INTERNATIONAL STANDARD ISO 1620

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Cryolite, natural and artificial – Determination of silica content – Reduced molybdosilicate spectrophotometric method

Cryolithe, naturelle et artificielle – 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 1620 and found it technically suitable for transformation. International Standard ISO 1620 therefore replaces ISO Recommendation R 1620-1970 to which it is technically identical.

ISO Recommendation R 1620 was approved by the Member Bodies of the following countries :

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United Kingdom
U.S.S.R.
Yugoslavia

The Member Body of the following country expressed disapproval of the Recommendation on technical grounds :

Canada

No Member Body disapproved the transformation of ISO/R 1620 into an International Standard.

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INTERNATIONAL STANDARD ISO 1620-1976 (E)

Cryolite, natural and artificial – 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 natural and artificial cryolite and of natural and synthetic materials having a molar ratio (NaF/AlF_3) between 3 and 1,7 approximately.

The method is applicable to products the phosphorus(V) oxide (P_2O_5) content of which does not exceed 0,02 % (*m/m*).

1.1 Special case (under study)

Phosphorus(V) oxide contents greater than 0,02 % (*m/m*).

2 REFERENCE

ISO 1619, *Cryolite, natural and artificial – Preparation and storage of test samples.*

3 PRINCIPLE

Alkaline fusion of a test portion by means of a mixture of sodium carbonate and boric acid. Dissolution of the fused mass in excess nitric acid so that the final pH of the solution is between 0,7 and 0,9 after dilution to 500 ml, or between 0,3 and 0,5 after dilution to 250 ml.

Formation, in a suitable aliquot, of the (yellow) oxidized molybdosilicate under clearly defined conditions of acidity, concentration of reagents, temperature and time.

Selective reduction of the complex in a high-acidity sulphuric medium 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 recognized 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, ρ approximately 1,40 g/ml, about 68 % (*m/m*) solution, with water to 1 000 ml.

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

In a polytetrafluoroethylene (PTFE) beaker, dissolve 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.

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

4.7 Reducing solution.

Use either 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, after cooling each time in a desiccator, do not differ by more than 0,001 g, 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 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 550 ± 25 °C.

5.3 Electric furnace, capable of being controlled at 740 ± 25 °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 Test portion

Weigh, to the nearest 0,001 g, exactly 1 g of the test sample, dried at 110 °C (see 3.3 of ISO 1619).

6.2 Preparation of the calibration graph

6.2.1 *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 550 ± 25 °C, taking care to isolate the dish from the floor of the furnace. Maintain at 550 ± 25 °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 at 750 ± 25 °C, taking care to isolate it, as before, from the floor of the furnace. It must not stay at this temperature for more than 5 min. Remove the dish from the furnace and allow 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 20 ml of the nitric acid solution (4.3). Carefully wash the dish and lid with 18 ml of the nitric acid solution and then with hot water, collecting the washings in the PTFE beaker; heat gently for a few minutes at a temperature near to the boiling point.

Allow to cool somewhat and transfer the solution quantitatively to a 100 ml one-mark volumetric flask. After cooling, dilute to the mark and mix.

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

Transfer 20 ml of the base solution (6.2.1) to a beaker of suitable capacity. Add to the beaker 15 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 slowly adding, drop by drop, by means of a graduated pipette or burette, mixing after each addition, the required quantity of the nitric acid solution (4.3). Dilute, if necessary, so that the final volume of the solution, after the addition of the nitric acid solution, is 65 ml and again check the pH value (between 0,85 and 0,90).

Note the volume of the nitric acid solution added to correct the pH and discard the solution.

6.2.3 *Preparation of the standard colorimetric solutions,* for spectrophotometric measurements using a cell having an optical path length of 1 cm

Into each of a series of six 100 ml one-mark volumetric flasks, place 20 ml of the base solution (6.2.1) and then add the volume of the nitric acid solution (4.3) used to adjust the pH in the preliminary test (6.2.2).

Then add to the flasks the volumes of the standard silica solution (4.10) shown in the following table :

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 approximately 60 ml.

