

TC 65

International Standard **ISO** 4300



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Manganese ores and concentrates — Determination of lead content — Polarographic methods

Minerais et concentrés de manganèse — Dosage du plomb — Méthodes polarographiques

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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. They are approved in accordance with ISO procedures requiring at least 75 % approval by the member bodies voting.

International Standard ISO 4300 was prepared by Technical Committee ISO/TC 65, *Manganese and chromium ores*.

ISO 4300 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 lead content — Polarographic methods

1 Scope and field of application

This International Standard specifies two polarographic methods for the determination of the lead content of manganese ores and concentrates

method A : applicable to products having lead contents from 0,002 to 0,01 % (m/m);

method B : applicable to products having lead contents from 0,01 to 1,0 % (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 Method A : For lead contents from 0,002 to 0,01 % (m/m)

3.1 Principle

Decomposition of a test portion by treatment with hydrochloric and nitric acids, and evaporation of the solution to dryness. Dissolution of the dry residue in hydrochloric acid, filtration of the insoluble residue and reservation of the filtrate as the main solution. Ignition of the filter containing the residue and treatment with nitric and hydrofluoric acids. Fusion of the ignited residue with sodium carbonate. Dissolution of the melt in hydrochloric acid in the presence of hydroxylammonium chloride solution, and combination with the main solution. Evaporation of the combined solution to dryness and dissolution of the dry residue in 2 mol/l hydrochloric acid.

Separation of the lead from other components by means of anionite, followed by elution of the lead with 0,02 mol/l hydrochloric acid.

Polarographic determination of the lead content at $-0,35$ to $-0,75$ V in a perchloric/phosphoric acid medium as a background.

3.2 Reagents and materials

3.2.1 Sodium carbonate, anhydrous.

3.2.2 Nitric acid, distilled, ρ 1,35 g/ml.

3.2.3 Hydrochloric acid, distilled, ρ 1,16 g/ml.

3.2.4 Hydrochloric acid, distilled, diluted 1 + 1.

3.2.5 Hydrochloric acid, distilled, diluted 1 + 19.

3.2.6 Hydrochloric acid, distilled, 2 mol/l.

3.2.7 Hydrochloric acid, distilled, 0,02 mol/l.

3.2.8 Hydrofluoric acid, ρ 1,14 g/ml, 40 % (m/m).

3.2.9 Perchloric acid (HClO_4), ρ 1,51 g/ml, 57 % (m/m) solution.

3.2.10 Phosphoric acid (H_3PO_4), diluted 1 + 3.

3.2.11 Ammonium thiocyanate (NH_4CNS), 400 g/l solution.

3.2.12 Hydroxylammonium chloride ($\text{NH}_2\text{OH}^+\text{Cl}^-$), 100 g/l solution.

3.2.13 Sodium chloride, 360 g/l solution.

3.2.14 Sodium hydroxide, 100 g/l solution.

3.2.15 Sodium hydroxide, 50 g/l solution.

3.2.16 Silver nitrate, 2,5 g/l solution.

3.2.17 Lead, standard solution, corresponding to 0,1 g of Pb per litre.

Weigh 0,1 g of metallic lead [purity 99,95 % (m/m)] from which the oxide film has been removed, place it in a 100 ml beaker, add 20 ml of nitric acid solution (diluted 1 + 1) and heat to dissolve. Evaporate the solution to dryness. Add 10 ml of hydrochloric acid (3.2.3) to the dry residue and evaporate again to dryness. Repeat the evaporation twice with the same hydrochloric acid. Dissolve the dry residue in 2 ml of the same hydrochloric acid and 100 ml of water and mix after dissolution. Transfer the solution to a 1 000 ml one-mark volumetric flask, make up to the mark with water and mix.

1 ml of this standard solution contains 0,1 mg of Pb.

3.2.18 Lead, standard solution, corresponding to 0,001 g of Pb per litre.

Transfer 10 ml of lead standard solution (3.2.17) to a 1 000 ml one-mark volumetric flask, make up the mark with water and mix.

1 ml of this solution contains 0,001 mg of Pb.

3.2.19 Phenolphthalein, indicator, 1 g/l alcoholic solution.

3.2.20 Anionite, of medium or strong basic capacity.

3.2.21 Inert gas, argon or nitrogen.

3.3 Apparatus

Usual laboratory apparatus and

3.3.1 Polarograph.

3.3.2 Ion-exchange (chromatographic) column, 10 to 12 mm in diameter, 480 mm in height (see the figure).

3.3.3 Platinum crucible.

3.4 Sample

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

3.5 Procedure

3.5.1 Preparation of ion-exchange column

3.5.1.1 Crush the anionite (3.2.20) to a grain size of 0,25 to 0,5 mm. Weigh 100 to 200 g of the crushed anionite into a 500 ml beaker, add the sodium chloride solution (3.2.13) and allow to stand for 24 h, stirring periodically. Then run off the sodium chloride solution, wash the anionite with water eight to 10 times by decanting, add hydrochloric acid (3.2.5) and allow to stand for 10 to 12 h, stirring periodically. Transfer the anionite together with the acid to a 500 ml separating funnel and wash it with hydrochloric acid (3.2.5) until complete elimination of iron [i.e. until a negative reaction for iron(III) is obtained with the ammonium thiocyanate solution (3.2.11)].

