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# International Standard



# 7990

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## Manganese ores and concentrates — Determination of total iron content — Titrimetric method after reduction and sulfosalicylic acid spectrophotometric method

*Minerais et concentrés de manganèse — Dosage du fer total — Méthode titrimétrique après réduction et méthode spectrophotométrique à l'acide sulfosalicylique*

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## Foreword

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International Standard ISO 7990 was prepared by Technical Committee ISO/TC 65, *Manganese and chromium ores*.

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STANDARD PREVIEW  
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# Manganese ores and concentrates – Determination of total iron content – Titrimetric method after reduction and sulfosalicylic acid spectrophotometric method

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

### 1 Scope and field of application ISO 7990:1985 **2 References**

<https://standards.iteh.ai/catalog/standards/sist/8864aca3-49f4-4c0b-b178-900000000000/iso-7990-1985>

This International Standard specifies two methods for the determination of the total iron content of manganese ores and concentrates:

**method A:** titrimetric method after reduction, applicable to products having a total iron content from 1 to 25 % (*m/m*);

**method B:** sulfosalicylic acid spectrophotometric method, applicable to products having a total iron content from 0,2 to 2 % (*m/m*).

ISO 4296/1, *Manganese ores – Sampling – Part 1: Incremental sampling.*

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

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

It should be read in conjunction with ISO 4297.

## Section one: Method A — Titrimetric method after reduction

### 3 Principle

In the case of ores which are easy to decompose, decomposition of a test portion by treatment with hydrochloric acid.

In the case of ores which are difficult to decompose, decomposition of a test portion either by treatment with hydrochloric acid in the presence of sodium fluoride, or by treatment with hydrochloric acid; separation of the residue, fusion with potassium disulfate, extraction of the melt with hydrochloric acid, precipitation of the iron and redissolution and combination with the main solution.

Reduction of the iron(III) with tin(II) chloride solution. Oxidation of excess of reducing agent with mercury(II) chloride solution. Titration of the iron(II) against potassium dichromate standard volumetric solution, using sodium diphenylamine-sulfonate as indicator.

### 4 Reagents

**4.1 Potassium disulfate** ( $K_2S_2O_7$ ).

**4.2 Sodium fluoride** (NaF).

**4.3 Hydrofluoric acid**,  $\rho$  1,14 g/ml, 40 % (m/m) solution.

**4.4 Hydrochloric acid**,  $\rho$  1,19 g/ml.

**4.5 Hydrochloric acid** (4.4), diluted 1 + 2.

**4.6 Hydrochloric acid** (4.4), diluted 1 + 4.

**4.7 Hydrochloric acid** (4.4), diluted 1 + 50.

**4.8 Sulfuric acid**,  $\rho$  1,84 g/ml, diluted 1 + 1.

**4.9 Sulfuric acid-orthophosphoric acid mixture.**

Pour 150 ml of sulfuric acid (4.8) carefully, while stirring, into 300 ml of water. After cooling add 150 ml of orthophosphoric acid ( $\rho$  1,70 g/ml), dilute to 1 000 ml with water and mix.

**4.10 Ammonia**,  $\rho$  0,91 g/ml, 25 % (m/m) solution.

**4.11 Ammonia solution** (4.10), diluted 1 + 50.

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

**4.13 Tin(II) chloride dihydrate** ( $SnCl_2 \cdot 2H_2O$ ), 100 g/l solution.

Dissolve 100 g of tin(II) chloride dihydrate, while heating, in 200 ml of hydrochloric acid (4.4), cool, dilute to 1 000 ml with

water, mix and add a small quantity of granular or mossy tin metal.

Store the solution in a brown glass bottle.

**4.14 Mercury(II) chloride** ( $HgCl_2$ ), 50 g/l solution.

**4.15 Potassium permanganate** ( $KMnO_4$ ), 30 g/l solution.

**4.16 Potassium dichromate**, standard volumetric solutions.

**4.16.1 Solution A**,  $c(K_2Cr_2O_7) = 0,016\ 67$  mol/l.

Weigh 4,903 5 g of potassium dichromate, recrystallized and dried at 140 to 150 °C, into a 300 ml beaker and dissolve in 100 ml of water. Transfer the solution to a 1 000 ml volumetric flask, dilute to the mark and mix.

