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Manganese ores and concentrates — Determination of aluminium content — Photometric and gravimetric methods

*Minerais et concentrés de manganèse — Dosage de l'aluminium — Méthodes photométrique
et gravimétrique*

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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 4295 was prepared by Technical Committee ISO/TC 65, *Manganese and chromium ores*.

This second edition cancels and replaces the first edition (ISO 4195 : 1979), of which it constitutes a technical revision.

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Manganese ores and concentrates — Determination of aluminium content — Photometric and gravimetric methods

1 Scope and field of application

This International Standard specifies the following methods for the determination of the aluminium content of manganese ores and concentrates :

- **method A** : photometric method, applicable to products having aluminium contents from 0,1 to 1,5 % (*m/m*);
- **method B** : oxine gravimetric method, applicable to products having aluminium contents over 1,5 % (*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 — Photometric method for aluminium contents from 0,1 to 1,5 % (*m/m*)

3.1 Principle

Decomposition of a test portion by treatment with hydrochloric and nitric acids and double evaporation of the solution with hydrochloric acid to dryness. Dissolution of the dry residue in hydrochloric acid with addition of hydroxylammonium chloride solution. Separation of the insoluble residue by filtration, the filtrate being reserved as the main solution.

Ignition of the filter containing the residue and treatment with sulfuric and hydrofluoric acids. Fusion of the ignited residue with sodium carbonate. Dissolution of the melt in hydrochloric acid and combination of the solution obtained with the main solution.

Separation of iron from aluminium by precipitation as hydroxide, with strong potassium hydroxide solution, in the presence of zinc chloride and boric acid.

Photometric determination in the presence of ascorbic acid and polyvinyl alcohol.

3.2 Reactions

The method is based on the interaction of aluminium with chromazurol-S in the presence of polyvinyl alcohol in acetate buffer solution (pH 6-7) with the formation of a coloured complex between the aluminium and chromazurol-S with a molecular ratio 1 : 3. The influence of iron(III) is eliminated by precipitation with an alkaline borate mixture which prevents sorption of aluminium by the hydroxides.

3.3 Reagents

Use only reagents of recognized analytical grade and only distilled water or water of equivalent purity.

3.3.1 Ammonium acetate ($\text{CH}_3\text{COONH}_4$).

3.3.2 Boric acid.

3.3.3 Sodium tetraborate, anhydrous ($\text{Na}_2\text{B}_4\text{O}_7$).

3.3.4 Sodium carbonate, anhydrous.

3.3.5 Sodium acetate trihydrate ($\text{CH}_3\text{COONa}\cdot 3\text{H}_2\text{O}$).

3.3.6 Fusion mixture : three parts of sodium carbonate (3.3.4) and one part of sodium tetraborate (3.3.3).

3.3.7 Buffer solution, pH 6-7.

Dissolve 274 g of ammonium acetate (3.3.1) in 400 ml of water. Dissolve 109 g of sodium acetate (3.3.5) in 250 ml of water. Combine the solutions, dilute to 1 000 ml with water and mix.

3.3.8 Hydroxylammonium chloride ($\text{NH}_2\text{OH}\cdot\text{HCl}$), 100 g/l solution.

3.3.9 Potassium hydroxide, 470 g/l solution, free from aluminium.

3.3.10 Potassium hydroxide, 50 g/l solution, free from aluminium.

3.3.11 Ascorbic acid ($C_6H_8O_6$), 50 g/l solution.

Prepare fresh as needed.

3.3.12 Nitric acid, ρ 1,40 g/ml.

3.3.13 Nitric acid, ρ 1,40 g/ml, diluted 1 + 1.

3.3.14 Hydrochloric acid, ρ 1,19 g/ml.

3.3.15 Hydrochloric acid, ρ 1,19 g/ml, diluted 1 + 1.

3.3.16 Hydrochloric acid, ρ 1,19 g/ml, diluted 1 + 50.

3.3.17 Sulfuric acid, ρ 1,84 g/ml, diluted 1 + 1.

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

3.3.19 Polyvinyl alcohol [$-CH_2CH(OH)CH_2CH(OH)-$] $_n$, 40 g/l solution.

Dissolve 4 g of polyvinyl alcohol in 100 ml of water while heating. Cool and filter the solution.

