

HYGIENIC REQUIREMENTS ON METALLIC MATERIALS USED FOR PRODUCTS IN CONTACT WITH DRINKING WATER.

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1 General

In the European Drinking Water Directive (DWD) a high level of protection for the consumers is established. Member States are required to ensure, that substances and materials used in preparation and distribution of drinking water do not reduce that level of protection (Council Directive 98/83/EC on the Quality of Water Intended for Human Consumption) [1]. The compliance point is at the consumer's tap.

These requirements imply first a need for monitoring water quality at the tap and second a control of all products in contact with drinking water (PDW).

In water supply networks and drinking water installations metal release into drinking water is mainly caused by corrosion of metallic materials. The interactions between materials and water are controlled by chemical and physical laws and are in general very complex.

Corrosion does not only attack metallic materials and deteriorates the water but also leads to the build-up of corrosion product layers, which effect further corrosion and metal release. Layers formed under favourable conditions might be protective and may reduce metal release during operation to a harmless level.

During experiments two different periods of metal release had been observed, which can be described as short term and long term behaviour. The initial period during the first month is mainly influenced by the surface characteristics of the product (e.g. lead film on the surface), while the long term behaviour is characterized by the corrosion of the bulk metallic material and the physical and chemical properties of the formed layers (figure 1).

Formation of protective layers needs time. Therefore limited exceeding of parametric values is accepted in the first month of operation.

2 Actual European evolution

During the last years the German ordinance on the quality of water intended for human consumption (drinking water directive / Trinkwasserverordnung – TrinkwV 2001) and the German standard DIN 50930-6 had been revised [2]. In parallel a new document concerning the assessment of metallic materials and the listing of accepted metallic materials in contact with drinking water had been developed by 5 member states of the European community. It has to be noted that the following documents and the discussion only concern hygienic aspects. Corrosion resistance and mechanical stability of metallic materials are not dealt.

The revision of the DIN 50930-6 and the development of the composition list are documenting the scientific progress while the revision of the German drinking water directive has to be regarded as administrative progress concerning control and regulation of products in contact with drinking water (PDW) [2, 3, 5].

2.1 DIN 50930-6

The actual German standard DIN 50930-6 “Corrosion of metals - Corrosion of metallic materials under corrosion load by water inside of tubes, tanks and apparatus - Part 6: Influence of the composition of drinking water” (version 08/2001) will be separated into two documents [4].

The draft standard DIN 50930-6 “Corrosion of metals - Corrosion of metallic materials under corrosion load by water inside of pipes, tanks and apparatus - Part 6: Evaluation process and requirements regarding the hygienic suitability in contact with drinking water” (01/2013) [3] will now describe the requirements of the testing procedure according to the European standard EN 15664-1/2, the guideline for interpretation of test results and the assessment procedure [6, 7]. The title of the revised standard had been adapted to the modified content.

The restrictions of water composition concerning the use of copper and galvanized steel will remain included in the DIN 50930-6. It has to be noted, that the accepted value of the water parameter acidity concerning the use of galvanized steel will be lowered from 0,5 to 0,20 mmol/L.

The tables with the maximum accepted contents of alloying elements of copper alloys will be removed from the standard and replaced by a separate list of metallic materials suitable for contact with drinking water, which contains all tested and accepted metallic materials. The material list is led by the members of the 4MS Joint Management Committee (revision 02/2013). Responsible authority of the German version of the list is the German Federal Environment Agency (Umweltbundesamt / UBA) [8, 9].

2.2 4MS Common Approach

The 5 member states France, Germany, the Netherlands, the United Kingdom and Portugal (since 1.1.2013) work together in the framework of the 4MS Common Approach as laid down in the Declaration of Intent (January 2011) [11]. After the fail of the European Acceptance Scheme (EAS) this common approach aims for convergence of the respective national approval schemes for materials and products in contact with drinking water. These states have agreed on collaboration in the harmonization of tests for the hygienic suitability of products in contact with drinking-water. In Germany the Federal Environment Agency is actively involved in this process. This cooperation includes all materials used for drinking water – metallic, plastic and other non-metallic materials.

The 4MS intend to adopt common or directly comparable practices for:

- The acceptance of the constituents used in materials in contact with drinking water
- The testing of materials
- The use of common test methods and setting acceptance levels
- The specification of tests to be applied to products
- Reviewing factory production control and setting audit testing requirements
- Assessing the capabilities of certification and testing bodies.

The 4MS are committed to make the documents that set out their agreed policies and practices public when they are fully agreed. The documents that are now available are:

“Acceptance of metallic materials used for products in contact with drinking water;
4MS Common Approach
Part A – Procedure for the acceptance
Part B – 4MS Common Composition List” [9].

