INTERNATIONAL STANDARD

ISO 4531-1

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Vitreous and porcelain enamels — Release of lead and cadmium from enamelled ware in contact with food —

Part 1:
Method of test

Émaux vitrifiés — Émission de plomb et de cadmium d'articles émaillés en contact avec les aliments —

Part 1: Méthode d'essai

Foreword

ISO (the International Organization for Standardization) is a worldwide federation of national standards bodies (ISO member bodies). The work of preparing International Standards is normally carried out through ISO technical committees. Each member body interested in a subject for which a technical committee has been established 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. ISO collaborates closely with the International Electrotechnical Commission (IEC) on all matters of electrotechnical standardization.

International Standards are drafted in accordance with the rules given in the ISO/IEC Directives, Part 3.

Draft International Standards adopted by the technical committees are circulated to the member bodies for voting. Publication as an International Standard requires approval by at least 75 % of the member bodies casting a vote.

International Standard ISO 4531-1 was prepared by Technical Committee ISO/TC 107, *Metallic and other inorganic coatings*, Subcommittee SC 6, *Vitreous and porcelain enamels*.

ISO 4531 consists of the following parts, under the general title *Vitreous and porcelain enamels — Release of lead and cadmium from enamelled ware in contact with food*:

— *Part 1: Method of test*

— *Part 2: Permissible limits*

The Bibliography is for information only.

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Introduction

The problem of lead and cadmium release from enamelled ware requires effective means of control to ensure the protection of the population against possible hazards arising from the use of improperly formulated, applied and fired enamels and/or decorations on the food contact surfaces of enamelled ware used for the preparation, serving and storage of foodstuffs.

NOTE Articles which are highly coloured or decorated on their food contact surfaces or which have a high surface area/volume ratio are more likely than other articles to release lead and/or cadmium.

As a secondary consideration, different requirements from country to country for the control of the release of toxic materials from the surfaces of enamelled ware present non-tarif barriers to international trade in these commodities. Accordingly, there is a need to establish internationally accepted methods of testing enamelled ware for the 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 [6]. A further meeting was convened by the WHO in November 1979 [7].

The method of test specified in this part of ISO 4531 is based on those WHO recommendations, because it was the sense of the WHO meeting that the term "ceramic" includes ceramics, glass, vitreous enamels and glass ceramics. The description of the test method is largely in accordance with EN 1388-2 dealing with the determination of the release of lead and cadmium from silicate surfaces other than ceramic ware.

The amount of lead and/or cadmium determined by the method of test specified in this part of ISO 4531 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 [8]. If WHO recommendations were to include hot testing at any time then a new edition of this part of ISO 4531 should be considered.

Vitreous and porcelain enamels — Release of lead and cadmium from enamelled ware in contact with food —

Part 1:
Method of test

1 Scope

This part of ISO 4531 specifies a simulating method of test for determination of the release of lead and cadmium from enamelled ware which are intended to come into contact with food (including drinks).

This part of ISO 4531 is applicable to enamelled ware including tanks and vessels which are intended to be used for the preparation, serving and storage of food.

This part of ISO 4531 is applicable to enamelled ware including tanks and vessels which can be used for the preparation, serving and storage of food.

This part of ISO 4531 also specifies a method of test for determining the release of lead and/or cadmium from a drinking rim.

It is not applicalble to ceramic ware, glassware or glass-ceramic ware.

2 Normative References

The following normative documents contain provisions which, through reference in this text, constitute provisions of this part of ISO 4531. For dated references, subsequent amendments to, or revisions of, any of these publications do not apply. However, parties to agreements based on this part of ISO 4531 are encouraged to investigate the possibility of applying the most recent editions of the normative documents indicated below. For undated references, the latest edtion of the normative document referred to applies. Members of ISO and IEC maintain registers of currently valid International Standards.

ISO 385-2, *Laboratory glassware — Burettes — Part 2: Burettes for which no waiting time is specified.*

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

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

ISO 2723, *Vitreous and porcelain enamels for sheet steel — Production of specimens for testing.*

ISO 2724, *Vitreous and porcelain enamels for cast iron — Production of specimens for testing.*

ISO 3585, *Borosilicate glass 3.3 — Properties.*

ISO 3696, *Water for analytical laboratory use — Specification and test methods.*

ISO 4531-2, *Vitreous and porcelain enamels — Release of lead and cadmium from enamelled ware in contact with food — Part 2: Permissible limits.*

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

3 Definitions

For the purposes of this part of ISO 4531, the following definitions apply.

