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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

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.

The procedures used to develop this document and those intended for its further maintenance are described in the ISO/IEC Directives, Part 1. In particular, the different approval criteria needed for the different types of ISO documents should be noted. This document was drafted in accordance with the editorial rules of the ISO/IEC Directives, Part 2 (see [www.iso.org/directives](http://www.iso.org/directives)).

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. Details of any patent rights identified during the development of the document will be in the Introduction and/or on the ISO list of patent declarations received (see [www.iso.org/patents](http://www.iso.org/patents)).

Any trade name used in this document is information given for the convenience of users and does not constitute an endorsement.

For an explanation of the voluntary nature of standards, the meaning of ISO specific terms and expressions related to conformity assessment, as well as information about ISO's adherence to the World Trade Organization (WTO) principles in the Technical Barriers to Trade (TBT), see [www.iso.org/iso/foreword.html](http://www.iso.org/iso/foreword.html).

This document was prepared by Technical Committee ISO/TC 132, *Ferroalloys*.

This third edition cancels and replaces the second edition (ISO 4298:1984), which has been technically revised.

The main changes are as follows:

- in [Clause 4](#), the description of reaction has been reworded to better explain the method;
- in [5.12](#) (previously in 5.10), the detailed specification of “electrolytic manganese” has been added and described as “electrolytic manganese metal flakes”;
- in [5.13](#) (previously in 5.11), the commercially available standard solution has been added as an alternative, and variations in concentration shall be taken into account for the calculation of the results in [9.1](#);
- in [5.14](#) (previously 5.11.1), the amount of aliquot portion of the manganese standard reference solution and the saturated sodium pyrophosphate solution has been reduced, and the specification of the beaker has been changed;
- in [5.15](#) (previously 5.11.2), the amount of aliquot portion of the potassium permanganate solution and the saturated sodium pyrophosphate solution has been reduced, and the specification of the beaker has been changed;
- in [Clause 6](#), the description of pH meter has been replaced with a list of potentiometric titration apparatus in line with the current status of the development of the instrument, including the apparatus for potentiometric titration in [6.1](#), pH determination in [6.2](#) and titration assembly in [6.3](#);
- in [Clause 8](#), a new paragraph of the definition of test portion has been added in [8.1](#) and the amount of test portion in [8.1](#) (previously 8.2) has been reduced from 1,0 g to 0,50 g;
- in [Clause 8](#), a new paragraph of the definition and requirement of determination of hygroscopic moisture content has been added in [8.3](#);

- in [8.4](#) (previously 8.2), the amount of acids has been reduced, the times of washing have been changed, and the detailed usage of watch-glass and the provision of filter volume have been added;
- in [8.6](#) (previously 8.4), the amount of aliquot portion of the solution and the saturated sodium pyrophosphate solution has been reduced, and the specification of one-mark volumetric flask and the beaker have been changed;
- in [9.1](#), the formula of the manganese content has been replaced with three new calculating formulae which take into account the hygroscopic moisture content of the test portion;
- in [9.2](#), the paragraph of the “permissible tolerances on results” has been replaced with the “general treatment of results”;
- [Clause 10](#), the test report has been added;
- [Annex A](#), “Additional information on the international interlaboratory test” has been added;
- [Annex B](#), “Flow sheet of the procedure for the acceptance of test results” has been added.

Any feedback or questions on this document should be directed to the user’s national standards body. A complete listing of these bodies can be found at [www.iso.org/members.html](http://www.iso.org/members.html).

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

## 1 Scope

This document specifies a potentiometric method for the determination of the manganese content of manganese ores and concentrates with manganese content equal to or greater than a mass fraction of 15 %.

## 2 Normative references

The following documents are referred to in the text in such a way that some or all of their content constitutes requirements 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 310, *Manganese ores and concentrates — Determination of hygroscopic moisture content in analytical samples — Gravimetric method*

ISO 648, *Laboratory glassware — Single-volume pipettes*

ISO 1042, *Laboratory glassware — One-mark volumetric flasks*

ISO 3696, *Water for analytical laboratory use — Specification and test methods*

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

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

ISO 80000-1:2009, *Quantities and units — Part 1: General*

## 3 Terms and definitions

No terms and definitions are listed in this document.

ISO and IEC maintain terminology databases for use in standardization at the following addresses:

- ISO Online browsing platform: available at <https://www.iso.org/obp>
- IEC Electropedia: available at <https://www.electropedia.org/>

## 4 Principle

The method is based on the titration of manganous ion with permanganate ion in neutral pyrophosphate solution, the manganese(II) being oxidized, the permanganate ion reduced, to a pyrophosphate complex of the +3 state (the stoichiometry ratio of  $\text{Mn}^{2+}$  to  $\text{MnO}_4^-$  is 4:1).

