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# International Standard



# 6233

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INTERNATIONAL ORGANIZATION FOR STANDARDIZATION • МЕЖДУНАРОДНАЯ ОРГАНИЗАЦИЯ ПО СТАНДАРТИЗАЦИИ • ORGANISATION INTERNATIONALE DE NORMALISATION

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## Manganese ores and concentrates — Determination of calcium and magnesium contents — EDTA titrimetric method

*Minerais et concentrés de manganèse — Dosage du calcium et du magnésium — Méthode titrimétrique à l'EDTA*

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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 6233 was developed by Technical Committee ISO/TC 65, *Manganese and chromium ores*, and was circulated to the member bodies in March 1982.

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

Australia	India	Romania
Austria	Italy	South Africa, Rep. of
Brazil	Japan	Spain
Czechoslovakia	Mexico	Thailand
Egypt, Arab Rep. of	Netherlands	United Kingdom
Germany, F. R.	Poland	USSR

The member bodies of the following countries expressed disapproval of the document on technical grounds :

China  
France

# Manganese ores and concentrates — Determination of calcium and magnesium contents — EDTA titrimetric method

## 1 Scope and field of application

This International Standard specifies an EDTA titrimetric method for the determination of calcium and magnesium content of manganese ores and concentrates.

The method is applicable to products having calcium and magnesium contents greater than 0,3 % (*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*.<sup>1)</sup>

ISO 4296/2, *Manganese ores — Sampling — Part 2: Preparation of samples*.<sup>1)</sup>

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

## 3 Principle

Decomposition of the test portion with hydrochloric and nitric acids. Separation of silicon by evaporation of the solution to dryness. Dissolution of salts in hydrochloric acid, any insoluble residue being filtered off and the filtrate being reserved as the main solution.

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

Fusion of the residue with sodium carbonate.

Dissolution of the melt in water and filtration of the solution obtained. Dissolution of the residue in hydrochloric acid and combination with the main solution.

Separation of barium [when its content exceeds 1 % (*m/m*)] as barium sulfate.

Separation of interfering elements (iron, aluminium, manganese, copper, lead and others) from the main solution (after separation of barium sulfate or without it) with hexamethylenetetramine and sodium diethyldithiocarbamate.

Titration of calcium with standard volumetric EDTA solution at pH 13 and titration of magnesium at pH 10 (after its separation from calcium as hydroxide) on a photoelectrode titrimeter in the presence of Eriochrome blue SE indicator, or visual titration of calcium with standard volumetric EDTA solution at pH 13 in the presence of a mixture of fluorexon and thymolphthalein as indicator and of calcium plus magnesium at pH 10 in the presence of Eriochrome black T indicator.

## 4 Reagents

4.1 Potassium disulfate ( $K_2S_2O_7$ ).

4.2 Sodium carbonate, anhydrous.

4.3 Ammonia solution,  $\rho$  0,90 g/ml.

4.4 Nitric acid,  $\rho$  1,40 g/ml.

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

4.6 Hydrofluoric acid,  $\rho$  1,14 g/ml.

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

4.8 Sulfuric acid, 2 % (*m/m*) solution.

4.9 Hydrochloric acid, diluted 1 + 1.

4.10 Hydrochloric acid, diluted 1 + 4.

4.11 Hydrochloric acid, diluted 1 + 50.

4.12 Potassium hydroxide, 200 g/l solution.

Store the solution in a tightly stoppered polyethylene bottle.

4.13 Potassium hydroxide, 2 g/l solution.

4.14 Sodium-diethyldithiocarbamate, 100 g/l solution.

Prepare before use.

1) At present at the stage of draft.

**4.15 Sodium carbonate**, 10 g/l solution.

**4.16 Sucrose** (C<sub>12</sub>H<sub>22</sub>O<sub>11</sub>), 40 g/l solution.

**4.17 Hexamethylenetetramine** (C<sub>6</sub>H<sub>12</sub>N<sub>4</sub>), 100 g/l solution.

**4.18 Disodium dihydrogen(ethylenedinitrilo) tetraacetate** (EDTA), 4,6 g/l standard solution.

**4.18.1 Preparation of the solution**

Dissolve 4,6 g of the EDTA in 100 ml of water while gently heating, filter through a medium-texture filter paper into 1 000 ml one-mark volumetric flask, dilute with water to the mark and mix.

**4.18.2 Standardization of the solution**

**4.18.2.1 Standardization of the solution in case of photometric titration**

Place, in a 250 ml beaker, the aliquot portions of the standard calcium solution (4.20) and the standard magnesium solution (4.21) containing 4 to 5 mg of the above elements, and titrate with the EDTA solution (4.18) in accordance with 7.5.1 and 7.5.2.1.

