

Limits for Metals – Trace Elements or Poison?

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Introduction

This paper deals with the content of metals in foodstuffs and in drinking water. Some of these metals are vital trace elements, others are undesirable but unavoidable accompanying elements. The levels, the recommended limits and minimum daily amounts from the WHO and other health organisations as well as my own limits were investigated. The values are critically compared and contrasted with quantities present in foodstuffs. The test procedure is likewise critically examined.

In July 2013 the German Federal Environment Agency presented a draft regarding guidelines for materials which come into contact with drinking water [1]. This new guideline will replace the previously valid KTW Recommendation [2] from the Agency. In this guideline 27 elements are approved for contact with drinking water, 15 of these 27 elements have limits imposed upon them. Up to now there has been no guideline for vitreous enamel or ceramics in contact with drinking water. This new guideline introduced a paper for this medium for the first time. At the same time a basis for evaluation [3] was presented as rationale for the limits in which the limits are explained. The results of this guideline being generally very low limits. The approach is to use the limits for water and to split them between the other materials so that, in a worst case scenario, the total cannot exceed the original limit. The guideline was presented in June 2014 and will become legally binding from July 2016. Due to the 4MS Initiative [4] the guideline will become valid in four European countries at the same time. These countries are France, Germany, the Netherlands and the United Kingdom. Portugal has already made an application regarding cooperation in the JMC. Also the English WRAS will be adapted accordingly. In the near future Spain and Italy as well as at least one Scandinavian country would also like to become involved. From our daily food we absorb all of the 15 metals which are subject to limits.

Method/Discussion

The method of testing materials in contact with drinking water is laid down in EN 12873-1 [5]. EN 12873-1 requires test water with a maximum conductivity of 2mS/m. The basis for evaluation additionally requires ultrapure, fully demineralized water as test water [1]. The use of ultrapure water (specific resistance > 1M Ω cm) as a substitute for drinking water is questionable. In ultrapure water the attack does not happen due to a chemical process, it is only controlled by osmosis and all materials disintegrate [6]. The conclusion that the migration of materials into this test water can be applied to the behaviour in real drinking water is incorrect. This finding was already known to the UBA but ignored [7]. In EN 15664-2 three types of drinking water are characterized which cover the range of drinking waters in Europe [8]. It would be necessary to adhere to this Standard when choosing a substitute otherwise one has no reference to drinking water anymore. The reason for using ultrapure water as a substitute seems reasonable because such water has to be used for the ICP-MS. It is therefore a useful mistake. The necessity of making this mistake will become clearer when one looks at the analytical requirements more closely.

In order to make a graphic comparison let us consider the accuracy of clocks. A mechanical clock with a 5Hz balance spring as a frequency generator has a deviation of some 13 seconds per day: this corresponds to some 0.15 parts per thousand. A quartz clock with an oscillation frequency of 215Hz achieves an accuracy of 15 seconds per month: this corresponds to an accuracy of some 5ppm (parts per million). The concentrations of the metals which are to be measured lie in the ppb (parts per billion) range. 1 ppb corresponds to a deviation of one second over 33 years. In order to be able to analyse to this accuracy one cannot afford refilling or diluting processes anymore as these actions

already cause errors in the parts per thousand range. The wish to be able to measure such low concentration levels therefore requires the necessity of enforcing a chemically incorrect approach.

Results

In the European Commission's 84/500/EEC from 1984 the limits for lead and cadmium for ceramic objects were regulated. These limits were also used for ISO 4531-1 and ISO 4531-2 which standardize the testing and limits for enamelled objects. This regulation is said to be revised. Lead and cadmium are not trace elements and have no positive influence on humans or animals at all – they are, however, constant accompanying elements in all foodstuffs. Thereafter the essential trace elements of metals and the semi-metal boron will be discussed.

Lead

In the past lead was ubiquitously spread in the environment via the burning of fuel in cars and via external house paints. The consequence is high lead contamination of the soil and all foodstuffs. Leaded petrol has been banned in the EU since 2000 and the contamination levels are declining. In March 2010 a margin of exposure (MoE) was recommended by the European Food Safety Authority (EFSA) of 10.5 µg/kg and week [11]. This is equivalent to a maximum lead intake of 90 µg per day for a person weighing 60 kg. On the basis of data acquired from the BfR (German Federal Institute for Risk Assessment) one can read a mean value of 32 µg of lead from daily food [12]. The maximum level for lead in drinking water must not exceed 10 µg/l (10ppb) [13]. From this value a 5% exhaustion for enamelled objects is allowed, reaching a limit of 0.5 µg/l [3].

