

Rapid determination of copper in copper ores

T. H. RAO, B. V. RAO and S. L. N. ACHARYULU

LOW grade copper ores and copper ores in association with considerable quantities of other elements such as iron, lead, zinc and vanadium, require a separational step wherein copper is generally separated as sulphide either with sodium thio-sulfate¹ or with thioacetamide.² In these methods, the precipitated copper sulfide is ignited to cupric oxide, dissolved in dilute nitric acid and titrated iodometrically. In a recent method³ wet oxidation of precipitated copper sulfide is effected with nitric acid and titrated with disodium ethylene diamine tetra-acetate (EDTA). The authors' work on the beneficiation of low grade copper ores and extraction of copper from these ores has necessitated developing a rapid and accurate method for the determination of copper. A separational step wherein cupric ion could be precipitated as cuprous oxide has been introduced to avoid ignition of copper sulfide to cupric oxide, which is time consuming.

This paper presents a method for the rapid and accurate determination of copper ores and concentrates. Copper is separated as cuprous oxide with ascorbic acid in dilute acetic acid medium. The precipitated cuprous oxide is dissolved in dilute nitric acid and titrated iodometrically or alternatively with EDTA using murexide or pyrocatechol violet as indicator. This method is quite rapid and accurate and yields results which are comparable with those obtained by electro-gravimetric method.⁴

Reagents

0.05 N sodium thiosulfate solution was prepared by dissolving 12.5 grams of sodium thiosulfate (A.R., B.D.H.) in 1000 ml distilled water and standardised with standard potassium dichromate solution.⁵

0.05 M EDTA solution was prepared by dissolving 18.613 gm reagent grade disodium ethylenediamine tetra-acetate dihydrate in 1000 ml distilled water and standardised against nearly neutralised zinc chloride solution prepared from a known weight A.R. zinc pellets.⁶

SYNOPSIS

A rapid and accurate method for the estimation of copper in high and low grade copper ores and concentrates is described. After the decomposition in the usual manner with acids, copper is separated by precipitation as cuprous oxide with ascorbic acid in dilute acetic acid medium. The cuprous oxide is dissolved in nitric acid and titrated iodometrically or alternatively with EDTA using either pyrocatechol violet or murexide as indicator. The results are comparable to those obtained by electrogravimetric method.

Standard copper solution

2 gm electrolytic copper was dissolved in 10 ml concentrated nitric acid and the solution was heated till oxides of nitrogen ceased to evolve. The solution was cooled and transferred to 1000 ml volumetric flask, diluted to mark with distilled water.

Ascorbic acid (Merck) was employed as a reagent for cuprous oxide precipitation.

Determination of copper

A known volume (containing 25–100 mg.) of copper solution was transferred to a 250 ml beaker, rendered ammoniacal with 1 : 4 ammonia and acidified with 1 : 4 acetic acid. Ascorbic acid (1 gm) was added and the solution was boiled. The precipitated cuprous oxide was filtered through filter pulp and washed with hot water. Cuprous oxide was dissolved in warm 1 : 1 nitric acid and washed with 2% nitric acid. The solution and the washings were collected in a conical flask. Urea (2 gm) was added and the solution was boiled. After cooling the solution, ammonia was added to remove free mineral acid. The solution was acidified with acetic acid and cooled to room temperature. 1 gm potassium iodide was added. The liberated iodine was titrated with standard sodium thiosulfate solution using 1% starch solution as indicator.

Alternatively, the solution and the washings were diluted to 100 ml ; 2 to 3 drops of aqueous solution of murexide followed by small volumes of ammonium chloride—ammonia buffer (pH 10) to give yellowish green color were added. This solution was titrated with 0.05 M EDTA to a violet-blue end point.

Messrs T. H. Rao, B. V. Rao, S. L. N. Acharyulu, Defence Metallurgical Research Laboratory, Hyderabad.