3.1
vitreous enamel (USA: porcelain enamel)
substance resulting from smelting or fritting of inorganic compounds to form a vitreous material fused, or capable of being fused (see frit), in one or more layers on to a metallic base

3.2
enamelled ware
metallic articles coated with vitreous and porcelain enamel

3.3
foodware
articles which are intended to be used for the preparation, cooking, serving and storage of food or drinks including tanks and vessels

3.4
flat ware
articles which cannot be filled and articles which can be filled, the internal depth of which, measured from the lowest point to the horizontal plane passing through the upper rim, does not exceed 25 mm

NOTE Flatware also includes the test specimens for testing vitreous porcelain enamelled equipment, containers and water heaters.

3.5
hollow ware
articles which can be filled the internal depth of which, measured from the horizontal plane passing through the lowest point of the upper rim, exceeds 25 mm, excepting hollow ware items having a filling volume exceeding 3 litres which are classed as storage vessels; examples of such articles are kitchen utensils such as pots, pans and kettles

3.6
cooking ware
foodware, specifically intended to be heated in the course of preparation of food and drinks by means such as steaming, boiling, braising, stewing, roasting, baking or by microwaves; examples of such articles are for instance casseroles, bakers, roasters, soufflés, percolators and saucepans

3.7
storage vessel
tank
articles with a capacity of equal to or greater than 3 litres

3.8
drinking rim
20 mm wide section of the external surface of a drinking vessel, measured downwards from the upper edge along the wall of the vessel

3.9
test solution
solution used to extract lead and cadmium from silicate surfaces

3.10
extract solution
aqueous acidic solution obtained from the exposure of a silicate surface to the test solution

3.11
sample measuring solution
solution used for measuring the concentration of the analyte, and perhaps the extract solution or an appropriately diluted extract solution

3.12
analyte
element or constituent to be determined

3.13
stock solution
solution of appropriate composition containing the analyte, in a known high concentration

3.14
standard solution
solution containing the analyte, in known concentration suitable for the preparation of calibration solutions

3.15
set of calibration solutions
set of simple or synthetic calibration solutions having different analyte concentrations. The zero number is, in principle, the solution having zero concentration of the analyte

3.16
atomic absorption spectrometry (AAS)
method for determining chemical elements based on measurement of the absorption of characteristic electromagnetic radiation by atoms in the vapour phase

3.17
optimum working range
range of concentrations of an analyte in solution over which the relationship between absorption and concentration is linear, or sufficiently approximates to linearity so that any divergence at the prescribed limit of concentration does not discernably affect any analytical determination

3.18
direct method of determination
analytical-curve technique
method consisting of inserting the measure obtained in the analytical function, and deducing from it the concentration of the analyte

3.19
analytical function
calibration function
function relating the value of the concentration to the characteristic value obtained from the set of calibration solutions

NOTE The graph of this function is called the "analytical curve (calibration graph)"

3.20
bracketing technique
method consisting of bracketing the measured absorbance or intensity of the sample solution between two measurements made on calibration solutions of neighbouring concentrations

4 Principle

Enamelled surfaces are placed in contact with 4 % (*V*/*V*) acetic solution for 24 h at 22 °C to extract lead and/or cadmium, if present, from the surfaces of the articles or test specimens.

The proportions of extracted lead and cadmium are determined by flame atomic absorption spectrometry (FAAS).

NOTE In routine tests, other equivalent analysis methods can be used.

5 Reagents

During the determination, use only reagents of recognized analytical grade and only distilled water, or water of equivalent purity (grade 3 water complying with the requirements of ISO 3696).

It is permissible to prepare proportionately greater quantities of test solution and analytical solutions than specified in 5.2, 5.4 and 5.5.

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

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

By means of a graduated measuring cylinder (6.7) add, to 500 ml of water, 40 ml ± 1 ml of glacial acetic acid (5.1) and make up to 1 l. Prepare the test solution freshly prior to use and in sufficient quantity to enable the whole of any group of tests and analysis to be completed.

5.3 Analytical stock solutions

5.3.1 Stock lead solution (1 g of lead per litre)

Prepare an analytical stock solution containing 1 000 mg ± 1 mg of lead per litre in the test solution (5.2).

