RELEASE OF METALS FROM CERAMIC ARTICLES IN CONTACT WITH FOOD: EFFECTS OF SIMULANT, PH, TEMPERATURE, CONTACT DURATION AND MIGRATION TIMES

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Abstract–Directive 84/500/EEC (a regulation which specifies migration limits of lead (Pb) and cadmium (Cd) from ceramic articles intended to come into contact with food), is currently under revision by the European Commission, both for defining new *Specific Migration Limits* (SMLs) for Pb and Cd and for considering an extension to other elements, with validated testing methods. In this study, we investigated how much various parameters (nature of acid as simulants, pH, temperature, contact duration and repeated exposure) influence the release of metals from decorated ceramic articles during their use. The amounts of a series of 17 elements (including lithium, aluminium, chromium, barium, lead and cadmium) leaching from ceramic articles were measured simultaneously by ICP-OES. For each piece of ceramic vessel under testing: (1) the amounts of metals released rose with a decrease in pH (in the range-2.05-2.97) in a non-linear mode, but this growth will not continue as much as the rise of the amount of hydrogen ions; (2) The amounts decreased with the repeated migration tests. Detailed studies of migration kinetics and behaviour at three temperatures (20°C, 40°C and 60°C) confirmed a rise with longer contact time, according to a logarithmic curve. Our data indicate that it is necessary to revise the Directive beyond the case of Pb and Cd, and to define SMLs for the potential migration of a series of metals. The test conditions with respect to all the parameters studied are discussed.

Keywords: *ceramic articles; food contact materials; metal release; parameters; chemical risks*

1. INTRODUCTION

Ceramic articles are commonly used in food preparation, cooking, serving and storage. When ceramic articles come into contact with foodstuffs, a release of metals may endanger the health of consumers.

Migration of metals depends on several parameters, including the characteristics and state of the specimen (glaze composition, oxides and firing temperature) and conditions of use or of testing (pH of the solution, migration temperature, contact time etc.). The composition of glaze will influence the leaching of metals especially for lead.

Somogyi et al (1999) has shown that the more the simulant acid, the higher the metal release is. A decrease in pH can promote the release of metals and a linear relationship has been observed (Bolle et al, 2012; Demont et al, 2012). However, studies also showed that 4% acetic acid represented the strongest extract capability, followed by 6%, 8% and 2% acetic acid (Abou-Arab, 2001). Some studies (Yoon et al, 1976; Somogyi, 1999; Bolle et al, 2012) have reported an exponential relation between migration values and temperature, whereas others indicated a linear relationship of migration values as function of temperature (Demont et al, 2012; Dong et al, 2014). With regard to the relationship between migration and contact duration, either an exponential or a linear relationship has been observed (Dong et al, 2014; Demont et al, 2012).

Directive 84/500/EC, a European level regulation, sets the requirements for ceramic articles intended to come into contact with foodstuffs. It regulates the specific migration limits (SMLs) of lead (Pb) and cadmium (Cd) and the test conditions (Directive 84/500/EC). The commission is currently revising this Directive in order to reduce existing limits for Pb and Cd, to extend the policy to other metals and to optimize the test methods.
In this context and with reference to Bolle's work (2013), this study aimed at investigating testing parameters which can influence the release of metals from ceramic articles after their manufacture. This work studied the leaching of elements under controlled external conditions of pH, food simulants, temperature, contact duration and migration times. Various tests with acetic or citric acid have been performed in a range of pH from 2.05 to 2.97, representing more aggressive extracting solutions than the conditions used in other studies. Moreover, the kinetics of metal release from ceramic articles at different temperature has been explored for a better understanding of the migration behaviour. Due to the fact that ceramic articles present on the market are designed for repeated use in daily life, we also performed consecutive migration tests. In addition, besides Pb and Cd, the leaching of Lithium (Li), Beryllium (Be), Aluminum (Al), Vanadium (V), Chromium (Cr), Manganese (Mn), Iron (Fe), Cobalt (Co), Nickel (Ni), Copper (Cu), Zinc (Zn), Arsenic (As), Molybdenum (Mo), Antimony (Sb), Barium (Ba), Silver (Ag) and Tin (Sn) is evaluated in support of the European Commission objectives to extend the "Ceramic Directive" to other metals.

