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Vitreous and porcelain enamels — Release from enamelled articles in contact with food — Methods of test and limits

Émaux vitrifiés — Libération depuis les articles émaillés en contact avec les aliments — Méthode d'essai et limites

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Foreword

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The procedures used to develop this document and those intended for its further maintenance are described in the ISO/IEC Directives, Part 1. In particular, the different approval criteria needed for the different types of ISO documents should be noted. This document was drafted in accordance with the editorial rules of the ISO/IEC Directives, Part 2 (see www.iso.org/directives).

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Any trade name used in this document is information given for the convenience of users and does not constitute an endorsement.

For an explanation of the voluntary nature of standards, the meaning of ISO specific terms and expressions related to conformity assessment, as well as information about ISO's adherence to the World Trade Organization (WTO) principles in the Technical Barriers to Trade (TBT), see www.iso.org/iso/foreword.html.

This document was prepared by the European Committee for Standardization (CEN) Technical Committee CEN/TC 262, *Metallic and other inorganic coatings, including for corrosion protection and corrosion testing of metals and alloys*, in collaboration with ISO Technical Committee ISO/TC 107, *Metallic and other inorganic coatings*, in accordance with the agreement on technical cooperation between ISO and CEN (Vienna Agreement).

This second edition cancels and replaces the first edition (ISO 4531:2018), which has been technically revised.

The main changes are as follows:

— the release limit and explanatory information on release limit for aluminium has been updated;

— the Bibliography has been updated;

— the requirement to carry out testing on the same day has been added;

— the requirements of test reports have been updated.

Any feedback or questions on this document should be directed to the user's national standards body. A complete listing of these bodies can be found at www.iso.org/members.html.

Introduction

The release of metal-ions from enamelled articles requires effective means of control to ensure protection against possible hazards arising from the use of improperly formulated, applied and fired enamels and/or inorganic decorations on food contact surfaces of enamelled articles used for the preparation, cooking, serving and storage of foodstuffs.

As a secondary consideration, different requirements from country to country for the control of the release of ions from the surfaces of enamelled articles present non-tariff barriers to international trade in these commodities. Accordingly, there is a need to establish internationally accepted methods of testing enamelled articles for the release of metal-ions.

Vitreous and porcelain enamels — Release from enamelled articles in contact with food — Methods of test and limits

1 Scope

This document specifies a simulating method of test for determination of the release of metal-ions from enamelled articles, which are intended to come into contact with food.

This document also specifies limits for the release of metal-ions from enamelled articles, which are intended to come into contact with food.

This document is applicable to enamelled articles, including tanks and vessels, which are intended to be used for the preparation, cooking, serving and storage of food.

2 Normative references

The following documents are referred to in the text in such a way that some or all of their content constitutes requirements of this document. For dated references, only the edition cited applies. For undated references, the latest edition of the referenced document (including any amendments) applies.

ISO 648, *Laboratory glassware — Single-volume pipettes*

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

ISO 3585, *Borosilicate glass 3.3 — Properties*

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

ISO 4788, *Laboratory glassware — Graduated measuring cylinders*

ISO 28764, *Vitreous and porcelain enamels — Production of specimens for testing enamels on sheet steel, sheet aluminium and cast iron*

3 Terms and definitions

No terms and definitions are listed in this document.

ISO and IEC maintain terminological databases for use in standardization at the following addresses:

— ISO Online browsing platform: available at https://www.iso.org/obp

— IEC Electropedia: available at https://www.electropedia.org/

4 Principle

For the release of metal-ions, if present, from the surfaces of articles or test specimen, a mass fraction of 3 % (density) of an acetic acid solution shall be used. Three consecutive release tests shall be performed on the same day using the same sample and a fresh test solution per test. The first two release test solutions (M1, M2) are discarded. Only the third release test solution (M3) shall be used for analysis. A blank test (B1, B2, B3) is required for each release test, of which only the third release test solution (B3) shall be used for analysis.

5 Reagents

During the determination, use only reagents of recognized analytical grade and only distilled water, or water of equivalent purity, grade 3 water conforming to the requirements of ISO 3696.

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

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

5.2 Test solution, acetic acid, a 3 % (density) solution.

By means of a graduated measuring cylinder (6.4) add, to 500 ml of water, (30 ± 1) g (28,6 ml) of concentrated 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, the standard stock solutions or multi-element solutions, used for ICP-analysis shall be used.

5.4 Dishwashing agent, commercially available, non-acidic dishwashing detergent in common dilution.

6 Apparatus

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

6.1 ICP spectrometer, with a limit of detection at least six times lower than the release limits in Table 1. Other analysis equipment that achieves the equivalent performance may also be used (e.g. AAS/GF).

