INTERNATIONAL STANDARD

ISO 10204

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Iron ores — Determination of magnesium — Flame atomic absorption spectrometric method

Minerais de fer — Dosage du magnésium — Méthode par spectrométrie d'absorption atomique dans la flamme

Reference number
ISO 10204:2006(E)

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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 10204 was prepared by Technical Committee ISO/TC 102, *Iron ore and direct reduced iron*, Subcommittee SC 2, *Chemical analysis*.

This second edition cancels and replaces the first edition (ISO 10204:1992), which has been technically revised. It has been updated to alter the manner in which precision data are presented.

Iron ores — Determination of magnesium — Flame atomic absorption spectrometric method

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

1 Scope

This International Standard specifies a flame atomic absorption spectrometric method for the determination of the mass fraction of magnesium in iron ores.

This method is applicable to mass fractions of magnesium between 0,25 % and 3,5 % in natural iron ores, 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 7764, *Iron ores — Preparation of predried test samples for chemical analysis*

3 Principle

The test portion is decomposed by treatment with hydrochloric acid and a small amount of nitric acid.

The solution is evaporated to dehydrate silica, followed by dilution and filtration.

The residue is ignited and silica is removed by evaporation with hydrofluoric and sulfuric acids. The residue is fused with sodium carbonate and the cooled melt is dissolved in the filtrate.

The solution is aspirated into the flame of an atomic absorption spectrometer using an air/acetylene burner.

Absorbance values obtained for magnesium are compared with those obtained from the calibration solutions.

NOTE A dinitrogen oxide/acelylene flame may be used for the determination, in which case the sensitivity is decreased by a factor of about 3.

4 Reagents

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

4.1 Sodium carbonate (Na_2CO_3), anhydrous.

4.2 Hydrochloric acid, ρ 1,19 g/ml.

4.3 Hydrochloric acid, ρ 1,19 g/ml, diluted 1 + 9.

4.4 Nitric acid, ρ 1,4 g/ml.

4.5 Hydrofluoric acid, ρ 1,13 g/ml, 40 % (m/m), or ρ 1,185 g/ml, 48 % (m/m).

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

4.7 Background solution.

Dissolve 10 g of iron wire [minimum purity 99,9 % (mass fraction), of mass fraction of magnesium less than 0,000 2 %] in 50 ml of hydrochloric acid (4.2) and oxidize by adding nitric acid (4.4) drop by drop. Evaporate until a syrupy consistency is obtained. Add 20 ml of hydrochloric acid (4.2) and dilute to 200 ml with water. Dissolve 17 g of sodium carbonate (4.1) in water, add carefully to the iron solution and heat to remove carbon dioxide. Transfer the cooled solution to a 1 000 ml one-mark volumetric flask, dilute to volume with water and mix.

4.8 Lanthanum chloride solution.

Dissolve 50 g of lanthanum chloride ($LaCl_3 \cdot xH_2O$) [of mass fraction of magnesium less than 0,002 %] in 50 ml of hydrochloric acid (4.2) and 300 ml of hot water. Cool and dilute to 1 litre.

4.9 Mangnesium standard solution, 15 µg Mg/ml.

Dissolve 0,300 0 g of oxide-free magnesium metal [minimum purity 99,9 % (mass fraction)] by slowly adding 75 ml of hydrochloric acid (4.2), diluted 1 + 3. When dissolved, cool, transfer to a 1 000 ml one-mark volumetric flask, dilute to volume with water and mix. Transfer 10 ml of this solution to a 200 ml one-mark volumetric flask, dilute to volume with water and mix.

4.10 Magnesium calibration solutions.

Using pipettes, transfer 2,0 ml; 5,0 ml; 10,0 ml; 20,0 ml; 40,0 ml; and 50,0 ml portions of the magnesium standard solutions (4.9) to 200 ml volumetric flasks (see next paragraph). Add 6 ml of hydrochloric acid (4.2), 60 ml of background solution (4.7) and 40 ml of lanthanum chloride solution (4.8) to each flask. Dilute all the solutions to volume with water and mix. Prepare a zero magnesium calibration solution by transferring 60 ml of the background solution to a 200 ml volumetric flask. Then add 6 ml of hydrochloric acid (4.2) and 40 ml of lanthanum chloride solution. Dilute all the solutions to volume with water and mix.

The range of magnesium that can be covered may vary from instrument to instrument. Attention should be paid to the minimum criteria given in 5.3. For instruments having high sensitivity, smaller portions of standard solution or a more diluted standard solution can be used.

