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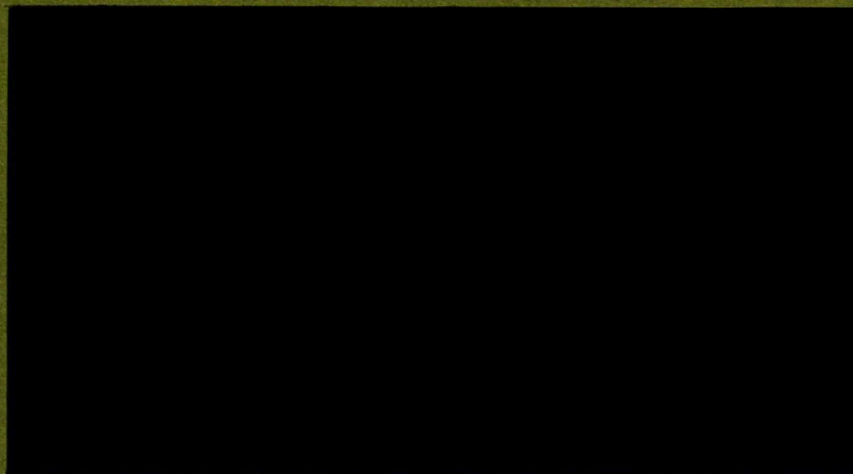
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CANADA

DEPARTMENT OF ENERGY, MINES AND RESOURCES

OTTAWA



Mines Branch

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AN EVALUATION OF CERTAIN MODIFICATIONS OF THE
VOLUMETRIC (IODOMETRIC) METHOD FOR THE
DETERMINATION OF COPPER IN COPPER CONCENTRATES

by

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INTRODUCTION

At the request of Placer Development Limited, Vancouver, British Columbia, the Mines Branch agreed to evaluate certain procedures for the volumetric (iodometric) determination of copper in copper concentrates. This request arose because certain analytical laboratories associated with the Canadian producers of the concentrates frequently obtain significantly higher copper values than those associated with the Japanese purchasers (Nippon Mining Company), and because the two groups of laboratories have not been able to establish, or come to a satisfactory agreement on, the source of the discrepancy in the methods (results) between themselves.

Accordingly, Mr. J.A. Ganshorn, transportation manager of Placer Development Limited, made available to the author copies of six methods used by various laboratories associated with the parties in dispute. All of these methods are essentially variations of the well-known "long" and "short" iodide methods for the volumetric determination of macroscopic amounts of copper. Although the amount of procedural detail given in the written accounts of these methods varied considerably, sufficient information was available so that five of the six methods could be adequately evaluated.

This report describes how these methods were evaluated by applying them, under essentially similar conditions, to the analysis of a United States National Bureau of Standards certified chalcopyrite concentrate (SRM 332) containing 28.45% of copper. This work shows that, under certain conditions, the method used by the Nippon Mining Company may yield lower and less precise results than the other methods. Experimental evidence that explains this difference is presented.

GENERAL

Identification of methods to be evaluated

As indicated previously, five of the six methods submitted to the author contained information sufficiently detailed for experimental evaluation of the methods. These methods and their source are identified as follows:

Short iodide methods:

- Method I - Daniel C. Griffith (Canada) Ltd.,
Vancouver, B. C.
- Method II - Warnock Hersey International Ltd.
- Method III - Marcopper Mining Corporation, Tapan,
Santa Cruz, Marinduque.

Long iodide methods:

- Method IV - Nippon Kogyo Mining Company.
- Method V - Marcopper Mining Corporation.

In the Experimental section to follow, it is indicated when a procedure deviated significantly from that given in the account submitted.

National Bureau of Standards copper concentrate SRM 332

This material was chosen for use in the evaluation tests because of its accurately known copper content (28.45%) and because it is mineralogically similar to the chalcopyrite concentrates to which the above-listed methods are normally applied.

A microscopical and electron-probe examination of SRM 332 showed that it is essentially 95% chalcopyrite, by volume, and that it contains minor amounts of pyrite, potassium-feldspar and quartz, and trace amounts of digenite, bornite, covellite, sphalerite, rutile and molybdenite.

In all the evaluation tests to be described, three 0.5-g samples of SRM 332 were used.

