International Standard 1776

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Glass — Resistance to attack by hydrochloric acid at 100 °C — Flame emission or flame atomic absorption spectrometric method

Verre — Résistance à l'attaque par l'acide chlorhydrique à 100 °C — Méthode de détermination par spectrométrie d'absorption atomique de flamme ou d'émission de flamme

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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. They are approved in accordance with ISO procedures requiring at least 75 % approval by the member bodies voting.

International Standard ISO 1776 was prepared by Technical Committee ISO/TC 48, *Laboratory glassware and related apparatus*.

It cancels and replaces ISO Recommendation R 1776-1970, of which it constitutes a technical revision.

Users should note that all International Standards undergo revision from time to time and that any reference made herein to any other International Standard implies its latest edition, unless otherwise stated.

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INTERNATIONAL STANDARD **ISO 1776-1985 (E)**

Glass — Resistance to attack by hydrochloric acid at 100 °C — Flame emission or flame atomic absorption spectrometric method

1 Scope

This International Standard specifies flame emission spectrometric (FES) and flame atomic absorption spectrometric (FAAS) methods for determining the amounts of alkali metal oxides released from the surfaces of glassware when subjected to attack by an aqueous solution of hydrochloric acid at 100 °C. The amount of alkali metal oxides determined is a measure of the acid resistance of the glass.

2 Field of application

This International Standard applies to pieces of glass, preferably flat but, if necessary, curved, cut from articles of laboratory glassware, from components of glass plant, pipeline or fittings or from any other articles used for purposes which may be described as "chemical".

The acid resistance of glass "as delivered", i.e. the acid resistance of the original fire-polished surfaces, may be determined when the surface area of the cut and smoothed edges does not exceed 10 % of the total surface area of the sample.

The acid resistance of the glass "as a material" may be determined when the original surface has been removed by the hydrofluoric acid treatment described in 7.3. This preliminary acid treatment shall be applied to all samples of borosilicate glass 3.3 taken from components of glass plant, pipeline or fittings.

The distinction between the acid resistance of glass "as delivered" and "as a material" may be of importance in cases where articles have been given a surface treatment during or after production.

3 References

ISO 719, *Glass — Hydrolytic resistance of glass grains at 98 °C — Method of test and classification.*

ISO 720, *Glass — Hydrolytic resistance of glass grains at 121 °C — Method of test and classification.*

ISO 835/2, *Laboratory glassware — Graduated pipettes — Part 2: Pipettes for which no waiting time is specified.*

ISO 1042, *Laboratory glassware — One-mark volumetric flasks.*

ISO 1773, *Laboratory glassware — Boiling flasks (narrow-necked).*

ISO 3585, *Glass plant, pipeline and fittings — Properties of borosilicate glass 3.3.*

ISO 3696, *Water for laboratory use — Specifications.*[1]

ISO 3819, *Laboratory glassware — Beakers.*[1]

ISO 6955, *Analytical spectroscopic methods — Flame emission, atomic absorption, and atomic fluorescence — Vocabulary.*

4 Principle

The method is a test for glass "as delivered" or for glass "as a material".

Attacking of sample pieces of 30 to 40 cm^2 by an aqueous hydrochloric acid solution, $c(HCl) = 6$ mol/l, at 100 °C for 3 h.

Determination of the amount of alkali metal oxides extracted per unit area by flame emission or flame atomic absorption spectrometric methods.

5 Reagents

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

5.1 Grade 2 water, complying with the requirements of ISO 3696.

5.2 Hydrochloric acid, solution, $c(HCl) = 6 \pm 0,2$ mol/l, prepared by adding 1 volume of concentrated hydrochloric acid solution ($\varrho = 1,18$ g/ml) to 1 volume of grade 2 water (5.1). The alkali (Na_2O and K_2O) contents of this solution shall be less than 0,2 µg/ml per oxide.

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[1] At present at the stage of draft.

Hydrochloric acid of analytical grade quality mostly meets this requirement. This shall be ensured for every new bottle of hydrochloric acid delivered.

If the alkali metal contents are higher, the hydrochloric acid solution shall be purified, for example, by using the procedure described in the annex.