2. EXPERIMENTAL

2.1. Samples and instrument

Decorated ceramic dinnerware articles for purpose of contact with food were bought from the Belgian market, with three replicates for each subset of tests. All the analysis was carried out with an Inductively Coupled Plasma Optical Emission Spectrometer (ICP-OES) (Perkin-Elmer, Optima 8300, USA).

2.2. Influence of simulant and pH

Testing samples were filled with either acetic acid (AA) or citric acid (CA) as the leaching agent. The concentration and pH of test simulants were listed in Table 1. The samples were left at ambient temperature for 24 hours.

Table 1.Concentration and pH of simulants.

Simulant	pH
0.25% acetic acid	2.97
4% acetic acid	2.48
20% acetic acid	2.05
0.5 g/L citric acid	2.97
5 g/L citric acid	2.48
50 g/L citric acid	2.05

2.3. Influence of migration times

After the first migration, the samples were rinsed with Milli-Q water and dried. The same procedure was repeated for further migration test up to 10 successive exercises.

2.4. Influence of temperature and migration kinetics

Samples filled with 4% acetic acid or 5g/L citric acid were placed in the oven at a temperature either of 20 or 40 or 60 °C. Aliquots of 5 mL were taken at given time intervals (30, 60, 90, 120, 180, 240, 360, 480 and 1440 min).

3. RESUTLS AND DISCUSSION

3.1. Influence of simulant

In spite of a similar appearance of tested samples, significant differences could be observed for the release of metals. For some pieces, the release of Co, Zn and Pb was extremely high and could reach levels about 100 times than the amounts released by other replicates. A scrutiny of these pieces revealed slight differences in the shades of the blue colour, suggesting that pieces in the same series have different compositions. Such heterogeneity can be a confounding factor in distinguishing differences in metals extraction capabilities of simulants.

That one same label may include pieces manufactured in different ways has to be addressed in revision the directive and risks control procedures.
The results below will consider acetic acid (AA) and citric acid (CA) groups as distinct samples.

3.2. Influence of pH

The amounts of metals released rose with a decrease in pH, and the increase varied from elements. These amounts of metal released from samples with three levels of acid concentration for AA and CA were shown in Figure 1. In the AA group, a higher acidity of the simulant induced a larger release, especially for cobalt and zinc; whereas in the CA group, the amounts of metals released were not significantly different at the three acidity levels.
The iron exchange mechanism provides a plausible explanation for these observations: the leaching of metals is driven by hydrogen or hydronium ions from attacking agent, higher acidity dissociates larger amount of hydrogen or hydronium ions, which displaces greater quantity of metals. Therefore, a larger amount of metals is extracted with 20% acetic acid. In the case of the CA group, the added elements in samples are not as much as that in acetic acid group, and thereby 0.5g/L citric acid can extract approximately all the elements in samples, which justify the increase of acidity in citric acid group did not result in greater quantity of metals.

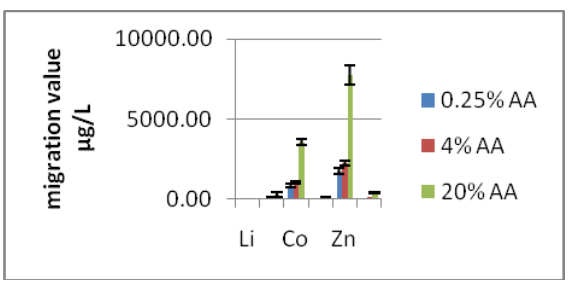

Figure 1a.Migration of metals with acetic acid.

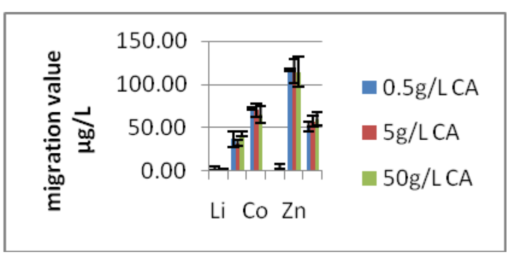

Figure 1b.Migration of metals with citric acid.