Decomposition of a test portion by treatment with hydrochloric acid, nitric, perchloric and hydrofluoric acids. Separation of 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.

## 5 Reagents

During the analysis, unless otherwise stated, use only reagents of recognized analytical grade and only grade 3 water as specified in ISO 3696.

**5.1 Sodium carbonate ( $\text{Na}_2\text{CO}_3$ ), anhydrous.**

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

**5.3 Hydrofluoric acid,  $\rho = 1,14$  g/ml.**

**5.4 Perchloric acid,  $\rho = 1,51$  g/ml.**

**5.5 Nitric acid,  $\rho = 1,40$  g/ml.**

**5.6 Potassium permanganate, degree of purity not less than 99,5 %.**

**5.7 Sodium carbonate, 50 g/l solution.**

**5.8 Hydrochloric acid, diluted 1 + 4.**

**5.9 Saturated sodium pyrophosphate solution.** Dissolve 120 g of sodium pyrophosphate decahydrate ( $\text{Na}_4\text{P}_2\text{O}_7 \cdot 10\text{H}_2\text{O}$ ) with 1 000 ml of water. After 24 h, the supernatant is obtained for use.

**5.10 Potassium-permanganate ( $\text{KMnO}_4$ ), recrystallized.** Dissolve 250 g of potassium permanganate (5.6) 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 (6.5). 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 (6.5) 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 °C to 100 °C for 2 h to 3 h in a drying oven. Then transfer it to a stoppered brown glass bottle.

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

**5.11 Bromothymol blue indicator, 0,4 g/l solution.**

**5.12 Manganese, standard reference solution,** corresponding to 1 g of Mn per litre. Place 10,00 g of electrolytic manganese metal flakes (purity not less than 99,95 %) in a 400 ml or 500 ml beaker. Add a mixture of 50 ml of water and 5 ml of the nitric acid (5.5) 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 1,00 g of the treated electrolytic manganese in a 400 ml or 500 ml beaker, and add 20 ml of sulfuric acid ( $\rho = 1,84$  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.



**5.13 Potassium permanganate**, standard volumetric solution,  $c(1/5 \text{ KMnO}_4) \approx 0,1 \text{ mol/l}$ . Dissolve 3,20 g of potassium permanganate (5.6) in 1 000 ml of water, allow to stand for six days, then transfer to a brown glass bottle and mix.

Alternatively, commercially available standard solutions of known concentration can be used instead of standard solutions produced in the laboratory. Variations in concentration shall be taken into account for the calculation of the results.

#### 5.14 Standardization with the manganese standard reference solution (5.12).

Transfer 50,00 ml of the manganese standard reference solution (5.12) into a 400 ml beaker and add, while stirring, 150 ml of the saturated sodium pyrophosphate solution (5.9). Adjust the pH of the solution to 7,0 with hydrochloric acid (5.8) [check the pH using either the pH electrode (6.2) or the bromothymol blue indicator (5.11)] and titrate with the potassium permanganate solution (5.13) using the potentiometric titration apparatus (6.1, 6.2, 6.3) 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,  $\rho_1$ , is given by Formula (1):

$$\rho_1 = \frac{m_1}{V_1 - V_2} \quad (1)$$

where

$m_1$  is the mass, in grams, of manganese present in the aliquot portion of the manganese standard reference solution (5.12);

$V_1$  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.

#### 5.15 Standardization with the potassium permanganate (5.10).

Place 1,50 g of potassium permanganate (5.10) in a 250 ml or 300 ml fluoroplastic or polytetrafluoroethylene beaker, add 30 ml to 40 ml of water and mix thoroughly. Add 20 ml of hydrochloric acid (5.2), 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 perchloric acid (5.4) and 20 ml of hydrofluoric acid (5.3) to the cooled solution and evaporate until dense white fumes of perchloric acid appear. Cool the solution, add 20 ml of hydrochloric acid (5.8) 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 50,00 ml aliquot portion and transfer it with continuous stirring into a 400 ml beaker containing 150 ml of the saturated sodium pyrophosphate solution (5.9). Adjust the pH of the solution to 7,0 with hydrochloric acid (5.8) or the sodium carbonate solution (5.7) [check the pH using either the pH electrode (6.2) or the bromothymol blue indicator (5.11)] and titrate with the potassium permanganate solution (5.13) using the potentiometric titration apparatus (6.1, 6.2, 6.3) 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,  $\rho_2$ , is given by Formula (2):

$$\rho_2 = \frac{m_2 \times 0,3476}{V_3 - V_4} \quad (2)$$

where

- $m_2$  is the mass, in grams, of the potassium permanganate (5.10) 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;
- 0,347 6 is the conversion factor from potassium permanganate to manganese.

