UDC 661.8 : 553.634 : 546.28 : 543.422

Ref. No. : ISO/R 1620-1970 (E)

ISO

INTERNATIONAL ORGANIZATION FOR STANDARDIZATION

# ISO RECOMMENDATION

# R 1620

## CRYOLITE (NATURAL AND ARTIFICIAL)

## DETERMINATION OF SILICA CONTENT

## SPECTROPHOTOMETRIC METHOD USING THE REDUCED SILICOMOLYBDIC COMPLEX

1st EDITION

August 1970

For each individual country the only valid standard is the national standard of that country.

Printed in Switzerland

Also issued in French and Russian. Copies to be obtained through the national standards organizations.

## BRIEF HISTORY

The ISO Recommendation R 1620, *Cryolite (natural and artificial) – Determination of silica content – Spectrophotometric method using the reduced silicomolybdic 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. 1620, which was circulated to all the ISO Member Bodies for enquiry in March 1969. It was approved, subject to a few modifications of an editorial nature, by the following Member Bodies :

Australia
Austria
Belgium
Brazil
Chile
Czechoslovakia
France
Germany
Greece
Hungary
India
Iran
Israel
Italy
Netherlands
New Zealand
Norway
Peru
Poland
Romania
South Africa, Rep. of
Spain
Sweden
Switzerland
Thailand
Turkey
U.A.R.
United Kingdom
U.S.S.R.
Yugoslavia

The following Member Body opposed the approval of the Draft :

Canada

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

ISO Recommendation | R 1620 | August 1970

## CRYOLITE (NATURAL AND ARTIFICIAL)

## DETERMINATION OF SILICA CONTENT

## SPECTROPHOTOMETRIC METHOD USING THE REDUCED SILICOMOLYBDIC COMPLEX

### 1. SCOPE

This ISO Recommendation describes a spectrophotometric method, using the reduced silicomolybdic complex, for determining the silica content in natural and artificial cryolite.

### 2. FIELD OF APPLICATION

The method can be applied to the determination of the silica present in natural and artificial cryolite provided that the $P_2O_5$ content does not exceed 0.02 %.

NOTE. – The method is suitable for application to both the natural and synthetic materials whose ratio of NaF to $AlF_3$ is between 3 and 1.7.

### 2.1 **Special case** (under preparation)

Determination of silica when $P_2O_5$ contents greater than 0.02 % are present.

### 3. PRINCIPLE

Alkaline fusion of a test portion by means of a mixture of sodium carbonate and boric acid. Solution of the fused mass in excess nitric acid so that the pH of the final solution is between 0.7 and 0.9 after being diluted to 500 ml or between 0.3 and 0.5 after being diluted to 250 ml.

Formation, in a suitable aliquot, of the (yellow) oxidized silicomolybdic complex 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 complex at a wavelength of about 815 nm.

## 4. REAGENTS

Redistilled water should be used in the test.

**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 $\rho$ 1.4 (g/ml), 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 ($Na_2MoO_4.2H_2O$) in hot water and, after cooling, dilute to 100 ml.

Transfer the solution to a plastics** bottle and, if necessary, filter before use.

**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.

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

**4.7** *Reducing solution.*

Either of the following solutions 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 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/l of silica ($SiO_2$).

Into a platinum crucible weigh to the nearest milligramme

- either 0.500 g of $SiO_2$ obtained from pure silicic acid ($H_2SiO_3$), ignited to constant mass at 1000 °C and cooled in a desiccator;
- or 0.500 g of finely ground pure quartz, previously ignited at 1000 °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 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. Transfer immediately to a plastics** bottle.

1 ml of this standard solution contains 0.500 mg of $SiO_2$.

**4.9** *Silica, standard solution* containing 0.020 g/l of silica ($SiO_2$).

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.

1 ml of this standard solution contains 20 $\mu$g of $SiO_2$.

This solution should be prepared just before use.

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* Polytetrafluorethylene

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

4.10 *Silica, standard solution* containing 0.005 g/l of silica ($SiO_2$).

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 5 $\mu$g of $SiO_2$.

This solution should be prepared just before use.

## 5. APPARATUS

Glassware should be carefully washed with hot chromic-sulphuric acid, thoroughly rinsed with water and finally with redistilled water; do not dry. Avoid the use of glass vessels for alkaline solutions.

Ordinary laboratory apparatus and

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 550 ± 25 °C.

5.3 *Electric furnace* controlled at 750 ± 25 °C.

5.4 *pH-meter*, provided with a glass electrode.

5.5 *Spectrophotometer.*

## 6. PROCEDURE

### 6.1 Test portion

Weigh, to the nearest 1 mg, exactly 1 g of the dried test sample*.

### 6.2 Preparation of the calibration curve

6.2.1 *Preparation of the base solution.* Into the platinum dish (5.1) weigh

- 12 g of sodium carbonate (4.1),
- 4 g of 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, until the reaction has ended, taking care to isolate the dish from the floor of the furnace.

Then transfer the dish to the electric furnace (5.3) controlled at a temperature of 750 ± 25 °C, isolating it, as before, from the floor of the furnace. It must not stay in this furnace for more than 5 minutes. Remove the dish from the furnace and allow to cool in the 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), and carefully wash the dish and lid with 18 ml of the nitric acid solution (4.3) and then with hot water, collecting the whole quantity in the PTFE beaker; heat gently for a few minutes at a temperature near to the boiling point.

Allow to cool somewhat and transfer 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), 5 ml of the sodium molybdate solution (4.4), mix and check the pH value with the pH-meter (5.4). This value should be between 0.85 and 0.90, but if 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 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 nitric acid solution (4.3) used to correct the pH and discard the solution.

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* See ISO Recommendation R 1619, *Cryolite (Natural and artificial) – Preparation and storage of test samples*, clause 2.3.

6.2.3 *Preparation of the standard matching solutions*, for spectrophotometric measurements using a 1 cm cell.

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 quantity of nitric acid solution (4.3) used to correct 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 :

| **Volume of standard silica solution (4.10)** | **Corresponding mass of $SiO_2$** |
|---|---|
| ml | µg |
| 0 * | 0 |
| 5.0 | 25 |
| 10.0 | 50 |
| 15.0 | 75 |
| 20.0 | 100 |
| 25.0 | 125 |

* Compensation solution

Then dilute the solutions to approximately 60 ml.

6.2.4 *Development of the colour.* To each flask add 5 ml of the sodium molybdate solution (4.4), mix and allow to stand for between 15 and 25 minutes at a temperature of 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). Make up to volume and mix.

6.2.5 *Spectrophotometric measurements.* After 10 minutes, but not longer than 40 minutes, carry out 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 8.2).

6.2.6 *Preparation of the calibration chart.* Prepare a calibration chart having, for example, the silica content, in milligrammes of $SiO_2$, per 100 ml of standard matching solution, as abscissae and the corresponding values of optical density as ordinates.

## 6.3 Determination

### 6.3.1 *Preparation of the sample solution*

6.3.1.1 FUSION OF THE TEST PORTION. Into the platinum dish (5.1) weigh 12 g of sodium carbonate (4.1) and 4 g of boric acid (4.2).

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 it 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 minutes).

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

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