The regulation (EC) no. 1881/2006 setting maximum levels for certain contaminants allows in appendix (3.1) for example a lead content of 20 µg/kg for milk, infant formulae and follow-on formulae. Bivalve molluscs are permitted to contain up to 1500 µg/kg of lead. In the regulation (EC) no. 629/2008 amending regulation (EC) no. 1881/2006 the limit for lead in food supplements (footnote: as sold) is increased to 3000 µg/kg [15]. In 2013 the Council of Europe (CoE) gave a limit for objects in contact with foodstuffs of 40 ppb which is adapted to the performance of a standard ICP [16, 17]. The UBA limit can only be measured with an ICP-MS [9].

Table 1: Limits and Average Daily Amounts for Lead

Values for lead	µg/d	Concentration/ ppb
Maximum daily value (EFSA)[11]:	90	
Average daily amount from food [12]:	32	
Drinking water limit [13]:		10
CoE objects in contact with foodstuffs [17]		40
Maximum for milk and follow-on formulae [14]:		20
Maximum value for bivalve molluscs [14]:		1500
Food supplements [15]:		3000
UBA limit for vitreous enamel from 2016 [1]:		0.5
Limit of determination in an ICP (radial) [16]:		24

Cadmium

Cadmium enters the environment via natural phenomena such as the weathering of rock and volcanic eruptions. For many years it has been distributed into the soil and water sediments by mining, industry and agriculture. Due to the absorption of cadmium in plants and animals this heavy metal has found its way into nearly all foodstuffs. Cadmium can contribute here negatively to health causing damage to kidneys, bone demineralization and lung, bladder and breast cancer [18].

Cadmium is used in solder for pipe welding and is found accompanying zinc and can find its way into water when zinc coatings disintegrate.

Smokers can absorb cadmium on the same scale as from foodstuffs through the consumption of tobacco products. Cadmium typically occurs in foodstuffs at a concentration of 2-70 µg/kg. Particularly high levels are found in sheep's and bovine liver as well as in kidney and wheat grain [19]. In January 2009 a TWI (tolerable weekly intake) of 2.5 µg/kg of bodyweight was set by the European Food Safety Authority (EFSA) regarding the absorption of cadmium [20].

The weekly absorption of cadmium is just under 1.5 µg/kg of bodyweight [12].

Drinking water contains on average 1.0 µg Cd [19].

In the drinking water-VO from 2001 a limit of 3 µg/l was given [13]. In order to find a test value for enamelled goods in contact with drinking water the UBA allows a 5% exhaustion of this value and arrives at a limit of 0.15 µg/l [1].

The 2nd regulation (EC) no. 1881/2006 setting maximum levels for certain contaminants in foodstuffs allows in the annex (section 3.2) a limit of 200 µg/kg for leaf vegetables, wheat, rice, soybeans; for kidney of bovine animals, sheep, pig, poultry and horse and for bivalve molluscs 1000 µg/kg are granted [14].

The regulation (EC) no. 629/2008, amending regulation (EC) no. 1881/2006 setting maximum levels for certain contaminants in foodstuffs increases some limits: Paragraph 3 states however:

“On the basis of new information, good agricultural and fisheries practices do not allow keeping levels of lead, cadmium and mercury in certain aquatic species and fungi as low as required.... It is therefore necessary to revise the maximum levels fixed for those contaminants while maintaining a high level of consumer health protection.”

The limits for fungi (except common mushroom, shiitake and oyster mushroom 200 µg/kg) are therefore raised to 1000 µg/kg. Food supplements must likewise not exceed 1000 µg/kg of cadmium – food supplements, derived mainly from seaweed, may contain up to 3000 µg/kg of cadmium [15]. In view of the high levels in foodstuffs it would have been sensible here to be able to adjust the limit of the performance of a standard ICP [16]. The UBA's limit can only be measured with an ICP-MS [9]. In 2013 the Council of Europe set this limit for foodstuffs at 20 ppb [17].