6.2 One-mark volumetric flasks, capacities 100 ml and 1 000 ml, conforming to 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.

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

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

6.5 Vessels, containers, stoppers and connectors shall consist of a material, such as glass or polytetrafluoroethylene (PTFE).

6.6 Vessels made of borosilicate glass, in accordance with ISO 3585, internal diameter 80 mm, external diameter 90 mm, height 36 mm, 10 mm diameter of the filling hole.

The calculation of the surface/volume (S/V) ratio is reported below.

Each chamber has an internal diameter of 80 mm. Therefore, the tested area, a, of one test plate is 5 025 mm^2 ($a = \pi \cdot r^2$) where r is the radius of the test plate.

The volume of the chamber, V, with a height, h, of 36 mm and a gasket thickness, e, of 2 mm is calculated from Formula (1):

$$V = (h + 2 \cdot e) \cdot a \tag{1}$$

V = (36 mm + 2·2 mm)·5 025 mm^2 = 201 000 mm^3

The S/V ratio can be calculated from Formula (2):

$$\frac{S}{V} = \frac{5\,025\ \text{mm}^2}{201\,000\ \text{mm}^3} = 0{,}025\ \text{mm}^{-1} \tag{2}$$

The S/V ratio for two plates that shall be used, therefore, is equal to 0,05 mm^{-1}.

6.7 Silicone gaskets, internal diameter 80 mm, external diameter of minimum 90 mm, thickness 2 mm.

6.8 Silicon stoppers, diameter 10 mm, 20 mm length.

6.9 PTFE-thermo insulating plate, dimension of minimum 105 mm × 105 mm, 2 mm thickness.

6.10 Blank samples plate made of borosilicate glass, in accordance with ISO 3585 and dimensions of minimum 105 mm × 105 mm, 2 mm thickness.

6.11 Flange frame, of corrosion resistant steel.

6.12 Heating apparatus, able to support the release test temperature, e.g. (95 ± 2) °C.

6.13 Beaker, to preheat the test solution made of borosilicate glass, of minimum 600 ml volume. The beaker is also used as a blank sample container when testing articles.

6.14 Borosilicate glass lid, in accordance with ISO 3585.

6.15 Release test lab apparatus, see 10.1.1.

7 Samples

The laboratory sample shall consist of four single test plates or two articles, identical in material, shape, dimensions and decoration. The sample may be specifically produced test plates or actual industrially produced articles.

For testing vitreous and porcelain enamelled tanks and vessels, test specimens prepared in accordance with ISO 28764 shall be used. These test specimens shall be tested as flat ware.

If a different enamel product is used for the rim or lid of a tableware article it shall also be tested.

8 Preparation of samples

Wash the samples briefly in an aqueous solution at (40 ± 5) °C containing 1 ml/l of dishwashing agent (5.4). Rinse the samples thoroughly with tap water, then with distilled water and allow to drain. Wipe dry with clean filter paper. Do not use any sample that shows residual staining.

Do not handle the surface to be tested after it has been cleaned or prepared.

For articles, an alternative cleaning procedure shall be used if specified in the article's product manual.

9 Test conditions

For enamelled surfaces that are used at room temperature only, the test conditions shall be 24 h at (40 ± 2) °C.

For enamelled surfaces that are used for hot fills, the test conditions shall be 2 h at (70 ± 2) °C.

For enamelled surfaces used for grills and barbecues, due to the short exposure time, the test condition shall be 30 min at (95 ± 2) °C.

For enamelled surfaces that are used for high temperature applications, including cooking, the test conditions shall be 2 h at (95 ± 2) °C.

Where tests are performed using the 2 h at 95 °C condition, there shall be no requirement to perform tests at other conditions specified, as the 2 h at 95 °C condition is the most severe.

For all test temperatures, ensure that the temperature of the simulant refers to the required temperature and not only the temperature of the oven or the bath.

The use of 95 °C instead of boiling conditions is specified to eliminate variability that is caused by atmospheric and other influences on the boiling conditions.

The concentration of metal-ions released is determined with an inductively coupled plasma (ICP) spectrometer.

10 Procedure

10.1 Release test

10.1.1 Release test lab apparatus

The release test apparatus shall be assembled vertically creating three adjacent cells, one for a blank test in the centre and two stagnation test cells on either side of it (see Figure 1).

