Food Contact materials in Europe: a challenge for the enamel industry

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Introduction

The European Directive 84/500/EEC of October 1984, relating to ceramic articles intended to come into contact with foodstuffs, was one of the first directives dealing with potential release of substances during contact with food. This directive specifies the migration limit of Pb and Cd from glass, ceramics or porcelain/vitreous enameled articles. The European standard EN1388-2 was created to standardize the determination of the release of those elements from silicate surfaces in acetic acid at room temperature.

Since 1984, directives have been made for other materials in contact with food. A lot of research has been done on the influence of other elements on the human metabolism and new analytical instruments with lower detection limits for metals have become available.

In 2012, the European Commission decided to have a complete revision of the directive on ceramic articles. In a first phase, the testing method and the existing limits for Pb and Cd will be revised. And in a second phase, also other metals could be included and the directive could be extended to glass, enamels and technical ceramics.

Existing directives and regulations for porcelain enamel used as FCM

The main porcelain enameled articles that are used to come into contact with foodstuffs are tableware, cookware and baking trays in kitchen ovens.

For the porcelain enamels that are used as Food Contact Material (FCM), there are a lot of European Regulations / Directives that have to be fulfilled. The three most known ones are :

- Regulation 1907/2006/EC: All chemicals used in the enamels are covered by REACH (Registration, Evaluation and Authorisation of CHemicals). This has a big impact on the use of a lot of elements in porcelain enamels, especially on the use of Ni in the glass matrix of the enamel frits.
- Directive 2002/95/EC: For the enamels used in kitchen ovens, which are electrical and therefore classed as electronic equipment, the RoHS Directive (Restriction of Hazardous Substances) restricts the use of hazardous substances in order to facilitate the recycling. For the inorganic elements, the use of Pb, Cd, Cr6+, Hg is very much restricted/forbidden.
- Directive 84/500/EEC, which has been amended in 2005 (2005/31/EC): This specifies a migration limit of Pb and Cd from glass, ceramics and porcelain enameled articles during contact with food.

Aside of these comprehensive directives/regulation, there are also two other general regulations that have to be respected: regulation 1935/2004/EC “framework regulation on materials and articles intended to come into contact with food” and regulation 2023/2006/EC “good manufacturing practice for materials and articles intended to come in contact with food”. These two regulations put the responsibility on the manufacturer, who is obliged to manufacture FCM in compliance with good manufacturing practice (GMP) so; that they do neither release substances into food in quantities which could endanger human health; bring about an unacceptable change in the composition of the food; or bring about deterioration in the organoleptic characteristics thereof. GMP in accordance with Regulation 2023/2006/EC requires manufacturers to operate documented quality assurance systems and quality control systems. Quality assurance covers the selection of starting materials and the control of all manufacturing operations in view of a safe final material. This implies that manufacturers need to know the toxicological hazard posed by the substance and the potential exposure of the consumer by the FCM application. But not all manufacturers have all this knowhow, and as there are no specific parameters, criteria nor migration limits given in these regulations, compliance cannot be verified neither. This was clearly demonstrated by some incidents that took place, e.g. with printing inks used as FCM.

For that reason, the European Commission Directorate General for Health and Consumers (DG SANCO), has started the initiative to ensure a uniformly high level of food safety for FCM throughout the EU and their free trading in the internal market, by setting out where necessary minimum specific requirements (SANCO- E6, 07/2012). Although the focus will be on those materials for which no specific EU legislation is existing and for which there is a high risk from transfer of its constituents into food (esp. printing inks, coatings, silicones, adhesives, rubber, metals, paper & board), they also started a revision of the existing EU directive 84/500/EEC !

Revision directive 84/500/EEC

The revision can be separated into 9 phases, of which the most important ones are setting new limits for Pb and Cd, setting limits of other metals and reviewing the testing method.

