THE COPPER ASSAY BY THE IODIDE METHOD.

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FROM time to time the writer has seen statements reflecting on the accuracy of the iodide method for copper. The strictures are undoubtedly, in the main, perfectly just, according to the experience of their authors. When the writer first published his modification of the method, the preliminary experiments and the actual assaying of many ores seemed to justify all the statements then made. Continued use of the method, however, upon all kinds of material, eventually resulted in the discovery of slight inaccuracies under certain conditions not always recognized or understood at the time. Much attention has naturally been paid to the elimination of these troubles and apparently with success. As a result, the assay as now carried out in the writer's laboratory, while essentially the same as originally described, is nevertheless different in many of its details. It appears to leave but little to be desired on the score of accuracy and is perhaps of sufficient general interest to warrant publication.

DESCRIPTION OF THE METHOD.

Standardization of the Thiosulphate Solution.—Prepare a solution of sodium thiosulphate containing about 19 grams of the pure crystals to the liter. Standardize as follows: Weigh accurately about 0.200 gram of pure copper foil and place in a flask of about 250 cc. capacity. Dissolve by warming with 5 cc. of a mixture of equal volumes of strong nitric acid (sp. gr. 1.42) and water and then dilute to about 50 cc. Boil for a few moments to partially expel the red fumes and then add 5 cc. of strong bromine water and boil until the bromine is thoroughly expelled. The bromine is to ensure the complete destructon or removal of the red fumes. Remove from the heat and add a slight excess of strong ammonia water. Ordinarily it suffices to add 7 cc. of ammonia water of 0.90 sp. gr. Again boil until the excess of ammonia is expelled, as shown by a change of color of the liquid and a partial precipitation of the copper as hydroxide or oxide. Now add strong acetic acid in slight excess, perhaps 3 or 4 cc. of the 80 per cent. acid in all, and boil again for a moment if necessary to redissolve the copper. Cool to room temperature and add about 3 grams of potassium iodide, or 6 cc. of a solution of the salt containing 50 grams in 100 cc. Cuprous iodide will be precipitated and iodine liberated according to the reaction

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

The free iodine colors the mixture brown. Titrate at once with the thiosulphate solution until the brown tinge has become weak and then add sufficient starch liquor to produce a marked blue coloration. Continue the titration cautiously until the color due to free iodine has entirely vanished. The blue color changes towards the end to a faint lilac. If at this point the thiosulphate be added drop by drop and a little time be allowed for complete reaction after each addition, there is no difficulty in hitting the end-point within a single drop. 1 cc. of the thiosulphate solution will be found to correspond to about 0.005 gram of copper, or about 1 per cent. in the case of an ore where 0.5 gram has been taken for assay. The reaction between the thiosulphate and the iodine is

$$2(Na_2S_2O_3) + 2I = 2NaI + Na_2S_4O_6.$$

Sodium iodide and tetrathionate are formed. The starch liquor may be made by boiling about 0.5 gram of starch with a little water and diluting with hot water to about 250 cc. The liquor should be homogeneous and free from lumps or grains. It should be used cold and must be prepared frequently, as it does not keep well. The thiosulphate solution made from the pure crystals and distilled water appears to be quite stable, showing little or no variation in a month under reasonable conditions.

