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Aluminium oxide primarily used for the production of aluminium — Determination of silica content — Reduced molybdosilicate spectrophotometric method

Oxyde d'aluminium principalement utilisé pour la production de l'aluminium — Dosage de la silice — Méthode spectrophotométrique au molybdosilicate réduit

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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.

Prior to 1972, the results of the work of the Technical Committees were published as ISO Recommendations; these documents are now in the process of being transformed into International Standards. As part of this process, Technical Committee ISO/TC 47 has reviewed ISO Recommendation R 1232 and fount it technically suitable for transformation. International Standard ISO 1232 therefore replaces ISO Recommendation R 1232-1970 to which it is technically identical.

ISO Recommendation R 1232 was approved by the Member Bodies of the following countries :

Austria
Belgium
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France
Germany
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Hungary
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South Africa, Rep. of
Spain
Sweden
Switzerland
Turkey
United Kingdom
U.S.S.R.

No Member Body expressed disapproval of the Recommendation.

No Member Body disapproved the transformation of ISO/R 1232 into an International Standard.

Printed in Switzerland

Aluminium oxide primarily used for the production of aluminium — Determination of silica content — Reduced molybdosilicate spectrophotometric method

1 SCOPE AND FIELD OF APPLICATION

This International Standard specifies a reduced molybdosilicate spectrophotometric method for the determination of the silica content of aluminium oxide primarily used for the production of aluminium.

The method is applicable to products having an SiO_2 content between 0,005 and 0,025 % (*m/m*), provided that the content of $(P_2O_5 + V_2O_5)$ does not exceed 0,02 % (*m/m*).

1.1 Special cases

1.1.1 SiO_2 content between 0,025 and 0,25 % (*m/m*) [$(P_2O_5 + V_2O_5)$ content not exceeding 0,02 % (*m/m*)].

1.1.2 $(P_2O_5 + V_2O_5)$ content exceeding 0,02 % (*m/m*) (under study).

2 REFERENCES

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

ISO 804, *Aluminium oxide primarily used for the production of aluminium — Preparation of solution for analysis — Method by alkaline fusion.*

ISO 2927, *Aluminium oxide primarily used for the production of aluminium — Sampling.*

3 PRINCIPLE

Formation of the oxidized molybdosilicate (yellow) under well-defined conditions of acidity, concentration of reagents, temperature and time.

Selective reduction of the complex in a highly acidic medium of sulphuric acid and in the presence of tartaric acid.

Spectrophotometric measurement of the reduced coloured complex at a wavelength of about 815 nm.

4 REAGENTS

During the analysis, use only reagents of analytical grade and only redistilled water.

4.1 Sodium carbonate, anhydrous.

4.2 Boric acid (H_3BO_3).

4.3 Nitric acid, approximately 8 N solution.

Dilute 540 ml of nitric acid solution, ρ approximately 1,40 g/ml, about 68 % (*m/m*), with water to 1 000 ml.

4.4 Sodium molybdate, 195 g/l solution (approximately 0,8 N).

Dissolve in a polytetrafluorethylene (PTFE) beaker 19,5 g of sodium molybdate dihydrate ($Na_2MoO_4.2H_2O$) in hot water and, after cooling, dilute to 100 ml.

Transfer the solution to a bottle made of silica-free material and, if necessary, filter before use.

4.5 Tartaric acid, 100 g/l solution.

4.6 Sulphuric acid, approximately 16 N solution.

Add carefully 450 ml of sulphuric acid, ρ approximately 1,84 g/ml, about 96 % (*m/m*), to about 500 ml of water. Cool, dilute to 1 000 ml and mix.

4.7 Reducing solution.

Use one of the following two solutions :

4.7.1 4-Amino-3-hydroxy-1-naphthalene sulphonic acid, 1,5 g/l solution.

a) Dissolve 7 g of anhydrous sodium sulphite (Na_2SO_3) in 50 ml of water. Add 1,5 g of 4-amino-3-hydroxy-1-naphthalene sulphonic acid ($C_{10}H_9NO_4S$).

b) Dissolve 90 g of anhydrous sodium metabisulphite ($Na_2S_2O_5$) in 900 ml of water.

