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The effect of copper on iron reduction and its application to the determination of total iron content in iron and copper ores by potassium dichromate titration

Hanjun Hu [a], Yang Tang [a], Haisong Ying [b], Minghai Wang [c], Pingyu Wan [a], X. Jin Yang [a,*]

[a] *Beijing Key Laboratory of Membrane Science and Technology, Beijing University of Chemical Technology, Beijing 100029, China*
[b] *Iron Ore Testing Centre, Ningbo Entry-Exit Inspection and Quarantine Bureau, Ningbo 315800, China*
[c] *Central Iron and Steel Research Institute, Beijing 100081, China*

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ABSTRACT

The International Standard Organization (ISO) specifies two titrimetric methods for the determination of total iron content in iron ores using potassium dichromate as titrant after reduction of the iron(III) by tin (II) chloride and/or titanium(III) chloride. These two ISO methods (ISO2597-1 and ISO2597-2) require nearly boiling-point temperature for iron(III) reduction and suffer from copper interference and/or mercury pollution. In this study, potassium borohydride was used for reduction of iron(III) catalyzed by copper ions at ambient temperatures. In the absence of copper, iron(III) reduction by potassium borohydride was sluggish while a trace amount of copper significantly accelerated the reduction and reduced potassium borohydride consumption. The catalytic mechanism of iron(III) reduction in sulfuric acid and hydrochloric acid was investigated. Potassium borohydride in sodium hydroxide solution was stable without a significant degradation within 24 h at ambient conditions and the use of potassium borohydride prepared in sodium hydroxide solution was safe and convenient in routine applications. The applicability of potassium borohydride reduction for the determination of total iron content by potassium dichromate titration was demonstrated by comparing with the ISO standard method using iron and copper ore reference materials and iron ore samples.

1. Introduction

Iron is the world's first most-used metal and iron ore ranks second to crude oil as a commodity in commerce and industrial use [1,2]. Typical concentrations of total iron content in iron ore and its concentrates range between 55% and 72% and the accurate determination of total iron in iron ores is important for iron smeltry. The international standard organization (ISO) prescribes titrimetric methods with potassium dichromate ($K_2Cr_2O_7$) as the standard method (ISO 2597-1) [3], in which Fe(III) is reduced to Fe(II) by excessive tin(II) chloride ($SnCl_2$). The excess of $SnCl_2$ is then removed by mercuric chloride and Fe(II) is titrated with $K_2Cr_2O_7$ standard solution using sodium diphenylamine sulfonate as indicator. This method is not environmentally friendly due to the use of mercury chloride and many mercury pollution-free methods have been developed [4–11]. These methods include ethylene diamine tetraacetic acid (EDTA) titration and the use of silver [5,6], bromine [7], titanium(III) chloride ($TiCl_3$) [4,8–10], potassium borohydride (KBH_4) [11], hydroxylamine hydrochloride, ascorbic acid as reductant followed by titration with dichromate or cerous sulfate ($Ce(SO_4)_2$) titration. Among these methods, the $TiCl_3$ reduction approach was adopted as the standard method in 1990 (ISO 9507) [8], in which the majority of Fe(III) is reduced by $SnCl_2$, the remainder of Fe(III) is reduced by $TiCl_3$ at a slight excess, and the excessive Ti(III) is oxidized by either dilute $K_2Cr_2O_7$ or perchloric acid ($HClO_4$). The ISO 9507 method [8] was recently updated [9] by correcting errors in the presentation of statistical information of previous editions. However, experience in routine analysis has shown that meticulous reduction conditions (high temperatures near boiling point and careful control of the concentration of the reductant $SnCl_2$ and $TiCl_3$) and copper interference make the procedure of the ISO standard methods complicated. For samples containing more than 0.1% of copper in weight, a separation step is required to remove copper prior to Fe(III) reduction. The copper separation is carried out by precipitation of iron hydroxide with ammonia solution. The precipitate is thoroughly washed with hot ammonia solution. The separation is a tedious and labor-intensive process.

In a previous study, KBH_4 was used for the reduction of Fe(III) in the dichromate titration method for the determination of total

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* Corresponding author. Fax: +86 10 6442 1030.
E-mail address: yangxj@mail.buct.edu.cn (X. Jin Yang).

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iron in copper ores [11]. The advantages of the KBH_4 reduction were rapid reduction of Fe(III) at ambient temperatures and no copper interferences in sulfuric acid (H_2SO_4) solutions. However, the determination was significantly interfered in hydrochloric acid (HCl) solutions [11]. This has limited the application of the KBH_4 approach because the acid decomposition using HCl is a common method for ores and minerals. In this study, we investigated the role of copper ions in iron redox processes and the mechanism of the copper interferences, developed a strategy for elimination of copper interference and made a comparison of the borohydride reduction method with the ISO standard methods for the determination of total iron content in both iron and copper ores.