Standard copper solution

This was prepared by dissolving 2 - 5 g of British Chemical Standards No. 197 d copper (purity 99.90%) in nitric and sulphuric acids and evaporating the solution to fumes of sulphur trioxide to remove nitric acid. The solution was subsequently diluted with water so that 1 ml contained 10 mg of copper.

Standardization of sodium thiosulphate solution and minor modifications in the titration procedures

Before each series of evaluation tests, the sodium thiosulphate solution (0.1 N) was standardized against aliquots (containing 200 mg of copper) of the standard copper solution, under the identical conditions employed for the titration of the sample solutions. In all cases, except Method I, aliquots of the standard copper solution were evaporated to dryness to remove excess sulphuric acid prior to the standardization of the thiosulphate solution.

In standardizing the sodium thiosulphate solution, as well as in the titration of the sample solutions, the maximum recommended amounts of potassium iodide, alkali thiocyanate, and ammonium bifluoride (if specified) were added as solutions (50%, 40% and 40% w/v, respectively) rather than as

solid reagents. Furthermore, in Methods I, II, and IV, 5 ml of freshly prepared 5% iodine indicator in 5% potassium iodide solution were used as indicator rather than starch solution. These changes were made for consistency and convenience and because the concentration of starch solution was not specified in some of the methods.

EXPERIMENTAL EVALUATION OF METHODS

Short iodide methods

Methods I, II, and III were evaluated in two series of tests, each involving three replicate determinations (Table 1). In the first series, the samples were decomposed and analyzed as described in the submitted accounts of the methods, except for the minor changes described below. In the second series, the acid-insoluble residue remaining after sample decomposition was removed by filtration and the paper and residue were treated with 10 ml each of concentrated nitric, perchloric and hydrochloric acids. The subsequent solution was evaporated to dryness, the resultant residue was boiled with dilute hydrochloric acid, the solution was filtered to remove insoluble material, and copper was finally determined by atomic-absorption spectrophotometry.

Description of minor modifications

Method I - The sample solution was not boiled to eliminate the small excess of ammonium hydroxide present after the neutralization step, and 8 ml of concentrated acetic acid, rather than the specified 7 - 10 ml, were added after neutralization.

Method II - Because the amount of fluoride used to complex iron was not specified in the account of the method, 5 ml of 40% ammonium bifluoride solution were arbitrarily employed for this purpose.

Method III - Because the concentration of potassium biphthalate solution was not specified in this method, a 10% solution was used for acidification of the sample solution after the neutralization step. Sodium thiocyanate solution (2.5 ml of 40% solution), which was not specified in the method, was added near the end of the titration to sharpen the end-point.

Long iodide methods

In the evaluation tests of Methods IV and V (Table 2), either the filtrates remaining after the separation of copper as the sulphide and/or the acid-insoluble residues remaining after sample decomposition (after treatment as described under Short iodide methods) were analyzed for copper by atomic-absorption spectrophotometry. In all the tests, 2.5 ml of 40% sodium thiocyanate solution, which was not specified in the methods, was added before the end of the titration to sharpen the end-point.

Method IV - Procedural details regarding the volume of the initial filtrate in which copper is precipitated as the sulphide, the time required for digestion of the precipitate, and the dissolution of the sulphide precipitate are not given in, or readily apparent from, the submitted flow-diagram of the method or accompanying notes. Consequently, copper was determined by the procedures described in tests A to E below which, except for test E, were considered to include the actual conditions employed by the users of the method. In all these tests, the initial filtrate was evaporated to 60 - 70 ml so that the sulphuric acid concentration of the solution, after the addition of 50 ml of hydrogen sulphide-saturated water, would be approximately 0.2 M during the precipitation of copper sulphide. Because the standard copper concentrate used for evaluation purposes contains an appreciable amount of iron, and molybdenum (which is not separated from copper during the hydrogen sulphide precipitation step), the volume of 25% ammonium fluoride solution, recommended in the notes of the method, was added before each titration step.

