

International Standard



4298

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Manganese ores and concentrates — Determination of manganese content — Potentiometric method

Minerais et concentrés de manganèse — Dosage du manganèse — Méthode potentiométrique

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Foreword

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International Standard ISO 4298 was prepared by Technical Committee ISO/TC 65, *Manganese and chromium ores*.

ISO 4298 was first published in 1978. This second edition cancels and replaces the first edition, of which it constitutes a minor revision.

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Manganese ores and concentrates — Determination of manganese content — Potentiometric method

1 Scope and field of application

This International Standard specifies a potentiometric method for the determination of the manganese content of manganese ores and concentrates having a manganese content equal to or greater than 15 % (m/m).

It 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*.

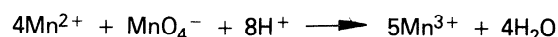
ISO 4297, *Manganese ores and concentrates — Methods of chemical analysis — General instructions*.

3 Principle

Decomposition of a test portion by treatment with hydrochloric, nitric, perchloric and hydrofluoric acids. Separation of the insoluble residue, and reservation of the filtrate as the main solution. Ignition of the residue, fusion with sodium carbonate, leaching of the melt with hydrochloric acid and combination with the main solution. Addition of an aliquot portion of the resulting solution to sodium pyrophosphate solution, adjustment of the pH to 7,0, and potentiometric titration with potassium permanganate standard volumetric solution.

4 Reaction

The method is based on the oxidation of manganese(II) ions to manganese (III) ions by potassium permanganate in a neutral medium in the presence of sodium pyrophosphate:



Iron and other interfering elements are eliminated by binding them into soluble pyrophosphate complexes.

5 Reagents

5.1 Sodium carbonate (Na_2CO_3), anhydrous.

5.2 Sodium carbonate, 50 g/l solution.

5.3 Sodium pyrophosphate decahydrate ($\text{Na}_4\text{P}_2\text{O}_7 \cdot 10\text{H}_2\text{O}$), 120 g/l solution.

This solution shall be prepared 24 h before use.

5.4 Hydrochloric acid, ρ 1,19 g/ml.

5.5 Hydrochloric acid, diluted 1 + 4.

5.6 Hydrofluoric acid, ρ 1,14 g/ml.

5.7 Perchloric acid, ρ 1,51 g/ml.

5.8 Nitric acid, ρ 1,40 g/ml.

5.9 Potassium permanganate (KMnO_4), degree of purity not less than 99,5 %, recrystallized.

Dissolve 250 g of potassium permanganate (purity not less than 99,5 %) with 800 ml of hot water (90 °C) in a 1 000 ml beaker. Filter the solution under vacuum through a filter crucible with a sintered glass plate No. 3. Cool the filtered solution in an ice-bath to 10 °C, while stirring vigorously. Allow the fine-grained precipitate to settle. Then pour out the solution, transfer the crystalline mass to the crucible with sintered glass plate No. 3 and place under suction. Repeat the recrystallization.

After thorough suction, transfer the crystalline mass thus obtained to a glass or porcelain dish and dry in air in the dark, protecting from dust. When the crystalline mass no longer sticks together when crushed with a glass rod, dry it at 80 to 100 °C

for 2 to 3 h in a drying oven. Then transfer it to a stoppered brown glass bottle.

Potassium permanganate thus obtained contains 34,76 % (m/m) of manganese and is non-hygroscopic.

5.10 Manganese, standard reference solution, corresponding to 1 g of Mn per litre.

Place 10 g of electrolytic manganese (purity not less than 99,95 %) in a 400 or 500 ml beaker. Add a mixture of 50 ml of water and 5 ml of the nitric acid (5.8) and leave for a few minutes until the surface becomes bright. Wash the treated manganese six times with water, then with acetone, and dry at 100 °C for 10 min.

Place 1 g of the treated electrolytic manganese in a 400 or 500 ml beaker, and add 20 ml of sulfuric acid (ρ 1,84 g/ml, diluted 1 + 1) and about 100 ml of water. Boil the solution for a few minutes, cool, transfer to a 1 000 ml one-mark volumetric flask, dilute to the mark with water and mix.

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

5.11 Potassium permanganate, standard volumetric solution, $c(1/5 \text{ KMnO}_4) \approx 0,1 \text{ mol/l}$.

Dissolve 3,20 g of potassium permanganate in 1 000 ml of water, allow to stand for 6 days, then transfer to a brown glass bottle and mix.

5.11.1 Standardization with the manganese standard reference solution (5.10)

Transfer 100 ml of the manganese standard reference solution (5.10) into a 500 to 800 ml beaker and add, while stirring, 250 ml of the sodium pyrophosphate solution (5.3). Adjust the pH of the solution to 7 with the hydrochloric acid (5.5) [check the pH using either a pH meter or the bromothymol blue indicator (5.12)] and titrate with the potassium permanganate solution (5.11) using the pH meter (6.1) until the maximum peak deflection on the voltmeter is observed.

Carry out a blank test, omitting the standard manganese solution.

The mass concentration of the potassium permanganate solution, ρ , is given by the equation

$$\rho = \frac{m_1}{V_1 - V_2}$$

where

m_1 is the mass, in grams, of manganese present in the aliquot portion of the manganese standard reference solution (5.10);

V_1 is the volume, in millilitres, of the potassium permanganate solution used for titration of the manganese standard reference solution;

V_2 is the volume, in millilitres, of the potassium permanganate solution used for titration of the blank test solution.

