International Standard 315

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Manganese ores and concentrates — Determination of nickel content — Dimethylglyoxime spectrometric method and flame atomic absorption spectrometric method

Minerais et concentrés de manganèse — Dosage du nickel — Méthode spectrométrique à la diméthylglyoxime et méthode par spectrométrie d'absorption atomique dans la flamme

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Foreword

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Draft International Standards adopted by the technical committees are circulated to the member bodies for approval before their acceptance as International Standards by the ISO Council.

International Standard ISO 315 was developed by Technical Committee ISO/TC 65, *Manganese and chromium ores*, and was circulated to the member bodies in February 1983.

It has been approved by the member bodies of the following countries:

Austria	Italy	South Africa, Rep. of
Bulgaria	Japan	Thailand
China	Mexico	United Kingdom
Czechoslovakia	Netherlands	USSR
France	Poland	
Germany, F.R.	Romania	

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Australia

This International Standard cancels and replaces ISO Recommendation R 315-1963, of which it constitutes a technical revision.

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Manganese ores and concentrates — Determination of nickel content — Dimethylglyoxime spectrometric method and flame atomic absorption spectrometric method

1 Scope and field of application

This International Standard specifies two methods for the determination of the nickel content of manganese ores and concentrates

method A: dimethylglyoxime spectrometric method, applicable to products having a nickel content of 0,01 to 1,0 % (*m/m*);

method B: flame atomic absorption spectrometric method, applicable to products having a nickel content of 0,005 to 1,0 % (*m/m*).

This International Standard 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 Method A: Dimethylglyoxime spectrometric method

3.1 Principle

Decomposition of test portion by treatment with sulfuric acid in the presence of hydrogen peroxide.

Separation of the insoluble residue, the filtrate being reserved as the main solution.

Ignition of the filter containing the residue and treatment with sulfuric and hydrofluoric acids.

Fusion of the ignited residue with potassium disulfate.

Dissolution of the melt in sulfuric acid and combination of the solution obtained with the main solution.

Separation of manganese in the form of manganese dioxide.

Spectrometric determination at 460 to 470 nm in the presence of tartaric acid, sodium hydroxide, ammonium persulfate and dimethylglyoxime.

3.2 Reactions

The method is based on the interaction of nickel ions with dimethylglyoxime in an alkaline medium (pH 10 to 11) in the presence of ammonium persulfate with the formation of a coloured complex. Iron and other elements are prevented from interfering with the reaction by the formation of soluble complexes with tartaric acid. Manganese is separated in the form of manganese dioxide.

3.3 Reagents

3.3.1 Potassium bromate ($KBrO_3$).

3.3.2 Potassium disulfate ($K_2S_2O_7$).

3.3.3 Hydrochloric acid, ϱ 1,19 g/ml.

3.3.4 Sulfuric acid, diluted 1 + 4.

3.3.5 Sulfuric acid, diluted 1 + 20.

3.3.6 Hydrofluoric acid, ϱ 1,14 g/ml, 40 % (*m/m*) solution.

3.3.7 Tartaric acid (HOOC – CHOH – CHOH – COOH), 200 g/l solution.

3.3.8 Hydrogen peroxide, 30 % (*m/m*).

3.3.9 Sodium hydroxide, 50 g/l solution.

3.3.10 Ammonium persulfate [$(NH_4)_2S_2O_8$], 30 g/l solution.

3.3.11 1,2-dimethylglyoxal dioxime [Dimethylglyoxime] ($C_4H_8O_2N_2$), 10 g/l solution.

Dissolve 1 g of dimethylglyoxime in 100 ml of sodium hydroxide (3.3.9).

3.3.12 Nickel, standard solution corresponding to 1 g of Ni per litre.

Weigh 1,000 0 g of metallic nickel (purity 99,95 %) into a beaker of capacity 250 ml. Dissolve the nickel in 20 ml of an acid mixture of three parts by volume hydrochloric acid (3.3.3) and one part by volume nitric acid, ϱ 1,40 g/ml.

Boil the solution until nitrogen oxides cease to evolve. Cool the solution, transfer to a one-mark volumetric flask of capacity 1 000 ml, dilute with water to the mark and mix.

1 ml of this standard solution contains 1 mg of Ni.

3.3.13 Nickel, standard solution corresponding to 0,01 g of Ni per litre.

Pipette 10 ml of standard nickel solution (3.3.12) into a one-mark volumetric flask of capacity 1 000 ml, dilute with water to the mark and mix.

1 ml of this standard solution contains 0,01 mg of Ni.

3.4 Apparatus

Usual laboratory apparatus and

3.4.1 Platinium crucible.

3.4.2 Spectrometer, with selectors for continuous or discontinuous variation, suitable for measurements at 460 to 470 nm, with matching cells.

3.5 Sample

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

Use a test sample which has been crushed to a size not exceeding 100 µm (checked on a sieve of appropriate aperture size) and air dried under laboratory conditions.

