International Standard ISO 7953

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Manganese ores and concentrates — Determination of calcium and magnesium contents — Flame atomic absorption spectrometric method

Minerais et concentrés de manganèse — Dosages du calcium et du magnésium — Méthode par spectrométrie d'absorption atomique dans la flamme

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Foreword

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International Standard ISO 7953 was prepared by Technical Committee ISO/TC 65, *Manganese and chromium ores*.

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Manganese ores and concentrates — Determination of calcium and magnesium contents — Flame atomic absorption spectrometric method

1 Scope and field of application

This International Standard specifies a flame atomic absorption spectrometric method for the determination of calcium and/or magnesium contents of manganese ores and concentrates.

The method is applicable to products having calcium contents from 0,01 to 15 % (m/m) and magnesium contents from 0,01 to 4 % (m/m).

It should be read in conjunction with ISO 4297.

2 References

ISO 4296/1, *Manganese ores — Sampling — Part 1 : Increment sampling.*

ISO 4296/2, *Manganese ores — Sampling — Part 2 : Preparation of samples.*

ISO 4297, *Manganese ores and concentrates — Methods of chemical analysis — General instructions.*

3 Principle

Decomposition of a test portion by treatment with hydrochloric and nitric acids. Filtration of any insoluble residue after evaporation and dehydration, the filtrate being reserved as the main solution.

Ignition of the filter containing the residue. Treatment with hydrofluoric and sulfuric acids. Fusion with a fusion mixture. Dissolution of the melt in hydrochloric acid and combination of the solution obtained with the main solution.

Aspiration of the solution into the flame of an atomic absorption spectrometer in the presence of lanthanum using a dinitrogen oxide/acetylene burner for calcium, and an air/acetylene burner for magnesium.

Comparison of absorbance values obtained for calcium and/or magnesium with those obtained from the calibration solutions.

NOTE — If a dinitrogen oxide flame is used for the determination of magnesium, the sensitivity is decreased by a factor of about 3.

4 Reagents

All standard solutions shall be stored in polythene bottles.

Any slight surface oxidation on the manganese and magnesium shall be removed by rinsing in dilute hydrochloric acid, distilled water and acetone prior to drying and weighing.

4.1 Hydrochloric acid, ϱ 1,19 g/ml.

4.2 Hydrochloric acid, diluted 1 + 1.

4.3 Hydrochloric acid, diluted 1 + 50.

4.4 Nitric acid, ϱ 1,40 g/ml.

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

4.6 Hydrofluoric acid, ϱ 1,14 g/ml.

4.7 Fusion mixture, consisting of 3 parts by mass of potassium carbonate and 1 part by mass of boric acid.

4.8 Background solution.

Dissolve 12,50 g of manganese [purity 99,95 % (m/m)], 1,25 g of iron [purity > 99,9 % (m/m)], 18,75 g of potassium carbonate and 6,25 g of boric acid by adding 625 ml of hydrochloric acid (4.2) and 25 ml of nitric acid (4.4) while heating. Cool, transfer to a 1 000 ml one-mark volumetric flask, dilute to the mark with water and mix.

4.9 Lanthanum chloride solution, containing 100 g of La per litre.

Dissolve 26,6 g of lanthanum chloride heptahydrate ($LaCl_3{\cdot}7H_2O$) in water, dilute to 100 ml and mix.

1 ml of this solution contains 0,1 g of La.

4.10 Calcium, standard solution corresponding to 50 mg of Ca per litre.

Dissolve 2,497 5 g of calcium carbonate (dried at 200 °C) in 50 ml of hydrochloric acid, diluted 1 + 4, while heating. When dissolution is complete, cool, dilute with water to 1 000 ml in a one-mark volumetric flask and mix.

Transfer 25 ml of this solution to a 500 ml one-mark volumetric flask, dilute to the mark with water and mix.

1 ml of this standard solution contains 50 µg of Ca.

4.11 Magnesium, standard solution corresponding to 25 mg of Mg per litre.

Dissolve 1,000 0 g of magnesium [purity 99,95 % (*m*/*m*)] in 20 ml of hydrochloric acid (4.2) while heating. When dissolution is complete, cool, dilute with water to 1 000 ml in a one-mark volumetric flask and mix.

Transfer 5 ml of this solution to a 200 ml one-mark volumetric flask, dilute to the mark with water and mix.

1 ml of this solution contains 25 µg of Mg.