2. Materials and methods

2.1. Reagents, chemicals and samples

Concentrated H_2SO_4 (1.84 g mL^{-1}), HNO_3 (1.4 g mL^{-1}), HCl (1.18 g mL^{-1}), phosphoric acid (H_3PO_4) ($\geq$ 1.71 g mL^{-1}), hydrofluoric acid (HF, 1.15 g mL^{-1}), hydrogen peroxide (H_2O_2, 30%), $CuSO_4 \cdot 5H_2O$, $K_2Cr_2O_7$, NaOH, sodium peroxide (Na_2O_2), Na_2CO_3, KBH_4, $SnCl_2 \cdot 2H_2O$, titanium(III) chloride solution (200 g L^{-1}), sodium tungstate dihydrate ($Na_2WO_4 \cdot 2H_2O$) and sodium diphenylamine sulphinate were analytical grade and were purchased from Sigma-Aldrich, Shanghai, China and Beijing Chemicals, China. Certified reference materials (iron ores GBW(E)010343, GBW07830, W88301a and GBW07272 and copper ores GBW07166 and GBW07170) were obtained from National Center for Standard Reference Materials, National Institute of Metrology, China. High-purity water (18 MΩ), obtained from a Milli-Q system, was used throughout the study.

Potassium dichromate standard solution (4.9047 g L^{-1}): $K_2Cr_2O_7$ reagent (6 g) was pulverized in an agate mortar, dried at 140–150 °C for 2 h, and cooled to room temperature in a desiccator. Then, 4.9047 g of this material was dissolved in 300 mL of water and the solution was transferred quantitatively to a 1000 mL volumetric flask and made up to volume with water after cooling to 20 °C. One mL of this standard solution corresponds to 5.585 mg of iron.

Potassium borohydride solution (20 g L^{-1}): 2 g of potassium borohydride were dissolved in 100 mL of 10 g L^{-1} NaOH solution. The solution was prepared fresh as needed and was stable without a significant degradation within 24 h when it was placed at an ambient condition.

Cupric sulfate solution (20 g L^{-1}): Dissolve 2 g of $CuSO_4 \cdot 5H_2O$ in 100 mL water.

Sulfuric acid-phosphoric acid mixture: 150 mL of concentrated sulfuric acid were slowly poured into about 500 mL of water, with stirring, and 150 mL of concentrated phosphoric acid were added with stirring. The mixture was cooled and diluted to 1 L with water. The beaker for preparation of the solution was cooled in the ice-water bath during the preparation.

Tin(II) chloride solution (100 g L^{-1}): Dissolve 10 g $SnCl_2 \cdot 2H_2O$ in 20 mL concentrated hydrochloric acid with heating the solution in a water bath. Cool the solution and dilute with water to 100 mL. Prepare fresh solution as needed. Alternatively, store the solution in a brown glass bottle with a small quantity of granular tin metal.

Titanium(III) chloride solution (20 g L^{-1}): Dilute one volume of titanium(III) chloride solution (200 g L^{-1}) with nine volumes of HCl (1+1). Prepare fresh solution as needed.

Sodium tungstate solution (250 g L^{-1}): Dissolve 25 g of $Na_2WO_4 \cdot 2H_2O$ in 95 mL water. Then, add 5 mL phosphoric acid to the solution.

Iron standard solution (5.585 g L^{-1}): Transfer 5.585 g of pure iron (> 99.99% purity) to a 500-mL Erlenmeyer flask and place a small filter funnel in the neck. Add 75 mL of hydrochloric acid (1+1) in small increments and heat until dissolved. Cool and oxidize with 5 mL of hydrogen peroxide (30%) added in small portions. Heat to boiling and boil to decompose the excess hydrogen peroxide and to expel chlorine. Cool, transfer to a 1000 mL volumetric flask and mix well. 1.00 mL of this solution is equivalent to 1.00 mL of the standard potassium dichromate solution (4.9047 g L^{-1}).

2.2. Decomposition of the sample

Acid decomposition (for samples containing mass fraction $\leq$ 0.05% of vanadium): Transfer 0.3–0.4 g sample (weighted to 0.1 mg) to a 300-mL beaker, add 20 mL of concentrated hydrochloric acid, cover with a watch glass, heat gently at about 80 °C for 1 h, and continue heat without boiling at a higher temperature for about 10 min. Wash the watch glass with a jet of water, and dilute to 50 mL with warm water. Filter the insoluble residue on a close-textured filter paper. Wash the residue with warm hydrochloric acid (1+50) until the yellow color of Fe(III) chloride is no longer observed. Then wash with warm water six to eight times. Collect the filtrate and washings in a 600 mL beaker. Begin the evaporation of this main solution without boiling to 70 mL.