3.6 Procedure

3.6.1 Test portion

Weigh a mass of the test sample, chosen from table 1 in accordance with the expected nickel content.

3.6.2 Blank test

Carry out a blank test through all stages of the analysis.

3.6.3 Decomposition of test portion

Place the test portion (3.6.1) in a beaker of capacity 250 ml, moisten with a few drops of water and dissolve in 30 ml of sulfuric acid (3.3.4) while heating and adding hydrogen peroxide solution (3.3.8) drop by drop to decompose the ore.

Evaporate the solution until dense white fumes of sulfuric acid appear. Cool, dilute with 40 to 50 ml of water and filter the insoluble residue on a medium-texture filter paper containing a small quantity of paper pulp, then wash with hot water six to eight times. Reserve the filtrate as the main solution.

3.6.4 Treatment of residue

Transfer the filter containing the residue to a platinum crucible (3.4.1), dry and ignite at 500 to 600 °C. Cool the crucible, moisten the residue with water, add 2 or 3 drops of sulfuric acid (3.3.4) and 5 to 7 ml of hydrofluoric acid (3.3.6).

Evaporate to dryness, then ignite the residue at 500 to 600 °C until sulfuric acid fuming ceases. Cool the crucible, add 2 to 3 g of potassium disulfate (3.3.2) and fuse at 600 to 650 °C. Leach the melt in 10 to 20 ml of sulfuric acid (3.3.5), then wash the crucible with water. Add the solution thus obtained to the main solution (3.6.3).

NOTE — If it is known that the ore does not contain insoluble nickel compounds, then the procedure described in 3.6.4 can be omitted.

3.6.5 Preparation of solution for spectrometric measurement

Dilute or evaporate the combined solution (3.6.3 and 3.6.4) to about 150 ml, add 1 g of potassium bromate (3.3.1), heat the solution to boiling and boil for 5 min. Filter through a medium-texture filter paper and wash with hot water eight to ten times. Discard the filter with the residue.

Evaporate the solution until sulfuric acid fuming ceases, cool and dissolve the salts in 10 ml of hydrochloric acid (3.3.3). Transfer the solution to a one-mark volumetric flask chosen in accordance with table 1, dilute with water to the mark and mix.

Table 1

Expected nickel content	Mass of test portion	Dilution	Aliquot portion of solution	Nickel content of aliquot portion of solution
% (*m*/*m*)	g	ml	ml	mg
> 0,01 to 0,05	1,0	100	10	0,010 to 0,050
> 0,05 to 0,10	1,0	250	10	0,020 to 0,040
> 0,10 to 0,50	1,0	250	5	0,020 to 0,100
> 0,50 to 1,0	0,5	250	5	0,050 to 0,100

Pipette two equal aliquot portions of the solution, chosen in accordance with table 1, into two one-mark volumetric flasks, each of capacity 100 ml. Then to each of the flasks add 10 ml of tartaric acid solution (3.3.7), 40 ml of sodium hydroxide solution (3.3.9) and 10 ml of ammonium persulfate solution (3.3.10).

Then add 10 ml of dimethylglyoxime (3.3.11) into one aliquot portion and 10 ml of sodium hydroxide (3.3.9) into the other aliquot portion (background solution). Mix the solution after the addition of each reagent. Allow the solution to stand for 5 to 10 min until a stable coloration appears, then dilute with water to the mark and mix.

3.6.6 Spectrometric measurement

Measure the absorbance of the solution in a cell, using the spectrometer (3.4.2) at 460 to 470 nm in order to obtain the optimum absorbance, against water as reference.

3.6.7 Preparation of calibration graph

Into each of a series of seven one-mark volumetric flasks of capacity 100 ml, introduce, using a burette, 0,0; 1,0; 2,0; 4,0; 6,0; 8,0 and 10,0 ml of the nickel standard solution (3.3.13), corresponding to 0,0; 0,010; 0,020; 0,040; 0,060; 0,080 and 0,100 mg of nickel. The first volumetric flask serves for the preparation of the calibration compensation solution. Add 10 ml of tartaric acid solution (3.3.7), 40 ml of sodium hydroxide solution (3.3.9), 10 ml of ammonium persulfate solution (3.3.10) and 10 ml of dimethylglyoxime solution (3.3.11).

Mix the solution after addition of each reagent. Allow the solution to stand for 5 to 10 min until a stable coloration appears, then dilute with water to the mark and mix.

Measure the absorbance of each solution as specified in 3.6.6.

Prepare a calibration graph by plotting the absorbance values (deducting the absorbance value of the calibration compensation solution) against the nominal nickel contents of the calibration solutions.

3.7 Expression of results

3.7.1 Calculation

Convert the net absorbance reading for the test solution (obtained by subtracting the absorbance reading of the blank test and background solution from that of the test solution) to nickel content by means of the calibration graph (3.6.7).

