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# Lead Migration from Ceramicware in Contact with Foodstuff: Effect of Glaze, Temperature, pH and Food Simulant

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**Abstract:** Lead (Pb) release from non-conforming flatwares and artisanal hollowwares was measured by ICP-AES. Influence of acidic beverages (tomato juice, vinegar and lemon juice), food simulants (acetic acid, citric acid, and malic acid) at pH (2.37-5.00), contact time (t) (30 min-2 days), temperature (T) (20 °C-90 °C), and glaze were investigated. Pb release was lowest in tomato juice and highest in lemon juice (t = 24 h; T = 22 °C). In acetic acid 4% (v/v) Pb release was 14% less than in lemon juice. Variability between the flatwares used for experiments in lemon juice and acetic acid 4% (v/v) corresponds to 3.48% and 7.03% respectively. According to the set of experiments where three food simulants were compared, it appeared that acetic acid, citric acid, and malic acid have the same leaching capacity above pH 3, but at pH < 3, citric acid appears to be the strongest extractant. Moreover, the influence of the applied ceramic glaze played an important role in lead release, in certain cases doubling the extracted amount of Pb. It has also been demonstrated that migration kinetics in citric acid is stronger. At 90 °C, after 2 h, the amount of extracted lead is 18% more important than at 20 °C after 24 h in acetic acid 4% (v/v) which may question the capacity of consumer protection of ED 84/500/EEC.

**Key words:** Lead migration, ceramicware, glaze, food simulant, pH, temperature, European Directive 84/500/EEC.

## 1. Introduction

Persistence of lead (Pb) in our life environment poses an ongoing challenge in the field of public health. Lead poisoning causes permanent neurological, haematological and growth problems [1, 2]. It has been shown that the mean blood Pb levels of infants and young children, more vulnerable to the neurotoxicity of lead, were consistently higher than those of adults [3].

Currently, dietary intake is considered to be the major Pb vector due to decreased environmental concentrations (for non-occupationally exposed adults)

[4, 5]. Food and beverage contamination by lead occurs either in a direct way or by contact with packaging, cooking, serving, and/or storing materials. In this study, we were interested in lead migration into food in contact with glazed ceramicwares. Despite studies showing that producing high quality ceramicware without lead is feasible [6], lead oxide (PbO) is still used in the glaze structure. In fact, its excellent properties and wide processing latitude in the glaze structure make it an ideal glaze component over a wide range of ceramicware compositions and firing ranges [7]. When properly processed, the amount of lead oxide extracted by food substances is extremely low, below the established limits set by European Directive (ED) 84/500/EEC, FDA (Food

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and Drug Administration) and other regulatory groups [5, 8]. High lead release is measured when: (1) glaze is improperly formulated and did not contain the proper mixture of ceramic oxides, (2) proper firing practices were not followed and PbO was incompletely combined with the silicate glaze matrix, and (3) decorations and/or colouring agents were inappropriately used [9-11]. Efforts to minimize the amount of lead in contact with food have been made since high toxicity of lead was recognized in the mid 1960s; however, it is still possible to find ceramicware exceeding the limit set by regulatory groups [12]. Current standards set the limit of extracted Pb not to exceed to 0.8 mg/dm<sup>2</sup> for flatwares (internal depth smaller than 2.5 cm), 4 mg/L for small hollowwares ( $\leq 3$  L) and 1.5 mg/L for big hollowwares ( $> 3$  L) and are excerpted in Table 1. The standard test method conditions are defined by ED 84/500/EEC as follows: extractant: 4% acetic acid, temperature (T) =  $22 \pm 2$  °C, contact time (t) =  $24 \pm 0.5$  h [13].

The presence of non-conforming ceramicware still available on the market and in use in households is mostly explained by: (1) massive importation making it impossible to test every product entering the country from regions where use of lead for glazes is less controlled or regulated; and (2) ceramicware dating before the first legislations handed down from previous generations or purchased on the flea market, or in antique stores [14, 15].