Table 2: Limits and Average Daily Amounts for Cadmium

Values for cadmium:	µg/d	Concentration/ ppb
Maximum daily value (EFSA)[20]:	21	
Average daily amount from food [12]:	13	
Drinking water limit [13, 19]:	3	3 (1)
CoE objects in contact with foodstuffs [17]		20
Leaf vegetables, wheat, rice, soybeans [14]:		200
Kidney of bovine animals, sheep, pig, poultry and bivalve molluscs, mushrooms [14]:		1000
Food supplements, derived from seaweed [15]:		3000
UBA limit for vitreous enamel from 2016 [1]:		0,15
Limit of determination in an ICP (radial) [16]:		1,5

Cobalt

Cobalt is vital to humans and animals. This trace element is stored in the liver and excess is excreted very quickly by the kidneys. Cobalt is prescribed for therapeutic reasons to humans and animals with anaemia. Cobalt is present in numerous foodstuffs e.g. yeast, milk, egg yolk, peanuts, oysters, fish, mussels, offal, dried lentils, leaf vegetables and black tea. Typical levels lie around 10-600 µg/kg. There is up to 600 µg/kg in leaf vegetables, 200 µg/kg in liver and kidney and 100 µg/kg in meat. Some 30 µg are consumed each day in food. An increased cobalt level in food is well tolerated.

Symptoms of a cobalt deficiency in humans and livestock are more well-known than cobalt poisoning itself. 500,000 µg CoCl₂ are acutely toxic to humans [19].

Cobalt is reabsorbed up to 25% in the upper segment of the small intestine, and up to 30% in the lungs. The toxicity of cobalt is low [21]. Up to now there has been no clear idea regarding a limit and the first tentative tests are cautious.

- In one region of the USA a level of 107 µg/l Co was measured in household tap water [22]. This is an unusually high value for drinking water, however, despite continued intake no recognizable or measureable effects were observed.

From this one can derive a NOEL (no observed effect level): 107 µg/l (with an intake of 2 litres drinking water/per day) and 30 µg/d from food = 244 µg/kg.

- The DSV (discussion starting value) from DG Sanco is given as 84 µg/kg based on a TDI of 1.4 µg/kg [23]. This value correlates with the value also used by the UBA [3] and goes back to the publication of Paley et al [24].

DG Sanco did not take into account the reabsorption rate of 25% which is why the limit must be corrected: 1.4 µg/kg/25% *60 kg = 336 µg/kg.

The UBA halved the uncorrected value of 1.4 µg/kg (safety factor of 2) and calculated with an additional safety factor of 10% exhaustion in drinking water 10 µg/l.

Comparison: According to the German regulation on drinking water [13] the limit of 10 µg per litre for trichloroethene and tetrachloroethylene together is set. Tetrachloroethylene is classified as a carcinogenic category 3 hazardous material. Chronic intake leads to liver and kidney damage and is suspected of being toxic to reproduction. Trichloroethene is damaging to health and highly narcotic. It was categorized by the MAK Commission as cancer-causing (above all cancer of the kidney) (category 2) and mutagenic (category 3b). It must be labelled as poisonous. With regard to drinking water cobalt is treated the same as these substances – incomprehensible.

Table 3: Limits and Average Daily Amounts for Cobalt

Values for cobalt:	µg/d	Concentration/ ppb
Maximum daily value:	340	
Average daily amount from food [19]:	30	
Drinking water limit [1]:		10
CoE objects in contact with foodstuffs [17]:		100
Meat [19]:		100
Liver, kidney [19]:		200
Leaf vegetables [19]:		600
UBA limit for vitreous enamel from 2016 [1]:		9
Limit of determination in an ICP(radial) [16]:		3,6

Nickel

A person weighing 70 kg contains some 15 mg of nickel [25]. For plants nickel is very important. Each molecule of urease, a bean enzyme, contains two nickel atoms. This enzyme is required to convert urea into ammonium and carbonate ions [26]. Plants absorb nickel from the soil. The average nickel content of plant tips is 50 µg/kg. In total there are about 70 nickel enriching plants. Nickel is present everywhere. On average air contains 6 µg/m³ (in the country) up to 150 µg/m³ (in cities) [27]. The average daily amount of nickel inhaled by city dwellers is estimated at 2-14 µg (equivalent to the intake from about 1-7 cigarettes), on average smokers take in an additional 15 µg [28].

