

Food contact Material Vitreous and Porcelain Enamel : Migration from enamelled articles made for food contact – Method of test and permissible limits

Forword

Producers of porcelain enamelled articles, testing institutes and national reference labs have no clear references on how to test porcelain enamelled surfaces for food contact compliancy after regulation 1935/2004/EC. Porcelain enamels do not fit in any of the 17 FCM groups mentioned in annex I of the Framework Regulation (EC) N°1935/2004. The group 3, Ceramics, is very similar to Porcelain Enamels, and for this group the European Directive 84/500/EEC of October 1984 is used for testing food contact compliancy. This directive is also still used by some institutes for testing porcelain enamel , but others believe it is not (longer) valid for porcelain enamels and want to test at elevated temperatures. Because of the fact that the regulation 10/2011/EC contains a testing method for contact with acidic food (pH < 4,5) at elevated temperature , this testing method and the specific migration limits for plastics, are sometimes wrongly used for testing porcelain enamelled articles.

The fact that within the European Union there is no general accepted testing method for porcelain enamels also makes that there exist different requirements, often not specific, from country to country for the control of the migration from the surfaces of enamelled ware, and this creates non-tarif barriers to international trade in these products.

The migration of metal-ions 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 inorganic decorations on the food contact surfaces of enamelled ware used for the preparation of foodstuffs. The European Enamel Authority has for this reason, written following testing method and permissible limits.

1 Scope

The simulating method of test for determination of the migration of metal-ions from enamelled cook and bake ware, which are intended to come into contact with food, is described. And the permissible limits are given.

This testing method has to be used for testing if enamelled articles which are intended to be used for the preparation (cooking, baking, grill, frying,...) of food, are fit for use.

2 Definitions

The definitions used in this testing method, can be found in EN 15826

3 Material specific properties to be considered when testing this class of FCM

The enamelled surface described in this testing method are inorganic coatings. They are best described as porcelain enamels or vitreous enamels. They are applied on a metallic substrate and represent a

functional and impermeable barrier. The organic coatings that are also sometimes called “enamelled surfaces” are not within the scope of this testing method.

4 Test Procedure

To simulate the migration of metal-ions, if present, from the surfaces of articles or test specimen into food, a 3 % (V/V) acetic acid solution shall be used.

For enamelled surfaces that are used for cooking, baking of food, the test conditions shall be 3 migrations of 2 hours +/- 1 min at 95 +/- 2 °C.

For enamelled surfaces that are only used for short frying/grilling of food, the testing time can be reduced to 3 migrations of 30min +/- 1min at 95 +/- 2 °C.

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

The volume/ surface-ratio to be used : 1liter per 2,5 dm². This corresponds with a casserole with diameter 22 cm, filled for 14cm or with a piece of meat of 1kg with contact area of 20 X 12.5 cm. If another Volume/Surface ratio is used, a recalculation has to be made.

Solution :

Acetic acid, (CH₃COOH), concentrated, density $\rho = 1,05$ g/ml – diluted with distilled or demineralised water to a 3% (V/V) solution : By means of a graduated measuring cylinder add, to 500 ml of water, 30 ml \pm 1 ml of concentrated acetic acid 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.

Test specimen :

The test specimen can be :

- Enamelled article : in this case the volume/surface ratio has to be calculated and the analysed migration of metal-ions has to be recalculated to a theoretical volume/surface ratio of 1 liter/2.5dm²
- Enamelled sheet : these can be made under lab conditions or industrial conditions, a good practice is to cut them out from the bottom of the enamelled article. A special testing equipment shall be used existing of material that does not contain the elements that have to be analysed, and with a volume/enamelled surface ratio of 1 liter / 2.5 dm². The advantage of this working method is that many specimen can be tested at the same time. Two different types of used equipments are shown in annex 1

Within 2h before testing, the enameled surface shall be cleaned using a commercially available non-acidic manual dishwashing detergent in common dilution at 40°C. After cleaning, rinse the samples thoroughly with tap water, then with distilled or demineralised water and allow to drain. Wipe dry with clean filter paper

If the manual of the article describes a specific cleaning method to be applied before the first use of the article, this shall be done before the cleaning with the dishwashing detergent.

Testing :

The article or testing equipment and the acetic acid solution have to be preheated at 95°C.

After filling the article or testing equipment with the test solution, it must be kept at 95 °C ± 2 °C for the correct time : 2hours +- 1 min for cook ware and bake ware or 30 min +- 1 min for articles that are only used for frying.

An article has to be filled for 2/3 of the height.

Evaporation during the test of an article has to be avoided, by covering the article with a borosilicate glass, even if the article is sold together with a lid. If the article is sold with a lid, the lid has to be tested for food contact compliance in accordance with the guideline for the used material.

