Determination of Iron in Iron Ores Using Enthalpimetric Flow Injection Analysis

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A method is described in which a dissolved sample of iron ore is injected into a flow manifold, after passing through a silver reductor column. The sample then merges with a dichromate solution and generates an enthalpimetric signal due to the oxidation of iron(II). The precision of the proposed method is approximately 0.3% and the sampling rate is 85 samples per hour. Interference from vanadium was negligible and titanium did not interfere. The results of the analysis of samples of iron ores by the proposed method agree with those obtained by titrimetric analysis.

Keywords: *Iron determination; flow enthalpimeter; flow injection analysis; iron ores*

The determination of iron in iron ores and other materials is usually carried out using oxidation - reduction titrimetry. In this procedure, the iron(III) is reduced with tin(II) chloride and the excess of tin(II) chloride is eliminated by treatment with mercury(II) chloride. A potential pollution hazard exists[1] because of the question of the disposal of the mercury residues. For this reason, procedures that do not employ mercury compounds have been sought, and the use of the silver reductor[2] has been proposed.[1,3]

Enthalpimetric methods have been reported[4] for the determination of iron in ores and other materials. Also, automated procedures are desirable because of the enhancement of the sampling rate, and the use of flow injection analysis has been suggested.[5] This paper describes an enthalpimetric method for the determination of iron in iron ores using flow injection analysis. Reduction of iron(III) to iron(II) is achieved by passing the sample through a column packed with metallic silver, followed by injection into a carrier stream that merges with a dichromate solution.

Experimental

Apparatus

A flow enthalpimeter described recently[6] was used. It consists of a peristaltic pump that impels the fluids toward an insulated 8-l water-bath, inside which the injector and flow manifolds are placed. Temperature differences are measured with two twin thermistors connected to a d.c. Wheatstone bridge, whose output voltage is monitored with a strip-chart recorder.

Manifold

Fig. 1 shows the manifold used in the determination of iron in iron ores. Polyethylene tubing of 0.5 mm i.d. was used for the sample, reagent and carrier streams. Pulse dampers (D_1 and D_2) similar to those described earlier[7] were used for the reagent and carrier streams. After entering the water-bath and also after the indicator cell (T_i), the fluids pass through temperature equilibration coils (E_1–E_4), which are stainless-steel tubes 0.5 mm i.d. and 1 m long. A laboratory-made acrylic proportional injector[8] (I) was used for the introduction of a volume of 100 µl of sample. The indicator (T_i) and reference (T_r) flow cells have a volume of about 17 µl and are laboratory-made acrylic blocks modelled as T-connectors, with the thermistor mounted perpendicular to the fluid stream. The reactor (R) is polyethylene tubing, 0.8 mm i.d. and 10 cm long, coated with Tygon tubing (Norton Specialty Plastics Division) of 1.5 mm i.d. and 3.5 mm o.d. The silver reductor column (C) consists of Tygon tubing, 3 mm i.d. and 10 cm long. The column was constructed and regenerated after use following a procedure given in the literature.[2] A sample commuter (S) was used to prevent air bubbles entering the reductor column.

Procedure

Analytical-reagent grade chemicals were used throughout.

About 0.1 g of sample (100 mesh, dried at 100 °C for 1 h) was accurately weighed and transferred into a 50-ml beaker. About 10 ml of concentrated hydrochloric acid were added and the beaker was covered with a watch-glass. The sample was digested on a hot-plate (60 °C) until dissolution was complete. In the samples analysed, no dark residues were observed and therefore no other treatment[4] for dissolution was applied. The watch-glass was removed from the beaker and the liquid was boiled off. The solid residue was dissolved with 1 M hydrochloric acid and the solution was cooled, filtered into a 100-ml calibrated flask and diluted to volume with 1 M hydrochloric acid. This sample solution was used to measure the enthalpimetric signal, using the flow manifold shown in Fig. 1. The concentration of iron in the sample solution, C_{Fe} (mg per 100 ml), was found by comparison with the signal from standard solutions of iron. These solutions were obtained by dissolving the metal in hot hydrochloric acid - water (1 + 1), boiling off the liquid, dissolving the residue in 1 M hydrochloric acid and standardising it titrimetrically against potassium dichromate solution. The percentage of total iron in the iron ore was found using the equation $Fe(\%) = (C_{Fe} \times 100)/m$, where m (mg) is the mass of sample initially taken.

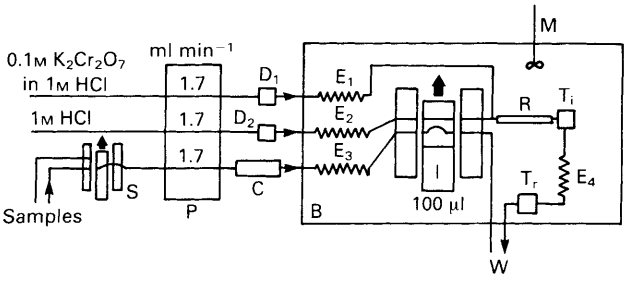

Fig. 1. Flow manifold for the determination of iron in iron ores. S, Sample commuter; P, peristaltic pump; D_1 and D_2, pulse dampers; C, silver reductor column; E_1–E_4, equilibration coils; B, insulated water-bath; I, injector; R, reactor tube; M, overhead stirrer; T_i and T_r, indicator and reference thermistor cells; W, waste. Sample introduction (100 µl) is accomplished by moving the central part of the injector (I) in the direction indicated by the arrow. Likewise, the change of samples is made by moving the central part of the sample commuter (S)

