0463	—0.0002
4	0.0465	0.0461	—0.0004
5	0.0093	0.0093	0.0000
6	0.0093	0.0092	—0.0001

We again tried the influence of various interfering elements, first upon potassium thiocyanate, and then upon silver nitrate. As previously stated, the only other element precipitated by potassium thiocyanate in acid solution is silver. It was, however, found that arsenic in the oxidized state gave a precipitate with silver nitrate, which seriously affected the results, so that this method could not be used with copper ores containing arsenic.

ACIDIMETRIC METHOD.[1]

The copper in the copper sulphate solution was precipitated with ammonium thiocyanate as in Rivot's method, and the cuprous thiocyanate filtered through a Gooch crucible. The crucible containing the cuprous thiocyanate was put into a porcelain dish, 25 cc. normal sodium hydroxide added, and the solution heated until the reaction

$$Cu_2(CNS)_2 + 2NaOH = Cu_2(OH)_2 + 2NaCNS$$

was complete. The cuprous hydroxide was filtered off and the filtrate titrated to neutrality with normal hydrochloric acid, using methyl orange as the indicator. One cc. normal sodium hydroxide = 0.0636 gram copper. Three determinations gave the following results:

	Copper taken. Gram.	Copper found. Gram.	Diff.
1	0.0939	0.0941	+0.0002
2	0.0939	0.0941	+0.0002
3	0.0939	0.0935	—0.0004

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[1] Garrigues: This Journal, **19**, 940 (1897).

The three results obtained with a pure copper sulphate solution show a good agreement among themselves, also with the theoretical amount of copper in the solution.

TITRATION OF THIOCYANIC ACID WITH POTASSIUM PERMANGANATE.

Guess[1] precipitates the copper from an acid solution with an alkaline thiocyanate, and then decomposes the cuprous thiocyanate with sodium hydroxide, according to the equation

$$Cu_2(CNS)_2 + 2NaOH = Cu_2(OH)_2 + 2NaCNS.$$

The sodium thiocyanate formed is made acid with sulphuric acid and the free thiocyanic acid titrated with a standard solution of potassium permanganate. According to the equation

$$10HCNS + 12KMnO_4 + 8H_2SO_4 = 6K_2SO_4 + 12MnSO_4 + 10HCN + 8H_2O,$$

the iron factor multiplied by 0.1892 should give the theoretical amount of copper. Guess found that by using 0.192 instead of 0.1892 as the factor, he obtained results which more nearly express the exact amount of copper. As the author does not give any experimental data, we have made a series of determinations with a pure copper sulphate solution, so that the results obtained by this method can be compared with the results obtained by other methods.

Our method of procedure was as follows: After precipitating the copper in the copper sulphate solution according to the method of Rivot, the precipitate was filtered on a Gooch filter and washed until free from ammonium thiocyanate. Then a hot solution of sodium hydroxide was poured through the filter and the cuprous hydroxide washed free from sodium thiocyanate, or the Gooch filter and precipitate were removed to a porcelain dish and then treated with hot sodium hydroxide, the precipitate stirred to insure intimate contact with the sodium hydroxide, then filtered and washed thoroughly. The strength of the sodium hydroxide was varied to see if it in any way altered the results. The sodium thiocyanate was then made decidedly acid with sulphuric acid, and titrated with a standard solution of potassium permanganate.

The potassium permanganate solution was carefully stand-

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[1] This Journal, 24, 208.

ardized against ferrous ammonium sulphate and the copper value computed by multiplying the iron value by 0.192.

$$1 \text{ cc. } KMnO_4 = 0.005448 \text{ gram iron}$$

or

$$1 \text{ cc. } KMnO_4 = 0.001046 \text{ gram copper.}$$

The following results were obtained by this method.

	Strength of NaOH to decompose $Cu_2(CNS)_2$. Per cent.	Copper taken. Gram.	Copper found. Gram.	Diff.
1	10	0.0939	0.0925	—0.0004
2	10	0.0939	0.0942	+0.0002
3	10	0.0939	0.0935	—0.0004
4	10	0.0939	0.0930	—0.0009
5	2	0.0939	0.0929	—0.0010
6	2	0.0939	0.0931	—0.0008
7	2	0.0939	0.0930	—0.0009
8	1	0.0929	0.0920	—0.0009
9	1	0.0929	0.0922	—0.0007
10	1	0.0465	0.0459	—0.0006
11	1	0.0465	0.0459	—0.0006
12	10	0.0188	0.0173	—0.0015
13	10	0.0188	0.0173	—0.0015
14	10	0.0188	0.0176	—0.0012

With a single exception our results are lower than the theoretical values, although we used the higher factor 0.192 instead of the factor 0.1892 computed from the equation given above.