5 Apparatus

Ordinary laboratory apparatus and

5.1 Platinum crucible.

5.2 Flame atomic absorption spectrometer, equipped with an air/acetylene and a dinitrogen oxide/acetylene burner.

The atomic absorption spectrometer used in this method will be satisfactory if it meets the following criteria :

a) Minimum sensitivity — the absorbance of the highest calibration solution (see 7.4) shall be at least 0,3.

b) Graph linearity — the slope of the calibration graph covering the top 20 % 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 % concentration range determined in the same way.

c) Minimum stability — the standard deviation of the absorbance of the most concentrated calibration solution and the standard deviation of the absorbance 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 solution.

An atomic absorption spectrometer shall be preferably attached to a chart recorder and/or digital readout device and capable of measuring absorbance at the following wavelengths :

calcium	422,7 nm
magnesium	285,2 nm

6 Sampling and samples

For the sampling of manganese ores, see ISO 4296/1. For the preparation of samples, see ISO 4296/2.

7 Procedure

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.

7.1 Test portion

Weigh about 2 g of the test sample.

7.2 Treatment of test portion

7.2.1 Decomposition

Transfer the test portion (7.1) to a 250 ml beaker, moisten with a few drops of water and dissolve in 40 ml of the hydrochloric acid (4.2) while heating.

After dissolution of the test portion, add 2 ml of nitric acid (4.4), heat the solution till oxides of nitrogen cease to evolve and evaporate the solution to dryness.

Add 10 ml of hydrochloric acid (4.1) to the dry residue and again evaporate the solution to dryness. Heat the salts on a hotplate at 130 °C for 40 to 60 min. After cooling add 20 ml of hydrochloric acid (4.1), heat to dissolve the salts, add 50 to 60 ml of hot water and filter the solution through a medium paper containing some filter pulp [previously washed with hot hydrochloric acid (4.3) and water].

Carefully remove all adhering particles with a rubber-tipped glass rod or moistened filter paper. Wash the filter and residue three or four times with hydrochloric acid (4.3), then several times with hot water and reserve the filtrate (main solution).

7.2.2 Treatment of the residue

Transfer the paper and residue to the platinum crucible (5.1) and ignite at 500 to 600 °C. Cool the crucible, moisten with a few drops of water, add 1 ml of the sulfuric acid (4.5), 5 to 10 ml of the hydrofluoric acid (4.6) and evaporate until sulfuric acid fuming ceases. Ignite the residue at 400 to 500 °C. Cool the crucible, add 2,0 g of the fusion mixture (4.7) to the residue and fuse over a Meker burner or in a muffle furnace until a clear melt is obtained (about 1 000 °C for 5 min).

Dissolve the cool melt in 10 ml of hydrochloric acid (4.2) in a 200 ml beaker while heating, remove and wash the crucible (the volume of the solution obtained should not exceed 50 ml).

Combine the solution obtained with the main solution (7.2.1).

NOTE — If the solution is cloudy at this stage it should be filtered through a filter paper containing some filter pulp, the filter being washed with hot hydrochloric acid (4.3) and water.

7.2.3 Preparation of the test solution

Transfer the solution obtained (7.2.2) to a 200 ml one-mark volumetric flask, dilute to the mark with water and mix. Transfer a suitable aliquot of this solution (see table 1) to a 100 or 200 ml one-mark volumetric flask and add the amounts of the lanthanum chloride solution (4.9) and background solution indicated in table 1; dilute to the mark with water and mix.

7.3 Preparation of the blank test

To prepare the blank test solution, dissolve 1 g of manganese [purity 99,95 % (*m/m*)] and 0,10 g of iron [purity > 99,9 % (*m/m*)] in 40 ml of hydrochloric acid (4.2) in a 200 ml beaker. Carry out the blank test through all stages of the analysis.

7.4 Preparation of the set of calibrating solutions

7.4.1 Calcium and magnesium calibration solutions

From the standard calcium solution (4.10) and standard magnesium solution (4.11) prepare calibration solutions as follows.

To each of a series of 100 ml one-mark volumetric flasks transfer quantities of standard calcium solution (4.10) and standard magnesium solution (4.11) according to table 2, add 5 ml of lanthanum chloride solution (4.9) and 20 ml of background solution (4.8), dilute to the mark with water and mix.

