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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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Contents

| | Page |
|---|-----------|
| Foreword..... | iv |
| 1 Scope | 1 |
| 2 Normative references | 1 |
| 3 Principle | 1 |
| 4 Reaction | 1 |
| 5 Reagents | 1 |
| 6 Apparatus | 4 |
| 6.1 Potentiometric titration apparatus..... | 4 |
| 6.2 Platinum crucible..... | 4 |
| 6.3 Filter crucible with a sintered glass plate No.3..... | 4 |
| 7 Sampling | 4 |
| 8 Procedure | 4 |
| 8.1 Test portion..... | 4 |
| 8.2 Blank test..... | 5 |
| 8.3 Determination of hygroscopic moisture content..... | 5 |
| 8.4 Decomposition of test portion..... | 5 |
| 8.5 Treatment of residue..... | 5 |
| 8.6 Titration..... | 5 |
| 9 Expression of results | 5 |
| 9.1 Calculation of manganese content..... | 5 |
| 9.2 General treatment of results..... | 6 |
| 9.2.1 Expression of precision..... | 6 |
| 9.2.2 Determination of analytical result..... | 7 |
| 9.2.3 Between-laboratories precision..... | 7 |
| 9.2.4 Check for trueness..... | 8 |
| 9.2.5 Calculation of final result..... | 8 |
| 10 Test report | 8 |
| Annex A (normative) The original data of verification test | 10 |
| Annex B (normative) The graphic presentation of the data | 12 |
| Annex C (normative) Flow sheet for the procedure for the acceptance of analytical value for test samples | 13 |
| Bibliography | 14 |

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).

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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 with the following changes:

- [Clause 2](#), the description of reaction has been reworded to better explain the method;
- [Clause 4](#), 4 normative references have been added;
- [Clause 5](#), a requirement of reagent used in method has been added in the first paragraph;
- [Clause 5](#), the order of reagents has been renumbered, starting with the commercial reagents and the prepared reagents backwards;
- [Clause 5](#), “potassium permanganate, degree of purity not less than 99,5 %” has been added as a reagent, and the description for potassium-permanganate in [5.10](#) (previously [5.9](#)) has been replaced with “potassium-permanganate (KMnO₄), recrystallized”;
- in [5.11](#) (previously in [5.10](#)), the detailed specification of “electrolytic manganese” has been added and described as “electrolytic manganese metal flakes”;
- in [5.12](#) (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 [5.12.1](#) (previously 5.11.1), reduce the amount of aliquot portion of the manganese standard reference solution and the saturated sodium pyrophosphate solution, and change the specification of the beaker;
- in [5.12.2](#) (previously 5.11.2), reduce the amount of aliquot portion of the potassium permanganate solution and the saturated sodium pyrophosphate solution, and change the specification of the beaker;

- in [5.12.1](#), [5.12.2](#) and [8.6](#) (previously in [5.11.1](#), [5.11.2](#) and [8.4](#)), the sodium pyrophosphate solution ([5.3](#)) has been replaced with “the saturated sodium pyrophosphate solution ([5.9](#))”;
- [Clause 6](#), a requirement of volumetric glassware used in method has been added in the first paragraph;
- in [6.1](#), the paragraph of the description of pH meter has been replaced with the paragraph of potentiometric titration apparatus to in line with the current status of the development of the instrument, including the description for potentiometric titration in [6.1.1](#), pH determination in [6.1.2](#) and titration assembly in [6.1.3](#);
- [Clause 6](#), filter crucible with a sintered glass plate No.3 has been added as an apparatus;
- [Clause 8](#), a new paragraph of the definition of test portion has been added in [8.1](#) and reduce the amount of test portion in [8.1](#) (previously [8.2](#)) from 1.0 g to 0.50 g;
- [Clause 8](#), a new paragraph of the definition and requirement of determination of hygroscopic moisture content has been added in [8.3](#);
- [Clause 8](#), the order of items [8.1](#), [8.2](#), [8.3](#) and [8.4](#) previously has been renumbered to [8.2](#), [8.4](#), [8.5](#) and [8.6](#);
- in [8.4](#) (previously [8.2](#)), reduce the amount of acids, change the times of washing, and add the detailed usage of watch-glass and the provision of filter volume;
- in [8.5](#) (previously [8.3](#)), the volume of the filtrate after filtration and the temperature for ashing and volatilization of alkali salts has been added;
- in [8.6](#) (previously [8.4](#)), reduce the amount of aliquot portion of the solution and the saturated sodium pyrophosphate solution and change the specification of one-mark volumetric flask and the beaker;
- in [9.1](#), the formula of the manganese content has been replaced with three new calculating formulas which took 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](#) The original data of verification test” has been added;
- “[Annex B](#) The graphic presentation of the data” has been added;
- “[Annex C](#) Flow sheet of the procedure for the acceptance of analytical value for test samples” has been added;
- Bibliography of ISO 5725-2 and ISO Guide 35 referred in [9.2.1](#) and [9.2.4](#) has been inserted at the end of the document;

