INTERNATIONAL STANDARD

ISO 9682-2

First edition
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Iron ores — Determination of manganese content —

Part 2: Periodate spectrophotometric method

Minerais de fer — Dosage du manganèse

Partie 2: Méthode spectrophotométrique au periodate

Reference number
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Foreword

ISO (the International Organization for Standardization) is a worldwide federation of national standards bodies (ISO member bodies). The work of preparing International Standards is normally carried out through ISO technical committees. Each member body interested in a subject for which a technical committee has been established has the right to be represented on that committee. International organizations, governmental and non-governmental, in liaison with ISO, also take part in the work. ISO collaborates closely with the International Electrotechnical Commission (IEC) on all matters of electrotechnical standardization.

International Standards are drafted in accordance with the rules given in the ISO/IEC Directives, Part 2.

The main task of technical committees is to prepare International Standards. Draft International Standards adopted by the technical committees are circulated to the member bodies for voting. Publication as an International Standard requires approval by at least 75 % of the member bodies casting a vote.

Attention is drawn to the possibility that some of the elements of this document may be the subject of patent rights. ISO shall not be held responsible for identifying any or all such patent rights.

ISO 9682-2 was prepared by Technical Committee ISO/TC 102, *Iron ore and direct reduced iron*, Subcommittee SC 2, *Chemical analysis*.

This first edition of ISO 9682-2 cancels and replaces ISO 3886:1986, which has been technically revised. It has been updated to alter the manner in which precision data are presented.

ISO 9682 consists of the following parts, under the general title *Iron ores — Determination of manganese content*:

— *Part 1: Flame atomic absorption spectrometric method*

— *Part 2: Periodate spectrophotometric method*

Iron ores — Determination of manganese content —

Part 2:
Periodate spectrophotometric method

WARNING — This part of ISO 9682 may involve hazardous materials, operations and equipment. This part of ISO 9682 does not purport to address all of the safety problems associated with its use. It is the responsibility of the user of this part of ISO 9682 to establish appropriate health and safety practices and determine the applicability of regulatory limitations prior to use.

1 Scope

This part of ISO 9682 specifies a spectrophotometric method using sodium periodate for the determination of the mass fraction of manganese in iron ores.

This method is applicable to a mass-fraction range of 0,02 % to 8 % of manganese in natural iron ores, and iron ore concentrates and agglomerates, including sinter products.

2 Normative references

The following referenced documents are indispensable for the application of this document. For dated references, only the edition cited applies. For undated references, the latest edition of the referenced document (including any amendments) applies.

ISO 648, *Laboratory glassware — One-mark pipettes*

ISO 1042, *Laboratory glassware — One-mark volumetric flasks*

ISO 3082, *Iron ores — Sampling and sample preparation procedures*

ISO 3696, *Water for analytical laboratory use — Specification and test methods*

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

3 Principle

A test portion is decomposed by one of the following methods:

a) treatment with hydrochloric, nitric and perchloric acids;

b) sintering with sodium peroxide, followed by treatment with hydrochloric and perchloric acids.

The mixture is filtered and the residue is ignited, followed by treatment with hydrofluoric and sulfuric acids, and fusion with sodium carbonate. The cooled melt is dissolved in the main solution.

Managanese in an aliquot is oxidized to permanganate ion, using sodium periodate in sulfuric acid/phosphoric acid medium.

The absorbance due to the permanganate ion is measured spectrophotometrically at a wavelength of about 535 nm.

4 Reagents

During the analysis, use only reagents of recognized analytical grade, and only water that conforms to grade 2 of ISO 3696 except that water which is free from organic matter (4.1) shall be used for the spectrophotometric measurement.

4.1 Water, free from organic matter.

Add 20 ml of sulfuric acid (4.9) to 1 litre of water, bring to the boil, add several crystals of sodium periodate, continue boiling for 10 min, then cool.

4.2 Sodium peroxide (Na_2O_2), powder.

Sodium peroxide should be kept away from humidity and should not be used once it has begun to agglomerate.