The world production of nickel is about 2,490,000 tons per year (2013) [29]. The vast majority of the production is used in the production of stainless steel and nickel alloys (87%) and about 9% is used for plating (electroplating, costume jewellery). Nickel is also used as an electrode material in nickel-cadmium batteries. Pure nickel metal is used in finely distributed form as a catalyst (Raney nickel,

Urushibara catalyst) in the hydrogenation of unsaturated fatty acids (cooking oil and margarine). The fields of application for nickel are seemingly inexhaustible.

The amount of nickel taken in daily from food 300-600 µg is toxicologically harmless [27]. Only 10% of the nickel is reabsorbed when taken in orally, 50-100% when inhaled [28].

Nickel is the most common cause of contact allergies e.g. dermatitis. There is reason to believe that nickel taken in orally can lead to a recurrence or deterioration of nickel-induced contact dermatitis. The effect only occurs when the amount of nickel taken in by far exceeds what is usually taken in from food [30].

Absorption from the air via breathing has been proven to be harmful, the reabsorbed part is also greater. Breathing in inorganic nickel compounds is associated with an increased risk of cancer in the lungs and upper airways [31]. Nickel is mainly excreted in urine, sweat and via hair and skin. 90% of nickel taken in orally is passed in faeces without being absorbed [32].

The main dietary sources of nickel are fruit and vegetables (potatoes: 260 µg/kg). Particularly high levels of nickel are found in fats and oils (margarine: 185 µg/kg; peanut butter: 1,467 µg/kg), cocoa powder (12,300 µg/kg), milk chocolate (1,500 µg/kg), soybeans (7,000 µg/kg), wheat flour (135 µg/kg) and ice cream (323 µg/kg) [33].

The additional daily intake as a result of nickel migration from stainless steel cooking utensils is about 100 µg and from electric kettles about 50 µg [34].

A cigarette contains on average 2.2 µg nickel [27], which is absorbed as nickel tetracarbonyl (highly poisonous). Nickel will only be carcinogenic, damage fertility and act mutagenically if inhaled.

In 1995 the WHO specified a PTWI (provisional tolerable weekly intake) of 5 µg/kg of bodyweight (300 µg/week). A limit for drinking water of 20 µg/l was set which is still valid today [35]. With regard to a limit for nickel taken in orally Ohnesorge recommended following the upper values of the usual daily pollution levels for nickel (600 µg/person and day). Thereby, in principle, an acceptable intake could be specified.

In 2008 the WHO specified a TDI of 12 µg/kg for nickel (720 µg/day; 60 kg person). The EFSA does not give a value. From this TDI a limit of 5040 µg/week results [37]. These values are in accord with Ohnesorge's recommendation.

The intake of nickel via foodstuffs is estimated at 600 µg/day and 20 µg/day (2l drinking water) by drinking water. The Council of Europe has specified a limit of 600 µg/kg for objects in contact with foodstuffs [17].

The DSV from Sanco was 72 µg/day and was derived from the WHO recommendation from 2008 with a 10% starting point.

As the inhaled intake from enamelled objects can be excluded and the oral intake is largely harmless the most significant danger is the sensitizing effect of dermal contact. This results in 2.0 µg/l for nickel as a test value for the basis of evaluation for enamel with a 10% exhaustion of the drinking water limit [3]. Nickel is considerably more dangerous than cobalt, the EU's high limit takes into consideration the extensive everyday use of nickel.

