SLOVENSKI STANDARD
SIST ISO 10204:1998

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Ģelezove rude ï Doloļevanje magnezija - Metoda plamenske atomske absorpcijske spektrometrije

Iron ores -- Determination of magnesium content -- Flame atomic absorption spectrometric method

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

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INTERNATIONAL STANDARD

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Iron ores — Determination of magnesium content — 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

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.

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.

International Standard ISO 10204 was prepared by Technical Committee ISO/TC 102, *Iron ores*, Sub-Committee SC 2, *Chemical analysis*.

ISO 10203 and ISO 10204 cancel and replace ISO 4692:1980, of which they constitute a technical revision.

Annex A forms an integral part of this International Standard. Annexes B and C are for information only.

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

1 Scope

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

This method is applicable to magnesium contents between 0,01 % (*m*/*m*) and 3,0 % (*m*/*m*) in natural iron ores, iron ore concentrates and agglomerates, including sinter products.

2 Normative references

The following standards contain provisions which, through reference in this text, constitute provisions of this International Standard. At the time of publication, the editions indicated were valid. All standards are subject to revision, and parties to agreements based on this International Standard are encouraged to investigate the possibility of applying the most recent editions of the standards indicated below. Members of IEC and ISO maintain registers of currently valid International Standards.

ISO 648:1977, *Laboratory glassware — One-mark pipettes.*

ISO 1042:1983, *Laboratory glassware — One-mark volumetric flasks.*

ISO 3081:1986, *Iron ores — Increment sampling — Manual method.*

ISO 3082:1987, *Iron ores — Increment sampling and sample preparation — Mechanical method.*

ISO 3083:1986, *Iron ores — Preparation of samples — Manual method.*

ISO 7764:1985, *Iron ores — Preparation of predried test samples for chemical analysis.*

3 Principle

Decomposition of the test portion by treatment with hydrochloric acid and a small amount of nitric acid.

Evaporation to dehydrate silica, followed by dilution and filtration.

Ignition of the residue and removal of silica by evaporation with hydrofluoric and sulfuric acids. Fusion with sodium carbonate and dissolution of the cooled melt in the filtrate.

Aspiration of the solution obtained into the flame of an atomic absorption spectrometer using an air-acetylene burner.

Comparison of the absorbance values obtained for magnesium with those obtained from the calibration solutions.

NOTE 1 A dinitrogen oxide-acetylene 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 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 pure iron wire [minimum purity 99,9 % (*m*/*m*), of magnesium content less than 0,000 2 % (*m*/*m*)] 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 ($LaCl_3.xH_2O$) [of magnesium content less than 0,002 % (*m*/*m*)] in 50 ml of hydrochloric acid (4.2) and 300 ml of hot water. Cool and dilute to 1 litre.

4.9 Magnesium standard solution, 15 µg Mg/ml.

Dissolve 0,300 0 g of oxide-free magnesium metal [minimum purity 99,9 % (*m*/*m*)] by slowly adding 75 ml of hydrochloric acid (ρ 1,19 g/ml), 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 note 2). 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, 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.

NOTE 2 The range of magnesium which 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

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.

NOTES

3 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.

4 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 in accordance with ISO 3081 or ISO 3082 and prepared in accordance with ISO 3082 or ISO 3083. In the case of ores having significant contents of combined water or oxidizable compounds, use a particle size of minus 160 µm.

NOTE 5 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 6 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.

NOTE 7 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.

NOTE 8 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.

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.

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 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, 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 9), 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 9 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 cover (see note 10).

NOTE 10 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 note 11). (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.)

NOTE 11 The dilutions shown in table 1 will provide magnesium contents 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 magnesium content (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 magnesium content

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

$$w_{Mg} = \frac{\rho_{Mg} \times 200}{m \times 10\ 000} = \frac{\rho_{Mg}}{m \times 50} \qquad \ldots (1)$$

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 which may have been made.

Table 1 — Dilution guide for test solution

Expected magnesium content of 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

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]:

$$r = 0{,}021\,7\,X + 0{,}027\,0 \qquad \ldots (2)$$

$$P = 0{,}118\,4\,X - 0{,}010\,2 \qquad \ldots (3)$$

$$\sigma_r = 0{,}007\,7\,X + 0{,}009\,5 \qquad \ldots (4)$$

$$\sigma_L = 0{,}041\,9\,X - 0{,}006\,1 \qquad \ldots (5)$$

where

X is the magnesium content, expressed as a percentage by mass, 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 (8.2.3) of the two laboratories;

r is the permissible tolerance within a laboratory (repeatability);

P is the permissible tolerance between laboratories;

σ_r is the within-laboratory standard deviation;

σ_L is the between-laboratories standard deviation.

8.2.2 Acceptance of analytical values

The result obtained for the certified reference material shall be such that the difference between this result and the certified value of the reference material is statistically insignificant. For a reference material that has been analysed by at least 10 laboratories using method(s) that are comparable both in accuracy and in precision with this method, the following condition shall be used to test the significance of the difference:

$$|A_c - A| \leqslant 2\sqrt{\frac{s_{Lc}^2 + \frac{s_{Wc}^2}{n_{Wc}}}{N_c} + \sigma_L^2 + \frac{\sigma_r^2}{n}} \qquad \ldots (6)$$

where

A_c is the certified value;

A is the result or the mean of results obtained for the certified reference material;

s_{Lc} is the between-laboratories standard deviation of the certifying laboratories;

s_{Wc} is the within-laboratory standard deviation of the certifying laboratories;

n_{Wc} is the average number of replicate determinations in the certifying laboratories;

N_c is the number of certifying laboratories;

n is the number of replicate determinations on the reference material (in most cases $n = 1$);

σ_L and σ_r are as defined in 8.2.1.

If condition (6) is satisfied, i.e. if the left-hand side is less than or equal to the right-hand side, then the difference $|A_c - A|$ is statistically insignificant; otherwise, it is statistically significant.

When the difference is significant, the analysis shall be repeated, simultaneously with an analysis of the test sample. If the difference is again significant, the procedure shall be repeated using a different certified reference material of the same type of ore.

When the range of the two values for the test sample is outside the limit for r calculated according to equation (2) in 8.2.1, one or more additional tests shall be carried out in accordance with the flowsheet presented in annex A, simultaneously with an analysis of a certified reference material of the same type of ore.

Acceptability of the results for the test sample shall in each case be subject to the acceptability of the results for the certified reference material.

NOTE 12 The following procedure should be used when the information on the reference material certificate is incomplete:

a) if there are insufficient data to enable the between-laboratories standard deviation to be estimated, delete the expression s_{Wc}^2/n_{Wc} and regard s_{Lc} as the standard deviation of the laboratory means;

b) if the certification has been made by only one laboratory or if the interlaboratory results are missing, it is advisable that this material not be used in the application of the standard. In case its use is unavoidable, use the condition

$$|A_c - A| \leqslant 2\sqrt{2\sigma_L^2 + \frac{\sigma_r^2}{n}} \qquad \ldots (7)$$

1) Additional information is given in annexes B and C.