Treatment of Ores.—To 0.5 gram of the ore in a flask of 250 cc. capacity add about 6 cc. of strong nitric acid and boil gently nearly to dryness. Then add 5 cc. of strong hydrochloric acid and again heat. As soon as the incrusted matter has dissolved add 6 cc. of strong sulphuric acid (sp. gr. 1.84) and boil until the more volatile acids are expelled and the fumes of sulphuric acid are coming off freely. This is best done over a naked flame. Allow to cool, add 25 cc. of cold water and heat the mixture to boiling. Allow to stand, hot, until any anhydrous ferric sulphate is entirely dissolved and then filter to remove more especially any lead sulphate. Receive the filtrate in a beaker about 6 cm. in diameter. Wash the flask and filter with either hot or cold water and make the volume of the filtrate about 75 cc. Place in the beaker a piece of sheet-aluminum prepared as follows: Cut a strip of stout sheet-aluminum 2.5 cm. wide and about 14 cm. long and bend this into a triangle so it will stand upon its edge in the beaker. The same aluminum may be used repeatedly as it is but little attacked each time. Add one large drop of a mixture of equal volumes of strong hydrochloric acid and water, cover the beaker and heat to boiling. Allow to boil from seven to ten minutes, which should be sufficient to precipitate all the copper in any case, provided the bulk of the solution does not much exceed 75 cc. Avoid boiling to a very small bulk, as, in that case, some of the precipitated copper may redissolve. The aluminum should now appear clean, the precipitated copper being detached or only loosely adhering. Remove from the heat and wash down the cover and sides of the beaker with cold water. There is danger of the finely divided copper being slightly oxidized and dissolved during the subsequent washing. To prevent this, and at the same time to precipitate any traces of copper still remaining in solution, add about 15 cc. of strong hydrogen sulphide water. If the copper in the ore does not much exceed 20 per cent. proceed as follows: Decant the supernatant liquid through a 9 cm. filter. Add 10 cc. of strong hydrogen sulphide water to the residue in the beaker and then transfer the liquid and precipitate to the filter. Wash thoroughly with cold water, without delay, to avoid oxidation. Now place the clean original flask under the funnel. Pour over the aluminum in the beaker 5 cc. of a mixture of equal volumes of strong nitric acid (sp. gr. 1.42) and water. Any adhering particles of copper will be thus dissolved. Heat to boiling but do not prolong the latter or the aluminum will be unnecessarily attacked. Pour the hot acid very slowly over the precipitate on the filter so as to dissolve all the copper, lifting the fold if necessary. Now, without washing, pour 5 cc. of a cold, saturated, aqueous solution of bromine into the filter and then wash the beaker and filter with hot water. Finally remove the filter and open it. If there remains a residue that might possibly contain copper it may be rinsed into the flask. The bromine has several functions. It cleanses the separated sulphur left on the filter, it ensures the highest state of oxidation of any arsenic or antimony present, and it also effects the complete destruction or removal of the red fumes, which is a matter of great importance. If 5 cc. of bromine water are insufficient to impart a permanent tinge to the filtrate, more must be added. Boil the filtrate, which usually does not exceed 75 cc. in bulk, to thoroughly expel the excess of bromine, but avoid boiling to such a small bulk as to cause decomposition of bromides, etc. Remove from the heat and add ammonia water in slight excess (ordinarily 7 cc. of strong ammonia). Boil off the excess of ammonia, as shown by the change of color of the solution, and then acidify with acetic acid, again boiling if necessary to redissolve any precipitate containing copper. The addition of 3 or 4 cc. of the 80 per cent. acid is usually sufficient. A large excess of acetic acid does no harm but is not necessary except in the presence of sufficient arsenic to cause a precipitate of copper arsenate. This may require considerable acetic acid for its solution, perhaps 10 cc. If not mostly dissolved at this stage, it is taken up slowly later on and the titration may become very tedious before the true end-point is finally reached. Proceed with the acetic acid solution, after cooling to room temperature, precisely as described in the standardization of the thiosulphate and calculate the percentage of copper from the amount of the latter required.

In titrating low percentages of copper great care should be taken not to pass the end-point. Always work slowly towards the end and stop short of complete decolorization and then continue only when the liquid, after standing a minute or two, still persists in a tinge of color.

With high percentages it is usually advisable to wash the precipitated copper by decantation instead of on the filter. Proceed as follows: Transfer the liquid and copper in the beaker (to which hydrogen sulphide solution has been added) to the original flask and set the beaker and aluminum aside temporarily. Allow to settle, decant through the filter and wash the copper three or four times by decantation, the first time with hydrogen sulphide water and then with cold water, using about 20 cc. each time. Now place the flask and residue under the funnel, heat the 5 cc. of acid in the beaker as before and pour it through the filter. Do not add the bromine for the moment but remove the flask, replacing it under the funnel with the beaker, and heat the acid until all the copper is dissolved and the red fumes are mostly expelled. Now return the flask under the funnel, add the bromine, proceed with the washing of the beaker and filter, and continue as described above.

Owing to the fact that the end-pont is somewhat sharper as the amount of copper present is less, the operator may perhaps find it advantageous in the case of very rich material to take only 0.25 gram instead of 0.5 gram for assay. As there seems to be no difficulty in doing accurate work by either plan, this is perhaps best left a matter of choice.

Notes.—According to the equation previously given, 0.5 gram of copper requires 2.62 grams potassium iodide. While direct experiment shows this to be apparently true, yet when only the theoretical amount of potassium iodide is present the reaction is slow and in fact does not appear to proceed to completion until during the titration, which is thereby unduly prolonged. It is best, therefore, to always use an excess, but as the iodide is expensive the quantity used should be governed by the amount of copper present, which can always be estimated approximately. Allow say 1 gram potassium iodide for every 15 per cent. copper, when 0.5 gram of ore is taken for assay. It is convenient to prepare a solution containing 50 grams of potassium iodide in 100 cc. A 2 cc. pipette will thus deliver 1 gram of the salt. No error will be introduced in a doubtful case by adding more potassium iodide after the titration is apparently finished and resuming the operation if the blue color is thereby restored.

Zinc and silver do not interfere with the assay. Lead and bismuth are without effect, except that by forming colored iodides they may mask the approach of the end-point before adding starch. Arsenic and antimony, when fully oxidized as described, have no influence. The return of the blue tinge in the titrated liquid after long standing is of no significance, but a quick return, which an additional drop or two of the thiosulphate does not permanently destroy, is usually an evidence of faulty work.

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