The nickel (Ni) content, expressed as a percentage by mass, is given by the formula

$$\frac{m_1 \times 100}{m_0 \times 1\,000} \times K = \frac{m_1}{m_0 \times 10} \times K$$

where

m_0 is the mass, in grams, of the test portion corresponding to the aliquot portion of the test solution;

m_1 is the mass, in milligrams, of nickel in the aliquot portion of the test solution, obtained from the calibration graph;

K is the conversion factor for the expression of the nickel content on the dry basis.

3.7.2 Permissible tolerances on results of parallel determinations

Table 2

Values as percentages by mass

Nickel content	Permissible tolerance	
	Three parallel determinations	Two parallel determinations
> 0,005 to 0,01	0,003	0,002
> 0,01 to 0,02	0,005	0,004
> 0,02 to 0,05	0,007	0,006
> 0,05 to 0,1	0,01	0,008
> 0,1 to 0,2	0,02	0,015
> 0,2 to 0,5	0,03	0,02
> 0,5 to 1,0	0,04	0,03

4 Method B: Flame atomic absorption spectrometric method

4.1 Principle

Decomposition of the test portion by treatment with hydrochloric and nitric acids.

Filtration of any insoluble residue, the filtrate being reserved as the main solution.

Ignition of the filter containing the residue and treatment with hydrofluoric and sulfuric acids.

Fusion with sodium carbonate. 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 using an air-acetylene burner and measurement of the absorbance at 232 nm.

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

4.2 Reagents

4.2.1 Sodium carbonate, anhydrous.

4.2.2 Hydrochloric acid, ϱ 1,19 g/ml.

4.2.3 Hydrochloric acid, diluted 1 + 4.

4.2.4 Hydrochloric acid, diluted 1 + 50.

4.2.5 Nitric acid, ϱ 1,40 g/ml.

4.2.6 Sulfuric acid, diluted 1 + 1.

4.2.7 Hydrofluoric acid, ϱ 1,14 g/ml, 40 % (m/m) solution.

4.2.8 Background solutions.

4.2.8.1 Solution A

Dissolve 20 g of high purity metallic manganese in 150 ml of hydrochloric acid (4.2.3) while heating in a beaker of capacity 500 ml. Cool the solution, transfer to a one-mark volumetric flask of capacity 1 000 ml, dilute with water to the mark and mix.

4.2.8.2 Solution B

Dissolve 20 g of high purity metallic manganese in 150 ml of hydrochloric acid (4.2.3) while heating in a beaker of capacity 500 ml. Add 40 g of sodium carbonate (4.2.1) previously dissolved in water. Cool the solution, transfer to a one-mark volumetric flask of capacity 1 000 ml, dilute with water to the mark and mix.

4.2.9 Nickel, standard solution corresponding to 1 g of Ni per litre.

Weigh 1,000 0 g of metallic nickel (purity 99,95 %) into a beaker of capacity 250 ml. Dissolve the nickel in 20 ml of an acid mixture of three parts by volume hydrochloric acid (4.2.2) and one part by volume nitric acid (4.2.5).

Boil the solution until nitrogen oxides cease to evolve. Cool the solution, transfer to a one-mark volumetric flask of capacity 1 000 ml, dilute with water to the mark and mix.

1 ml of this standard solution contains 1 mg of Ni.

4.2.10 Nickel, standard solution corresponding to 0,05 g of Ni per litre.

Pipette 10 ml of standard nickel solution (4.2.9) into a one-mark volumetric flask of capacity 200 ml. Dilute with water to the mark and mix.

1 ml of this standard solution contains 0,05 mg of Ni.

4.3 Apparatus

Usual laboratory apparatus and

4.3.1 Platinum crucible.

4.3.2 Atomic absorption spectrometer, equipped with an air-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 4.5.8) shall be at least 0,3;

b) curve linearity — the slope of the calibration curve 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 calibration compensation 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 read-out device.

Instrument parameters may vary with each instrument. The parameters given in table 3 can be used as guidelines.

Table 3

Parameter	Value
Nickel hollow cathode lamp	30 mA
Slit width	0,1 mm
Wavelength	232,0 nm
Air flow rate	11,2 l/min
Acetylene flow rate	1,2 l/min

4.4 Sample

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

Use a test sample which has been crushed to a size not exceeding 100 µm (checked on a sieve of appropriate aperture size) and air dried under laboratory conditions.

4.5 Procedure

4.5.1 Test portion

Weigh 1 g of the test sample.

4.5.2 Blank test

Carry out a blank test through all stages of the analysis.

4.5.3 Decomposition of test portion

Place the test portion (4.5.1) in a beaker of capacity 250 ml, moisten with a few drops of water and dissolve in 10 ml of hydrochloric acid (4.2.2) while heating. Add 1 ml of nitric acid (4.2.5).

Evaporate the solution to dryness. Cool, add 10 ml of hydrochloric acid (4.2.2), then heat to dissolve the soluble salts. Dilute with about 30 ml of hot water and filter the solution through a medium-texture filter paper containing a small quantity of paper pulp, then wash with hot hydrochloric acid (4.2.4) five or six times, then with hot water seven or eight times. Reserve the filtrate as the main solution.