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4MSI Common Approach: ACCEPTANCE OF ENAMELS AND CERAMIC MATERIALS USED FOR PRODUCTS IN CONTACT WITH DRINKING WATER

Part A – Methodologies for testing and accepting compositions to be included in the 4MSI Positive List of compositions for enamels and ceramic materials

Part B – 4MSI Positive List of compositions for enamels and ceramic materials

Part C – Procedure and methods for testing and accepting products or components made of enamels or ceramic materials

Draft 24th February 2021

France, Germany, the Netherlands, the United Kingdom and Denmark (4MSI) work together in the framework of the 4MS Common Approach as laid down in the Declaration of Intent (January 2011). This common approach aims for convergence of the respective national approval schemes for materials and products in contact with drinking water. It might also be used as a starting point for harmonized European requirements, which will have to be implemented under the revised Drinking Water Directive (DWD).

Part A of this document includes a common basis for accepting enamel and ceramic compositions as prerequisite for testing products.

Part B of this document includes a Positive List of enamel and ceramic compositions accepted in all of the 4MSI following the procedure described in Part A and a corresponding list of parameters to be investigated when products are tested according to Part C.

Part C includes a procedure and methods for testing and accepting products or components made of enamels or ceramics in a certifying or approval process.

Further information may be obtained from any of the competent authorities of the 4MSI.

Bundesministerium für Gesundheit (Deutschland)

Ministère du Travail, de l'Emploi et de la Santé (France)

Ministerie van Infrastructuur en Milieu (Nederland)

Department for Environment, Food and Rural Affairs (United Kingdom)

Miljøministeriet, and Trafik-, Bygge- og Boligstyrelsen (Denmark)

Part C – Procedure and methods for testing and accepting products made of enamels and ceramic materials

1 General Approach

The hygienic suitability for use in drinking water systems must be proved for the components made of enamel or ceramic.

Based on the risk for the contamination of the drinking water, which is defined based on the conversion factor for the component, a compliance test with the accepted compositions according to Part B and a migration test is required.

2 Risked based testing program

Depending on the type of product and the relative contact area of its parts, the requirements, tests and depth of evaluation are differentiated. Products with a smaller conversion factor (reflecting smaller surface area in contact with drinking water) are considered to be of lower risk to the drinking water quality and can be evaluated with a reduced set of requirements. This is elaborated in a 'risk table' where all products are divided into one of five risk groups. For each risk group, a set of requirements is given (see Table 1).

Table 1: Risked based testing program

Risk group	Conversion factor CF in d/dm	Composition Testing	Specific migration testing
RG 1	≥ 4	Yes	Yes, on product or component. Enamels: test plates (produced by enameller)
RG 2	≥ 0.4 and < 4	Yes	Yes, on product or component. Enamels: test plates (produced by enameller)
RG 3	≥ 0.04 and < 0.4	Yes	Yes, on product or component. Enamels: test plates (produced by enamel manufacturer)
RG 4	≥ 0.004 and < 0.04	Yes	No
RG 5	< 0.004	No	No

3 Testing of the composition

3.1 Examination

3.1.1 Enamel

An analysis of the composition of the component or test specimen has to be performed. This may be done using X-ray fluorescence analysis or a wet chemical method.

The objective of composition testing is:

1) to verify the requirement that enamels only contain constituents as listed in Part B (Table *Accepted constituents of enamel*)

   and

2) to identify the product.

3.1.2 Ceramic Materials

An analysis of the composition of the component or test specimen has to be performed. The objective of composition testing is:

1) to verify the requirement that ceramic materials have the composition specified in the respective Positive List (s. Part B Table *Accepted constituents of Al2O3 and SiO2 ceramics* to *Accepted constituents of silicon nitride (SN) ceramics*)

2) to define the elements to be assessed in the migration waters, and

3) to identify the product.

3.1.3 Ceramic Materials Made of Carbon

For ceramic materials made of carbon an analysis of the composition is not required.

3.2 Requirements

All constituents with a content exceeding 0.02% (w/w) in the material must be specified.

Enamels may only contain constituents listed in Part B Table *Accepted constituents of enamel*. Lead and cadmium may be present only as impurities in small quantities that are technically unavoidable and may not be added intentionally. The content of these elements must be less than 0.02% (w/w) and has to be declared for the product or components.

