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A RAPID AND MERCURY POLLUTION-FREE REDOXIMETRY DETERMINATION OF TOTAL IRON IN COPPER ORE*

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Summary—A rapid and mercury pollution-free method for the determination of total iron in the presence of copper is described. The sample was decomposed either by an acid attack of hydrochloric acid–nitric acid (1 + 2) or by fusion with sodium peroxide. The ferric ion in the sample solution was amenable to direct reduction to ferrous ion with potassium borohydride in sulphuric acid medium under the catalysis of cupric ion, followed by titration with potassium dichromate using sodium diphenylaminesulfonate as an indicator. After reduction, the iron (II) in the solution was stable for 300 min. The proposed method is free of interference from copper and has been successfully used for the large-scale routine determination of total iron in copper ores showing the same or better degree of precision and accuracy as those obtained by the classic standard stannous chloride–mercuric chloride method with the separation of iron from copper.

The copper sulphide ores (chalcopyrite, chalcocite, *etc.*) usually contain a considerable amount of iron, which is required to be accurately measured for copper ore smelting. In the analysis of such ores, the classic standard method for the determination of total iron[1,2] involves the separation of iron from copper with precipitation using excess of aqueous ammonia, the reduction of iron (III) to iron (II) with stannous chloride, the excess of which is removed by mercuric chloride, followed by titration of ferrous ion with standard dichromate solution with sodium diphenylaminesulfonate as indicator. It is obvious that this standard method is time-consuming and the mercuric salt used is a health hazardous chemical leading to environmental pollution. This conventional standard method is increasingly rejected in many countries for environmental reasons, which has led many analysts to search for mercury pollution-free methods.[3-12] However, most of these published methods were complicated, tedious and also time-consuming and only applied to iron ores containing no copper. That is to say, these methods do not tolerate the presence of copper. Sastri[13] developed a titrimetric method for the determination of iron in the presence of copper, but it used mercuric perchlorate.

A mercury pollution-free method for the determination of iron in copper ores using non-aqueous stannous chloride solution as titrant was reported,[14] but it required not only non-aqueous conditions but also the separation of iron from copper using ammonium chloride–aqueous ammonia. Ko *et al.*[15] described a mercury pollution-free method for the determination of iron in the presence of copper, which involved the reduction of iron (III) with stannous chloride-titanous chloride, the removal of the excess of titanous ion by oxidization with dissolved oxygen and the titration of ferrous ion with cerium sulfate. However, it is difficult to apply these two methods[14,15] to the routine analysis of copper ores. In addition, among the published methods, the titration should be immediately carried out within a few minutes after iron (III) was reduced and the excess of reductant removed, which makes the methods less attractive for large-scale routine determinations. Therefore, the aim of this work is to develop a mercury pollution-free method in the presence of copper for the routine determination of iron. Since borohydride has been widely used in the field of analytical chemistry and was found to reduce iron (III) to iron (II) in acidic medium, a detailed study was undertaken for the determi-

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nation of iron in the presence of copper with potassium borohydride as the reducing agent. The proposed method replaced the conventional stannous chloride–mercuric chloride method in the Laboratory of Chemical Analysis of Guixi Smeltry (Jiangxi, China) and has been successfully carried out for five years.

EXPERIMENTAL

Reagents

*Ferric sulfate solution (*10 *mg/ml).* A 2.5000 g sample of high-purity iron was dissolved in dilute sulfuric acid with hydrogen peroxide as the oxidizing agent and made up to 250 ml in 0.25M sulfuric acid medium in a standard flask.

Potassium dichromate solution. A 4.9747 g amount of potassium dichromate (guaranteed-reagent grade) was dried at 150°C in 300 ml of water, transferred to a 1000-ml standard flask, diluted to volume and mixed; 1 ml of the standard solution corresponds to 5.666 mg of iron.

Potassium borohydride solution (2%, w/v). Potassium borohydride (2 g was dissolved) in 100 ml of water with the addition of a small amount of sodium hydroxide. It was prepared fresh as needed.

Cupric sulfate solution (5%, w/v).

Sulfuric acid–phosphoric acid mixture. Concentrated sulfuric acid (150 ml) was slowly poured into 700 ml of water, with stirring, and 150 ml of concentrated phosphoric acid added with stirring. It was cooled and diluted to 1 l. with water.