5.3 Hydrochloric acid, solution, $c(\text{HCl}) \approx 2$ mol/l, prepared by adding 1 volume of concentrated hydrochloric acid solution ($\varrho = 1{,}18$ g/ml) to 5 volumes of grade 2 water (5.1).

5.4 Hydrochloric acid, solution, $c(\text{HCl}) \approx 1$ mol/l.

5.5 Hydrofluoric acid, solution, HF ≈ 40 % (*m*/*m*).

5.6 Ionization buffer, for precise alkali metal determination, especially when glasses with higher lime contents are extracted. The alkali (Na_2O and K_2O) contents of the ionization buffer when measured in a solution of 10 % (*V*/*V*) ionization buffer in grade 2 water (5.1) shall be less than 0,5 µg/ml per oxide.

NOTE — The ionization buffer can be prepared by dissolving 250 g of aluminium nitrate nonahydrate [$Al(NO_3)_3 \cdot 9H_2O$] and 50 g of caesium chloride (CsCl) in grade 2 water (5.1), and diluting to 1 litre. Commercially available solutions, such as "Schuhknecht-Schinkel-Buffer", may also be used.

5.7 Ethanol (C_2H_5OH) or **acetone** (CH_3COCH_3).

6 Apparatus

Ordinary laboratory apparatus, and

6.1 Drying oven, capable of maintaining a temperature of 100 ± 1 °C.

6.2 Drying oven, suitable for operation at a temperature up to 130 °C.

6.3 Flame emission or flame atomic absorption spectrometer.

6.4 Linear measuring instruments, suitable for measuring lengths and diameters to an accuracy of 0,2 mm.

6.5 Dishes, made of high density pressed polytetrafluorethylene (PTFE) of extremely low porosity, having a capacity of about 70 ml (overflow capacity), a wall thickness of about 5 mm, an inner diameter of about 60 mm and an inner height of about 25 mm. The dish should be closed with a screw-threaded lid.

The dish should be equipped with a suitable rack, made of polytetrafluorethylene (PTFE), or with four peaks, made of PTFE, about 3 mm high and fixed on the bottom to keep the samples at this distance from the bottom.

NOTE — The lid may be fitted with an opening of up to 5 mm in diameter so that a thermocouple can be inserted so that the temperature can be measured and controlled at 100 ± 1 °C inside the dish, e.g. an iron-copper/nickel (Fe-CuNi) thermocouple.

6.6 Tongs, tipped with a suitable chemically resistant material, e.g. platinum or resistant plastics. The tips should be pretreated with the hydrochloric acid solution (5.3) and should be washed in grade 2 water (5.1) immediately before use.

6.7 Beaker, made of plastics, having a capacity of 250 ml, fitted with a rack (see figure 1), made of platinum wire, to hold the samples during the preliminary acid treatment.

6.8 Beakers, having a capacity of 50 ml, complying with the requirements of ISO 3819 and made of borosilicate glass 3.3 complying with the requirements of ISO 3585.

Each new beaker or contaminated beaker shall be pretreated in the following manner: The beaker shall be immersed in hydrochloric acid (5.3) and boiled for 2 h. The beaker shall then be rinsed with water, immersed in water and heated, as above, for two periods of 1 h, using fresh water each time.

6.9 Boiling flasks (e.g. conical or volumetric flasks), having a capacity of 50 ml, complying with the requirements of ISO 1773 and made of polypropylene or vitreous silica. The neck of the polypropylene flasks shall be shortened to a length sufficient to hold the flasks in the heating bath (6.10). A thin layer of aluminium shall be wrapped round the neck of vitreous silica flasks for insulating purposes.

NOTE — Polypropylene withstands temperatures ≈ 130 °C.

6.10 Heating bath, for example oil, capable of maintaining a temperature of 125 ± 5 °C.

NOTE — For flasks of vitreous silica, a sand bath may also be used.

