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INTERNATIONAL ORGANIZATION FOR STANDARDIZATION

**ISO RECOMMENDATION**

**R 1232**

ALUMINIUM OXIDE  
PRIMARILY USED FOR THE PRODUCTION OF ALUMINIUM

**DETERMINATION OF SILICA CONTENT**

SPECTROPHOTOMETRIC METHOD AS THE REDUCED SILICOMOLYBDATE COMPLEX

1st EDITION

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## BRIEF HISTORY

The ISO Recommendation R 1232, *Aluminium oxide primarily used for the production of aluminium – Determination of silica content – Spectrophotometric method as the reduced silicomolybdate complex*, was drawn up by Technical Committee ISO/TC 47, *Chemistry*, the Secretariat of which is held by the Ente Nazionale Italiano di Unificazione (UNI).

Work on this question led to the adoption of Draft ISO Recommendation No. 1169, which was circulated to all the ISO Member Bodies for enquiry in May 1967. It was approved by the requisite majority of Member Bodies. In the meantime, the ISO/TC 47 Secretariat studied the extension of the method to the determination of silicon contents greater than 0.025 %, and a new section on this subject was added to Draft No. 1169. Thus completed, this Draft was circulated in September 1968 to all the ISO Member Bodies for enquiry as second Draft ISO Recommendation No. 1169. It was approved, subject to a few modifications of an editorial nature, by the following Member Bodies :

Austria	Hungary	South Africa, Rep. of
Belgium	India	Spain
Canada	Iran	Sweden
Chile	Israel	Switzerland
Czechoslovakia	Italy	Turkey
France	Netherlands	U.A.R.
Germany	Portugal	United Kingdom
Greece	Romania	U.S.S.R.

No Member Body opposed the approval of the second Draft.

This second Draft ISO Recommendation was then submitted by correspondence to the ISO Council, which decided to accept it as an ISO RECOMMENDATION.

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1. SCOPE

This ISO Recommendation describes a spectrophotometric method using the reduced silicomolybdate complex for the determination of silica in aluminium oxide primarily used for the production of aluminium.

2. FIELD OF APPLICATION

The method is applicable to the determination of silica in the industrial product having an  $\text{SiO}_2$  content between 0.005 and 0.025 % provided that the content of  $\text{P}_2\text{O}_5 + \text{V}_2\text{O}_5$  does not exceed 0.02 %.

2.1 Special cases

2.1.1  $\text{SiO}_2$  content between 0.025 and 0.25 % ( $\text{P}_2\text{O}_5 + \text{V}_2\text{O}_5$  content not exceeding 0.02 %).

2.1.2  $\text{P}_2\text{O}_5 + \text{V}_2\text{O}_5$  content exceeding 0.02 % (in course of study).

3. PRINCIPLE

Formation of the oxidized silicomolybdate complex (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 coloured complex at a wavelength of about 815 nm.

4. REAGENTS

Only redistilled water should be used in the test.

4.1 *Sodium carbonate*, anhydrous.

4.2 *Boric acid* ( $\text{H}_3\text{BO}_3$ ).

4.3 *Nitric acid*, approximately 8 N solution.

Dilute 540 ml of nitric acid solution,  $\rho$  1.4 (g/ml) approximately, 68 % (m/m) approximately, with water to 1000 ml.

4.4 *Sodium molybdate*, 195 g/l (0.8 M approximately) solution.

Dissolve in a PTFE\* beaker, 19.5 g of sodium molybdate dihydrate ( $\text{Na}_2\text{MoO}_4 \cdot 2\text{H}_2\text{O}$ ) in hot water and, after cooling, dilute to 100 ml. Transfer the solution to a plastics\*\* bottle and, if necessary, filter before use.

\* Polytetrafluorethylene.

\*\* For example, PTFE, polypropylene and polyethylene may be used.

4.5 *Tartaric acid*, 100 g/l solution.

Dissolve 10 g of tartaric acid in water and dilute to 100 ml.