Preparation of sample solution

(a) *Acid decomposition.* A 0.2–0.3 g dried 100 mesh sample (weighed to 0.1 mg) was transferred to a 250–ml beaker, to which 5 ml of concentrated hydrochloric acid was added, and then heated on a hot-plate to boil for 2 min. It was cooled slightly and 10 ml concentrated nitric acid added and heated. If sulphur appeared, 0.5–1 ml of bromine was added to decompose it. When all the sample has completely dissolved, it was evaporated gently to about 5 ml solution, 5 ml of sulfuric acid (1 + 1) was added and heated and evaporated to sulfur oxide fumes for 5 min so as to remove hydrochloric acid. It was removed from the heat source, cooled and the cover and walls of the beaker rinsed. The resulting salts were dissolved in water and made up to 50 ml in *ca.* 0.25M sulfuric acid medium.

(b) *Fusion decomposition.* Powdered sodium peroxide (3 g) was transferred into a dry 50-ml nickel or corundum crucible, 0.2–0.3 g of sample (accurately weighed to 0.1 mg) added to the crucible and the contents mixed with a dry stainless-steel spatula. The mixture was covered with a thin layer of powdered sodium peroxide and fused over a muffle furnace at 750°C for 5–10 min. The crucible was removed from the heat and cooled in air for 2–3 min, then placed in a dry 250-ml beaker, 1–2 ml sulfuric acid (1 + 1) added and then 15 ml of water added to the crucible and the beaker covered with a watch-glass. After effervescence had ceased, the contents of the crucible were washed into the beaker with 15–20 ml of water. The crucible was rinsed into the beaker with 5 ml of sulfuric acid (1 + 10) and then with water. The solution was boiled in the beaker for 3–5 min to remove hydrogen peroxide. The watch-glass and walls of the beaker were washed with water and made up to 50 ml in *ca.* 0.25M sulfuric acid medium.

Procedure for the reduction of iron (III) and the titration of iron (II)

Potassium borohydride solution (2%) prepared freshly dropwise from a burette was added to the sample solution, with stirring, until the disappearance of the light blue colour of cupric ion (the sample solution, *e.g.* iron ores, contained no copper, 5–10 drops of 5% copper sulphate solution was added before the reduction step). It was treated again until the appearance of a turbidity of brown-yellow colour due to the appearance of very fine ground metallic copper, which did not fade within 30 sec. Next, the walls of the beaker were rinsed with water and diluted to 100 ml and stood until the disappearance of the brown-yellow colour and the appearance of light blue colour of cupric ion, which took 10–15 min. Then, 10–15 ml of sulfuric–phosphoric acid mixture were added and three drops of 1% sodium diphenylaminesulfonate indicator added and the solution was titrated with standard potassium dichromate solution until the appearance of a permanent deep blue-violet.

RESULTS AND DISCUSSION

Effect of medium and acidity

The effect of hydrochloric acid and sulfuric acid concentration on the determination of iron was studied (Table 1). It was found that completion of the reduction step in chloride medium

Table 1. Effect of HCl and H_2SO_4 concentration on the determination of 25 mg of iron (copper added, 15 mg)

Acidic conc. (*M*)	HCl Fe found (*mg*)	HCl Error (%)	H_2SO_4 KBH_4 (*ml*)	H_2SO_4 Fe found (*mg*)	H_2SO_4 Error (%)
0.01	26.12	+4.48	1.2	25.10	+0.4
0.1	28.80	+15.20	1.4	24.92	−0.3
0.3	29.57	+18.28	2.9	24.99	−0.04
0.5	29.79	+19.16	3.8	25.08	+0.3
1.0	30.04	+20.16	5.4	24.75	−1.0
2.0	32.83	+31.32	7.5	24.88	−0.48
3.0	35.93	+43.80	10.6	25.05	+0.2

was difficult to judge visually and the results gave serious errors because of the titration of cuprous chloride (Table 1). In sulfuric acid medium, copper did not interfere with the determination of iron and the sulfuric acid concentration of 0.01–0.5M remained suitable. The high concentration of sulfuric acid in the solution caused the violent decomposition of potassium borohydride, and as a result, the efficiency of utilization of the reducing agent decreased.

Effect of copper on the reduction of iron (III)

The results for the effect of copper on the reduction of iron (III) are outlined in Table 2. The reduction of iron (III) by potassium borohydride in sulfate medium without the presence of cupric ion was very slow, whereas in the presence of cupric ion the reduction reaction was fast. During the reduction of iron (III) in the presence of copper, the appearance of a turbidity of brown-yellow colour when adding the potassium borohydride solution dropwise and the immediate disappearance of this colour when stirring were observed until the excess of potassium borohydride reduced the cupric ion to very fine ground metallic copper, which can be taken as indication that iron (III) has been completely reduced. The above experimental results (Tables 1 and 2) demonstrated the catalysis of cupric ion on the reduction of iron (III) in sulfate medium ($Cu^{2+} \rightarrow Cu^0 \rightarrow Cu^{2+}$). Copper sulphate is, therefore, both an indicator of the end point of the reduction of iron (III) and a catalyst of the redox reaction. Hence, for the sample containing no or extremely low content of copper, the sample solution should have additional added copper.