Place the filter paper and residue in a platinum crucible (should be precleaned), dry then char the paper and finally ignite at 750–800 °C. Allow the crucible to cool, moisten the residue with sulfuric acid (1+1), add about 5 mL of hydrofluoric acid (40%) and heat gently to remove silica and sulfuric acid. Add 2 g of potassium pyrosulfate to the cold crucible, heat gently at first then strongly until a clear melt is obtained. Cool, place the crucible in a 250 mL beaker, add about 25 mL of water and about 5 mL of hydrochloric acid (1.16–1.19 g mL^{-1}) and warm to dissolve the melt. Remove and wash the crucible. Combine this solution with the main solution, evaporate without boiling to about 100 mL. This solution is ready for the reduction of Fe(III) with titanium(III) chloride in accordance with ISO 2597-2. For the reduction with KBH_4, continue to evaporate the solution without boiling to about 5 mL. Add 5 mL of sulfuric acid (1+1) and evaporate to white fumes for 10 min. Cool, rinse the walls with water and make the solution to 100 mL with 0.25 M sulfuric acid.

Fusion decomposition (for samples containing more than 0.05% mass fraction of vanadium and/or samples not being decomposed by the acid-decomposition): Powdered sodium peroxide (3 g) and sodium carbonate (1 g) were transferred into a dry 50-mL corundum crucible, a portion of 0.3–0.4 g of sample (weighed to 0.1 mg) was added to the crucible and the contents were 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 10 min. The crucible was removed from the furnace and was heated over a burner to melt the sinter within 30 s and, swirling gently, was continued with heating to allow a total heating time of 2 min. The crucible was cooled in air for 2–3 min and then placed in a dry 300-mL beaker. About 100 mL of warm water were added and heated on a hot-plate with a watch glass for a few minutes to dissolve the melt. The crucible was removed from the beaker and washed with 5 mL of sulfuric acid (1+10) and then with warm water (the washings were added to the solution). The solution was boiled in the beaker for 35 min to remove hydrogen peroxide. A mixed acid (0.2 M HCl – 1 M H_2SO_4) was added to the beaker until the hydroxide precipitate was completely dissolved. Then, the solution was evaporated without boiling to about 100 mL and was ready for the reduction by KBH_4. If the solution was reduced with titanium(III) chloride in accordance with ISO 2597-2, hydrochloric acid was used to dissolve the hydroxide precipitates.

2.3. Reduction of Fe(III) and titration of Fe(II) with ISO 2597-2 [9]

Reduction of Fe(III): After sample decomposition and preparation, the sample solution was maintained at 90–95 °C and the beaker's inside wall and the cover were washed with hot water (the washes were combined with the solution). Immediately, $SnCl_2$ solution was added dropwise to reduce iron(III) while the solution in the beaker was swirled until only a faint yellow tint of the iron (III) chloride solution remained. It was essential that some iron(III) remained unreduced. If the solution was made colorless by the excessive addition of tin(II) chloride solution, hydrogen peroxide was added dropwise until the solution changed to a faint yellow tint. It was convenient to use dilute $K_2Cr_2O_7$ solution as a reference solution for establishing the desired slight yellow tint of the sample solution. The dilute $K_2Cr_2O_7$ solution was prepared by diluting 5 mL of $K_2Cr_2O_7$ standard solution to 100 mL with water. The inside wall of the beaker was washed using a small amount of hot water. A sodium tungstate solution of 3 drops was added as indicator and then $TiCl_3$ solution was added drop by drop with swirling until it turned blue and lasted for at least 5 s. Then, dilute $K_2Cr_2O_7$ solution was added drop by drop to oxidize the excess of titanium(III), until the solution became colorless (the temperature of the solution at this time should be > 70 °C). If indigo carmine solution was added as indicator, the solution turned blue and then colorless with the addition of $TiCl_3$ solution at a slight excess (2–3 drops). The removal of the excessive titanium(III) by dilute $K_2Cr_2O_7$ solution was indicated by blue color which lasted for at least 5 s.

Titration of Fe(II): The sample solution was placed in a cooling bath for several minutes and diluted to about 300 mL using cold water. The solution was titrated with the $K_2Cr_2O_7$ standard solution, while swirling, until the amount of the titrate reached 10 mL. 30 mL of sulfuric acid-phosphoric acid mixture was added and the titration was continued with addition of 0.5 mL sodium diphenylamine sulfonate solution as an indicator. The end point was reached when the green color of the solution changed to a bluish green and a final drop of the titrant imparted a violet color.

2.4. Reduction of Fe(III) and titration of Fe(II) with the proposed KBH_4 method

After sample decomposition and preparation, the sample solution was cooled to room temperature and KBH_4 solution was added drop by drop to the solution with swirling until red-brown particles lasted at least for 5 s (2–3 drops of copper sulfate solution was added to the sample solution prior to KBH_4 reduction if the ore sample contained $< 2\%$ copper in mass fraction). The inside wall of the beaker was rinsed with a small amount of water. When the red-brown particles disappeared and the solution turned to light-blue or colorless (depending on the concentration of Cu in the solution), the solution was titrated with dichromate standard solution (see above).

