EVALUATION CRITERIA

30th July 2013

Umwelt Bundes Amt
Für Mensch und Umwelt

Draft

Evaluation criteria for enamels and ceramic materials in contact with drinking water (enamel/ceramic evaluation criteria)[1]

[1] The evaluation criteria will be notified before publication

1 Introduction

According to § 17 Par. 2 Section 1 of the German Drinking Water Ordinance 2001, materials used for the erection of new facilities or the maintenance of facilities used to produce, treat or distribute drinking water that come into contact with drinking water may not

1. directly or indirectly impair human health as defined by the German Drinking Water Ordinance 2001,
2. impair or change the odour or the taste of the water or
3. release quantities of substances into the drinking water that exceed the limits that are unavoidable when complying with generally accepted code of practice.

This draft of an evaluation criteria in compliance with § 17 Par. 3 of the German Drinking Water Ordinance 2001 specifies the general hygienic requirements for the materials listed in the application scope.

Materials in the application scope of this evaluation criteria correspond to the requirements of § 17 Par. 2 Section 1 of the German Drinking Water Ordinance 2001, if they comply to the requirements of this evaluation criteria.

According to § 17 Par. 3 Section 4 of the German Drinking Water Ordinance 2001, this evaluation criteria is valid two years after publication[2] (i.e. from [insert: publication date plus two years]) and, from this date onwards, the company owners and other owners of water supply systems must take steps to ensure that only those enamels and ceramic materials that comply with this evaluation criteria are used to erect new facilities or maintain facilities used to produce, treat or distribute drinking water. Proof that a product meets the requirements of this evaluation criteria can be provided for instance via a certificate from a certification body accredited for the drinking water field.

Via the regulations in § 17 Par. 3 of the German Drinking Water Ordinance 2001 and the specific requirements stated in this evaluation criteria, the Federal Republic of Germany implements Article 10 of the Directive 98/83/EC on the quality of water intended for human consumption by the Council dated 3rd November 1998, which obligates the member states of the European Union to regulate the requirements for materials that come into contact with drinking water. Currently there are no harmonised European regulations for products that come into contact with drinking water. The four EU member states Germany, France, The Netherlands and the United Kingdom (4MS) are working together to harmonize their national requirements. The draft of these evaluation criteria is put forward as a proposal for joint requirements within the scope of this cooperation.

2 Scope

The evaluation criteria apply to enamels and ceramic materials that have direct contact with drinking water.

[2] The date for the binding nature does **not** refer to the publication date of the draft.

3 Evaluation principle

Enamels and ceramic materials may only contain certain oxides.

The release of certain elements is examined in a migration test of the finished product or a representative specimen (e.g. enamelled plate).

The requirements in terms of the release of elements are designed so that the corresponding limit values of the German Drinking Water Ordinance 2001 or, if these do not exist, other guidelines of the Federal Environment Agency (UBA) or World Health Organization (WHO) are not completely exhausted by the release from enamels or ceramic materials.

4 Terms

Test value (PW)

> This is the maximum allowed concentration of an element in drinking water arising through migration from the enamel or ceramic materials.

Conversion factor (F_C)

> This is a part-specific conversion factor that is used in combination with the experimental surface/volume ratio and the contact time applied in the test to calculate the maximum concentration (c_{Tap}) expected at the consumers' tap.

Part

> This is a manufactured component that is used directly or after installation in another product for contact with drinking water.

Test water

> This is completely demineralised (VE) water used for the migration test.

Migration water

> This is the test water after contact with the test specimen(s) under the defined contact conditions.

5 Description of the materials

5.1 Enamel

Enamel is a glass-like material created by melting at 1200 °C – 1300 °C and fritting; it is inorganic and has a predominantly oxide structure (see Table 1).