Table 2. Effect of the amount of copper on the reduction of iron (III) and the determination of 25 mg of iron

Cu added (*mg*)	Cu:Fe ratio	Reducting period (*min*)	KBH_4 (*ml*)	Fe found (*mg*)
0	0:1	10-12	8.8	24.94
2.5	0.1:1	7	4.0	24.93
5	0.2:1	5	3.8	25.11
10	0.4:1	2	2.5	25.02
15	0.6:1	2	2.4	24.92
25	1:1	2	2.4	25.05
50	2:1	2	2.5	24.90
100	4:1	2	2.5	24.88

There seemed to be no difference in the effect of excess potassium borohydride in the range 20–100% and the excess of the reductant can be removed by the automatic spontaneous escape of hydrogen produced in the decomposition of the reluctant by standing for 10–15 min.

Effect of temperature on the reduction

The effect of temperature on the reduction of iron (III) was examined. The results showed that there was no difference for temperatures of 25, 50 and 80°C. Hence it is convenient to carry out the reduction after the preparation of the sample solution. It is well known that in the conventional $SnCl_2$–$HgCl_2$ method,[1,2,16] the reduction of iron (III) by $SnCl_2$ solution at room temperature is sluggish and it should be carried out in nearly boiling solution (at least over 80°C).

Stability of the iron (II) solution

In the conventional $SnCl_2$–$HgCl_2$ method the hot solution containing the iron (II) after the reduction of iron (III) is required to be rapidly cooled, and, after the oxidization of the excess of Sn(II) with mercuric chloride, the titration should be carried out within a few minutes. In Kallmann *et al.*'s method[8] the standing period of the iron (II) solution should not exceed 30 min. In the present work, the stability of the iron (II) in the sample solution after the reduction was examined and the results (Table 3) show that when the standing period was varied from 15 to 300 min, little change in the determined value was noted, thus indicating that the iron (II) in the solution was stable for 300 min. It is without doubt that the long-term stability of the iron (II) solution is very beneficial to the large-scale routine determinations.

Effect of potential interfering ions

Synthetic solutions containing iron and other ions were used for studying possible interferences. The results for the effect of potential interfering ions are summarized in Table 4. The tolerance limit was set as the amount of foreign ion causing interference of a relative error of

Table 3. The stability of the iron (II) in the sample solution after reduction

Sample	Weight (*g*)	Titration (*ml*)	Standing period (*min*)	Fe found (%)	Error (%)
1# copper ore*	0.2009	9.75	15	27.50	—
	0.2002	9.71	60	27.49	0.04
	0.2009	9.74	150	27.47	0.11
	0.2020	9.79	210	27.46	0.15
	0.2010	9.72	300	27.40	0.36
11# gold ore*	0.2007	7.90	15	22.30	—
	0.2008	7.90	60	22.29	0.04
	0.2025	7.95	150	22.24	0.27
	0.2017	7.92	210	22.25	0.22
	0.2000	7.85	300	22.24	0.27
3# copper ore†	0.3212	19.33	15	34.10	—
	0.3114	18.69	30	34.01	0.26
	0.3016	18.02	150	33.85	0.73

*Acid decomposition.
†Fusion decomposition.

<2% in the determination. Three milligrams of Mo(VI) and Sb(V) and 10 mg of Sn(IV) did not interfere with the determination, and 5 mg of Se(VI), As(V) and Te(IV) did. The latter caused the wrong end point indication of the reduction. The interference of As and Sb could be eliminated by adding hydrobromic acid to the sample solution followed by evaporating to remove As and Sb, and that of Se and Te could be removed by adding excess potassium borohydride and precipitating Se and Te. It should be pointed out that the concentrations of these ions in copper ores are generally much lower than the maximum levels tested, so there is usually little interference from these ions.