In real life, ceramicware fulfils different functions when it comes to food. It can be used for cooking, serving, storing, and packaging. As a consequence, ceramicware is used in a wide range of temperature, pH, and time. The aim of this study was to verify the relationships between lead release and the formerly mentioned parameters and to study whether the conditions laid down by ED 84/500/EEC represents the most extreme situation a ceramicware could be used in contact with food in real. It has already been showed that lead glazes are more soluble at higher temperatures [16-18] and that solubility was enhanced

**Table 1 European Directive 84/500/EEC relating to ceramic articles intended to come into contact with foodstuffs.**

Category	Specification	Pb level
Flatware	Internal depth $\leq 25$ mm	0.8 mg/dm <sup>2</sup> <sup>1,2</sup>
Small hollowware	Volume $< 3$ L	4 mg/L <sup>1,2</sup>
Large hollowware	Volume $> 3$ L	1.5 mg/L <sup>1,2</sup>

<sup>1</sup> The average value obtained for four similar objects should not exceed these norm concentrations.

<sup>2</sup> The individual values should not exceed the norm concentration by  $> 50\%$ .

These complements to the first directive were inspired by the obvious spread observed for ceramic ware of the same batch.

at lower pH [16, 19]. A study by R.W. Sheet and C. Bonnet et al. [15, 20] also tackled the subject of lead release in contact with different food simulants, other than acetic acid. The question is whether lead migration into food is more important by carrying out experiments under more realistic conditions where temperature, pH, contact time and nature of the acid in contact with the ceramicware are varied.

For migration experiments, both flat- and hollowware were used. Hollowwares were purchased from local artisan. Ceramic flatware, imported from China, was received for conformity test. Temperature was varied between 20 °C and 90 °C, pH between 2.37 and 5.00, the contact time was extended to 4 days, and the influence of the following acids were investigated: acetic acid, citric acid, and malic acid. These acids are naturally present in various foods and food products, among others: white vinegar, lemon juice and tomato juice.

## 2. Materials and Methods

### 2.1 Instrumentation

ICP-AES measurements were performed by an Optima 4300 DV spectrometer (Perkin-Elmer). Calibration was performed with external standards. Details on the instrumentation and the operating conditions are summarized in Table 2.

### 2.2 Chemicals and Reagents

The highest quality reagents were used to eliminate

**Table 2 Instrumental operating conditions for ICP-AES.**

Spectrometer	Optima 4300 DV (Perkin-Elmer, Norwalk, CT, USA)
Plasma	
RF generator	Frequency: 40 MHz, power: 1,300 W
Gas flow rate (L min <sup>-1</sup> )	Plasma: 15, auxiliary: 0.2, nebulizer: 0.5
Solution uptake rate	1 mL min <sup>-1</sup>
Optical viewing	Axial
Resolution	High
Data acquisition	Peak area; number of replicates 3
Spectral lines (nm)	Pb: 220.353 217.000 261.418

contamination and to ensure accuracy of results. Ultrapure, deionized Milli-Q<sup>®</sup> water (Millipore, Milford, MA, USA, specific resistivity > 18 MΩcm<sup>-1</sup>) was used throughout the study. Standard solution of Pb was purchased at Fluka Chemika. Citric acid (> 99.5% w/w) and malic acid (> 99.5% w/w), both purchased at Merck, and acetic acid (> 99%, BDH Prolabo) were used as extractants and standard solutions in dilutions.

### 2.3 Experimental Design

Acidic beverages, food simulant, pH, and temperature were varied during experiments in order to investigate the capacity of ED 84/500/EEC. Table 3 summarizes the studied parameters and conditions. Ceramic flatwares were obtained in original manufacturer packages from a local retail store. Three flatwares were taken for each series of experiments, except for the standard migration method testing the conformity of the ceramicwares where four plates were taken from each three boxes to provide a total of 12 plates. Ceramic hollowwares with different glaze each (Table 4) studying the influence of food simulant on Pb migration were purchased from local artisan. Tests were repeated on three identical hollowwares.