Ceramic materials may only contain constituents listed for the relevant material in (s. Part B Table *Accepted constituents of Al2O3 and SiO2 ceramics* to *Accepted constituents of silicon nitride (SN) ceramics*).

Lead and cadmium may be present only as impurities in small quantities that are technically unavoidable and may not be added intentionally. The content of these elements must be less than 0.02% (w/w) and has to be declared for the mixture.

For ceramic materials made of carbon, there are no specific composition requirements provided that the manufacturing methods meet the requirements listed under Part B / Chapter *Ceramic materials made of carbon*.

4 Migration Test

4.1 Examination

4.1.1 Test Principle

The migration test has to be performed according to EN 12873-1.[1]

In repeated contact tests with fully demineralised water (test water) at 23 °C ± 2 °C (cold-water test), 60 °C ± 2 °C (warm-water test) or 85 °C ± 2 °C (hot-water test), the test specimens are assessed for migration of the constituents. In Table 2, test conditions for the various components are listed depending on their intended use.

Table 2: Test conditions for components

Component group	Test conditions
Components intended exclusively for cold-water use	Cold water test at 23 °C ± 2 °C
Components normally in contact with both warm and cold water (e.g. mixing blocks on a tap)	Warm water test at 60 °C ± 2 °C
Components for drinking-water heaters	Warm water test at 60 °C ± 2 °C
Components for drinking-water heaters that normally dispense hot water near the boiling point	Hot water test at 85 °C ± 2 °C

4.1.2 Test Specimens

The respective component or product is to be used as test specimens.

For testing enamels, purposely produced plates (test plates) may be used as test specimens. These must be made of the same material as the component to be enamelled. Plates of dimensions 105 mm x 105 mm should be used. For attachment, a hole of about 5 mm in diameter should be drilled in the samples, with the centre 4 mm from the edge. Pre-treatment and enamelling must reflect normal production conditions. The obverse of the sample is protected against corrosion by means of a thin enamel layer. After drying, the enamel layer is burning in the test specimens together with the regular products, under otherwise normal conditions. In case the test is not executed on the component but on purposely produced test plates instead, a report of the production of the sample shall be compiled and attached to the test report (see chapter 11 of EN 12873-1).

4.1.3 Test Performance

Sample preparation and subsequent migration testing shall be done according to EN 12873-1 and EN 12873-2.

A demineralised test water according to EN 12873-1 shall be used.

To determine the release of elements from enamelled products or products with ceramic components, glass containers or glass recipients must not be used. Migration testing of

[1] Note: Migration testing of ceramic membranes can be performed according to EN 12873-1. For testing according to EN 12873-4 it has to be evaluated whether the same requirements for the assessment of the test results can apply.

carbon-containing ceramics and subsequent analysis of polycyclic aromatic hydrocarbons in turn shall be done exclusively in glass containers or glass recipients.

At least two parallel migration tests and one blind test shall be performed simultaneously.

When testing components, a test surface to water volume (S/V) ratio of at least 5 dm^{-1} shall be configured. When testing purposely produced test plates as referred to in section Part C / 3.1.2, the test setup shall be dimensioned such that a test surface to water volume (S/V) ratio of 5 dm^{-1} ± 10% is obtained.

Figure 1 shows an appropriate setup for migration testing on enamelled plates. Of the three test chambers in the setup, the test water in two of the chambers is in contact with two enamelled plates each, whereas the blank trial runs in the middle chamber.

However, different test setups are possible. Figure 2 shows a test setup where funnels containing the migration water are pressed against the enamel plates.

In warm-water and hot-water testing, the test water must reach the required test temperature after at most one hour. This may be ensured e.g. by using pre-heated test water.

In cold-water testing, at least the three migration periods described in EN 12873-1 should be implemented. If c_{tap} (for calculation see Part C / 3.1.5) is above the criterion for at least one element in the third migration period (see Part B, Tables *Reference concentration*) or shows an increasing trend, the test may be extended by performing 9 migration periods pursuant to Annex 1 In the additional migration periods, the migration waters have to be analysed only for those parameters that have failed to meet the requirements during the regular test.

For the warm-water and hot-water tests, at least the first seven migration periods as defined in Annex 2 should be performed. If c_{tap} (for calculation see Part C / 3.1.5) is above the criterion for at least one element in the seventh migration period (see Part B, Tables *Reference concentration*) or shows a rising trend, the test may be extended to 22 migration periods according to Annex 2. In the additional migration periods, the migration waters have to be analysed only for those parameters that have failed to meet the requirements during the regular test.