Table 1: Complete list of the accepted oxides in enamels that come into contact with drinking water

Substance	Content in %		Substance	Content in %		Substance	Content in %	
	Min.	Max.		Min.	Max.		Min.	Max.
SiO_2	25	80	MgO	0	5	Fe_2O_3	0	5
B_2O_3	0.1	20	CeO_2	0	15	MoO_3	0	5
Na_2O	0	30	ZnO	0	10	P_2O_5	0	5
K_2O	0	10	Al_2O_3	0	5	SnO_2	0	5
Li_2O	0	10	CoO	0	5	TiO_2	0	10
CaO	0	10	NiO	0	3	ZrO_2	0	30
BaO	0	15	CuO	0	3	F	0	10
SrO	0	5	MnO_2	0	5	Cr_2O_3	0	3

The ground enamel frit is applied to ferrous metals in a melting process at a temperature in excess of 480 °C. The resulting enamel combines the strength and elasticity of metals with the hardness and chemical resistance of glass.

In the enamelling process, the enamel and metal react to each other in an electro-chemical reaction and a compound material is created allowing the enamel to adhere to the metal surface with a bonding strength of up to 100 N mm^{-2}. The enamelling cannot be infiltrated and is diffusion-resistant. The enamelling is temperature resistant up to 300 °C.

Enamels used in the drinking water field should be highly resistant to water. Enamel does not impact on the taste of the drinking water, which means that this does not need to be tested. Neither is it necessary to test for microbial growth because the smooth surface and the lack of organic nutrients in the material prevent growth.

Enamelled parts that satisfy the requirements of these evaluation criteria are hygienically suitable for use with all drinking water.

5.2 Ceramic materials

Ceramic is an inorganic and non-metallic material. To manufacture ceramic products, a ceramic raw material (e.g. kaolin, clay), which is either available as a granulate for dry pressing or in a plastic form, is usually shaped at room temperature. The subsequent sintering process leads to the typical properties. Depending on the material, the sintering temperatures lie between 1,250 °C and 2,500 °C. This produces crystalline structures, some of which also contain a percentage of glassy phase.

Ceramics are very strong and hard; they are corrosion resistant and can usually be used up to slightly below the sintering temperature.

Ceramics are also highly resistant to water. Drinking water is not impaired in either appearance or taste, so that relevant testing is not necessary. Neither is it necessary to test for microbial growth because the smooth surface (typically created by sanding and polishing) and the lack of organic nutrients in the material prevent growth.

Ceramic materials that are used for direct contact with drinking water must have a composition as shown in Table 2.

Table 2: Complete list of the accepted oxides in ceramic that have contact with drinking water

Substance	Content in %		Substance	Content in %	
	Min.	Max.		Min.	Max.
Al_2O_3	94.0	98.0	Fe_2O_3	0.0	1.0
SiO_2	2.0	5.0	MgO	0.0	1.3
TiO_2	0.0	2.5	BaO	0.0	0.1
Na_2O	0.1	0.5	CaO	0.0	1.0
K_2O	0.0	0.2	SrO	0.0	0.5
MnO_2	0.0	3.0			

6 Hygienic requirements in terms of enamel and ceramic materials

6.1 Requirements in terms of the oxide structure

Enamels may only contain oxides listed in Table 1. They may not contain lead or cadmium as consciously added elements.

Ceramic materials may only contain oxides listed in Table 2. They may not contain lead or cadmium as consciously added elements.

6.2 Requirements in terms of the element release

When enamelled products or products with ceramic parts are used as intended, the release of the elements may not lead to an exceedance of the limit values of the German Drinking Water Ordinance 2001 in distributed drinking water. If the drinking water ordinance does not specify limit values for certain elements, the guideline values of the WHO or the UBA are valid.

The test values (Table 3) are restricted to percentages of the limit or guideline values to take into account other possible release sources. The percentages differ for the various elements. The release should be as low as possible according to the minimisation obligation (§ 6 Par 3 German Drinking Water Ordinance 2001, § 17 Par. 2 No. 3 German Drinking Water Ordinance 2001). Therefore the basic principle is that the percentage of the test value of the limit /guideline value is limited to 10 % in terms of the release of elements coming from the enamel or ceramic materials. The percentage of the test value is limited to 5 % for non-permitted components (lead and cadmium) that may be

contained as impurities in the product. Cobalt, manganese and aluminium are important components of enamels. In terms of cobalt, no further release pathways into the drinking water are known; for this reason, the percentage of the test value of the guideline value can be set to 90 % for cobalt. In the case of manganese and aluminium, no releases from other materials that are used in the distribution of drinking water are expected. For this reason, the percentage of the test values of the limit value of the German Drinking Water Ordinance 2001 is set to 50 %. The 50 % rule also applies to cerium, titanium and zirconium, because no other relevant release pathways into drinking water are known. The test values are summarised in the following Table 3.