Test A - The samples were decomposed solely with mixed acid (approximately 24.5 and 2.5% nitric and sulphuric acids by volume, respectively). The subsequent copper sulphide precipitates were allowed to digest for varying periods of time (Table 2) and, after filtration and washing, the bulk of each precipitate was transferred, with a jet of water, to the beaker that initially contained the precipitate. The small amount of each precipitate remaining on the filter paper was dissolved with a mixture of 25 ml of bromine-saturated water and 20 ml of mixed acid, and the paper was washed three times with hot water and discarded. The bulk of the precipitates in the beakers did not dissolve even after the addition of more mixed acid and repeated additions of bromine-saturated water. Decomposition of the precipitates was finally achieved by evaporating the solutions to approximately 50 ml, adding 10 ml of concentrated nitric acid and 5 ml of concentrated perchloric acid, and washing down the sides of the beakers with bromine-saturated water during repeated evaporations of the solutions to fumes of perchloric acid and finally to dryness prior to the determination of copper.

Test B - The samples were decomposed with mixed acid and 20 ml of 50% hydrochloric acid as described in the notes accompanying the method. The copper sulphide precipitates were allowed to digest for varying periods of time (Table 2) before being filtered and decomposed as described in Test A.

Test C - The samples were decomposed as described in Test A and the precipitates were allowed to digest for 5 minutes before filtration. An attempt was made to dissolve the precipitates directly with bromine-saturated water, as implied in the flow-diagram of the method. However, a considerable

portion remained undissolved even after the addition of approximately 400 ml of bromine-saturated water. The filter papers and remaining precipitates were finally transferred to beakers and decomposed with 10 ml each of concentrated nitric and perchloric acids as described in Method V. After evaporation of the resultant solutions to fumes of perchloric acid, they were added to the corresponding initial solutions and the combined solutions were evaporated to dryness prior to the determination of copper.

Test D - The samples were decomposed as described in Test B. The precipitates were allowed to digest for 15 minutes before filtration and the papers and precipitates were decomposed with concentrated nitric and perchloric acids as described in Test C. The resulting solutions were evaporated to dryness before the determination of copper.

Test E - The samples were decomposed and the precipitates were treated as described in Test D. Copper was ultimately determined using the titration procedure described in Method I.

Method V - The samples were decomposed and treated as described in the submitted account of the method. Because procedural details regarding the volume of the initial filtrate in which copper is precipitated as the sulphide with sodium thiosulphate, and the amount of potassium iodide required for titration are not given in the method, copper was precipitated in approximately 175 ml of the filtrate, and 10 ml of 50% potassium iodide solution were added before each titration.

RESULTS AND DISCUSSION

The results obtained for the National Bureau of Standards copper concentrate by the different modifications of the volumetric short and long iodide methods for copper are shown in Tables 1 and 2, respectively. With the exception of Method IV, no difficulties were encountered in applying any of the methods to the analysis of the standard copper concentrate.

Tables 1 and 2 show that, except in the cases of Methods II and IV, the copper results are in good agreement with the certified value for the concentrate. Method II yielded average results for copper that are approximately 0.1% lower than the certified value. The subsequent test of this method, in which the acid-insoluble residue was removed by filtration and re-treated with nitric, perchloric and hydrochloric acids, showed that only a small amount (0.01 - 0.02%) of copper is retained in the residue. Consequently, this is not a source of significant error in this method. Tests showed that the pH of the sample solution before the addition of potassium iodide is approximately the same (i. e., 4.4) as that obtained in Method I. Furthermore, the titration procedure is similar, except that the concentrations of potassium iodide and acetic acid are lower and higher, respectively, in the solution to be titrated. However, it was noted that the end-point obtained in Method II is not as sharp as that obtained in Method I, and the blue starch-iodine colour returns relatively quickly after the end-point. This could be caused by excess acetate ion which is known to interfere by decreasing the rate of the reaction between copper (II) and potassium iodide.¹ It is suggested that the method could probably be improved in this regard by using less acetic acid and more potassium iodide.

TABLE I

Determination of Copper in N. B. S. Copper Concentrate[†]
by the Short Iodide Methods

Method	Nature of test procedure	Cu found, %			Total % Cu	Average % Cu
		According to method	In filtrate	In residue		
I	According to submitted procedure	28.40	--	--	--	28.40
		28.33	--	--	--	
		28.47	--	--	--	
	Residue filtered off and re-treated with acids	--	28.43	0.041	28.47	28.48
		--	28.45	0.015	28.47	
		--	28.43	0.081	28.51	
II	According to submitted procedure	28.35	--	--	--	28.35
		28.35	--	--	--	
		28.34	--	--	--	
	Residue filtered off and re-treated with acids	--	28.32	0.010	28.33	28.33
		--	28.32	0.015	28.34	
		--	28.31	0.015	28.33	
III	According to submitted procedure	28.42	--	--	--	28.41
		28.38	--	--	--	
		28.43	--	--	--	
	Residue filtered off and re-treated with acids	--	28.46	0.016	28.48	28.40
		--	28.41	0.018	28.43	
		--	28.28	0.018	28.30	

[†] Certified value for copper - 28.45%; uncertainty figure - 0.08%.