Table 1 — Dilution guide for test solution

Element	Expected content of element in sample	Aliquot portion I	Dilution of aliquot I	Aliquot portion II	Dilution of aliquot II	Lanthanum chloride solution (4.9) to be added	Background solution (4.8) to be added	Element content in the solution measured
	% (*m/m*)	ml	ml	ml	ml	ml	ml	µg/ml
Ca	0,01 up to 0,1	50	100	—	—	5	0	0,5 up to 5,0
	0,1 up to 0,5	25	100	—	—	5	10	2,5 up to 12,5
	0,5 up to 2,5	10	200	—	—	10	36	2,5 up to 12,5
	2,5 up to 5,0	20	100	10	100	5	19	5,0 up to 10,0
	5,0 up to 15,0	20	200	20	200	10	38	5,0 up to 15,0
Mg	0,01 up to 0,02	50	100	—	—	5	0	0,5 up to 1,0
	0,02 up to 0,05	25	100	—	—	5	10	0,5 up to 1,25
	0,05 up to 0,2	10	100	—	—	5	16	0,5 up to 2,0
	0,2 up to 0,4	5	100	—	—	5	18	1,0 up to 2,0
	0,4 up to 1,0	20	100	10	100	5	19	0,8 up to 2,0
	1,0 up to 2,0	20	200	20	200	10	38	1,0 up to 2,0
	2,0 up to 4,0	20	200	10	200	10	39	1,0 up to 2,0

Table 2 — Preparation of calcium and magnesium calibration solutions

Ca				Mg	
Expected percentage in sample [% (*m/m*)]				Expected percentage in sample [% (*m/m*)]	
0,01 up to 0,1		0,1 up to 15		0,01 up to 4	
Standard solution 50 mg/l (4.10)	**Content in calibration solution**	**Standard solution 50 mg/l (4.10)**	**Content in calibration solution**	**Standard solution 25 mg/l (4.11)**	**Content in calibration solution**
ml	µg/ml	ml	µg/ml	ml	µg/ml
1	0,5	2	1,0	2	0,5
2	1,0	4	2,0	3	0,75
3	1,5	6	3,0	4	1,0
6	3,0	10	5,0	6	1,5
10	5,0	20	10,0	8	2,0
		30	15,0		

NOTE — The range of calcium or magnesium which can be covered may vary from instrument to instrument. Attention should be paid to the minimum criteria given in 5.2. For instruments with high sensitivity, smaller portions of the standard solution or a more diluted standard solution can be used.

7.4.2 Zero calibration solution

Transfer 20 ml of background solution (4.8) to a 100 ml one-mark volumetric flask, add 5 ml of lanthanum chloride solution (4.9), dilute to the mark with water and mix.

7.5 Calibration and determination

7.5.1 Adjustment of atomic absorption spectrometer

Optimize the response of the instrument as described in 5.2. Set the wavelength for calcium (422,7 nm) or magnesium (285,2 nm) to obtain minimum absorbance. After 10 min preheating of the burner, adjust fuel and burner to obtain maximum absorbance while aspirating the highest calibration solution (see 7.4.1).

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

7.5.2 Spectrometric measurements

Aspirate water until the initial reading is again obtained. Aspirate the calibration solution and the final test solution in the order of increasing absorption, starting with the reagent blank solution, the zero calibration solution (7.4.2) and the final test solution being aspirated at the appropriate points in the series. When a stable response is obtained for each solution, record the readings. Aspirate water between each calibration and test solution. Repeat the measurements at least twice more.

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

Convert the net absorbance values of the test solution to micrograms of calcium or magnesium per millilitre by means of the calibration curve.

8 Expression of results

8.1 Calculation

The calcium or magnesium content, expressed as a percentage by mass, is given by the formula

$$\frac{\varrho V}{m \times 10^4} \times K$$

where

ϱ is the concentration, expressed in micrograms per millilitre, of calcium or magnesium in the test solution;

V is the volume of the final solution;

m is the mass, in grams, of sample represented in the volume of the test solution;

K is the conversion factor for expression of the calcium or magnesium content on the dry basis.

8.2 Permissible tolerances on results of parallel determinations

Table 3 — Permissible tolerances on calcium content

Calcium content	Permissible tolerance	
	Three parallel determinations	Two parallel determinations
% (m/m)	% (m/m)	% (m/m)
From 0,01 to 0,10	0,007	0,006
From 0,10 to 0,25	0,03	0,025
From 0,25 to 0,50	0,08	0,07
From 0,50 to 1,0	0,12	0,10
From 1,0 to 2,0	0,17	0,15
From 2,0 to 5,0	0,25	0,20
From 5,0 to 8,0	0,35	0,30
From 8,0 to 15,0	0,45	0,40

Table 4 — Permissible tolerances on magnesium content

Magnesium content	Permissible tolerance	
	Three parallel determinations	Two parallel determinations
% (m/m)	% (m/m)	% (m/m)
From 0,01 to 0,05	0,006	0,005
From 0,05 to 0,25	0,012	0,01
From 0,25 to 0,5	0,06	0,05
From 0,5 to 1,0	0,09	0,07
From 1,0 to 2,0	0,12	0,10
From 2,0 to 4,0	0,15	0,12