The values for Pb and Cd that DG SANCO has been given as “discussion starting values” are very drastic (see table 1). Not only if we compare them with the existing limits dating back to 1984, but also if we compare them with more recent legislation outside Europe. The limits for Pb and Cd would be 10 times lower than the strictest “warning limits” which currently exists in the world , i.e. the Californian Prop.65, which requires to put a warning on the article if migration exceeds the warning limit (the article may still be sold).

		Pb	Cd
Existing European directive 84/500/EEC	Articles that cannot be filled or with small depth (<25mm)	0.8 mg/dm²	0.07 mg/dm²
	Articles that can be filled with depth >25mm	4 mg/l	0.3 mg/l
	Cook ware with vol. > 3 l	1.5 mg/l	0.1 mg/l
DSV	Hollow ware	0.01 mg/kg food	0.005 mg/kg food

Table 1: existing migration limit of 84/500/EEC and new DSV (Discussion Starting Values)

A list with all discussion starting values (DSV) for in total 21 elements is given by DG SANCO (see table 2). Those values are based on available toxicological studies, but should not be seen as proposed migration limits. To come to migration limits other pertinent factors will be taken into account, which shall be part of the discussion with all stakeholders. And once the migration limits for ceramics and porcelain enamels are determined, an adaptation period with gradual transition of the limits can be defined.

In table 2, also the migration limits for the metals & alloys (EDQM, 2013) and for plastics intended to come into contact with food (regulation 10/2011/EC) are given. For some elements, there are big differences between the three values. It is clear that depending on the material, the DSV can easily be reached for some elements (and even lower migration limits are possible) while for other elements, the DSV cannot be reached at all. For plastics, the migration limit for Zn is almost 17 times higher than the DSV. For metals, the migration limit for Fe is 16 times higher and even the limit for Ni is almost doubled. At the same time, it seems possible to lower the limit for Co with a factor 4 and for Li with a factor 12.5. For porcelain enamels, it is especially the DSV for Co that is much too low and will have to be increased (see test results further on). The fact that for this element the migration out of metallic and plastic FCM is very low makes it acceptable to increase the migration limit for porcelain enameled cookware, because people eat food prepared in different FCM. So, the total daily intake will not become too high.

	DG SANCO DSV (mg/kg)	CoE – **metals & alloys** SRL (mg/kg)	Ratio metal SRL/DSV	10/2011/EC, annex 2 – **plastics** SML (mg/kg)	Ratio Plastic SML/DSV
Al	1	5	**5 X**	-	
Ba	1	1.2	**1.2 X**	1	1 X
Co	0.084	0.020	<u>0.24 X</u>	0.050	<u>0.59 X</u>
Cr	0.1 (soluble) 10 (insoluble)	0.25		-	
Cu	1	4	**4 X**	5	**5 X**
Fe	2.5	40	**16 X**	48	**19.2 X**
Li	0.6	0.048	<u>0.08 X</u>	0.6	1 X
Mn	0.4	1.8	**4.5 X**	0.6	**1.5 X**
Sb	0.04	0.04	1 X	-	
V	1.2	0.01	<u>0.008 X</u>	-	
Zn	1.5	5	**3.33 X**	25	**16.67 X**
Pb	0.01	0.01	1 X	-	
Cd	0.005	0.005	1 X	-	
Sn	50	100	**2 X**	-	
As	0.018	0.002	<u>0.11 X</u>	-	
Ag	0.05	0.08	**1.6 X**	-	
Hg	0.009	0.003	<u>0.33 X</u>	-	
Mo	0.01	0.12	**12 X**	-	
Ni	0.072	0.14	**1.94 X**	-	
Se	0.024	-		-	
Tl	0.0004	0.0001	<u>0.25 X</u>	-	

Table 2: DG SANCO Discussion Starting Values (DSV) for migration limits of 21 metals, the Specific Release Limits (SRL) specified by the Council of Europe for metals and alloys and the Specific Migration Limits (SML) of the European regulation 10/201/EC on plastics. (all limits in mg/kg food or food simulant)