5 Apparatus

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

5.1 Platinum crucible, of minimum capacity 30 ml.

5.2 Muffle furnace, capable of maintaining a temperature of approximately 1 100 °C.

5.3 Atomic absorption spectrometer, equipped with an air/acetylene burner.

The atomic absorption spectrometer used in this method shall meet the following criteria:

a) Minimum sensitivity: the absorbance of the most concentrated magnesium calibration solution (4.10) shall be at least 0,3.

b) Graph linearity: the slope of the calibration graph covering the top 20 % of the concentration range (expressed as a change in absorbance) shall not be less than 0,7 of the value of the slope for the bottom 20 % of the concentration range determined in the same way.

c) Minimum stability: the standard deviation of the absorbance of the most concentrated calibration solution and that of the zero calibration solution, each being calculated from a sufficient number of repetitive measurements, shall be less than 1,5 % and 0,5 %, respectively, of the mean value of the absorbance of the most concentrated calibration solution.

The use of a strip chart recorder and/or digital readout device is recommended to evaluate criteria a), b) and c) and for all subsequent measurements.

NOTE Instrument parameters may vary with each instrument. The following parameters were successfully used in several laboratories and they can be used as guidelines. An air/acetylene flame was used.

Hollow cathode lamp, mA	15
Wavelength, nm	285,2
Air flow rate, l/min	22
Acetylene flow rate, l/min	4,2

In systems where the values shown above for gas flow rates do not apply, the ratio of the gas flow rates may still be a useful guideline.

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 way that it is representative of the whole contents of the container. Dry the test sample at 105 °C ± 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 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 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 will become necessary.

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 Determination

7.4.1 Decomposition of the test portion

Transfer the test portion (7.2) to a 250 ml beaker. Moisten with a few millilitres of water, add 25 ml of hydrochloric acid (4.2), cover with a watch-glass and heat gently. Increase the heat and digest just below boiling, until no further attack is apparent. Add 2 ml of nitric acid (4.4) and digest for several minutes. Remove the watch-glass and evaporate the solution to dryness. Heat the salts on a hot-plate at 105°C to 110°C for 30 min. Add 5 ml of hydrochloric acid (4.2), cover the beaker with a watch-glass, and warm for several minutes. Add 50 ml of water, stirring to avoid the hydrolysis of titanium, and heat to boiling. Wash the watch-glass and the walls of the beaker, and filter the solution through a medium-texture paper, containing some filter pulp, into a 250 ml beaker. Carefully remove all adhering particles with a rubber-tipped glass rod or moistened filter paper and transfer to the filter, washing three times with dilute hydrochloric acid (4.3), then with hot water until the paper is free of iron. Transfer the paper and residue to a platinum crucible (5.1). Evaporate the filtrate to about 100 ml and retain it.

7.4.2 Treatment of the residue

Ignite the filter paper and residue in a platinum crucible (5.1) at a low temperature (500 °C to 800 °C). Cool, moisten with a few drops of water, add 3 or 4 drops of sulfuric acid (4.6) and 10 ml of hydrofluoric acid (4.5). Evaporate slowly to expel silica and then fume to remove the excess sulfuric acid. Ignite at about 700°C. Add 1,0 g of sodium carbonate (4.1) to the residue (see note), cover the crucible, and fuse over a burner or in a muffle furnace (5.2) until a clear melt is obtained (at about 1 100 °C for 15 min).

NOTE If difficulties are experienced with the fusion, 2 g of sodium carbonate (4.1) may be used, in which case it is advisable to double the amount of sodium carbonate and the volume of hydrochloric acid (4.2) in the background solution (4.7).

7.4.3 Preparation of the test solution

Dissolve the cooled melt in the retained filtrate (see 7.4.1), then remove and wash the crucible and the cover (see next paragraph).

If the solution is cloudy at this stage, indicating the presence of substantial amounts of hydrolysed titanium, it should be filtered prior to the transfer to the 200 ml volumetric flask.

Transfer the solution to a 200 ml one-mark volumetric flask, dilute to volume with water and mix. Transfer an appropriate aliquot of this solution (see Table 1) to a 200 ml one-mark volumetric flask and add 40 ml of lanthanum chloride solution (4.8). Add the amount of background solution (4.7) and hydrochloric acid (4.2) indicated in Table 1, dilute to volume with water and mix (see last paragraph). (This solution is the final test solution.)

