INTERNATIONAL STANDARD 3699

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Anhydrous hydrogen fluoride for industrial use — Determination of water content — Karl Fischer method

Fluorure d'hydrogène anhydre à usage industriel — Dosage de l'eau — Méthode de Karl Fischer

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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.

International Standard ISO 3699 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 :

Austria	India	Switzerland
Belgium	Israel	Turkey
Bulgaria	Poland	United Kingdom
Czechoslovakia	Portugal	U.S.S.R.
France	Romania	Yugoslavia
Germany	South Africa, Rep. of	
Hungary	Spain	

No Member Body expressed disapproval of the document.

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Anhydrous hydrogen fluoride for industrial use — Determination of water content — Karl Fischer 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 method for the determination of the water content of anhydrous hydrogen fluoride for industrial use. This method, that of Karl Fischer, is intended for reference purposes.

NOTE — Attention is drawn to ISO 3700[1], which describes an alternative method suitable for routine purposes.

2 FIELD OF APPLICATION

The method is applicable to products having water contents between 0,01 and 0,5 % (*m/m*).

3 REFERENCES

ISO/R 760, *Determination of water by the Karl Fischer method.*

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

4 SAMPLING

For the preparation of the laboratory sample, use the method specified in section one of ISO 3137.

5 PRINCIPLE

Addition of a cooled test portion to cooled, dry pyridine containing 5 % of anhydrous hydrogen fluoride. Electrometric titration of the water with Karl Fischer reagent.

6 REAGENTS

During the analysis, use only reagents of recognized analytical grade.

6.1 Karl Fischer reagent, water equivalent 4 to 6 mg/ml (see ISO/R 760).

6.2 Pyridine solvent.

In a polyethylene bottle, cool 1 000 ml of dry pyridine to −50 °C in a mixture of dry ice and methanol. Stir vigorously and continue cooling while slowly adding 50 ml of anhydrous hydrogen fluoride. Store in the polyethylene bottle.

7 APPARATUS

Ordinary laboratory apparatus and

7.1 Apparatus for measurement of test portion and titration (see figures 1 and 2), comprising :

7.1.1 Cooling coil, stainless steel, mounted vertically in a cylindrical cooling bath constructed of mild steel.

7.1.2 Vessel, for the measurement of the test portion, comprising a body constructed of stainless steel fitted with windows made of a sandwich consisting of polytetrafluoroethylene (PTFE) foil/glass sheet/PTFE foil. The front window is marked at a volume of about 40 ml.

The construction is shown in detail in figure 2.

1) At present at the stage of draft.

7.1.3 Titration bottle, for the test portion, PTFE, capacity 700 to 1 000 ml. The inlet tube carried by the screw cap of the bottle is rigidly joined to valve D. In order to introduce the test portion below the surface of the solvent, the inlet tube is extended by means of a PTFE tube as shown in figure 1. The screw cap also carried two platinum wire electrodes, a tip connected to a burette containing Karl Fischer reagent and an outlet connected to the overflow bottle (7.1.4).

7.1.4 Overflow bottle, polypropylene, about 500 ml capacity, for collecting the anhydrous hydrogen fluoride used for purging the apparatus.

7.1.5 Air dryer : polypropylene bottle of about 750 ml capacity, packed with anhydrous calcium chloride, and vented to an extraction system.

7.1.6 Stirring bar, PTFE-coated.

7.1.7 Magnetic stirrer.

7.1.8 Flange joint, stainless steel, with PTFE gasket (F_1).

7.1.9 Threaded couplings, of stainless steel (C_1, C_2, C_3, C_4).

7.1.10 Valves, stainless steel needle valves (B, C, D, E).

7.1.11 Cooling bath, removable, for the titration bottle (7.1.3).

7.2 Detection equipment, for electrometric titration : as specified in ISO/R 760.

8 PROCEDURE

8.1 Standardization of Karl Fischer reagent

Proceed as specified in ISO/R 760.