4.3 Sodium carbonate (Na_2CO_3), anhydrous.

4.4 Hydrochloric acid, ρ 1,16 g/ml to 1,19 g/ml.

4.5 Hydrochloric acid, ρ 1,16 g/ml to 1,19 g/ml, dilute 1 + 9.

4.6 Nitric acid, ρ 1,4 g/ml.

4.7 Perchloric acid, 60 % (by mass) (ρ 1,54 g/ml) or 70 % (by mass) (ρ 1,67 g/ml).

4.8 Hydrogen peroxide, 3 % (by volume).

4.9 Sulfuric acid, ρ 1,84 g/ml, diluted 1 + 1.

4.10 Sulfuric acid, ρ 1,84 g/ml, diluted 1 + 100.

4.11 Hydrofluoric acid, 40 % (by mass) (ρ 1,13 g/ml).

4.12 Sulfuric acid/phosphoric acid mixture.

Carefully pour 100 ml of sulfuric acid (ρ 1,84 g/ml) into about 600 ml of water while stirring, cool, add 150 ml of phosphoric acid (ρ 1,70 g/ml) and dilute to 1 000 ml with water.

4.13 Sodium periodate ($NaIO_4$) solution, 50 g/l.

4.14 Sodium nitrite ($NaNO_2$) solution, 10 g/100 ml.

4.15 Manganese, standard solutions.

4.15.1 Stock solution

Dissolve 0,500 g of pure metallic manganese in 20 ml of nitric acid (4.6), add 20 ml of sulfuric acid (4.9) and heat to dense white fumes for about 10 min to expel all oxides of nitrogen. Cool, add about 100 ml of water to dissolve the salt, transfer into a 500 ml volumetric flask, dilute to the mark with water and mix.

1 ml of stock solution contains 1,00 mg of manganese.

4.15.2 Standard solution A

Take 100 ml of stock solution (4.15.1) and dilute to 1 000 ml in a volumetric flask.

1 ml of this standard solution contains 0,100 mg of manganese.

4.15.3 Standard solution B

Take 250 ml of standard solution A (4.15.2) and dilute to 1 000 ml in a volumetric flask.

1 ml of this standard solution contains 0,025 mg of manganese.

5 Apparatus

Ordinary laboratory equipment, including one-mark pipettes and volumetric flasks complying with the specifications of ISO 648 and ISO 1042, and the following.

5.1 Spectrophotometer, suitable for the measurement of absorbance at approximately 535 nm.

5.2 Nickel crucible, free of manganese.

5.3 Pletinum crucible, of capacity 25 ml to 30 ml.

6 Sampling and samples

6.1 Laboratory sample

For analysis, use a laboratory sample of minus 100 µm particle size which has been taken and prepared in accordance with ISO 3082. In the case of ores having 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 predried test samples

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

WARNING — Perchloric acid vapour may cause explosions in the presence of ammonia, nitrous fumes or organic matter in general.

7.1 Number of determinations

Carry out the analysis at least in duplicate in accordance with Annex A, independently, on one predried test sample.

NOTE The expression “independently” means that the second and any subsequent result is not affected by the previous result(s). For this particular analytical method, this condition implies that the repetition of the procedure is carried out either by the same operator at a different time or by a different operator, including, in either case, appropriate recalibration.

7.2 Test portion

Taking several increments, weigh, to the nearest 0,000 2 g, approximately 1 g of the predried test sample obtained in accordance with 6.2.

The test portion should be taken and weighed quickly in order to avoid reabsorption of moisture.

7.3 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 predried test sample of the certified reference material shall be prepared as specified in 6.2.

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. Where a certified reference material is not available, a reference material may be used (see 8.2.4).

Where 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.

Where 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.

7.4 Calibration

7.4.1 Samples containing more than 0,1 % (by mass) of manganese

7.4.1.1 Set of calibration solutions and formation of the absorbing compound

Into a series of five 300 ml beakers, introduce 2,0 ml; 5,0 ml; 10,0 ml; 15,0 ml and 20,0 ml of manganese standard solution A (4.15.2). Add 30 ml of sulfuric acid/phosphoric acid mixture (4.12), and dilute to about 60 ml with water (4.1).

Add 10 ml of sodium periodate solution (4.13) to each solution, cover each beaker with a watch-glass, heat to boiling, and maintain just below boiling point for 10 min after colour development of the permanganate ion. Cool each solution, transfer to a series of five 100 ml volumetric flasks, make up to the mark with water (4.1) and mix.

7.4.1.2 Calibration compensation solution

Prepare a calibration compensation solution according to 7.4.1.1, but omitting the manganese standard solution A.

7.4.1.3 Spectrophotometric measurements

Transfer a part of each solution (7.4.1.1) to a spectrophotometric cell of suitable thickness, and measure the absorbance of each, A_{i1}, where i is 1 to 5 cm optical path length, with the spectrophotometer (5.1), at the wavelength of maximum absorbance near 535 nm, after having adjusted the instrument to zero absorbance against the calibration compensation solution (7.4.1.2).