#### Experiment 1: conformity test

Flatwares were filled with 240 mL of 4% acetic acid (HAc) and left for 24 hours at ambient temperature (22 °C).

#### Experiment 2: influence of acidic beverage on lead

release

Flatwares were filled with 240 mL of tomato juice, white vinegar, lemon juice and 4% HAc, at pH 4.1; 2.47; 2.42; and 2.46 respectively, and left for 24 hours at ambient temperature (22 °C) as listed in Table 3.

Experiment 3: influence of food simulant on lead release

All hollowwares were fired at 900 °C. The base glaze used was 89329. On the top of the base glaze, different glazes were added, as listed in Table 4. For analysis, hollowwares were filled with 650 mL of HAc, citric acid (HCit), and malic acid (HMal), respectively, at different concentrations corresponding to pH 2.37, 2.68, 2.90, 3.18, 3.63 and 2.34, 2.68, 2.93, 3.07, 3.63 and 2.43, 2.68, 2.97, 3.11, 3.62 respectively (Table 3). Hollowwares filled with the respective food simulant were left for 24 hours at ambient temperature (22 °C).

#### Experiment 4: migration kinetics and contact time

Flatwares were filled with 240 mL HAc and HCit at different concentrations corresponding to pH 2.37, 3.0, 3.5, 4.0, 5.0 and 2.34, 2.92, 3.07, 3.63, respectively.

Leachates of 5 mL were taken for analysis 10 and 12 times at different intervals (at 30, 60, 120, 240, 360, 480, 600, 1,440, 2,880, 4,320 min and at 15, 30, 45, 60, 75, 90, 105, 120, 180, 240, 1,440, 2,880 min) for HAc and HCit respectively (Table 3).

Portions of fresh extractants were added to flatwares immediately after aliquots were removed for analysis.

#### Experiment 5: influence of temperature

Flatwares were filled with 240 mL of 4% HAc and placed in the oven at different temperatures (20, 40, 70, 90 °C).

When operating at 40, 70, and 90 °C, leachates of 5 mL were taken 13 times at different intervals (at 5, 10, 15, 20, 25, 30, 35, 40, 45, 50, 55, 60, and 120 min).

When the migration was investigated at 20 °C, leachates of 5 mL were taken 14 times at different intervals (at 15, 30, 45, 60, 75, 90, 105, 120, 150, 210, 240, 300, 360, and 1,440 min).

**Table 3 Parameters and conditions.**

Ceramic ware	Surface (dm <sup>2</sup> )	Conditions				
		Extractant	Volume (mL)	Contact time (h)	pH	Temperature (°C)
Experiment 1						
Flatware	2.92	HAc 4%	240	24	2.46	22
Experiment 2						
Flatware	2.92	Tomato juice	240	24 and 48	4.1	22
		Vinegar	240	24	2.47	
		Lemon juice	240	24	2.41	
		HAc 4%		24	2.46	
Experiment 3						
Hollowware <sup>1</sup>	4.02	HAc	650	24	2.37, 2.68 <sup>6</sup> , 2.90, 3.18 <sup>6</sup> , 3.63	22
		HCit			2.34, 2.68 <sup>6</sup> , 2.93, 3.07 <sup>6</sup> , 3.63	
		HMal			2.43, 2.68 <sup>6</sup> , 2.97, 3.11 <sup>6</sup> , 3.62	
Experiment 4						
Flatware	2.92	(1) HAc	240	A <sup>2</sup>	2.37, 3, 3.5, 4, 5	22
		(2) HCit		B <sup>3</sup>	2.34, 2.92, 3.07, 3.63	
Experiment 5						
Flatware	2.92	HAc 4%	240	C <sup>4</sup>	2.46	20
				D <sup>5</sup>		40
				D <sup>5</sup>		70
				D <sup>5</sup>		85