The 4MS have adopted Part A of this document as a common basis for implementing the concept of accepting metallic materials in their national regulations. The document is subject to revisions agreed by the 4MS. Part B of this document includes a Composition List of metallic materials accepted in all of the 4MS following the procedure described in Part A. Concerning Germany the revised DIN 50930-6 will be in compliance with Part A and vice versa and the composition lists will be identical.

3 Assessment procedure and Composition List

3.1 Structure of the composition list

The structure of the composition list is declared in the 4 MS document. The composition list contains different categories of metallic materials:

A **Category** is defined as a group of materials with the same characteristics in respect of their field of application, behaviour in contact with drinking water and restrictions with regard to water composition and/or surface area. The composition list contains the categories' range of compositions. Each category has one reference material.

A **Reference Material** is defined as a material falling within a category for which the characteristics of metal release into drinking water are known and reproducible, the composition is strictly controlled and the elements of interest will be at or near the upper limit of acceptability. Possible effects of some constituents to inhibit the metal release have to be taken into account.

Under each category **commercially available metallic materials** accepted for use in PDW will be listed.

The composition list is not complete. It is an open list. Tested and accepted materials will be added according to the rules of the 4MS approach document and to the UBA rules of internal procedure for the updating of the list of metallic materials [5].

An example for a category of the UBA material list is presented in table 3.

3.2 Product groups for metallic materials

The materials may only be used for certain products due to the restrictions with respect to the wetted surface area (Table 1). The former so called installation parameters (wetted surface area ratio) of the DIN 50930-6 [4] with the values of 0,04 and 0,14 had been utilized to the wetted surface ratio (assumed contact surface) of 0,1 respectively 10 %. The product groups for metallic materials are summarized in table 1.

Table 1: Product groups for metallic materials

Product Group	Examples of products or parts of products	Assumed contact surface
A	Pipes in buildings installation Uncoated pipelines in water supply systems	100 %
B	Fittings Ancillaries Parts of pumps in buildings installations Parts of valves in buildings installations	10 %
C	Moving parts in water meters Parts of pumps in water supply systems Parts of valves in water supply systems	1 %

3.3 Acceptable contributions and reference concentrations for acceptance of metallic constituents of metallic PDW

In Table 2 the acceptable assessment values and DWD parametric parameters of elements which may potentially be released from the metallic materials of distribution systems into the drinking water are summarized. The acceptable contributions were derived using the following principles:

- 90 % for elements for which metallic PDW constitute the only major source of contamination;
- 50 % for elements for which other sources of contamination are possible.

On the contrary to the assessment criteria of the DIN 50930-6, the actual assessment values must not tap the full potential of the drinking water parameters. Though zinc is not toxic it has been limited due to the aesthetic acceptability of water (WHO, 2004).

Table 2: Acceptable contributions and reference concentrations for acceptance of metallic constituents of metallic PDW.

Parameter	Acceptable contribution from metallic PDW	DWD parametric value or proposed reference value in DW in µg/l	Reference concentration "RC" for Acceptance Scheme in µg/l
Part B: Chemical parameters			
Antimony	50 %	5	2.5
Arsenic	50 %	10	5
Chromium	50 %	50	25
Cadmium	50 %	5	2.5
Copper	90 %	2000	1800
Lead	50 %	10	5
Nickel	50 %	20	10
Selenium	50 %	10	5
Part C: Indicator parameters			
Aluminium	50 %	200	100
Iron	50 %	200	100
Manganese	50 %	50	25
Others: not listed in DWD			
Bismuth	90 %	10	9
Molybdenum	50 %	20	10
Tin	50 %	6000	3000
Titanium	50 %	15	7,5
Zinc	90 %	3000	2700

Table 3: List of metallic materials suitable for contact with drinking water; Version of German UBA, 23.04.2013; Extract, example of one listed material.

2 Kupfer-Zink-Arsen-Legierungen (Vorläufige Listung)

2.1 Kategoriegrenzen

Legierungsbestandteile (% (m/m)):

Cu	Zn	As
≥ 61,0%	Rest	0,02% - 0,15%

Unvermeidbare Begleitelemente (% (m/m)):

Al	Fe	Mn	Ni	Pb	Sn
≤ 0,1%	≤ 0,5%	≤ 0,1%	≤ 0,3%	≤ 0,2%	≤ 0,5%

2.2 Referenzwerkstoff

Legierungsbestandteile (% (m/m)):

Cu	Zn	As
61,5% - 63,5%	Rest	0,10% - 0,15%

Unvermeidbare Begleitelemente (% (m/m)):

Al	Fe	Mn	Ni	Pb	Sn
≤ 0,1%	≤ 0,1%	≤ 0,1%	0,21% - 0,35%	0,15% - 0,25%	≤ 0,1%

Bei Vergleichsuntersuchungen im Kontaktwasser zu bestimmende Elemente: Arsens, Blei, Kupfer, Nickel, Zink

