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Iron ores — Determination of total iron content — Volumetric method

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FOREWORD

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International Standard ISO 2597 was drawn up by Technical Committee ISO/TC 102, *Iron ores*, and circulated to the Member Bodies in February 1972.

It has been approved by the Member Bodies of the following countries :

Australia	Japan	Sweden
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The Member Bodies of the following countries expressed disapproval of the document on technical grounds :

Belgium
France

Iron ores — Determination of total iron content — Volumetric method

1 SCOPE AND FIELD OF APPLICATION

This International Standard specifies two volumetric methods for the determination of the total iron content in iron ores, using potassium dichromate after reduction of the trivalent iron by stannous chloride (method 1) or hydrogen sulphide (method 2).

Both methods are applicable to natural iron ores, concentrates and agglomerates, including sinter products. For an unknown iron ore it is recommended that the iron content be determined by both methods to check that the stannous chloride reduction method is satisfactory.

2 REFERENCES

ISO 2596, *Iron ores — Determination of hygroscopic moisture in analytical samples.*

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

ISO 3082, *Iron ores — Increment sampling — Mechanical method.*¹⁾

ISO 3083, *Iron ores — Preparation of samples.*

3 PRINCIPLE

3.1 Method 1 : Reduction by stannous chloride

Decomposition of the test portion :

a) *for samples not containing more than 0,1 % vanadium, 0,1 % molybdenum or 2 % copper* : by treatment with hydrochloric acid, the residue being filtered off, ignited, treated with hydrofluoric and sulphuric acids and fused with sodium carbonate. 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 % 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 stannous chloride. Oxidation of excess reductant with mercuric chloride.

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

3.2 Method 2 : Reduction by hydrogen sulphide

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

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

4 REAGENTS

Distilled water or deionized water shall be used in the preparation of reagents and throughout the analysis. Except where otherwise stated, all reagents shall be of recognized analytical reagent quality.

	Method
4.1 Hydrochloric acid ($d = 1,19$)	1 and 2
4.2 Hydrochloric acid, diluted 1 + 1.	1
4.3 Hydrochloric acid, diluted 1 + 2.	1
4.4 Hydrochloric acid, diluted 1 + 10.	1
4.5 Hydrochloric acid, diluted 1 + 50.	1 and 2
4.6 Sulphuric acid ($d = 1,84$).	
4.7 Sulphuric acid, diluted 1 + 1.	1 and 2

1) In preparation.

	Method		Method
4.8 Sulphuric acid , diluted 1 + 19.		4.19 Sodium diphenylaminesulphonate solution.	1 and 2
4.9 Phosphoric acid ($d = 1,70$).		Dissolve 0,2 g of powdered sodium diphenylaminesulphonate ($C_6H_5NHC_6H_4.SO_3Na$) in a small volume of water and dilute with water to 100 ml.	
4.10 Hydrofluoric acid , 40 % ($d = 1,13$).	1 and 2	Store the solution in a brown glass bottle.	
4.11 Sulphuric acid-phosphoric acid mixture.	1 and 2	4.20 Ferrous ammonium sulphate solution,	1 and 2
Pour 150 ml of sulphuric acid (4.6) into about 300 ml of water while stirring, cool in a water bath, add 150 ml of phosphoric acid (4.9) and dilute with water to 1 l.		approximately 0,1 N.	
4.12 Ammonia solution ($d = 0,90$).	1	Dissolve 40 g of ferrous ammonium sulphate [$FeSO_4 \cdot (NH_4)_2SO_4 \cdot 6H_2O$] in sulphuric acid (4.8).	
4.13 Stannous chloride solution , 100 g/l.	1	Transfer to a 1 l volumetric flask and dilute to volume with the same acid. Standardize against the standard potassium dichromate solution (4.18), using diphenylaminesulphonate as indicator (see 7.3.4).	
Place 200 ml of hydrochloric acid (4.1) into a 1 l beaker and add 100 g of crystalline stannous chloride ($SnCl_2 \cdot 2H_2O$) in small increments, while heating the solution on a water bath.		4.21 Sodium carbonate	1 and 2
Cool the solution and dilute with water to 1 l.		4.22 Sodium peroxide	1
This solution should be stored in a brown glass bottle with the addition of a small quantity of granular or mossy tin metal.		4.23 Sodium hydroxide , 20 g/l solution.	1
4.14 Hydrogen sulphide.	2	5 APPARATUS	
The hydrogen sulphide may be taken from a cylinder. Alternatively a Kipp generator can be used (see Note 9.1).		Ordinary laboratory apparatus.	
4.15 Sulphuric acid-hydrogen sulphide wash solution.	2	6 SAMPLING AND SAMPLE PREPARATION	
To 900 ml of water add 10 ml of sulphuric acid (4.6). Dilute to 1 l and pass a rapid stream of hydrogen sulphide gas through the solution for at least 10 min.		Use an air-dried sample of minus 160 μm in size, which has been taken in accordance with ISO 3081 or ISO 3082 and prepared in accordance with ISO 3083.	
4.16 Mercuric chloride ($HgCl_2$) solution, 50 g/l.	1	7 PROCEDURE	
4.17 Potassium permanganate ($KMnO_4$) solution, 30 g/l.	1	7.1 Number of analyses, determination of hygroscopic moisture, application of standard sample and blank test	
4.18 Potassium dichromate , standard volumetric solution, 0,1 N.	1 and 2	The analysis shall be carried out generally in duplicate, independently (see Note 9.3), on one ore sample.	
Pulverize about 6 g of potassium dichromate standard reagent (see Note 9.2), in an agate mortar, dry in an air-bath at 105 to 110 °C for 3 to 4 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.		Simultaneously with the analysis, two 10 g test portions shall be taken to determine the hygroscopic moisture of the sample in accordance with ISO 2596.	
		In each run, one analysis of a standard sample of the same type of ore (see Note 9.4) or, in default, a sample of chemically pure ferric oxide and one blank test shall be carried out in parallel with the analysis of one ore sample, under the same conditions.	
		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 standard sample may be used.