Table 4: Limits and Average Daily Amounts for Nickel

Values for nickel:	µg/d	Concentration/ ppb
Maximum daily value (WHO) [37]:	720	
Average daily amount from food [28]:	600	
Drinking water limit [3, 28]:		20 (10)
CoE objects in contact with foodstuffs limit [17]		600
Stainless steel cooking utensils, elec. kettle [34]:	100, 50	
margarine [33]:		185
potatoes [33]:		260
peanut butter [33]:		1467
soya beans [33]:		7000
cocoa powder [33]:		12300
UBA limit for vitreous enamel from 2016 [1]:		2
Limit of determination in an ICP (radial) [16]:		6,3

Boron

Borax is found on the bed and shore of alkaline, dried-up seas. Boron is essential for growth in higher plants: a lack of boron has similar effects to a lack of calcium – the leaves turn yellow in colour and then curl up and fall off. Boron is extraordinarily important for the growth of pollen. It is also required for the formation of the fiber substance pectin. As a trace element, boron plays an important role in the metabolism of magnesium and calcium in humans. There is a link between a lack of boron and osteoporosis. Israel has high levels of boron in the ground and the fewest cases of osteoporosis (the opposite is true for Jamaica). Boron is used to treat the symptoms of arthritis [38]. Boron is present in all human tissues and bones – the highest concentration being in tooth enamel.

Borax and boric acid are utilized as a flux for soldering gold, in the glass industry, in the detergents industry, for cosmetics (hair-care products, shaving cream), in pesticides and as a flame retardant for wood and synthetics as well as in pyrotechnics for green fireworks. In nuclear technology the isotope ^{10}B is used in rubber and synthetic material as a neutron absorber for protective clothing. 1cm ^{10}B has the same shielding effect as 5m of concrete or 20cm of lead. Boron carbide is used in bulletproof vests and armour-plating for seats in helicopters. Boric acid is used as an antiseptic in ointments.

A lethal dosis of boric acid for children is 3,000,000 - 6,000,000 μg and for adults 15,000,000 – 20,000,000 μg [40]. In animal experiments fertility disorders were detected in male animals under long-term exposure. In 2010 borax (use 100,000 – 1m tons/annum in the EU) at Denmark's suggestion and boric acid (use 10,000 – 100,000 tons/annum in the EU) at Germany's suggestion were included on the candidate list by the ECHA as a SVHC material [41, 42]. In Turkey no fertility disorders were observed with boron levels in drinking water of 29,000 $\mu\text{g/l}$ [43]. Boric acid and borax are excreted by the body unchanged via the kidneys up to 90% [40].

The best natural sources of boron are avocado (14,300 $\mu\text{g/kg}$), nuts (6,000 $\mu\text{g/kg}$), grape juice and wine (3,500 $\mu\text{g/kg}$), fruit (pear, tomato, grape, apricot, peach approx. 3,000 $\mu\text{g/kg}$) and vegetables (cauliflower, broccoli, celeriac, salad leaves and carrots approx. 2,000 $\mu\text{g/kg}$) [44, 40]. Food supplements such as multivitamins contained up to 10,000 μg but have since been banned [45].

A NOAEL of 576,000 $\mu\text{g/day}$ is specified from animal experiments [46]. A safety factor of 10 for variation between species and an additional safety factor of 6 for individual variations in humans is assumed. A limit for objects in contact with foodstuffs of 6,600 $\mu\text{g/day}$ can be derived from the known exposures. Sanco did not release a DSV.

As such high levels of leaching from enamelled products is improbable, a review of this limit is not necessary for ceramic or enamelled objects.

Table 5: Limits and Average Daily Amounts for Boron

Values for boron:	$\mu\text{g/d}$	Concentration/ ppb
Maximum daily value NOAEL animal [46]:	576000	
Average daily amount from food [40]:	1500	
Drinking water limit [1]:		1000
CoE objects in contact with foodstuffs limit [17]:		-
Avocado [44]:		14000
Nuts [44]		6000
Grape juice, wine [44]		3500
Fruit [40]:		3000
Vegetables [40]:		2000
UBA limit for vitreous enamel from 2016 [1]:		100
Limit of determination in an ICP (radial) [16]:		4,5

Molybdenum

Molybdenum should be considered as an example of a very important trace element essential to humans. The same applies to chromium and manganese.

Molybdenum is used extensively in stainless steel and dental alloys and also highly acid-resistant enamels. Its occurrence in foodstuffs is as follows: whole grain, soya, sunflower seeds, eggs and liver. High levels are found in milk and milk products, offal, pulses, nuts as well as various grains [47].