A blank sample should be tested. The total iron content is calculated by $Fe\% = (V_1 - V_2)/m \times 5.585 \times 100$ where V_1 is the volume (mL) of potassium dichromate standard solution used for the titration of the test sample, V_2 is the volume (mL) of potassium dichromate standard solution used for the titration in the blank test, m is the mass (mg) of the test sample. When necessary, the total iron content in mass fraction should be corrected by the hygroscopic moisture content, determined in accordance with ISO 2596[12].

3. Results and discussion

In the standard $TiCl_3$ reduction method, sodium tungstate or indigo carmine is employed as indicator for reduction of Fe(III) and removal of excessive $TiCl_3$ by dilute $K_2Cr_2O_7$ solution through the change of solution color (sodium tungstate: yellow – colorless – blue – colorless; indigo carmine: yellow – colorless – blue – colorless – blue). The appearance of the tungstate blue color lasting at least for 5 s indicates a full completion of Fe(III) reduction and a slight excess of $TiCl_3$. Then, the addition of dilute $K_2Cr_2O_7$ solution drop by drop removes the excessive $TiCl_3$ through fading of the blue color. It was found that the tungstate blue was not able to last for 5 s for copper ore samples (the separation of copper and iron by ammonium hydroxide precipitation was carried out on the sample solution prior to the reduction). We speculated that this was likely due to the presence of a trace amount of copper because of incomplete separation of copper and iron by ammonia precipitation. Therefore, the reduction of synthetic samples containing 28 mg of Fe and different amounts of Cu (0, 0.4 and 28 mg) was investigated. The results showed that 1 mL of $SnCl_2$ solution (100 g L^{-1}) followed by 0.2 mL $TiCl_3$ (20 g L^{-1}) was sufficient to completely reduce 28 mg of Fe(III) and the tungstate blue color lasted for longer than 15 s without the presence of Cu (see Entry 1 of Table 1). In contrast, the presence of Cu at a trace amount (0.4 mg) was not able to hold the blue color for 5 s even with a large excess of $TiCl_3$ solution. It was therefore considered that Cu^{2+} was likely to have a catalytic effect on the oxidation of Ti(III) by air oxygen in the solution. In summary, the complete reduction of Fe(III) by the standard $TiCl_3$ reduction method is difficult to achieve when copper is present, leading to negative biases on the determination of total iron.

When KBH_4 is employed as reductant, red-brown fine particles occur when KBH_4 solution is added to mixtures of Fe^{3+} and Cu^{2+} solution drop by drop and disappear instantly upon swirling of the solution. The red-brown particles are metallic copper and their disappearance becomes slower when more KBH_4 is added. The mechanism of the reduction was considered to be the reduction of Cu^{2+} to zero-valent Cu^0 at first ($Cu^{2+} + 2e^- = Cu^0$, $E^0 = 0.342$ V) and then a quick re-oxidation of Cu^0 by Fe^{3+} ($Cu + 2Fe^{3+} = 2Fe^{2+} + Cu^{2+}$, $Fe^{3+} + e^- = Fe^{2+}$, $E^0 = 0.771$ V). When the metallic Cu particles held in the solution for at least 5 s, the reduction of Fe(III) to Fe(II) was considered to be complete. This was confirmed by determining Fe recovery from synthetic samples at different reduction stages. The re-dissolution of Cu particles was the consequence of Cu oxidation by air oxygen ($2Cu + O_2 + 4H^+ = Cu^{2+} + 2H_2O$, $E^0 = 0.887$ V).

It was observed that the observation of the reduction process was somewhat different in between H_2SO_4 and HCl solutions. In H_2SO_4, the red-brown particles were relatively large when the reduction of Fe(III) was completed and the solution became light-blue or colorless (depending on the concentration of Cu^{2+}) when the particles were re-dissolved (Fig. 1). In HCl, the solution turned

Table 1
Determination of total iron in synthetic samples by the $TiCl_3$ reduction standard method (ISO 2597-2).

Synthetic sample (Fe/Cu, mg/mg)	$SnCl_2$ (mL)	$TiCl_3$ (mL)	Time for tungstate blue (s)	Fe recovery (%)
28/0	1	0.2	> 15	100.1
28/28[a]	1	0.2	< 2	98.7
28/28[a]	1	1.0	< 2	97.3
28/28[a]	1	2.5	< 2	95.7
28/0.4[b]	1	0.6	< 2	98.0
28/0.4[b]	1	1.5	< 2	97.8
28/0.4[b]	1	2.5	< 2	97.0

[a] Prior to reduction by $SnCl_2$, the separation of copper by ammonium hydroxide precipitation was carried out (iron hydroxide precipitates were filtered and rinsed with hot ammonia solution of 11.33 g L^{-1} for 8–9 times to remove $Cu(NH_3)_4^{2+}$ from the $Fe(OH)_3$ precipitates).

[b] No separation of copper was carried out.

