International Standard 7086/1

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Glassware and glass ceramic ware in contact with food — Release of lead and cadmium — Part 1 : Method of test

Articles en verre et en vitro céramique en contact avec les aliments — Émission de plomb et de cadmium — Partie 1 : Méthode d'essai

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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 7086/1 was developed by Technical Committee ISO/TC 166, *Ceramic ware, glassware and glass ceramic ware in contact with food*, and was circulated to the member bodies in May 1981.

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

Austria	France	Poland
Brazil	Germany, F. R.	Romania
Canada	Ireland	South Africa, Rep. of
Czechoslovakia	Israel	Spain
Denmark	Japan	United Kingdom
Egypt, Arab Rep. of	Mexico	USA

No member body expressed disapproval of the document.

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Glassware and glass ceramic ware in contact with food — Release of lead and cadmium — Part 1 : Method of test

0 Introduction

The problem of lead and cadmium release from glassware and glass ceramic ware requires effective means of control to ensure the protection of the population against possible hazards arising from the use of improperly formulated, applied or fired glazes and/or decorations on the food contact surfaces of glassware and glass ceramic ware used for the preparation, serving and storage of food and drinks. As a secondary consideration, different requirements from country to country for the control of the release of toxic materials from the surfaces of glassware and glass ceramic ware present non-tariff barriers to international trade in these commodities. Accordingly, there is a need to establish internationally accepted methods of testing glassware and glass ceramic ware for lead and cadmium release.

An expert panel convened by the World Health Organization (WHO) met in Geneva, in June 1976, and recommended the adoption of sampling methods, testing procedures and limits for the release of toxic materials from ceramic ware.[1] A further meeting was convened by WHO in November 1979.[2]

The method of test specified in this International Standard is based on the WHO recommendations, because it was the sense of the WHO meeting that the term "ceramic" includes ceramics, glass, vitreous enamels, and glass ceramics.

It has been proved that the amount of lead and/or cadmium determined by the method of test specified in this International Standard will not be less than, and in the vast majority of cases will be greater than, the quantities released into acidic foods and drinks over a period of time.[3]

The results of an international survey showed that cooking ware made from glass or glass ceramics is not normally decorated on the food contact surfaces. For that reason this International Standard does not address cooking ware.

1 Scope

This part of ISO 7086 specifies a simulative method of test for the release of lead and cadmium from glassware and glass ceramic ware which may be used in contact with food (including drinks).

2 Field of application

This part of ISO 7086 is applicable to glassware and glass ceramic ware which may be used for the preparation, serving and storage of food.

It does not necessarily apply to glassware made from borosilicate glass or soda-lime-silicate glass, which is not glazed or decorated on any food contact surface, nor need it apply to glass ceramic ware which is not glazed or decorated on any food contact surface.

It does not apply to vitreous and porcelain enamel ware, nor to ceramic ware.

3 References

ISO 385/2, *Laboratory glassware — Burettes — Part 2 : Burettes for which no waiting time is specified.*[4]

ISO 648, *Laboratory glassware — One-mark pipettes.*

1) See WHO/Food Additives 77.44. *Ceramic Foodware Safety, Sampling, Analysis and Limits for Release* (Report of a WHO meeting, Geneva, 8-10 June 1976).

2) See WHO/Food Additives HCS/79.7. *Ceramic Foodware Safety, Critical Review of Sampling, Analysis and Limits for Lead and Cadmium Release* (Report of a WHO meeting, Geneva, 12-14 November 1979).

3) Frey, E., Scholze, H. *Blei- und Cadmiumlässigkeit von Schmelzfarben, Glasuren und Emails in Kontakt mit Essigsäure und Lebensmitteln und unter Lichteinwirkung* (Lead and cadmium release from fused colours, glazes and enamels in contact with acetic acid and foodstuffs and under the influence of light). *Ber. Dt. Keram. Ges.* **56** (1979) No. 10, pp. 293-297.

4) At present at the stage of draft. (Partial revision of ISO/R 385-1964.)

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

ISO 4788, *Laboratory glassware — Graduated measuring cylinders.*

ISO 7086/2, *Glassware and glass ceramic ware in contact with food — Release of lead and cadmium — Part 2 : Permissible limits.*

4 Definitions

For the purpose of this International Standard, the following definitions apply.

4.1 glass : An inorganic, non-metallic material produced by the complete fusion of raw materials at high temperature into a homogeneous liquid which is then cooled to a rigid condition, essentially without crystallization.

4.2 glass ceramic : An inorganic, non-metallic material produced by the complete fusion of raw materials at high temperatures into a homogeneous liquid which is then cooled to a rigid condition with a certain degree of crystallization. It may be translucent or opaque.