Dimensions in millimetres

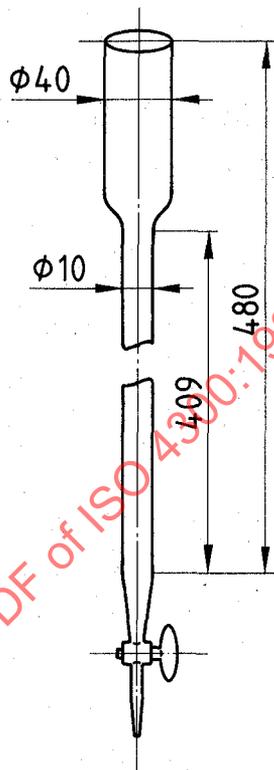


Figure — Ion-exchange (chromatographic) column (3.3.2)

Run off the hydrochloric acid, wash the anionite in the separating funnel, first with water, and once or twice with the sodium hydroxide solution (3.2.15) and then with the sodium hydroxide solution (3.2.14) until a negative reaction for the chloride ion is obtained with the silver nitrate solution (3.2.16). Then wash the anionite with boiled and cooled water free from carbon dioxide until the washings are neutral to the phenolphthalein solution (3.2.19). Then add hydrochloric acid (3.2.6) to the anionite and store it in a bottle with a ground glass stopper.

3.5.1.2 Transfer the anionite treated as specified in 3.5.1.1 to the ion-exchange column (3.3.2) filled with water (with glass wool at the bottom). The height of the anionite layer in the column shall be 120 to 150 mm.

The anionite shall not come into contact with air.

Before passing the test solution through the column, wash the anionite with 100 ml of hydrochloric acid (3.2.7) and then with 100 ml of hydrochloric acid (3.2.6) at a rate of 1 to 2 ml/min.

Add hydrochloric acid (3.2.6) to the column so that its level is 5 to 10 mm above that of the anionite.

The ion-exchange column is then ready for use.

3.5.2 Test portion

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

Table 1

Expected lead content % (m/m)	Mass of test portion g
> 0,002 to 0,005	1,0
> 0,005 to 0,010	0,5

3.5.3 Decomposition of test portion

Place the test portion (3.5.2) in a 100 or 200 ml beaker and dissolve in 10 to 30 ml of the hydrochloric acid (3.2.3) while heating. Add 1 ml of the nitric acid (3.2.2), boil for 1 to 2 min and evaporate to dryness. Repeat the evaporation with hydrochloric acid two or three times until complete elimination of nitric acid. Dissolve the dry residue in 2 or 3 ml of hydrochloric acid (3.2.3), add 10 ml of water and filter through a medium-texture filter containing a small quantity of paper pulp. Wash the residue on the filter five or six times with hydrochloric acid (3.2.5) and five times with warm water. Reserve the filtrate as the main solution.

3.5.4 Treatment of residue

Transfer the filter containing the residue to a platinum crucible, dry and ignite at 500 to 600 °C, until the carbonaceous matter is removed. After cooling, add to the residue 1 or 2 drops of water, 2 or 3 drops of the nitric acid (3.2.2) and 6 to 7 ml of the hydrofluoric acid (3.2.8) and evaporate to dryness. Ignite the dry residue at 500 to 600 °C, cool, add 0,5 to 1,0 g of the sodium carbonate (3.2.1) and fuse at 900 to 1 000 °C.

Leach the melt in 40 ml of hydrochloric acid (3.2.4) containing 0,5 ml of the hydroxylammonium chloride solution (3.2.12). Add the solution thus obtained to the main solution.

3.5.5 Separation of lead from accompanying elements

Evaporate the combined solution to dryness, and then dissolve the residue in 7 ml of hydrochloric acid (3.2.3) and 10 ml of water. Add 50 to 60 ml of hydrochloric acid (3.2.6) to the solution and mix.

Transfer the hydrochloric solution to the prepared ion-exchange column (3.5.1) and pass it through at a rate of 1 ml/min. Lead and zinc will be absorbed by the anionite, and other elements will pass into solution. The level of the last portion of the test solution shall be no more than 5 mm above that of the anionite. For complete washing-off of other components, pass 100 ml of hydrochloric acid (3.2.6) through the column at a rate of 1,5 ml/min, taking care that the anionite does not come into contact with air. Discard the percolate.

3.5.6 Desorption of lead

For elution of the lead, pass 150 ml of hydrochloric acid (3.2.7) through the column at a rate of 2 ml/min. Collect the lead-

containing eluate in a 200 ml beaker, and evaporate the solution to 10 ml.

3.5.7 Preparation and polarographic analysis of solution

Add to the solution 1 ml of the perchloric acid solution (3.2.9), evaporate to fuming and cool. Dissolve the salts in 7 ml of the phosphoric acid solution (3.2.10). Pour the solution into a 25 ml one-mark volumetric flask, make up to the mark with water and mix.