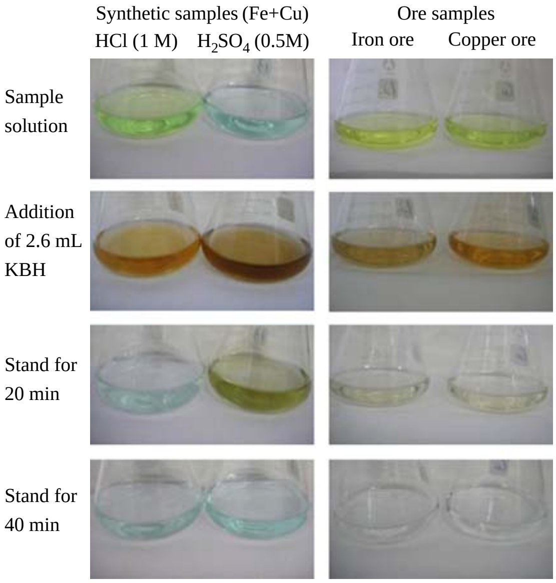

Fig. 1. Color changes of synthetic samples (28 mg Fe+58 mg Cu) and iron ore samples before and after addition of KBH_4. The iron ore sample contained 52.96% Fe and the copper ore contained 29.6% Fe and 24.2% Cu. 4.8 mg Cu was added to the iron ore sample solution prior to the addition of KBH_4. (For interpretation of the references to color in captions of this figure, Table 2 and Figure 2, the reader is referred to the web version of this article.)

Table 2
Effect of standing period after KBH_4 reduction on the determination of iron in synthetic samples containing 28 mg Fe and 28 mg Cu at pH 1.0 (the use of 20 g $L^{-1}KBH_4$ was 1.9 mL).

Standing period (min)	HCl solution		H_2SO_4 solution	
	Color of solution	Recovery (%)	Color of solution	Recovery (%)
0		134.0		102.9
5		124.8		101.5
15		111.6		100.5
30		100.7		100.5
60		98.8		100.3

into a clear brown-yellow solution first and red-brown particles in a much finer size (as compared to H_2SO_4 solution) then occurred at the end of reduction. When the fine Cu particles were re-dissolved, the sample became clear brown-yellow solution again. Finally, the brown-yellow faded and the solution became light-blue or colorless (Fig. 1). Significant positive errors were observed when the dichromate titration was performed before the sample solution turned into light-blue or colorless (Table 2). Based on the above observations, we hypothesized that the reduction of Fe(III) by KBH_4 was catalytically promoted by Cu^{2+} via $Cu^{2+} \rightarrow Cu^0 \rightarrow Cu^{2+}$ (in H_2SO_4) and $Cu^{2+} \rightarrow Cu^+ \rightarrow Cu^0 \rightarrow Cu^+ \rightarrow Cu^{2+}$ (in HCl) (Table 3). The brown-yellow solution was due to the formation of Cu^+ complexes with Cl^- [13–15]. This mechanism was verified by electrochemical reduction in cyclic voltammetry (Fig. 2). A single pair of oxidation/reduction peaks in H_2SO_4 was attributed to $Cu^{2+}+2e^- \leftrightarrow Cu$. In comparison, two pairs of oxidation/reduction peaks were observed in HCl and they were related to $Cu \leftrightarrow CuCl^+_{ads}+e^-$ and $CuCl^+_{ads} \leftrightarrow Cu^{2+}+e^-$ where $CuCl^+_{ads}$ denoted the copper(I)-chloride complexes.

Table 3
Reactions during the process of Fe(III) reduction by KBH_4 in the presence of Cu(II) ions in H_2SO_4 and HCl solutions.

Medium	Reactions	E^0 (V)
H_2SO_4	$Cu^{2+}+2e^-=Cu$	0.342
	$Cu+2Fe^{3+}=2Fe^{2+}+Cu^{2+}$	0.435
	$2Cu+O_2+4H^+=Cu^{2+}+2H_2O$	0.887
	$O_2+4H^++4e^-=2H_2O$	1.229
HCl	$Cu^{2+}+2e^-=Cu$	0.342
	$Cu+FeCl_2^+=Fe^{2+}+CuCl_2^-$	
	$Cu^{2+}+e^-=Cu^+$	0.153
	$Cu^++e^-=Cu$	0.521
	$Cu+Cu^{2+}+4Cl^-=2CuCl_2^-$	
	$Cu^{2+}+Cl^-+e^-=CuCl$	0.538
	$CuCl_2^-+e^-=Cu+2Cl^-$	
	$CuCl+e^-=Cu+Cl^-$	0.137
	$4CuCl_2^-+O_2+4H^+=4Cu^{2+}+2H_2O+8Cl^-$	