Also the testing method has been reviewed. The current testing method of 84/500/EEC (4% acetic acid, 24h±30 min, 22°C±2°C) is applied worldwide and acknowledged as being designed to be significantly over predictive of the actual leaching into food due to the aggressive nature of 4% acetic acid compared to real foods. All European and

International standards dealing with release of elements out of amorphous (glass) structures are using this testing method. For porcelain enamel, the test method is described in ISO4531-1/2 (1998) and EN 1388-2 (1995).
A new study was made by European Union Reference Lab (EURL) to compare the release of elements out of ceramic hollow-ware into the benchmarking foodstuff tomato sauce (pH3.5), and into the food simulants acetic acid (4%,20°C,24h) and citric acid (0.5%,70°C, 2h) (Peltzer, Beldi, & Simoneau, 2014). The conclusions confirmed that both food simulants presented higher migration than the benchmarking food. So, both simulants are giving a worst case scenario. Because of the facts that tests at room temperature have significant advantages over tests at elevated temperature and that the acetic acid test is used worldwide, the decision has been taken to keep using the 4% acetic acid as food simulant.
For porcelain enamels, the migration in 0.5% citric acid and 4% acetic acid is very similar (see results further on).

A lot of studies (Marshall & Roberts, 1978) have clearly shown that there is no increase in migration over time linked to the possible ware of the surface of the porcelain enamel or ceramics, which is a fundamental difference compared to e.g. plastics. And recent studies show a very sharp drop in migration when a ceramic surface is washed and tested for a second and third time. Performing the test on a new piece is therefore not relevant, because the concluded migration levels are significantly higher than levels found with cook ware / baking trays, used repeatedly in real life during many years. In the second part of this paper, we show a lot of results on porcelain enameled articles, which clearly demonstrate this drop in migration.

Migration tests on porcelain enamel

Samples and migration procedure:

In order to study the migration of metal ions out of a porcelain enamel coating on steel into food, 5 different enamel coatings have been tested, using as food simulants acetic acid 4% and citric acid 0.5% at different temperatures (20°C till 100°C) and times (30 minutes till 3 days). The boiling tests were done with a boiling reflux of 8ml/3 min, corresponding with EN ISO28706-2.

The used porcelain enamels are commercial products which are industrially used and which were fired using standard firing conditions:

- Formulation A (Blue), B (Black) and C (Grey) are direct on enamels with a decreasing chemical resistance after EN ISO28706-1 (A is better than B, B is better than C). All formulations contain CoO and NiO as adherence oxides. Direct on enamels are typically used for baking trays and cavities in kitchen ovens. Using a ground + cover coat would create problems due to the higher enamel layer thickness.
- Formulation D and E are very resistant cover coats (class AA). Form D is Ti-white and Form E is transparent.

As no decoration (screen print, transfer paper, etc.) is used on the porcelain enamel side that is in contact with the food, only non-decorated enamel surfaces were tested.

Enameled steel sheets were used for the trials. Different test equipment was used for the non-boiling and for the boiling tests (see figure 1), causing a different volume/surface ratio. For that reason, the analyzed concentrations were first calculated in mg/dm² and then recalculated in mg/l using a realistic volume/surface ratio of 1liter pro 2.5 dm². This corresponds with a casserole with diameter 22 cm, filled for 14cm. And this corresponds also with a piece of meat of 1kg with contact area of 20 X 12.5 cm on a baking tray in the oven.

Figure 1: used test equipment to test the migration at 20°C-40°C-70°C (6 migration tests together) and to test the migration into boiling food simulant (test equipment of EN ISO28706-2).

The migration equipment and the food simulants were preheated to the migration temperature before filling. Samples of 15 ml were taken at specific intervals and blanco solution (at the right temperature) was added to ensure the same volume/surface ratio was used. The drop in concentration caused by these samplings (adding the blanco solution) was taken into account.