4.3 borosilicate glass : A glass containing a sufficient amount of boric oxide to influence its properties, in particular producing high chemical and thermal resistances.

Lead and cadmium are present only in trace amounts as adventitious impurities. The release of these elements will be below the limits of detection of the method of test specified in this International Standard.

4.4 soda-lime-silicate glass : A glass in which the main constituents are normally sodium oxide, calcium oxide, and silica.

Lead and cadmium are present only in trace amounts as adventitious impurities. The release of these elements will be below the limits of detection of the method of test specified in this International Standard.

4.5 foodware : Articles produced from glass and glass ceramics which are intended to be used for the preparation, cooking, serving, and storage of food or drinks, including packaging.

4.6 flatware : Articles having an internal depth not exceeding 25 mm, measured from the lowest internal point to the horizontal plane passing through the point of overflow.

4.7 hollow-ware : Articles having an internal depth greater than 25 mm, measured from the lowest internal point to the horizontal plane passing through the point of overflow.

Hollow-ware may be termed large or small according to its capacity (filling volume, see 8.3.1) as follows :

a) large hollow-ware : hollow-ware with a capacity of 1,1 litres or more;

b) small hollow-ware : hollow-ware with a capacity of less than 1,1 litres.

5 Principle

Filling test specimens with 4 % (*V*/*V*) acetic acid solution and keeping them for 24 h at 22 °C in the absence of light.

This solution extracts lead and/or cadmium, if present, from the surfaces of the test specimens.

Determination of the amounts of lead and/or cadmium extracted by atomic absorption spectrometry (AAS).

6 Reagents

All reagents shall be of recognized analytical grade. Unless otherwise specified, distilled water or water of equivalent purity shall be used throughout.

6.1 Acetic acid (CH_3COOH), glacial, ϱ = 1,05 g/ml.

Store this reagent in darkness.

6.2 Test solution : acetic acid, 4 % (*V*/*V*) solution.

Add 40 ml of the glacial acetic acid (6.1) to water, and dilute to 1 000 ml. This solution shall be freshly prepared for use.

6.3 Lead carbonate ($PbCO_3$) or **lead acetate trihydrate** [$Pb(CH_3COO)_2.3H_2O$].

NOTE — Commercially available standard solutions may also be used. (See the note to 6.4).

6.4 Lead, standard solution corresponding to 1 g of Pb per litre.

Dissolve 1,289 6 g of the lead carbonate (6.3), or 1,830 8 g of the lead acetate (6.3), in 40 ml of the glacial acetic acid (6.1) in a 400 ml beaker (7.6). Warm gently to dissolve, then cool the solution and transfer it quantitatively to a 1 000 ml one-mark volumetric flask (7.3). Dilute to the mark with water and mix.

Determine the exact concentration of the solution by a recognized standardized procedure, such as a complexometric titration.

1 ml of this standard solution contains 1 mg of lead.

NOTE — Alternatively, an appropriate, commercially available, standardized lead solution for atomic absorption spectrometry may be used. Prepare the standard solution (6.4) by diluting, as appropriate, with the test solution (6.2) or with 2 % (*V*/*V*) nitric acid (HNO_3) solution.

6.5 Lead, standard solution corresponding to 0,1 g of Pb per litre.

By means of a pipette (7.4), transfer 10 ml of the standard lead solution (6.4) to a 100 ml one-mark volumetric flask (7.3), make up to the mark with the test solution (6.2) and mix well. Renew this solution every four weeks.

1 ml of this standard solution contains 0,1 mg of lead.

6.6 Lead, standard matching solutions for calibration.

By means of a burette (7.7), or a graduated pipette (7.5), transfer 0 — 0,5 — 1,0 — 2,0 — 5,0 and 10,0 ml aliquot portions of the standard lead solution (6.5) into separate 100 ml one-mark volumetric flasks (7.3), dilute each to the mark with the test solution (6.2) and mix. These solutions have lead concentrations of 0 — 0,5 — 1,0 — 2,0 — 5,0 and 10,0 mg/l respectively. These solutions shall be freshly prepared for use.

6.7 Cadmium oxide (CdO).

NOTE — Commercially available standard solutions may also be used. (See the note to 6.8).

6.8 Cadmium, standard solution corresponding to 1 g of Cd per litre.

Dissolve 1,142 3 g of the cadmium oxide (6.7) in 40 ml of the glacial acetic acid (6.1) in a 400 ml beaker (7.6). Warm gently to dissolve, then cool the solution and transfer it quantitatively to a 1 000 ml one-mark volumetric flask (7.3). Dilute to the mark with water and mix.

Determine the exact concentration of the solution by a recognized standardized procedure such as a complexometric titration.

1 ml of this standard solution contains 1 mg of cadmium.