6.11 Magnetic stirrer, with a plastics-coated rotor.

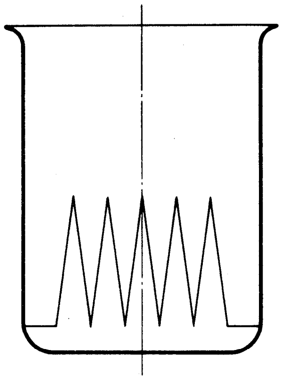

Figure 1 — Beaker with rack to hold samples during the preliminary acid treatment

6.12 One-mark volumetric flasks, having a capacity of 5 ml, complying with the requirements specified for class A one-mark volumetric flasks in ISO 1042, made of glass of hydrolytic resistance grain class HGA 1 as specified in ISO 720[1].

6.13 Graduated pipette for partial delivery, having a capacity of 2 ml and complying with the requirements for type 1 pipettes of class A in ISO 835/2.

7 Preparation of sample pieces

7.1 Condition of sample pieces for preparation

The sample pieces shall have a total surface of 30 to 40 cm^2, and shall be taken from the glassware which has been delivered well annealed. Remove from the edges any sharp angles, "hackles" or splinters by a minimum of grinding. Do not fire-polish the edges.

7.2 Measurement of linear dimensions

Measure all dimensions to the nearest 0,2 mm and calculate the actual total surface area.

7.3 For testing glass "as a material" and glass for glass plant, pipeline and fittings (preliminary acid treatment)

Place the sample pieces of any thickness in the rack (6.7) fitted inside the beaker (6.7), as shown in figure 1. Insert the rotor of the stirrer (6.11) and then add, carefully, down the wall of the beaker, a mixture containing 1 part of the hydrofluoric acid solution (5.5) and 9 parts of the hydrochloric acid solution (5.3) until the sample pieces are completely immersed. The temperature of the mixture should be about ambient temperature. Stir the mixture magnetically for 10 min. Holding the sample pieces in position with a plastics rod, pour out the mixture. Fill the beaker with grade 2 water (5.1) and again decant the liquid. Remove each sample piece, using the tongs (6.6), and wash thoroughly in grade 2 water. Finally rinse the sample pieces with the ethanol (5.7) or the acetone (5.7) and dry them for 30 min in the drying oven (6.2) at about 115 °C.

7.4 For testing glass "as delivered"

The thickness of the sample pieces shall not exceed ≈ 2 mm for a total surface of 30 to 40 cm^2. That means that the new cut surface area is not more than about 10 % of the total surface area.

Wash the sample pieces thoroughly with grade 2 water (5.1), then rinse with the ethanol (5.7) or the acetone (5.7). Dry the sample pieces in the drying oven (6.2) for 30 min at about 115 °C.

8 Procedure

8.1 Number of determinations

Test three sample pieces and three blank solutions as specified in 8.2.

8.2 Acid leaching and blank tests

Heat the drying oven (6.2) to 115 °C and the other drying oven (6.1) to 100 ± 1 °C. Put each sample piece (prepared in accordance with clause 7) by means of the tongs (6.6) into a separate dish (6.5), close the three dishes loosely with the lids and put them into the hot drying oven (6.2) overnight. In the same way, heat three more dishes for blank tests omitting the sample pieces, and another one for temperature control.

Next day heat seven portions of exactly 25 ml of the hydrochloric acid solution (5.2) in the beakers (6.8) until boiling. Then transfer the hot dish for the temperature control (without a sample piece) to a fume cupboard and pour in the boiling hydrochloric acid solution. Cover and close the dish, insert the thermocouple, and replace the dish in the other drying oven (6.1) at 100 °C. Repeat the filling procedure with the three other dishes without sample pieces (for the blank tests), and finally with the three dishes containing the sample pieces (i.e. the extraction solutions). Count the period of 3 h from the time when the first dish containing a sample piece was placed back in the drying oven.

NOTE — The period before a dish is placed back in the drying oven shall not exceed 2 min. Protect, as well as possible, the dishes in the drying oven from cold air entering through the drying oven door.

Measure the temperature in one dish and correct the temperature of the drying oven (6.1), if necessary, to maintain the temperature at 100 ± 1 °C.

After 3 h remove the dishes from the drying oven and decant the extraction solutions and the blank test solutions into separate boiling flasks (6.9), except the dish for the temperature control. Dip, as deep as possible, the flasks into the heating bath (6.10) at 120 to 130 °C. Remove the sample piece from a dish using the tongs. Wash thoroughly with a few jets of grade 2 water (5.1). According to the evaporation of the solutions in the flasks, add the washings and complete the cleaning of the dishes with more jets of the water.