Table 3: Test values (PW) for various elements

Element	***Source of the test value***	***Percentage of test value of limit value/guideline***	**Test value in µg/l**
Aluminium	German Drinking Water Ordinance 2001	50 %	100
Barium	WHO	10 %	70
Lead	German Drinking Water Ordinance 2001	5 %	0.5
Boron	German Drinking Water Ordinance 2001	10 %	100
Cadmium	German Drinking Water Ordinance2001	5 %	0.15
Chromium	German Drinking Water Ordinance 2001	10 %	5.0
Cerium	UBA	50 %	20.0
Cobalt	UBA[3]	90 %	9.0
Copper	German Drinking Water Ordinance 2001	10 %	200
Manganese	German Drinking Water Ordinance 2001	50 %	25.0
Molybdenum	WHO	10 %	7.0
Nickel	German Drinking Water Ordinance 2001	10 %	2.0
Strontium	UBA	10 %	210
Titan	UBA	50 %	70
Zirconium	UBA	50 %	5.0

[3] No TDI has yet been defined for the element cobalt; however, there is a preliminary, life-long maximum acceptable value of 10 µg Co/l that was derived as part of the work by LAWA 2001-2004 when establishing the no-effect thresholds (GFS) for groundwater.

7 Test

7.1 Parts test – materials test

The hygienic suitability must be verified on the part that is enamelled or made of ceramic.

However in the case of enamel, it is also possible to examine treated enamel frits, whose composition is subjected to a monitoring procedure that takes into account the specific procedural condition of the enamelling, in place of the enamelled parts produced from this. In this case, the corresponding enamelled parts do not need to be examined again in accordance with these evaluation criteria.

7.2 Inspection of the oxide structure

The oxide structure of the part or test piece must be analysed in an X-ray-fluorescence procedure.

The inspection of the oxide structure serves to:

1) examine the requirement that the enamels or ceramic materials only contain the oxides listed in Table 1 or Table 2 (see 5.1 and 5.2) and
2) identify the product.

7.3 Migration test

7.3.1 Principle of the procedure

In a repeated contact test with fully demineralised water (VE-water = test water) at 23 °C ± 2° C (cold water test) or 60 °C ± 2 °C (warm water test) or 85 °C ± 2 °C (hot water test), the test pieces are tested for migration of the components. Table 4 lists the test conditions of the various parts according to their intended use.

Table 4: Test conditions for assemblies

Assembly	Test conditions
Parts only designed for use with cold water	Cold water test at 23 °C ± 2 °C
Parts that only have contact with warm and cold water (e.g. mixer cartridges of a tap)	Cold water test at 23 °C ± 2 °C and Warm water test at 60 °C ± 2 °C
Parts for drinking water heaters	Warm water test at 60 °C ± 2 °C
Parts for drinking water heaters designed to provide boiling hot water	Hot water test at 85 °C ± 2 °C

The migration test is carried out in compliance with DIN EN 12873-1. Each test piece is subjected to a pre-treatment process comprising a rinsing, stagnation and further rinsing phase. The pre-treatment of the samples is followed by migration periods at a defined ratio of test piece surface to water volume. At the end of this migration period, the migration water must be emptied and replaced with fresh water. The migration water from the defined migration periods is used for further examinations.

7.3.2 Test specimens

The part must be used as the test specimen.

Specially produced plates (test plates) can be used to test enamels. They must be made of the same material in the same gauge as the part that is to be enamelled. Plates with the dimensions 105 x 105 mm must be used. For attachment purposes, a borehole with a diameter of around 5 mm is made in the plate, the centre of which is 4 mm from the edge. The pre-treatment and enamelling processes must correspond to the actual production process. The reverse side of the sample is protected from corrosion with a thin enamel layer. Once dry, the enamel layer on the test piece is branded together with the regular products under the same standard conditions.[4]

In case specially produced plates are used instead of the part itself, a record of the production of the test piece must be drawn up and attached to the test report (section 8).