NOTE — Alternatively, an appropriate, commercially available standardized cadmium solution for atomic absorption spectrometry may be used. Prepare the standard solution (6.8) by diluting, as appropriate, with the test solution (6.2) or with 2 % (*V*/*V*) nitric acid (HNO_3) solution.

6.9 Cadmium, standard solution corresponding to 0,01 g of Cd per litre.

By means of a pipette (7.4), transfer 10 ml of the standard cadmium solution (6.8) into a 1 000 ml one-mark volumetric flask (7.3), make up to the mark with the test solution (6.2) and mix well. Renew this solution every four weeks.

1 ml of this standard solution contains 0,01 mg of cadmium.

6.10 Cadmium, standard matching solutions for calibration.

By means of a burette (7.7), or a graduated pipette (7.5), transfer 0 — 1,0 — 2,0 — 5,0 — 10,0 and 20,0 ml aliquot portions of the standard cadmium solution (6.9) into separate 100 ml one-mark volumetric flasks (7.3), dilute each to the mark with the test solution (6.2) and mix. These solutions have cadmium concentrations of 0 — 0,1 — 0,2 — 0,5 — 1,0 and 2,0 mg/l respectively. These solutions shall be freshly prepared for use.

7 Apparatus

Laboratory glassware shall comply with the requirements of the appropriate International Standards, wherever such International Standards are available. It shall be made of borosilicate glass, as specified in ISO 3585.

Usual laboratory apparatus, and in particular

7.1 Atomic absorption spectrometer, having a minimum sensitivity of 0,50 mg of lead per litre, and 0,05 mg of cadmium per litre, for 1 % absorption. It shall be operated in accordance with the manufacturer's instructions. A digital concentration reader (DCR) attachment is optional, but is useful for rapid analysis.

7.2 Line sources for lead and cadmium.

7.3 One-mark volumetric flasks, of capacities 100 and 1 000 ml, complying with the requirements of ISO 1042, class A.

7.4 One-mark pipettes, of capacities 10 and 100 ml, complying with the requirements of ISO 648, class A.

7.5 Graduated pipettes, of capacities 10 and 25 ml, complying with the requirements of ISO 835/2, class A.

7.6 Beakers.

7.7 Burette, of capacity 25 ml, graduated in divisions of 0,05 ml, complying with the requirements of ISO 385/2, class A.

7.8 Watch-glasses, of different sizes, for covering the test specimens during the test.

7.9 Graduated measuring cylinder, of capacity 500 ml complying with the requirements of ISO 4788.

7.10 Opaque devices, of a suitable shape for covering opaque specimens during the test.

8 Sampling and preparation of test specimens

8.1 Priority

Articles which are highly coloured or decorated on their food contact surfaces or which have a high surface area/volume ratio should be especially selected for testing.

8.2 Sample size

It is desirable to develop a system of control that is regarded as appropriate to the circumstances. If available, six articles shall be tested. Each of the articles (test specimens) shall be identical in size, shape, colour and decoration.

8.3 Preparation of test specimens

8.3.1 Determination of filling volume

Select one from the group of identical test specimens, place it on a flat, horizontal surface and fill it with water to 5 mm from overflowing, as measured along the surface of the specimen. Measure and record the volume V of water to an accuracy of ± 2 %.

8.3.2 Determination of reference surface area for flatware

Invert the specimen on graph paper marked in millimetre squares and draw the contour round the rim. Calculate the area enclosed by the contour and record this as the reference surface area S_R in square decimetres to two decimal places. For circular articles the reference surface area may be calculated from the diameter of the specimens.

8.3.3 Preparation of articles which cannot be filled

Articles which cannot be filled to 5 mm from overflowing as specified in 8.3.1 shall be regarded as non-fillable. These articles shall be coated on all surfaces except the reference surface with beeswax or paraffin wax and tested as specified in 9.1.2.2.

8.4 Cleaning the specimens

The specimens shall be clean and free from grease or other matter likely to affect the test results.

Briefly wash them at a temperature of about 40 °C with a solution containing a non-acidic detergent. Rinse in tap water and then in distilled water. Drain and dry either in a drying oven or by wiping with a new filter paper to avoid any stains. Do not handle the surface to be tested after it has been cleaned.

Articles which cannot be filled and which are protected according to 8.3.3 with wax shall be cleaned on the non-protected surface by the same procedure, but shall not dried in an oven.

9 Procedure

9.1 Extraction

9.1.1 Test temperature

Carry out the extraction at a temperature of 22 ± 2 °C; the test solution and the specimens to be tested shall be allowed to attain this temperature before extraction is commenced.

9.1.2 Filling the specimens

9.1.2.1 Place the specimens on a flat, horizontal surface. Add a volume of the test solution (6.2) equal to the filling volume (see 8.3.1), using the measuring cylinder (7.9).

