INTERNATIONAL STANDARD

ISO 10204

Third edition
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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
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Foreword

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The procedures used to develop this document and those intended for its further maintenance are described in the ISO/IEC Directives, Part 1. In particular the different approval criteria needed for the different types of ISO documents should be noted. This document was drafted in accordance with the editorial rules of the ISO/IEC Directives, Part 2 (see www.iso.org/directives).

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. Details of any patent rights identified during the development of the document will be in the Introduction and/or on the ISO list of patent declarations received (see www.iso.org/patents).

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For an explanation on the meaning of ISO specific terms and expressions related to conformity assessment, as well as information about ISO's adherence to the WTO principles in the Technical Barriers to Trade (TBT) see the following URL: Foreword - Supplementary information.

The committee responsible for this document is ISO/TC 102, *Iron ore and direct reduced iron*, Subcommittee SC 2, *Chemical analysis*.

This third edition cancels and replaces the second edition (ISO 10204:2006), which has been technically revised.

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

WARNING — This International Standard might 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 0,010 % and 2,00 % in natural iron ores, iron ore concentrates, and agglomerates, including sinter products.

2 Normative references

The following documents, in whole or in part, are normatively referenced in this document and are indispensable for its application. 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 — Single-volume 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*

ISO 9516-1, *Iron ores — Determination of various elements by X-ray fluorescence spectrometry — Part 1: Comprehensive procedure*

ISO 80000-1:2009, *Quantities and units — Part 1: General*

ISO Guide 35, *Reference materials — General and statistical principles for certification*

3 Principle

The test portion is decomposed by the treatment with hydrochloric acid and a small amount of nitric acid and then 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 obtained is aspirated into the flame of an atomic absorption spectrometer using an air-acetylene burner.

The absorbance values obtained for magnesium are compared with those obtained from calibration solutions.

NOTE A dinitrogen oxide/acetylene flame can 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 grade and only water that complies with Grade 2 of ISO 3696.

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 % (mass fraction) or ρ 1,185 g/ml, 48 % (mass fraction).

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

4.7 Pure iron, minimum purity 99,9 % (mass fraction), of mass fraction of magnesium less than 0,0002 %.

4.8 Background solution

Dissolve 5,0 g pure iron (4.7) 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.

4.9 Lanthanum chloride solution

Dissolve 50 g of lanthanum chloride ($LaCl_3 \cdot 7H_2O$) (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 l.

4.10 Magnesium standard solution, 25 µg Mg/ml.

Dissolve 0,500 0 g of oxide-free magnesium metal [minimum purity 99,9 % (mass fraction)] or 0,829 2 g of analytical grade magnesium oxide (dried and weighed in accordance with 4.9 in ISO 9516-1) 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.

4.11 Magnesium calibration solutions

Using pipettes, transfer 2,0 ml, 5,0 ml, 10,0 ml, 15,0 ml, and 20,0 ml portions of magnesium standard solution (4.10) to 200 ml volumetric flasks (see next paragraph). Add 6 ml of hydrochloric acid (4.2), 60 ml of background solution (4.8), and 40 ml of lanthanum chloride solution (4.9) to each flask. Dilute the solution to volume with water and mix. Prepare a zero magnesium calibration solution by transferring 60 ml of background solution (4.8) to a 200 ml volumetric flask. Then add 6 ml of hydrochloric acid (4.2) and 40 ml of lanthanum chloride solution (4.9). Dilute the solution 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 with a lid, 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.

WARNING — Follow the manufacturer's instructions for igniting and extinguishing the dinitrogen oxide/acetylene flame to avoid possible explosion hazards. Wear tinted safety glasses whenever the flame is burning.

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 (see 4.11) shall be at least 0,3.

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

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 can vary with each instrument. The following parameters were successfully used in several laboratories and they can be used as guidelines. Solutions were aspirated into an air-acetylene burner.

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

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

6 Sampling and samples

6.1 Laboratory sample

For analysis, use a laboratory sample of −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 −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 0,5 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

7.3.1 Blank test

7.3.1.1 Preparation of blank test solution

Using pure iron (4.7) with a 60 % mass of the test portion in place of the test portion, carry out the same procedure described from 7.4.1 to 7.4.3 as the test portion in parallel with it.

7.3.1.2 Measurement of blank value

Carry out in accordance with 7.4.5.

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 that the reagents used are from the same reagent bottles.

