

---

---

**Iron ores — Determination of manganese  
content —**

Part 1:  
**Flame atomic absorption spectrometric  
method**

*Minerais de fer — Dosage du manganèse —*

*Partie 1: Méthode par spectrométrie d'absorption atomique dans la  
flamme*

ISO 9682-1:2009

<https://standards.iteh.ai/catalog/standards/sist/a7db0c0d-0844-400f-ba07-33083b19cdb3/iso-9682-1-2009>



**PDF disclaimer**

This PDF file may contain embedded typefaces. In accordance with Adobe's licensing policy, this file may be printed or viewed but shall not be edited unless the typefaces which are embedded are licensed to and installed on the computer performing the editing. In downloading this file, parties accept therein the responsibility of not infringing Adobe's licensing policy. The ISO Central Secretariat accepts no liability in this area.

Adobe is a trademark of Adobe Systems Incorporated.

Details of the software products used to create this PDF file can be found in the General Info relative to the file; the PDF-creation parameters were optimized for printing. Every care has been taken to ensure that the file is suitable for use by ISO member bodies. In the unlikely event that a problem relating to it is found, please inform the Central Secretariat at the address given below.

**iTeh STANDARD PREVIEW**  
**(standards.iteh.ai)**

ISO 9682-1:2009

<https://standards.iteh.ai/catalog/standards/sist/a7db0c0d-0844-400f-ba07-33083b19cdb3/iso-9682-1-2009>



**COPYRIGHT PROTECTED DOCUMENT**

© ISO 2009

All rights reserved. Unless otherwise specified, no part of this publication may be reproduced or utilized in any form or by any means, electronic or mechanical, including photocopying and microfilm, without permission in writing from either ISO at the address below or ISO's member body in the country of the requester.

ISO copyright office  
Case postale 56 • CH-1211 Geneva 20  
Tel. + 41 22 749 01 11  
Fax + 41 22 749 09 47  
E-mail [copyright@iso.org](mailto:copyright@iso.org)  
Web [www.iso.org](http://www.iso.org)

Published in Switzerland

# Contents

Page

Foreword .....	iv
<b>1 Scope .....</b>	<b>1</b>
<b>2 Normative references .....</b>	<b>1</b>
<b>3 Principle .....</b>	<b>1</b>
<b>4 Reagents .....</b>	<b>2</b>
<b>5 Apparatus .....</b>	<b>2</b>
<b>6 Sampling and samples .....</b>	<b>3</b>
6.1 Laboratory sample .....	3
6.2 Preparation of predried test samples .....	3
<b>7 Procedure .....</b>	<b>4</b>
7.1 Number of determinations .....	4
7.2 Safety precautions .....	4
7.3 Test portion .....	4
7.4 Blank test and check test .....	4
7.5 Determination .....	4
7.5.1 Decomposition of the test portion .....	4
7.5.2 Treatment of the test solution .....	5
7.5.3 Adjustment of the atomic absorption spectrometer .....	6
7.5.4 Atomic absorption measurements .....	6
<b>8 Expression of results .....</b>	<b>7</b>
8.1 Calculation of mass fraction of manganese .....	7
8.2 General treatment of results .....	7
8.2.1 Repeatability and permissible tolerance .....	7
8.2.2 Determination of analytical result .....	8
8.2.3 Between-laboratories precision .....	8
8.2.4 Check for trueness .....	8
8.2.5 Calculation of final result .....	9
8.3 Oxide factor .....	9
<b>9 Test report .....</b>	<b>10</b>
<b>Annex A (normative) Flowsheet of the procedure for the acceptance of analytical values for test samples .....</b>	<b>11</b>
<b>Annex B (informative) Derivation of repeatability and permissible tolerance equations .....</b>	<b>12</b>
<b>Annex C (informative) Precision data obtained by international analytical trials .....</b>	<b>13</b>

## 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.

International Standards are drafted in accordance with the rules given in the ISO/IEC Directives, Part 2.

The main task of technical committees is to prepare International Standards. 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.

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.

ISO 9682-1 was prepared by Technical Committee ISO/TC 102, *Iron ore and direct reduced iron*, Subcommittee SC 2, *Chemical analysis*.