Alternatively, appropriate commercially available lead solutions may be used, provided that the concentrations of such solutions are known to an equivalent accuracy.

1 ml of this stock solution ≙ mg of lead.

5.3.2 Stock cadmium solution (1 g of cadmium per litre)

Prepare an analytical stock solution containing 1 000 mg ± 1 mg of cadmium per litre in the test solution (5.2).

1 ml of this stock solution ≙ 1 mg of cadmium.

5.4 Analytical standard solutions

5.4.1 Standard lead solution (0,1 g of lead per litre)

By means of a one-mark pipette (6.4), transfer 10 ml of the stock lead solution (5.3.1) to a 100 ml one-mark volumetric flask (6.3), make up to the mark with the test solution (5.2) and mix well. Renew this solution every four weeks.

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

From this solution prepare appropriate calibration solutions by dilution with the test solution (5.2) using the burette (6.5), and keep them in suitably prepared containers. Renew these solutions every four weeks. It is also permissible to prepare lead calibration solutions directly from the stock solution by using one-mark glass pipettes or precision piston pipettes with a fixed stroke and 500 ml to 2 000 ml volumetric flasks.

5.4.2 Standard cadmium solution (0,01 g of cadmium per litre)

By means of a one-mark pipette (6.4), transfer 1 ml of the stock cadmium solution (5.3.2) to a 100 ml one-mark volumetric flask (6.3), make up to the mark with the test solution (5.2) and mix well. Renew this solution every four weeks.

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

From this solution prepare appropriate calibration solutions by dilution with the test solution (5.2), using the burette (6.5), and keep them in suitably prepared containers. Renew these solutions every four weeks. It is also permissible to prepare cadmium solutions directly from the stock solution by using one-mark glass pipettes or precision piston pipettes with a fixed stroke and 500 ml to 2 000 ml volumetric flasks.

5.5 Paraffin wax, high melting point.

NOTE Suitable wax is specified e. g. in the European Pharmacopoeia.

5.6 Washing agent, commercially available non-acidic manual dishwashing detergent in common dilution.

5.7 Silicone sealant, in a tube or dispenser, enabling a ribbon of silicone sealant approximately 6 mm to be formed.

6 Apparatus

Use only laboratory glassware, complying with the requirements of appropriate International Standards, where they exist, and made of borosilicate glass as specified in ISO 3585.

6.1 Flame atomic absorption spectrometer, with a detection limit of Pb equal to or smaller than 0,1 mg/l (in 4 % (*V*/*V*) acetic acid) and of Cd equal to or smaller than 0,01 mg/l (in 4 % (*V*/*V*) acetic acid) where the detection limit is the mass concentration of analyte for which the absorbance is three times the standard deviation of the background noise of the system.

NOTE The background noise of the system can be derived either from a series of absorbance measurements made on a solution which contains lead or cadmium at a concentration distinctly detectable above, but close to, the composition of solvent blanks, or directly by suitable flame atomic absorption spectrometers measuring the absorbance of a solvent blank.

6.2 Line sources, for lead and cadmium.

6.3 One-mark volumetric flasks, capacities 100 ml and 1 000 ml, complying with the requirements specified for class B or better one-mark volumetric flasks in ISO 1042. Other sizes of one-mark volumetric flasks may also be required.

6.4 One-mark pipettes, capacities 10 ml and 100 ml, complying with the requirements specified for class B or better one-mark pipettes in ISO 648. Other sizes of one-mark pipettes may also be required.

6.5 Burette, capacity 25 ml, graduated in divisions of 0,05 ml, complying with the requirements specified for class B or better burettes in ISO 385-2.

6.6 Covers, for the articles under test, e. g. plates, watch-glasses, petri dishes of different sizes and opaque if no darkroom is available.

6.7 Graduated measuring cylinders, capacities 50 ml and 500 ml, complying with the requirements specified in ISO 4788. Other sizes of graduated measuring cylinders may also be required.

6.8 Straightedge, strip of metal, or other material, having at least one clearly identifiable edge, cut straight and which does not deviate from straightness by the equivalent of more than one millimetre in one metre. The straight edge may incorporate a spirit level.

6.9 Depth-gauge or rule, calibrated in millimetres, to be used in conjunction with the straight edge (6.8).

7 Samples

The laboratory sample shall consist of four similar single articles, identical in material, shape, dimensions and decoration.