7.3.2 Check test

In each run, 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 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 until dry. 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 diluted hydrochloric acid (4.3), then with hot water until the filter 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, and then add three or four 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) can 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 (4.8).

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 cover (see next paragraph).

If the solution is cloudy at this stage, indicating the presence of substantial amounts of hydrolyzed 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.

When the mass fraction of magnesium in sample is expected to be ≤0,10 %, add 40 ml of lanthanum chloride solution (4.9), dilute to volume with water, and mix. This solution is the final test solution for the low Mg sample.

When the mass fraction of magnesium in sample is expected to be >0,10 %, 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 (4.9). Add the amount of background solution (4.8) 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 for the high Mg sample.

The dilutions shown in Table 1 will provide mass 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.

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 (4.8) to be added ml	Hydrochloric acid (4.2) to be added ml
$0,10 < w_{Mg} \leq 1,0$	20	0,05	55	5
$1,0 < w_{Mg} \leq 2,0$	5	0,0125	60	6

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 4.11). Then evaluate the criteria in 5.3.

When the sensitivity of the instrument is too high to meet the criteria, it is permitted to set analytical conditions by which the absorbance is not the maximum. In this case, the criteria in 5.3 shall be met and the conditions shall not be changed during the measurements of all solutions prepared in each independent analysis.

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 (4.11), the blank test solution (7.3.1.1), and the final test solution (see 7.4.3) in order of increasing absorption, starting with the 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. 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 blank test solution and 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 Formula (1):

$$w_{\mathrm{Mg}} = \frac{(\rho_{\mathrm{Mg}} - \rho_{\mathrm{MgB}}) \times 200}{m \times 10\,000} = \frac{\rho_{\mathrm{Mg}} - \rho_{\mathrm{MgB}}}{m \times 50} \qquad (1)$$

where

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

ρ_{MgB} is the mass concentration, in micrograms per millilitre, of magnesium in the blank 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 which might 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 formulae:

NOTE Additional information is given in Annex B and Annex C.

$$R_{\mathrm{d}} = 0{,}030\,39\, X^{0{,}817\,28} \qquad (2)$$

$$P = 0{,}049\,46\, X^{0{,}790\,88} \qquad (3)$$

$$\sigma_{\mathrm{d}} = 0{,}010\,74\, X^{0{,}817\,28} \qquad (4)$$

$$\sigma_{\mathrm{L}} = 0{,}017\,61\, X + 0{,}000\,59 \qquad (5)$$

where

R_{d} is the independent duplicate limit;

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

- within-laboratory Formula (2) and Formula (4): the arithmetic mean of the duplicate values;
- between-laboratories Formula (3) and Formula (5): the arithmetic mean of the final laboratory results (8.2.2) of the two laboratories;

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 Formula (1), compare them with the independent duplicate limit (R_d), using the procedure given in Annex A and obtain the final laboratory result, μ, which calculated to five decimal places for mass fractions of magnesium less than 1 % and to four decimal places for mass fractions greater than 1 %.

8.2.3 Between-laboratories precision

Between-laboratories precision is used to determine the agreement between the final laboratory results reported by two laboratories.

Compute the following quantity using Formula (6):

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

where

μ_{12} is the mean of final results;

μ_1 is the final result reported by laboratory 1;

μ_2 is the final result reported by laboratory 2.

Substitute μ_{12} for X in Formula (3) and calculate P.

If $\left|\mu_1 - \mu_2\right| \leq P$, 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).

Calculate the analytical result (μ_C) for the CRM using the procedures in 8.1 and compare it with the certified value A_C. The following are two possibilities:

a) $\left|\mu_c - A_C\right| \leq C$ in which case, the difference between the reported result and the certified value is statistically insignificant;

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

where

μ_c is the final result for the certified reference material;

A_C is the reference value for the CRM;

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

Certified reference materials used for this purpose should be prepared and certified in accordance with ISO Guide 35.

C shall be calculated as given by Formula (7):

$$C = 2\sqrt{\frac{s_c^2}{N_c} + \sigma_L^2 + \frac{\sigma_d^2}{n}} \qquad (7)$$

where

s_c is the standard deviation of laboratory means (each value for calculating the standard deviation is the average value in each certifying laboratory) of the CRM;

N_c is the number of certifying laboratories;

n is the number of replicate determinations carried out on the CRM;

σ_d is the independent duplicate standard deviation;

σ_L is the between-laboratories standard deviation.