Reabsorption via the intestinal tract occurs within 4 hours. A reabsorption rate of approx. 50% for humans can be assumed for soluble compounds, possibly also even higher rates. About 40% is excreted by the kidneys and the rest via the gall bladder within 72 hours of exposure. An accumulation of molybdenum in mammals can be excluded [48]. Molybdenum is a constituent part of about 20 enzymes. Flavoenzymes catalyse various degradative reactions, for example the carcinogenic nitrosamines. Xanthinoxidase is responsible for the degradation of nitrogen compounds in the body and controls the synthesis of urea. The most well-known enzyme is nitrogenase which is found in the root nodules of legumes and enables the absorption of nitrogen from the soil there [49]. In the blood molybdenum is firmly attached to the erythrocytes and plasma proteins. Generally speaking molybdenum compounds are classified as being relatively low toxic for humans particularly because the element is essential and when intake is completely lacking deficiency disease can occur. In metabolism molybdenum is closely associated with copper [48]. The daily requirement of molybdenum for humans is given as about 300 µg [48, 49]. The Council of Europe placed the limit for contact with foodstuffs at 600 ppb [17]. The UBA's limit of 7 ppb is based on a 10% exhaustion of a WHO value from 2011. The WHO did not think it necessary to set a limit for drinking water as toxicologically relevant amounts are not present in it [3].

Table 6: Limits and Average Daily Amounts for Molybdenum

Values for molybdenum:	µg/d	Concentration/ ppb
Maximum daily value NOAEL [50]:	54000	
Average daily amount from food [50]:	100	
CoE objects in contact with foodstuffs limit [17]:		600
Milk [47]		60
Beef [47]:		280
Pig's liver [47]:		2000
Buckwheat [47]:		4850
Soya beans [47]		2100
UBA limit for vitreous enamel from 2016 [1]:		7
Limit of determination in an ICP (radial) [16]:		6

Conclusion

The creation of a new guideline opens up opportunities; the latest data can be compared and a good consensus found for the decades to come. The approach of fixing a limit for water in proportions and to apply this to different materials leads to very low proportion values for materials in contact with drinking water. These low test values bring with them the problem of their measurability and are partly incommensurate with the amounts contained in foodstuffs which makes little sense. The necessity to then want to measure extraordinarily low values leads to the mistake of using ultrapure water as test water. Thus the reference to drinking water is lost and with it makes the entire basis of evaluation meaningless. The values measured have nothing more to do with the behaviour of the material when in contact with genuine drinking water. It is hoped that the Council of Europe (with higher authority) will revise the limits in the guideline and pass more reasonable ones, whereby the use of an ICP-MS is superfluous and a drinking water-compatible water can be used as a substitute.

