

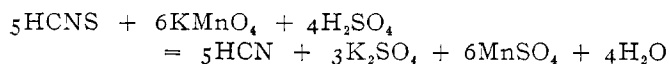
### THE SULFOCYANATE-PERMANGANATE METHOD FOR COPPER IN ORES

By D. J. DEMOREST

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Under the proper conditions copper may be precipitated practically completely as cuprous sulfocyanate. It is true that a qualitative test for copper may be obtained in the filtrate from the cuprous sulfocyanate when potassium ferrocyanide is added but this is due to the presence of only about 0.0001 gram of copper, as the writer has found by colorimetric measurements. Furthermore, the writer has found that practically all the copper added to the solution before precipitation may be recovered from the precipitate by electrolysis.

In Guess's method for copper the cuprous sulfocyanate is dissolved on the filter with sodium hydroxide, leaving the cuprous hydroxide on the filter while sodium sulfocyanate goes through. The filtrate is then made acid with sulfuric acid and is titrated with permanganate. Theoretically, the titration reaction is



Practically, however, the oxidation in acid solution is never complete and an empirical factor must be used amounting to about 5 per cent. of the copper present, according to Guess's tables of correction given in Low's "Technical Methods of Ore Analysis." This is also in accord with the writer's experience and with that of Grossman and Hölter.<sup>1</sup>

It occurred to the writer that if the permanganate were added to the sulfocyanate in alkaline solution until about as much was added as would be required to titrate the sulfocyanate in acid solution and if then the solution were made acid, the titration might be finished by a few drops, and in this way complete oxidation might be brought about and no empirical factor would be needed.

It is easy to tell when enough permanganate has been added to the alkaline solution by testing a drop or so on a white plate with a drop of an acid solution of ferric chloride. If not enough permanganate has been added a red color develops but if enough has been added no red appears. It is not necessary to run in permanganate until no red is obtained on testing. When the red color of the test is very faint the solution may be made acid and the titration finished in the usual way.

#### PROCESS OF ANALYSIS

Weigh out enough of the ore to have from 0.05 gram to 0.30 gram of copper present. Transfer the sample to a 200 cc. beaker, add 5 cc. of strong hydrochloric acid and heat for several minutes; then add 10 cc. of nitric acid and digest on a hot plate until the ore is completely decomposed. Then add 10 cc. of 1 : 1 sulfuric acid and boil down until fumes of  $\text{SO}_3$  appear. Cool and add 50 cc. of water containing 3 grams of tartaric acid and heat until all soluble salts are in solution. Cool and add ammonia until

the solution turns a deep blue, then add sulfuric acid until the liquid becomes acid, then add one cc. more. Now add one gram of sodium sulfite dissolved in 20 cc. of water, heat nearly to boiling and add slowly and with vigorous stirring one gram of potassium sulfocyanate dissolved in 20 cc. of water. Heat at a nearly boiling temperature for several minutes to coagulate the precipitate and dissolve out of it all tartaric acid. Cool somewhat and filter while still hot through, preferably, an asbestos mat on a Gooch filter. Wash well with water and rinse out the suction flask. Then pour through the crucible 30 cc. of a hot 10 per cent. sodium hydroxide solution and wash well with water.

Warm the filtrate to about 50° and proceed to titrate. Run in slowly at first, while the flask is vigorously shaken, the standard permanganate solution. The solution in the flask turns green, due to the  $\text{K}_2\text{MnO}_4$  formed. After about 10 cc. have been run in take out a drop of the solution and place it in a drop of strong hydrochloric acid on a paraffined white plate; then add a drop of a 10 per cent. solution of ferric chloride. If a red color appears continue to add the permanganate solution, testing after each 5 cc. until the red becomes weak, then test more frequently until the red color of a test becomes quite faint. Then add 30 cc. of 1 : 1 sulfuric acid and shake the flask until the  $\text{MnO}_2$  all dissolves and finish the titration to the usual permanganate end point. This will require perhaps one cc. of permanganate.

#### NOTES ON THE PROCESS

Fairly close results may be obtained by titrating carefully in the alkaline solution until five drops of the solution give no red color with ferric chloride. But it is easier and more accurate to titrate only to an approximate end in the alkaline solution and finish in an acid solution. It is important that the precipitation be made as above directed with vigorous stirring and that the solution be digested on the hot plate after precipitation.

Under the conditions of titration the permanganate is reduced in the alkaline solution thus:  $2\text{KMnO}_4 = \text{K}_2\text{MnO}_4 + \text{MnO}_2 + 2\text{O}$ . The oxygen possibly oxidizes the sulfocyanate to tetrathionate, but of this the writer is not sure. He has proved by filtering off the  $\text{MnO}_2$  and weighing it and by titrating the manganate in the filtrate that the permanganate is reduced as above written. However, it makes no difference what reaction takes place in the oxidation of the sulfur in the alkaline solution, since the test for sulfocyanic acid is made on the plate in a strongly acid solution and the reaction between the sulfocyanate and the manganate and manganese dioxide completes itself there. The manganese dioxide does not settle out of the solution unless it stands a long time.

According to the titration reaction given in the second paragraph of this article 5 atoms of copper are equivalent to 6 molecules of  $\text{KMnO}_4$  or 30 atoms of iron. Therefore, the iron value of the permanganate multiplied by  $\text{Cu}/6\text{Fe}$  or 0.1897 gives the copper value of the permanganate. The permanganate used

<sup>1</sup> Grossman and Hölter, *Chem. Ztg.*, **33**, 348.

by the writer equals 0.01 gram Fe, or 0.001897 gram Cu per cc.