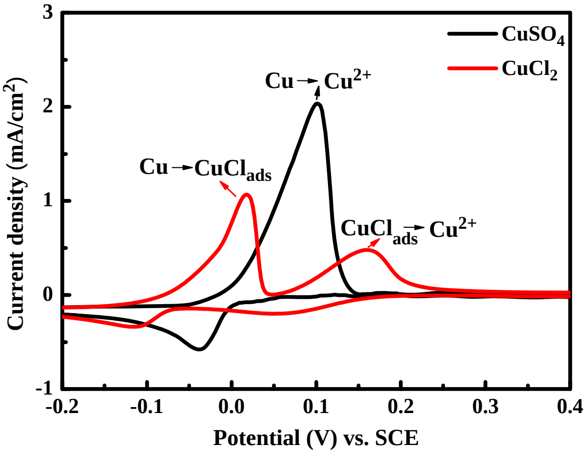

Fig. 2. Cyclic voltammograms of $CuSO_4$ and $CuCl_2$ solutions at pH 1.0 (Pt electrode at a scan rate of 20 mV s^{-1}, [$CuSO_4$]: = 1.6 g L^{-1}, [$CuCl_2$] = 1.3 g L^{-1}, the pH of $CuSO_4$ solution was adjusted with H_2SO_4 and that of $CuCl_2$ solution was done with HCl).

The catalytic effect of Cu on the reduction of Fe(III) was further demonstrated by examining the effect of copper concentration (Table 4). The presence of a small amount of copper (4.8 mg L^{-1} or 0.48 mg) significantly accelerated the reduction and reduced the volume of KBH_4 consumed and the presence of 0.48–28.8 mg of Cu did not interfere with the determination of 28 mg of Fe.

Fig. 3(A) shows the effect of acid concentration (HCl and H_2SO_4) on the recovery of 28 mg of Fe. The presence of 4.8 mg Cu did not affect the recovery regardless of HCl concentration but significant positive errors were observed in the presence of 28.8 mg Cu when HCl concentration was greater than 0.25 M. In comparison, the presence of 28.8 mg Cu did not interfere with the Fe determination in 0.1–2 M H_2SO_4. Fig. 3(B) shows the effect of the amount of Cu (0.48–28.8 mg) on the determination of 28 mg Fe in 1 M HCl. The results indicate that up to 6 mg of Cu did not interfere with the determination of Fe. Table 5 shows the effect of NaCl concentration on the determination of Fe in the presence of 4.8 and 28 mg Cu. The amount of 4.8 mg Cu did not influence the determination of Fe between 0 and 1.5 M NaCl whereas the determination of Fe was in a significantly positive bias when NaCl concentration was greater than 0.3 M in the presence of 28 mg Cu. In summary, the condition for the determination of Fe in HCl is that the HCl concentration should be less than 0.25 M or the amount of Cu is not greater than 6 mg.

After reduction, the stability of Fe(II) solution is important in routine analysis. The ISO methods require that the dichromate titration be performed immediately after Fe(III) reduction and removal of excessive reductant. We found that the Fe(II) solution obtained by KBH_4 reduction was more stable in H_2SO_4 than in HCl (Fig. 4). If the sample is prepared in HCl, the titration should be carried out immediately after the reduced sample solution becomes colorless or light-blue from brown-yellow. If prepared in dilute H_2SO_4 solutions, the reduced sample solution is stable in 30 min (0.05 M H_2SO_4) and 150 min (0.5 M H_2SO_4).

Table 6 gives the variation coefficient for the determination of 5.6–280 mg iron by potassium borohydride reduction and dichromate titration. The variation coefficient for the determination of 17–280 mg is less than 1%. For a portion of 0.4 g sample taken for analysis, 17–280 mg of Fe corresponds to 4–70% mass fraction of Fe. This indicates that the proposed method is of capability to determine a wide range of iron content. The ISO methods are applicable to 30–72% mass fraction of Fe in ore samples, which is equivalent to 120–288 mg of Fe for a test portion of 0.4 g sample.

In the ISO 2597-2 method [9], the proceeding of Fe(III) reduction by $SnCl_2$ is judged by solution color change from yellow color of Fe(III) solution to the faint yellow tint and it is essential that a small amount of Fe(III) remains unreduced prior to the addition of $TiCl_3$. The Fe(III) reduction by $SnCl_2$ is sluggish and the temperature of the reduction must be maintained at 90–95 °C. Our experience showed that the reduction at such high temperatures was not convenient in routine determinations and that it was not straightforward to ensure a small amount of Fe(III) unreduced. The ISO method [9] states that if the solution is made colorless by the excessive addition of $SnCl_2$ solution, hydrogen peroxide is required to re-oxidize Fe(II) and Sn(II) until the solution changes to a faint

Table 4
Effect of copper concentration on reduction time, volume of KBH_4 solution and recovery of iron (Fe 28 mg, pH 1.0).