This second edition cancels and replaces the first edition (ISO 9682-1:1991), which has been technically revised.

ISO 9682 consists of the following parts, under the general title *Iron ores — Determination of manganese content*:

— *Part 1: Flame atomic absorption spectrometric method*

— *Part 2: Periodate spectrophotometric method*

iTeh STANDARD PREVIEW  
(standards.iteh.ai)

<https://standards.iteh.ai/catalog/standards/sist/a7db0c0d-0844-400f-ba07-33083b19c4b3/iso-9682-1-2009>

# Iron ores — Determination of manganese content —

## Part 1: Flame atomic absorption spectrometric method

**WARNING** — This part of ISO 9682 may involve hazardous materials, operations and equipment. This part of ISO 9682 does not purport to address all of the safety problems associated with its use. It is the responsibility of the user of this part of ISO 9682 to establish appropriate health and safety practices and determine the applicability of regulatory limitations prior to use.

### 1 Scope

This part of ISO 9682 specifies a flame atomic absorption spectrometric method for the determination of the mass fraction of manganese in iron ores.

This method is applicable to a mass-fraction range of 0,01 % to 2,5 % of manganese in natural iron ores, iron ore concentrates and agglomerates, including sinter products.

### 2 Normative references

The following referenced documents are indispensable for the application of this document. 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 7764, *Iron ores — Preparation of predried test samples for chemical analysis*

### 3 Principle

The test portion is decomposed by one of the following methods.

- Fusion of the test portion in sodium carbonate/sodium tetraborate flux and dissolution of the cooled melt in hydrochloric acid.
- Treatment with hydrochloric acid, with the addition of a small amount of nitric acid. Evaporation to dehydrate silica, addition of hydrochloric acid, dilution and filtration. Ignition of the residue and removal of silica by evaporation with hydrofluoric and sulfuric acids. Fusion with sodium carbonate and sodium tetraborate and dissolution of the cooled melt in the filtrate.

The solution obtained, in both cases, is aspirated into the flame of an atomic absorption spectrometer using a dinitrogen oxide/acetylene flame.

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

## 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** ( $\text{Na}_2\text{CO}_3$ ), anhydrous.
- 4.2 **Sodium tetraborate** ( $\text{Na}_2\text{B}_4\text{O}_7$ ), anhydrous.
- 4.3 **Hydrochloric acid**,  $\rho$  1,16 g/ml to 1,19 g/ml.
- 4.4 **Hydrochloric acid**,  $\rho$  1,16 g/ml to 1,19 g/ml, diluted 1 + 1.
- 4.5 **Nitric acid**,  $\rho$  1,4 g/ml.
- 4.6 **Hydrofluoric acid**,  $\rho$  1,13 g/ml, 40 % (by mass), or 1,19 g/ml, 48 % (by mass).
- 4.7 **Sulfuric acid**,  $\rho$  1,84 g/ml.
- 4.8 **Sulfuric acid**,  $\rho$  1,84 g/ml, diluted 1 + 1.
- 4.9 **Background solution.**

Dissolve 12 g of metallic iron (wire or powder) or 17 g of iron oxide (in both cases with a mass fraction of manganese less than 0,003 %) in 100 ml of hydrochloric acid (4.3) by heating in a covered 1 000 ml beaker. If metallic iron is used, oxidize by adding nitric acid (4.5) drop by drop. Cool and add 300 ml of hydrochloric acid (4.3). Dissolve 32 g of sodium carbonate (4.1) and 16 g of sodium tetraborate (4.2) in 300 ml of water, add carefully to the iron solution and heat to remove carbon dioxide. Cool, transfer to a 1 000 ml one-mark volumetric flask, dilute to volume with water and mix.

### 4.10 Manganese standard solutions

#### 4.10.1 Manganese stock solution, 500 $\mu\text{g}$ Mn/ml.

Dissolve 0,500 g of high-purity manganese metal [minimum purity 99,9 % (by mass)] in 25 ml of hydrochloric acid (4.4) in a covered tall-form beaker, while heating. When dissolution is complete, cool, transfer the solution to a 1 000 ml one-mark volumetric flask, dilute to volume with water and mix.

