

INTERNATIONAL STANDARD



4295

INTERNATIONAL ORGANIZATION FOR STANDARDIZATION • МЕЖДУНАРОДНАЯ ОРГАНИЗАЦИЯ ПО СТАНДАРТИЗАЦИИ • ORGANISATION INTERNATIONALE DE NORMALISATION

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

ISO (the International Organization for Standardization) is a worldwide federation of national standards institutes (ISO member bodies). The work of developing International Standards is carried out through ISO technical committees. Every member body interested in a subject for which a technical committee has been set up 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.

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.

International Standard ISO 4295 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	Germany, F.R.	Poland
Austria	Hungary	Romania
Bulgaria	India	South Africa, Rep. of
Czechoslovakia	Iran	Turkey
Egypt, Arab Rep. of	Italy	U.S.S.R.
France	Japan	Yugoslavia

No member body expressed disapproval of the document.



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AMENDMENT SLIP

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

MODIFICATION TO FOREWORD (*Inside front cover*)

The following sentence is to be added at the end of the foreword :

“This International Standard cancels and replaces ISO Recommendation R 318-1963.”

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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 0,02 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 REFERENCE

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

3 METHOD A — PHOTOMETRIC METHOD FOR ALUMINIUM CONTENTS FROM 0,02 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 sulphuric 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.

Photometric determination in the presence of ascorbic acid, chromazurol-S, polyvinyl alcohol and buffer solution.

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) with the formation of a coloured complex with the aluminium to chromazurol-S molecular ratio 1 : 3. The influence of iron(III) is eliminated by precipitation with an alkaline borate mixture which prevents absorption of aluminium by hydroxides.

3.3 Reagents

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 the sodium carbonate (3.3.4) and one part of the sodium tetraborate (3.3.3).

3.3.7 Buffer solution, pH 6.

Dissolve 274 g of the ammonium acetate (3.3.1) in 400 ml of water. Dissolve 109 g of the 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 ($\text{C}_6\text{H}_8\text{O}_6$), 50 g/l solution.

Prepare fresh as needed.

3.3.12 Nitric acid, ρ 1,40 g/ml.

3.3.13 Nitric acid, diluted 1 + 1.

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

3.3.15 Hydrochloric acid, diluted 1 + 1.

3.3.16 Hydrochloric acid, diluted 1 + 50.

3.3.17 Sulphuric acid, diluted 1 + 1.

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

3.3.19 Methanol (CH_3OH).

3.3.20 Polyvinyl alcohol [$-\text{CH}_2\text{CH}(\text{OH})\text{CH}_2\text{CH}(\text{OH})-$] $_n$, 40 g/l solution.

Dissolve 4 g of polyvinyl alcohol in 10 ml of the methanol (3.3.19), add 70 ml of water and heat to boiling; filter the solution, cool, transfer to a 100 ml one-mark volumetric flask, dilute with water to the mark and mix.

This solution should be stable for months.

3.3.21 Chromazurol-S, 1 g/l solution.

Dissolve 1 g of chromazurol-S in 6 ml of the nitric acid (3.3.13), add 500 ml of the ethanol (3.3.23) 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.

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

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

3.3.23 Ethanol ($\text{C}_2\text{H}_5\text{OH}$).

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

Weigh 0,100 0 g of metallic aluminium (purity 99,95 %) into a 300 ml beaker and dissolve in 25 ml of the hydrochloric acid (3.3.15) while heating. Evaporate the solution until moist salts form, then add 5 ml of the 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.

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

Pipette 10 ml of the standard aluminium solution (3.3.24) 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.

