INTERNATIONAL STANDARD ISO 3390

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Aluminium oxide primarily used for the production of aluminium — Determination of manganese content — Flame atomic absorption method

Oxyde d'aluminium principalement utilisé pour la production de l'aluminium — Dosage du manganèse — Méthode par absorption atomique dans la flamme

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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.

International Standard ISO 3390 was drawn up by Technical Committee ISO/TC 47, *Chemistry,* and was circulated to the Member Bodies in May 1974.

It has been approved by the Member Bodies of the following countries :

Austria	Hungary	South Africa, Rep. of
Belgium	India	Spain
Bulgaria	Israel	Sweden
Chile	Italy	Switzerland
Czechoslovakia	Netherlands	Thailand
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France	Poland	United Kingdom
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No Member Body expressed disapproval of the document.

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Aluminium oxide primarily used for the production of aluminium — Determination of manganese content — Flame atomic absorption method

1 SCOPE AND FIELD OF APPLICATION

This International Standard specifies a flame atomic absorption method for the determination of the manganese content of aluminium oxide primarily used for the production of aluminium.

The method is applicable to products of which the manganese content, expressed as Mn, is between 0,000 2 and 0,005 % (*m/m*) (0,000 258 and 0,006 46 % (*m/m*), expressed as MnO).

NOTE — If the apparatus available does not have a sufficient sensitivity for the lower contents of manganese, it is recommended that there should be prior extraction of the manganese, by the method specified in annex A.

2 REFERENCES

ISO 802, *Aluminium oxide primarily used for the production of aluminium — Preparation and storage of test samples.*

ISO 2073, *Aluminium oxide primarily used for the production of aluminium — Preparation of sample solution for analysis — Method by means of attack by hydrochloric acid under pressure.*

3 PRINCIPLE

Dissolution of a test portion by heating in a sealed borosilicate tube with hydrochloric acid at a controlled temperature of 250 °C.

Aspiration of the solution in an air-acetylene flame and determination of manganese by spectrophotometric measurement of the absorption of the 279,5 nm line emitted by a manganese hollow cathode lamp.

4 REAGENTS

During the analysis, use only reagents of recognized analytical grade and only water with a conductivity less than or equal to 50 μS/m.

4.1 Hydrochloric acid, ρ approximately 1,19 g/ml, about 12 N solution.

4.2 Aluminium, acid solution (base solution).

Pickle 60 g of extra pure aluminium (assay 99,999 %), in the form of shavings obtained by turning or drilling, in a little nitric acid, ρ approximately 1,40 g/ml. Wash the cleaned shavings with water and then dry them by washing with acetone.

Weigh, to the nearest 0,02 g, 53,0 g of the dried shavings, place in a beaker of convenient capacity and add 600 ml of the hydrochloric acid solution (4.1) and 300 ml of water.

Introduce 1 drop of mercury to facilitate the attack. Wait until the reaction subsides and then place the beaker on a sand bath or hot-plate and heat gently until all the aluminium has been dissolved. Add another 120 ml of the hydrochloric acid solution (4.1).

Allow to cool, transfer quantitatively to a 1 000 ml one-mark volumetric flask, dilute to the mark and mix.

4.3 Manganese, standard solution, corresponding to 0,500 g of Mn per litre.

1 ml of this standard solution, prepared according to 4.3.1 or 4.3.2, contains 0,000 5 g of Mn.

4.3.1 Weigh, to the nearest 0,000 1 g, 1,802 g of manganese(II) chloride tetrahydrate ($MnCl_2.4H_2O$), dissolve in water, transfer quantitatively to a 1 000 ml one-mark volumetric flask, dilute to the mark and mix.

4.3.2 Weigh, to the nearest 0,000 1 g, 0,500 g of manganese, extra pure, place in a beaker of convenient capacity (for example 200 ml) and add 6 ml of water and 6 ml of the hydrochloric acid solution (4.1). Cover the beaker with a clock-glass and warm until the manganese has completely dissolved. Cool to ambient temperature and transfer the solution quantitatively to a 1 000 ml one-mark volumetric flask, dilute to the mark and mix.