TITRATION OF THE IRON EQUIVALENT OF COPPER BY MEANS OF POTASSIUM PERMANGANATE.

According to Meade[1] the copper is again precipitated as cuprous thiocyanate, and treated with sodium hydroxide as in the previous method. The cuprous hydroxide is then dissolved in a dilute sulphuric acid solution of ferric chloride or ferric sulphate, the cuprous hydroxide dissolving, and reducing a corresponding amount of iron from the ferric to the ferrous state.

$$Cu_2(OH)_2 + Fe_2(SO_4)_3 + H_2SO_4 = 2CuSO_4 + 2FeSO_4 + 2H_2O.$$

The ferrous sulphate is then titrated with a standard solution of potassium permanganate. According to the author the iron value of the permanganate used, multiplied by 1.125, gives the amount of copper.

We precipitated the copper with ammonium thiocyanate and decomposed the cuprous thiocyanate with sodium hydroxide as

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[1] This Journal, **20**, 610.

before. Various strengths of sodium hydroxide, both hot and cold, were used to decompose the cuprous thiocyanate. The cuprous hydroxide was then dissolved in a solution of ferric chloride, or ferric sulphate containing a little sulphuric acid, care being taken to have the iron salt in large excess. The Gooch crucible containing the cuprous hydroxide was either put into a porcelain dish, the dissolving solution added, and the dish warmed and stirred until the cuprous hydroxide had gone into solution and then filtered; or, the warm dissolving solution was poured through the Gooch crucible. In each case a little sodium carbonate, and dilute sulphuric acid were put into the flask into which the solution of reduced ferric salt was to be filtered. In this way sufficient carbon dioxide was generated to expel the air from the flask, and prevent any oxidation of the ferrous iron by the oxygen of the air. The reduced ferric chloride, or ferric sulphate solution was then titrated with a standard solution of potassium permanganate and the amount of copper calculated.

Meade multiplies the iron value of the permanganate by 1.125 to obtain the copper value. From the equation

$$Cu_2(OH)_2 + Fe_2(SO_4)_3 + H_2SO_4 = 2CuSO_4 + 2FeSO_4 + 2H_2O,$$

this would mean Fe:Cu as 56.63. Taking the atomic weight of Fe = 55.9 and Cu = 63.6, as given in the table of international atomic weights for 1905, we would obtain a factor which equals 1.138. In our determinations the results have been computed separately for each factor, as the following tables show.

	Strength of NaOH used to decompose $Cu_2(CNS)_2$. Per cent.	Copper taken. Gram.	F=1.125 Copper found. Gram.	Diff.	F=1.128 Copper found. Gram.	Diff.
1	2–4	0.0939	0.0843	—0.0096	0.0852	—0.0087
2	2–4	0.0939	0.0873	—0.0066	0.0883	—0.0056
3	2–4	0.0939	0.0742	—0.0197	0.0750	—0.0189
4	2–4	0.0939	0.0674	—0.0265	0.0682	—0.0257
5	2–4	0.0939	0.0742	—0.0197	0.0750	—0.0189
6	2	0.0939	0.0674	—0.0265	0.0682	—0.0257
7	2	0.0939	0.0803	—0.0136	0.0812	—0.0127
8	10	0.0939	0.0631	—0.0308	0.0638	—0.0301
9	10	0.0939	0.0592	—0.0347	0.0599	—0.0340

Nos. 1 and 2 were dissolved in a solution of 1 gram ferric ammonium sulphate, 25 cc. distilled water and a little sulphuric acid.

Nos. 3 to 9 were dissolved in a solution of 0.5 gram ferric chloride, 25 cc. distilled water and a little sulphuric acid.

In No. 6 the cuprous thiocyanate was decomposed with sodium hydroxide at room temperature. In the other eight determinations, hot sodium hydroxide was used for the decomposition of the cuprous thiocyanate.

