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Phosphoric acid for industrial use — Determination of soluble silica content — Reduced molybdosilicate spectrophotometric method

Acide phosphorique à usage industriel — Dosage de la silice soluble — Méthode spectrophotométrique au molybdosilicate réduit

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FOREWORD

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INTERNATIONAL STANDARD **ISO 3361-1975 (E)**

Phosphoric acid for industrial use — Determination of soluble 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 soluble silica content of phosphoric acid for industrial use.

The method can be used for the determination of 1 μg of soluble silica (SiO_2) in the presence of 20 mg of P_2O_5. It is thus, for example, applicable to the determination of soluble silica (SiO_2) contents greater than 30 mg/kg if the phosphoric acid contains 60 % of P_2O_5.

2 PRINCIPLE

Depolymerization of any polymerized silica by treatment with hydrofluoric acid and boric acid. Formation of the oxidized molybdosilicate (yellow) under well-defined conditions of acidity (pH 1 ± 0,05).

Selective reduction of the complex in a strong sulphuric acid medium in the presence of oxalic acid to eliminate interference by phosphates.

Spectrophotometric measurement of the coloured complex at the wavelength of maximum absorption (about 795 nm).

3 REAGENTS

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

3.1 Sulphuric acid, approximately 4 N solution.

3.2 Sulphuric acid, approximately 16 N solution.

3.3 Sodium molybdate, 274 g/l solution.

Dissolve 27,4 g of sodium molybdate dihydrate ($Na_2MoO_4 \cdot 2H_2O$) in warm water in a beaker of material free from silica, of suitable capacity, and, after cooling, dilute to 100 ml. Transfer the solution to a bottle of material free from silica and filter, if necessary, before use.

3.4 Oxalic acid, 100 g/l solution.

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

3.5 Ascorbic acid, 25 g/l solution.

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

Store the solution in a bottle of material free from silica and protect it from light.

Prepare this solution at the time of use.

Or as an alternative :

3.6 Reduction solution

3.6.1 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 by grinding.

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

3.6.3 Mix the two solutions 3.6.1 and 3.6.2 and dilute to 1 000 ml. Filter if necessary, and store in an opaque bottle of material free from silica, in a cool place.

3.7 Sodium fluoride, 20 g/l solution.

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

3.8 Boric acid, solution saturated at ambient temperature.

3.9 Standard silica solution, corresponding to 0,200 g of SiO_2 per litre.

Weigh, to the nearest 0,001 g, 0,200 g of SiO_2, obtained by heating pure silicic acid (H_2SiO_3) at 1 000 °C until constant mass (that is to say, until two consecutive weighings do not differ by more than 1 mg) and cooling in a desiccator, into a platinum crucible of convenient capacity. Add 2 g of anhydrous sodium carbonate to the crucible. Mix well, preferably with a platinum spatula, and carefully fuse the mixture. Add warm water directly to the crucible, heat gently until the contents are completely dissolved and transfer quantitatively to a beaker of material free from silica, of suitable capacity.

Cool, 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 bottle of material free from silica.

1 ml of this standard solution contains 0,200 mg of SiO_2.

3.10 Standard silica solution, corresponding to 2,00 mg of SiO_2 per litre.

Place 10,0 ml of the standard silica solution (3.9) in a 1 000 ml one-mark volumetric flask, dilute to the mark and mix.

1 ml of this standard solution contains 2,0 µg of SiO_2.

Prepare this solution at the time of use.

4 APPARATUS

Ordinary laboratory apparatus and

4.1 Beakers, 50 ml capacity, of material free from silica.

4.2 One-mark volumetric flasks, 50 ml, fitted with stoppers, of material free from silica.

4.3 pH meter, fitted with a glass measuring electrode and a calomel reference electrode, sensitivity 0,05 pH unit.

4.4 Spectrophotometer.

NOTE — The glassware shall be thoroughly washed, taking the necessary precautions, with chromic acid, thoroughly rinsed with water and finally with redistilled water. Do not dry either in an oven or by means of compressed air.

5 PROCEDURE

5.1 Test portion and preparation of the test solution

Weigh by difference, to the nearest 0,000 2 g, a quantity of the test sample containing a maximum quantity of about 1,3 g of P_2O_5.

Place in a 1 000 ml one-mark volumetric flask, dilute to the mark and mix. Transfer the solution immediately to a dry receiver of material free from silica, filtering, if necessary, through a dry filter paper.

5.2 Blank test

Carry out a blank test at the same time as the determination, following the same procedure and using the same quantities of all the reagents as used for the determination, but replacing the volume of the test solution by the same volume of water.

5.3 Preparation of the calibration graph

5.3.1 *Preliminary test for control and correction of the pH*

Place 10,0 ml of the standard silica solution (3.10) in one of the beakers (4.1). Add the quantity of water to bring the volume to 15 ml and then 5,0 ml of the sodium molybdate solution (3.3), 1 ml of the sodium fluoride solution (3.7) and 5 ml of the boric acid solution (3.8), mix and measure the pH with the pH meter (4.3). Adjust the pH to 1,0 ± 0,05 by adding slowly, using a graduated pipette or a burette, drop by drop, mixing after each addition, the necessary quantity of the sulphuric acid solution (3.1) (normally about 4,5 ml).