4.4 Manganese, standard solution, corresponding to 0,010 g of Mn per litre.

Place 10,0 ml of the standard manganese solution (4.3) in a 500 ml one-mark volumetric flask, dilute to the mark and mix.

1 ml of this standard solution contains 0,010 mg of Mn.

4.5 Manganese, standard solution, corresponding to 0,001 g of Mn per litre.

Place 50,0 ml of the standard manganese solution (4.4) in a 500 ml one-mark volumetric flask, dilute to the mark and mix.

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

5 APPARATUS

Ordinary laboratory apparatus and :

5.1 Apparatus specified in ISO 2073 (clause 5).

5.2 Atomic absorption spectrophotometer, fitted with a burner fed by air and acetylene (a 100 mm burner is suitable).

5.3 Manganese hollow cathode lamp.

6 PROCEDURE

6.1 Test portion

Weigh, to the nearest 0,001 g, 2,00 g of the dried test sample, prepared according to ISO 802 (sub-clause 3.3). clause 3.3).

6.2 Preparation of calibration graph

6.2.1 *Preparation of the standard matching solutions*

Into each of a series of nine 500 ml one-mark volumetric flasks, place 100 ml of the aluminium base solution (4.2) and then respectively the volumes of the standard manganese solutions (4.5 or 4.4) indicated in the following table.

Dilute to the mark and mix.

Standard manganese solution		Corresponding Mn content	
No.	ml	mg/l	%[1]
	0[2]	0	–
4.5	5,0	0,01	0,000 05
	15,0	0,03	0,000 15
	30,0	0,06	0,000 3
	50,0	0,10	0,000 5
4.4	10,0	0,20	0,001 0
	20,0	0,40	0,002 0
	35,0	0,70	0,003 5
	50,0	1,00	0,005 0

1) In the test conditions : 2 g of test portion in 100 ml of final solution.

2) Blank test on reagents for the calibration graph.

6.2.2 *Spectrophotometric measurements*

Mount the manganese hollow cathode lamp (5.3). Switch on the apparatus (5.2) a sufficient time in advance for it to reach stabilization. Adjust the wavelength to 279,5 nm and select a slit small enough to separate the 279,5 nm line from the manganese triplet (279,5 – 279,8 – 280,1 nm). Adjust the air and acetylene pressures according to the characteristics of the burner so as to obtain an oxidizing flame. Control the rate of aspiration to between 2,5 and 5 ml/min.

Aspirate the standard matching solutions (6.2.1) in the flame and measure the intensity of the non-absorbed radiations.

Take care to maintain the quantity of solution aspirated in the flame constant with respect to time during all the measurements.

Spray water through the burner after each measurement.

NOTE – Light scattering in atomic absorption spectroscopy is caused by solid particles (mainly refractories) in the flame deflecting the light from the hollow cathode lamp, resulting in a high absorbance reading. When using the method without the prior extraction of manganese specified in annex A and if the concentration of aluminium oxide is 2 g per 100 ml of final solution, there is a considerable degree of light scattering. It is therefore necessary to check the calibration blank solution to determine whether the high absorbance reading is due to light scattering (in which case there is no correction to the result) or to traces of manganese present in the aluminium or in the reagents used to prepare the standard matching solutions (in which case a correction must be applied), or to a combination of the two.

Carry out the determination of light scattering as follows :

1) note the absorbance X of the calibration blank solution, measured at the normal wavelength of 279,5 nm;

2) select a non-absorbing wavelength close to the absorbing wavelength (for example 270,2 nm) and adjust the gain control until the same baseline as for 1) is obtained. Note the absorbance Y measured at this wavelength; $(X - Y)$ then gives the corrected calibration blank Z;

3) deduct the corrected reading Z from the readings for the standard matching solutions and prepare a calibration graph by plotting absorbance values against the nominal manganese contents of the solutions.