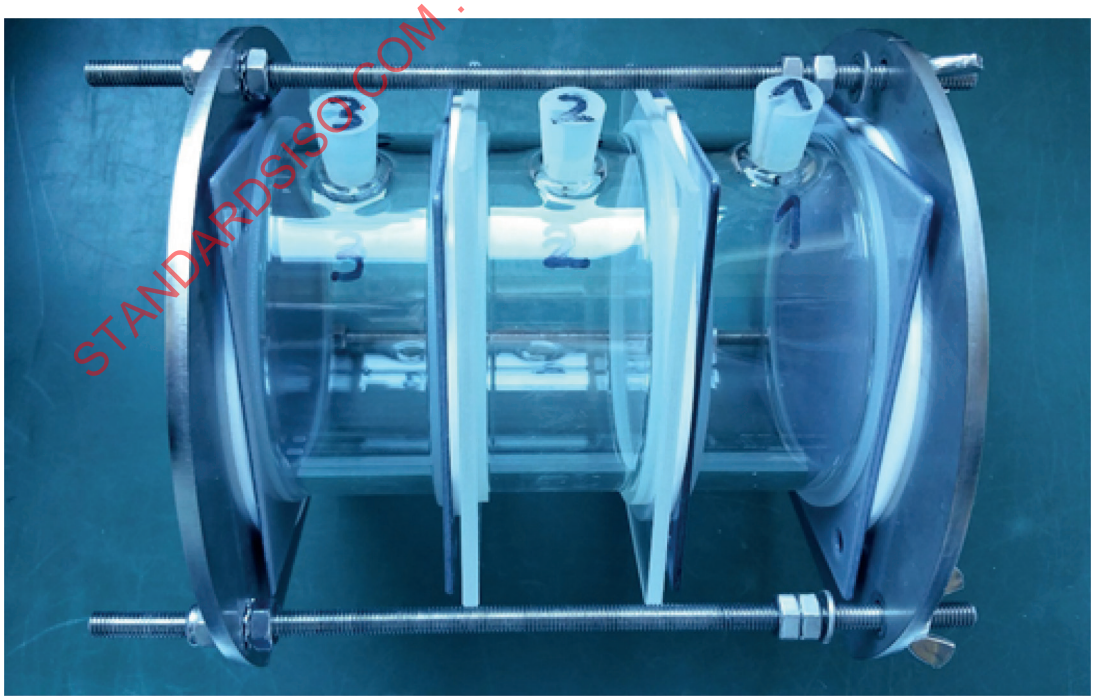

Figure 1 — Release test apparatus with three testing chambers

Borosilicate plates are used as blank sample plates (6.10) instead of enamelled plates.

Place a PTFE insulating plate (6.9) between the enamelled sample plate, in contact with the non-enamelled face and the steel flange (6.11). Very carefully mount the silicone gaskets (6.7) between the glass ring (6.6) and the sample plates on each side, taking care to prevent the silicone gaskets coming out of the glass ring rim. In this way, each of the two test cells have two enamelled coated faces in contact with the test solution. The middle chamber has two blank sample plates in contact with the test solution.

Fix the screws, then place the cell horizontally. Fill the single parts of the apparatus with the test solution (5.2), preheated to the required test temperature, from the beaker (6.13), taking care to eliminate all the air bubbles that form near the walls. Then, close the apparatus with the stoppers (6.8) and put in the heating apparatus (6.12); this starts the release test procedure. Rinsing of the enamelled samples or blank sample plates between each release test is not necessary, however, the test solution shall be completely removed between each release test.

10.1.2 Release from enamelled articles

The S/V ratio used shall be always the same: 5 dm^{-1}. This corresponds, for example, with a small sized casserole article used for cooking. If it is not possible to achieve the requested ratio, a mathematical recalculation of the results shall be done using Formula (3):

$$M3 = M3 \times 5/(S/V) \tag{3}$$

Preheat the articles to the required test temperature. Also preheat the test solution to the required test temperature in the beaker (6.13). Fill the preheated articles with the preheated test solution (5.2) to a level of two-thirds of their height. For articles that cannot be filled, immerse the preheated articles in a borosilicate glass container of an appropriate shape and fill the container with preheated test solution, ensuring that the correct S/V ratio is achieved. In order to eliminate evaporation, cover the articles or glass container with a borosilicate glass lid (6.14).

Along with the articles under test, a blank test is required. The blank test is performed using a beaker (6.13) and a S/V ratio of 5 dm^{-1}. In order to eliminate evaporation, cover the beaker with a borosilicate glass lid (6.14).

Put the articles and the blank in the heating apparatus (6.12); this starts the release test procedure. Rinsing of the articles or blank between each release test is not necessary, however, the test solution shall be completely removed between each release test.