4.6 *Sulphuric acid*, approximately 16 N solution.

Add carefully 450 ml of sulphuric acid,  $\rho$  1.84 (g/ml) approximately, 96 % (m/m) approximately, to about 500 ml of water. Cool and dilute to 1000 ml.

4.7 *Reducing solution*

Either of the solutions given below may be used.

4.7.1 *1-amino, 2-naphthol, 4-sulphonic acid*, 1.5 g/l solution.

(a) Dissolve 7 g of anhydrous sodium sulphite in 50 ml of water. Add 1.5 g of 1-amino, 2-naphthol, 4-sulphonic acid.

(b) Dissolve 90 g of anhydrous sodium metabisulphite ( $\text{Na}_2\text{S}_2\text{O}_5$ ) in 900 ml of water.

Mix the two solutions (a) and (b) and dilute to 1000 ml. Filter if necessary.

Store in an amber coloured bottle, in a cool place.

4.7.2 *Ascorbic acid*, 20 g/l solution.

Dissolve 2 g of ascorbic acid in water and dilute to 100 ml.

Use a freshly prepared solution.

4.8 *Silica, standard solution* containing 0.500 g of  $\text{SiO}_2$  per litre.

Into a platinum crucible of suitable capacity, weigh to the nearest milligramme, either

- 0.500 g of  $\text{SiO}_2$  obtained from pure silicic acid ( $\text{H}_2\text{SiO}_3$ ), ignited to constant mass at  $1000^\circ\text{C}$  and cooled in a desiccator; or
- 0.500 g of finely ground pure quartz, previously ignited at  $1000^\circ\text{C}$  for 1 hour and cooled in a desiccator.

Add to the crucible 5 g of sodium carbonate (4.1).

Mix thoroughly, preferably with a platinum spatula, and fuse carefully.

Add hot water directly to the crucible, heat gently to complete the dissolution and transfer the solution quantitatively into a PTFE beaker.

Cool, dilute to about 500 ml, transfer quantitatively to a 1000 ml one-mark volumetric flask, dilute to the mark and mix thoroughly.

Transfer immediately to a plastics\* bottle.

1 ml of this standard solution contains 0.500 mg of  $\text{SiO}_2$ .

4.9 *Silica, standard solution* containing 0.020 g of  $\text{SiO}_2$  per litre.

Transfer 40.0 ml of the standard silica solution (4.8) to a 1000 ml one-mark volumetric flask, dilute to the mark and mix thoroughly.

1 ml of this standard solution contains 20  $\mu\text{g}$  of  $\text{SiO}_2$ .

This solution should be prepared just before use.

4.10 *Silica, standard solution* containing 0.005 g of  $\text{SiO}_2$  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 thoroughly.

1 ml of this standard solution contains 5  $\mu\text{g}$  of  $\text{SiO}_2$ .

This solution should be prepared just before use.

\* For example, PTFE, polypropylene and polyethylene may be used.

## 5. APPARATUS

Ordinary laboratory apparatus together with

- 5.1 *Platinum dish*, flat bottomed, diameter approximately 70 mm, height approximately 35 mm, fitted with a platinum lid.
- 5.2 *Electric furnace*, controlled at  $500 \pm 50$  °C.
- 5.3 *Electric furnace*, controlled between 1000 and 1025 °C.
- 5.4 *pH meter*.
- 5.5 *Spectrophotometer*.

NOTE. – Glassware should be carefully washed with chromic-sulphuric acid, 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 sample solution (principal solution P)

Follow the instructions given in clauses 5.1, 5.2 and 5.3 of ISO Recommendation R 804, *Aluminium oxide primarily used for the production of aluminium – Preparation of sample solution for analysis*.

This sample solution should be prepared immediately before use.

### 6.2 Test portion

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

Volume of the principal solution (6.1)	Aliquot portion		Volume of water to be added to the aliquot portion taken
	Volume to be taken	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 chart

#### 6.3.1 Preparation of the base solution. Weigh into the platinum dish (5.1)

- 12 g of sodium carbonate (4.1) and
- 4 g of boric acid (4.2)

and mix thoroughly, preferably with a platinum spatula.