6.2.4 *Colour development*

To each flask, add 5 ml of the sodium molybdate solution (4.4), mix and allow to stand for 15 to 25 min at 20 to 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.

6.2.5 *Spectrophotometric measurements*

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

NOTE — Calibrate accurately the cells used for the measurements.

6.2.6 *Plotting the calibration graph*

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

6.3 Determination

6.3.1 *Preparation of the test solution*

6.3.1.1 Fusion of the test portion

Into the platinum dish (5.1), weigh 12 g of the sodium carbonate (4.1) and 4 g of the boric acid (4.2), and mix carefully. Add the test portion (6.1) and mix the whole quantity carefully, preferably with a platinum spatula.

Cover the dish with its lid and place it in the electric furnace (5.2), controlled at 550 ± 25 °C, taking the precaution of isolating the dish from the floor of the furnace by means of a support from which there is no risk of introducing impurities.

Maintain at 550 ± 25 °C until the reaction subsides (time required : approximately 30 min).

Then transfer the dish to the electric furnace (5.3), controlled at 750 ± 25 °C, taking care to isolate it from the floor of the furnace in the same manner as before.

The dish shall stay at this temperature for 30 min and the operator must ensure that the temperature of 750 ± 25 °C is maintained for at least 20 min.

6.3.1.2 Dissolution of the fused mass

Remove the dish from the furnace and allow to cool in air. Add boiling water to the dish, heating moderately until dissolution occurs.

After cooling slightly, transfer the contents of the dish to a beaker (for example PTFE) of suitable capacity, containing 20 ml of the nitric acid solution (4.3).

Dissolve the residue (mainly iron(III) oxide) still adhering to the walls of the dish, with 18 ml of the nitric acid solution and carefully wash the dish and lid in hot water, collecting the washings in the plastics beaker.

Heat for a few minutes at a temperature approaching boiling point until complete dissolution occurs. Allow to cool, transfer the solution quantitatively to a 250 ml one-mark volumetric flask, dilute to the mark and mix.

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

6.3.2 *Coloured reaction*

6.3.2.1 Taking of aliquot portions

Take two 50,0 ml aliquot portions from the test solution (6.3.1.2) and place one in a beaker of suitable capacity and the other in a 100 ml one-mark volumetric flask.

6.3.2.2 Preliminary test for the control and adjustment of pH

Add 5 ml of the sodium molybdate solution (4.4) to the aliquot portion of the test solution in the beaker and mix. Check the pH value using the pH meter (5.4), adjust to a value of between 0,85 and 0,90 as specified in 6.2.2 and discard this solution.

6.3.2.3 COLOUR DEVELOPMENT

To the aliquot portion of the test solution in the 100 ml one-mark volumetric flask, add the volume of the nitric acid solution (4.3) used to adjust the pH in the preliminary test (6.3.2.2), adjust the volume to about 60 ml and mix. Then proceed with development of the coloured reaction as specified in 6.2.4.

6.3.2.4 SPECTROPHOTOMETRIC MEASUREMENT

Carry out the spectrophotometric measurement according to the procedure specified in 6.2.5, after having adjusted the instrument to zero absorbance against water.

6.3.3 *Blank test*

6.3.3.1 PREPARATION OF THE SOLUTION

Prepare the blank test solution according to the procedure specified in 6.2.1, but dilute to a final volume of 250 ml.

6.3.3.2 COLOUR DEVELOPMENT

Develop the colour as specified in 6.3.2.3.

6.3.3.3 SPECTROPHOTOMETRIC MEASUREMENT

Carry out the spectrophotometric measurement as specified in 6.3.2.4.

7 EXPRESSION OF RESULTS

By reference to the calibration graph (see 6.2.5), determine the quantities of silica corresponding to the values of the spectrophotometric measurements of the aliquot portion of the test solution and of the blank test solution.

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

$$(m_0 - m_1) \times \frac{500}{1\ 000} = \frac{m_0 - m_1}{2}$$

where

m_0 is the mass, in milligrams, of silica (SiO_2) found in the aliquot portion of the test solution (containing 0,200 g of the dried test sample) taken 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.

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 operations not included in this International Standard or in the International Standard to which reference is made, or regarded as optional.