

# INTERNATIONAL STANDARD

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**9681**

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## **Manganese ores and concentrates — Determination of iron content — Flame atomic absorption spectrometric method**

*Minerais et concentrés de manganèse — Dosage du fer — Méthode par  
spectrométrie d'absorption atomique dans la flamme*



Reference number  
ISO 9681:1990(E)

## Foreword

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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 9681 was prepared by Technical Committee ISO/TC 65, *Manganese and chromium ores*.

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# Manganese ores and concentrates — Determination of iron content — Flame atomic absorption spectrometric method

## 1 Scope

This International Standard specifies a flame atomic absorption spectrometric method for the determination of iron content in manganese ores and concentrates. The method is applicable to products having an iron content from 0,2 % (m/m) to 10 % (m/m).

This International Standard should be read in conjunction with ISO 4297.

## 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 310:1981, *Manganese ores — Determination of hygroscopic moisture content in analytical samples — Gravimetric method.*

ISO 4296-1:1984, *Manganese ores — Sampling — Part 1: Increment sampling.*

ISO 4296-2:1983, *Manganese ores — Sampling — Part 2: Preparation of samples.*

ISO 4297:1978, *Manganese ores and concentrates — Methods of chemical analysis — General instructions.*

## 3 Principle

**Method 1:** Decomposition of the test portion by treatment with hydrochloric, perchloric and hydrofluoric acids. Separation of the insoluble resi-

due, fusion of the residue with a fusion mixture and dissolution of the cooled melt in the test solution. Aspiration of the test solution into an air-acetylene flame in an atomic absorption spectrometer and measurement of the absorbance at a wavelength of 248,3 nm or 344,06 nm.

**Method 2:** Decomposition of the test portion by treatment with hydrochloric, nitric and perchloric acids and filtration of the insoluble residue. Removal of silica by volatilization with sulfuric and hydrofluoric acids, fusion of the residue with a fusion mixture and dissolution of the cooled melt in the test solution. Aspiration of the test solution into an air-acetylene flame in an atomic absorption spectrometer and measurement of the absorbance at a wavelength of 248,3 nm or 344,06 nm.

## 4 Reagents

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

- 4.1 **Metallic manganese**, 99,9 % purity.
- 4.2 **Hydrochloric acid**,  $\rho$  1,19 g/ml.
- 4.3 **Hydrochloric acid**,  $\rho$  1,19 g/ml, diluted 1 + 50.
- 4.4 **Hydrofluoric acid**,  $\rho$  1,14 g/ml.
- 4.5 **Perchloric acid**,  $\rho$  1,61 g/ml.
- 4.6 **Nitric acid**,  $\rho$  1,40 g/ml.
- 4.7 **Nitric acid**,  $\rho$  1,40 g/ml, diluted 1 + 1.
- 4.8 **Sulfuric acid**,  $\rho$  1,84 g/ml, diluted 1 + 1.

Slowly and with great care, pour 1 volume of concentrated sulfuric acid into an equal volume of water.

**4.9 Hydrogen peroxide**, 30 % (m/m) solution.

**4.10 Fusion mixture.**

Mix anhydrous sodium carbonate and anhydrous sodium tetraborate, in the proportion 3 + 1.

**4.11 Background solution A**, for ores having CaO content less than 5 % (m/m).

Dissolve 5 g of manganese (4.1) in 40 ml of nitric acid (4.7). Add 30 ml of perchloric acid (4.5). Heat until fumes of perchloric acid appear. Cool the solution and dilute with water. Add 7,5 g of anhydrous sodium carbonate, 2,5 g of anhydrous sodium tetraborate and 30 ml of hydrochloric acid (4.2). After dissolution, transfer the solution to a 500 ml one-mark volumetric flask, dilute to the mark with water and mix.

**4.12 Background solution B**, for ores having CaO content greater than 5 % (m/m).

Dissolve 4 g of manganese (4.1) and 1,8 g of calcium carbonate in 40 ml of nitric acid (4.7) and proceed as in 4.11.

**4.13 Iron**, standard solutions.

**4.13.1 Iron**, standard solution A corresponding to 4 g of Fe per litre.

Dissolve 4,000 g of carbonyl iron (purity 99,99 %) in 40 ml of nitric acid (4.6). Add 40 ml of perchloric acid (4.5) and evaporate until fumes of perchloric acid appear. Cool the solution and dilute with water. Transfer the solution to a 1000 ml one-mark volumetric flask, dilute to the mark with water and mix.

1 ml of this standard solution contains 4 mg of Fe.

**4.13.2 Iron**, standard solution B corresponding to 0,1 g of Fe per litre.

Transfer 5 ml of iron standard solution A (4.13.1) to a 200 ml one-mark volumetric flask, dilute to the mark with water and mix.