TABLE I Amount of copper in mg

Taken	Found (by thiosulfate)	% Error	Found (by EDTA)	% Error
25.0	24.85	0.60	24.87	0.52
50.0	49.77	0.46	49.82	0.36
75.0	74.73	0.36	74.75	0.33
100.0	99.54	0.46	99.75	0.25

Alternatively, the solution and the washings were diluted to 100 ml ; 0.5 gm ammonium nitrate, 4-5 drops of 0.1 per cent aqueous solution of pyrocatechol violet indicator were added. The acidity of the solution was adjusted with 0.5 M ammonia until the blue color of the copper pyrocatechol violet complex just appears. 2 gm sodium acetate was added and the solution was titrated against 0.05 M EDTA solution to a sharp yellowish-green end point.

Determination of copper in ores and concentrates

2 gm copper ore or 0.5 gm concentrate was weighed into a 500 ml conical beaker. 20 ml of mixed concentrated hydro-chloric, sulfuric and nitric acids (1:1:1) was added and gently heated until the digestion was complete. 5 ml of concentrated sulfuric acid was added and the heating was continued till sulfur trioxide fumes were evolved. The contents were cooled to room temperature. 100-150 ml water was added and the solution was gently heated till all the salts formed were dissolved. The solution was filtered and the residue was washed with 5% sulfuric acid and subsequently with hot water. The filtrate and the washings were collected into a 400 ml beaker. Citric acid or tartaric acid (5 gm) was added to complex Fe (III) and neutralised with ammonia. The solution was rendered slightly acidic with 1 : 4 acetic acid and heated gently. 2 gm ascorbic acid was added and the solution was then boiled. The cuprous oxide thus precipitated was filtered through filter pulp and washed with 2% acetic acid and hot water. The washed precipitate was dissolved in minimum quantity of warm 1 : 1 nitric acid and washing was effected with hot 2% nitric acid. The solution was allowed to cool and was made up to 250 ml in a standard volumetric flask. Aliquots of the copper solution were taken and the copper was determined iodometrically. Alternatively, copper solution was titrated with 0.05 M EDTA using pyrocatechol violet or murexide as indicator.

TABLE II Determination of copper in ores and concentrates

	Per cent copper found		
	by THIO	by EDTA	by electro-gravimetry
*Ore concentrate	23.71	23.83	23.87
†Ore sample A	4.69	4.62	4.64
B	4.19	4.16	4.12
C	1.07	1.10	1.12

*Mysore ore.

†A, B and C are the hand picked ore samples obtained from Khetri, Kalihan and Agnigundala.

Results

Typical results for the determination of copper in pure copper solutions by the above mentioned procedure are given in Table I. The results are reproducible and accurate to within about 0.5 per cent. Various ore samples from Khetri, Kalihan and Agnigundala mines (hand picked and sampled) and ore concentrate from Mysore ore were analysed for copper and the results are presented in Table II. An aliquot of sample solution before the precipitation of cuprous oxide was taken and the percentage of copper was determined by electro-gravimetric method. In Table II results obtained with the proposed method are compared with values obtained by electro-gravimetric method.

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Discussions

Mr M. Totlani (Bhabha Atomic Research Centre, Bombay) : Can this method be used in the case of concentrates, which in addition to Cu, also contain Ni, Co, Mo and Fe?

Mr S. L. N. Acharyulu (Author) : The method proposed can be applied for the determination of copper in the case of concentrates containing nickel, cobalt, molybdenum and iron, because :

- (a) ascorbic acid has no reducing action on nickel (ii) and cobalt (ii)
- (b) ascorbic acid reduces molybdenum (vi) to molybdenum (v) only, and
- (c) iron (iii) complexed with citrate does not interfere.

Dr Sharma (Khetri Copper Project) : I would request the author to explain the advantages of his method over the short iodide process. In our works we are analysing about 100 samples by three analyses with two attendants for every eight-hour shift. In the method described by the author what would be the time and number of men required for analysing 100 samples per eight-hour shift?

Mr S. L. N. Acharyulu (Author): As the short iodide process does not involve a separational step, it is rapid but does not yield accurate results. The proposed method is more advantageous when accurate analysis is required. These two methods cannot, therefore, be compared in terms of time requirements.