1 ml of this solution corresponds to 0,005 585 g of iron.

**4.16.2 Solution B**,  $c(K_2Cr_2O_7) = 0,008\ 33$  mol/l.

Weigh 2,451 7 g of potassium dichromate into a 300 ml beaker and dissolve in 100 ml of water. Transfer the solution to a 1 000 ml volumetric flask, dilute with water to the mark and

mix.

1 ml of this solution corresponds to 0,002 792 g of iron.

**4.17 Iron**, standard solution, corresponding to 5,58 g of Fe per litre.

Place 5,58 g of metallic iron [purity 99,95 % (m/m)] in a 500 ml conical flask. Insert a small funnel into the neck of the flask.

Add 110 ml of the hydrochloric acid (4.5) in small portions and heat until the iron is dissolved. Cool the solution and oxidize with 5 ml of hydrogen peroxide (4.12). Cool the solution, transfer to a 1 000 ml one-mark volumetric flask, dilute to the mark with water and mix.

1 ml of this standard solution corresponds to 1 ml of potassium dichromate standard volumetric solution A.

**4.18 Sodium diphenylaminesulfonate indicator** ( $C_{12}H_{10}O_3NSNa$ ), 0,8 g/l.

### 5 Apparatus

Ordinary laboratory apparatus, and

Platinum or suitable platinum alloy crucible.

### 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

### 7.1 Test portion

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

Table 1

Expected total iron content	Mass of test portion
% (m/m)	g
From 1,0 to 10,0	1,0
From 10,0 to 25,0	0,5

### 7.2 Blank test

Carry out a blank test in parallel with the determination, by the same procedure, but using 1 ml of iron standard solution (4.17) instead of the test portion.

### 7.3 Decomposition of test portion

#### 7.3.1 For ores which are easy to decompose

Place the test portion (7.1) in a 500 ml conical flask, moisten with water, and add 15 ml of hydrochloric acid (4.4).

Cover the flask with a watch-glass and heat the solution gently without boiling, swirling from time to time to decompose the ore. Proceed according to 7.4.

#### 7.3.2 For ores which are difficult to decompose

Place the test portion (7.1) in a 300 ml beaker, moisten with water, and add 0,5 g of sodium fluoride (4.2) and 15 ml of hydrochloric acid (4.4).

Cover the beaker with a watch-glass and heat to just below the boiling point to decompose the ore. Proceed according to 7.4.

In case of incomplete decomposition of the ore, place the test portion (7.1) in a 300 ml beaker, moisten with water, and add 15 ml of hydrochloric acid (4.4).

Cover the beaker with a watch-glass and heat to just below the boiling point to decompose the base mass of the test portion. Add 30 to 40 ml of hot hydrochloric acid (4.7) and filter the insoluble residue on a medium texture filter paper with a small quantity of paper pulp. Wash the residue four or five times with hydrochloric acid (4.7) and four or five times with warm water. Collect the filtrate and washings in a 500 ml conical flask and reserve as the main solution.

Place the filter containing the residue in a platinum crucible, dry, ash and ignite at 600 to 700 °C until the carbonaceous matter is removed. After cooling, moisten the residue with water, add 3 or 4 drops of sulfuric acid (4.8) and 5 to 6 ml of hydrofluoric acid (4.3) and evaporate until the fuming of sulfuric acid ceases. Add 2 g of potassium disulfate (4.1) to the residue, cover the crucible with a lid and fuse at 600 to 700 °C until a clear melt is obtained. Allow the melt to cool,

place the platinum crucible in a 100 ml beaker and leach the melt in 25 to 30 ml of hydrochloric acid (4.6). Remove the crucible and the lid from the beaker and rinse it with water.