**4.18.2.2 Standardization of the solution in case of visual titration**

Place, in a 250 ml conical flask, the aliquot portion of the standard calcium solution (4.20) containing 4 to 5 mg of Ca and titrate with the EDTA solution (4.18) in accordance with 7.5.3.

Place, in a 250 ml conical flask, aliquot portions of the standard calcium solution (4.20) and standard magnesium solution (4.21) containing 4 to 5 mg of the above elements and titrate with EDTA solution (4.18) in accordance with 7.5.4.

**4.18.3 Calculation**

The concentration, *c*, of the EDTA solution, expressed in grams of calcium or magnesium per millilitre, is given by the formula

$$c = \frac{m}{V}$$

where

*m* is the mass, in grams, of calcium or magnesium in the aliquot portion of the corresponding standard solution;

*V* is the volume, in millilitres, of the EDTA solution taken for titration of the aliquot portion of standard calcium or magnesium solution.

**4.19 Disodium dihydrogen(ethylenedinitrilo) tetraacetate** (EDTA), 2,3 g/l standard volumetric solution.

Dissolve 2,3 g of EDTA in 100 ml of water while gently heating. Prepare the solution and determine the concentration in accordance with 4.18 but taking aliquot portions of the standard calcium solution (4.20) and the standard magnesium solution (4.21) containing 1 to 2 mg of calcium and magnesium.

**4.20 Calcium**, standard solution corresponding to 1 g of Ca per litre.

Place 2,497 5 g of calcium carbonate, previously dried at 200 °C and cooled in a desiccator, in a 250 ml beaker, dissolve in 50 ml of the hydrochloric acid (4.10) and boil till removal of carbon dioxide. Allow the solution to cool, transfer in a 1 000 ml one-mark volumetric flask, dilute with water to the mark and mix.

1 ml of this standard solution contain 1 mg of Ca.

**4.21 Magnesium**, standard solution corresponding to 1 g of Mg per litre.

Dissolve 1,000 0 g of magnesium (purity 99,95 %) in 20 ml of the hydrochloric acid (4.9) while heating. Allow the solution to cool, transfer to a 1 000 ml one-mark volumetric flask, dilute with water to the mark and mix.

1 ml of this standard solution contain 1 mg of Mg.

**4.22 Buffer solution, pH 10**

Dissolve 35 g of ammonium chloride in 200 ml of the ammonia solution (4.3) and dilute with water to 500 ml.

**4.23 Eriochrome blue SE**, indicator {disodium 3-[(5-chloro-2-hydroxyphenyl)azo]-4,5-dihydroxy-2,7-naphthalenedi-sulfonate} (C<sub>16</sub>H<sub>9</sub>ClN<sub>2</sub>Na<sub>2</sub>O<sub>9</sub>S<sub>2</sub>), C.I. 16680, 0,5 % (*m/m*) solution.

Dissolve 0,5 g of Eriochrome blue SE in water in the presence of 2 g of ammonium chloride and 10 ml of ammonia solution (4.3), and dilute with water to 100 ml.

**4.24 Malachite green**, indicator {4-[4-(dimethylamino)- $\alpha$ -phenylbenzylidene]-2,5-cyclohexadienylidene} dimethylammonium chloride (C<sub>23</sub>H<sub>25</sub>ClN<sub>2</sub>), C.I. 42000, 1 % (*m/m*) aqueous solution.

**4.25 Eriochrome black T**, indicator, {sodium 3-hydroxy-4-[(1-hydroxy-2-naphthyl)azo]-7-nitro-1-naphthalenesulfonate} (C<sub>20</sub>H<sub>12</sub>N<sub>3</sub>NaO<sub>7</sub>S), C.I. 14645, mixed with potassium chloride in the mass ratio 1 : 100.

**4.26 Indicator mixture.**

Mix fluorexon {fluorescein-2', 7'-diylbis(methylenenitrilo) tetraacetic acid} (C<sub>30</sub>H<sub>26</sub>N<sub>2</sub>O<sub>13</sub>), thymolphthalein (3,3-bis (4-hydroxy-5-isopropyl-*o*-tolyl) phthalide) (C<sub>28</sub>H<sub>30</sub>O<sub>4</sub>) and potassium chloride in the mass ratio 1 : 1 : 100 and grind thoroughly in an agate mortar.