References

- [1] UBA Fachgebiet II 3.4: Bewertungsgrundlage für Emails und keramische Werkstoffe im Kontakt mit Trinkwasser (Email/Keramik-Bewertungsgrundlage), http://www.umweltbundesamt.de/sites/default/files/medien/419/dokumente/anlage_1_130730_email-bwgl.pdf, 2013, 1-16.
- [2] UBA: Leitlinie zur hygienischen Beurteilung von organischen Materialien im Kontakt mit Trinkwasser (KTW-Leitlinie), <http://www.umweltbundesamt.de/sites/default/files/medien/419/dokumente/ktwleitlinie.pdf>, 2008, 1-18.
- [3] UBA Fachgeb. II 3.4/ II 3.6: Begründung der Prüfwerte der Bewertungsgrundlage für Emails und keramische Werkstoffe im Kontakt mit Trinkwasser (Email/Keramik-Bewertungsgrundlage), http://www.umweltbundesamt.de/sites/default/files/medien/419/dokumente/anlage_2_130730_begrue ndung_pruefwerte.pdf, 2013, 1-25.
- [4] 4MS: Declaration of intent, http://www.umweltbundesamt.de/sites/default/files/medien/419/dokumente/4ms_declaration_of_intent_signed.pdf, 2011, 1-7.
- [5] DIN EN 12873-1: Einfluss von Materialien auf Trinkwasser - Einfluss infolge der Migration - Teil 1: Prüfverfahren für fabrikmäßig hergestellte Produkte aus oder mit organischen oder glasartigen Materialien (Emails/Emailierungen), Ausgabe Feb. 2014.
- [6] Gabler, R.; Hegde, R.; Hughes, D.: Degradation of High Purity Water on Storage, Journal of liquid Chromatography 6 (13) 1983, pp: 2565-2570.
- [7] 4MS: Acceptance of metallic materials used for products in contact with drinking water – Procedure for the acceptance of metallic materials for PDW, http://www.umweltbundesamt.de/wassere/themen/downloads/trinkwasser/4ms_scheme_for_metallic_materials_part_a.pdf, 2011, 1-31.
- [8] EN 15664-2: Influence of metallic materials on water intended for human consumption - Dynamic rig test for assessment of metal release - Part 2: Test waters; 2010.
- [9] UBA: Richtlinie zur chemischen Analyse Bestimmung von Elementgehalten in Umwelt-proben durch ICP-MS, http://www.ime.fraunhofer.de/content/dam/ime/de/documents/AOe/UPB_SOP_ICP-MS_de.pdf, Ausgabe: Feb. 2011.
- [10] Council Directive 84/500/EEC of 15 October 1984 on the approximation of the laws of the Member States relating to ceramic articles intended to come into contact with foodstuffs, 1984.
- [11] EFSA: Scientific Opinion on Lead in Food, <http://www.efsa.europa.eu/de/search/doc/1570.pdf>, EFSA Journal 2010; 8(4):1570, 1-151.
- [12] BfR: Aufnahme von Umweltkontaminanten über Lebensmittel; http://www.bfr.bund.de/cm/350/aufnahme_von_umweltkontaminanten_ueber_lebensmittel.pdf, 2010, 1-60.
- [13] Trinkwasser VO 2001: Verordnung über die Qualität von Wasser für den menschlichen Gebrauch (Trinkwasserverordnung – TrinkwV 2001) vom 21. Mai 2001, BGBl I 959-980.
- [14] Commission Regulation (EC) No 1881/2006 setting maximum levels for certain contaminants in foodstuffs; 2006.
- [15] Commission Regulation (EC) No 629/2008 amending Regulation (EC) No 1881/2006 setting maximum levels for certain contaminants in foodstuffs; 2008.

- [16] Agilent: Agilent 710 Series ICP-OES - Specifications, Accurate, Robust, Reliable. 2010, 1-8.
- [17] OMCL Network & HealthCare (DBO): specific release limits (SRLs) during the transitional period to legislation, letter, 2013.
- [18] Cadmium in food – Scientific Opinion of the Panel on Contaminants in the Food Chain; <http://www.efsa.europa.eu/de/scdocs/doc/980.pdf>, EFSA Journal (2009) 980: 1-139.
- [19] Daunderer, M.: Handbuch der Umweltgifte, Hüthig Jehle Rehm Verlag ,Ausgabe 6/2006.
- [20] EFSA: Statement on tolerable weekly intake for cadmium, <http://www.efsa.europa.eu/de/efsajournal/doc/1975.pdf>, EFSA Journal (2011) 9(2):1975, 1-19.
- [21] Biesalski, H.K.; Fürst, P.; Kasper, H.; Kluthe, R.; Pöler, W.; Puchstein, C.; Stähelin, H.B.: Ernährungsmedizin, 3. Aufl. 2004, Thieme, Stuttgart, 178.
- [22] WHO: Concise International Chemical Assessment Document 69 - COBALT AND INORGANIC COBALT COMPOUNDS, <http://www.who.int/ipcs/publications/cicad/cicad69%20.pdf?ua=1>, World Health Organization, 2006, 11.
- [23] RIVM: report 711701 025 - Re-evaluation of human-toxicological maximum permissible risk levels, <http://www.rivm.nl/bibliotheek/rapporten/711701025.pdf>, march 2001, RIVM, the Netherlands, 58-61.
- [24] Paley, K.R.; Sobel, E.S.; Yalow, RS: Effect of oral and intravenous cobaltous chloride on thyroid function, J. Clin. Endocrin. Metabol. 18 (1958), 850 – 859.
- [25] [Kaim](#), W.; Schwederski, B.: Bioanorganische Chemie, 4. Auflage, Teubner, 2005.
- [26] Wikipedia: Urease, <http://de.wikipedia.org/wiki/Urease>
- [27] Daunderer, M.: ecomed Medizin - Nickel, Verlagsgruppe Hüthig Jehle Rehm GmbH, 2006.
- [28] Koch, R.: Umweltchemikalien: Physikalisch-chemische Daten, Toxizitäten, Grenz- und Richtwerte, Umweltverhalten, Wiley & Sons 2008, S.291.
- [29] U.S. Geological Survey: Mineral Commodity Summaries, 2014.
- [30] Bekanntmachung des UBA- Nickel: Bundesgesundhbl. – Gesundheitsforsch. – Gesundheitsschutz 44 (2001) 12, S.1243-1248.
- [31] Jürgen Strutz, Olaf Arndt, Wolfgang Mann: Praxis der HNO-Heilkunde, Kopf- und Halschirurgie, Thieme, 2001, S.386.
- [32] Sunderman, F. W. Jr.: A review of the metabolism and toxicology of nickel. Ann. Clin. Lab. Sci. (1977) 7, S.377-398.
- [33] Policy statement concerning metals and alloys: Guidelines on metals and alloys used as food contact materials, Council of Europe 2002, S.81-88.
- [34] NiDI (1994): Status report. Nickel Development Institute. SR-0003.
- [35] Policy statement concerning metals and alloys: Guidelines on metals and alloys used as food contact materials, Council of Europe 2002, S.44.
- [36] Ohnesorge F.K.: Toxikologische Bewertung von Arsen, Blei, Cadmium, Nickel, Thallium und Zink, Fortschritt-Berichte VDI. Reihe 15, Umwelttechnik, Düsseldorf (1985) 38.