Prepare this solution at the time of use.

3.3.20 Chromazurol-S, 1 g/l solution.

Dissolve 1 g of chromazurol-S in 6 ml of nitric acid (3.3.13), add 500 ml of ethanol (3.3.22) and 200 ml of water and mix. Transfer the solution to a 1 000 ml one-mark volumetric flask, dilute with water to the mark and mix.

This solution can be used for 14 days.

3.3.21 Zinc chloride, 104,6 g/l solution.

Dissolve 104,6 g of zinc chloride in water, adding 10 ml of hydrochloric acid (3.3.14), dilute to 1 000 ml with water and mix.

3.3.22 Ethanol (C_2H_5OH).

3.3.23 Aluminium, 0,1 g/l standard solution.

Weigh 0,100 0 g of metallic aluminium (purity 99,95 %) into a 250 ml beaker and dissolve in 25 ml of hydrochloric acid (3.3.15) while heating. Evaporate the solution until moist salts form. Add 5 ml of hydrochloric acid (3.3.15), wash the beaker with water and heat the solution until the salts have dissolved. Cool the solution, transfer 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 aluminium.

3.3.24 Aluminium, 0,01 g/l standard solution.

Pipette 10 ml of standard aluminium solution (3.3.23) into a 100 ml one-mark volumetric flask, dilute with water to the mark and mix.

1 ml of this standard solution contains 0,01 mg of aluminium.

3.3.25 Iron, 1 g/l standard solution.

Place 1 g of metallic iron (purity 99,95 %) in a 250 ml beaker, add 15 ml of hydrochloric acid (3.3.14) and heat the solution until dissolution of the iron is complete. Then add 3 to 5 ml of nitric acid (3.3.12) and boil the solution until it is free from nitrogen oxides. Cool the solution, transfer to a 1 000 ml one-mark volumetric flask, dilute with water to the mark and mix.

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

3.4 Apparatus

Ordinary laboratory apparatus, and

3.4.1 Spectrophotometer or photocolormeter.

3.5 Sampling and samples

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

3.6 Procedure

3.6.1 Number of determinations

Carry out the analysis at least in duplicate, independently, on one test sample.

3.6.2 Test portion

Weigh 1 g of the test sample into a 100 or 250 ml beaker.

3.6.3 Determination

3.6.3.1 Decomposition of test portion

Add 10 to 20 ml of hydrochloric acid (3.3.14) to the beaker containing the test portion (3.6.2) and dissolve while heating. Add 1 ml of nitric acid (3.3.12), boil the solution and then evaporate to dryness. Moisten the dry residue with 10 ml of hydrochloric acid (3.3.14) and again evaporate to dryness. Repeat the evaporation with 10 ml of the same hydrochloric acid. Dissolve the dry residue in 5 to 10 ml of hydrochloric acid (3.3.14) while heating for 3 to 5 min, add 30 to 40 ml of hot water and 1 ml of hydroxylammonium chloride solution (3.3.8) and heat to boiling.

Filter off the insoluble residue on a medium-texture filter paper containing a small quantity of paper pulp, then wash with hydrochloric acid (3.3.16) four or five times and with hot water six to eight times. Reserve the filtrate as the main solution.

3.6.3.2 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 1 or 2 drops of sulfuric acid (3.3.17) and 8 to 10 ml of hydrofluoric acid (3.3.18) and evaporate until the fuming of sulfuric acid ceases. Ignite the residue at 400 to 500 °C, cool, add 0,5 to 1 g of sodium carbonate (3.3.4) and fuse at 1 100 °C for 15 min. If difficulty is encountered in dissolving the sample, fuse with 1 g of the fusion mixture (3.3.6) at the same temperature.