Transfer corresponding amounts of blank test solution to a 200 ml one-mark volumetric flask, add the same volumes of lanthanum chloride solution (4.8), background solution (4.7) and hydrochloric acid (4.2) as used for the test solution. Dilute to volume with water and mix. (This solution is the diluted blank test solution.)

Table 1 — Dilution guide for test solution

Expected mass fraction of magnesium in sample w_{Mg} %	Aliquot ml	Equivalent mass of sample g	Background solution (4.7) to be added ml	Hydrochloric acid (4.2) to be added ml
$0{,}01 \leqslant w_{Mg} \leqslant 0{,}1$	60	0,30	40	4
$0{,}1 \leqslant w_{Mg} \leqslant 0{,}25$	40	0,20	50	4
$0{,}25 \leqslant w_{Mg} \leqslant 1{,}25$	10	0,05	60	6
$1{,}25 \leqslant w_{Mg} \leqslant 3{,}00$	2	0,01	60	6

The dilutions shown in Table 1 will provide concentrations of magnesium falling within the range of the calibration solutions. For instruments having high sensitivity, smaller portions of the test solution may be preferable. Avoid aliquot portions of less than 2 ml by making a preliminary dilution. Treat the blank test solution similarly. In this case, the amounts of background solution (4.7) and hydrochloric acid (4.2) should be adjusted.

7.4.4 Adjustment of the atomic absorption spectrometer

Set the wavelength for magnesium (285,2 nm) to obtain minimum absorbance. Fit the correct burner and, in accordance with the manufacturer's instructions, light the appropriate flame. After 10 min of preheating the burner, adjust the fuel flow and burner to obtain maximum absorbance while aspirating the calibration solution of highest mass fraction of magnesium (see 4.10). Then evaluate the criteria in 5.3.

Aspirate water and the calibration solution to establish that the absorbance reading is not drifting and then set the initial reading for water to zero absorbance.

7.4.5 Atomic absorption measurements

Aspirate the calibration solutions (4.10) and the final test solution (see 7.4.3) in order of increasing absorption, starting with the diluted blank test solution and the zero calibration solution, with the final test solution being aspirated at the appropriate point in the series. Aspirate water between each solution and record the readings when stable responses are obtained.

Repeat the measurements at least twice.

If necessary, convert the average of the readings for each solution to absorbance. Obtain the net absorbance of each calibration solution by subtracting the absorbance of the zero calibration solution. In a similar manner, obtain the net absorbance of the final test solution by subtracting the absorbance of the diluted blank test solution. Prepare a calibration graph by plotting the net absorbance values of the calibration solutions against the concentration of magnesium, in micrograms per millilitre.

Convert the net absorbance values of the final test solution to micrograms of magnesium per millilitre by means of the calibration graph.

8 Expression of results

8.1 Calculation of mass fraction of magnesium

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

$$w_{\mathrm{Mg}} = \frac{\rho_{\mathrm{Mg}} \times 200}{m \times 10\,000}$$

$$= \frac{\rho_{\mathrm{Mg}}}{m \times 50} \tag{1}$$

where

ρ_{Mg} is the concentration, in micrograms per millilitre, of magnesium in the final test solution;

m is the mass, in grams, of sample contained in a 200 ml volume of the final test solution, taking into account any preliminary dilution that may have been made.

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:[1)]

$$R_{\mathrm{d}} = 0{,}0607\, X^{0{,}7230} \tag{2}$$

$$P = 0{,}0801\, X^{0{,}8496} \tag{3}$$

$$\sigma_{\mathrm{d}} = 0{,}0215\, X^{0{,}7230} \tag{4}$$

$$\sigma_{\mathrm{L}} = 0{,}0237\, X^{0{,}9077} \tag{5}$$

where

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

- within-laboratory Equations (2) and (4): the arithmetic mean of the duplicate values,
- between-laboratories Equations (3) and (5): the arithmetic mean of the final results (8.2.5) of the two laboratories;

[1)] Additional information is given in Annexes B and C.

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.

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_c (see 8.2.5).

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 same procedure as described in 8.2.2.

Compute the following quantity:

$$\mu_{12} = \frac{\mu_1 + \mu_2}{2} \tag{6}$$

where

μ_1 is the final result reported by laboratory 1;

μ_2 is the final result reported by laboratory 2;

μ_{12} is the mean of final results.

