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British Standard

Analysis of iron ores

Part 4. Methods for the determination of total iron content

Section 4.1 Titrimetric methods

[ISO title: Iron ores — Determination of total iron content — Titrimetric methods]

Analyse des minerais de fer

Partie 4. Méthodes de dosage du fer total

Section 4.1 Méthodes titrimétriques

Analyse von Eisenerzen

Teil 4. Verfahren zur Bestimmung des Gesamteisengehaltes

Abschnitt 4.1 Maßanalytische Verfahren

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National foreword

This Section of BS 7020 has been prepared under the direction of the Iron and Steel Standards Committee. It supersedes BS 4158 : Part 1 : 1967, which is withdrawn. It is identical with ISO 2597-1985 'Iron ores — Determination of total iron content — Titrimetric methods' published by the International Organization for Standardization (ISO).

Terminology and conventions. The text of the international standard has been approved as suitable for publication as a British Standard without deviation. Some terminology and certain conventions are not identical with those used in British Standards; attention is drawn especially to the following.

The comma has been used as a decimal marker. In British Standards it is current practice to use a full point on the baseline as the decimal marker.

In British Standards it is current practice to use the spelling 'sulphur' etc., instead of 'sulfur', etc.

Wherever the words 'International Standard' appear, referring to this standard, they should be read as 'Section of BS 7020'.

Cross-references

International standard	Corresponding British Standard
ISO 2596-1984	BS 7020 Analysis of iron ores Part 2 : 1988 Methods for the determination of hygroscopic moisture in analytical samples (Identical)
ISO 3081-1986	BS 5660 Methods of sampling iron ores Part 1 : 1987 Manual method of increment sampling (Identical)
ISO 3082-1987	Part 2 : 1987 Mechanical method of increment sampling and sample preparation (Identical)
ISO 3082-1986	BS 5661 : 1987 Method for preparation of samples of iron ores by manual means (Identical)
ISO 7764-1985	BS 7020 Analysis of iron ores Part 1 : 1988 Method for the preparation of pre-dried test samples for chemical analysis (Identical)

The reference to ISO 5725 is for information only.

Additional information. In clause 2 the footnotes to ISO 3081, ISO 3082 and ISO 3083 no longer apply as these standards have now been published.

Compliance with a British Standard does not of itself confer immunity from legal obligations.

British Standard

Analysis of iron ores

Part 4. Methods for the determination of total iron content

Section 4.1 Titrimetric methods

1 Scope and field of application

This International Standard specifies two titrimetric methods for the determination of the total iron content in iron ores using potassium dichromate after reduction of the trivalent iron by tin(II) chloride (method 1) or hydrogen sulfide (method 2).

Both methods are applicable to a concentration range of 30 to 72 % (m/m) of iron in natural iron ores, and iron ore concentrates and agglomerates including sinter products. For an unknown ore, it is recommended that the iron content be determined by both methods to check that the tin(II) chloride reduction method is satisfactory.

2 References

ISO 2596, *Iron ores — Determination of hygroscopic moisture in analytical samples — Gravimetric and Karl Fischer methods.*

ISO 3081, *Iron ores — Increment sampling — Manual method.*¹⁾

ISO 3082, *Iron ores — Increment sampling and sample preparation — Mechanical method.*²⁾

ISO 3083, *Iron ores — Preparation of samples — Manual method.*³⁾

ISO 7764, *Iron ores — Preparation of predried test samples for chemical analysis.*

3 Principle

3.1 Method 1: Reduction by tin(II) chloride

Decomposition of the test portion:

- a) for samples containing less than 0,1 % (m/m) vanadium, 0,1 % (m/m) molybdenum or 0,1 % (m/m) copper: by treatment with hydrochloric acid, the residue

being filtered off, ignited, treatment with hydrofluoric and sulfuric acids to remove silica and fused with potassium pyrosulfate.

Dissolution of the melt in hydrochloric acid, precipitation of iron with ammonia solution, redissolution of the precipitate in hydrochloric acid, and addition of this solution to the main solution.

- b) for samples containing more than 0,1 % (m/m) vanadium: by fusion with alkali, the melt being leached with water and filtered, the filtrate being discarded. Dissolution of the residue in hydrochloric acid.

Reduction of trivalent iron in the solution, using tin(II) chloride. Oxidation of excess reductant with mercury(II) chloride.

Titration of the reduced iron with potassium dichromate solution, using sodium diphenylaminesulfonate as indicator.