7.2 Test portion

Weigh, to the nearest 0,000 2 g, approximately 0,40 g of the test sample.

7.3 Determination — Method 1: Reduction by stannous chloride

7.3.1 Decomposition of test portion

7.3.1.1 FOR SAMPLES NOT CONTAINING MORE THAN 0,1 % VANADIUM 0,1 % MOLYBDENUM AND 2 % COPPER

Place the test portion (7.2) in a 300 ml beaker, add 30 ml of hydrochloric acid (4.1), cover the beaker with a watch glass, and heat the solution gently without boiling, to decompose the ore (see Notes 9.5, 9.6 and 9.7). Wash the watch glass with a spray of water, and dilute the solution to about 50 ml with warm water. Filter the insoluble residue on a close-texture paper and wash with warm hydrochloric acid (4.5) until the yellow colour of ferric chloride is no longer observed. Then wash it with warm water six to eight times. Collect the filtrate and washings in a 600 ml beaker and concentrate by heating. (Main solution.)

Place the filter paper and the residue in a platinum crucible, dry, char the paper and finally ignite at 750 to 800 °C. Allow the crucible to cool. Moisten the residue in the crucible with sulphuric acid (4.7), add about 5 ml of hydrofluoric acid (4.10), and heat gently to remove silica and sulphuric acid.

Add to the cool crucible 2 g of sodium carbonate (4.21); heat gently at first and then strongly, until a clear melt is obtained. Allow the melt to cool, place the platinum crucible in a 300 ml beaker, add about 100 ml of warm water and about 5 ml of hydrochloric acid (4.1), and heat gently to dissolve the melt. Rinse and remove the platinum crucible.

Adjust this solution to slight alkalinity by the addition of ammonia solution (4.12), boil the solution for a few minutes and remove from the source of heat.

When the precipitate has settled, collect the precipitate of iron hydroxide on a rapid filter paper, and wash six to eight times with warm water. Discard the filtrate and washings.

Place the beaker containing the main solution under the funnel and dissolve the precipitate on the filter paper by pouring over it 10 ml of hot hydrochloric acid (4.3); wash the filter, first six to eight times with warm hydrochloric acid (4.5), then twice with hot water, and follow the procedure given under 7.3.2.

7.3.1.2 FOR SAMPLES CONTAINING MORE THAN 0,1 % VANADIUM

Place the test portion (7.2) in an alumina crucible, add about 4 g of fusion mixture [1 + 2 mixture of sodium carbonate (4.21) and sodium peroxide (4.22)], mix thoroughly, and heat to fusion. Allow the melt to cool, place the crucible in a 300 ml beaker, add about 100 ml of warm water, and boil for a few minutes to leach the melt. Take out the crucible, wash with warm water, and preserve the crucible. Cool the solution and filter through a filter paper of dense texture. Wash the filter six to eight times with sodium hydroxide solution (4.23) and discard the filtrate and washings.

Transfer the precipitate on the filter into the original beaker by washing with water, add 10 ml of hydrochloric acid (4.1), and warm to dissolve the precipitate. Dissolve the remaining precipitate in the alumina crucible with hot hydrochloric acid (4.2) and wash the crucible with hot water. The filter is to be washed three times with warm hydrochloric acid (4.3), several times with warm hydrochloric acid (4.5), and finally with warm water until the washings are no longer acid. Combine the solution and washings in a 500 ml beaker, evaporate this solution to about 30 ml and follow the procedure given under 7.3.2.

7.3.2 Reduction

Heat the solution, now containing all the iron, to just below the boiling point and add three to five drops of potassium permanganate solution (4.17). Maintain at this temperature for 5 min to oxidize any arsenic and organic matter and evaporate to about 30 ml. Wash the cover and inside wall of the beaker with a small amount of hot hydrochloric acid (4.4). Immediately add stannous chloride solution (4.13), drop by drop, while swirling the liquid in the beaker. When the yellow colour of the ferric chloride has disappeared, add one additional drop of the stannous chloride solution and cool the solution in a water cooler. Add all at once 8 ml of the mercuric chloride solution (4.16), mix gently, and allow the solution to stand for 5 min.