#### 4.10.2 Manganese standard solution, 50 $\mu\text{g}$ Mn/ml.

Transfer 50 ml of manganese stock solution (4.10.1) to a 500 ml one-mark volumetric flask, dilute to volume with water and mix.

### 4.11 Manganese calibration solutions.

To a series of 100 ml one-mark volumetric flasks, transfer 0 ml; 5,0 ml; 10,0 ml; 20,0 ml; 30,0 ml, respectively, of manganese standard solution (4.10.2). Add 25,0 ml of background solution (4.9) to each flask, dilute to volume with water and mix.

The range of manganese concentrations that can be covered may vary from one instrument to another. Attention should be paid to the minimum performance criteria described in 5.5. For instruments with high sensitivity, the solution of highest concentration shown above may be deleted from the series and an additional solution included at the lower end, e.g. 2,0 ml of manganese standard solution (4.10.2).

## 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 or suitable platinum alloy crucibles**, of minimum capacity 25 ml.
- 5.2 **Muffle furnace**, to provide a minimum temperature of 1 020 °C.
- 5.3 **Combined magnetic stirrer/hotplate**.
- 5.4 **Stirring bars**, polytetrafluoroethylene (PTFE)-coated, 10 mm long.
- 5.5 **Atomic absorption spectrometer**, equipped with 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 most concentrated manganese calibration solution (4.11) is at least 0,27.
- b) **Graph linearity**: the slope of the calibration graph covering the top 20 % of the concentration range (expressed as a change in absorbance) is not 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, are 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 read-out 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 a dinitrogen oxide/acetylene flame of a premix burner.

		ISO 9682-1:2009
Hollow cathode lamp, mA	5	<a href="https://standards.iteh.ai/catalog/standards/sist/a7db0c0d-0844-400f-ba07-33083b19cdb3/iso-9682-1-2009">https://standards.iteh.ai/catalog/standards/sist/a7db0c0d-0844-400f-ba07-33083b19cdb3/iso-9682-1-2009</a>
Wavelength, nm	279,5	
Dinitrogen oxide flow rate, l/min	7,5	
Acetylene flow rate, l/min	4,0	

In systems where the values shown above for gas flow rates do not apply, the ratio of the gas flow rates can 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 and prepared in accordance with ISO 3082. In the case of ores with significant contents of combined water or oxidizable compounds, use a particle size of minus 160 µm.

NOTE Guidance 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 manner 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 both cases, appropriate recalibration.

### 7.2 Safety precautions

**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 in operation.

### 7.3 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.

### 7.4 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.

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 both cases, 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.

### 7.5 Determination

#### 7.5.1 Decomposition of the test portion

If the decomposition is to be based on fusion, proceed as specified in 7.5.1.1. If it is to be based on acid attack, proceed as specified in 7.5.1.2.

##### 7.5.1.1 Alkali fusion

Add 0,80 g of sodium carbonate (4.1) to a platinum or suitable platinum alloy crucible (5.1), transfer the test portion (7.3) to the crucible and mix well using a platinum or stainless-steel rod. Add 0,40 g of sodium tetraborate (4.2) and repeat the mixing using the metal rod. Place the crucible in a muffle furnace (5.2), with the temperature maintained at 1 020 °C to 1 040 °C, for 30 min.

Remove the crucible and gently swirl the melt as it solidifies. Allow to cool, then place a PTFE-coated stirring bar (5.4) in the crucible and place the crucible on its side in a 150 ml low-form beaker. Add 20 ml of hydrochloric acid (4.4) and 30 ml of water, cover and heat while stirring on a magnetic stirrer/hotplate (5.3) until dissolution of the melt is complete.



NOTE 1 The crucible might need to be rolled to ensure complete dissolution of the fused melt.

NOTE 2 As an alternative to a magnetic stirrer/hotplate, an ultrasonic bath can be used to facilitate dissolution of the fused melt.