Blanco trials showed that no relevant migration from the test equipment occurs. The analyzed values of the blanco trials were NOT distracted from the analyzed test results. All analyses were done with ICP-OES. The elements As, Ag, Hg, Se and Tl have not been studied.

Results at room temperature (= 20°C):

The difference in migration into acetic acid and citric acid was studied for the migration of the critical element Co. From figure 2, one can conclude that there are no relevant differences between both food simulants in the range of 2 ppb to 2 ppm. These results confirm the results of EURL done on ceramics. All other results of this paper are based on migrations into acetic acid.

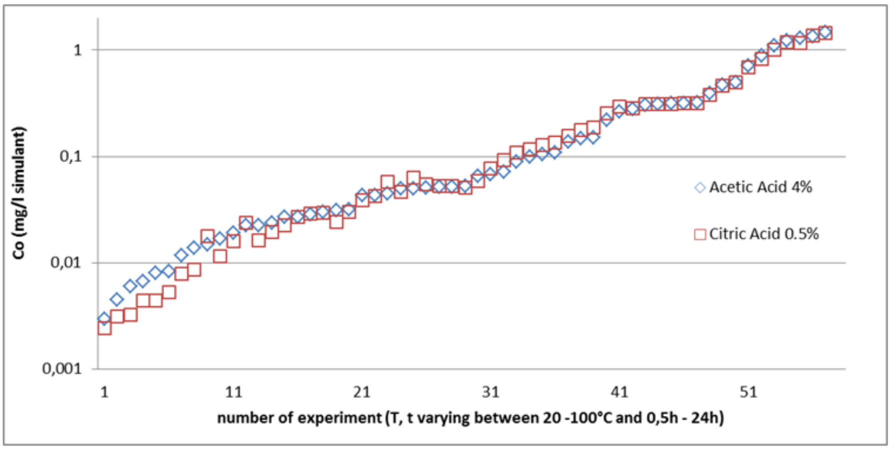


Figure 2: Migration of Co into food simulant acetic acid and citric acid.

In order to study the migration and migration speed of the different metals, following migration times were used:

- 0.5h, 1h, 1.5h, 2h, 2.5h, 3h, 6h, 24h=1day=M1 (no renewal of solution)

- M2 = M1+1day; M3 = M2+1day (renewal of solution + drying/wiping the enamel surface after 1day and 2 days)
- M1* = 1day after preconditioning. The precondition at room temperature was done with 10% acetic acid during 5h at 20°C with the purpose to compare M1* with M3.

The DSV for cover coat enamels (form. D and E) were never exceeded. The white cover coat showed however relative high migration of Al during the first hours of migration (see fig.3). The used frit contains 1.5% Al_2O_3 with Al in the clay and kaolin used as a milling addition. The migration speed of Al decreases very fast: from 0.88 mg/l.h during the first 30 min to 0.005 mg/l.h during the third day (migration period M3).