Cu (mg or mg L^{-1})	HCl solution			H_2SO_4 solution		
	Time (min)	KBH_4 (mL)	Recovery (%)	Time (min)	KBH_4 (mL)	Recovery (%)
0 mg (0 mg L^{-1})	6	17.5	98.8	7.5	22.8	100.9
0.48 mg (4.8 mg L^{-1})	1–2	5.8	99.3	1–2	4.8	101.5
0.96 mg (9.6 mg L^{-1})	1–2	4.3	100. 7	1–2	4.2	101.1
4.8 mg (48 mg L^{-1})	< 1	2.6	98.4	1–2	3.3	100.9
9.6 mg (96 mg L^{-1})	< 1	1.8	98.4	1–2	2.7	101.1
19.2 mg (192 mg L^{-1})	< 1	1.5	100.5	< 1	2.1	101.3
28.8 mg (288 mg L^{-1})	< 1	1.3	99.0	< 1	1.7	101.5

Table 5
Effect of NaCl concentrations on the determination of 28 mg Fe in the presence of 4.8 and 28 mg Cu.[a]

NaCl (M)	4.8 mg Cu+28 mg Fe		28 mg Cu+28 mg Fe	
	Fe found (mg)	Recovery (%)	Fe found (mg)	Recovery (%)
0.0	27.68	98.8	27.85	99.5
0.3	27.62	98.6	30.74	109.8
0.6	28.13	100.5	37.62	134.4
0.9	27.90	99.7	38.93	139.0
1.5	28.47	101.7	42.34	151.2

[a] The solutions were adjusted to pH 1.0 using HCl.

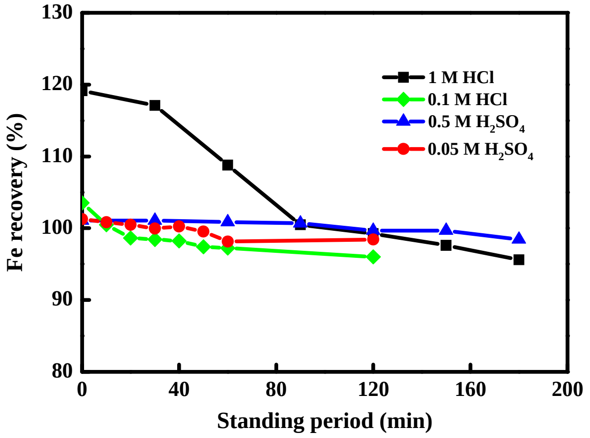

Fig. 4. Effect of standing period after KBH_4 reduction on recovery of Fe (each sample solution contained 28 mg Fe and 28.8 mg Cu in different acid concentrations).

Table 6
The determination of different amounts of iron.

Iron added [a] (mg)	KBH_4 (mL)	Iron found [b] (mg)	Recovery (%)	RSD (%)
5.6	0.8	5.65 ± 0.14	100.8	2.48
16.8	1.3	16.64 ± 0.12	99.0	0.72
28.0	1.6	27.90 ± 0.14	99.6	0.50
39.2	1.9	38.89 ± 0.34	99.2	0.87
56.0	2.5	55.70 ± 0.26	99.5	0.47
112	5.7	111.9 ± 0.34	99.9	0.31
168	6.2	167.6 ± 0.07	99.7	0.04
224	8.9	224.1 ± 0.23	100.0	0.10
280	10.5	279.9 ± 0.55	99.9	0.20

[a] 4.8 mg Cu was added and the solution was adjusted to pH 1.0 using HCl.
[b] Mean ± SD of three parallel determinations.

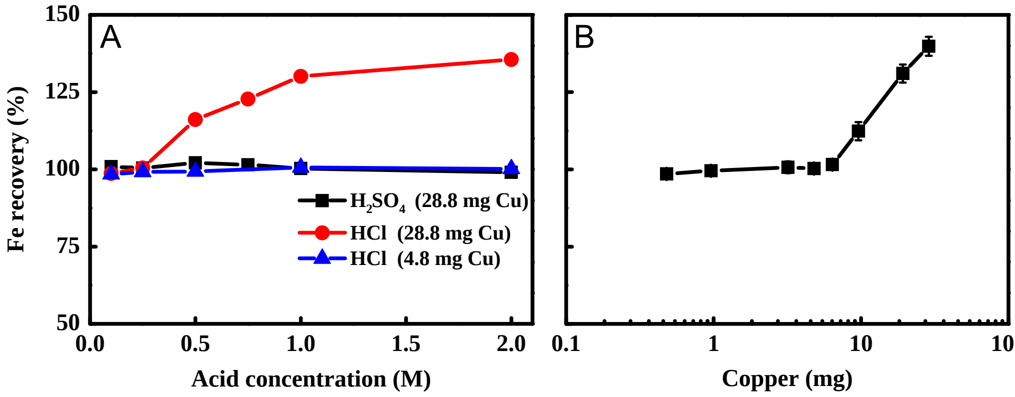

Fig. 3. Effect of (A) H_2SO_4 and HCl concentrations and (B) the amount of copper (in 1 M HCl) on the determination of 28 mg iron.

Table 7
Comparison of the standard and proposed methods for the determination of total iron content in iron and copper ores.