Add sodium nitrite solution (4.14), drop by drop, to the solutions in the volumetric flasks, while mixing, until 1 drop in excess decolorizes the pink colour of the permanganate ion; transfer a part of each solution to the corresponding spectrophotometric cell, and measure the absorbances, A_{i2}, as described in the first paragraph.

NOTE An increase in the volume of the solution by addition of sodium nitrite solution is disregarded.

The measurement of absorbance should not be postponed unduly after decoloration of the pink colour of the permanganate ion by sodium nitrite solution, because reoxidation of the manganese ion occurs on standing.

7.4.1.4 Plotting the calibration graph

Plot a calibration graph showing the differences between the absorbances, $A_{i1} - A_{i2}$, of the set of calibration solutions as a function of the quantities of manganese contained in these solutions.

7.4.2 Samples containing less than 0,1 % manganese

7.4.2.1 Set of calibration solutions and formation of the absorbing compound

As in 7.4.1.1, but using manganese standard solution B (4.15.3) instead of manganese standard solution A.

For mass fractions of manganese below 0,1 %, the heating time should be approximately 30 min and, if necessary, water (4.1) should be added to maintain the volume.

7.4.2.2 Calibration compensation solution

Prepare a calibration compensation solution according to 7.4.2.1, but omitting the manganese standard solution B.

7.4.2.3 Spectrophotometric measurements

Proceed as in 7.4.1.3, but using the solutions from 7.4.2.1.

7.4.2.4 Plotting the calibration graph

See 7.4.1.4.

7.5 Determination

7.5.1 Decomposition of the test portion

If the decomposition is to be based on acid attack, proceed as instructed in 7.5.1.1. If the decomposition is to be based on alkali sintering, proceed as instructed in 7.5.1.2.

7.5.1.1 Acid attack

Place the test portion (7.2) in a 300 ml beaker, add 30 ml of hydrochloric acid (4.4), cover the beaker with a watch-glass and heat the solution gently without boiling.

For decomposition of the test portion, place the beaker for about 1 h on the low temperature zone (60 °C to 100 °C) of the hotplate, then transfer to a higher temperature zone and heat for about 10 min at just under boiling point.

Add 5 ml of nitric acid (4.6), 20 ml of perchloric acid (4.7), and 0,2 ml of sulfuric acid (4.9), cover the beaker again with the watch-glass, heat until dense white fumes of perchloric acid appear, and maintain a steady refluxing of acid on the walls of the beaker for about 10 min.

Allow the beaker to cool, add about 50 ml of warm water and a few drops of hydrogen peroxide (4.8), heat the mixture to dissolve the soluble salts, and boil to decompose the excess of hydrogen peroxide.

Filter the solution through a close-texture paper. Wash the beaker with water, scrubbing the wall with a rubber-tipped glass rod. Wash the residue first with three or four portions of sulfuric acid (4.10) and then with warm water. Collect the filtrate and washings in a 300 ml beaker and reserve as the main solution. Keep the filter paper with the residue and continue according to 7.5.2.

7.5.1.2 Alkali sinter attack

Place the test portion (7.2) in a 40 ml nickel crucible free of manganese (see Note 1), add about 3 g of sodium peroxide powder (4.2), mix well using a platinum or nickel spatula, and tamp the mixture. Place the crucible for 1 or 2 min at the entrance of a muffle furnace, the temperature of which is regulated at 400 °C ± 20 °C, and then into the closed furnace for about 1 h to effect sintering. Take the crucible out of the furnace and cool.

Transfer the sintered mass to a 300 ml beaker, add 30 ml of water (see Note 2) and cover the beaker with a watch-glass.

Rinse the crucible first with water and then once with hydrochloric acid (4.5), and add the washings to the bulk solution. Acidify slowly with 30 ml of hydrochloric acid (4.4) and heat the solution gently to decompose the sintered mass. Add 30 ml of perchloric acid (4.7) and 0,2 ml of sulfuric acid (4.9), cover the beaker again with the watch-glass, heat until dense white fumes of perchloric acid appear and maintain a steady refluxing of acid on the walls of the beaker for about 10 min.

Continue according to 7.5.1.1, starting with “Allow the beaker to cool,...”.

NOTE 1 An alkali-resistant alumina crucible free of manganese may be used in place of a nickel crucible.