10.2 Sampling the release test solution for analysis (sample measuring solution)

Using the pipette, remove a quantity of the release test solution and allow it to run back into the sample several times, avoiding dilution or evaporation loss in the process. Alternatively, the whole sample solution can be transferred in a suitable vessel and then, after cooling (with a cover), into a sample vial.

Transfer the release test solution or a part of it to a suitable vessel. This is the sample measuring solution. Perform the analysis as quickly as possible.

All three release tests will be done using the same test plates or enamelled articles. Only the test solution of the final release (M3) shall be used for measuring. The blank sample shall be measured as well (B3).

11 Expression of results

11.1 Reporting

The result, which is compared with the limits, is the arithmetical mean of the differences of the metal-ion analysis M3 from the samples/articles tested and the blank sample solution B3 for each tested metal.

The release limit shall be greater than M3 – B3.

Both results of the sample solutions, as well as their mean value, shall be expressed together with the limits for all metal-ions.

The results shall be expressed as precisely as 1 µg/l.

An article is deemed to comply with specified limits when these are not exceeded by the values of the metal-ions released, determined as specified in Table 1.

Table 1 — Release limits

Element	Release limit µg/l
Al	1 000
Ag	80
As	2
Ba	1 200
Cd	5
Co	100
Cr	250
Cu	4 000
Li	480
Mn	1 800
Mo	120
Ni	140
Pb	10
Sb	40
V	10
Zn	5 000

NOTE Annex A provides explanatory information on the limits.

If the results from the test exceeds specified limits up to a maximum of 20 %, the enamel concerned is nevertheless deemed to comply with the limits if a second test is made and the mean value of the two tests does not exceed the specified limit.

11.2 Test report

The test report shall include the following information:

a) a reference to this document, i.e. ISO 4531:2022;

b) an identification of the articles tested, including their type, origin and designation;

c) the place and date of sampling;

d) the date of receipt and date of testing the sample;

e) the S/V ratio of the test;

f) details of the sample cleaning procedure if different to that specified in Clause 8;

g) the number of samples tested;

h) each single result, in accordance with 11.1, and the mean value for each metal-ion expressed as µg/l;

i) whether the article tested satisfies the requirements for release limits specified in this document;

j) any relevant information relating to uncertainty of measurement;

k) any unusual features noted during the testing;

l) any deviations from the procedure.

Annex A
(informative)

Explanatory information on release limits

A.1 General

The method described in this document provides a process to obtain a test solution simulating the release of metals into the food under worst-case conditions. The concentration of the metals within this solution (µg/l) correspond to the concentration that would be equivalent in 1 kg of cooked food. All data are based on the model of European Food Safety Authority (EFSA), whereby a standard human of 60 kg body weight consumes 1 kg of food per day. Therefore, the limits in µg/d or µg/kg are similar. As the specific gravity of the test solution is also close to one, the resulting concentration in µg/l corresponds to the searched value of µg/kg or µg/d.

A.2 Release limits

NOTE The derivation of toxicologically justified limits related to metal intake has not been undertaken in the preparation of this document.

In the absence of published legal limits, the limits laid down in this document correspond to limits published by the Council of Europe in Resolution CM/Res(2013)9 on metals and alloys used in food contact materials and articles[1]. It is noted that this document only uses the limits from Resolution CM/Res(2013)9 and not the test method protocols. The test method protocols identified in this document are relevant and applicable for vitreous and porcelain enamel.

As Resolution CM/Res(2013)9 and the correspondent technical guide Reference [2], do not cover the field on vitreous and porcelain enamels, an exception had to be made for two elements: lithium and cobalt. The elements beryllium, mercury and thallium are not detected in vitreous and porcelain enamels. Therefore, no observation is needed.

The release limits given in this document can change when new knowledge regarding risk assessment on human health related to metal intake is available or in the event that legal limits become available.

A.3 Lithium

For vitreous and porcelain enamels, lithium is a necessary matrix element and a network transformer providing flow to the enamel, whereas in the field of metals and alloys it is regarded as a contaminant or an impurity. Therefore, the application of an allowance of 10 % is deemed to be incorrect. In deviation to Reference [2], no allowance is applied for the purpose of this document.

A.4 Cobalt

For vitreous and porcelain enamels, cobalt oxide is a necessary oxide providing adherence on steel substrates and acting as an intermediate oxide in the glass matrix. In deviation to Reference [2], no allowance is applied for the purpose of this document.

A.5 Mercury

All mercury compounds decompose on heating above 500 °C. It is not possible to maintain mercury inside vitreous and porcelain enamels. Any mercury would evaporate either during the smelt or during