It is clear that the low results given in the above table are not due to the difference in the value of the factor, but are due to some other cause. It was noticed that the cuprous hydroxide, after the treatment with sodium hydroxide solution, often appeared quite black on the surface, probably due to a slight oxidation by the hot sodium hydroxide solution. In No. 6, sodium hydroxide at room temperature was used to decompose the cuprous thiocyanate; while the cuprous hydroxide did not blacken as much as in the other tests, where hot sodium hydroxide was used, no better result was obtained. The asbestos in the Gooch crucible was then treated with nitric acid and found to contain considerable copper, but by no means enough to make up the theoretical amount of copper taken. We next tried a larger excess of ferric salt. The following are the results obtained:

	Strength of NaOH used to decompose $Cu_2(CNS)_2$. Per cent.	Copper taken. Gram.	F=1.125. Copper found. Gram.	Diff.	F=1.138. Copper found. Gram.	Diff.
10	10	0.0929	0.0925	—0.0004	0.0936	+0.0007
11	5	0.0929	0.0956	+0.0027	0.0966	+0.0037
12	10	0.0929	0.0971	+0.0042	0.0983	+0.0054
13	10	0.0929	0.0950	+0.0021	0.0961	+0.0021
14	4	0.0929	0.0968	+0.0039	0.0979	+0.0050
15	4	0.0929	0.0971	+0.0042	0.0983	+0.0054
16	4	0.0929	0.0959	+0.0030	0.0970	+0.0041
17	10	0.0188	0.0180	—0.0008	0.0182	+0.0006
18	10	0.0188	0.0190	+0.0002	0.0192	+0.0004

No. 10 was dissolved in a solution of 2 grams ferric chloride, 25 cc. distilled water and 2 cc. sulphuric acid.

No. 11 was dissolved in a solution of 2.5 grams ferric chloride, 25 cc. distilled water and 4 cc. sulphuric acid.

Nos. 12, 13, 14, 17 and 18 were dissolved in a solution of 2.5 grams ferric chloride, 25 cc. distilled water and 3 cc. sulphuric acid. Before titrating No. 14, 20 cc. of the titrating mixture were added.

Nos. 15 and 16 were dissolved in a solution of 5 grams ferric ammonium sulphate, 25 cc. water and 3 cc. sulphuric acid.

In all the above tests Nos. 10 to 18, the cuprous hydroxide was dissolved by pouring the acid solution of ferric chloride or sulphate through the Gooch crucible, until all the cuprous hydroxide was dissolved. This procedure was more rapid than to remove the asbestos with the cuprous hydroxide to a dish, dissolve the cuprous hydroxide, and then filter; in the greater number of cases the asbestos was free from copper after this treatment. The ferric chloride and ferric ammonium sulphate used for the above determinations were free from ferrous salts; still the results are too high whether we use the factor 1.125 or 1.138. Believing that the iron value of our permanganate solution was too high, we again restandardized our permanganate solution, but obtained the same results as at first.

Recalculating the six results obtained by Meade,[1] with a copper sulphate solution of known strength, on the basis of $F = 1.138$, we find his results to be on an average too high by 0.0012 gram, while with $F = 1.125$ to be on an average too low by 0.0011 gram. We were unable to obtain as concordant results by this method as were desired, either with the copper sulphate solution, or with a chalcopyrite ore.

Taking the average of the seven results, Nos. 10 to 16, and computing the factor by which we would have to multiply the iron value of the permanganate, in order to obtain the theoretical amount of copper, we obtain $F = 1.092$. While this new factor may approximately express the value for a solution containing a quantity of copper = 0.0929 gram, a smaller or larger amount of copper may require some other factor. In order to determine whether the factor varies with the amount of copper, a series of determinations with smaller and larger amounts of copper will be necessary. At best the method is longer and more painstaking than the previous method of titrating the thiocyanic acid with permanganate, and the results have been less satisfactory.

ANALYSIS OF CHALCOPYRITE.