NOTE 2 If the volume of water added is insufficient, bumping may occur on subsequent heating. Therefore the volume, for safety, may be increased up to 100 ml.

7.5.2 Treatment of the residue

Place the residue from 7.5.1 with the filter in a platinum crucible, dry, ash the paper, and finally ignite at 950 °C to 1 050 °C. Allow the crucible to cool, then moisten the residue with sulfuric acid (4.9). Add 5 ml to 15 ml of hydrofluoric acid (4.11), depending on the silica content, heat gently to expel silica, and fume off sulfuric acid. Allow the crucible to cool, add 2 g of sodium carbonate (4.3), and heat, gently at first, then finally to dull red, to fuse the residue.

Allow the melt to cool, place the crucible in the beaker containing the main solution from 7.5.1, and heat gently to dissolve the melt. Take out the crucible and rinse it with water.

7.5.3 Treatment of the test solution

Evaporate the solution to approximately 50 ml. Cool to room temperature, transfer directly, or filter if necessary, into a 100 ml volumetric flask for mass fractions of manganese less than 4,0 %, or a 500 ml volumetric flask for mass fractions of manganese between 4,0 %, and 8,0 %, and dilute with water to the mark, shaking at intervals.

7.5.4 Spectrophotometric measurements

7.5.4.1 Formation of the absorbing compound

Transfer to a 300 ml beaker an aliquot of the solution from 7.5.3, chosen in accordance with Table 1, and add 30 ml of sulfuric acid/phosphoric acid mixture (4.12). Dilute to about 60 ml with water.

Table 1 — Aliquots

Expected mass fraction of manganese %	Aliquots
0,02 up to 0,1	take a 25,0 ml aliquot out of 100 ml
0,1 up to 1,0	take a 20,0 ml aliquot out of 100 ml
1,0 up to 2,0	take a 10,0 ml aliquot out of 100 ml
2,0 up to 4,0	take a 5,0 ml aliquot out of 100 ml
4,0 up to 8,0	take a 10,0 ml aliquot out of 500 ml

Add 10 ml of sodium periodate solution (4.13), cover the beaker with a watch-glass, heat to boiling, and maintain just below boiling point for 10 min after colour development of the permanganate ion. Cool the solution, transfer to a 100 ml volumetric flask, make up to the mark with water (4.1) and mix.

For mass fractions of manganese below 0,1 %, the heating time should be approximately 30 min and, if necessary, water (4.1) should be added to maintain the volume.

7.5.4.2 Spectrophotometric measurements

Transfer a part of the solution into a spectrophotometric cell having a suitable thickness, and measure the absorbance, A_1, with the spectrophotometer (5.1), at a wavelength of the maximum absorption located near 535 nm, after having adjusted the instrument to zero absorbance against water (4.1).

Add sodium nitrite solution (4.14), drop by drop, to the solution in the volumetric flask, while mixing, until 1 drop in excess decolorizes the pink colour of the permanganate ion. Transfer a part of this solution to the same spectrophotometric cell, and measure the absorbance, A_2, as described in the first paragraph. Rinse the spectrophotometric cell carefully after each measurement.

NOTE An increase in the volume of the solution by addition of sodium nitrite solution is disregarded.

The measurement of absorbance should not be postponed unduly after decoloration of the pink colour of the permanganate ion by sodium nitrite solution, because reoxidation of the manganese ion occurs on standing.

Determine the quantity of manganese from the difference between these absorbances, $A_1 - A_2$, by using the calibration graph prepared as instructed, specified in 7.4.1.4 or 7.4.2.4.

8 Expression of results

8.1 Calculation of mass fraction of manganese

The mass fraction of manganese, w_{Mn}, expressed as a percentage, is calculated to four decimal places using the equation

$$w_{Mn} = \frac{m_1 V_0}{m_0 V_1} \times 100 \qquad (1)$$

where

m_0 is the mass, in grams, of the test portion (7.2);

m_1 is the mass, in grams, of manganese in the aliquot of sample solution in Table 1, after correction for the blank value (7.3), obtained from the calibration graph;

V_0 is the total volume, in millilitres, of the test solution depending on the mass fraction of manganese (7.5.3);

V_1 is the volume, in millilitres, taken as an aliquot from Table 1.

The mass fraction of manganese shall be expressed to the fourth decimal place.