7.3.3 Execution

The preparation of the samples and the subsequent migration tests are carried out in compliance with DIN EN 12873-1.

VE-water with a conductibility of < 1 µS cm^{-1} must be used as test water.

No glass vessels or glass containers may be used.

At least two parallel migration tests and a blind test must be carried out at the same time.

When testing the test plates in accordance with section 7.3.2, the test setup must be dimensioned so that a ratio of test surface to water volume (S/V) of 5 dm^{-1} ± 10 % is achieved. When testing other parts, a ratio of test surface to water volume (S/V) of at least 5 dm^{-1} must be set.

Figure 1 shows an apparatus used for migration testing of enamelled plates. In the three test chambers of the apparatus the test water has contact to 2 enamelled plates, whilst a blind test is carried out in the middle chamber.

It is also possible to design the test differently. Figure 2 shows a test setup in which funnels are pressed onto the enamel plates that contain the migration water.

[4] The test specimens correspond to the samples in compliance with DIN 4753-3: 2011

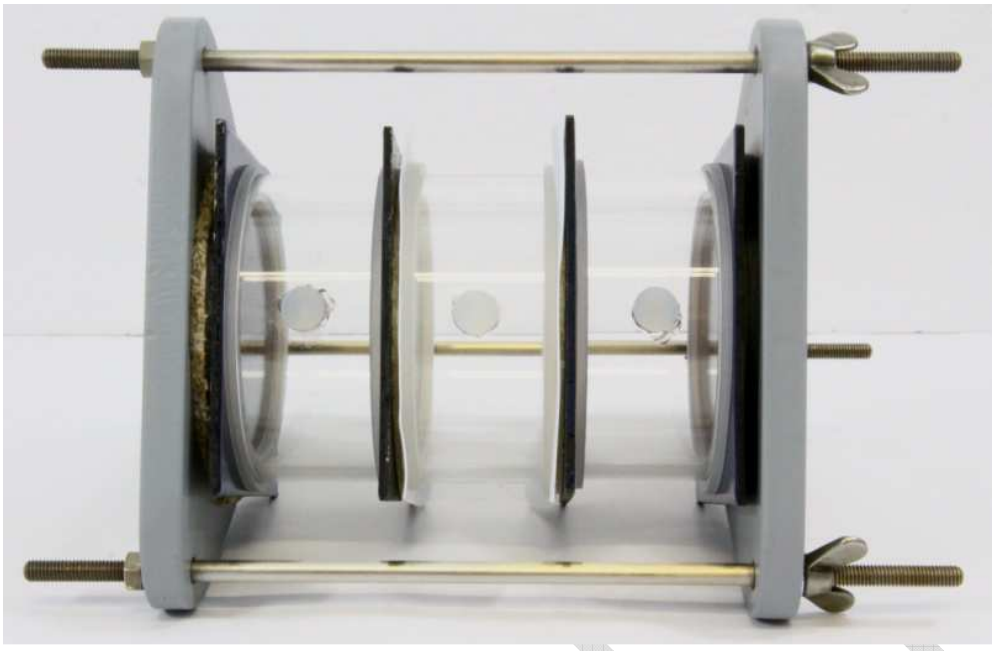

Figure 1: Example of a setup for migration testing of enamelled test plates (for demonstration reasons, the setup has glass parts, however these may not be used in the test) (Photo: TÜV Süd)

Figure 2: Alternative test setup (Photo: Federal Environment Agency)

The test water must reach the specified test temperature within one hour for the warm or hot water test. This can be ensured by e.g. preheating the test water.

At least 3 migration periods stipulated by DIN EN 12873-1 must be executed for the cold water test. If c_{Tap} (see 7.3.4) exceeds the test value for one or several of the parameters in the 3rd migration period (see 7.3.4) or has an upward tendency, the examination can be expanded to 9 migration periods according to Attachment 1 of these evaluation criteria.

