International Standard 6382

INTERNATIONAL ORGANIZATION FOR STANDARDIZATION•МЕЖДУНАРОДНАЯ ОРГАНИЗАЦИЯ ПО СТАНДАРТИЗАЦИИ•ORGANISATION INTERNATIONALE DE NORMALISATION

General method for determination of silicon content — Reduced molybdosilicate spectrophotometric method

Méthode générale de dosage du silicium — Méthode spectrophotométrique au molybdosilicate réduit

First edition — 1981-11-01

UDC 543.422 : 546.284-31 **Ref. No. ISO 6382-1981 (E)**

Descriptors : chemical compounds, tests, determination of content, silicon, spectrophotometric analysis, calibrating.

Price based on 5 pages

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 6382 was developed by Technical Committee ISO/TC 47, *Chemistry*, and was circulated to the member bodies in October 1979.

It has been approved by the member bodies of the following countries :

Australia
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No member body expressed disapproval of the document.

This International Standard was also approved by the International Union of Pure and Applied Chemistry (IUPAC).

Printed in Switzerland

General method for determination of silicon content — Reduced molybdosilicate spectrophotometric method

WARNING — Attention is drawn to the dangers involved in the use of some of the reagents (see the corresponding notes).

1 Scope

This International Standard specifies a general method for the determination of silicon by spectrophotometric measurement of reduced molybdosilicate.

It describes a technique for the determination of the content of silicon in a solution. Reference should be made, for the preparation of the test solution, to the International Standard relating to the product to be analysed, which should indicate the modifications necessary to make the method applicable to that product.

2 Field of application

The method is applicable to the determination of quantities of silicon, expressed as SiO_2, between 2 and 200 µg in the aliquot portion of the test solution taken for the determination.

The ions, elements and compounds given in the table in annex A do not interfere with the determination when they are present separately up to the limits indicated. In certain cases, this table gives guidance on the treatment to be applied to reduce or suppress interferences.

3 Principle

Depolymerization of any polymerized silica by treatment with sodium fluoride in the presence of hydrochloric acid.

Formation of the oxidized (yellow) molybdosilicate at a pH of 1,1 ± 0,2 in the presence of boric acid to suppress interference by fluoride ion.

Selective reduction of this complex in the presence of oxalic acid and in a sulphuric acid medium of acidity sufficiently high to eliminate interference by phosphates.

Spectrophotometric measurement of the blue-coloured complex at the wavelength corresponding to maximum absorption (about 800 nm).

4 Reagents

During the analysis, use only reagents of recognized analytical grade, as far as possible silica-free, and water which has been double-distilled from a quartz apparatus or water of equivalent purity.

NOTE — Demineralized water is not suitable.

Store all the reagents in flasks of material free from silica (for example, polyethylene).

4.1 Sulphuric acid, approximately 400 g/l solution.

Add, taking all necessary precautions, 240 ml of sulphuric acid, ϱ 1,84 g/ml [98 % (m/m) solution], to 500 ml of water, dilute to 1 000 ml and mix.

4.2 Hydrochloric acid, approximately 150 g/l solution.

Dilute, taking all necessary precautions, 340 ml of hydrochloric acid, ϱ 1,19 g/ml [38 % (m/m) solution], to 1 000 ml with water.

4.3 Boric acid, solution saturated at room temperature (approximately 48 g/l).

4.4 Oxalic acid dihydrate [$(COOH)_2.2H_2O$], 100 g/l solution.

NOTE — Harmful in contact with skin and if swallowed. Avoid contact with skin and eyes.

4.5 Sodium fluoride, 20 g/l solution.

Store this solution in a flask of material free from silica.

NOTE — Toxic by inhalation, in contact with skin and if swallowed. In case of contact with eyes, rinse immediately with plenty of water and seek medical advice.

In case of feeling unwell, seek medical advice (show the label where possible).

4.6 *Di*sodium molybdate dihydrate, 140 g/l solution.

Dissolve, in a polyethylene beaker, 35 g of *di*sodium molybdate dihydrate ($Na_2MoO_4.2H_2O$) in 200 ml of water at about 50 °C. Allow to cool to ambient temperature, transfer to a 250 ml one-mark volumetric flask and dilute to the mark. Transfer the solution to a flask of material free from silica and, if necessary, filter before use.