Aside of the enamelled article(s)/sheet(s) to be tested, a blank test has to be performed as well. The permissible migration limits are very low and the used analytical instruments are so accurate, that there will always be found small amounts of the elements to be analysed, in the blank test solution. This amount should be deducted from the amount found in the migration solutions. The blank test should be done using an article/sheet that does not contain the elements to be analysed. A borosilicate beaker/plate is recommended.

REMARK : Duran® and Pyrex® are two trade names of borosilicate glass, and both glass plates and beakers can be bought in this glass quality.

Analysis :

The solution of the third migration (M3) is analysed using an ICP with detection limits below the permissible migration limits.

Also the third migration solution of the blank test is analysed and called B3

For each enamelled article/ sheet, the migration pro element is calculated as M3-B3.

The migration is given in µg/l

REMARK : 1 liter corresponds with an enamelled surface of 2.5 dm². If an article is tested with a different volume / enamelled surface ratio, the migration has to be recalculated to a theoretical V/S of 1liter/2.5 dm²

5 Evaluation of test results

Permissible migration limits for Porcelain Enamels

An article complies when for each element, the migration M3-B3 is below the permissible migration limit given in Annex 2.

If the results from an article exceed the specified permissible limits, but by no more than 50 %, the article concerned is nevertheless deemed to comply with the permissible limits if at least three other similar articles tested provide results such that the arithmetic mean of the metal-ion, released from these articles does not exceed the permissible limit or limits and none of the articles exceeds the permissible limit or limits by more than 50 %.

Report :

The test report shall contain the following information:

- reference to this testing method
- an identification of the articles tested, including their type, origin and designation;
- the place and date of sampling;
- the date of receipt and date of testing the sample;
- the fact if a recalculation was needed to obtain the requested volume/ enamelled surface of 1 liter / 2.5 dm²
- the number of samples tested;
- For each element, each single result, M3-B3, in µg/l and the permissible migration limit
- whether the article tested satisfies the requirements for permissible limits specified

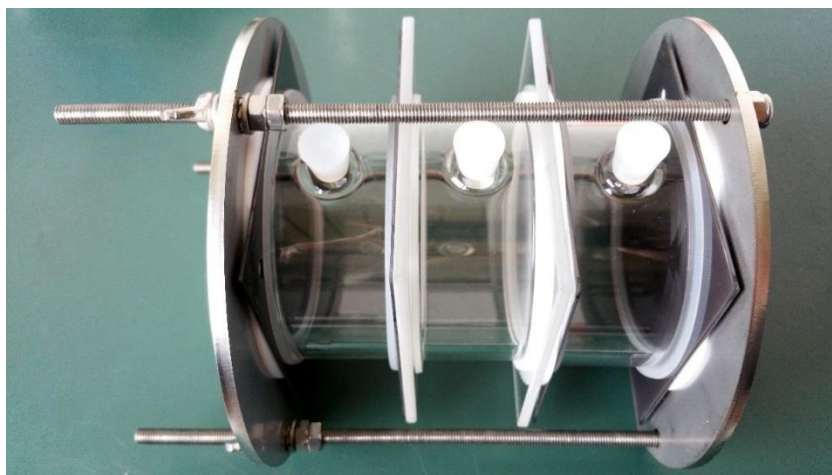
Annex 1 : possible testing equipment for testing enamelled sheet specimen

for the testing of enamelled sheet specimen, one can create its own testing equipment, taking into account that the volume/surface ratio has to be respected as described in the testing method, and that the material used for the equipment, that is in contact with the testing solution, may contain none of the migration elements that have to be analysed.

Possible testing equipments that are in used are given below. If you need more info on those equipments, please contact EEA : <http://www.european-enamel-authority.org>

Both equipment shown below use following dimensions :

- One enamelled sheet per chamber: diameter of 80mm -> tested area = 0,5025 dm².
- Volume of the chambers (incl the seal, the height of the cylinder is 40 mm) = 0,201 dm³.
- Tested area / Volume = 0,5025 dm²/ 0,201 dm³ = 2,5 dm⁻¹.



Annex 2 : Permissible migration limits for porcelain enamel

Taking into account the relevant references, a risk assessment was made on elements used in porcelain enamels for food contact, resulting in the below listed permissible migration limits :

Element	Permissible migration Limit µg/l
Ba	1200
Cd	5
Co	250
Cr	250
Cu	1000
Li	600
Mn	600
Mo	120
Ni	140
Pb	10
Sb	40
Zn	7000

Annex 3 : references :

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

ISO 4788, Laboratory glassware — Graduated measuring cylinders.

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

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

EN 12873-1, Influence of materials on water for human consumption – Influence due to migration – Part 1: Test method for factory made products made from or incorporating organic or glassy (porcelain/vitreous enamel) materials

EN15826, vitreous and porcelain enamels - Terminology

Simoneau, C: Annual Activity Report 2013: European Union Reference Laboratory for Food Contact Materials; EUR – Scientific and Technical Research series, ISBN 978-92-79-38469-1 (2014), S.15