TABLE 2

Determination of Copper in N. B. S. Copper Concentrate^{*}
by the Long Iodide Methods

Method	Digestion period before filtration of precipitate (minutes)	Cu found, %				Average total % Cu
		In precipitate	In residue	In filtrate	Total	
IV <u>Test A</u> - Decomposition with mixed acid. Copper sulphide precipitate washed into beaker and finally decomposed with nitric and perchloric acids.	0	27.94	--	0.002	--	--
	15	28.18	--	0.002	--	--
	30	28.00	--	0.002	--	--
<u>Test B</u> - Decomposition with mixed acid + hydrochloric acid. Precipitate treated as in Test A.	0	28.15	--	0.003	--	--
	15	28.05	--	0.003	--	--
	30	28.23	--	0.002	--	--
<u>Test C</u> - Decomposition as in Test A. Precipitate partly dissolved in bromine-saturated water. Paper and remainder of precipitate decomposed with nitric and perchloric acids.	5	28.26	0.005	0.083	28.35	28.34
	5	28.35	0.007	0.003	28.36	
	5	28.29	0.008	0.004	28.30	
<u>Test D</u> - Decomposition as in Test B. Paper and precipitate decomposed with nitric and perchloric acids.	15	28.25	0.021	0.003	28.27	28.30
	15	†	0.032	2.15	--	
	15	28.29	0.027	0.003	28.32	
<u>Test E</u> - Decomposition as in Test B. Paper and precipitate decomposed as in Test D. Titrated as in Method I.	15	28.41	0.043	0.002	28.46	28.46
	15	28.45	0.031	0.002	28.48	
	15	28.41	0.037	0.002	28.45	
V	--	28.41	0.031	--	28.44	28.44
	--	28.39	0.059	--	28.45	
	--	28.37	0.045	--	28.42	

*Certified value for copper - 28.45%; uncertainty figure - 0.08%.

† Sample solution titrated past end-point.

Tables 1 and 2 also show that, in Methods I, III, IV and V, some copper is retained in the acid-insoluble material remaining after sample decomposition. In all cases, except for Methods II and III, in which the samples are decomposed directly (i. e., in the absence of water) with concentrated nitric acid and bromine and with concentrated nitric acid and potassium chlorate, respectively, it was noted that the oxidation of elemental sulphur formed during digestion was slow and incomplete. After evaporation to dryness or to fumes of sulphur trioxide, depending on the method, a varying amount of black material was found in the solutions. A microprobe analysis of this material showed that it was essentially elemental sulphur coated with metallic-like flakes of a molybdenum-sulphur compound and small amounts of a copper-iron-sulphur compound. Correspondingly, Tables 1 and 2 show that, except for Test C (Table 2), the amount of copper found in the acid-insoluble residues in which this material was present (i. e., Methods I, IV, and V) is significantly greater than that found in the residues remaining after sample decomposition as described in Methods II and III. Consequently, more accurate results would probably be obtained by these methods if the insoluble material is included in the analysis. This can be accomplished by igniting the residue and fusing it with potassium pyrosulphate, followed by dissolution of the melt in water or dilute acid, filtration, and addition of the resultant solution to the initial filtrate.

Table 2 shows that low and erratic results were obtained in Tests A to D of Method IV in which the samples were decomposed with mixed acid only or in conjunction with hydrochloric acid, and in which the copper sulphide precipitates were dissolved by various methods. Despite the inference made in the flow-diagram of the method, it was found that the precipitate is not readily soluble in bromine-saturated water; tests showed that an impractically large volume (>400 ml) was required for the dissolution. Subsequent work showed that the precipitate and filter paper can be readily decomposed by treatment with concentrated nitric and perchloric acids as described in Method V. The results obtained in Tests A, B and E show

