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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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International Standard ISO 4300 was developed by Technical Committee ISO/TC 65, *Manganese and chromium ores*, and was circulated to the member bodies in May 1977.

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

Australia
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The member body of the following country expressed disapproval of the document on technical grounds :

France

This International Standard cancels and replaces ISO Recommendation R 323-1963, of which it constitutes a technical 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 is applicable to products having lead contents from 0,002 to 0,01 % (*m/m*), and method B to products having lead contents from 0,01 to 1,0 % (*m/m*).

This International Standard should be read in conjunction with ISO 4297.

2 REFERENCE

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, followed by 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 N hydrochloric acid solution.

Separation of the lead from other components by means of anionite, followed by elution of the lead with 0,02 N hydrochloric acid solution.

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

3.2.1 Inert gas : argon or nitrogen.

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

3.2.3 Hydroxylammonium chloride ($NH_2OH.HCl$), 100 g/l solution.

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

3.2.5 Nitric acid, distilled, diluted 1 + 1.

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

3.2.7 Hydrochloric acid, distilled, diluted 1 + 1.

3.2.8 Hydrochloric acid, distilled, diluted 5 + 95.

3.2.9 Hydrochloric acid, distilled, 2 N solution.

3.2.10 Hydrochloric acid, distilled, 0,02 N solution.

3.2.11 Hydrofluoric acid, ρ 1,14 g/ml, 40 % (*m/m*) solution.

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

3.2.13 Phosphoric acid (H_3PO_4), ρ 1,70 g/ml.

3.2.14 Phosphoric acid, diluted 1 + 3.

3.2.15 Sodium chloride, 360 g/l solution.

3.2.16 Sodium carbonate, anhydrous.

3.2.17 Sodium hydroxide, 100 g/l solution.

3.2.18 Sodium hydroxide, 50 g/l solution.

3.2.19 Silver nitrate ($AgNO_3$), 2,5 g/l solution.

3.2.20 Lead, 0,1 g/l standard solution.

Weigh 0,1 g of metallic lead (purity 99,95 %) from which the oxide film has been removed, place it in a 100 ml beaker, add 20 ml of the nitric acid solution (3.2.5) and heat to dissolve. Evaporate the solution to dryness. Add 10 ml of the hydrochloric acid (3.2.6) 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, dilute with water to the mark and mix.

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

3.2.21 Lead, 0,001 g/l standard solution.

Transfer 10 ml of the standard lead solution (3.2.20) to a 1 000 ml one-mark volumetric flask, dilute with water to the mark and mix.

1 ml of this standard solution contains 0,001 mg of lead.

3.2.22 Anionite, of medium or strongly basic capacity.

3.2.23 Phenolphthalein, 1 g/l alcoholic indicator solution.

3.3 Apparatus

Ordinary 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).

Dimensions in millimetres

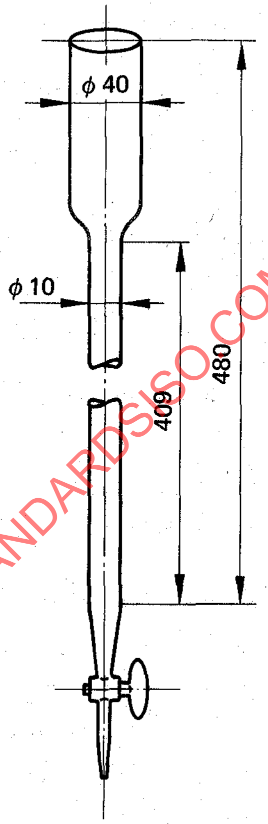

FIGURE – **Ion-exchange (chromatographic) column (3.3.2)**

3.4 Procedure

3.4.1 *Preparation of ion-exchange column*

3.4.1.1 Crush the anionite (3.2.22) 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 (3.2.15) and allow to stand for 24 h, stirring periodically. Then run off the sodium chloride solution, wash the anionite with water eight to ten times by decanting, add the hydrochloric acid (3.2.8) 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 (3.2.8) until complete elimination of iron [i.e. until a negative reaction for iron(III) is obtained with the ammonium thiocyanate solution (3.2.2)].

Run off the hydrochloric acid, wash the anionite in the separating funnel, first with water, and once or twice with the sodium hydroxide solution (3.2.18) and then with the sodium hydroxide solution (3.2.17) until a negative reaction for the chloride ion is obtained with the silver nitrate solution (3.2.19). Then wash the anionite with boiled and cooled water free from carbon dioxide until the washings are neutral to the phenolphthalein solution (3.2.23). Then add the hydrochloric acid solution (3.2.9) to the anionite and store it in a bottle with a ground glass stopper.

3.4.1.2 Transfer the anionite treated as specified in 3.4.1.1 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 the hydrochloric acid solution (3.2.10) and then with 100 ml of the hydrochloric acid solution (3.2.9) at a rate of 1 to 2 ml/min.

Add the hydrochloric acid solution (3.2.9) 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.

3.4.2 *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		Mass of test portion
% (*m*/*m*)		g
from	to	
0,002	0,005	1,0
0,005	0,010	0,5

3.4.3 *Decomposition of test portion*

Place the test portion (3.4.2) in a 100 or 200 ml beaker and dissolve in 10 to 30 ml of the hydrochloric acid (3.2.6) while heating. Add 1 ml of the nitric acid (3.2.4), 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 (3.2.6), 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 the hydrochloric acid solution (3.2.8) and five times with warm water. Reserve the filtrate as the main solution.