In each case 0.5 gram of ore was used. It was dissolved and treated by familiar methods employed for copper ores. It might, however, be said that aluminum was used to precipitate the copper from the solution. After thoroughly washing the copper by decantation, it was redissolved in nitric acid. The solution was boiled until the brown fumes disappeared. The solution was diluted,

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[1] This Journal, **20**, 613.

ammonium hydroxide was added to alkaline reaction and again boiled. Now we acidified with acetic acid, and allowed the solution to assume the room temperature. Three grams of potassium iodide were added and the liberated iodine titrated with a tenth-normal thiosulphate solution.

In determining the copper as cuprous thiocyanate, according to Rivot, the ore was again decomposed as before. The solution was slightly acid with sulphuric acid and saturated with sulphur dioxide, and the copper precipitated with ammonium thiocyanate. The precipitated cuprous thiocyanate was finally weighed in a Gooch crucible. The two permanganate methods were carried out as previously described when pure copper sulphate was used. The results obtained are as follows:

	Electrolytic.		Iodide.		$Cu_2(CNS)_2$.			$KMnO_4$ of HCNS.		$KMnO_4$ of $Cu_2(OH)_2$.	
	Copper found. Gram.	Copper. Per cent.	Copper found. Gram.	Copper. Per cent.	Found. Gram.	Copper. Gram.	Copper. Per cent.	Copper found. Gram.	Copper. Per cent.	Copper found. Gram.	Copper. Per cent.
1	0.1686	33.72	0.1685	33.70	0.3158	0.1650	33.00	0.1662	33.24	0.1767	35.34
2	0.1685	33.70	0.1682	33.64	0.3176	0.1660	33.20	0.1692	33.84	0.1711	34.22
3	....	......	0.1685	33.70	....	....	......	....	......	....	......

The results in the above table show that the iodide method compares very favorably with the electrolytic method. The three results agree very well among themselves and give an average of 33.68 per cent. copper, as compared with an average of 33.71 per cent. copper by the electrolytic method, a difference of 0.03 per cent. This slight difference is insignificant, and can easily be accounted for in filtering, washing, etc. We found that all the copper is precipitated by the aluminum strip, for neither the ammonia nor hydrogen sulphide test showed any copper in the filtrates of the chalcopyrite ore or the copper sulphate solution. Thorn Smith[1] claims that all the copper is not precipitated by means of aluminum; this may be the case with more complicated ores, containing arsenic, antimony, etc., and which we have not analyzed. As far as we have worked with the iodide method, we find that when one has once mastered the manipulations, it is rapid, and, excluding the item of expense, an excellent method for the determination of copper.

The two results in which the copper was weighed as cuprous thiocyanate gave low results. When, however, the thiocyanic acid was titrated with potassium permanganate, results were

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[1] *Eng. Min. J.*, p. 1023, Dec., 1904.

obtained which agree very favorably with those obtained with pure copper sulphate solutions.

In No. 1 of the last method we used as the dissolving solution, a solution of 2.5 grams ferric chloride, 25 cc. distilled water and 3 cc. sulphuric acid, but before titrating added 20 cc. of titrating mixture. In No. 2 the ferric chloride was replaced by ferric sulphate, but no titrating mixture was used. In making the computations the iron factor was multiplied by 1.138 to give the copper value. Recalculating the results, using the factor 1.092, we obtain 33.90 per cent. and 32.84 per cent., or an average of 33.37 per cent. copper,—a result which approximates the results obtained by the other methods.

In nearly all of the above methods, the determinations were carried out by each of us independently. In this way the weak points of the methods were brought out more clearly, and gave us a check on our work.

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THE CAUSTIC SODA METHOD OF DETERMINING MOLYBDENUM IN STEEL.[1]

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THIS method as described by the writer in the *Iron Age*, November 20, 1902, was taken up by Cruger and Miller,[2] tested by them and compared with a method of their own which they suggest and describe, and which differs from the writer's method in that the iron is separated from the molybdenum by hydrogen sulphide instead of by caustic soda. The conclusion that their experiments bring them to is that the caustic soda method gives results that are about 0.30 per cent. too high in steels, and about 2.00 per cent. too high in ferro-molybdenums, on account of the formation of a molybdate of iron soluble in caustic soda or ammonia. It seemed to the writer that this conclusion was based on insufficient evidence. It is true that the fact that in their experiments, the caustic soda results are lower than results by their own method as above stated is a

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[1] Read at the June Meeting of the Philadelphia Section of the American Chemical Society.

[2] This Journal, **26**, 675.