At least the first 7 migration periods as stated in Attachment 2 of these evaluation criteria must be carried out for the warm and hot water test. If c_{Tap} exceeds the test value for one

or several of the elements in the 7th migration period (see 7.3.4) or has an upward tendency, the examination can be expanded to 22 migration periods as stated in Attachment 2.

The migration water that is to be analysed is defined in Attachment 1 for the cold water test and in Attachment 2 for the warm and hot water test. This migration water must be immediately acidified to 2 % with concentrated HNO_3.

To test the enamels, all the elements listed in Table 3 - regardless of the oxide structure - need to be determined by means of ICP-MS in compliance with DIN EN ISO 17294-1.

To test ceramic materials, the elements listed in Table 3 except boron, chromium, cerium, cobalt, copper, molybdenum, nickel and zirconium - regardless of the oxide structure – need to be determined. ICP-MS in compliance with DIN EN ISO 17294-1 must be applied as the analysis procedure.

7.3.4 Analysis of test results

The concentrations measured via the migration examinations ($c_{measured}$) are converted to the maximum expected concentrations (c_{Tap}) at the consumers' tap:

$$c_{Tap} = \frac{F_C \, (c_{measured} - c_{blank})}{S/V \quad t} \qquad (1)$$

The following applies:

c respective element concentration in µg l^{-1}

c_{blank} respective element concentration of the blind test in µg l^{-1}

F_C part-specific conversion factor according to Table 5 in d dm^{-1}

S/V surfaces/volume ratio in dm^{-1}, whereby S is the surface of the part in dm^2 and V the volume of the part brought into contact in dm^3

t the contact time in d

Table 5: Assemblies with the associated conversion factors

Assembly	Conversion factor F_c in d dm^{-1}
Tubes with DN[5] < 80 mm (drinking water installation)	20
Tubes with 80 mm ≤ DN < 300 mm (supply lines)	10
Tubes with DN ≥ 300 mm (main lines)	5
Ancillaries (fittings, apparatus, tube connectors, pumps) for	
Tubes with DN < 80 mm	4
Tubes with 80 mm ≤ DN < 300 mm	2
Tubes with DN ≥ 300 mm	1
Parts of ancillaries (fittings, apparatus, tube connectors, pumps) that in total do not make up more than 10 % of the total surface that comes into contact with the water for	
Tubes with DN < 80 mm	0.4
Tubes with 80 mm ≤ DN < 300 mm	0.2
Tubes with DN ≥ 300 mm	0.1
Tanks in the drinking water installation including repair systems	4
Tanks outside the drinking water installation including repair systems	1

The results of the parallel migration examinations (double determination) must be listed singly in the test report. The mean value ($\overline{c}_{Tap}$) of the double determination must be used for the evaluation.

The requirements are deemed fulfilled for the **cold water test,** if the following apply for all elements that are to be determined:

$\overline{c}_{Tap} \leq PW$ for the 3rd or 9th migration period

The requirements are deemed fulfilled for the **warm and hot water test,** if the following apply for all elements that are to be determined:

$\overline{c}_{Tap} \leq PW$ for the 7th or 22nd migration period

Also, the concentration of the elements that are to be determined may not display an upward trend.

8 Test report

The test report based on these evaluation criteria must satisfy the specifications for test reports as defined in the standard DIN EN 12873-1.

When testing specially produced test plates, it is important to specifically state the conditions under which the test plates were produced and also where and by whom.