2.3 Trinkwasserhygienisch geeignete Werkstoffe

2.3.1 Vorläufige Listung

Bezeichnung	Produktgruppe
CW511L (CuZn38As)	B und C

Legierungsbestandteile (% (m/m)):

Cu	Zn	As
61,5% - 63,5%	Rest	0,02% - 0,15%

Unvermeidbare Begleitelemente (% (m/m)):

Al	Fe	Mn	Ni	Pb	Sn
≤ 0,05%	≤ 0,1%	≤ 0,1%	≤ 0,3%	≤ 0,2%	≤ 0,1%

3.4 Assessment Procedure

The assessment procedure is described in the draft DIN 50930-6 and in the 4MS document, "Acceptance of metallic materials used for products in contact with drinking water; 4MS Common Approach, Part A – Procedure for the acceptance" [4]. The procedure is rather complex because of the complexity of corrosion reactions. Assessment procedure is an iterative process and will be adapted according to the requirements [8].

Experimental tests have to be carried out according to the European standard EN 15664-1 with test waters according to EN 15664-2. Main parameters for the assessment procedure are the arithmetic mean values of a complete stagnation curve ($0,1 * MEP(T)$ values) and the weekly measured concentrations after 4 hours stagnation ($0,1 * CEP(T, 4h)$ values). $0,1 * MEP(T)$ and $0,1 * CEP(T, 4h)$ values have to be calculated from all relevant elements.

As an example test results of 3 typical brasses are plotted in figure 1. The tests were carried out in 2001/2002 and it has to be noted, that the used test water was not in compliance with the requirements of EN 15664-2, which was published several years later. Concentrations of neutral salts and TOC were lower than required. The fundamental requirements are:

- 1) After 15 weeks of operation, $0,1 * MEP(T)$ values must be in compliance with the assessment values – e.g. $5 \mu\text{g/L Pb}$.
- 2) $0,1 * MEP(T)$ values must not increase after 12 weeks of operation.

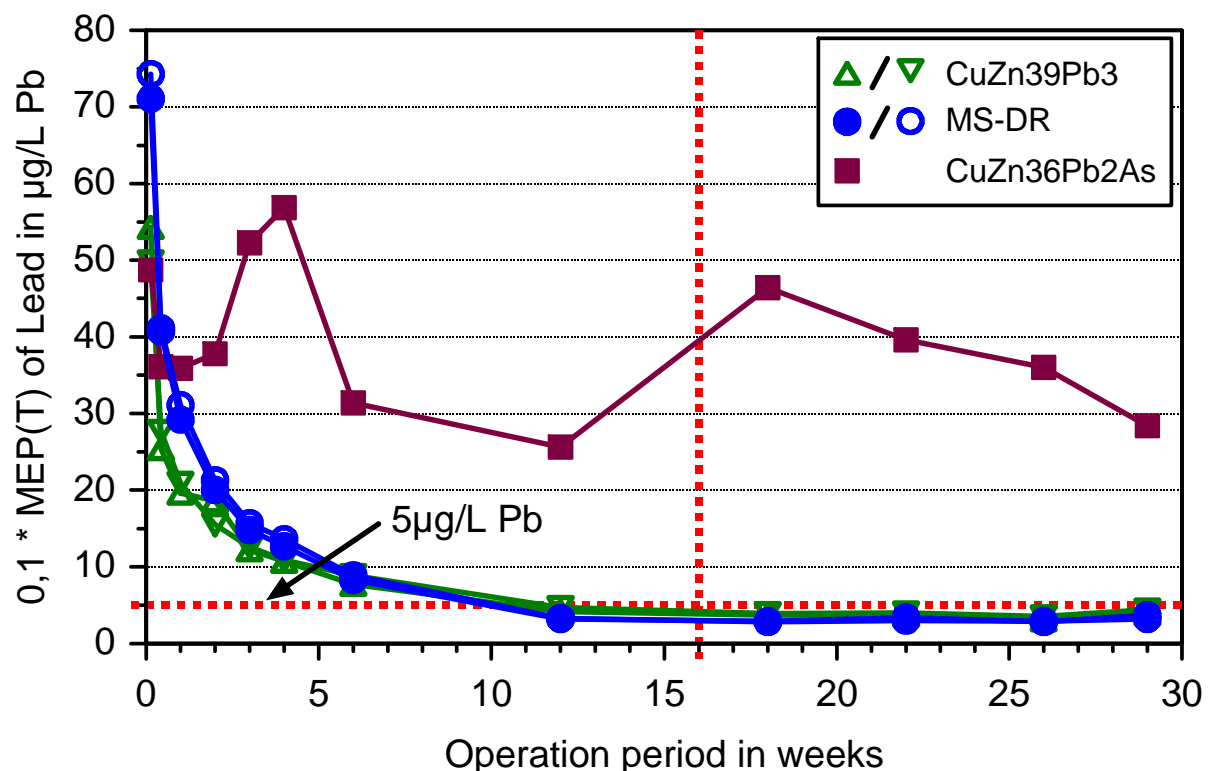


Figure 1: Run-time curves of $0,1 * MEP(T)$ values of lead concentrations of different brasses used for drinking water applications.