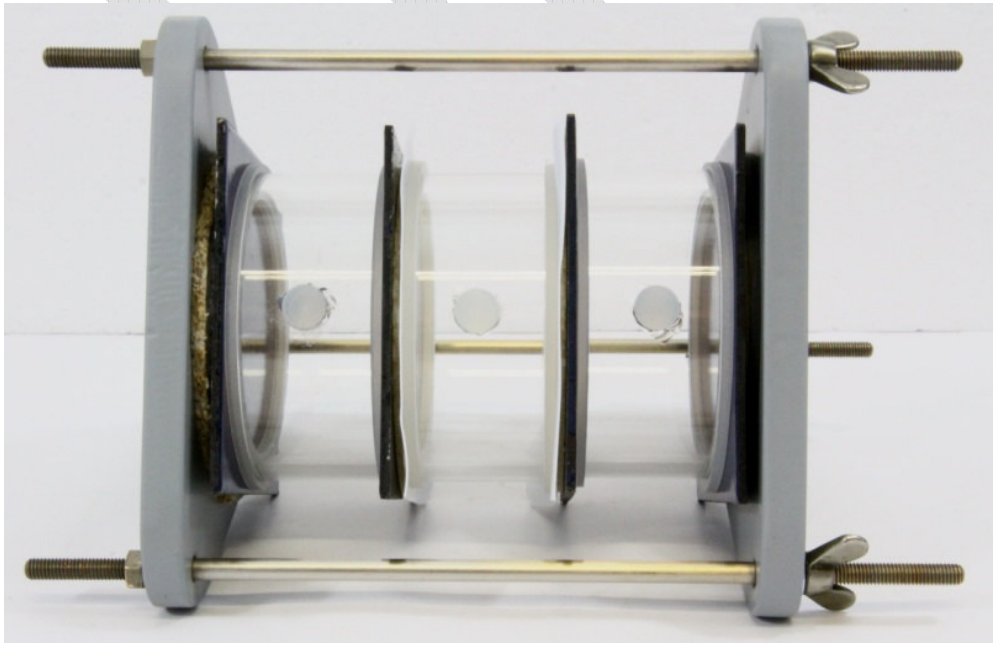

Figure 1: Exemplary setup for migration testing of enamelled test plates (for a better view, the setup shown contains glass parts, which should not be used in actual testing) (photo: TÜV Süd)

Figure 2: Alternative test setup (photo: German Environment Agency)

4.1.4 Analysis of migration waters

Annex 1 lists the migration water samples to be retrieved for the relevant migration periods in the analyses of the cold-water test, Annex 2 correspondingly lists relevant samples for the warm water and hot water tests. The migration waters should be acidified immediately with concentrated HNO_3 to yield 2% (v/v) acid to prepare the sample for element content determination (not for PAH testing).

The elements and substances as listed for the respective accepted composition (see Part B) have to be analysed.

4.1.5 Evaluation of the test results

The concentrations measured in the migration tests ($c_{measured}$) are converted into maximum expected concentrations at the tap (c_{tap}):

$$c_{tap} = \frac{CF\ (c_{measured} - c_{blind})}{S/V \quad t}$$

$c_{measured}$	respective element concentration in µg/l
c_{blind}	respective element concentration of the blind trial in µg/l
CF	component-specific conversion factor according to Table 3 in d/dm
S/V	surface-to-volume ratio in dm^{-1}, where S is the surface area of the component in dm^2 brought into contact with test water, and V the volume of test water in dm^3 brought into contact with the component
t	contact time in d