[5] Inner diameter

Attachment 1: Migration sequence of the prolonged cold water test

Week	Migration cycle	Total contact time in days	End of the migration period	Contact period in days per migration	Analysis
1	0 (Pre-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

Attachment 2: Migration sequence of the prolonged warm or hot water test

Week	Migration cycle	Total contact time in days	End of the migration period	Contact period in days per migration	Analysis
1	0 (Pre-treatment)	1	Tuesday		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

Attachment 3 Declaration of conformity (informative attachment)

A 3.1 Enamel

The following are required to confirm conformity of part enamelling with the specifications of this evaluation criteria:

Responsibilities of the manufacturer of the enamel frit and the enameller:

1. Joint application for a declaration of conformity from an independent body by the manufacturer of the enamel frit and the enameller.
   The following must be submitted to the independent body:
   a. Designation of the enamel frit
   b. Oxide structure of the enamel frit
   c. Production site of the enamel frit and the enamelling
   d. Names of the enamelled products
2. Internal production control:
   a. The manufacturer of the enamel frit must implement production controls that verify the constant composition and quality of the supplied enamel frit. A functional QM system can be used for this purpose.
   b. The enameller must carry out an incoming inspection of the supplied enamel frit and control the part enamelling process to ensure the constant quality of the enamelled parts. It is recommended using a functional QM system for this purpose.
3. Additional testing of the specimens taken in the factory:
   The frit manufacturer must regularly determine or have determined the oxide structure of the enamel frit.

Responsibilities of the independent body:

4. Initial test of the product:
   A full test and assessment based on this evaluation criteria is necessary. To do this, the independent body must arrange for test plates to be enamelled in the enamelling factory for the initial inspection in accordance with section 5 and then test these accordingly.
5. Initial inspection of the factory:
   The independent office must carry out an initial inspection of the enamel frit manufacturer's factory and that of the enameller. Steps should be taken to test whether the manufacturer of the enamel frit is principally in a position to supply enamel frits in a constant quality and if the enameller is able to produce enamelled parts during regular production that comply with these evaluation criteria. Also, the monitoring procedures of the manufacturer of the enamel frit and the enameller must be defined in accordance with number 2.

6. Continuous surveillance:
   The independent body must carry out an inspection of the enamel frit manufacturer's factory and that of the enameller every 3 years. This should include an inspection and assessment of the internal production controls. At the same time, test plates should be enamelled again under supervision and inspected based on these evaluation criteria.
7. If necessary, additional audit-testing:
   If there is a suspicion that enamelled products on the market whose hygienic suitability is confirmed by the independent body do not satisfy the requirements of these evaluation criteria, the independent body can carry out an additional inspection of the manufacturer's factory and arrange for the test plates to be enamelled for inspection purposes.

Confirmation of conformity can be provided in the shape of a test certificate or similar document.

A 3.2 Ceramic materials

For parts produced of the same ceramic materials under the same production conditions in a factory, it is possible to issue a common document confirming the conformity of these products with the specifications of these evaluation criteria.

The following are required for the confirmation of conformity:

Manufacturer responsibilities:

1. Application for a declaration of conformity from an independent body by the manufacturer.
   The following must be submitted to the independent body:
   a. Designation of the manufactured parts
   b. Oxide structure of the ceramic materials
   c. Production site
   d. Description of the production process
2. Internal production control:

   The manufacturer of the enamel frit must implement production controls that verify the constant composition and quality of the supplied ten parts. A functional QM system can be used for this purpose.
3. Additional testing of the specimens taken in the factory:
   The manufacturer must regularly determine or have determined the oxide structure of the manufactured parts.

Responsibilities of the independent body:

4. Initial test of the product:
   A full test and assessment based on this evaluation criteria is necessary. To do this, the independent body must sample manufactured parts for the initial inspection in the factory according to section 5 and then test these accordingly.
5. Initial inspection of the factory:
   The independent body must carry out an initial inspection of the manufacturer's factory. Steps should be taken to test whether the manufacturer is principally in a position to supply parts in a constant quality. Also, the monitoring procedures of the manufacturer must be defined in accordance with section 2.
6. Continuous surveillance:
   The independent body must carry out an inspection of the manufacturer's factory every 3 years. This should include an inspection and assessment of the internal production controls. At the same time, parts should be removed from the factory again and inspected based on these evaluation criteria.
7. If necessary, additional audit-testing:
   If there is a suspicion that parts on the market whose hygienic suitability is confirmed by the independent body do not satisfy the requirements of these evaluation criteria, the independent body can carry out an additional inspection of the manufacturer's factory and take parts from the factory for inspection purposes.

Confirmation of conformity can be provided in the shape of a test certificate or similar document.