Talanta 125 (2014) 425–431

Contents lists available at ScienceDirect

Talanta

journal homepage: www.elsevier.com/locate/talanta

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

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ARTICLE INFO

Article history:
Received 19 October 2013
Received in revised form
26 February 2014
Accepted 10 March 2014
Available online 19 March 2014

Keywords:
Total iron content
Iron and copper ores
Potassium borohydride
Colorimetry
Dichromate titration

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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http://dx.doi.org/10.1016/j.talanta.2014.03.008
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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.