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INTERNATIONAL STANDARD 3701

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Anhydrous hydrogen fluoride for industrial use — Determination of hexafluorosilicic acid content — Reduced molybdosilicate photometric method

Fluorure d'hydrogène anhydre à usage industriel — Dosage de l'acide hexafluorosilicique — Méthode photométrique au molybdosilicate réduit

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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 3701 was drawn up by Technical Committee ISO/TC 47, *Chemistry,* and was circulated to the Member Bodies in February 1975.

It has been approved by the Member Bodies of the following countries :

Belgium	India	Spain
Brazil	Israel	Switzerland
Bulgaria	Italy	Turkey
France	Poland	United Kingdom
Germany	Romania	U.S.S.R.
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Anhydrous hydrogen fluoride for industrial use — Determination of hexafluorosilicic acid content — Reduced molybdosilicate photometric method

WARNING — Anhydrous hydrogen fluoride is a highly corrosive liquid which boils at 19,5 °C. It attacks glass, has a great affinity for water and the vapour is irritant and toxic. Its action on the skin and eyes is strongly corrosive, producing severe and painful burns which may not be immediately evident and which respond slowly to treatment.

Samples should be handled only inside a well-ventilated fume cupboard. Rubber gloves, boots and gown of a suitable size to give adequate protection to the individual and full head and face protection must be worn when handling the material.

In the event of contact or suspected contact, flood with water and seek immediate medical attention. The manufacturers' literature should be consulted for further information.

1 SCOPE

This International Standard specifies a reduced molybdosilicate photometric method for the determination of the hexafluorosilicic acid content of anhydrous hydrogen fluoride for industrial use.

2 FIELD OF APPLICATION

The method is applicable to products having hexafluorosilicic acid (H_2SiF_6) contents between 0,01 and 0,2 % (*m/m*).

3 REFERENCE

ISO 3137, *Anhydrous hydrogen fluoride for industrial use — Sampling.*

4 SAMPLING

For the preparation of the laboratory and test samples, use the methods specified in ISO 3137.

5 PRINCIPLE

Formation of oxidized molybdosilicate (yellow), in weakly acid medium, in the presence of boric acid to suppress interference by fluorine. Selective reduction of this complex, after addition of 9 N sulphuric acid solution and oxalic acid to eliminate interference from phosphates. Photometric measurement of the blue-coloured complex at a wavelength of about 795 nm.

6 REAGENTS

During the analysis, use only reagents of recognized analytical grade and only distilled water or water of equivalent purity.

Store all the reagents in polyethylene flasks and carry out all operations in apparatus of this material, except where specified otherwise.

6.1 Sulphuric acid, approximately 9 N solution.

6.2 Hydrochloric acid, approximately 2 N solution.

6.3 Boric acid, 40 g/l solution.

6.4 Oxalic acid, anhydrous, 100 g/l solution.

6.5 Ammonium molybdate, 100 g/l solution.

Dissolve 25 g of ammonium molybdate tetrahydrate [$(NH_4)_6Mo_7O_{24}.4H_2O$] in 200 ml of water at about 50 °C. Allow to cool to ambient temperature, transfer to a 250 ml one-mark volumetric flask, dilute to the mark, mix and transfer to a polyethylene flask.

Discard the solution when a precipitate appears.

6.6 Reducing solution

6.6.1 Dissolve 7 g of anhydrous *di*sodium sulphite (Na_2SO_3) in 50 ml of water. Add 1,5 g of 4-amino-3-hydroxynaphthalene-1-sulphonic acid and dissolve by trituration.

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

6.6.3 Mix the two solutions 6.6.1 and 6.6.2 and dilute to 1 000 ml. Filter, if necessary, and store the solution in a cool place, away from direct sunlight. Renew it every 15 to 20 days.

6.7 Silica, standard solution corresponding to 1,00 g of hexafluorosilicic acid (H_2SiF_6) per litre.

Weigh, to the nearest 0,001 g, into a platinum crucible, either :

— 0,417 g of silica (SiO_2), obtained by heating pure silicic acid (H_2SiO_3) at 1 000 °C to constant mass (that

is, until two consecutive weighings do not differ by more than 1 mg) and allowing to cool in a desiccator;

or

— 0,417 g of pure quartz, finely ground and previously heated for 1 h at 1 000 °C and allowed to cool in a desiccator.

Add 5 g of anhydrous sodium carbonate to the crucible. Mix well, preferably with a platinum spatula, and fuse together gently. Allow to cool, add warm water, warm moderately until completely dissolved, cool, transfer quantitatively to a 1 000 ml one-mark volumetric flask, dilute to the mark and mix.

Transfer immediately to a polyethylene flask.

1 ml of this solution contains the equivalent of 1,00 mg of H_2SiF_6.

Prepare a fresh solution at least every month.

6.8 Silica, standard solution corresponding to 20 mg of hexafluorosilicic acid (H_2SiF_6) per litre.

Take 20,0 ml of the standard silica solution (6.7), transfer to a 1 000 ml one-mark volumetric flask, dilute to the mark and mix.

1 ml of this solution contains the equivalent of 20 µg of H_2SiF_6.

Prepare this solution at the time of use.

7 APPARATUS

Ordinary laboratory apparatus and

7.1 Spectrophotometer, fitted with cells of optical path length 2, 4 or 5 cm, or

7.2 Photoelectric absorptiometer, fitted with the same cells and with filters allowing a maximum transmission at about 795 nm.