Mix the two solutions a) and b), dilute to 1 000 ml and mix. Filter if necessary.

Store in a cool place in an amber-coloured bottle made of silica-free material.

4.7.2 Ascorbic acid, 20 g/l solution.

Prepare this solution just before use.

4.8 Silica, standard solution corresponding to 0,500 g of SiO_2 per litre.

Into a platinum crucible of suitable capacity, weigh, to the nearest 0,001 g, either

- 0,500 g of SiO_2 obtained from pure silicic acid (H_2SiO_3), ignited at 1 000 °C to constant mass, i.e. until the results of two consecutive weighings do not differ by more than 0,001 g, after cooling each time in a desiccator, or
- 0,500 g of finely ground pure quartz, previously ignited at 1 000 °C for 1 h and cooled in a desiccator.

Add to the crucible 5 g of the sodium carbonate (4.1). Mix thoroughly, preferably with a platinum spatula, and fuse carefully. Add hot water to the crucible, heat gently to complete the dissolution and transfer the solution quantitatively into a beaker made of silica-free material. Cool, dilute to about 500 ml, transfer quantitatively to a 1 000 ml one-mark volumetric flask, dilute to the mark and mix.

Transfer the solution immediately to a bottle made of silica-free material.

1 ml of this standard solution contains 0,500 mg of SiO_2.

4.9 Silica, standard solution corresponding to 0,020 g of SiO_2 per litre.

Transfer 40,0 ml of the standard silica solution (4.8) to a 1 000 ml one-mark volumetric flask, dilute to the mark and mix.

1 ml of this standard solution contains 0,020 mg of SiO_2.

Prepare this solution just before use.

4.10 Silica, standard solution corresponding to 0,005 g of SiO_2 per litre.

Transfer 50,0 ml of the standard silica solution (4.9) to a 200 ml one-mark volumetric flask, dilute to the mark and mix.

1 ml of this standard solution contains 0,005 mg of SiO_2.

Prepare this solution just before use.

5 APPARATUS

Ordinary laboratory apparatus and

5.1 Platinum dish, flat bottomed, of diameter approximately 70 mm, and height approximately 35 mm, fitted with a platinum lid.

5.2 Electric furnace, capable of being controlled at 500 ± 50 °C.

5.3 Electric furnace, capable of being controlled between 1 000 and 1 025 °C.

5.4 pH meter.

5.5 Spectrophotometer.

NOTE — Glassware shall be carefully washed with hot chromic-sulphuric acid, taking all necessary precautions, thoroughly rinsed with water and finally with redistilled water. It should not be dried.

Avoid the use of glass vessels for alkaline solutions.

6 PROCEDURE

6.1 Preparation of the principal solution P

Follow the procedure specified in 6.1, 6.2 and 6.3 of ISO 804.

Prepare this principal solution immediately before use.

6.2 Aliquot portion of principal solution (test portion)

Take two aliquot portions of the principal solution P (6.1) according to the directions given in table 1; transfer one aliquot portion to a beaker of suitable capacity and the other to a 100 ml one-mark volumetric flask, and add the volume of water stated.

TABLE 1

Principal solution P (6.1)	Aliquot portion to be taken		Water to be added to the aliquot portion taken
	Volume	Corresponding mass of test portion	
ml	ml	g	ml
500	50	0,50	0
250	25	0,50	25

6.3 Preparation of the calibration graph

6.3.1 *Preparation of the base solution*

Weigh into the platinum dish (5.1) 12 g of the sodium carbonate (4.1) and 4 g of the boric acid (4.2), and mix carefully, preferably with a platinum spatula.

Cover the dish with its lid and place it in the electric furnace (5.2), controlled at 500 ± 50 °C, taking care to isolate the dish from the floor of the furnace. Maintain at 500 ± 50 °C until the reaction subsides.

NOTE — Avoid contact of the platinum vessel with refractory materials. To isolate it from the floor of the furnace, use, for example, platinum supports.

Transfer the dish to the electric furnace (5.3), controlled between 1 000 and 1 025 °C, taking care to isolate it, as before, from the floor of the furnace. The time at this temperature shall not exceed 5 min.