3.2 Method 2: Reduction by hydrogen sulfide

Decomposition of the test portion by treatment with hydrochloric acid, the residue being filtered off, ignited, treated with hydrofluoric and sulfuric acids to remove silica, and fused with potassium pyrosulfate. Dissolution of the melt in the main solution, addition of sulfuric acid and evaporation to expel all chlorides. Dissolution of the sulfates in water.

After adjustment of the acidity, reduction of the trivalent iron in the solution, using hydrogen sulfide. Boiling to remove excess hydrogen sulfide. After cooling, titration of the reduced iron with potassium dichromate solution using sodium diphenylaminesulfonate as indicator.

4 Reagents

During the analysis, use only reagents of recognized analytical grade, and only distilled water or water of equivalent purity.

1) At present at the stage of draft. (Revision of ISO 3081-1973.)

2) At present at the stage of draft.

3) At present at the stage of draft. (Revision of ISO 3083-1973.)

	Method
4.1 Hydrochloric acid , ρ 1,16 to 1,19 g/ml.	1 and 2
4.2 Hydrochloric acid , ρ 1,16 to 1,19 g/ml, diluted 1 + 1.	1
4.3 Hydrochloric acid , ρ 1,16 to 1,19 g/ml, diluted 1 + 2.	1
4.4 Hydrochloric acid , ρ 1,16 to 1,19 g/ml, diluted 1 + 10.	1
4.5 Hydrochloric acid , ρ 1,16 to 1,19 g/ml, diluted 1 + 50.	1 and 2
4.6 Sulfuric acid , ρ 1,84 g/ml, diluted 1 + 1.	1 and 2
4.7 Hydrofluoric acid , 40 % (m/m), ρ 1,13 g/ml, or 48 % (m/m), ρ 1,19 g/ml.	1 and 2
4.8 Ammonia solution , ρ 0,90 g/ml.	1
4.9 Hydrogen sulfide .	2

CAUTION — Hydrogen sulfide is highly toxic and shall be used only in a fume cupboard.

The hydrogen sulfide may be taken from a cylinder. Alternatively a Kipp generator can be used.

NOTE — The hydrogen sulfide gas from a Kipp generator should be passed through a water trap to remove any entrained iron salts.

4.10 Sodium carbonate (Na_2CO_3), anhydrous.	1
Heat for 30 min at 500 °C, or confirm that the water content is not more than 1 % (m/m) (by heating a test portion for 30 min at 500 °C and measuring the loss in mass).	
4.11 Sodium peroxide (Na_2O_2), dry powder.	1
4.12 Potassium pyrosulfate ($\text{K}_2\text{S}_2\text{O}_7$), fine powder.	1 and 2
4.13 Sulfuric acid-phosphoric acid mixture .	1 and 2
Cautiously pour 150 ml of sulfuric acid (ρ 1,84 g/ml) into about 300 ml of water while stirring, cool in a water-bath, add 150 ml of phosphoric acid (ρ 1,70 g/ml) and dilute with water to 1 litre.	
4.14 Tin(II) chloride , 100 g/l solution.	1

Place 200 ml of the hydrochloric acid (4.1) into a 1 litre beaker and add 100 g of crystalline tin(II) chloride dihydrate ($\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$) in small increments, while heating the solution on a water-bath.

Cool the solution and dilute with water to 1 litre.

Store this solution in a brown glass bottle with the addition of a small quantity of granular or mossy tin metal.

NOTE — The tin(II) chloride solution may be prepared in 250 ml lots.

4.15 Sulfuric acid-hydrogen sulfide wash solution .	2
To 900 ml of water, add 10 ml of sulfuric acid (ρ 1,84 g/ml). Dilute to 1 litre and pass a rapid stream of hydrogen sulfide gas through the solution for at least 10 min.	
4.16 Mercury(II) chloride (HgCl_2), 50 g/l solution.	1
4.17 Potassium permanganate (KMnO_4), 30 g/l solution.	1
4.18 Sodium diphenylaminesulfonate solution .	1 and 2

Dissolve 0,2 g of powdered sodium diphenylaminesulfonate ($\text{C}_6\text{H}_5\text{NHC}_6\text{H}_4\text{SO}_3\text{Na}$) in a small volume of water and dilute with water to 100 ml.

Store the solution in a brown glass bottle.

4.19 Ammonium iron(II) sulfate , approximately 0,1 mol/l solution.	1 and 2
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Dissolve 40 g of ammonium iron(II) sulfate hexahydrate [$\text{Fe}(\text{NH}_4)_2(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}$] in sulfuric acid (ρ 1,84 g/ml, diluted 1 + 19).