## 6 Apparatus

All volumetric glassware shall be Class A, in accordance with ISO 648 and ISO 1042. Ordinary laboratory apparatus and the following shall be used.

**6.1 Apparatus for potentiometric titration:** Indicator electrode (of platinum) with reference electrode (of tungsten, platinum, calomel or silver/silver chloride) or combined electrode of equivalent performance.

**6.2 Apparatus for pH determination:** Glass electrode and reference electrode, or combined electrode of equivalent performance.

**6.3 Titration assembly,** consisting of a 400 ml beaker, two 20 ml or 25 ml dosing units and a magnetic stirrer.

**6.4 Platinum crucible**

**6.5 Filter crucible with a sintered glass plate No.3.**

## 7 Sampling

The sampling of manganese ores shall be in accordance with ISO 4296-1. The preparation of samples shall be in accordance with ISO 4296-2.

## 8 Procedure

### 8.1 Test portion

Weigh, to the nearest 0,000 1 g, approximately 0,50 g of the test sample.

### 8.2 Blank test

Carry out a blank test in parallel with the determination.

### 8.3 Determination of hygroscopic moisture content

Determine the hygroscopic moisture content in accordance with ISO 310, simultaneously with the taking of the test portion (8.1) for the determination of manganese content.

## 8.4 Decomposition of test portion

Place the test portion (8.1) in a 250 ml or 300 ml fluoroplastic or polytetrafluoroethylene beaker, moisten with a few drops of water, add 10 ml of hydrochloric acid (5.2) and 2 ml of nitric acid (5.5), cover the beaker with a watch-glass and heat until nitrous fumes cease to be evolved, and cool. Add 5 ml of perchloric acid (5.4) and heat, gently at first, and then strongly to decompose the ore. Cool the solution, rinse the watch-glass, transferring the washings into the beaker. Add 5 ml of hydrofluoric acid (5.3) and evaporate until dense white fumes of perchloric acid appear. Cool the solution, add 10 ml of hydrochloric acid (5.8) 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 8 to 10 times. The filter volume should be no more than 120 ml. Reserve the filtrate (A).

## 8.5 Treatment of residue

Place the filter paper containing the residue in a platinum crucible (6.4), dry, char the paper at 600 °C to 700 °C and finally fuse with 2 g of sodium carbonate (5.1) at 900 °C to 1 000 °C. Cool the crucible containing the melt, place in a 250 ml beaker, add 10 ml of hydrochloric acid (5.2) and 30 ml 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).

## 8.6 Titration

Transfer the combined solution into a 250 ml one-mark volumetric flask, dilute to the mark with water and mix.

Take a 50,00 ml aliquot portion of the solution and transfer it with continuous stirring into a 400 ml beaker containing 150 ml of the saturated sodium pyrophosphate solution (5.9).

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 the saturated sodium pyrophosphate solution (5.9).

Adjust the pH of the solution to 7,0 with hydrochloric acid (5.8) or the sodium carbonate solution (5.7) [check the pH using either the pH electrode (6.2) or the bromothymol blue indicator (5.11)] and titrate with the potassium permanganate solution (5.13) using the potentiometric titration apparatus (6.1, 6.2, 6.3) until the maximum peak deflection on the voltmeter is observed.

## 9 Expression of results

### 9.1 Calculation of manganese content

The manganese (Mn) content, expressed as a percentage mass fraction,  $\omega_{\text{Mn}}$  (%), is given by Formula (3), (4) or (5):

$$\omega_{\text{Mn}} = \frac{\rho_1 \times (V_5 - V_6) \times 100}{m_3 \times \gamma} \times \frac{100}{100 - K} \quad (3)$$

$$\omega_{\text{Mn}} = \frac{\rho_2 \times (V_5 - V_6) \times 100}{m_3 \times \gamma} \times \frac{100}{100 - K} \quad (4)$$

$$\omega_{\text{Mn}} = \frac{\rho_3 \times (V_5 - V_6) \times 4 \times 54,938 \times 100}{m_3 \times \gamma \times 1000} \times \frac{100}{100 - K} \quad (5)$$

where

$\rho_1$  is the concentration obtained by Formula (1), expressed in grams of manganese per millilitre, of the potassium permanganate solution (5.13);