8.2 Determination

8.2.1 *Pre-titration of pyridine solvent*

Add 200 ml of the pyridine solvent (6.2) to the titration bottle (7.1.3) containing the stirring bar (7.1.6). Stopper the titration bottle and weigh, to the nearest 0,1 g. Remove the stopper and connect the titration bottle to the apparatus. Close the electrical circuit of the detection equipment (7.2) and switch on the magnetic stirrer (7.1.1). Slowly add Karl Fischer reagent, stirring continuously, until the galvanometer shows a sudden increase in current which remains stable.

8.2.2 *Test portion*

Remove the threaded stopper from one end of the transverse passageway of the sample cylinder (see ISO 3137) and connect the latter to valve B by means of the threaded union coupling C_1. Place the cooling bath (7.1.11) in position around the titration bottle (7.1.3) and cool it and the cooling coil (7.1.1), using a mixture of dry ice and methanol, stirring continuously for 15 min. Purge the apparatus by opening valves A and C and, carefully opening valve B, fill the measuring vessel (7.1.2) with the laboratory sample. Close valve B. Empty the measuring vessel through valve E and then close this valve. Open valve B and transfer approximately 40 ml of the laboratory sample, stirring continuously, to the measuring vessel (7.1.2). Close valves A and B. Stir the contents of the titration bottle and, depending on the expected water content of the sample, add a suitable volume of the sample at a rate of about 3 ml/min through valve D. Close valve D and open valve E.

8.2.3 *Titration and weighing*

Remove the cooling bath from the titration bottle and, when the reaction mixture is at about ambient temperature, titrate with Karl Fischer reagent as specified in 8.2.1, stirring continuously. Disconnect the titration bottle from the apparatus, stopper, dry carefully and reweigh to the nearest 0,1 g.

9 EXPRESSION OF RESULTS

The water content, expressed as a percentage by mass, is given by the formula

$$V_1 \times T \times \frac{1}{1\,000} \times \frac{100}{m_3 - [m_1 + (V_1 + V_2)\rho]} = \frac{V_1 \times T}{10\,[m_3 - (m_1 + m_2)]}$$

where

V_1 is the volume, in millilitres, of Karl Fischer reagent used in the titration of the test portion (see 8.2.3);

V_2 is the volume, in millilitres, of Karl Fischer reagent used in the pre-titration of the solvent (see 8.2.1);

T is the water equivalent, in milligrams per millilitre, of the Karl Fischer reagent;

m_1 is the initial mass, in grams, of the stoppered titration bottle and its contents (see 8.2.1);

m_2 is the sum of the masses, in grams, of Karl Fischer reagent added in 8.2.1 and 8.2.3, given by the formula $m_2 = (V_1 + V_2)\rho$;

m_3 is the final mass, in grams, of the stoppered titration bottle and its contents (see 8.2.3);

ρ is the density, in grams per millilitre, of the Karl Fischer reagent (ρ is approximately equal to 1 g/ml).

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 Standards to which reference is made, or regarded as optional.