<sup>1</sup> see Table 4 for glazes.<sup>2</sup> leachates of 5 mL taken at 30, 60, 120, 240, 360, 480, 600, 1,440, 2,880, 4,320 min.<sup>3</sup> leachates of 5 mL taken at 15, 30, 45, 60, 75, 90, 105, 120, 180, 240, 1,440, 2,880 min.<sup>4</sup> leachates of 5 mL taken at 15, 30, 45, 60, 75, 90, 105, 120, 150, 210, 240, 300, 360, and 1,440 min.<sup>5</sup> leachates of 5 mL taken at 5, 10, 15, 20, 25, 30, 35, 40, 45, 50, 55, 60, and 120 min.<sup>6</sup> Pb extraction measured only in ceramicware glazed with glazes barium chromate and chrome oxide.**Table 4 List of the glazes used for Experiment 3.**

Name	Abbreviation
Base glaze	89329
Zircon oxide	ZrO
Iron Chromate	FeCr
Lid oxide	SnO
Barium chromate	BaCrO
Chrome oxide	CrO
Borax	Bo
Antimony oxide	SbO
Aluminium chromate	AlCrO

## 2.4 Methods

Prior to migration tests, ceramicwares were washed in a detergent solution to remove small dust particles and rinsed with Milli-Q<sup>®</sup> water.

Plastic labware and acid-cleaning procedures were used as necessary to eliminate contamination. Disposable 15 and 50 mL Falcon tubes with caps (Falcon 2097 and 2098) were used to hold solutions.

Dilutions due to replacing the taken leachate at different contact times by fresh extractant were not negligible. To calculate the actual mass of the extracted lead in a given time, the following expressions were used:

$$t_0 \quad c_0 V_t = m_{t_0} \quad (1)$$

$$t_1 \quad c_1 V_t - c_0 V_t = m_{t_1-t_0} \quad (2)$$

$$t_2 \quad c_2 V_t - (c_1 (V_t - V_l) + c_0 V_l) = m_{t_2-t_1} \quad (3)$$

$$\vdots$$

$$t_n \quad c_n V_t - (c_{n-1} (V_t - V_l) + c_0 V_l) = m_{t_n-t_{n-1}} \quad (4)$$

Where:  $t_n$  : elapsed time,  $V_t$  : total volume of extractant,  $V_l$  : volume of extractant taken for analysis,  $c_n$  : concentration measured by ICP-AES at  $t_n$ ,  $m_{t_n-t_{n-1}}$  : mass of Pb extracted between  $t_{n-1}$  and  $t_n$ .

For Experiment 1, the samples were digested with nitric acid (Merck) and hydrogen peroxide (Merck), 5 mL, (4:1 v/v) at 120 °C in Teflon tubes. Once a

minimum level is reached ( $> 1$  mL), the mineralisation is stopped and the volume is completed with ultrapure Milli-Q<sup>®</sup> water.

### 2.5 Figures of Merits

Method controls (Falcons, filled with extractant, stirred, and sampled at the same contact times as test wares) were prepared with every leach cycle and analysed with the leachates. Limits of detection (LODs) were calculated on the basis of the  $3\sigma$  criterion from the standard deviation ( $\sigma$ ) [21]. Limits of quantification (LOQs) were calculated by adding  $3\sigma$  to the respective LODs. In Experiment 1; 2; and 5, the method blank was 4% HAc. In Experiment 3 and 4, the method blank was HAc, HCit and HMal at the required concentration for the corresponding series of experiment. Non-quantified values were treated according the following statistical approach: for samples in which no lead was detected (nd), values were assumed to be half the limit of detection ( $\frac{1}{2}LOD$ ) and for samples in which lead was seen to be below the LOQ, values were assumed to be half the limit of quantification ( $\frac{1}{2}LOQ$ ) [22].

Repeatability was calculated as the relative standard deviation of a sample with concentration values in the central region of the analytical range carried out during the same analytical run.

## 3. Results and Discussion

The present paper is structured in five experimental steps studying the influence of physical and chemical conditions on migration in order to investigate whether the conditions stipulated by the European Directive 84/500/EEC fully protects consumers using ceramicware in various conditions.