Transfer to a 1 000 ml one-mark volumetric flask and dilute to the mark with sulfuric acid (ρ 1,84 g/ml, diluted 1 + 19). Standardize the solution against the potassium dichromate solution (4.21) by taking a 25 ml aliquot of the solution and titrating as shown in 7.5.3.

4.20 Sodium hydroxide , 20 g/l solution.	1
4.21 Potassium dichromate , standard volumetric solution, $c(\text{K}_2\text{Cr}_2\text{O}_7) = 0,016\,67\text{ mol/l}$.	1 and 2

Pulverize about 6 g of potassium dichromate standard reagent in an agate mortar, dry in an air-bath at 140 to 150 °C for 2 h, and cool to room temperature in a desiccator. Dissolve 4,904 g of this dried and pulverized potassium dichromate in water and dilute the solution with water to exactly 1 000 ml.

Record on the stock bottle the temperature at which this dilution was made.

5 Apparatus

Ordinary laboratory apparatus, and

5.1 Zirconium, vitreous carbon or alkali-resistant sintered alumina crucibles, 25 to 30 ml capacity.

5.2 Weighing spatula, of a non-magnetic material or demagnetized stainless steel.

5.3 Cylinder of hydrogen sulfide or Kipp generator (method 2).

5.4 Muffle furnace, capable of being maintained at between 500 ± 10 and 800 ± 10 °C.

6 Sampling and samples

6.1 Laboratory sample

For analysis, use a laboratory sample of minus 100 μm particle size which has been taken in accordance with ISO 3081 or ISO 3082 and prepared in accordance with ISO 3082 or ISO 3083. In the case of ores with significant contents of combined water or oxidizable compounds, use a particle size of minus 160 μm .

NOTE — A guideline on significant contents of combined water and oxidizable compounds is incorporated in ISO 7764.

6.2 Preparation of test samples

Depending on the ore type, proceed in accordance with either 6.2.1 or 6.2.2.

6.2.1 Ores with significant contents of combined water or oxidizable compounds

Prepare an air-equilibrated test sample in accordance with ISO 2596 with the following types of ores:

- a) processed ores containing metallic iron;
- b) natural or processed ores in which the sulfur content is higher than 0,2 % (m/m);
- c) natural or processed ores in which the content of combined water is higher than 2,5 % (m/m).

6.2.2 Ores outside the scope of 6.2.1

Prepare a predried test sample as follows.

Thoroughly mix the laboratory sample and, taking multiple increments, extract a test sample in such a manner that it is representative of the whole contents of the container. Dry the test sample at 105 ± 2 °C as specified in ISO 7764. (This is the predried test sample.)

7 Procedure

7.1 Number of determinations

Carry out the analysis at least in duplicate in accord with annex A, independently, on one test sample (6.2).

NOTE — The expression “independently” implies that the repetition of the procedure shall be carried out at a different time.

7.2 Blank test and check test

In each run, one blank test and one analysis of a certified reference material of the same type of ore shall be carried out in parallel with the analysis of the ore sample(s) under the same conditions. A test sample of the certified reference material shall be prepared in the manner appropriate to the type of ore involved (see 6.2). (See note 1.)

When the analysis is carried out on several samples at the same time, the blank value may be represented by one test, provided that the procedure is the same and the reagents used are from the same reagent bottles.

When the analysis is carried out on several samples of the same type of ore at the same time, the analytical value of one certified reference material may be used.

NOTES

1 The certified reference material should be of the same type as the sample to be analysed and the properties of the two materials should be sufficiently similar to ensure that in either case no significant changes in the analytical procedure would become necessary.

2 The certified reference material is used only to validate the performance of the analytical procedure and expressly not to standardize the potassium dichromate solution.

7.3 Determination of hygroscopic moisture content

When the ore type conforms to the specifications of 6.2.1, determine the hygroscopic moisture content in accordance with ISO 2596, simultaneously with the taking of the test portion (7.4), for the determination of iron content.

7.4 Test portion

Taking several increments, weigh, to the nearest 0,000 2 g, approximately 0,4 g of the test sample (6.2) using a non-magnetic spatula (5.2).

NOTES

1 For samples of iron content higher than 68 % (m/m), weigh approximately 0,38 g.

2 When predried test samples are being used, the test portion should be taken and weighed quickly on the day of predrying to avoid re-absorption of moisture.

7.5 Determination — Method 1: Reduction by tin(II) chloride

7.5.1 Decomposition of the test portion

7.5.1.1 For samples containing less than 0,1 % (m/m) vanadium, 0,1 % (m/m) molybdenum and 0,1 % (m/m) copper