Prepare this solution at the time of use.

4.7 Reducing solution.

Use one of the following solutions :

4.7.1 4-amino-3-hydroxynaphthalene-1-sulphonic acid, 1,5 g/l solution.

a) Dissolve 7 g of anhydrous sodium sulphite (Na_2SO_3) in 50 ml of water. Then add 1,5 g of 4-amino-3-hydroxynaphthalene-1-sulphonic acid ($C_{10}H_9NO_4S$) and dissolve with trituration.

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

Mix the two solutions a) and b) and dilute to 1 000 ml. Filter if necessary, and store the solution in a dark flask of material free from silica.

Renew this solution every 2 or 3 weeks.

NOTE — **Irritating to skin and eyes.**

4.7.2 L-ascorbic acid, 25 g/l solution.

Dissolve 2,5 g of L-ascorbic acid in water, dilute to 100 ml and mix.

Prepare this solution at the time of use.

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

In a platinum dish, weigh, to the nearest 0,001 g,

- either 0,500 g of silica (SiO_2) obtained by heating pure silicic acid at 1 000 °C to constant mass (that is until two consecutive weighings do not differ by more than 1 mg) and allowed to cool in a desiccator containing diphosphorus pentaoxide, or

- 0,500 g of pure silica, finely ground and previously heated for 1 h at 1 000 °C and allowed to cool in a desiccator containing diphosphorus pentaoxide.

Add 5 g of anhydrous sodium carbonate to the dish. Mix well, preferably with a platinum spatula, and fuse carefully until a clear and transparent melt is obtained.

Allow to cool, add warm water, heat gently until completely dissolved and transfer the solution quantitatively to a beaker of material free from silica.

Allow to cool again, dilute the solution 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 flask of material free from silica.

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

Do not keep this solution for longer than 1 month.

4.9 Silica, standard solution corresponding to 0,010 g of SiO_2 per litre.

Take 20,0 ml of the standard silica solution (4.8), place in a 1 000 ml one-mark volumetric flask, dilute to the mark and mix.

1 ml of this solution contains 10 µg of SiO_2.

Prepare the solution at the time of use.

5 Appartus

Ordinary laboratory apparatus, and in particular material free from silica (see the note).

5.1 pH meter, fitted with a glass measuring electrode and a calomel reference electrode, calibrated at pH 1,1 using hydrochloric acid solution, $c(HCl) = 0,1$ mol/l.

5.2 Spectrophotometer, fitted with cells of optical path length 10 or 20 or 50 mm

NOTE — All the steps using alkaline solutions and any treatment involving the sodium fluoride solution (4.5) should be carried out in vessels free from silica (for example, polyethylene). Glass volumetric flasks can be used for dilutions if the glass is in good condition (neither chipped nor etched) and if the solutions are transferred immediately into flasks of material free from silica.

6 Procedure

6.1 Test portion and preparation of the test solution

The mass of the test portion and the details for preparation of the test solution are given in the International Standard relating to the product concerned.

NOTE — The pH of the test solution should be between 4 and 7, except in the presence of hydrolizable salts when the pH adjustment is carried out during the procedure.

6.2 Blank test

Carry out a blank test at the same time as the determination, using the same procedure and the same quantities of all the reagents (including the sodium fluoride solution and the aliquot portions of neutralizing solutions of the test solution) as used for the determination, but omitting the test portion.

6.3 Preparation of the calibration graph

6.3.1 Preparation of calibration solutions, for spectrophotometric measurements carried out with cells of optical path length 10 or 20 or 50 mm

According to the expected silica content of the test solution, place the volumes of the standard silica solution (4.9), shown in the following table, in a series of 100 ml beakers of material free from silica.

Expected silica content of the test solution, µg					
2 to 30		10 to 80		50 to 200	
Standard silica solution (4.9)	**Corresponding mass of SiO_2**	**Standard silica solution (4.9)**	**Corresponding mass of SiO_2**	**Standard silica solution (4.9)**	**Corresponding mass of SiO_2**
ml	µg	ml	µg	ml	µg
0*	0	0*	0	0*	0
0,20	2	1,0	10	5,0	50
0,50	5	2,0	20	10,0	100
1,00	10	4,0	40	15,0	150
2,00	20	6,0	60	20,0	200
3,00	30	8,0	80		
Optical path length of cells, mm					
50		20		10	

* Blank test of the reagents for calibration.