If the specimens are opaque, cover them with a suitable opaque inert material to avoid contamination. It is not necessary to carry out the extraction of such specimens in the dark.

If the specimens are transparent or translucent, cover them at once and place them in the dark.

9.1.2.2 Place specimens of articles which are non-fillable in a borosilicate glass vessel of suitable size and add the test solution (6.2) to completely cover the specimen. Measure and record the required volume V of test solution to an accuracy of ± 2 %. Cover the vessel with a watch-glass (7.8) and place it in the dark.

9.1.3 Duration of extraction

Allow the specimens to stand for 24 h ± 10 min.

9.2 Sampling the extraction solution for analysis

Prior to sampling the extraction solution to determine the lead and/or cadmium concentration(s), mix the extraction solution from each specimen by an appropriate method which avoids any loss of solution or any abrasion of the surface being tested (for example, using a pipette, remove and allow the extraction solution to run back on to, and into, the specimen several times). Do not dilute the extraction solution (for example by rinsing the specimen).

Transfer the extraction solution to a suitable storage container. It is not necessary to transfer all the extraction solution.

Analyse the extraction solution as soon as possible as there is a risk of adsorption of lead or cadmium on to the walls of the storage container, particularly when the metals are present in low concentrations.

9.3 Calibration

Establish and carefully standardize instrument operating techniques so as to utilize maximum sensitivity, as determinations of lead concentrations as low as 0,50 mg/l, or cadmium concentrations as low as 0,05 mg/l, require the full potential of most instruments (low noise levels).

Determine the absorbances of the standard matching lead solutions (6.6) or the standard matching cadmium solutions (6.10) and, for the determination, either use the bracketing technique or construct calibration curves having, for example, the absorbances of the standard matching solutions as abscissae and the corresponding lead or cadmium concentrations, in milligrams per litre, as ordinates.

Carry out a blank test on the reagents used for each set of determinations.

9.4 Determination of lead and/or cadmium

Determine the lead and/or cadmium concentrations of the extraction solutions by atomic absorption spectrometry following the instrument manufacturer's instructions.

If the lead concentration of the extraction solution is found to be higher than 20 mg/l, or the cadmium concentration higher than 2,0 mg/l, take a suitable aliquot portion and dilute it with the test solution (6.2) to reduce the concentration to less than 20 mg/l for lead or 2,0 mg/l for cadmium.

Alternatively, use standard matching solutions of higher concentrations for the bracketing measurements or for preparing new calibration curves.

10 Expression of results

10.1 Bracketing technique

The lead or cadmium concentration, c_0, expressed in milligrams per litre of extraction solution, is given by the equation

$$c_0 = \frac{A_0 - A_1}{A_2 - A_1} \times (c_2 - c_1) + c_1$$

where

A_0 is the absorbance corresponding to lead or cadmium of the extraction solution;

A_1 is the absorbance corresponding to lead or cadmium of the lower bracketing solution;

A_2 is the absorbance corresponding to lead or cadmium of the upper bracketing solution;

c_1 is the lead or cadmium concentration, expressed in milligrams per litre, of the lower bracketing solution;

c_2 is the lead or cadmium concentration, expressed in milligrams per litre, of the upper bracketing solution.

NOTE — If the extraction solution was diluted, an appropriate correction factor has to be used in the equation.

10.2 Calibration curve technique

Read the lead or cadmium concentration, expressed in milligrams per litre of extraction solution, directly from the calibration curve.

10.3 Calculation of release of lead and cadmium for flatware

The lead or cadmium released per unit surface area from flatware, a_0, expressed in milligrams per square decimetre, is given by the equation

$$a_0 = \frac{c_0 \times V}{S_R}$$

where

c_0 is the lead or cadmium concentration, expressed in milligrams per litre, of the extraction solution, calculated as specified in 10.1 or 10.2;

V is the volume, in litres, of test solution used for the extraction (see 9.1.2);

S_R is the reference surface area (see 8.3.2), expressed in square decimetres, of the test specimen.

10.4 Reporting

For hollow-ware, report the results to the nearest 0,1 mg/l for lead and to the nearest 0,01 mg/l for cadmium.

For flatware, report the results to the nearest 0,1 mg/dm² for lead and to the nearest 0,01 mg/dm² for cadmium.

11 Test report

The test report shall include the following information :

a) a reference to this International Standard;

b) identification of the articles tested, for example whether they were flatware or hollow-ware;

c) the number of specimens tested;

d) each single result, in accordance with 10.4;

e) any unusual features noted during the determination;

f) any operation not included in this International Standard, or regarded as optional;

g) whether each single specimen satisfies the requirements for permissible limits of release as specified in ISO 7086/2.

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