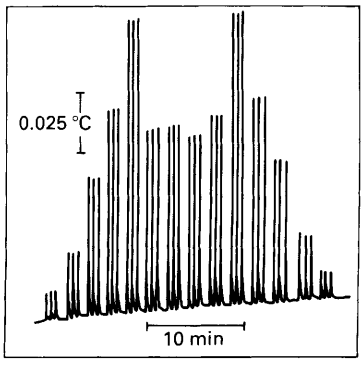

Fig. 2. Typical enthalpimetric signals for the determination of iron. Signals for four samples are shown in the centre of two calibration runs with standard solutions of concentrations equal to 13.92, 27.84, 55.69, 79.89 and 111.38 mg of iron per 100 ml. All measurements performed in triplicate

Table 1. Effect of interfering species on the determination of iron in iron ores

Species	ΔFe, %	Species	ΔFe, %
Cu(II)	4.6	Ni(II)	0.2
Mg(II)	0.0	Cr(III)	0.3
Ca(II)	0.0	Mo(VI)	0.8
Zn(II)	0.1	V(V)	0.4
Al(III)*	0.1	Ti(IV)†	0.1
Mn(II)	0.0		

* At 10% in the ore.
† At 20% in the ore.

Results and Discussion

A solid reagent is used for the reduction of iron(III), which has the advantage of quantitative reaction without the need to eliminate the excess of reductant. Also, the sample solution, the reagent and the carrier flow all have the same concentration of hydrochloric acid in order to avoid enthalpimetric effects due to heat of dilution. Under the experimental conditions employed, it was observed that no blank corrections were needed.

Experiments were conducted to determine how long the reductor column lasts before it needs to be regenerated. It was found that a column with about 1 g of silver can be used for more than 200 determinations of iron. Regeneration[2] is simple. Moreover, the reductor column has the advantage of self-indication of exhaustion, shown by the dark area that extends down the column.

Fig. 2 shows typical enthalpimetric signals for standard and sample solutions. Calibration runs performed with standard solutions of iron with concentations in the range 13–112 mg per 100 ml showed that the enthalpimetric signal, ΔT (°C), is related to the concentration of iron, C_{Fe} (mg per 100 ml), by the equation $\Delta T = -0.922 \times 10^{-3} + 1.192 \times 10^{-3} C_{Fe}$ with a correlation coefficient of 0.9999. As the average standard deviation of ten replicate analyses of five standard solutions in the range 13–112 mg per 100 ml was found to be 0.0004 °C, the precision with respect to iron concentration was approximately 0.3 mg per 100 ml.

In order to study the effect of potential interferences on the iron determination, several species were added, separately, to a 0.0100 M solution of iron(III) in 1 M hydrochloric acid. The amount of interfering species added was chosen to be equivalent to 5% *m/m* in the ore. Each solution, containing one such species, was passed through the reductor column and the iron concentration determined enthalpimetrically. The results are given in Table 1, expressed as the variation in the percentage of iron caused by the presence of the interference.

Table 2. Comparison of results of the analysis of samples of iron ores

Sample	Fe, % *m/m* Titrimetric method	Fe, % *m/m* Enthalpimetric method	Relative difference, %
IPT standard No. 21	68.55 ± 0.06*	68.4	−0.22
S_1	66.30	65.9	−0.60
S_2	63.88	63.9	+0.03
S_3	67.42	67.3	−0.18

* Certificated Fe content ± standard deviation.

Table 1 shows that the principal interfering species are copper and molybdenum, but these elements are usually not present in iron ores. Titanium, however, is normally found in iron ores but it does not interfere, even in large amounts. The result for the interference of titanium is in agreement with the findings of the manual method,[3] which uses the silver reductor. Vanadium can be reduced by metallic silver in 1 M hydrochloric acid.[2] Banerjee and Dutta[3] reported interference from vanadium in the determination of iron, affecting the end-point of the titration with dichromate. Table 1 shows that the interference of vanadium in the enthalpimetric method is small, considering the relatively large amount (5% *m/m*) added. This is probably due to the slow kinetics of the oxidation of vanadium by dichromate, which limits the extent of reaction taking place within the short time (around 3 s) that elapses between sample injection and detection. Taking into account the fact that the percentage of vanadium in iron ores is usually less than 1% *m/m*, its interference in the enthalpimetric method should be negligible.

Analyses of samples of iron ores, including a reference material [Instituto de Pesquisas Tecnológicas (IPT), SP, Brazil, standard No. 21], were performed by applying the proposed method and also by using titrimetric analysis with potentiometric detection. Table 2 shows the results obtained. For each sample the complete procedure, starting from sample dissolution, was repeated twice and the enthalpimetric signal was obtained in triplicate. The results indicate good agreement between the two methods, with an average relative difference of 0.26%.

The precision and accuracy of the enthalpimetric method are lower than those of the classical titrimetric method. However, the enthalpimetric procedure is faster, allowing a sampling rate of 85 samples per hour, with determinations in triplicate. The proposed method is free from pollution hazards due to the use of mercury compounds and also uses simple, inexpensive instrumentation.

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