Record the volume of the sulphuric acid solution (3.1) used for the pH correction and discard the solution.

5.3.2 *Preparation of the standard colorimetric solutions,* for photometric measurements carried out with cells of 4 or 5 cm optical path length.

Into a series of six of the beakers (4.1) place the volumes of the standard silica solution (3.10) indicated in the following table.

Standard silica solution (3.10)	Corresponding mass of SiO_2
ml	µg
0*	0
2,0	4,0
4,0	8,0
6,0	12,0
8,0	16,0
10,0	20,0

* Compensation solution.

Add to each beaker the quantity of water necessary to bring the volume to 15 ml and then the volume of the sulphuric acid solution (3.1) used for the pH correction in the preliminary test (5.3.1) and mix. Add 1 ml of the sodium fluoride solution (3.7) and allow to stand for 5 min.

5.3.3 *Colour development*

Add to each beaker 5 ml of the boric acid solution (3.8) and 5,0 ml of the sodium molybdate solution (3.3). Mix and allow to stand for 10 min. Add 5 ml of the oxalic acid solution (3.4) and 8 ml of the sulphuric acid solution (3.2) and allow to stand for 2 min. Add 2 ml of the ascorbic acid solution (3.5) or, as an alternative, 2 ml of the reduction solution (3.6), and allow to stand for 10 min. Transfer the solutions quantitatively to a series of the 50 ml one-mark volumetric flasks (4.2), dilute to the marks and mix.

5.3.4 *Spectrophotometric measurements*

Carry out the spectrophotometric measurements with the spectrophotometer (4.4), at the wavelength of maximum absorption (about 795 nm), after having adjusted the instrument to zero absorbance against the compensation solution.

NOTE — Carefully calibrate the cells used for the measurements.

5.3.5 *Preparation of the calibration graph*

Plot a graph having, for example, the masses, expressed in micrograms, of silica (SiO_2) contained in 50 ml of the standard colorimetric solutions as abscissae and the corresponding values of absorbance as ordinates.

5.4 Determination

5.4.1 *Treatment of the test solution*

Place a known, accurately measured, volume of not more than 15 ml of the test solution (5.1), containing not more than 20 mg of P_2O_5 and of which the silica content is between 0 and 20 μg, into one of the beakers (4.1). Add the quantity of water necessary to bring the volume to 15 ml, then the volume of the sulphuric acid solution (3.1) used for the pH correction in the preliminary test (5.3.1) and 1 ml of the sodium fluoride solution (3.7). Mix and allow to stand for 5 min.

5.4.2 *Colour development*

Develop the colour by the procedure specified in 5.3.3.

5.4.3 *Spectrophotometric measurements*

Carry out the spectrophotometric measurements by the procedure specified in 5.3.4 and at the same wavelength, after having adjusted the instrument to zero absorbance against water.

6 EXPRESSION OF RESULTS

By means of the calibration graph (see 5.3.5), determine the masses of silica corresponding to the values of the spectrophotometric measurements on the aliquot portion of the test solution and on the blank test solution, taken for the colour development.

The soluble silica content, expressed in milligrams of silica (SiO_2) per kilogram, is given by the formula

$$\frac{m_1 - m_2}{m_0} \times D$$

where

m_0 is the mass, in grams, of the test portion (5.1);

m_1 is the mass, in micrograms, of silica (SiO_2) found in the aliquot portion of the test solution taken for the colour development;

m_2 is the mass, in micrograms, of silica (SiO_2) found in the blank test solution;

D is the ratio between the volume of the test solution and the volume of the aliquot portion taken for the colour development.

7 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 regarded as optional.

ANNEX

PUBLICATIONS RELATING TO PHOSPHORIC ACID FOR INDUSTRIAL USE

ISO/R 847 – Determination of sulphate content – Volumetric method.

ISO/R 848 – Determination of calcium content – Volumetric method.

ISO/R 849 – Determination of iron content – 2,2′-bipyridyl spectrophotometric method.

ISO 2997 – Determination of sulphate content – Method by reduction and titrimetry.

ISO 3359 – Determination of arsenic content – Silver diethyldithiocarbamate photometric method.

ISO 3360 – Determination of fluorine content – Alizarin complexone and cerium chloride photometric method.

ISO 3361 – Determination of silica content – Reduced molybdosilicate spectrophotometric method.

ISO 3706 – Determination of total phosphorus(V) oxide content – Quinoline phosphomolybdate gravimetric method.

ISO 3707 – Determination of calcium content – Flame atomic absorption spectrophotometric method.

ISO 3708 – Determination of chlorides content – Potentiometric method.

ISO 3709 – Determination of oxides of nitrogen content – 3,4-xylenol photometric method.

ISO ... – Sampling technique.