As can be seen in figure 1 the standard brass and the MS-DR brass might be in compliance with the requirements of the assessment procedure (in the case of an adequate test water). The dezincification resistant Brass CW602N (CuZn36Pb2As) would fail because of too high lead concentrations. That's the reason why this copper alloy will not be listed.

4 Changes of the German drinking water ordinance 2012

Actually in Germany the guidelines of the Federal Environment Agency and the composition list have the status of a recommendation. This means that the published documents have to be recognized as state of the art, but they are not obligatory.

Due to the authorization on the basis of the modified § 17 of the last revision of the German drinking water ordinance in 2012 the Federal Environment Agency was tasked to produce mandatory standards for products for drinking water applications. With this authorisation the relevance of the health precautions as a sovereign task was confirmed [2].

The Federal Environment Agency is free in its decisions. It can use and modify existing standards or create new assessment standards. Two years after its publication an assessment standard will become obligatory.

According to the presented road map the Federal Environment Agency intends to publish on 1.12.1213 an assessment standard for metallic materials for drinking water applications. This assessment standard consists of a composition list and probably of the DIN 50930-6. Two years later (1.12.1215) the assessment standard will be obligatory and from that time on only products made from listed metallic materials will be permitted to be installed in drinking water installations.

5 Literature

- 1 **Council Directive 98/83/EC** of 3 November 1998 on the quality of water intended for human consumption
- 2 **TrinkwV**, Verordnung über die Qualität von Wasser für den menschlichen Gebrauch, (Trinkwasserverordnung – TrinkwV 2001); Bundesgesetzblatt; 2001, Teil 1; Nr.24; Zweite Verordnung zur Änderung der Trinkwasserverordnung vom 5. Dezember 2012; Bundesgesetzblatt Jahrgang 2012 Teil I Nr. 58, 12/2012
- 3 **DIN 50930-6**, Corrosion of metals - Corrosion of metallic materials under corrosion load by water inside of pipes, tanks and apparatus - Part 6: Evaluation process and requirements regarding the hygienic suitability in contact with drinking water; draft 01/2013
- 4 **DIN 50930-6**, Corrosion of metals - Corrosion of metallic materials under corrosion load by water inside of tubes, tanks and apparatus - Part 6: Influence of the composition of drinking water; 08/2001
- 5 **List of metallic materials suitable for contact with drinking water**; 04/2013
http://www.umweltbundesamt.de/wasser-e/themen/downloads/trinkwasser/4ms_scheme_for_metallic_materials_part_b.pdf
- 6 **EN 15664-1**, Influence of metallic materials on water intended for human consumption - Dynamic rig test for assessment of metal release - Part 1: Design and operation; 6/2008
- 7 **EN 15664-2**, Influence of metallic materials on water intended for human consumption - Dynamic rig test for assessment of metal release - Part 1: Design and operation; 6/2010
- 9 **4MS Common Approach**: Acceptance of metallic materials used for products in contact with drinking water
 - Part A – Procedure for the acceptance; 1st Revision 30.03.2011
 - Part B – 4MS Common Composition List; 2nd Revision 11.02.2013;http://www.umweltbundesamt.de/wasser-e/themen/downloads/trinkwasser/4ms_scheme_for_metallic_materials_part_a.pdf
http://www.umweltbundesamt.de/wasser-e/themen/downloads/trinkwasser/4ms_scheme_for_metallic_materials_part_b.pdf
- 10 **Geschäftsordnung des Umweltbundesamtes zur Führung der Liste der trinkwasserhygienisch geeigneten metallenen Werkstoffe**; [Rules of internal procedure for the updating of the list of metallic materials in German, PDF / 38 KB](#)
http://www.umweltbundesamt.de/wasser/themen/downloads/trinkwasser/liste_trinkwasserhygienisch_geeignete_metallene_werkstoffe_geschaeftsordnung.pdf
- 11 **DECLARATION of INTENT between the competent authorities of France, Germany, the Netherlands and the United Kingdom concerning the approval of products in contact with drinking water (drinking water quality)**; 1/2011
http://www.umweltbundesamt.de/wasser-e/themen/downloads/trinkwasser/4ms_declaration_of_intent_signed.pdf