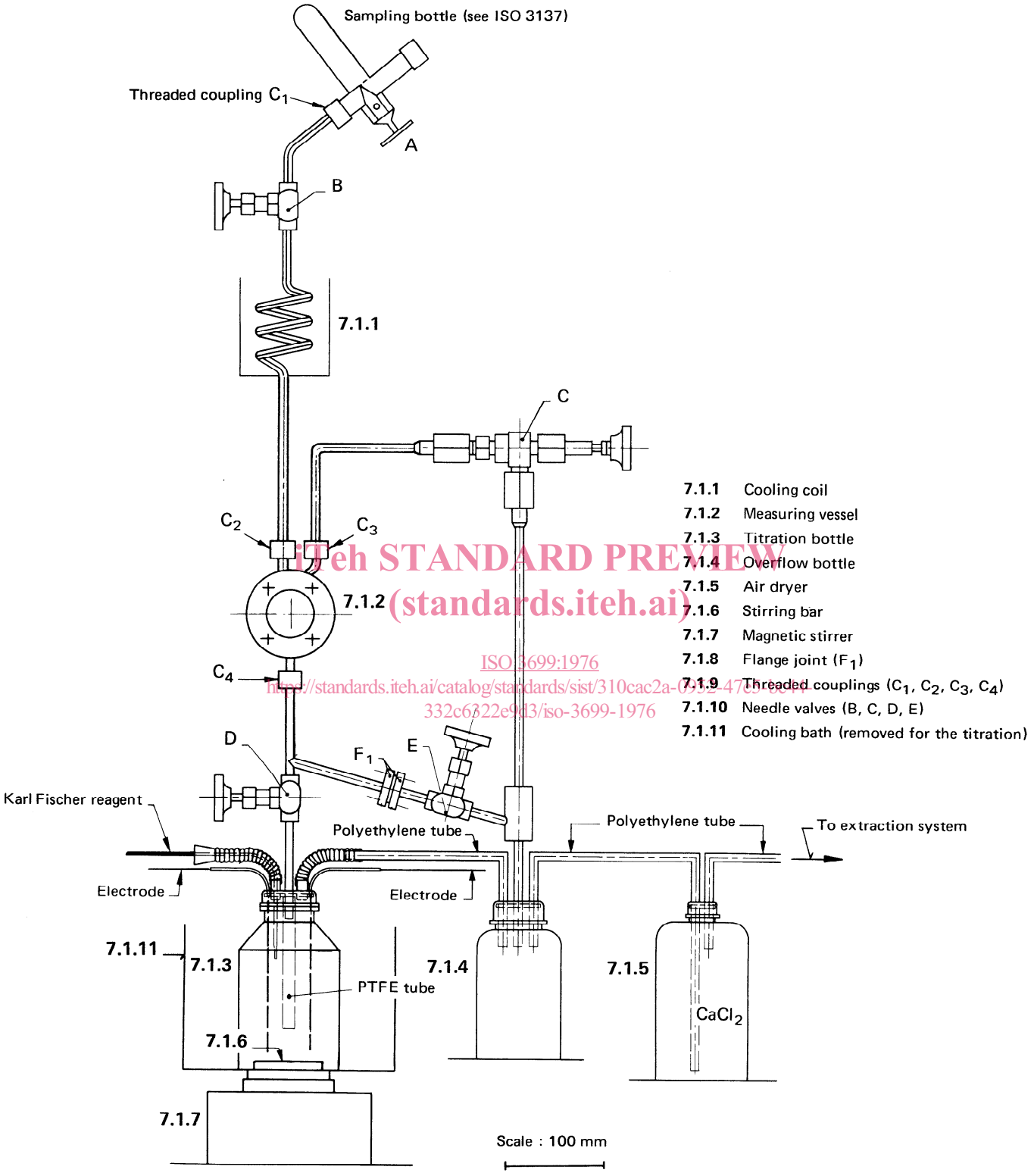
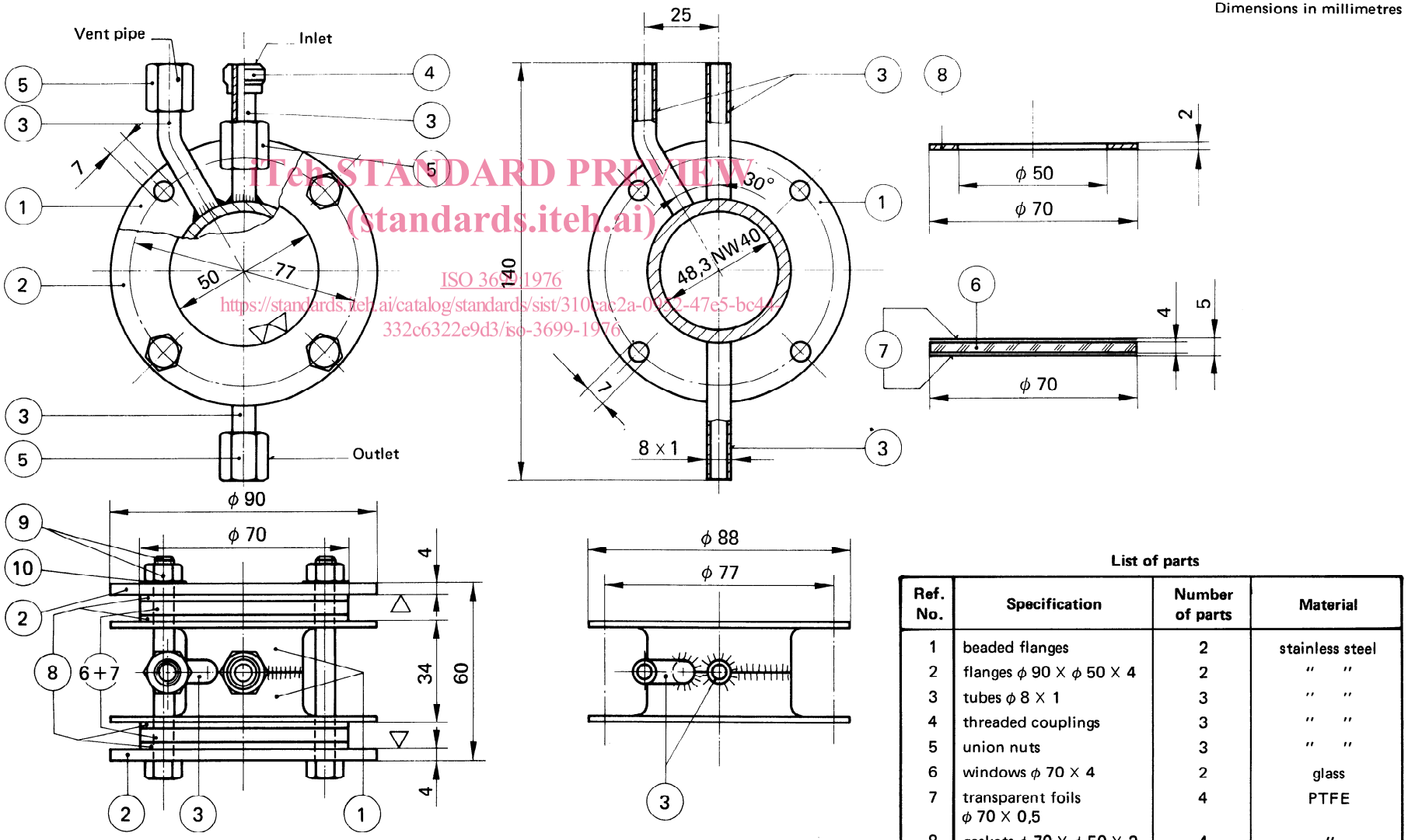


FIGURE 1 — **Apparatus for measurement of the test portion and titration (7.1)**

Dimensions in millimetres



List of parts

Ref. No.	Specification	Number of parts	Material
1	beaded flanges	2	stainless steel
2	flanges ϕ 90 X ϕ 50 X 4	2	" "
3	tubes ϕ 8 X 1	3	" "
4	threaded couplings	3	" "
5	union nuts	3	" "
6	windows ϕ 70 X 4	2	glass
7	transparent foils ϕ 70 X 0,5	4	PTFE
8	gaskets ϕ 70 X ϕ 50 X 2	4	"
9	screws and nuts	4	"
10	washers for No. 9	4	"

Scale : 100 mm

FIGURE 2 – **Measuring vessel (7.1.2)**

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.