Remove the dish from the furnace and allow it to cool in air.

Add boiling water to the dish and heat gently to complete dissolution.

After cooling slightly, transfer the contents of the dish to a PTFE beaker of suitable capacity, containing 35 ml of the nitric acid solution (4.3). Wash the dish and its lid carefully with hot water, add the washings to the PTFE beaker and stir. Carefully wash the contents of the PTFE beaker into a glass beaker. Simmer gently for a few minutes. Cool slightly and transfer the solution quantitatively to a 250 ml one-mark volumetric flask. After cooling, dilute to the mark and mix.

6.3.2 *Preliminary test for the control and adjustment of pH*

Transfer 25,0 ml of the base solution (6.3.1) to a beaker of suitable capacity. Add to the beaker 10 ml of water, 15 ml of the standard silica solution (4.10), and 5 ml of the sodium molybdate solution (4.4); mix and check the pH value with the pH meter (5.4).

This value should lie between 0,85 and 0,90. If it does not, adjust the pH by the slow addition, drop by drop, of the required volume of the nitric acid solution (4.3) from a graduated pipette or burette, mixing after each addition. Dilute, if necessary, so that the volume of the solution, after the addition of the nitric acid solution, is 65 ml and check the pH value again (between 0,85 and 0,90).

Note the volume of the nitric acid solution (4.3) used for the pH adjustment and discard the solution.

6.3.3 *Preparation of the standard colorimetric solutions*

for spectrophotometric measurement using a cell having an optical path length of 1 cm.

Into each of a series of six 100 ml one-mark volumetric flasks, transfer 25 ml of the base solution (6.3.1) and then add the volume of nitric acid solution (4.3) used for the adjustment of the pH in the preliminary test (6.3.2). Transfer respectively to the flasks the volumes of the standard silica solution (4.10) shown in table 2.

TABLE 2

Standard silica solution (4.10)	Corresponding mass of SiO_2
ml	mg
0*	0
5,0	0,025
10,0	0,050
15,0	0,075
20,0	0,100
25,0	0,125

* Compensation solution.

Dilute the solutions to about 60 ml.

6.3.4 *Colour development*

Add to each flask 5 ml of the sodium molybdate solution (4.4), mix and leave to stand for 15 to 25 min maximum at 20 to 25 °C. Then add 5 ml of the tartaric solution (4.5), 11 ml of the sulphuric acid solution (4.6) and finally 2 ml of the reducing solution (4.7.1 or 4.7.2). Mix, dilute to the mark and mix again.

6.3.5 *Spectrophotometric measurements*

After 10 min but not longer than 40 min, make the spectrophotometric measurements by means of the spectrophotometer (5.5) at a wavelength of about 815 nm, after having adjusted the instrument to zero absorbance against the compensation solution.

NOTE — Calibrate accurately the cells used for the measurements.

6.3.6 *Plotting of the calibration graph*

Plot a graph having, for example, as abscissae the values, expressed in milligrams, of the masses of SiO_2 per 100 ml of standard colorimetric solution and, as ordinates, the corresponding values of absorbance.

6.4 Determination

6.4.1 *Preliminary test for the control and adjustment of pH*

To the aliquot portion of the principal solution contained in the beaker (see 6.2), add 5 ml of the sodium molybdate solution (4.4) and mix. Check the pH value using the pH meter (5.4), adjust it to a value between 0,85 and 0,90 as indicated in 6.3.2 and discard this solution.

6.4.2 *Colour development*

To the aliquot portion of the principal solution contained in the 100 ml one-mark volumetric flask (see 6.2), add the volume of the nitric acid solution (4.3) used for the adjustment of the pH in the preliminary test (6.4.1), dilute the solution to about 60 ml and mix. Proceed as specified in 6.3.4 for the colour development.

6.4.3 *Spectrophotometric measurement*

Carry out spectrophotometric measurement following the procedure specified in 6.3.5, after having adjusted the instrument to zero absorbance against water.