Place the crucible containing the melt in a 250 ml beaker, and add 10 ml of hot hydrochloric acid (3.3.15), 20 ml of water and 0,5 ml of hydroxylammonium chloride solution (3.3.8). After dissolution of the melt, remove the crucible, rinsing it into the beaker with water. Boil the solution for 3 to 5 min to remove carbon dioxide and dissolve the aluminate. Add the solution thus obtained to the main solution.

3.6.3.3 Preparation of solution for photometric measurement

Evaporate the combined solution (3.6.3.2) to 50 to 60 ml, and add 5 ml of zinc chloride solution (3.3.21) and 1 g of boric acid (3.3.2). Heat the solution to boiling and pour carefully into a 250 ml silica beaker containing 30 ml of potassium hydroxide solution (3.3.9). While transferring the solution and then for 3 min, stir the solution using a magnetic stirrer. Cool, transfer to a 500 ml volumetric flask, dilute with water to the mark and mix. After the precipitate has settled, immediately filter the solution through a medium-texture double filter paper into silica beakers, discarding the first portions of the filtrate.

For the further determination, use the solution obtained or carry out the additional dilution as specified in table 1 in accordance with the expected aluminium content.

Pipette a 5 ml aliquot portion of the solution into a 50 ml beaker containing 1,5 ml of hydrochloric acid (3.3.15) and 15 ml of water. Then add 1 ml of ascorbic acid solution (3.3.11), allow to stand for 5 min, and adjust the pH of the solution to 1,5 by adding, drop by drop, potassium hydroxide solution (3.3.10) or hydrochloric acid (3.3.15), checking with a pH meter. Transfer the solution to a 100 ml one-mark volumetric flask, add 10 ml of chromazurol-S solution (3.3.20), while swirling, 5 ml of polyvinyl alcohol solution (3.3.19), and 20 ml of buffer solution (3.3.7), dilute with water to the mark and mix.

3.6.3.4 Photometric measurement

After 60 min, measure the absorbance of the solution at 610 to 620 nm in a 10 mm cell, using either the spectrophotometer or the photocolormeter, having set zero absorbance with reference to water.

3.6.3.5 Blank test

Carry out the blank test through all stages of the analysis, with the addition of iron solution (3.3.25) in a quantity corresponding to the iron content of the test sample.

3.6.3.6 Preparation of calibration graph

Introduce, using a burette, into each of a series of seven 50 ml beakers containing 5 ml of the blank test solution, 1,5 ml of hydrochloric acid (3.3.15) and 15 ml of water, 0,0 — 1,0 — 1,5 — 2,0 — 2,5 — 3,0 and 3,5 ml of standard aluminium solution (3.3.24), corresponding, respectively, to 0,0 — 0,010 — 0,015 — 0,020 — 0,025 — 0,030 and 0,035 mg of aluminium. Add 1 ml of ascorbic acid (3.3.11), mix and allow to stand for 5 min. Then adjust the pH of the solution to 1,5, adding, drop by drop, potassium hydroxide solution (3.3.10) or hydrochloric acid (3.3.15), checking with a pH meter. Transfer the solutions to 100 ml one-mark volumetric flasks, add to each solution, while swirling, 10 ml of chromazurol-S solution (3.3.20), 5 ml of polyvinyl alcohol solution (3.3.19), and 20 ml of buffer solution (3.3.7), dilute with water to the mark and mix.

After 60 min, measure the absorbance of each solution as specified in 3.6.3.4.

Prepare a calibration graph by plotting the absorbance values (deducting the absorbance value of the solution containing no aluminium) against the nominal aluminium contents of the solutions.

3.7 Expression of results

3.7.1 Method of calculation

Convert the absorbance reading for the test solution to aluminium content by means of the calibration graph (3.6.3.6), deducting the absorbance reading for the blank test.