Substitute μ_{12} 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 second paragraph of 7.3). Calculate the analytical result (μ_c) for the RM/CRM using the procedures in 8.1 and 8.2, 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 reference/certified value is statistically insignificant;

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

where

μ_c is the analytical result for the certified reference material;

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 certified by an interlaboratory test programme

$$C = 2\left[\sigma_{\mathrm{L}}^{2} + \frac{\sigma_{\mathrm{d}}^{2}}{n} + V\left(A_{\mathrm{c}}\right)\right]^{1/2}$$

where

$V(A_{\mathrm{c}})$ is the variance of the certified value A_{c} (= 0 for a CRM certified by only one laboratory);

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

A CRM certified by only one laboratory should be avoided unless it is known to have an unbiased certified value.

8.2.5 Calculation of final result

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.

The arithmetic mean of the acceptable analytical values, calculated to the fourth decimal place, is 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 where 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 discarded and the figure in the second decimal place is kept unchanged if it is 0, 2, 4, 6 or 8 and is 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:

$$w_{\mathrm{MgO}} = 1{,}658\ w_{\mathrm{Mg}}$$

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 International Standard;

d) details necessary for the identification of the sample;

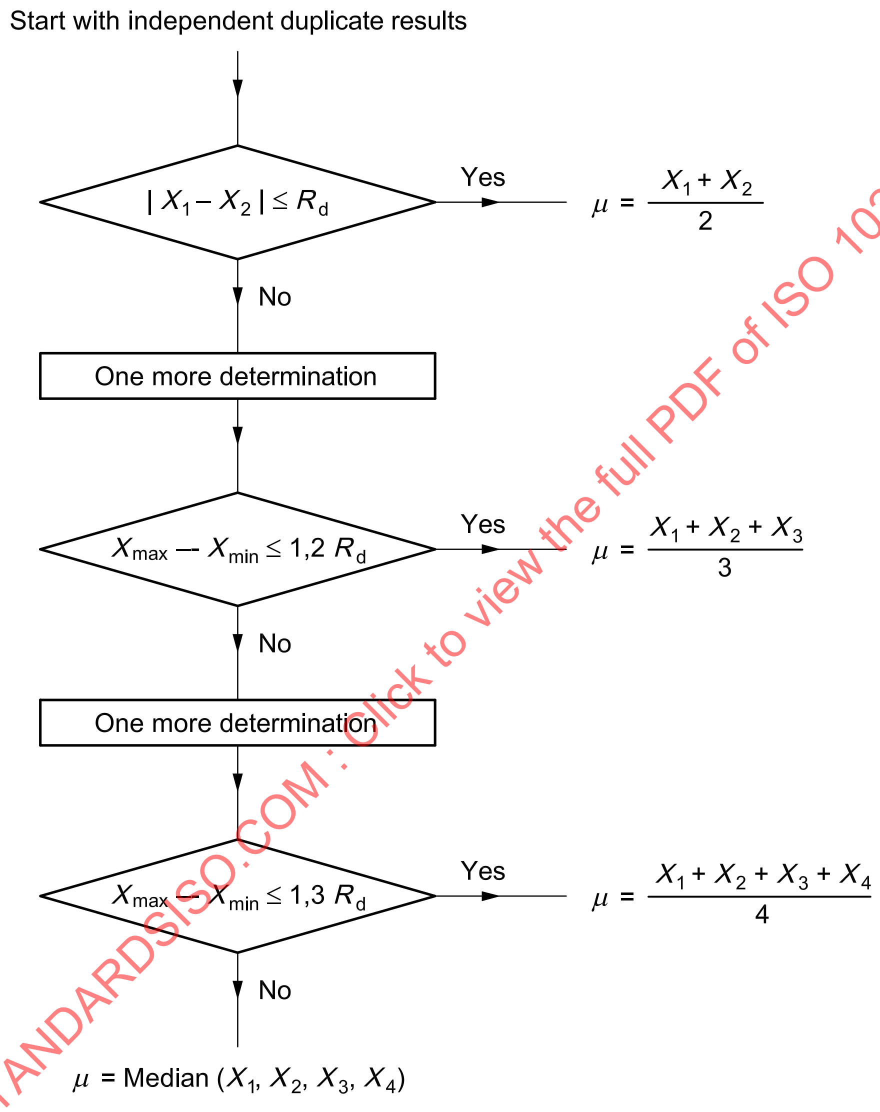
e) result of the analysis;

f) reference number of the result;

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

Annex A
(normative)

Flowsheet of the procedure for the acceptance of analytical values for test samples



R_d: as defined in 8.2.1.