Remove the crucible and stirrer and rinse, cool the solution and transfer to a 100 ml one-mark volumetric flask. Dilute to volume with water and mix. (This is the test solution.)

### 7.5.1.2 Acid attack

Transfer the test portion (7.3) to a 250 ml tall-form beaker. Add 20 ml of hydrochloric acid (4.3), cover with a watch-glass and heat for about 1 h on a hotplate adjusted to give a temperature of 100 °C in a test beaker containing a similar volume and depth of sulfuric acid (4.7).

NOTE When the amount of insoluble residue is high, continue heating on a higher temperature zone of the hotplate without boiling the solution.

Add 1 ml of nitric acid (4.5) and 0,2 ml of sulfuric acid (4.8), and digest for 15 min. Remove the watch-glass and evaporate the solution to dryness. Heat the salts for 30 min on a hotplate adjusted as before to give a temperature of 100 °C to 115 °C in sulfuric acid. Add 20 ml of hydrochloric acid (4.4), cover the beaker with a watch-glass and warm for several minutes. Add 30 ml of water and heat to boiling.

Cool, wash the watch-glass and the walls of the beaker, and filter the solution through a medium-texture filter paper containing filter pulp (0,3 g to 0,4 g dry mass) into a 150 ml low-form beaker. Carefully remove all adhering particles with a rubber-tipped glass rod or piece of moistened filter paper, and transfer to the filter, washing the paper with water until it is visibly free from iron. Reserve the filtrate. Transfer the filter paper and residue to a platinum or suitable platinum alloy crucible (5.1) and start evaporating the filtrate to a final volume of approximately 70 ml.

Dry and ignite the paper and residue in the platinum or suitable platinum alloy crucible (5.1) at approximately 800 °C. Cool, add 3 drops of sulfuric acid (4.8) and 2 ml of hydrofluoric acid (4.6) or, in the case of ores of high silica content, 5 ml of hydrofluoric acid. Evaporate slowly to expel silica and continue heating to remove the sulfuric acid. Ignite at approximately 800 °C for several minutes and cool. Add 0,4 g of sodium tetraborate (4.2) and 0,8 g of sodium carbonate (4.1) to the residue, mix and heat at 1 000 °C for 15 min in a muffle furnace (5.2) or over a pressurized air burner for a time sufficient to produce a clear melt.

Cool the melt and place the crucible on its side in the beaker containing the reserved filtrate evaporated to approximately 70 ml. Heat the solution until the fused salts are completely dissolved from the crucible. Remove and rinse the crucible, cool the solution and transfer to a 100 ml one-mark volumetric flask. Dilute to volume with water and mix. (This is the test solution.)

### 7.5.2 Treatment of the test solution

If the mass fraction of manganese in the test sample is between 0,01 % and 0,2 %, use the test solution, obtained in either 7.5.1.1 or 7.5.1.2 directly, without dilution. For a mass fraction of manganese between 0,2 % and 3,0 %, transfer an appropriate aliquot of the test solution (see Table 1) to a 100 ml one-mark volumetric flask, add the amount of background solution (4.9) indicated in Table 1, dilute to volume with water and mix. (This is the diluted test solution.)

If a diluted test solution has been prepared, prepare a corresponding diluted blank test solution as follows.

Transfer a corresponding amount of the blank test solution, and the amount of background solution (4.9) specified in Table 1, to a 100 ml one-mark volumetric flask. Dilute to volume with water and mix. (This is the diluted blank test solution.)

Table 1 — Dilution guide for test and blank test solution

Expected mass fraction, $w_{Mn}$ , of Mn in sample %	Aliquot ml	Volume of background solution (4.9) to be added ml
0,01 to 0,2	No dilution	0
0,2 to 0,6	50,0	12,5
0,5 to 1,5	20,0	20
1,0 to 3	10,0	22,5

NOTE The overlap in concentration ranges allows the mass fraction obtained to differ slightly from the mass fraction expected. When in doubt, use the first range specified.