3.4.4 *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 (3.2.4) and 6 to 7 ml of the hydrofluoric acid solution (3.2.11) and evaporate to dryness. Ingite the dry residue at 500 to 600 °C, cool, add 0,5 to 1,0 g of the sodium carbonate (3.2.16) and fuse at 900 to 1 000 °C.

Leach the melt in 40 ml of the hydrochloric acid solution (3.2.7) containing 0,5 ml of the hydroxylammonium chloride solution (3.2.3). Add the solution thus obtained to the main solution.

3.4.5 *Separation of lead from accompanying elements*

Evaporate the combined solution to dryness, and then dissolve the residue in 7 ml of the hydrochloric acid (3.2.6) and 10 ml of water. Add 50 to 60 ml of the hydrochloric acid solution (3.2.9) to the solution and mix.

Transfer the hydrochloric solution to the prepared ion-exchange column (3.4.1) 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 the hydrochloric acid solution (3.2.9) 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.

3.4.6 *Desorption of lead*

For elution of the lead, pass 150 ml of the hydrochloric acid solution (3.2.10) 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.

3.4.7 *Preparation and polarographic analysis of solution*

Add to the solution 1 ml of the perchloric acid solution (3.2.12), evaporate to fuming and cool. Dissolve the salts in 7 ml of the phosphoric acid solution (3.2.14). Pour the solution into a 25 ml one-mark volumetric flask, dilute with water to the mark and mix.

Transfer the solution from the flask to a polarographic cell, and purge it with the inert gas (3.2.1) 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).

3.4.8 *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 3.4.4). These solutions shall be analysed under the same conditions as the test sample.

3.5 Expression of results

3.5.1 *Calculation*

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

$$\frac{m_1 (h - h_b) \times 100}{m_2 (h_{st} - h_b)} \times K$$

where

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

m_2 is the mass, in grams, of the test portion (3.4.2);

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.

3.5.2 *Permissible tolerances on results of duplicate determinations*

TABLE 2

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

4.2.1 Inert gas : argon or nitrogen.

4.2.2 Ammonium hydroxide solution, ρ 0,91 g/ml.

4.2.3 Ammonium hydroxide, diluted 1 + 100.

4.2.4 Ammonium acetate (CH_3COONH_4), crystalline.

4.2.5 Hydroxylammonium chloride ($NH_2OH.HCl$), crystalline.

4.2.6 Hydrochloric acid, ρ 1,19 g/ml.

4.2.7 Hydrochloric acid, diluted 1 + 9.

4.2.8 Hydrofluoric acid, ρ 1,14 g/ml, 40 % (*m*/*m*) solution.

4.2.9 Acetic acid, glacial.

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

4.2.11 Sodium carbonate, anhydrous.

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

Dissolve 500 g of the ammonium acetate (4.2.4) in 400 ml of water, add 60 ml of the acetic acid (4.2.9) and 5 ml of the methyl red indicator (4.2.15), dilute with water to 1 000 ml and mix.

4.2.13 Lead, 1 g/l standard solution.

Weigh 1 g of metallic lead (purity 99,95 %) into a 250 ml conical flask, add 20 ml of the perchloric acid (4.2.10) 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 the ammonium acetate buffer solution (4.2.12), dilute with water to the mark and mix.

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

4.2.14 Lead, 0,1 g/l standard solution.

Transfer 100 ml of the standard lead solution (4.2.13) to a 1 000 ml one-mark volumetric flask, dilute with water to the mark and mix.

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

4.2.15 Methyl red, 2 g/l solution in ammonium hydroxide solution (4.2.3).

4.3 Apparatus

Ordinary laboratory apparatus and

4.3.1 Polarograph, operating on alternating or direct current.

4.4 Procedure

4.4.1 *Test portion*

Weigh a mass of the test sample, chosen from table 3 in accordance with the expected lead content.

TABLE 3

Expected lead content		Mass of test portion	Volume of test solution
% (*m*/*m*)		g	ml
from	to		
0,01	0,02	1,0	100
0,02	0,05	1,0	100
0,05	0,10	1,0	200
0,10	0,25	1,0	200
0,25	0,50	1,0	200
0,50	1,00	1,0	200

4.4.2 *Decomposition of test portion*

Place the test portion (4.4.1) in a 200 or 300 ml beaker, add 10 ml of the hydrochloric acid (4.2.6) and heat to dissolve. Evaporate the solution until almost dry, add 10 ml of the perchloric acid solution (4.2.10) and heat to white fumes of perchloric acid. After cooling the solution, add 100 ml of water, 1 g of the hydroxylammonium chloride (4.2.5) 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 the hydrochloric acid solution (4.2.7) and then ten times with hot water. Reserve the filtrate as the main solution.

4.4.3 *Treatment of residue*

Transfer the filter containing the residue to a platinum crucible, dry and ignite at 500 to 600 °C. Cool the crucible, moisten the residue with 2 or 3 drops of water, add 3 or 4 drops of the perchloric acid solution (4.2.10) and 5 to 10 ml of the hydrofluoric acid solution (4.2.8) and evaporate until perchloric acid fuming ceases. Slightly ignite