Table 1

Expected aluminium content	Aliquot portion of solution I	Dilution II	Aliquot portion of solution II	Aluminium content of aliquot portion of solution
% (m/m)	ml	ml	ml	mg
0,1 to 0,3	5	—	—	0,010 to 0,030
0,3 to 0,5	100	250	5	0,012 to 0,020
0,5 to 1,5	50	250	5	0,010 to 0,030

The aluminium (Al) content is given, as a percentage by mass, by the formula

$$\frac{m_1 \times 100}{m_2 \times 1\,000} \times K$$

$$= \frac{m_1}{m_2 \times 10} \times K$$

where

m_1 is the mass, in milligrams, of aluminium in the aliquot portion of the test solution, obtained from the calibration graph;

m_2 is the mass, in grams, of the test portion corresponding to the aliquot portion of the test solution;

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

3.7.2 Permissible tolerances on results of parallel determinations

Table 2

Aluminium content	Permissible tolerance	
	Three parallel determinations	Two parallel determinations
% (m/m)	% (m/m)	% (m/m)
From 0,10 to 0,20	0,025	0,02
From 0,20 to 0,50	0,04	0,03
From 0,50 to 1,0	0,08	0,07
From 1,0 to 1,5	0,10	0,08

4 Method B — Oxine gravimetric method for aluminium contents over 1,5 % (m/m)

4.1 Principle

Decomposition of a test portion by treatment with hydrochloric acid and evaporation of the solution to dryness. Dissolution of the dry residue in hydrochloric acid and separation of the silica by filtration, the filtrate being reserved as the main solution.

Ignition of the filter containing the residue and treatment with sulfuric and hydrofluoric acids. Fusion of the ignited residue with sodium carbonate. Dissolution of the melt in hydrochloric acid and addition of the solution obtained to the main solution.

Precipitation of the aluminium with ammonium monohydrogen phosphate solution in an acetic medium in the presence of sodium thiosulfate. Filtration of the solution and fusion of the precipitate with sodium carbonate after incineration.

Dissolution of the melt in hot water and separation of the insoluble residue by filtration. Precipitation of the aluminium in the filtrate with quinolin-8-ol in the presence of ammonium acetate. Separation of the precipitate by filtration. Ignition of the residue to constant mass.

4.2 Reactions

The method is based on the precipitation of the aluminium, in an acetic medium and in the presence of sodium thiosulfate, as an oxinate after its separation from most of the accompanying elements as their phosphates.

4.3 Reagents

Use only reagents of recognized analytical grade and only distilled water or water of equivalent purity.

4.3.1 Sodium tetraborate, anhydrous ($\text{Na}_2\text{B}_4\text{O}_7$).

4.3.2 Sodium carbonate, anhydrous.

4.3.3 Fusion mixture: three parts of sodium carbonate (4.3.2) and one part of sodium tetraborate (4.3.1).

4.3.4 Oxalic acid ($\text{H}_2\text{C}_2\text{O}_4$).

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

4.3.6 Ammonium nitrate, 20 g/l solution.

Dissolve 20 g of ammonium nitrate in 1 000 ml of hot water. Add ammonium hydroxide solution (4.3.5) until the colour of the solution turns yellow, using methyl red (4.3.21) as indicator.

4.3.7 Ammonium acetate ($\text{CH}_3\text{COONH}_4$), 200 g/l solution.

4.3.8 Ammonium monohydrogen phosphate [$(\text{NH}_4)_2\text{HPO}_4$], 100 g/l solution.

4.3.9 Nitric acid, ρ 1,40 g/ml.

4.3.10 Hydrochloric acid, ρ 1,19 g/ml.

4.3.11 Hydrochloric acid, ρ 1,19 g/ml, diluted 1 + 4.

4.3.12 Hydrochloric acid, ρ 1,19 g/ml, diluted 1 + 50.

4.3.13 Sulfuric acid, ρ 1,84 g/ml, diluted 1 + 1.

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

4.3.15 Acetic acid, glacial, ρ 1,05 g/ml.

4.3.16 Acetic acid, ρ 1,05 g/ml, diluted 1 + 1.

4.3.17 Sodium carbonate, 10 g/l solution.

4.3.18 Sodium thiosulfate pentahydrate ($\text{Na}_2\text{S}_2\text{O}_3 \cdot 5\text{H}_2\text{O}$), 50 g/l solution.