7.3.3 Titration

Dilute the solution to about 300 ml with cold water, add 30 ml of the sulphuric-phosphoric acid mixture (4.11), and titrate with the standard potassium dichromate solution (4.18) using five drops of the sodium diphenyl-aminosulphonate solution (4.19) as indicator. The end point is obtained when the green colour of the solution changes to bluish green and a final drop of the titrant imparts a violet colour.

7.3.4 Blank test

Determine the blank value of the reagents concurrently with the test determination, using the same amounts of all reagents and following all the steps of the procedure. Immediately before titrating with the potassium dichromate solution (4.18), add 1,0 ml of the ferrous ammonium sulphate solution (4.20) (see Note 9.8) and make the appropriate correction.

7.4 Determination — Method 2 : Reduction by hydrogen sulphide

7.4.1 Decomposition of test portion

Place the test portion (7.2) in a 300 ml beaker, add 30 ml of hydrochloric acid (4.1), cover the beaker with a watch glass, and heat the solution gently without boiling to decompose the ore (see Notes 9.5 and 9.7).

Wash the watch glass with a jet of water, and dilute to 50 ml with warm water. Filter the insoluble residue on a close-texture paper. Wash the residue with warm hydrochloric acid (4.5), until the yellow colour of ferric chloride is no longer observed. Then wash with warm water six to eight times. Collect the filtrate and washings in a 600 ml beaker. (Main solution.)

Place the filter paper and residue in a platinum crucible, dry and ignite at 750 to 800 °C. Allow the crucible to cool, moisten the residue with sulphuric acid (4.7) add about 5 ml of hydrofluoric acid (4.10), and heat gently to remove silica and sulphuric acid. Add to the cold crucible 2 g of sodium carbonate (4.21), heat gently at first and 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 (4.1), and warm to dissolve the melt. Remove and wash the crucible, and add this solution to the main solution.

7.4.2 Reduction

Add 10 ml of sulphuric acid (4.7) to the main solution and evaporate to copious fumes of sulphur trioxide (see Note 9.9). Dilute to about 350 ml, and heat until a clear solution is obtained. Pass hydrogen sulphide (4.14) through the warm solution for 15 min at a rate of about 1 l/min. Digest at about 60 °C for a further 15 min, filter through a small filter paper into a 1 l conical flask and wash 15 times with the hydrogen sulphide-sulphuric acid wash solution (4.15). Add to the filtrate 10 ml of sulphuric acid (4.7) and boil until free from hydrogen sulphide (see Note 9.10), and then for an additional 10 min. Cool to room temperature.

7.4.3 Titration

Dilute to about 300 ml with water, add 30 ml of the sulphuric acid-phosphoric acid mixture (4.11) and titrate this solution with standard potassium dichromate solution (4.18), using 5 drops of the sodium diphenyl-aminesulphonate (4.19) as indicator. The end point is obtained when the green colour of the solution changes to bluish green and a final drop of the titrant imparts a violet colour.

7.4.4 Blank test

Determine the blank value of the reagents concurrently with the test determination, using the same amounts of all reagents and following all the steps of the procedure. Immediately before titrating with the potassium dichromate (4.18), add 1.0 ml of the ferrous ammonium sulphate solution (4.20) (see Note 9.8), and make the appropriate correction.

8 EXPRESSION OF RESULTS

8.1 Calculation of total iron content

The total iron content, as a percentage by mass, is calculated from the following formula :

$$\text{Fe \% (m/m)} = \frac{V_1 - V_2}{m} \times 0,005\,584\,7 \times 100 \times K$$

where

V_1 is the volume, in millilitres, of potassium dichromate standard solution (4.18) used for titration of the analytical sample;

V_2 is the volume, in millilitres, of potassium dichromate standard solution (4.18) used for titration in the blank test;

m is the mass, in grams, of the test portion;

K is the conversion factor found from the following formula :

$$K = \frac{100}{100 - A}$$

where A is the hygroscopic moisture content, as a percentage by mass.

8.2 General treatment of analytical values

8.2.1 Blank value

The analytical values obtained shall first be corrected with the blank value and then the total iron content of each analysis shall be calculated as specified in 8.1.

Analytical results (total iron content) shall be calculated as a percentage by mass and recorded to the third decimal place, figures beyond the third decimal place being unconditionally discarded.

8.2.2 Adoption of analytical values

The analytical value of the sample shall be accepted when the analytical value of the corresponding standard sample (or pure ferric oxide) agrees with the standard value within the limit of permissible tolerance of a standard sample (or pure ferric oxide) and the difference between the two values of the analytical sample does not exceed the permissible tolerance for the analytical sample specified in the table in 8.3.

When the analytical value of the standard sample (or pure ferric oxide) is outside the limit of the permissible tolerance (see table, second column) a simultaneous analysis shall be carried out on one analytical sample and one standard sample of the same type of ore (or pure ferric oxide), with one blank test. The two analytical values of the standard sample shall be examined for adoption as above. This procedure shall be repeated until acceptable values are obtained.