During storing of the washings, the dishes shall be covered. When the liquids have almost completely evaporated, add four drops of the hydrofluoric acid solution (5.5) and continue the evaporation until dryness (total time about 3 h).

NOTES

1 If a vitreous silica flask has been used, the addition of hydrofluoric acid solution shall be omitted.

2 If dryness is not reached after 3 h (drops of solution remaining), put the flask into a drying oven at 125 °C for 30 min.

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1) Glass of hydrolytic resistance grain class ISO 719-HGB 1 adequately meets the requirements of class HGA 1 specified in ISO 720.

Once dryness is achieved, allow to cool and add to each flask, by means of the graduated pipette (6.13), 0,2 ml of the hydrochloric acid solution (5.3) and 2 ml of grade 2 water (5.1). Dissolve the residue by swirling the solution.

Transfer each solution into a separate one-mark volumetric flask (6.12), add, by means of the graduated pipette, 0,5 ml of the ionization buffer (5.6), rinse each boiling flask (6.9) with about 1,5 ml of water, add it to the one-mark volumetric flask, dilute to the mark with water and mix thoroughly.

8.3 Determination of the alkali metal oxide contents

Prepare standard solutions by dissolving dried chlorides of sodium and potassium, and calibration solutions of appropriate concentrations by adding 0,2 ml of the hydrochloric acid solution (5.3) and 0,5 ml of the ionization buffer (5.6) for each 5 ml of the final volume.

Establish and carefully standardize instrument techniques so as to utilize maximum sensitivity, as sodium oxide concentrations of about 0,1 mg/l may have to be measured.

The spectrometers shall be operated in accordance with the manufacturers' instructions, so that measurement can be made in the optimal working range specified.

Determine the alkali metal oxide contents of the extraction solutions and of the blank solutions (8.2) using the flame emission or flame atomic absorption spectrometer (6.3). Calculate the mean value for the three extraction solutions, and also for the three blank test solutions (in micrograms per millilitre).

If the single values of the blank test solutions differ by more than 0,2 µg/ml from their mean value, or if the absolute content of Na_2O is higher than 5 µg, contamination has occurred; while the subsequent measurements and calculations may be carried out, the values thus obtained are for information only. The test (8.2) shall be repeated. For this purpose

a) when testing glass "as a material", the preliminary acid treatment (7.3) shall be applied beforehand;

b) when testing glass "as delivered", sample pieces with the original surfaces (7.4) shall be tested.

If the blank values are sufficient, the final results shall be calculated.

9 Expression of results

Calculate the mean of the values obtained. If the highest and the lowest observed values differ by more than the permissible range given in the table, repeat the test.

Table — Permissible range of the values obtained

Mean of the values obtained µg of Na_2O per 100 cm^2	Permissible range of the values obtained
Up to and including 30	30 % of the mean
From 30 up to and including 70	20 % of the mean
From 70 upwards	15 % of the mean

Subtract the mean value of the alkali metal oxides, obtained from the blank test solutions, from the mean value, obtained from the extraction solutions. Calculate the amount of the alkali metal oxides extracted per 100 cm^2 of attacked surface. If the potassium oxide release is lower than 5 µg/100 cm^2, it shall be disregarded.

Express the result either as the mass of sodium oxide (Na_2O) or, if required, as the mass of the separate alkali metal oxide extracted, per 100 cm^2 of attacked surface.

10 Test report

The test report shall include the following information:

a) a reference to this International Standard;

b) an identification of the sample pieces;

c) a statement as to whether the test was applied to glass "as delivered" or to glass "as a material" after etching the surface;

d) the thickness of the glass tested, in millimetres, to the nearest 0,1 mm;

e) the surface tested, in square centimetres, to the nearest 0,1 cm^2;

f) the original concentration of sodium oxide measured in the extraction solutions, expressed as micrograms of Na_2O per millilitre, to the nearest 0,01 µg/ml;

g) the calculated release, expressed as micrograms of Na_2O per square decimetre, to the nearest 0,1 µg/dm^2, mean value;

h) any unusual features noted during the determination.