NOTE — If such filters are not available, operate at about 680 nm with cells of optical path length 4 or 5 cm.

8 PROCEDURE

8.1 Test portion

Introduce a quantity of the test solution, prepared by the method specified in ISO 3137, containing not more than 0,1 g of hydrogen fluoride, into a 100 ml polyethylene beaker. Determine the mass of this test portion to the nearest 0,001 g.

8.2 Blank test

Carry out a blank test at the same time as the determination, using the same procedure and the same quantities of all reagents as used in the determination, but omitting the test portion. The absorbance of the blank test solution should not be greater than that corresponding to 10 µg of hexafluorosilicic acid. Otherwise, better quality reagents should be used.

8.3 Preparation of calibration graph

8.3.1 *Preparation of standard colorimetric solutions*

Into a series of four 100 ml one-mark volumetric flasks, transfer the quantities of the standard silica solution (6.8) indicated in the following table.

Silica standard solution (6.8)	Corresponding mass of hexafluorosilicic acid (H_2SiF_6)
ml	µg
0*	0
2,0	40
5,0	100
10,0	200

* Blank test on reagents for calibration graph.

8.3.2 *Colour development*

Dilute the contents of each flask to 20 ml with water and add, while stirring, 4 ml of the hydrochloric acid solution (6.2) and 35 ml of the boric acid solution (6.3), and allow to stand for 5 min. Then add 10 ml of the ammonium molybdate solution (6.5), mix and allow to stand for 15 min.

Add, while stirring, 5,0 ml of the oxalic acid solution (6.4) and then 20 ml of the sulphuric acid solution (6.1). Mix and add 2 ml of the reducing solution (6.6), dilute to the mark and mix. Allow to stand for 15 to 25 min.

8.3.3 *Photometric measurements*

Using the spectrophotometer (7.1) adjusted to a wavelength of about 795 nm, or the photoelectric absorptiometer (7.3) fitted with suitable filters, carry out the photometric measurements using cells of optical path length 2 cm, after having adjusted the instrument to zero absorbance against water.

8.3.4 *Plotting of the calibration graph*

Deduct the absorbance of the blank test on reagents for the calibration graph from those of the standard colorimetric solutions. Plot a graph having, for example, the quantities, in micrograms, of hexafluorosilicic acid in the standard colorimetric solutions as abscissae and the corresponding values of the absorbance as ordinates.

NOTE — For hexafluorosilicic acid contents lower than 0,05 %, prepare the calibration graph by the same procedure except that the standard colorimetric solutions shall be prepared using 0 — 2,0 — 4,0 and 5,0 ml of the standard silica solution (6.8) and the photometric measurements shall be carried out in cells of 4 or 5 cm optical path length.

8.4 Determination

Dilute the test portion (8.1) to 20 ml with water, and add, while stirring, 4 ml of the hydrochloric acid solution (6.2) and 35 ml of the boric acid solution (6.3). Allow to stand for 5 min, add 10 ml of the ammonium molybdate solution (6.5), mix and allow to stand for 15 min.

NOTE — The specified operations result in a solution whose pH at this stage is in the range 1,0 to 1,2.

Add, while stirring, 5,0 ml of the oxalic acid solution (6.4) and then 20 ml of the sulphuric acid solution (6.1).

Transfer quantitatively to a 100 ml one-mark volumetric flask, mix, add 2 ml of the reducing solution (6.6), dilute to the mark and mix.

Allow to stand for 15 to 25 min and carry out the photometric measurements at the same wavelength as was used for the preparation of the calibration graph, on the test solution and on the blank test solution, following the instructions specified in 8.3.3, after having adjusted the instrument to zero absorbance against water, using cells of optical path length 2, 4 or 5 cm, according to the hexafluorosilicic acid content.

9 EXPRESSION OF RESULTS

By means of the calibration graph (8.3), determine the masses of H_2SiF_6 corresponding to the absorbances of the test solution and of the blank test solution.

The hexafluorosilicic acid content, expressed as a percentage by mass of H_2SiF_6, is given by the formula

$$(m_1 - m_2) \times \frac{1}{10^6} \times \frac{100}{m_0 \times C/100} = \frac{m_1 - m_2}{100\, m_0 \times C}$$

where

m_0 is the mass, in grams, of the test portion (8.1);

m_1 is the mass, in micrograms, of hexafluorosilicic acid (H_2SiF_6) found in the test solution;

m_2 is the mass, in micrograms, of hexafluorosilicic acid (H_2SiF_6) found in the blank test solution;

C is the concentration of anhydrous hydrogen fluoride, expressed as a percentage by mass, in the test sample (see ISO 3137, clause 12).

10 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 in the International Standard to which reference is made, or regarded as optional.

ANNEX

ISO PUBLICATIONS RELATING TO ANHYDROUS HYDROGEN FLUORIDE AND AQUEOUS HYDROFLUORIC ACID FOR INDUSTRIAL USE

ANHYDROUS HYDROGEN FLUORIDE

ISO 3137 — Sampling.

ISO 3138 — Determination of non-volatile acid content — Titrimetric method.

ISO 3699 — Determination of water content — Karl Fischer method.

ISO 3700 — Determination of water content — Conductimetric method.

ISO 3701 — Determination of hexafluorosilicic acid content — Reduced molybdosilicate photometric method.

ISO 3702 — Determination of sulphur dioxide content — Iodometric method.

AQUEOUS HYDROFLUORIC ACID

ISO 3139 — Sampling and methods of test.