[37] Commission staff working paper: Discussion of options and questionnaire to prepare the possible update and extension of the legislation on Ceramic Food Contact Materials - possibly including Glass and other Glazed materials, 2011.

[38] lex.referata.com/wiki/bor

[39] Vermeulen, F.: Homöopathische Substanzen - vom Element zum Arzneimittelbild, Georg Thieme Verlag, 2004, 78-80.

[40] Expert Group on Vitamins and Minerals: Part 3 Trace Elements – Risk assessment boron, <http://cot.food.gov.uk/committee/committee-on-toxicity/cotreports/cotjointreps/evmreport>, 2003, 164-171.

[41] ECHA: Draft background document for Disodium tetraborate, anhydrous, <http://echa.europa.eu/documents/10162/4a3e7046-abf0-4361-8a9a-28cb2227d480>, 2014, 1-5.

[42] ECHA: Draft background document for Boric acid, <http://echa.europa.eu/documents/10162/8ed82613-b492-4868-bcc0-3fab8a1e9ed9>, 2014, 1-4.

[43] Sayli, B.S., Tuccar, E., Elhan, A.H. (1998). An assessment of fertility in boron-exposed Turkish subpopulations. Reproductive Toxicology 12, 297-304.

[44] Meacham, S.; Karakas, S.;Wallace, A.; Altun, F.: Boron in Human Health: Evidence for Dietary Recommendations and Public Policies, The Open Mineral Processing Journal, 2010 (3), 36-53.

[45] BfR: Zusatz von Borsäure oder Borax in Nahrungsergänzungsmitteln, Gesundheitliche Bewertung Nr. 005, http://www.bfr.bund.de/cm/343/zusatz_von_borsaure_oder_borax_in_nahrungsergaenzungsmitt.pdf, 2006, 1-24.

[46] Price, C.J., Strong, P.L., Marr, M.C., Myers, C.B., Murray, F.J: Developmental toxicity NOAEL and postnatal recovery in rats fed boric acid during gestation, Fundamental and Applied Toxicology (32) 1996, 179-193.

[47] Schuchardt, J.P., Hahn, A.: Bedeutung der Spurenelemente Chrom, Mangan und Molybdän in der Ernährung des Menschen, Schweizer Zeitschrift für Ernährungsmedizin, 2011 (1), 25-33.

[48] Emsley, J.: Sonne, Sex und Schokolade – Chemie im Alltag II, Wiley-VCH, 1999, 63-64.

[49] Daunerer, M.: Klinische Toxikologie – 158. Erg.-Lfg. Molybdän, 2002, 20.

[50] SCF. Opinion of the Scientific Committee on Food on the tolerable upper intake level of molybdenum. Document SCF/CS/NUT/UPPLEV/22 Final. Brüssel 28.11.2000. http://ec.europa.eu/food/fs/sc/scf/out80_en.html