Add 1 or 2 drops of hydrogen peroxide (4.12) to the solution while mixing, dilute with water to 50 ml and add ammonia solution (4.10) until the ammoniacal smell persists. Heat the solution to boiling and allow to stand for 10 min in a warm place. After the precipitate has settled, filter on a rapid paper and wash four or five times with hot ammonia solution (4.11). Discard the filtrate. Dissolve the precipitate on the filter with 10 ml of hydrochloric acid (4.5), using small portions. Wash the filter four or five times with hot hydrochloric acid (4.7) and four or five times with hot water. Add the solution obtained to the main solution and evaporate to 25 or 30 ml.

### 7.4 Reduction

#### 7.4.1 For ores containing less than 0,02 % (m/m) vanadium

Heat the solution obtained to 90 to 100 °C, wash the walls of the flask with hot hydrochloric acid (4.7) immediately, add tin(II) chloride solution (4.13), while swirling, until the solution becomes colourless and then add 1 or 2 drops of the tin(II) chloride solution in excess.

Wash the walls of the flask with hot water, swirl the solution, then cool in a water cooler. When the solution has reached ambient temperature, add 5 ml of the mercury(II) chloride solution (4.14). A small quantity of a white precipitate of mercury(I) chloride should appear. If there is no precipitate or if there is too much of it and it has a dark colour owing to the presence of metallic mercury, repeat the analysis.

#### 7.4.2 For ores containing more than 0,02 % (m/m) vanadium

Dilute the solution obtained in 7.3 to 100 ml with water, heat to 90 to 100 °C, add tin(II) chloride solution (4.13), while swirling, until the solution becomes colourless and then add 0,5 ml of the tin(II) chloride solution in excess.

Add potassium permanganate solution (4.15) drop by drop, while swirling, until the colour of the solution becomes stable yellow and then again add tin(II) chloride solution (4.13) drop by drop, while swirling, until the yellow colour of the solution has disappeared. Then add one or two drops of the tin(II) chloride solution in excess.

Wash the walls of the flask with water, cool in a water cooler and add 5 ml of mercury(II) chloride solution (4.14). A small quantity of a white precipitate of mercury(I) chloride should appear. If there is no precipitate or if there is too much of it and it has a dark colour owing to the presence of metallic mercury, repeat the analysis.

### 7.5 Titration

Allow the solution obtained in 7.4 to stand for about 5 min, dilute with water to 200 ml, add to the solution 25 ml of the sulfuric acid-orthophosphoric acid mixture (4.9) and 2 ml of the sodium diphenylaminesulfonate indicator (4.18). Mix and immediately titrate with potassium dichromate solution (4.16).

The end-point is reached when the green colour of the solution changes to purple-blue.

For ores containing less than 5 % (*m/m*) of total iron, use potassium dichromate standard volumetric solution B (4.16.2) for titration; for ores containing more than 5 % (*m/m*) of total iron, use potassium dichromate standard volumetric solution A (4.16.1).

## 8 Expression of results

### 8.1 Calculation

The total iron content,  $w_{Fe}$  (%), expressed as a percentage by mass, is given by the equation

$$w_{Fe} (\%) = \frac{\rho(V_1 - V_2) \times 100}{m} \times K$$

where

$\rho$  is the titre of the potassium dichromate standard volumetric solution, expressed in grams of iron per millilitre (see 4.16);

$V_1$  is the volume, in millilitres, of potassium dichromate standard volumetric solution used for titration of the test solution;

$V_2$  is the volume, in millilitres, of potassium dichromate standard volumetric solution used for titration of the blank solution (deducting the volume of potassium dichromate standard volumetric solution A or B corresponding to 1 ml of iron standard solution);

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

$K$  is the conversion factor for the expression of the total iron content on the dry basis.

### 8.2 Permissible tolerances on results of parallel determinations

Table 2

Total iron content	Permissible tolerance	
	Three parallel determinations	Two parallel determinations
% ( <i>m/m</i> )	% ( <i>m/m</i> )	% ( <i>m/m</i> )
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
From 10,0 to 25,0	0,35	0,30

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## Section two : Method B – Sulfosalicylic acid spectrophotometric method

### 9 Principle

In the case of ores which are easy to decompose, decomposition of a test portion by treatment with hydrochloric acid.