6.5 Blank test

6.5.1 *Preparation of the solution*

Prepare the blank test solution without addition of extra-pure aluminium oxide, following the procedure specified in 6.4.2 of ISO 804.

6.5.2 *Colour development*

Carry out the development of the colour as specified in 6.4.2.

6.5.3 *Spectrophotometric measurement*

Carry out the spectrophotometric measurement as specified in 6.4.3.

7 EXPRESSION OF RESULTS

By means of the calibration graph (see 6.3.6), determine the silica contents corresponding to the values of the spectrophotometric measurements of the aliquot portion of the principal solution and of the blank test solution.

The silica (SiO_2) content, expressed as a percentage by mass, is given by the formula

$$\frac{(m_0 - m_1) \times D}{1\ 000 \times 5} \times 100 = \frac{m_0 - m_1}{5}$$

where

m_0 is the mass, in milligrams, of silica (SiO_2) found in the aliquot portion of the principal solution P used for the determination;

m_1 is the mass, in milligrams, of silica (SiO_2) found in the corresponding aliquot portion of the blank test solution;

D is the ratio of the volume of the principal solution P to the volume of the aliquot portion used for the determination; in the method specified, this ratio is equal to 10;

5 is the mass, in grams, of the test portion used for the preparation of the principal solution P.

8 SPECIAL CASE – SiO_2 CONTENT BETWEEN 0,025 AND 0,25 % (*m/m*)

8.1 Principle

See clause 3.

NOTE – To effect the colour reaction in the same environmental conditions and in the presence of the same quantities of reagents as used for the preparation of the calibration curve, an addition is made to the aliquot portion of the principal solution P – which should always be less than 50 ml – the amount of the blank test solution required to bring the volume to 50,0 ml.

8.2 Reagents

See clause 4.

8.3 Apparatus

See clause 5.

8.4 Procedure

8.4.1 *Preparation of the principal solution P*

Follow the procedure specified in 6.1, 6.2 and 6.3 of ISO 804, bringing the volume of the principal solution to 500 ml.

8.4.2 *Aliquot portion of principal solution (test portion)*

Take two aliquot portions of the principal solution (8.4.1), containing from 0,025 to 0,125 mg of SiO_2 in a volume not less than 5 ml; and transfer one aliquot portion to a beaker of suitable capacity and the other to a 100 ml one-mark volumetric flask. Then add to each the quantity of the blank test solution (8.4.5.1) necessary to bring the volume to 50,0 ml.

8.4.3 *Preparation of the calibration graph*

See 6.3.

8.4.4 *Determination*

See 6.4.

8.4.5 *Blank test*

8.4.5.1 PREPARATION OF THE SOLUTION

Prepare the blank test solution without addition of extra-pure aluminium oxide, following the procedure specified in 6.4.2 of ISO 804, bringing the volume to 500 ml.

8.4.5.2 COLOUR DEVELOPMENT

See 6.5.2; use a 50 ml aliquot portion.

8.4.5.3 SPECTROPHOTOMETRIC MEASUREMENT

See 6.5.3.

8.5 Expression of results

By means of the calibration graph (see 6.3.6), determine the silica contents corresponding to the values of the spectrophotometric measurements of the aliquot portion of the principal solution and of the blank test solution.

The silica (SiO_2) content, expressed as a percentage by mass, is given by the formula

$$\frac{(m_0 - m_1) \times D}{1\ 000 \times 5} \times 100 = \frac{(m_0 - m_1) \times D}{50}$$

where

m_0 is the mass, in milligrams, of silica (SiO_2) found in the aliquot portion of the principal solution P used for the determination;

m_1 is the mass, in milligrams, of silica (SiO_2) found in the aliquot portion of the blank test solution (50 ml);

D is the ratio of the volume of the principal solution P to the volume of the aliquot portion used for the determination;

5 is the mass, in grams, of the test portion used for the preparation of the principal solution P.

9 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

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 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/R 2070 – Determination of calcium content – Spectrophotometric method using naphthalhydroxamic acid.

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

ISO/R 2072 – Determination of zinc content – PAN photometric method.

ISO 2073 – Preparation of solution for analysis – Method by hydrochloric acid attack 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 adsorption index.

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