Verification of procedure

The determination of various amounts of iron (0.3–210 mg) in sulfate medium (Table 5) shows that the method can be applied to the iron content percentage of 0.5–70% corresponding to 0.3 g of sample with a relative maximum error of 1%. The error of the determined value of 0.3 mg of iron was caused by the error of the volume of titration. Because of the lack of a certified reference material for iron content in copper ore, the validity of the proposed analytical procedure was assessed by analysing the control copper ore samples and measuring the recovery of iron spiked in a control sample. The analytical results for the control samples are given in Table 6 and those for 1# control sample are compared by the proposed method, the conventional stannous chloride–mercuric chloride method with the separation of iron from copper using ammonia precipitation and the EDTA titration method, demonstrating that the proposed method is widely applicable and

Table 4. Effect of potential interfering ions

Fe added (*mg*)	Foreign ion (*mg*)	$K_2Cr_2O_7$ (*ml*)	Fe found (*mg*)	Error (%)
25		4.40	24.93	−0.28
	Sb(V) 5	4.95	28.05	+12.2
	5	4.34†	24.59	−1.6
	Se(VI) 5	1.00*		
	5	4.42§	25.04	+0.16
	Te(IV) 5	0.88*		
	5	4.41§	24.99	−0.04
	As(V) 3.75	1.58*		
	7.5	4.35†	24.65	−1.4
	Sn(IV) 5	4.47	25.33	+1.33
	10	4.48	25.35	+1.4
50	Sb(V) 3	8.98	50.88	+1.8
	4	9.87	50.82	+1.6
	8	9.30	52.69	+5.4
60	Mo(VI) 1	10.47	59.32	−1.1
	2	10.50	59.49	−0.85
	3	10.48	59.38	−1.0
	4	10.44	59.15	−1.5
	8	10.42	59.04	−1.6
	Sb(V) 2	10.47	59.32	−1.1
	3	10.44	59.15	−1.5

*The error was caused by the wrong end-point of the reduction.
†Add HBr to remove Sb and As.
§Add excess of KBH_4 and filter to remove Se and Te.

Table 5. Determination of various amounts of iron (copper added, 15 mg)

Fe added (*mg*)	Fe content* (%)	$K_2Cr_2O_7$ (*ml*)	Fe found (*mg*)	Error (%)
0.3	0.1	0.08	0.45	+50†
1.5	0.5	0.26	1.51	+0.7
6	2	1.05	5.95	−0.8
60	20	10.63	60.23	+0.4
150	50	26.32	149.1	−0.6
210	70	36.65	207.7	−1.1

*Calculated corresponding to 0.3 g of sample.
†The error was mainly caused by the error of titration volume.

Table 6. Determination of iron in control copper ore samples

Control sample	Suggested value (%)	Fe found (%)*		
		This method	$SnCl_2$–$HgCl_2$	EDTA
1# copper ore	27.47	27.45 ± 0.06†	27.39 ± 0.12†	27.62 ± 0.52†
		27.59 ± 0.07‡	—	—
3# copper ore	34.07	33.94 ± 0.10‡	—	—

*Mean ± S.D. of three parallel determinations.
†Acid decomposition.
‡Fusion decomposition.

has excellent precision and accuracy. The conventional $SnCl_2$–$HgCl_2$ method requires the separation of iron from copper with 10–12 times washing the iron hydroxide with 40–50 ml of hot ammonia solution per time and, as a result, the error is high. The error of the EDTA titration method is caused by the sluggish end-point. The spiking and recovery test was performed as follows: 0.2 g of sample was placed in a 250-ml beaker, to which ferric sulfate solution containing 50 mg iron was added; it was then treated according to the procedure of acid decomposition followed by the procedure for the reduction of iron (III) and the titration of iron (II) described as above. The results are given in Table 7, showing that the mean recovery of the spiked iron was 99.81%.

Advantages of the procedure

The proposed procedure has the following advantages: (1) it avoids the use of mercuric salt, (2) it removes the excess of reducing agent borohydride by spontaneous decomposition of reducing agent borohydride in acidic medium without adding any oxidizer, (3) copper does not interfere with the determination of iron, and is both indicator and catalyst of the reduction of iron (III), (4) the reduction of iron (III) with borohydride is not affected by the temperature, (5) the iron (II) in the sample solution after the reduction of iron (III) is stable for 300 min, and (6) the procedure is simple, rapid, precise and accurate. The above advantages make the proposed method most attractive for large-scale routine analyses.

Table 7. Recovery of iron spiked to copper ore (27.47% Fe)

Weight (*g*)	Fe present (*mg*)	Fe added (*mg*)	Titration (*ml*)	Fe found (%)	Recovery (%)
0.2025	55.63	50	18.61	105.44	99.62
0.2138	58.73	50	19.19	108.73	100

CONCLUSION

The proposed method for the determination of total iron in the presence of copper with the reduction of potassium borohydride followed by titration of a standard solution of potassium dichromate proved to be simple, rapid, accurate and precise. In sulfate medium, cupric ion is not only an indicator of the end-point of the reduction of iron (III) and a catalyst of the reduction reaction, but also does not interfere with the determination of iron. Moreover, the iron (II) solution is stable for 300 min, which is greatly superior to all of the previously published methods.

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