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.

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

1 Scope

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

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

3 Principle

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.

4 Reaction

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 Mn^{2+} to MnO_4^- is 4:1).

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 (Na_2CO_3), anhydrous.

5.2 **Hydrochloric acid**, ρ 1,19 g/ml.

5.3 **Hydrofluoric acid**, ρ 1,14 g/ml.

5.4 **Perchloric acid**, ρ 1,51 g/ml.

5.5 **Nitric acid**, ρ 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 (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 (6.3). 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 (6.3) 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.

5.11 **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 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 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.

5.12 **Potassium permanganate**, standard volumetric solution, c (1/5 KMnO_4) \approx 0,1 mol/l.

Dissolve 3,20 g of potassium permanganate (5.6) in 1 000 ml of water, allow to stand for 6 days, then transfer to a brown glass bottle and mix.

Or, 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.

5.12.1 Standardization with the manganese standard reference solution (5.11)

Transfer 50,00 ml of the manganese standard reference solution (5.11) 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 the hydrochloric acid (5.8) [check the pH using either the pH electrode (6.1.2) or the bromothymol blue indicator (5.13)] and titrate with the potassium permanganate solution (5.12) using the potentiometric titration apparatus (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_1 , is given by the 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 (5.11);
- 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.

5.12.2 Standardization with the potassium permanganate (5.10)

Place 1,50 g of the potassium permanganate (5.10) 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 (5.2), 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 the perchloric acid (5.4) and 20 ml of the 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 the 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 the hydrochloric acid (5.8) or the sodium carbonate solution (5.7) [check the pH using either the pH electrode (6.1.2) or the bromothymol blue indicator (5.13)] and titrate with the potassium permanganate solution (5.12) using the potentiometric titration apparatus (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_2 , is given by the [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;

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

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

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 Potentiometric titration apparatus

[ISO/DIS 4298](#)

6.1.1 For potentiometric titration

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Indicator electrode (of platinum) with reference electrode (of tungsten, platinum, calomel or silver/silver chloride) or combined electrode of equivalent performance.

6.1.2 For pH determination

Glass electrode and reference electrode, or combined electrode of equivalent performance.

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

6.2 Platinum crucible

6.3 Filter crucible with a sintered glass plate No.3

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 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 or 300 ml fluoroplastic or polytetrafluoroethylene beaker, moisten with a few drops of water, add 10 ml of the hydrochloric acid (5.2) and 2 ml of the 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 the 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 the hydrofluoric acid (5.3) and evaporate until dense white fumes of perchloric acid appear. Cool the solution, add 10 ml of the 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 (6.2), dry, char the paper at 600 to 700 °C and finally fuse with 2 g of the sodium carbonate (5.1) at 900 to 1000 °C. Cool the crucible containing the melt, place in a 250 ml beaker, add 10 ml of the hydrochloric acid (5.2) 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).

ISO/DIS 4298

8.6 Titration <https://standards.iteh.ai/catalog/standards/sist/d70d345a-a8a3-4e8d-b443-758c92c7024b/iso-dis-4298>

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 the hydrochloric acid (5.8) or the sodium carbonate solution (5.7) [check the pH using either the pH electrode (6.1.2) or the bromothymol blue indicator (5.13)] and titrate with the potassium permanganate solution (5.12) using the potentiometric titration apparatus (6.1) 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 by mass, ω_{Mn} (%), is given by the [Formula \(3\)](#), [\(4\)](#) or [\(5\)](#)

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