6.2.3 *Plotting of the calibration graph*

Plot a graph having, for example, the values, expressed as milligrams per litre, of the quantities of Mn (or MnO) contained in the standard matching solutions as abscissae and the corresponding values of absorbance, decreased by the corrected value Z measured for the blank on the reagents for the calibration curve, as ordinates.

6.3 Determination

6.3.1 *Preparation of the test solution*

Prepare the test solution by the procedure specified in ISO 2073, using for the attack 14,4 ml of the hydrochloric acid solution (4.1) and 4 ml of water, adjusting the final volume of the solution to 100 ml.

6.3.2 *Blank test*

Carry out a blank test at the same time as the determination, following the same procedure and using the same quantities of all the reagents used for the determination.

6.3.3 *Spectrophotometric measurements*

Carry out the measurements on the test solution (6.3.1) and on the blank test solution (6.3.2) at the same time as the spectrophotometric measurements on the standard matching solutions (6.2.1), as specified in 6.2.2.

7 EXPRESSION OF RESULTS

By means of the calibration graph (6.2.3), determine the masses of Mn corresponding to the absorbance of the test solution and of the blank test solution.

The manganese content, expressed as a percentage by mass of Mn, is given by the formula

$$\frac{(m_1 - m_2) \times 100}{m_0 \times 10 \times 1\,000} = \frac{m_1 - m_2}{m_0 \times 100}$$

where

m_0 is the mass, in grams, of the test portion (6.1);

m_1 is the mass, in milligrams, of Mn found in the test solution;

m_2 is the mass, in milligrams, of Mn found in the blank test solution.

The manganese content, expressed as a percentage by mass of MnO, is given by multiplying the above value by 1,291.

8 TEST REPORT

The test report shall include the following particulars :

a) the reference of the method used;

b) the results and the method of expression used;

c) any unusual features noted during the determination;

d) any operation not included in this International Standard or in the International Standards to which reference is made, or regarded as optional.

ANNEX A

PRIOR EXTRACTION OF MANGANESE

A.1 PRINCIPLE

After dissolving the test portion, separation of the manganese by extraction of the (2-methyl-8-quinolinol) manganese complex with chloroform from alkaline solution, after addition of tartaric acid and potassium cyanide, at a pH of 11,8. Evaporation of the chloroform and dissolution of the residue in hydrochloric acid.

A.2 REAGENTS

Reagents specified in clause 4 and :

A.2.1 Chloroform

A.2.2 Hydrochloric acid, approximately 0,1 N.

A.2.3 Tartaric acid, 200 g/l solution.

A.2.4 Potassium cyanide, 40 g/l solution. **(See clause A.3 "WARNING").**

A.2.5 Sodium hydroxide, 500 g/l solution.

A.2.6 2-Methyl-8-quinolinol, 20 g/l acetic solution.

Dissolve 2 g of 2-methyl-8-quinolinol ($C_{10}H_9NO$) in about 5 ml of glacial acetic acid, ρ approximately 1,05 g/ml, and dilute to 100 ml with water.

A.3 PREPARATION OF THE TEST SOLUTION

WARNING — Because potassium cyanide is extremely poisonous, it must only be handled with all necessary precautions. In particular, do not add acids to solutions containing cyanides, otherwise hydrogen cyanide will be released.

Follow the procedure specified in 6.3.1 up to the addition of the 14,4 ml of the hydrochloric acid solution (4.1) and 4 ml of water. Transfer the solution quantitatively into a beaker of suitable capacity. Cover the beaker and evaporate the solution on a hot-plate just to crystallization. Dissolve the residue in 60 ml of water and add 25 ml of the tartaric acid solution (A.2.3).

NOTE — The tartaric acid solution (A.2.3) is added before making the solution alkaline in order to avoid the precipitation of manganese hydroxide and incomplete extraction.