After the filtrate has cooled, a crystalline compound of tartaric acid may separate. Hence the solution should be filtered hot.

The following are some results obtained by the above method:

COPPER		COPPER	
Present	Found	Present	Found
0.1870	0.1890	0.0600	0.0596
0.1503	0.1511	0.0605	0.0603
0.1117	0.1125	0.1610	0.1630
0.1666	0.1668	0.0663	0.0667
0.0940	0.0930	0.1103	0.1109
0.2005	0.2017	0.1140	0.1147
0.2220	0.2224	0.1000	0.1001
0.2220	0.2210	0.1000	0.0999

The later results were the most accurate and were obtained after the necessity of digesting the precipitate in the hot solution was learned.

No elements interfere except, according to Low, silver. This is easily removed. If there is any lead present, the lead sulfate obtained after evaporating to fumes of  $\text{SO}_3$  should be filtered off after the soluble salts are dissolved.

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#### ELECTROLYTIC DETERMINATION OF COPPER IN ORES, CONTAINING ARSENIC, ANTIMONY OR BISMUTH

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Ores containing arsenic, antimony or bismuth have been best analyzed for copper by the iodide method, for the copper must be separated from these elements before it can be accurately determined electrolytically. To separate the copper from these interfering elements, by the old method of precipitating the sulfides, dissolving the arsenic and antimony sulfides in sodium sulfide and then the copper sulfide in potassium cyanide is tedious and troublesome. The following method greatly reduces the time required and gives very accurate results.

It has long been known that under the proper circumstances copper can be precipitated free from arsenic, antimony or bismuth as  $\text{CuCNS}$ . Guess's permanganate method is based upon this precipitation. However, owing to the solubility of the  $\text{CuCNS}$  as ordinarily precipitated, a considerable correction factor was necessary.

While working on the analysis of Babbitt metals high in antimony and tin, the writer observed that the copper was apparently entirely precipitated as  $\text{CuCNS}$  from a solution containing ammonium sulfate, ammonium tartrate and tartaric acid. When the method was applied to the analysis of impure ores, it proved successful. It is as follows:

One gram, or more if the sample is low in copper, is treated with 7 cc. of  $\text{HCl}$  and 7 cc. of  $\text{HNO}_3$ . The solution is heated until the ore is decomposed, then 5 cc. of sulfuric acid are added and the liquid evaporated to copious fumes of sulfuric acid. Now 30 cc. of water containing 3 grams of tartaric acid are added, and the

solution is heated until all soluble salts are dissolved; then it is cooled somewhat and ammonia is added until alkalinity is reached. Now  $\text{H}_2\text{SO}_4$  is added until the solution becomes acid, and then one cc. more. To the solution, which will now be hot, is added 2 grams of sodium sulfite, and the solution is stirred until it is all dissolved. Then 1 gram of  $\text{KCNS}$  dissolved in a few cc. of water is poured in. The copper precipitates immediately as  $\text{CuCNS}$ . The solution is stirred vigorously and heated to boiling; then the precipitate is allowed to settle for a few minutes. The precipitate is very dense. The solution is filtered through a dense filter and washed several times with a solution containing about 1 per cent. of  $\text{KCNS}$  and the same amount of tartaric acid.

Onto the filter paper, which should be held in a rather large funnel, is poured 18 cc. of 1 : 2 nitric acid and the funnel is immediately covered with a watch glass to prevent loss by spraying, due to the vigorous action of the nitric acid on the  $\text{CuCNS}$ . When the acid has run through, the filtrate is heated to boiling and poured through again; the paper, funnel and watch glass are washed well with water, care being taken to keep the volume of the filtrate as small as possible. The solution is now heated to vigorous boiling for five minutes to destroy the  $\text{HCNS}$ , water is added to make the volume about 125 cc., and the copper is precipitated by electrolysis, using a gauze cathode, a drop of potential of three volts and a current of three amperes. Precipitation should be complete in from thirty minutes to an hour. The copper should precipitate in a beautiful and crystalline condition. If it does not the solution was not boiled long enough.

If the ore contains lead, some will precipitate when the sodium sulfite is added, but this does no harm. The tartaric acid prevents the precipitation of antimonic acid.

The sulfocyanic acid must be completely destroyed before electrolysis or the copper will come down in a spongy and non-adherent form. Instead of dissolving the  $\text{CuCNS}$  in nitric acid, the precipitate and filter paper may be ignited in a porcelain crucible until all carbon is burned off and the  $\text{CuO}$  dissolved in 5 cc. of nitric acid, diluted and electrolyzed.

The following are some results obtained with the method:

Copper	GRAMS OF METALS PRESENT					GRAMS COPPER FOUND
	Arsenic	Antimony	Bismuth	Iron	Lead	
0.1000	0.07	0.07	0.100	0.100	0.100	0.0997
0.1000	0.07	0.07	0.100	0.100	0.100	0.0999
0.1000	0.07	0.07	0.100	0.100	0.100	0.0995
0.1000	0.07	0.07	0.100	0.100	0.100	0.1000
0.1500	0.07	0.07	0.100	0.100	0.100	0.1495
0.1500	0.07	0.07	0.100	0.100	0.100	0.1495
0.1500	0.07	0.07	0.100	0.100	0.100	0.1500
0.1500	0.07	0.07	0.100	0.100	0.100	0.1500
0.1500	0.07	0.07	0.100	0.100	0.100	0.1499

It is the writer's belief that this is the most accurate and usable electrolytic method for copper on ores containing arsenic, antimony or bismuth.

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