In the case of ores which are difficult to decompose, decomposition of a test portion either by treatment with hydrochloric acid in the presence of sodium fluoride, or by treatment with hydrochloric acid; separation of the residue, fusion with potassium disulfate, extraction of the melt with hydrochloric acid and combination with the main solution.

Spectrophotometric determination in the presence of sulfosalicylic acid and hydroxylammonium chloride at about 430 nm.

### 10 Reactions

The method is based on the interaction of iron with sulfosalicylic acid in alkaline solution (pH 8 to 12) with the formation of a coloured complex. The influence of manganese is eliminated by hydroxylammonium chloride.

### 11 Reagents

- 11.1 Sodium fluoride** (NaF).
- 11.2 Potassium disulfate** ( $K_2S_2O_7$ ).
- 11.3 Hydrofluoric acid**,  $\rho$  1,14 g/ml.
- 11.4 Hydrochloric acid**,  $\rho$  1,19 g/ml.
- 11.5 Hydrochloric acid** (11.4), diluted 1 + 4.
- 11.6 Hydrochloric acid** (11.4), diluted 1 + 50.
- 11.7 Sulfuric acid**,  $\rho$  1,84 g/ml, diluted 1 + 1.
- 11.8 Ammonia solution**,  $\rho$  0,91 g/ml, diluted 1 + 1.
- 11.9 Hydroxylammonium chloride**, 100 g/l solution.
- 11.10 Sulfosalicylic acid dihydrate** ( $C_7H_6O_6S \cdot 2H_2O$ ), 100 g/l solution.
- 11.11 Iron**, standard solutions.
- 11.11.1 Solution A**, corresponding to 0,100 0 g of Fe per litre.

Weigh 0,100 0 g of metallic iron [purity 99,95 % (*m/m*)] and dissolve in 50 ml of nitric acid (diluted 1 + 3).

Heat the solution until it is free from nitrogen oxides. Cool the solution, transfer to a 1 000 ml volumetric flask, dilute with water to the mark and mix.

1 ml of this standard solution contains 0,1 000 mg of Fe.

**11.11.2 Solution B**, corresponding to 0,010 0 g of Fe per litre.

Pipette 10 ml of iron standard solution A (11.11.1) into a 100 ml volumetric flask, dilute with water to the mark and mix.

1 ml of this standard solution contains 0,010 0 mg of Fe.

### 12 Apparatus

Usual laboratory apparatus and

**12.1 Platinum or suitable platinum alloy crucible.**

**12.2 Spectrophotometer**, with selectors for continuous or discontinuous variation, capable of measuring absorbance at 430 nm.

### 13 Sampling and samples

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

### 14 Procedure

#### 14.1 Test portion

Weigh 0,2 g of the test sample.

#### 14.2 Preparation of test solution

##### 14.2.1 For ores which are easy to decompose

Place the test portion (14.1) in a 100 ml beaker, moisten with water and dissolve in 5 ml of hydrochloric acid (11.4). Add 30 to 40 ml of hot hydrochloric acid (11.6) to the solution, and filter through a medium texture filter paper with a small quantity of paper pulp. Wash the filter four or five times with hydrochloric acid (11.6) and four or five times with hot water. Discard the filter. Proceed according to 14.2.3.

##### 14.2.2 For ores which are difficult to decompose

Place the test portion (14.1) in a 100 ml beaker, moisten with water, add 0,5 g of sodium fluoride (11.1) and dissolve in 5 ml of hydrochloric acid (11.4) to decompose the ore. Add 30 to 40 ml of hot hydrochloric acid (11.6) to the solution, and filter through a medium texture filter paper with a small quantity of paper pulp. Wash the filter four or five times with hydrochloric acid (11.6) and four or five times with hot water. Discard the filter. Proceed according to 14.2.3.



In case of incomplete decomposition of the ore, place the test portion (14.1) in a 100 ml beaker, moisten with water and dissolve in 5 ml of hydrochloric acid (11.4). Add 30 to 40 ml of hot hydrochloric acid (11.6) to the solution and filter the insoluble residue on a medium texture filter paper with a small quantity of paper pulp. Wash the filter four or five times with hydrochloric acid (11.6) and four or five times with hot water. Reserve the filtrate as the main solution.