## 5 Apparatus

Ordinary laboratory apparatus and

### 5.1 Photoelectrotrimeter.

## 6 Sample

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

## 7 Procedure

### 7.1 Test portion

Weigh 0,5 to 1 g of the sample for chemical analysis into a 250 ml beaker.

### 7.2 Decomposition of the test portion

Dissolve the test portion (7.1) in 15 to 20 ml of the hydrochloric acid (4.5) while heating. After complete dissolution, add the nitric acid (4.4), drop by drop, until the foaming of the solution ceases. Evaporate the solution to dryness, add 10 ml of the hydrochloric acid (4.5) to the dry residue and evaporate to dryness again. Then keep the dry residue for 40 to 60 min at 120 to 130 °C. Add 10 to 15 ml of the hydrochloric acid (4.5) to the dry residue, heat moderately for 3 to 5 min to dissolve the soluble salts, then add 30 to 40 ml of hot water, heat to boiling and filter off the insoluble residue on a rapid filter paper containing a small amount of paper pulp. Wash the residue on the filter paper 3 or 4 times with the hydrochloric acid (4.11) and then several times with hot water. Reserve the filtrate (the main solution).

### 7.3 Treatment of the residue

Transfer the filter paper with the residue to a platinum crucible, ignite and incinerate at 500 to 600 °C. After allowing the crucible to cool, moisten the residue with 2 or 3 drops of water, add 2 or 3 drops of the sulfuric acid (4.7), 5 to 7 ml of the hydrofluoric acid (4.6) and evaporate to dryness. Incinerate the dry residue at 500 to 600 °C, allow to cool, add 1 to 2 g of the sodium carbonate (4.2) and fuse at 900 to 1 000 °C for 15 to 20 min. Place the crucible with the melt in a 200 to 250 ml beaker, add 50 to 60 ml of hot water and heat till complete decomposition of the melt. Rinse the crucible with water and take it out of the beaker. Boil the solution for 2 to 3 min, then filter the solution through a medium-texture filter paper with a small amount of paper pulp. Wash the residue on the paper filter 4 or 5 times with the sodium carbonate solution (4.15). Discard the filtrate. Dissolve the washed residue on the filter paper in 10 to 15 ml of hot hydrochloric acid (4.10). Wash the filter paper 3 or 4 times with hot water. Boil the solution obtained and combine it with the main solution.

### 7.4 Separation of accompanying elements

#### 7.4.1 Separation of accompanying elements in case of ores containing not more than 1 % (m/m) of barium oxide

Evaporate the combined solution (7.3) till moist salts appear. Dissolve the salts in 10 ml of the hydrochloric acid (4.5), dilute

with water to the volume of 40 to 50 ml and mix. Add the ammonia solution (4.3) to the solution obtained till the first precipitate of iron hydroxides appears. Dissolve the precipitate at once in the hydrochloric acid (4.9), added drop by drop without any excess. For neutralization of the blank test solution, add ammonia solution in the same amount as for neutralization of the test solution.

Add 20 to 30 ml of the hexamethylenetetramine solution (4.17) to the neutralized solutions, depending on iron content, heat to 80 to 90 °C and allow to stand for 15 to 20 min on an air bath or on a slightly heated plate. Then allow the solution to cool, transfer the solution with the precipitate to a 250 ml one-mark volumetric flask, add a small amount of paper pulp add 80 ml of the sodium diethyldithiocarbamate solution (4.14), mix vigorously until the solution over the precipitate becomes transparent.

Dilute the solution to the mark with water and mix. Allow the precipitate to settle and filter through two dry, close-texture filter papers into a dry conical flask, discarding the first portions of the filtrate. If turbidity of the filtrate is considerable, allow the solution to stand for 1 to 2 h, then filter it once more through two close-texture filter papers (main solution). Slight turbidity of the solution caused by the products of decomposition of sodium diethyldithiocarbamate does not interfere with the further procedure of determination of calcium and magnesium contents.