8.2 General treatment of results

8.2.1 Repeatability and permissible tolerance

The precision of this analytical method is expressed by the following regression equations:

$$R_d = 0{,}015\,3X + 0{,}001\,5 \quad (2)$$

$$P = 0{,}038\,8X + 0{,}008\,6 \quad (3)$$

$$\sigma_d = 0{,}005\,4X + 0{,}000\,5 \quad (4)$$

$$\sigma_L = 0{,}012\,8X + 0{,}002\,9 \quad (5)$$

where

R_d is the independent duplicate limit;

P is the permissible tolerance between laboratories;

σ_d is the independent duplicate standard deviation;

σ_L is the between-laboratories standard deviation;

X is the mass fraction of manganese, expressed as a percentage, of the test sample, calculated as follows:

— for the within-laboratory Equations (2) and (4), the arithmetic mean of the duplicate values;

— for the between-laboratory Equations (3) and (5), the arithmetic mean of the final results (8.2.3) of the two laboratories.

See Annexes B and C.

8.2.2 Determination of analytical result

Having computed the independent duplicate results according to Equation (1), compare them with the independent duplicate limit (R_d), using the procedure given in Annex A, and obtain the final laboratory result μ (see 8.2.3).

8.2.3 Between-laboratories precision

Between-laboratories precision is used to determine the agreement between the final results reported by two laboratories. The assumption is that both laboratories followed the procedure described in 8.2.2.

Compute the following quantity:

$$\mu_{1,2} = \frac{\mu_1 + \mu_2}{2} \quad (6)$$

where

μ_1 is the final result reported by laboratory 1;

μ_2 is the final result reported by laboratory 2;

$\mu_{1,2}$ is the mean of the final results.

Substitute $\mu_{1,2}$ for X in Equation (3) and calculate P.

If $|\mu_1 - \mu_2| \leqslant P$, the final results are in agreement.

8.2.4 Check for trueness

The trueness of the analytical method shall be checked by applying it to a certified reference material (CRM) or a reference material (RM) (see the second paragraph of 7.3). Calculate the analytical result (μ) for the CRM/RM using the procedures in 8.1 and 8.2.1 to 8.2.3, and compare it with the reference or certified value A_c. There are two possibilities:

a) $|\mu_c - A_c| \leqslant C$ in which case, the difference between the reported result and the certified/reference value is statistically insignificant;

b) $|\mu_c - A_c| > C$ in which case, the difference between the reported result and the certified/reference value is statistically significant.

where

μ_c is the final result for the CRM/RM;

A_c is the certified/reference value for the CRM/RM;

C is a value dependent on the type of CRM/RM used.

Certified reference materials used for this purpose should be prepared and certified in accordance with ISO Guide 35:2006, *Reference materials — General and statistical principles for certification*.

For a CRM/RM certified by an interlaboratory test programme:

$$C = 2\sqrt{\sigma_L^2 + \frac{\sigma_d^2}{n} + V(A_c)}$$

where

$V(A_c)$ is the variance of the certified/reference value A_c (= 0 for a CRM/RM certified by only one laboratory);

n is the number of replicate determinations carried out on the CRM/RM.

CRMs certified by only one laboratory should be avoided unless they are known to have an unbiased certified value.

8.2.5 Calculation of final results

The final result is the arithmetic mean of the acceptable analytical values for the test sample, or as otherwise determined by the operations specified in Annex A, calculated to four decimal places and rounded off to the second decimal place as follows:

a) where the figure in the third decimal place is less than 5, it is discarded and the figure in the second decimal place is kept unchanged;

b) where the figure in the third decimal place is 5 and there is a figure other than 0 in the fourth decimal place, or when the figure in the third decimal place is greater than 5, the figure in the second decimal place is increased by one;

c) where the figure in the third decimal place is 5 and the figure 0 is in the fourth decimal place, the 5 is discharged and the figure in the second decimal place is kept unchanged if it is 0, 2, 4, 6 or 8 and increased by one if it is 1, 3, 5, 7 or 9.

8.3 Oxide factor

The oxide factor, expressed as a percent, is given by the following equation:

$$w_{MnO} = 1{,}291\ 2\ w_{Mn}$$

9 Test report

The test report shall include the following information:

a) name and address of the testing laboratory;

b) date of issue of the test report;

c) a reference to this part of ISO 9682;

d) details necessary for the identification of the sample;

e) result of the analysis;

f) reference number of the result;

g) any characteristics noticed during the determination, and any operations not specified in this part of ISO 9682 which may have had an influence on the result, either for the test sample or the certified reference material(s).