Experiment 1 allowed determining conformity of the flatwares received from local retail store. Variability caused by differences among individual vessels was also investigated. It is a well-known concern among ceramicwares. The observed deviations can be explained by differences in

fabrication procedure, such as different applications of pigments and/or other additives, insufficient homogenization of the original material, and improper or variable heating and glazing in the fabrication furnace. Every pottery specimen has glaze coating on its surface. It seems plausible that the glaze contributes predominantly to the Pb contamination; some release by the clay of the receptacle cannot be excluded though and this still remains a matter of concern [23]. In the present case, this variability corresponds to 9.7% which is acceptable compared to variability found in the literature concerning Pb release from ceramicware [24]. The mean lead release was equal to  $5.1 \text{ mg/dm}^2$ . The difference between means and medians (as % of the mean) was less than the variability of ICP-AES measurements, 0.92% and 4% or less, respectively. Mean results were therefore used throughout the study. Estimates of LODs, LOQs, repeatability, and variability are reported in Table 5.

In order to compare the extraction force of food products to the food simulant stipulated by ED 84/500/EEC, tomato juice, white vinegar, and lemon juice were put in non-conforming flatwares, as summarized in Experiment 2. It allows realizing the protection capacity of the ED 84/500/EEC. The pHs of the food products were equal to 4.10; 2.47; and 2.42 for tomato juice, white vinegar, and lemon juice, respectively. Conditions defined by ED 84/500/EEC were of application. Results are given in Table 6. Lead release corresponds to 2.85; 4.90; and  $5.81 \text{ mg/dm}^2$  in tomato juice, white vinegar, and lemon juice, respectively, whereas it corresponds to  $4.99 \text{ mg/dm}^2$  in acetic acid 4% in conditions stipulated by ED 84/500/EEC. The mean Pb migration is 3% smaller in the second set of flatwares than in the first set used in Experiment 1. The difference is, however, within the variability, 9.7%, and 7.0% for the first and the second set, respectively. The amount of extracted lead in lemon juice, shown in Table 6, is 14% higher than in acetic acid 4%. However, it is not straightforward to deduce that lemon juice is a more

**Table 5** Method detection limits (mg/L), quantification limits, repeatability (%), and variability.

	LOD (mg/L)	LOQ (mg/L)	Repeatability (%)	Variability (%)
Experiment 1				
HAc 4%	A	A	A	9.7
Experiment 2				
Tomato juice <sup>1</sup>	A	A	A	11.1
Tomato juice <sup>2</sup>	A	A	A	15.3
Vinegar	A	A	A	7.81
Lemon juice	A	A	A	3.48
HAc 4%	A	A	A	7.03
Experiment 3 <sup>3</sup>				
89329	A <sup>4</sup> , B <sup>5</sup> , C <sup>6</sup>	A, B, C	A, B, C	26.6
ZrO	A, B, C	A, B, C	A, B, C	19.9
FeCr	A, B, C	A, B, C	A, B, C	33.8
SnO	A, B, C	A, B, C	A, B, C	27.4
BaCrO	A, B, C	A, B, C	A, B, C	21.1
CrO	A, B, C	A, B, C	A, B, C	29.0
Bo	A, B, C	A, B, C	A, B, C	31.9
SbO	A, B, C	A, B, C	A, B, C	14.1
AlCrO	A, B, C	A, B, C	A, B, C	46.3
Experiment 4				
pH (HAc) 2.37	A	A	A	8.75
3.00	A	A	A	0.94
3.50	A	A	A	20.3
4.00	A	A	A	36.0
5.00	A	A	A	42.0
pH (HCit) 2.34	B	B	B	3.68
2.92	B	B	B	8.06
3.07	B	B	B	19.4
3.63	B	B	B	16.0
Experiment 5				
20 °C	A	A	A	14.9
40 °C	A	A	A	27.3
70 °C	A	A	A	2.27
90 °C	A	A	A	13.3