5.11.2 Standardization with the potassium permanganate (5.9)

Place 1,5 g of the potassium permanganate (5.9) in a 250 or 300 ml fluoroplastic or polytetrafluoroethylene beaker, add 30 to 40 ml of water and mix thoroughly. Add 20 ml of the hydrochloric acid (5.4), cover the beaker with a watch-glass and heat. When the reaction is complete, rinse the watch-glass, transferring the washings into the beaker. Add 10 ml of the perchloric acid (5.7) and 20 ml of the hydrofluoric acid (5.6) to the cooled solution and evaporate until dense white fumes of perchloric acid appear. Cool the solution, add 20 ml of the hydrochloric acid (5.5) and heat until the pink colour of the solution is discharged.

After cooling, transfer the solution to a 500 ml one-mark volumetric flask, dilute to the mark with water and mix. Take a 100 ml aliquot portion and transfer it with continuous stirring into a 500 to 800 ml beaker containing 250 ml of the sodium pyrophosphate solution (5.3). Adjust the pH of the solution to 7 with the hydrochloric acid (5.5) or the sodium carbonate solution (5.2) [check the pH using either a pH meter or the bromothymol blue indicator (5.12)] and titrate with the potassium permanganate solution (5.11) using the pH meter (6.1) until the maximum peak deflection on the voltmeter is observed.

Carry out a blank test, omitting the solid potassium permanganate.

The mass concentration of the potassium permanganate solution, ρ , is given by the equation

$$\rho = \frac{m_2 \times 0,3476}{V_3 - V_4}$$

where

m_2 is the mass, in grams, of the potassium permanganate (5.9) present in the aliquot portion of solution taken for titration;

V_3 is the volume, in millilitres, of the potassium permanganate solution used for titration of manganese;

V_4 is the volume, in millilitres, of the potassium permanganate solution used for titration of the blank test solution;

0,3476 is the conversion factor from potassium permanganate to manganese.

5.12 Bromothymol blue indicator, 0,4 g/l solution.

6 Apparatus

Ordinary laboratory apparatus and

6.1 pH meter, fitted with one of the following pairs of electrodes:

- a) for potentiometric titration:
 - platinum-saturated calomel;
 - platinum-tungsten;
 - platinum-platinum;

- b) for pH determination:
— glass-silver-silver chloride

6.2 Platinum crucible.

7 Sampling

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

8 Procedure

8.1 Blank test

Carry out a blank test in parallel with the determination.

8.2 Decomposition of test portion

Place a 1 g test portion in a 250 or 300 ml fluoroplastic or polytetrafluoroethylene beaker, moisten with a few drops of water, add 20 ml of the hydrochloric acid (5.4) and 2 to 3 ml of the nitric acid (5.8), heat until nitrous fumes cease to be evolved, and cool. Add 10 ml of the perchloric acid (5.7) and heat, gently at first, and then strongly to decompose the ore. Cool the solution, add 10 ml of the hydrofluoric acid (5.6) and evaporate until dense white fumes of perchloric acid appear. Cool the solution, add 20 ml of the hydrochloric acid (5.5) and heat until the salts dissolve. Filter the insoluble residue on a medium texture filter containing a small amount of paper pulp, and wash with warm water 10 to 12 times. Reserve the filtrate (A).

8.3 Treatment of residue

Place the filter containing the residue in a platinum crucible, dry, ignite and fuse with 2 g of the sodium carbonate (5.1). Cool the crucible containing the melt, place in a 250 ml beaker, add 10 ml of the hydrochloric acid (5.4) and 30 to 40 ml of water, and heat to dissolve the melt. Remove the crucible and rinse it into the beaker with water. Cool the solution and add it to the filtrate A.

8.4 Titration

Transfer the combined solution into a 500 ml one-mark volumetric flask, dilute to the mark with water and mix.

Take a 100 ml aliquot portion of the solution and transfer it with continuous stirring into a 500 to 800 ml beaker containing 250 ml of the sodium pyrophosphate solution (5.3).

The solution obtained should be clear. If a residue is formed, it is necessary to take either a small aliquot portion or a greater amount of sodium pyrophosphate solution.

Adjust the pH of the solution to 7 with the hydrochloric acid (5.5) or the sodium carbonate solution (5.2) [check the pH using either a pH meter or the bromothymol blue indicator (5.12)] and titrate with the potassium permanganate solution (5.11) using the pH meter (6.1) until the maximum peak deflection on the voltmeter is observed.

9 Expression of results

9.1 Calculation

The manganese (Mn) content, expressed as a percentage by mass, is given by the formula

$$\frac{\rho (V_5 - V_6) \times 100}{m_3} \times K$$

where

ρ is the concentration, expressed in grams of manganese per millilitre, of the potassium permanganate solution (5.11).

V_5 is the volume, in millilitres, of the potassium permanganate solution (5.11) used for the titration of the aliquot portion of the test solution;

V_6 is the volume, in millilitres, of the potassium permanganate solution (5.11) used for the titration of the blank test solution;

m_3 is the mass, in grams, of the test portion of ore or concentrate corresponding to the aliquot portion of the test solution;

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

9.2 Permissible tolerances on results of parallel determinations

Manganese content	Permissible tolerance	
	Three parallel determinations	Two parallel determinations
% (m/m)	% (m/m)	% (m/m)
From 15 to 40	0,30	0,25
From 40 to 50	0,40	0,30
Over 50	0,50	0,40

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