Dilute each solution to about 25 ml.

6.3.2 Colour development

Add to each beaker 4,0 ml of the hydrochloric acid solution (4.2), 1,0 ml of the sodium fluoride solution (4.5), stir and allow to stand for 5 min. Add, while stirring, 20,0 ml of the boric acid solution (4.3), wait for 5 min, and add 10,0 ml of the sodium molybdate solution (4.6). Stir and wait for 10 min. The pH of the solution should then be 1,1 ± 0,2.

Add, while stirring, 5 ml of the oxalic acid solution (4.4), wait for 5 min and transfer quantitatively into a 100 ml one-mark volumetric flask.

Then add, according to the reducing solution used,

- either 20 ml of the sulphuric acid solution (4.1), stir and then add 2 ml of the sulphonic acid reducing solution (4.7.1),
- or 30 ml of the sulphuric acid solution (4.1), mix and then add 2 ml of the L-ascorbic acid reducing solution (4.7.2).

Dilute to the mark and mix.

6.3.3 Spectrophotometric measurements

After 10 min, but before 40 min, carry out the spectrophotometric measurements, using the spectrophotometer (5.2), at the wavelength corresponding to maximum absorption (about 800 nm), using cells of appropriate optical path length (see the table in 6.3.1) after having adjusted the instrument to zero absorbance against water.

NOTE — As a guide, the absorbance of a solution containing 50 µg of SiO_2 in cells of optical path length 20 mm is about 0,34.

6.3.4 Plotting the calibration graph

Deduct the absorbance of the blank test of the reagents for calibration from that of each of the other calibration solutions.

Plot a graph having, for example, the masses, in micrograms, of silica (SiO_2) contained in 100 ml of each of the calibration solutions as abscissae and the corresponding values of absorbance as ordinates.

6.4 Determination

6.4.1 Treatment of the test solution

Place a volume of the test solution containing not more than 200 µg of silica in a 100 ml beaker of material free from silica. Dilute the content of the beaker to about 25 ml with water.

6.4.2 Colour development

Add to the beaker about 4 ml (see note 1) of the hydrochloric acid solution (4.2), 1,0 ml of the sodium fluoride solution (4.5), stir and allow to stand for 5 min. Add, while stirring, 20,0 ml of the boric acid solution (4.3), wait for 5 min, and add 10,0 ml of the sodium molybdate solution (4.6). Stir and wait for 10 min. The pH of the solution should then be 1,1 ± 0,2.

NOTES

1 In order to ensure that the pH is 1,1 ± 0,2 at this stage, a preliminary check using the pH meter (5.1) should be carried out to determine the amount of the hydrochloric acid solution (4.2) required.

2 The sodium fluoride, which is intended for the determination of silicon present in the form of polymerized silica, can be omitted if it is certain that the test solution does not contain silicon in this form. In this case, it is possible to prepare the solution directly in a 100 ml glass one-mark volumetric flask.

Add, while stirring, 5 ml of the oxalic acid solution (4.4), wait for 5 min and transfer quantitatively into a 100 ml one-mark volumetric flask. Then follow the instructions in 6.3.2, starting from the third paragraph ("Then add, according to the reducing solution ...").

6.4.3 Spectrophotometric measurements

Carry out the spectrophotometric measurements on the test solution and on the blank test solution according to the instructions given in 6.3.3, after having adjusted the instrument to zero absorbance against water.

7 Expression of results

By means of the calibration graph (6.3.4), determine the mass, in micrograms, of silica corresponding to the results of the spectrophotometric measurement on the aliquot portion of the test solution taken for colour development and that on the blank test solution.

The International Standard relating to the product concerned will give the formulae to be applied for the calculation.

NOTE — If the result is to be expressed in milligrams of silicon (Si) per kilogram, multiply the result obtained above by 0,468.

8 Test report

The test report shall contain the following particulars :

a) an identification of the sample;

b) the reference of the general method used and of the International Standard relating to the product concerned;

c) the results and the form in which they are expressed;

d) any unusual features noted during the determination;

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