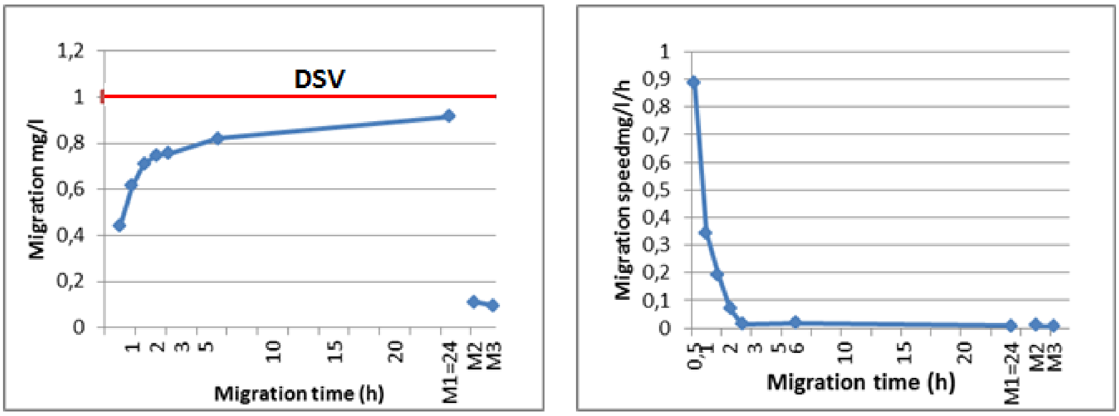
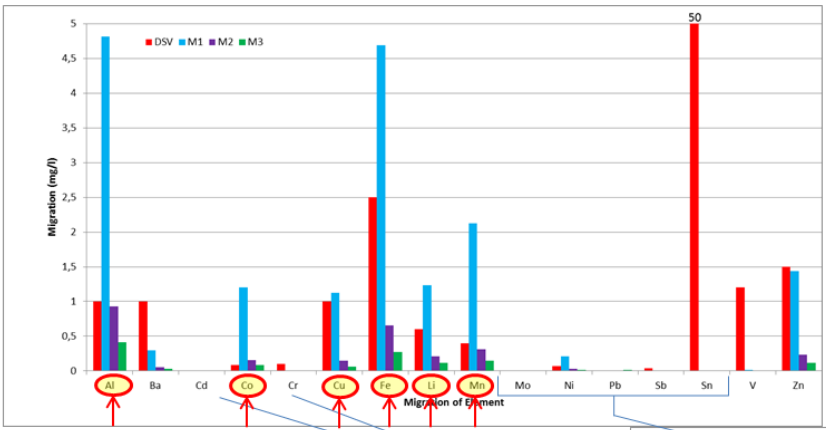


Figure 3: Migration of Al out of white cover coat (form.D) into acetic acid 4% at 20°Ct

For the direct on enamels, there is a clear relation between the chemical resistance after EN ISO 28706-1 and the migration of metals into the acetic acid. Formulation A fulfills all DSV from the first migration period (M1 = first 24h) onwards, form. B exceeds the DSV of Co and Ni during M1, and form C exceeds the DSV of Al, Co, Cu, Fe, Li and Mn during M1. The migration values during migration period 3 (M3) are all below DSV. Figure 4 gives an overview of the migration of all elements during M1-3 for form. C.



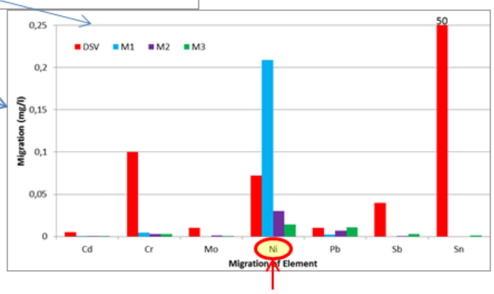


Figure 4: Migration of metals out of direct on enamel C (limited chemical resistance) during 3 consecutive days (M1-2-3) compared with DSV

Also for the direct on enamels, there is always a very important decrease in migration speed for all elements during the first hours. Figure 5 gives as example the migration speed for Co out of formulation A and C.