<sup>1</sup> After 24 h.<sup>2</sup> After 48 h.<sup>3</sup> Values averaged for HAc, HCit, and HMal over the whole range of pH.<sup>4</sup> A: for acetic acid: LOD = 0.252 mg/L; LOQ = 0.494 mg/L; Repeatability = 1.43%.<sup>5</sup> B: for citric acid: LOD = 0.092 mg/L; LOQ = 0.102 mg/L; Repeatability = 1.12%.<sup>6</sup> C: for malic acid: LOD = 0.153 mg/L; LOQ = 0.278 mg/L; Repeatability = 2.01%.

powerful extractant than acetic acid 4% because of the difference in pH. It is important to note that the nature of the acid occurring in majority in the food products are different, thus it may play a role as well in Pb

**Table 6** Lead release (mg/dm<sup>2</sup>) in tomato juice, white vinegar, lemon juice, acetic acid 4% under conditions defined by ED 84/500/EEC.

	pH	Contact time (h)	Pb released (mg/dm <sup>2</sup> )
Tomato Juice	4.10	24	2.85 ± 0.18
White vinegar	2.47	24	4.90 ± 0.40
Acetic acid 4%	2.46	24	4.99 ± 0.35
Lemon juice	2.42	24	5.81 ± 0.20
Tomato juice <sup>1</sup>	4.10	48	3.47 ± 0.30

<sup>1</sup> After 48 h.

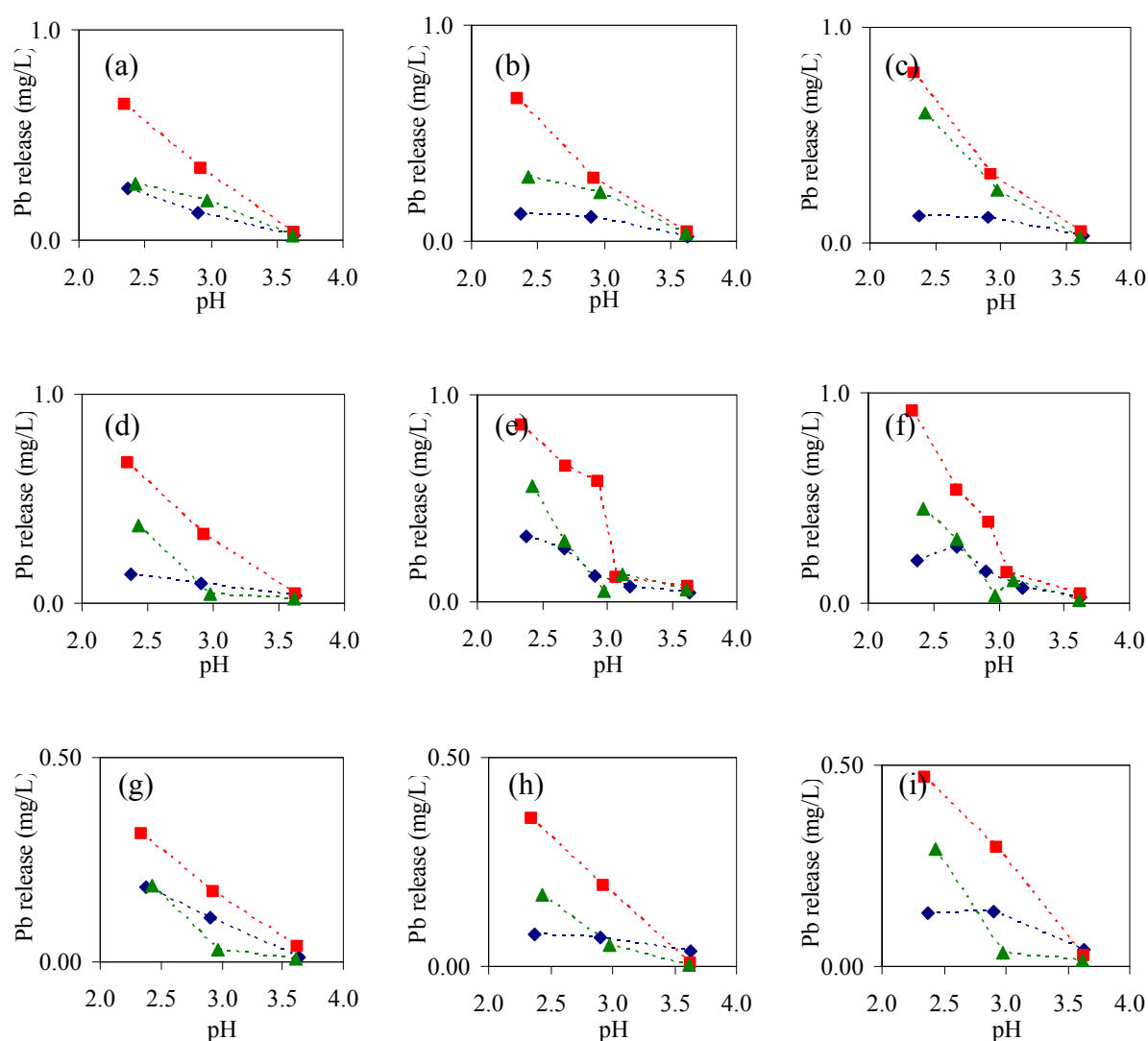
extraction. Therefore, in order to determine the influence of each parameter on the amount of extracted Pb, both pH and the nature of acid were investigated (Experiments 3 and 4).