1 ml of this standard solution contains 0,1 mg of Fe.

## 5 Apparatus

Ordinary laboratory equipment, and

**5.1 Platinum crucibles.**

**5.2 Polytetrafluoroethylene (PTFE) beakers.**

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

The atomic absorption spectrometer used will be satisfactory if it meets the following criteria.

- minimum sensitivity*: the absorbance of the calibration solution of highest iron content (7.4) shall be at least 0,25;
- curve linearity*: the slope of the calibration graph covering the top 20 % of the concentration range (expressed as a change in absorbance) shall be not less than 0,7 of the value of the slope for the bottom 20 % of the concentration range determined in the same way;
- minimum stability*: the standard deviation of the absorbance of the calibration solution of highest concentration 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 calibration solution of highest concentration.

## NOTES

1 The use of a strip chart recorder and/or digital readout device is recommended to evaluate the criteria and for all subsequent measurements.

2 Instrument parameters may vary with each instrument. The following parameters were successfully used in several laboratories and they can be used as guidelines.

Iron hollow cathode lamp: 20 mA  
Wavelength: 248,3 nm or 344,06 nm  
Air flow rate: 13,3 l/min  
Acetylene flow rate: 1,7 l/min.

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

## 6 Sampling and samples

For analysis, use a laboratory sample of minus 100 µm particle size which has been taken in accordance with ISO 4296-1 and prepared in accordance with ISO 4296-2.

## 7 Procedure

### 7.1 Test portion

Weigh 1 g of an air-dried sample or the sample dried at 105 °C to 110 °C.

NOTE 3 When using the sample dried at 105 °C to 110 °C, the test portion should be taken and weighed quickly in order to avoid reabsorption of moisture.

## 7.2 Blank test

Carry out a blank test using 0,5 g of manganese (4.1) through all stages of the analysis.

## 7.3 Determination

### 7.3.1 Decomposition of the test portion

Carry out decomposition by one of the following methods.

#### 7.3.1.1 Method 1

Place the test portion (7.1) in a 300 ml polytetrafluoroethylene beaker (5.2), moisten with water and dissolve, while heating gently without boiling, in 10 ml of hydrochloric acid (4.2) and 5 ml to 7 ml of hydrofluoric acid (4.4). After decomposition, add 10 ml of perchloric acid (4.5) and wash down the sides of the beaker with water. Heat until fumes of perchloric acid appear and allow the solution to cool. Wash down again the sides of the beaker with water and with 5 ml of hydrochloric acid (4.2) and heat until fumes of perchloric acid appear. Allow to cool, then add 20 ml of hot water and 2 or 3 drops of hydrogen peroxide (4.9). Heat to boiling and cool. Filter the residue on a medium-texture filter paper containing some filter pulp. Wash the filter paper with hot hydrochloric acid (4.3), then 7 or 8 times with hot water. Reserve the filtrate as the main solution.

#### 7.3.1.2 Method 2

Place the test portion (7.1) in a 300 ml borosilicate glass beaker, moisten with water and dissolve, while heating gently without boiling, in 10 ml of hydrochloric acid (4.2). After decomposition, add 1 ml of nitric acid (4.6) and 10 ml of perchloric acid (4.5) and wash down the sides of the beaker with water. Heat until fumes of perchloric acid appear and allow the solution to cool. Follow the procedure as in 7.3.1.1 from the words "Wash down again...".

### 7.3.2 Treatment of the residue

#### 7.3.2.1 Method 1

Transfer the filter paper and the residue to a platinum crucible (5.1). Ignite the paper and residue at 600 °C to 700 °C. Allow to cool.

Fuse the residue with 1 g of fusion mixture (4.10) at 950 °C to 1050 °C. Leach the melt in a beaker with 50 ml of hot water. Remove the crucible and rinse it into the beaker with water acidified with 3 ml of hydrochloric acid (4.2). Combine the solution with the main solution (7.3.1.1).

\* ) Zero calibration solution.

#### 7.3.2.2 Method 2

Transfer the filter paper with the silica and the residue to a platinum crucible (5.1). Ignite the paper and residue at 600 °C to 700 °C. Allow to cool. Moisten the residue in the crucible with several drops of water, and add 2 to 4 drops of sulfuric acid (4.8) and 5 ml to 7 ml of hydrofluoric acid (4.4).

Evaporate the solution to dryness and ignite the residue in the crucible at 400 °C to 500 °C until complete removal of sulfuric acid, then allow to cool. Follow the procedure as in 7.3.2.1 from the words "Fuse the residue...".

### 7.3.3 Preparation of the test solution

Transfer the combined solution (7.3.2.1 or 7.3.2.2) to a 250 ml one-mark volumetric flask, dilute to the mark with water and mix. For further steps in the determination, use the solution obtained or take an aliquot portion of the solution, as specified in table 1, in accordance with the expected iron content.