Place the filter containing the residue in a platinum crucible, dry, ash and ignite at 600 to 700 °C until the carbonaceous matter is removed. After cooling, moisten the residue with water, add 3 or 4 drops of sulfuric acid (11.7) and 5 to 6 ml of hydrofluoric acid (11.3) and evaporate until the fuming of sulfuric acid ceases. Add 2 g of potassium disulfate (11.2) to the residue, cover the crucible with a platinum lid and fuse at 650 to 700 °C until a clear melt is obtained. Allow the melt to cool, place the crucible in a 100 ml beaker and leach the melt in 25 to 30 ml of hydrochloric acid (11.5). Remove the crucible and the lid from the beaker and rinse it with water.

Filter the solution obtained through a medium texture filter paper and wash the filter four or five times with hot water. Discard the filter and add the filtrate to the main solution.

#### 14.2.3 Test solution

After cooling, evaporate the solution (14.2.1 or 14.2.2) if necessary to about 150 ml and transfer to a 200 ml volumetric flask. Dilute with water to the mark and mix.

#### 14.3 Blank test

Carry out a blank test in parallel with the determination.

#### 14.4 Calibration

##### 14.4.1 Preparation of the set of calibration solutions

Introduce, using a burette, into each of a series of nine 100 ml one-mark volumetric flasks, 0,0; 1,0; 2,0; 4,0; 6,0; 8,0; 10,0; 12,0; and 14,0 ml of iron standard solution B (11.11.2), corresponding to 0,00; 0,01; 0,02; 0,04; 0,06; 0,08; 0,10; 0,12; and 0,14 mg of iron.

##### 14.4.2 Formation of the absorbing compound

Add 10 ml of hydroxylammonium chloride solution (11.9), mix, and add 30 ml of sulfosalicylic acid solution (11.10). Add ammonia solution (11.8) until a stable yellow colour appears, and then 5 ml in excess. Dilute to the mark with water and mix.

##### 14.4.3 Spectrometric measurements

Measure the absorbance of the solutions over the range 420 to 480 nm (spectrometer with selectors for continuous variation) or at 430 nm (spectrometer with selectors for discontinuous variation) in a cell of thickness 50 mm, or any other suitable cell, against water as reference.

##### 14.4.4 Plotting the calibration graph

Prepare a calibration graph by plotting the absorbance (deducting the absorbance of the zero term) against the nominal iron contents of the solutions.

#### 14.5 Determination

##### 14.5.1 Formation of the absorbing compound

If the iron content is less than 1 % (m/m), pipette a 10 ml aliquot portion of the test solution (14.2.3) into a 100 ml one-mark volumetric flask; if the iron content is greater than 1 % (m/m), use a 5 ml aliquot portion.

Proceed as in 14.4.2.

##### 14.5.2 Spectrometric measurements

See 14.4.3.

### 15 Expression of results

#### 15.1 Calculation

After having deducted the absorbance reading for the blank test, convert the absorbance reading for the test solution to the total iron content by means of the calibration graph (14.4.4).

The total iron content,  $w_{Fe}$  (%), expressed as a percentage by mass, is given by the equation

$$w_{Fe} (\%) = \frac{m_1 \times 100}{m_2 \times 1\,000} \times K$$

where

$m_1$  is the mass, in milligrams, of total iron obtained from the calibration graph;

$m_2$  is the mass, in grams, of the test portion corresponding to the aliquot portion of the test solution;

$K$  is the conversion factor for the expression of total iron content on the dry basis.

#### 15.2 Permissible tolerances on results of parallel determinations

Table 3

Total iron content	Permissible tolerance	
	Three parallel determinations	Two parallel determinations
% (m/m)	% (m/m)	% (m/m)
From 0,20 to 0,40	0,04	0,03
From 0,40 to 1,0	0,07	0,06
From 1,0 to 2,0	0,10	0,09