Cover the dish with its lid. Place in the electric furnace (5.2) controlled at  $500 \pm 50$  °C, taking care to isolate the dish from the base of the furnace (see Note below). Keep at  $500 \pm 50$  °C until the reaction subsides.

Transfer the dish to the electric furnace (5.3), controlled between 1000 and 1025 °C, once again taking care to isolate it from the base of the furnace. The time at this temperature should not exceed 5 minutes.

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

Add boiling water directly 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 to a 250 ml one-mark volumetric flask. After cooling, dilute to the mark and mix.

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

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),
- 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 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 matching solutions* for spectrophotometric measurement using a 1 cm cell.

6.3.3.1 **TAKING ALIQUOT PARTS OF THE STANDARD SOLUTION.** 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 silica standard solution (4.10) shown in the following Table.

Volume of silica standard solution (4.10)	Corresponding mass of SiO <sub>2</sub>
ml	µg
0 *	0
5.0	25
10.0	50
15.0	75
20.0	100
25.0	125

\* Compensation solution.

Dilute the solutions to about 60 ml.

**6.3.3.2 DEVELOPMENT OF THE COLOUR.** Add to each flask 5 ml of the sodium molybdate solution (4.4), mix and leave to stand for 15 to a maximum of 25 minutes at a temperature between 20 and 25 °C. Then add 5 ml of the tartaric acid 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.

**6.3.4 Spectrophotometric measurements.** After 10 minutes but not longer than 40 minutes, make the spectrophotometric measurements by means of the spectrophotometer (5.5) at a wavelength of about 815 nm, having adjusted the instrument to zero optical density against the compensation solution (see clause 6.3.3.1).

NOTE. - Calibrate the cells used for the measurements.

**6.3.5 Plotting of the calibration chart.** Prepare a calibration chart having, for example, as abscissae the values, expressed in milligrammes, of the quantities of SiO<sub>2</sub> per 100 ml of standard matching solution, and the corresponding values of optical density as ordinates.

#### 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 clause 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 clause 6.3.2 and discard this solution.

**6.4.2 Development of the colour.** To the aliquot portion of the principal solution contained in the 100 ml one-mark volumetric flask (see clause 6.2) add the quantity of 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 indicated in clause 6.3.3.2 for the development of the colour.

**6.4.3 Spectrophotometric measurement.** Carry out spectrophotometric measurement following the procedure described in clause 6.3.4, after having adjusted the instrument to zero optical density against water.

#### 6.5 Blank test

**6.5.1 Preparation of the solution.** Prepare the blank solution without addition of pure aluminium oxide, following the instructions given in clause 5.4.2 of ISO Recommendation R 804, *Aluminium oxide primarily used for the production of aluminium - Preparation of sample solution for analysis*.

**6.5.2 Development of the colour.** Carry out the procedure described in clause 6.4.2.

**6.5.3 Spectrophotometric measurement.** Carry out the procedure described in clause 6.4.3.

### 7. EXPRESSION OF RESULTS

By means of the calibration chart (see clause 6.3.5) determine the silica contents corresponding to the value of the spectrophotometric measurement of the aliquot of the principal solution and to that of the blank solution.

The silica content (SiO<sub>2</sub>) is given as a percentage, by mass, by the formula

$$\frac{(A - B) \times D}{1000 \times 5} \times 100 = \frac{A - B}{5}$$

where

- A* is the mass, in milligrammes, of silica (SiO<sub>2</sub>) found in the aliquot of the principal solution used for the determination;
- B* is the mass, in milligrammes, of silica (SiO<sub>2</sub>) found in the corresponding aliquot of the blank solution;
- D* is the ratio of the volume of the principal solution to the volume of the aliquot used for the determination. In the method described this ratio is equal to 10;
- 5* is the mass, in grammes, of the test portion used for the preparation of the principal solution.