#### 7.4.2 Separation of accompanying elements in case of ores containing more than 1,0 % (m/m) of barium oxide

To the solution obtained (7.3), add 5 to 10 ml of the sulfuric acid solution (4.7) and evaporate the solution to dryness. To the dry residue, add 10 ml of the hydrochloric acid (4.5) and evaporate to dryness again. Repeat the treatment with hydrochloric acid. Moisten the dry residue with the hydrochloric acid (4.5), then dissolve in 200 ml of hot water while heating. Allow the solution to cool, neutralize with the ammonia solution (4.3) till the first precipitate of iron hydroxides appears, then dissolve it carefully by adding the hydrochloric acid (4.9), drop by drop, while mixing vigorously, then add excess of hydrochloric acid (4.9) [no more than 0,5 to 1 ml of hydrochloric acid for each 100 ml of the solution (the pH of the solution should be 1,6)]. Mix the solution and allow to stand for 2 to 3 h. Filter the precipitate of barium sulfate on a close-texture filter paper containing some paper pulp, wash 2 or 3 times with the sulfuric acid solution (4.8) and 5 or 6 times with warm water. Reserve the filtrate. Place the filter paper with the precipitate into the platinum crucible, ignite, incinerate and fuse with 2 to 3 g of the potassium disulfate (4.1) at 500 to 600 °C. Place the crucible in a 250 ml beaker and leach the melt in 100 ml of warm water, add 2 or 3 drops of the sulfuric acid (4.7), 2 ml of the hydrochloric acid (4.5), boil for 10 to 15 min and allow to stand till the solution is completely cool. Filter the residue on two close-texture filter papers containing paper pulp, wash the residue 5 or 6 times with warm sulfuric acid solution (4.8) and then 2 or 3 times with warm water. Discard the residue. Combine the filtrate obtained with the main solution, evaporate the solution to 40 to 50 ml and repeat the procedure in 7.4.1.

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

## 7.5 Determination

### 7.5.1 Determination of calcium content — Photometric titration

For the determination of calcium content, place the aliquot containing 1 to 5 mg of calcium from the solution obtained according to 7.4 in a 250 ml beaker inserted in the nest of the photoelectrotrimeter (5.1). If necessary, dilute the solution with water to 100 ml, add 1 or 2 drops of the malachite green indicator solution (4.24), which gives light turquoise colouring to the solution. Add 5 ml of the sucrose solution (4.16), then add the potassium hydroxide solution (4.12) till the solution becomes colourless, and 10 to 15 ml in excess (the pH of the solution should be 13). To the solution obtained, add 5 or 6 drops of the Eriochrome blue SE indicator solution (4.23) and titrate with the EDTA solution (4.18 or 4.19 depending on the calcium content) on the photoelectrotrimeter (5.1), using a filter having a maximum transmission 610 nm, till the pointer of the device stops.

### 7.5.2 Determination of magnesium content — Photometric titration

#### 7.5.2.1 Determination of magnesium content in case of ore with magnesium content not significantly less than calcium content

Carry out the determination using the aliquot portion used for the determination of the calcium content (7.5.1). Filter the precipitate of magnesium hydroxide on a medium-texture filter paper compacted with paper pulp. Wash the walls of the beaker twice with the potassium hydroxide solution (4.13). Wash the precipitate of magnesium hydroxide on the filter paper 4 to 7 times (depending on the magnesium content) with the potassium hydroxide solution (4.13). Then dissolve the precipitate in 50 ml of the hydrochloric acid (4.11), collecting the filtrate in the beakers in which the determination of calcium content has been carried out. Wash the filter paper 5 to 7 times with warm water. To the solution, add 4 ml of the ammonia solution (4.3), make up to 150 ml with water (the pH of the solution should be 10), add 3 or 4 drops of the Eriochrome blue SE indicator solution (4.23) and titrate with the EDTA solution (4.18 or 4.19 depending on the magnesium content) on the photoelectrotrimeter (5.1), using a filter having a maximum transmission 610 nm, till the pointer of the device stops.

#### 7.5.2.2 Determination of magnesium content in case of ores with magnesium content significantly less than calcium content

Take the aliquot portion containing 1 to 5 mg of magnesium from the solution obtained according to 7.4, the conditions for titration being the same as those specified in 7.5.1 for calcium. Without titration of calcium, filter the precipitate of magnesium hydroxide on the filter paper compacted with paper pulp, wash the beaker and the precipitate 4 or 5 times with the potassium hydroxide solution (4.13). Then dissolve the precipitate in 50 ml of the hydrochloric acid (4.11) and wash the filter paper 3 or 4 times with warm water. Adjust the pH of the solution obtained to 13 (see 7.5.1) with the potassium hydroxide solution (4.12), add 5 or 6 drops of the Eriochrome blue SE indicator (4.23) and

titrate the remaining calcium with the EDTA solution (4.18). Then filter the precipitate of magnesium hydroxide and complete the determination of magnesium content as specified in 7.5.2.1.