3.3. Influence of migration times

A decrease of release from ceramic articles was observed with consecutive test irrespective of simulant type. The first migration test presented the largest release of metals, after which the release of metals from ceramic articles remained at a much lower value (Figure 2).
The lower release of metals after repeated contact may result from the formation of a silica surface layer acting as barrier, preventing progressive diffusion from the inner layer (White 1992).

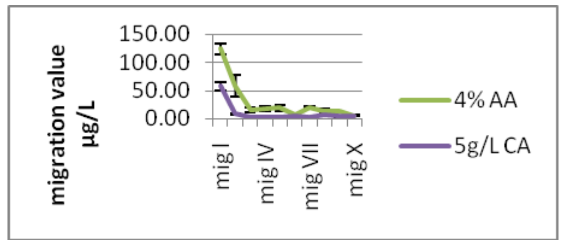

Figure 2. Migration of Pb after consecutive test with acetic acid and citric acid

3.4. Influence of contact duration and kinetics

The amounts of released metals were plotted as a function of time to represent migration kinetics. All the elements present a similar behaviour: the amounts of metals leaching from ceramic pieces increased with contact time.
The relationship between migration values and contact time fits a logarithmic regression was obtained (Figure 3) i.e. the release of metals increased considerably at the first place and slowed down afterwards, up to a marginal level.

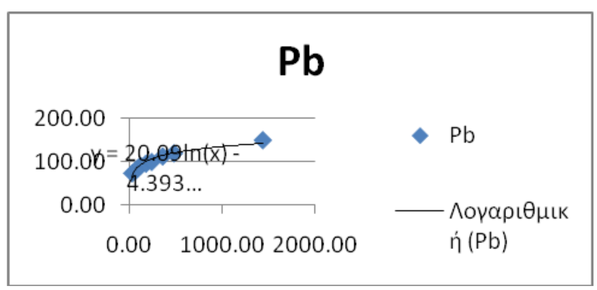

Figure 3. Migration of lead at 20°C with 4% acetic acid

The migration activity found in this lot indicates that the majority of migration occurs before the first 30 minutes of contact and that, for most elements, the release of metal rises more slightly after 180 min. The migration kinetics observed in this study is consistent with previous studies (Bolle et al, 2012; Demont et al; 2012).

3.5. Influence of temperature

The amounts of metals leaching in simulant as a function of contact time at three temperatures were compared. An increase of temperature resulted in a rise of migration level.

Figure 4 showed the migration kinetics at three temperatures in the case of lead. Tests data show that the rise of temperature between 20°C and 40°C affects release of lead much more than that between 40°C to 60°C. Indeed, the increase in migration level after 240min became very slight, again a logarithmic fit between migration values and contact time.

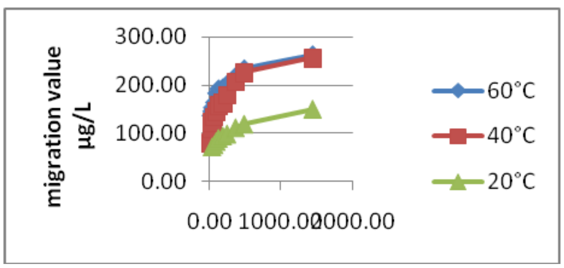

Figure 4. Migration of Pb at three temperatures

4. CONCLUSIONS

This study investigated various parameters which can influence the release of metals from ceramic articles after their manufacture, including pH, food simulants, temperature, contact duration and migration times. For this purpose, it used a series of ceramic pieces bought from the same store on the Belgian market.

Metal release grew with decreasing pH. Successive migrations generated a drop of release.

Migration kinetics appeared to follow a logarithmic curve. Higher temperatures promoted the release of metals from ceramic wares, although the relation of migration values as a function of temperature remains to be further determined.

Work is in process to further assess the extent and characteristics of multiple metals migrations related to the use of ceramic ware under various conditions, in the context of the revision of Directive84/500.

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