For CRMs certified by only one laboratory, C shall be calculated as given by Formula (8):

$$C = 2\sqrt{2\sigma_L^2 + \frac{\sigma_d^2}{n}} \qquad (8)$$

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 rounded off the final laboratory result to the third decimal place for mass fractions of magnesium less than 1 % and to the second decimal place for mass fraction greater than or equal to 1 % according to Rule A shown in ISO 80000-1:2009, B.3.

8.3 Oxide factor

The oxide factor, expressed as a percent, is given by Formula (9):

$$w_{MgO} = 1{,}658\ w_{Mg} \qquad (9)$$

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) reference to this International Standard, i.e. ISO 10204;

d) details necessary for the identification of the sample;

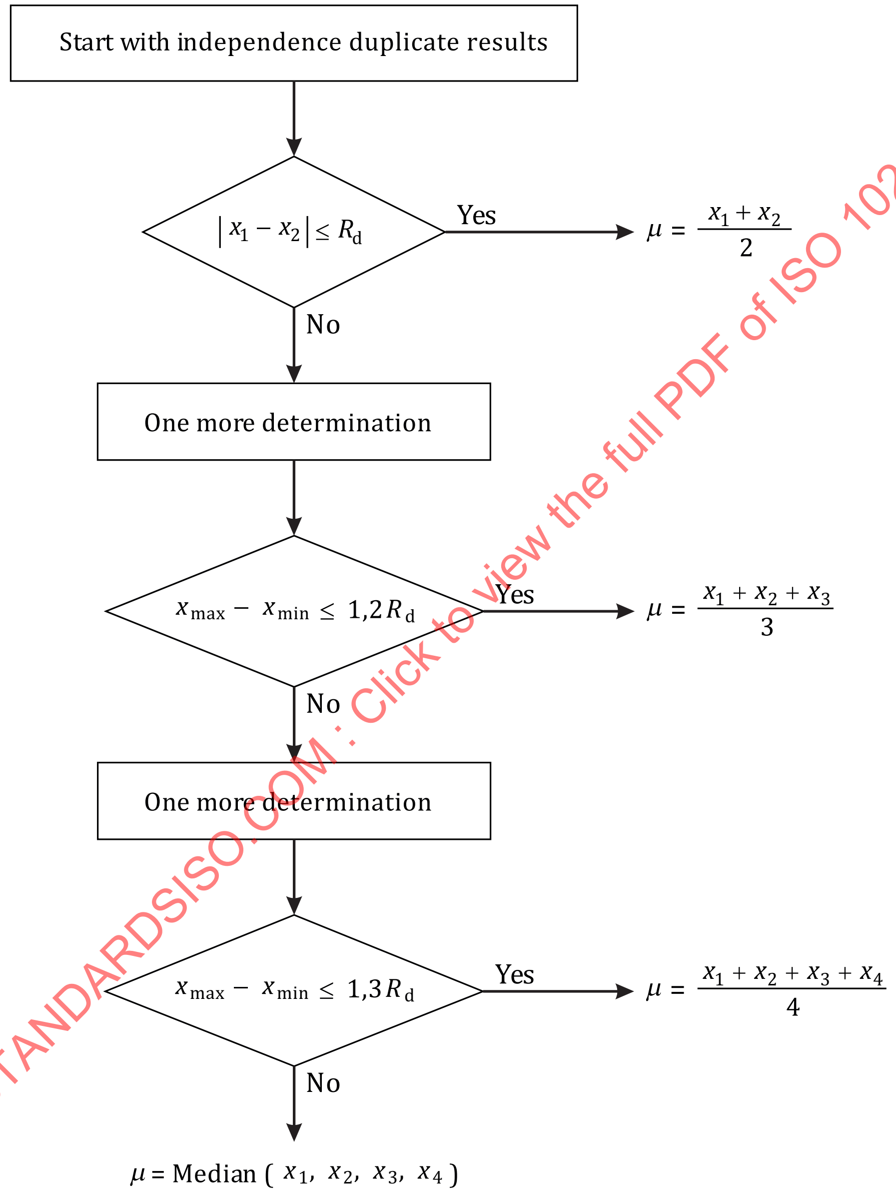
e) result of the analysis;

f) reference number of the result;

g) any characteristics noticed during the determination and any operations not specified in this International Standard which might 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



Key

R_d permissible tolerance within a laboratory(repeatability)

Figure A.1 — Flowsheet of the procedure for the acceptance of analytical values for test samples