### 7.5.3 Determination of calcium content — Visual titration

For the determination of calcium content, place the aliquot portion containing 1 to 5 mg of calcium from the solution obtained according to 7.4 in a 250 ml conical flask, add 100 ml of water and 5 ml of the sucrose solution (4.16). Add 1 or 2 drops of the malachite green indicator (4.24), which gives a light turquoise colouring to the solution, then add the potassium hydroxide solution (4.12) till the solution becomes colourless and 10 to 15 ml in excess (pH should be 13). To the solution obtained, add 40 to 50 mg of the indicator mixture (4.26), mix and immediately titrate with the EDTA solution (4.18), till greenish-blue colouring of the fluorescent solution changes to violet, fluorescence decreasing greatly. The solution may be illuminated from below.

### 7.5.4 Determination of calcium plus magnesium content — Visual titration

For the determination of calcium plus magnesium content, place the aliquot portion (in the same amount as for the determination of calcium content) from the solution obtained according to 7.4 in a 250 ml conical flask, add 50 ml of water, 10 ml of the buffer solution (4.22), 30 to 50 mg of the Eriochrome black T indicator (4.25), mix and immediately titrate with the EDTA solution (4.18), till the wine-red colour changes to blue.

## 8 Expression of results

### 8.1 Photometric titration

The calcium and magnesium contents, expressed as a percentage by mass, are given by the formula

$$\frac{c \times (V_0 - V_1) \times V_2 \times 100}{V_3 \times m_0} \times K$$

where

$c$  is the concentration of the standard volumetric EDTA solution (4.18 or 4.19), expressed as grams of calcium or magnesium per millilitre, calculated in accordance with 4.18.3;

$V_0$  is the volume, in millilitres, of the standard volumetric EDTA solution taken for the determination of calcium and magnesium content in the aliquot portion of the test solution (7.5.1 and 7.5.2);

$V_1$  is the volume, in millilitres, of the standard volumetric EDTA solution taken for titration of the aliquot portion of the corresponding blank test solution;

$V_2$  is the volume, in millilitres, of the test solution;

$V_3$  is the volume, in millilitres, of the aliquot portion of the test solution taken for the determination;

$m_0$  is the mass, in grams, of the test portion (7.1);

$K$  is the conversion factor for the expression of the calcium and magnesium contents on the dry basis.

**8.2 Visual titration**

**8.2.1** The calcium content, expressed as a percentage by mass, is given by the formula

$$\frac{c \times (V_4 - V_5) \times V_2 \times 100}{V_6 \times m_0} \times K$$

where

$c$  is the concentration of the standard volumetric EDTA solution (4.18), expressed as grams of calcium per millilitre, calculated in accordance with 4.18.3;

$V_2$  is the volume, in millilitres, of the test solution;

$V_4$  is the volume, in millilitres, of the standard volumetric EDTA solution (4.18) taken for the determination of calcium content in the aliquot portion of the test solution (7.5.3);

$V_5$  is the volume, in millilitres, of the standard volumetric EDTA solution (4.18) taken for titration of the aliquot portion of the corresponding blank test solution;

$V_6$  is the volume, in millilitres, of the aliquot portion of the test solution taken for the determination;

$m_0$  is the mass, in grams, of the test portion (7.1);

$K$  is the conversion factor for the expression of the calcium and magnesium contents on the dry basis.

**8.2.2** The magnesium content, expressed as a percentage by mass, is given by the formula

$$\frac{c \times (V_7 - V_8) \times V_2 \times 100}{V_6 \times m_0} \times K$$

where

$c$  is the concentration of the standard volumetric EDTA solution (4.18), expressed as grams of magnesium per millilitre, calculated in accordance with 4.18.3;

$V_2$  is the volume, in millilitres, of the test solution;

$V_6$  is the volume, in millilitres, of the aliquot portion of the test solution taken for the determination;

$V_7$  is the volume, in millilitres, of the standard volumetric EDTA solution (4.18) taken for the determination of calcium plus magnesium contents (7.5.4) in the aliquot portion of the test solution, reduced by the volume of the standard volumetric EDTA solution (4.18) taken for titration of the aliquot portion of the corresponding blank test solution;

$V_8$  is the volume, in millilitres, of the standard volumetric EDTA solution (4.18) taken for the determination of calcium content (7.5.3) in the aliquot portion of the test solution, reduced by the volume of the standard volumetric EDTA solution (4.18) taken for titration of the aliquot portion of the corresponding blank test solution;

$m_0$  is the mass, in grams, of the test portion (7.1);

$K$  is the conversion factor for the expression of the calcium and magnesium contents on the dry basis.

**8.3 Permissible tolerances on results of parallel determinations**

**8.3.1 Determinations of calcium content**

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

**8.3.2 Determinations of magnesium content**

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

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