7.5.3 Adjustment of the atomic absorption spectrometer

Set the wavelength of manganese (279,5 nm) to obtain minimum absorbance and adjust the read-out to zero absorbance. Light the dinitrogen oxide/acetylene flame, observing the safety precautions of 7.2. After 10 min of preheating the burner, aspirate the calibration solution with the highest mass fraction of manganese (4.11) and carefully adjust the fuel flow and burner position to obtain maximum absorbance.

Check that the conditions for zero absorbance were maintained while aspirating water and again aspirate the calibration solution with the highest mass fraction of manganese to establish that the absorbance reading is not drifting. Set the reading for water to zero absorbance.

7.5.4 Atomic absorption measurements (standards.iteh.ai)

Aspirate the calibration solutions (4.11) and the test solution or diluted test solution in order of increasing concentration, starting with the zero calibration solution and the blank test solution or diluted blank test solution. When stable responses have been obtained, record the readings in absorbance units. Aspirate water between each solution and repeat the measurements twice.

The reagents used for the preparation of the zero calibration solution should have a low enough mass fraction of manganese for the absorbance value not to significantly exceed 0,01 with high-performance instruments (absorbance for the highest calibration solution above 0,6), and 0,005 with instruments of average to low performance (approaching the criterion in 5.5).

NOTE If, with an instrument of high sensitivity, the solution of highest manganese concentration has been deleted from the calibration series (see 4.11), it can also be necessary to change the dilution guide in Table 1. In this case, move the values for the volumes of aliquots and background solution to the line above for each range of mass fraction of manganese, using, for the range of 1 % to 3 % Mn, a 5,0 ml aliquot with 23,8 ml of background solution.

Correct the absorbance values obtained for the calibration solutions by subtracting the absorbance of the zero calibration solution, and prepare a calibration graph by plotting the net absorbance values against micrograms of manganese per millilitre. If the graph is substantially linear, subtract the absorbance obtained for the blank test or diluted blank test from the absorbance obtained for the test solution or diluted test solution as appropriate and, using the graph, convert the net absorbance value of the test solution or diluted test solution to micrograms of manganese per millilitre.

If any curvature obtained approaches the limit specified in 5.5 b), replot the graph using uncorrected values for all solutions and establish the concentration of the zero calibration solution from the intercept of the graph on the negative side of the concentration axis. Add this value to the nominal concentration values of the calibration solutions and replot the graph to pass through the origin. Determine from the graph the concentration of manganese, in micrograms per millilitre, in the blank test and test solutions respectively, and correct the concentration of the test solution or diluted test solution with the concentration of the blank test or diluted blank test, as appropriate.

## 8 Expression of results

### 8.1 Calculation of mass fraction of manganese

The mass fraction of manganese,  $w_{\text{Mn}}$ , expressed as a percentage, is calculated to five decimal places for mass fractions of manganese below 0,5 % and to four decimal places for mass fractions of manganese between 0,5 % and 2,5 %, from Equation (1):

$$w_{\text{Mn}} = \frac{\rho_{\text{Mn}}}{m \times 100} \times \text{DF} \quad (1)$$

where

$\rho_{\text{Mn}}$  is the concentration, in micrograms per millilitre, of manganese in the test solution or diluted test solution;

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

DF is the dilution factor, calculated from  $100/V$ , when a dilution has been made using  $V$  ml of test solution. When no dilution has been made,  $\text{DF} = 1$ .

### 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:

for alkali fusion

$$R_d = 0,024 0X^{0,6087} \quad (2)$$

$$P = 0,037 4X + 0,002 9 \quad (3)$$

$$\sigma_d = 0,008 5X^{0,6087} \quad (4)$$

$$\sigma_L = 0,012 0X + 0,000 9 \quad (5)$$

for acid attack

$$R_d = 0,021 7X + 0,001 3 \quad (6)$$

$$P = 0,045 6X + 0,002 5 \quad (7)$$

$$\sigma_d = 0,007 7X + 0,000 4 \quad (8)$$

$$\sigma_L = 0,013 8X + 0,000 9 \quad (9)$$

where

$R_d$  is the independent duplicate limit;

$P$  is the permissible tolerance between laboratories;

$\sigma_d$  is the independent duplicate standard deviation;

$\sigma_L$  is the between-laboratories standard deviation;