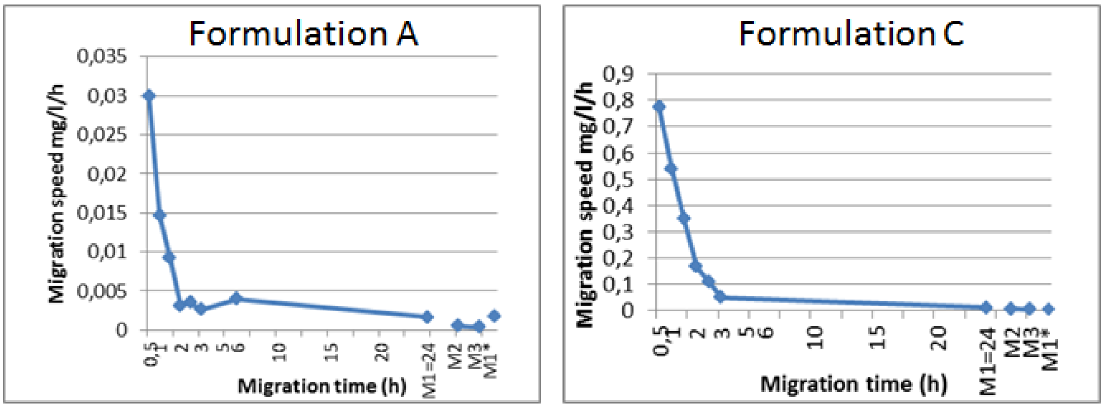


Figure 5:Migration speed of Co out of direct on enamel formulations A and C

On this figure, you also can notice that the migration speed during the 24h migration after preconditioning (M1*) is higher or equal to the migration during the third migration period of 24h (M3). This was the case for 86% of all analyses.

Results at elevated temperatures:

There is of course an important influence on the temperature on the migration. But one has to take into account that most of the cooking/baking is done within 1h! Also at elevated temperatures, we found a very important decrease in the migration after a "preconditioning" with 4% acetic acid of 2h at the same elevated temperature, as you can see in figure 6 for the migration of Co out of formulation A. But even after the preconditioning, the Co Migration exceeds the DSV (0.085mg Co/l) after 1.5h at 70°C and after 0.5h at 100°C. After preconditioning, apart from Co, no other element migrates more than DSV during 1h. The migration of Ni and Ba does become higher than DSV, but only at longer migration times: for Ba after 1.5 h at 100°C and for Ni after 2.5h at 100°C.

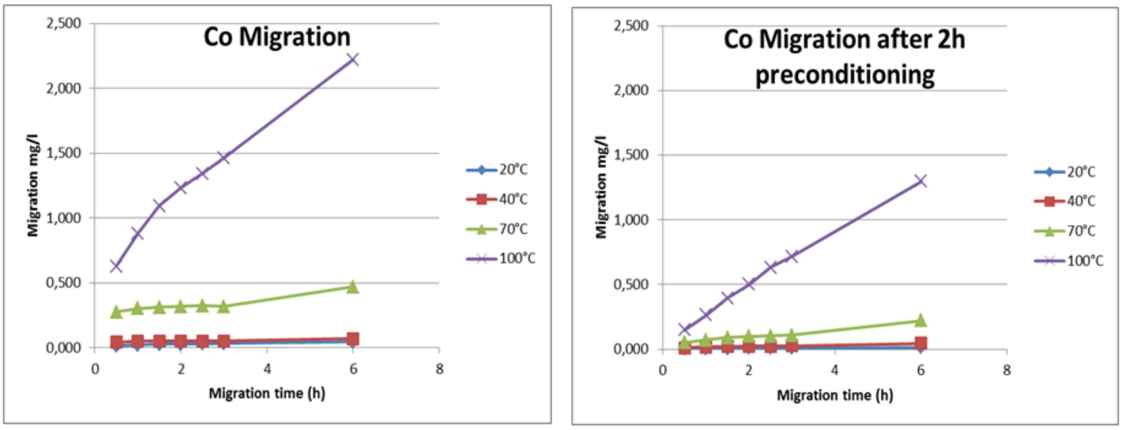


Figure 6 : Migration of Co out of direct on enamel formulation A

Figure 7 gives the migration of all elements out of formulations B and C during 1h at elevated temperatures and during 1h after a preconditioning of 2h at the same temperature. Due to the preconditioning the decrease can clearly be seen. Without preconditioning, the DSV are exceeded for the elements Al, Ba, Co, Cu, Fe, Li, Mn, Ni, Sb and Zn. After the preconditioning, the DSV is exceeded at 100°C for the elements Co and Ni (form B) and Al and Co (form C).