Sample	Certified Fe (%)	Certified Cu (%)	ISO 2597-2: 2008	Proposed method	Statistical analysis	
			Fe% (RSD%, n)	Fe% (RSD%, n)	*F*-value	*t*-value
Iron ore sample 1	–	–	62.09 (0.06, n=3)	62.31 (0.26, n=3)		
Iron ore sample 2	–	–	61.19 (0.16, n=3)	60.58 (0.75, n=3)		
Iron ore sample 3	–	–	55.46 (0.12, n=7)	55.48 (0.16, n=7)	0.4908[a]	0.1104[a]
Iron ore sample 4	–	–	59.74 (0.16, n=7)	59.77 (0.17, n=7)	0.8345[a]	0.1139[a]
GBW(E)010343	46.93	–	–	46.92 (0.13, n=7)		0.0842[a]
GBW07830	66.87	–	–	66.90 (0.14, n=7)		0.1354[a]
W88301a	64.88	–	64.98 (0.18, n=11)	64.72 (0.24, n=11)	0.3949[b]	0.2094[b]
GBW07272	52.96	–	53.01 (0.42, n=3)	53.07 (0.37, n=3)		
GBW 07166 (copper ore)	29.60	24.2	28.96 [c] (0.04, n=3)	29.80 [d] (0.82, n=3)		
GBW 07170 (copper ore)	12.76	12.59	–	12.30 [d] (0.37, n=3)		

[a] $F_{0.01}(6, 6)=8.47$, $t(0.01/2,6)=3.707$.

[b] $F_{0.01}(10, 10)=4.85$, $t(0.01/2,10)=3.169$.

[c] Separation of iron and copper was carried out by aqueous ammonia precipitation prior to Fe(III) reduction.

[d] No Cu separation was carried out.

Table 8
Comparison of ISO 2597 and the proposed method.

Method	ISO 2597-1: 2006	ISO 2597-2: 2008	Proposed method
Reductant	$SnCl_2$	$SnCl_2+TiCl_3$	KBH_4
Temperature of reduction	90–95 °C	90–95 °C	Room temperature
Indicator for Fe(III) reduction	Not required	Sodium tungstate or indigo carmine	Copper
Judgement for completion of Fe(III) reduction and removal of excessive reductant	Yellow → Colorless	Sodium tungstate: Yellow → Colorless → Blue → Colorless Indigo carmine: Yellow → Colorless → Blue → Colorless → Blue	Yellow → Colorless → Red-brown particles → Colorless
Precise control of excessive reductant	Required	Required	Not required
Oxidizing agent of excessive reductant	$HgCl_2$	$K_2Cr_2O_7$ or $HClO_4$	Not required
Tolerance of Cu (mg or % mass fraction)	< 0.4 or 0.1%	< 0.4 or 0.1%	< 100 or 25%
Range of Fe content (mg or %)	120–280 (30–72%)	120–280 (30–72%)	15–280 (5–72%)
Separation of Cu (Cu > 0.1%)	Required	Required	Not required

yellow tint. The reminder of Fe(III) is then reduced by Ti(III) chloride and the excess of Ti(III) is oxidized by adding dilute $K_2Cr_2O_7$ drop by drop using indigo carmine or sodium tungstate indicator. The complete reduction of Fe(III) using sodium tungstate indicator is indicated by a blue color which lasts at least for 5 s. This procedure requires that the copper content in the sample be less than 0.1% (corresponding to 0.4 mg Cu when a portion of 0.4 g sample is taken for analysis). Otherwise, copper and iron separation by ammonium hydroxide precipitation must be carried out prior to Fe(III) reduction. In comparison, the completion of Fe(III) reduction by KBH_4 is indicated by occurrence of red-brown particles and no chemicals are required to remove the excessive reductant after the reduction. The validity of the proposed method was examined by comparing the results of total iron content in certified reference materials of iron and copper ores and iron ore samples (Table 7). The results demonstrate that the proposed method has a similar degree of the accuracy and precision with the standard method. The characteristics of proposed method and the ISO standard methods (ISO 2597) are compared in Table 8. The advantages of the proposed method include (1) mercury pollution-free; (2) copper does not interfere with the titration but also has a catalytic effect on the reduction of Fe(III) and provides an clear indication to the completion of reduction; (3) the separation of copper is not required and thus the turn-around-time of the analysis is significantly reduced, particularly for copper ores; (4) the reduction is performed at ambient temperature and external oxidative reagents for removal of the excess of reductant are not required; (5) the procedure is simple and straightforward with a similar degree of accuracy and precision with the ISO standard methods.

4. Conclusions

The presence of a trace amount of copper ions significantly affects the accuracy of the International Standard Organization's tin (II) chloride and titanium(III) chloride reduction-potassium dichromate titrimetric method for the determination of total iron. The reduction of iron(III) by tin(II) chloride and titanium(III) chloride is sluggish and requires nearly boiling-point temperature and a precise control of the reductant and careful removal of excessive reductant. In comparison, iron(III) reduction by potassium borohydride catalyzed by copper ions is straightforward and rapid at ambient conditions. The use of potassium borohydride for dichromate titration in the determination of total iron content is of similar degrees of accuracy and precision with the ISO standard methods and is advantageous in terms of mercury pollution, reduction condition, copper interferences and turn-around-time of the analysis.

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