A.4 MANGANESE EXTRACTION

Slowly add about 18 ml of the sodium hydroxide solution (A.2.5) to the solution (A.3), with stirring, until the precipitated aluminium hydroxide has completely dissolved. Avoid an excess of sodium hydroxide. Add 10 ml of the potassium cyanide solution (A.2.4), 5 ml of the 2-methyl-8-quinolinol solution (A.2.6) and, with stirring, drop by drop, the sodium hydroxide solution (A.2.5) until the quinaldine precipitate has dissolved. Avoid an excess of sodium hydroxide.

Cool to ambient temperature and adjust the pH of the solution to 11,8 with the sodium hydroxide solution (A.2.5). If the pH is higher, correct it by addition of the hydrochloric acid solution (A.2.2).

NOTE — A black precipitate which disappears completely during the extraction is often noticed.

Transfer the solution quantitatively to a 200 ml separating funnel and extract with 10 ml portions of the chloroform (A.2.1) until the organic phase no longer turns green (four or five extractions are usually required).

Collect the chloroform phases in a 100 ml beaker and discard the aqueous solution.

NOTE — To safely dispose of the cyanide in the aqueous phase, add about 2 g of iron(II) sulphate heptahydrate ($FeSO_4.7H_2O$), mix well and discard.

Add about 0,5 ml of the hydrochloric acid solution (4.1) to the beaker, cover it and evaporate slowly to dryness on a hot-plate.

Dissolve the residue in several millilitres of the hydrochloric acid solution (A.2.2) and transfer quantitatively, washing with the same hydrochloric acid solution, to a 50 ml one-mark volumetric flask. Cool the solution to ambient temperature and dilute to the mark with the hydrochloric acid solution (A.2.2) and mix.

A.5 DETERMINATION

Continue as specified in 6.2 but in the preparation of the standard matching solutions omit the addition of the acid aluminium base solution (4.2).

Note that the extraction solution corresponds to 2 g of test portion in 50 ml, i.e. twice the concentration of the test solution prepared in 6.3.1.

ANNEX B

. ISO PUBLICATIONS RELATING TO ALUMINIUM OXIDE PRIMARILY USED FOR THE PRODUCTION OF ALUMINIUM

ISO 802 — Preparation and storage of test samples.

ISO 803 — Determination of loss of mass at 300 °C (conventional moisture).

ISO 804 — Preparation of sample solution for analysis — Method by alkaline fusion.

ISO 805 — Determination of iron content — 1,10-Phenanthroline photometric method.

ISO 806 — Determination of loss of mass at 1 000 and 1 200 °C.

ISO 900 — Determination of titanium content — Diantipyrylmethane photometric method.

ISO 901 — Determination of absolute density — Pyknometer method.

ISO 902 — Measurement of the angle of repose.

ISO 903 — Determination of untamped density.

ISO 1232 — Determination of silica content — Reduced molybdosilicate spectrophotometric method.

ISO 1617 — Determination of sodium content — Flame (emission) spectrophotometric method.

ISO 1618 — Determination of vanadium content — *N*-Benzoyl-*N*-phenylhydroxylamine photometric method.

ISO 2069 — Determination of calcium content — Flame atomic absorption method.

ISO 2070 — Determination of calcium content — Naphthalhydroxamic acid spectrophotometric method.

ISO 2071 — Determination of zinc content — Flame atomic absorption method.

ISO 2072 — Determination of zinc content — PAN photometric method.

ISO 2073 — Preparation of sample solution for analysis — Method by means of attack by hydrochloric acid under pressure.

ISO 2828 — Determination of fluorine content — Alizarin complexone and lanthanum chloride spectrophotometric method.

ISO 2829 — Determination of phosphorus content — Reduced phosphomolybdate spectrophotometric method.

ISO 2865 — Determination of boron content — Curcumin spectrophotometric method.

ISO 2926 — Particle size analysis — Sieving method.

ISO 2927 — Sampling.

ISO 2961 — Determination of an absorption index.

ISO 3390 — Determination of manganese content — Flame atomic absorption method.