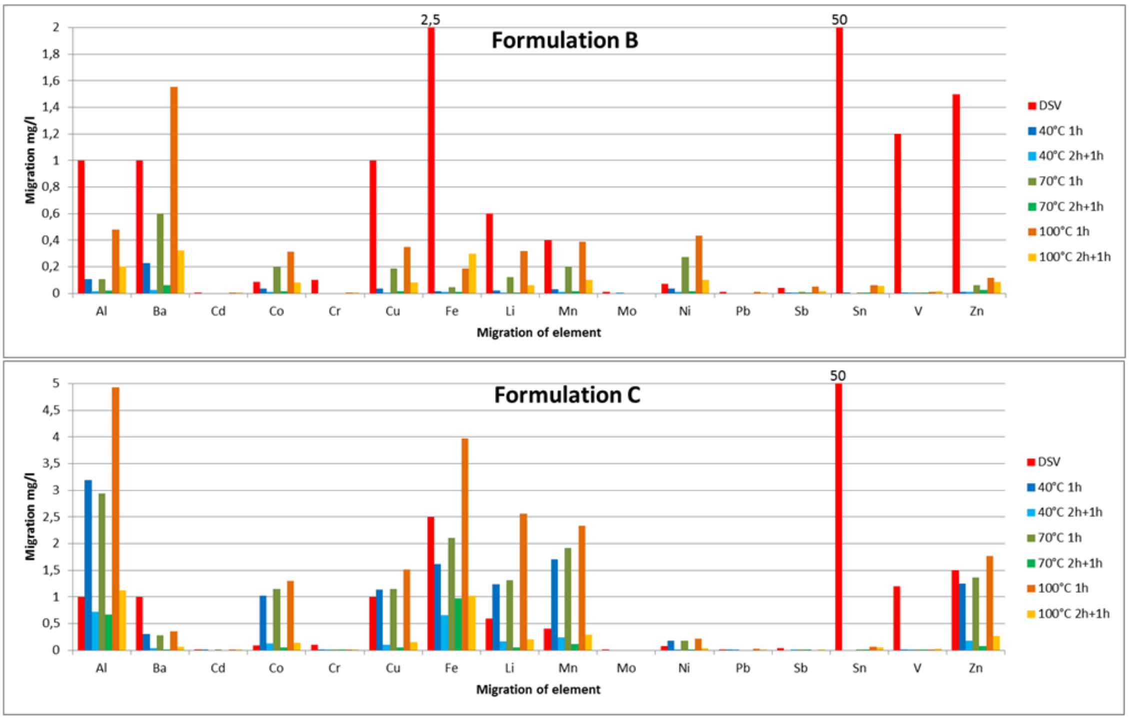


Figure 7 : Migration of all elements out of direct on enamel form B and C, compared with DSV

For the white cover coat, the DSV of Al is exceeded during 1h at 100°C, but the migration of all elements are below DSV after preconditioning. And for the transparent cover coat, the DSV of Mo is exceeded during 1h migration at 100°C (Mo is added to the transparent frit to improve surface aspect), but also here, all migration levels are below DSV after preconditioning.

Conclusions

In the coming years, a stringent migration regulation for ceramic articles / glass / porcelain enamel into contact with foodstuffs will be agreed upon between the European Commission and the industry. The best scenario would be to keep using the test method at room temperature for 24h. Porcelain enamel is mostly used at elevated temperatures for the cooking/baking of the food, but the migration time is much lower than 24h. This article clearly shows that most migration takes place during the first hours. As cookware is used for many years, an appropriate preconditioning would be realistic to simulate migration during a steady state daily use of the cookware. Even then, the migration limits of some essential elements for porcelain enamels, (especially Cobalt) will have to be brought to achievable levels for the direct on enamels.

This article was written in Sept.2014 and published in May 2015

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