3.3.26 Iron, 1 g/l standard solution.

Place 1 g of metallic iron (purity 99,95 %) in a 200 ml beaker, add 15 ml of the hydrochloric acid (3.3.14) and heat the solution until dissolution of the iron is complete. Then add 3 to 5 ml of the 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

3.4.1 Spectrophotometer or photocolormeter.

3.5 Procedure

3.5.1 Decomposition of test portion

Weigh 1 g of the test sample, place it in a 100 to 200 ml beaker and dissolve in 10 to 20 ml of the hydrochloric acid (3.3.14) while heating. Add 1 ml of the nitric acid (3.3.12), boil the solution and then evaporate to dryness. Moisten the dry residue with 10 ml of the 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 the hydrochloric acid (3.3.14) while heating for 3 to 5 min, add 30 to 40 ml of hot water and 1 ml of the 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 the hydrochloric acid (3.3.16) four or five times and with hot water six to eight times. Reserve the filtrate as the main solution.

3.5.2 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 the sulphuric acid (3.3.17) and 8 to 10 ml of the hydrofluoric acid (3.3.18) and evaporate until the fuming of sulphuric acid ceases. Ignite the residue at 400 to 500 °C, cool, add 0,5 to 1 g of the sodium carbonate (3.3.4) and fuse at 1 100 °C for 15 min. When difficulty is encountered in decomposing 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 200 ml beaker, and add 10 ml of the hot hydrochloric acid (3.3.15), 20 ml of water and 0,5 ml of the 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 decompose aluminate. Add the solution thus obtained to the main solution.

3.5.3 Preparation of solution for photometric measurement

Evaporate the combined solution (3.5.3) to 50 to 60 ml, and add 5 ml of the zinc chloride solution (3.3.22) and 1 g of the boric acid (3.3.2). Heat the solution to boiling and pour carefully into a 200 ml silica beaker containing 30 ml of the 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 the hydrochloric acid (3.3.15) and 15 ml of water. Then add 1 ml of the 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, the potassium hydroxide solution (3.3.10) or the 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 the chromazurol-S solution (3.3.21), while swirling, 5 ml of the polyvinyl alcohol solution (3.3.20), and 20 ml of the buffer solution (3.3.7), dilute with water to the mark and mix.

3.5.4 Photometric measurement

After 30 min, measure the absorbance of the solution using the spectrophotometer at 620 nm, in a 10 mm cell, or the photocolorimeter (3.4.1) at about 610 nm, in a 10 mm cell, against water as reference.

3.5.5 Blank test

Carry out the blank test through all stages of the analysis, with the addition of the standard iron solution (3.3.26) in a quantity corresponding to the iron content of the test sample.

3.5.6 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 the 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 the standard aluminium solution (3.3.25), corresponding to 0,0 – 0,010 – 0,015 – 0,020 – 0,025 – 0,030 and 0,035 mg of aluminium. Add 1 ml of the 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, the potassium hydroxide solution (3.3.10) or the 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 the chromazurol-S solution (3.3.21), 5 ml of the polyvinyl alcohol solution (3.3.20), and 20 ml of the buffer solution (3.3.7), dilute with water to the mark and mix.

TABLE 1

Expected aluminium content	Dilution I	Aliquot portion of solution I	Dilution II	Aliquot portion of solution II	Aluminium content of aliquot portion of solution
% (m/m)	ml	ml	ml	ml	mg
0,2 to 0,3	500	5	—	—	0,020 to 0,030
0,3 to 0,5	500	100	250	5	0,012 to 0,020
0,5 to 1,5	500	50	250	5	0,010 to 0,030

After 30 min, measure the absorbance of each solution as specified in 3.5.4.

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.

3.6 Expression of results

3.6.1 Calculation

Convert the absorbance reading for the test solution to aluminium content by means of the calibration graph (3.5.6), deducting the absorbance reading for the blank test.

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.

3.6.2 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)
0,20	0,02	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 sulphuric 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 thiosulphate. 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 8-oxyquinoline 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 as the oxinate after its separation from most of the accompanying elements as the phosphate in an acetic medium in the presence of sodium thiosulphate.

4.3 Reagents

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 the sodium carbonate (4.3.2) and one part of the 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 the ammonium hydroxide solution (4.3.5) until the colour of the solution turns yellow, using the 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, diluted 1 + 4.