Transfer the solution from the flask to a polarographic cell, and purge it with the inert gas (3.2.21) for 10 min. Then carry out the polarographic analysis at $-0,35$ to $-0,75$ V in relation to a mercury anode (half-wave potential is $-0,55$ V).

3.5.8 Analysis of standard solution, and blank test

Simultaneously with the analysis of a series of test solutions, a standard solution having a lead content close to that of the test solution, together with the blank test solution, shall be taken through all stages of the analysis except the operation of the treatment of residue (see 3.5.4). These solutions shall be analysed under the same conditions as the test sample.

3.6 Expression of results

3.6.1 Calculation

The lead (Pb) content is given, as a percentage by mass, by the formula

$$\frac{m_1 (h - h_b) \times 100}{m_0 (h_{st} - h_b)} \times K$$

where

m_0 is the mass, in grams, of the test portion (3.5.2);

m_1 is the mass, in grams, of lead in the standard lead solution taken through all stages of the analysis;

h is the height, in millimetres, of the polarographic wave of the test solution;

h_b is the height, in millimetres, of the polarographic wave of the blank test solution;

h_{st} is the height, in millimetres, of the polarographic wave of the standard lead solution taken through all stages of the analysis;

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

3.6.2 Permissible tolerances on results of duplicate determinations

Table 2

Lead content	Permissible tolerance
% (m/m)	(m/m)
0,002	0,000 5
> 0,002 to 0,005	0,001
> 0,005 to 0,01	0,002

4 Method B : For lead contents from 0,01 to 1,0 % (m/m)

4.1 Principle

Decomposition of a test portion by treatment with hydrochloric and perchloric acids in the presence of hydroxylammonium chloride, separation of the insoluble residue by filtration, and reservation of the filtrate as the main solution. Ignition of the filter containing the residue and treatment with perchloric and hydrofluoric acids. Fusion of the ignited residue with sodium carbonate. Dissolution of the melt in hydrochloric acid. Addition of the solution thus obtained to the main solution.

Polarographic determination of the lead content of the solution thus obtained using ammonium acetate buffer solution as a background in the presence of accompanying elements.

4.2 Reagents and materials

4.2.1 Hydroxylammonium chloride ($\text{NH}_3\text{OH}^+\text{Cl}^-$), crystalline.

4.2.2 Sodium carbonate, anhydrous.

4.2.3 Hydrochloric acid, ρ 1,19 g/ml.

4.2.4 Hydrochloric acid, diluted 1 + 9.

4.2.5 Hydrofluoric acid, ρ 1,14 g/ml, 40 % (m/m).

4.2.6 Perchloric acid (HClO_4), ρ 1,51 g/ml, 57 % (m/m).

4.2.7 Ammonium acetate, buffer solution having a pH of 6,0 to 6,2.

4.2.7.1 Methyl red, 2 g/l solution in ammonium hydroxide (diluted 1 + 100).

4.2.7.2 Preparation

Dissolve 500 g of crystalline ammonium acetate ($\text{CH}_3\text{COONH}_4$) in 400 ml water, add 60 ml of glacial acetic acid and 5 ml of methyl red indicator (4.2.7.1), dilute with water to 1 000 ml and mix.

4.2.8 Lead, standard solution corresponding to 1 g of Pb per litre.

Weigh 1 g of metallic lead [purity 99,95 % (m/m)] into a 250 ml conical flask, add 20 ml of perchloric acid (4.2.6) and heat to complete dissolution of lead. Evaporate the solution until fumes of perchloric acid appear, cool, add 50 ml of water and boil for 3 to 5 min, then transfer the solution to a 1 000 ml one-mark volumetric flask. Add 100 ml of ammonium acetate buffer solution (4.2.7), make up to the mark with water and mix.

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

4.2.9 Lead, standard solution corresponding to 0,1 g of Pb per litre.

Transfer 100 ml of lead standard solution (4.2.8) to a 1 000 ml one-mark volumetric flask, make up to the mark with water and mix.

1 ml of this standard solution contains 0,1 mg of Pb.

4.2.10 Inert gas, argon or nitrogen.

4.3 Apparatus

Usual laboratory apparatus and

4.3.1 Polarograph, operating on alternating or direct current.

4.3.2 Platinum crucible.

4.4 Sample

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

4.5 Procedure

4.5.1 Test portion

Weigh 1 g of the sample for chemical analysis.

4.5.2 Decomposition of test portion

Place the test portion (4.5.1) in a 200 or 300 ml beaker, add 10 ml of hydrochloric acid (4.2.3) and heat to dissolve. Evaporate the solution until almost dry, add 10 ml of the perchloric acid solution (4.2.6) and heat to white fumes of perchloric acid. After cooling the solution, add 100 ml of water, 1 g of the hydroxylammonium chloride (4.2.1) and boil for 3 to 5 min.

Filter off the insoluble residue on a medium-texture filter containing a small quantity of paper pulp, wash the residue with 2 to 3 ml of hydrochloric acid (4.2.4) and then 10 times with hot water. Reserve the filtrate as the main solution.