that no appreciable loss of copper to the filtrate occurs on washing the copper sulphide precipitate with warm water. However, tests C and D show that the precipitation of copper sulphide with hydrogen sulphide-saturated water is not always complete even after a 15-minute digestion period. Because tests C and D show that the low results obtained were not due primarily to copper retained in the acid-insoluble material, and also because erratic results were often obtained during the preceding standardization of the sodium thiosulphate solution, it was considered that the major source of error in the method must be in the final titration procedure. This supposition was confirmed by the results obtained in two series of tests in which duplicate 150-mg portions of copper (i.e., 15-ml aliquots of standard copper solution) were precipitated as the sulphide with hydrogen sulphide-saturated water and the paper and precipitates were decomposed with concentrated nitric and perchloric acids. The first series of solutions, which were titrated by the procedure described in Method IV in the presence of ammonium fluoride, yielded erratic results for both the test solutions and the pure copper solutions employed for standardization of the sodium thiosulphate solution. The second series, which was titrated by the procedure described in Method I, yielded satisfactory results (i.e., 150.0 and 149.8 mg of copper). Satisfactory results were subsequently obtained for the copper concentrate (Test E, Table 2), after separation of copper by the procedure described in Method IV, when the titration procedure described in Method I was employed for the final determination of copper.

Table 3 shows the results obtained (arranged in order of increasing pH) by titrating identical aliquots (containing 150 mg of copper) of a standard copper solution by the procedure described in Method IV, both in the absence and presence of ammonium fluoride, and by the procedure described in Method I. It is apparent that relatively precise and reproducible results are obtained by Method I, and by Method IV in the absence of ammonium fluoride. However, the results obtained by the latter method in the presence of ammonium fluoride decrease as the pH of the solution increases. An analysis

TABLE 3

Titration of Standard Copper Solutions by the Procedures
Described in Methods I and IV

Titration procedure	pH before addition of potassium iodide	Volume of 0.1N sodium thio- sulphate solution (ml)	Average volume (ml)	Standard deviation
Method IV in the absence of ammonium fluoride	4.04	23.24	23.29	0.051
	4.31	23.26		
	4.55	23.25		
	4.60	23.36		
	4.79	23.34		
	4.84	23.27		
Method IV in the presence of ammonium fluoride	5.06	23.30	23.20	0.091
	5.14	23.30		
	5.15	23.21		
	5.15	23.18		
	5.19	23.14		
	5.22	23.07		
Method I	4.52	23.29	23.31	0.043
	4.55	23.37		
	4.55	23.36		
	4.56	23.30		
	4.57	23.26		
	4.58	23.30		

Copper taken, 150 mg.

of variance showed that, in the presence of ammonium fluoride, the titration procedure described in Method IV yields results that are significantly (at the 90% confidence level) lower than those obtained in its absence. Moreover, the standard deviation in the presence of ammonium fluoride is essentially twice as large as that obtained in its absence. During these titration tests, it was noted that the end-points obtained by Method IV in the presence of ammonium fluoride were not as sharp as those obtained in its absence or by Method I, and that the blue starch-iodine colour returned relatively quickly after the end-point of the titration. The indistinct end-points and the variation of the results with the pH of the solution are presumably caused by the slow rate of reaction between copper (II) and iodide ion in weakly acid solutions in the neighborhood of pH 5.^{1,2}

From the results shown in Table 3, it is apparent that Method IV should yield satisfactory results for copper — provided that it is completely precipitated as the sulphide, that iron is not occluded or adsorbed by the precipitate, and that molybdenum is absent — when ammonium fluoride is not present during the final titration of the sample solution or during the standardization of the sodium thiosulphate solution. As shown in Table 2 (Tests A to D), erratic and generally low results will be obtained when ammonium fluoride is present during both the final titration and standardization procedures. Similarly, low and probably erratic results will be obtained when ammonium fluoride is present during the titration of the sample solution but not during the standardization procedure.

Methods III and V can be improved by adding sodium or potassium thiocyanate near the end of the titration to sharpen the end-point.^{2,3} Method IV can be improved by: (a) ensuring that the volume, and subsequently the acid concentration of the initial filtrate, is consistent with that required (i. e. , 0.1 - 0.25 M) for the complete precipitation of copper as the sulphide; (b) bubbling hydrogen sulphide gas through the solution to precipitate copper as the sulphide; (c) decomposing the filter paper and copper sulphide precipitate with concentrated nitric and perchloric acids; (d) determining copper

by a titration procedure similar to that described in Method I; and (e) using sodium or potassium thiocyanate to sharpen the end-point.

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