Table 3: Product groups with corresponding conversion factors

#	Product group	CF in day/dm
A	**Pipes and their linings**	
1	ID < 80 mm (domestic installations, buildings) [2]	20
2	80 mm ≤ ID < 300 mm (service piping)	10
3	ID ≥ 300 mm (mains piping)	5
B	**Fittings, ancillaries [3]**	
1	ID < 80 mm (domestic installations, buildings)	2
2	80 mm ≤ ID < 300 mm (service piping)	1
3	ID ≥ 300 mm (mains piping)	0.5
4	Housing of treatment steps and their coatings	0.05
5	Water abstraction devices	0.005
C	**Components of fittings, ancillaries [4]**	
1	ID < 80 mm (domestic installations, buildings)	0.2
2	80 mm ≤ ID < 300 mm (service piping)	0.1
3	ID ≥ 300 mm (mains piping)	0.05
4	Components of housing of treatment steps and their coatings	0.005
5	Components of water abstraction devices	0.0005
D	**Small Components of fittings, ancillaries [5]**	
1	ID < 80 mm (domestic installations, buildings)	0.02
2	80 mm ≤ ID < 300 mm (service piping)	0.01
3	ID ≥ 300 mm (mains piping)	0.005
4	Small components of housing of treatment steps and their coatings	0.0005
5	Small components of water abstraction devices	0.00005
E	**Storage systems (reservoirs)**	
1	In domestic installations, buildings; water volume < 10 l	4
2	In domestic installations, buildings; water volume from 10 l	2
4	In water supply	1
F	**Components of storage systems [6]**	
1	In domestic installations, buildings; water volume < 10 l	0.4
2	In domestic installations, buildings; water volume from 10 l	0.2
4	In water supply	0.1
G	**Small Components storage systems [7]**	
1	In domestic installations, buildings; water volume < 10 l	0.04

[2] If from a series of different diameter pipes made from the same raw and ancillary materials under the same manufacturing process (a so-called product family) the smallest diameter pipe is assessed and approved, then the whole series of different diameter pipes is allowed to be used for all application areas within the product group without further testing.

[3] Components (sum of components made of similar materials) of assembled products with a wetted surface fraction > 10% of the assembled products

[4] Components (sum of components made of similar materials) of assembled products with a wetted surface fraction ≤ 10% of the assembled products.

[5] Components (sum of components made of similar materials) of assembled products with a wetted surface fraction ≤ 1% of the assembled products.

[6] Components (sum of components made of similar materials) of assembled products with a wetted surface fraction ≤ 10% of the assembled products.

[7] Components (sum of components made of similar materials) of assembled products with a wetted surface fraction ≤ 1% of the assembled products.

2	In domestic installations, buildings; water volume from 10 l	0.02
4	In water supply	0.01
5	Elements of raw water basins, covering < 1‰ of the total surface	0.001

The results of the parallel migration tests (duplicate testing) shall be reported individually in the test report. For purposes of assessment, the average ($\overline{c}_{Tap}$) of the duplicate test results shall be used.

The requirements are regarded as fulfilled for the **cold water test** if for all parameters to be determined, it holds that:

$\overline{c}_{Tap} \leq RC$ for the third or ninth migration period

The requirements are regarded as fulfilled for the **warm water and hot water tests** if for all parameters to be determined, it holds that:

$\overline{c}_{Tap} \leq RC$ for the seventh or twenty second migration period

In addition, the concentrations of the elements to be determined must not show an increasing trend.

Annex 1 Migration periods for the extended cold-water testing

Week	Migration period	Total contact time in days	End of the migration period	Contact time in days per migration	Analysis
1	0 (preliminary treatment)	1	Tuesday	1	No
1	1	4	Friday	3	Yes
2	2	7	Monday	3	Yes
2	3	10	Thursday	3	Yes
3	4	14	Monday	4	No
3	5	17	Thursday	3	Yes
4	6	21	Monday	4	No
4	7	24	Thursday	3	Yes
5	8	28	Monday	4	No
5	9	31	Thursday	3	Yes

Annex 2 Migration periods for the extended warm-water or hot-water test

Week	Migration period	Total contact time in days	End of the migration period	Contact time in days per migration	Analysis
1	0 (preliminary treatment)	1	Tuesday	1	No
1	1	2	Wednesday	1	Yes
1	2	3	Thursday	1	Yes
1	3	4	Friday	1	Yes
2	4	7	Monday	3	No
2	5	8	Tuesday	1	No
2	6	9	Wednesday	1	Yes
2	7	10	Thursday	1	Yes
2	8	11	Friday	1	No
3	9	14	Monday	3	No
3	10	15	Tuesday	1	No
3	11	16	Wednesday	1	Yes
3	12	17	Thursday	1	Yes
3	13	18	Friday	1	No
4	14	21	Monday	3	No
4	15	22	Tuesday	1	No
4	16	23	Wednesday	1	Yes
4	17	24	Thursday	1	Yes
4	18	25	Friday	1	No
5	19	28	Monday	3	No
5	20	29	Tuesday	1	No
5	21	30	Wednesday	1	Yes
5	22	31	Thursday	1	Yes