Transfer the solution or the aliquot portion to a 100 ml one-mark volumetric flask. Add background solution A (4.11) or B (4.12), depending on the CaO content in the sample. Dilute to the mark with water and mix.

Table 1 — Volumes of aliquot portion and background solution

Expected iron content	Aliquot portion	Concentration of iron in the solution measured	Background solution (4.11 or 4.12) to be added
% (m/m)	ml	µg/ml	ml
0,2 to 1	25	2 to 10	15
1 to 5	5	2 to 10	20
2,5 to 10	—	100 to 400	—

## 7.4 Preparation of the set of calibration solutions

### 7.4.1 Iron content up to 5 % (m/m)

To each of a series of six 100 ml one-mark volumetric flasks, transfer, by means of a pipette, 0 ml<sup>\*)</sup>; 2,0 ml; 4,0 ml; 6,0 ml; 8,0 ml and 10,0 ml of standard iron solution B (4.13.2), corresponding to 0 mg; 0,002 mg; 0,004 mg; 0,006 mg; 0,008 mg and 0,010 mg of iron per millilitre. Add 20 ml of background solution A (4.11) or B (4.12), depending on the expected CaO content in the sample. Dilute to the mark with water and mix.

### 7.4.2 Iron content higher than 2,5% (m/m)

To each of a series of six 100 ml one-mark volumetric flasks, transfer, by means of a pipette, 0 ml<sup>\*)</sup>; 2,5 ml; 5,0 ml; 7,5 ml; 10,0 ml and 12,5 ml of standard iron solution A (4.13.1), corresponding to 0 mg; 0,1 mg; 0,2 mg; 0,3 mg; 0,4 mg and 0,5 mg of iron per millilitre. Add 20 ml of background solution A (4.11) or B (4.12), depending on the expected CaO content in the sample. Dilute to the mark with water and mix.

NOTE 4 The range of iron which can be covered may vary from instrument to instrument. Attention should be paid to the minimum criteria given in 5.3. For instruments with high sensitivity, smaller aliquots of the standard solution can be used.

## 7.5 Calibration and measurements

### 7.5.1 Spectrometric measurements

Optimize the response of the instrument as described in 5.3. After 10 min preheating of the burner and obtaining a stable response, aspirate the test solution or the diluted test solution (7.3.3). Set the wavelength for iron at 248,3 nm in the case of iron content from 0,2 % (m/m) to 5,0 % (m/m) or at 344,06 nm in the case of iron content above 2,5 % (m/m). In the concentration range of iron from 2,5 % (m/m) to 5,0 % (m/m), determination can be carried out at both wavelengths.

Aspirate water after the test solution to obtain zero absorbance.

Repeat the measurements at least twice. Obtain the net absorbance of the test solution by subtracting the absorbance of the reagent blank solution (7.2).

Convert the net absorbance values of the test solution to micrograms of Fe per millilitre by means of the calibration graph (7.5.2).

Simultaneously with the analysis of the test solution, analyse the series of calibration solutions (7.4).

### 7.5.2 Plotting the calibration graph

Obtain the net absorbance of each calibration solution (7.4.1 or 7.4.2) by subtracting the average absorbance of the zero calibration solution.

Prepare calibration graphs, by plotting the net absorbance values of the calibration solution against micrograms of Fe per millilitre.

## 8 Expression of results

### 8.1 Calculation

The iron content  $w_{\text{Fe}}$ , expressed as a percentage by mass, is given by the formula

$$w_{\text{Fe}} = \frac{\rho_{\text{Fe}} \cdot VK \times 100}{m \cdot 10^6}$$

$$= \frac{\rho_{\text{Fe}} \cdot VK}{m \cdot 10^4}$$

where

$\rho_{\text{Fe}}$  is the concentration, expressed in micrograms per millilitre, of iron in the test solution, obtained from the calibration graph;

$m$  is the mass, in grams, of the test portion represented in the final test solution;

$V$  is the volume, in millilitres, of the final test solution;

$K$  is the conversion factor for the expression of the iron content on the dry basis (for an air-dried sample, see ISO 4297).

### 8.2 Permissible tolerances on results of parallel determinations

See table 2.

Table 2 — Permissible tolerances on iron content

Values expressed as a percentage by mass

Iron content	Permissible tolerance	
	Three parallel determinations	Two parallel determinations
From 0,2 to 0,4	0,04	0,03
From 0,4 to 1,0	0,07	0,06
From 1,0 to 2,5	0,10	0,09
From 2,5 to 5,0	0,15	0,12
From 5,0 to 10,0	0,25	0,20

\*) Zero calibration solution.