The amount of Pb extracted in white vinegar is very close to that in acetic acid 4% as it could be expected from the physical-chemical properties of these two extractants (pH, main constituents). The difference of 2% is within the variability caused by the inherent differences between flatwares considered alike as discussed above. The beverage with the highest pH (tomato juice) appeared to be the weakest extractant. Tomato juice also differs from the three other acidic beverages by the nature of the acid it contains naturally. The acid occurring in appreciable quantities in tomato juice is malic acid. In order to investigate the influence of contact time in mild conditions (relatively high pH, ambient temperature), tomato juice was left for an extra day in contact with the ceramic flatware and leachate was analysed after 48 h. It appears that after 48 h, the leachate contained 3.47 mg/dm<sup>2</sup> Pb, 22% more Pb than after 24 hours. Considering that ceramicware is also used for storage, it is important to reconsider the contact time for testing ceramicwares intended to store food.

Experiments 3 and 4 aimed at highlighting the influence of the nature of the extractant, ceramic glaze, and the pH on lead extraction. As all experiments were carried out in triplicates, a large number of samples was necessary. Because of the number of flatwares limited, artisanal glazed hollowwares were used (for specifications on the studied glazes, see

Table 4). Three food simulants were put in contact with the hollowwares: acetic acid, citric acid, and malic acid, all of them present in important quantities in food and food products. It is recognized that glaze is the main source of Pb migration [25], thus it was straightforward to examine the influence of different, commercially available glazes listed in Table 4 in combination with different acids at different pH. On Figs. 1(a)-(i), Pb release from artisanal, glazed hollowwares in function of pH is represented. The data points are connected with dotted lines for better

visibility. Two conclusions can be drawn. First, concerning the glazes, they have a visible influence on Pb release. It appears that 89329, ZrO, FeO, SnO, BaCrO, and CrO release appreciatively 2 times more Pb than Bo, SbO, and AlCr at low pH. On the other hand, above pH 3.0-3.5, differences in lead release become less and less pronounced. Second, it could be noticed that for each glaze citric acid (■ in Fig. 1) appears to be the strongest extractant at low pH, but above pH 3.0-3.5, the difference is negligible. Malic acid (▲ in Fig. 1), in the studied pH range, seems to be



**Fig. 1** Lead release in acetic acid (◆), citric acid (■), and malic acid (▲) are represented in function of pH.

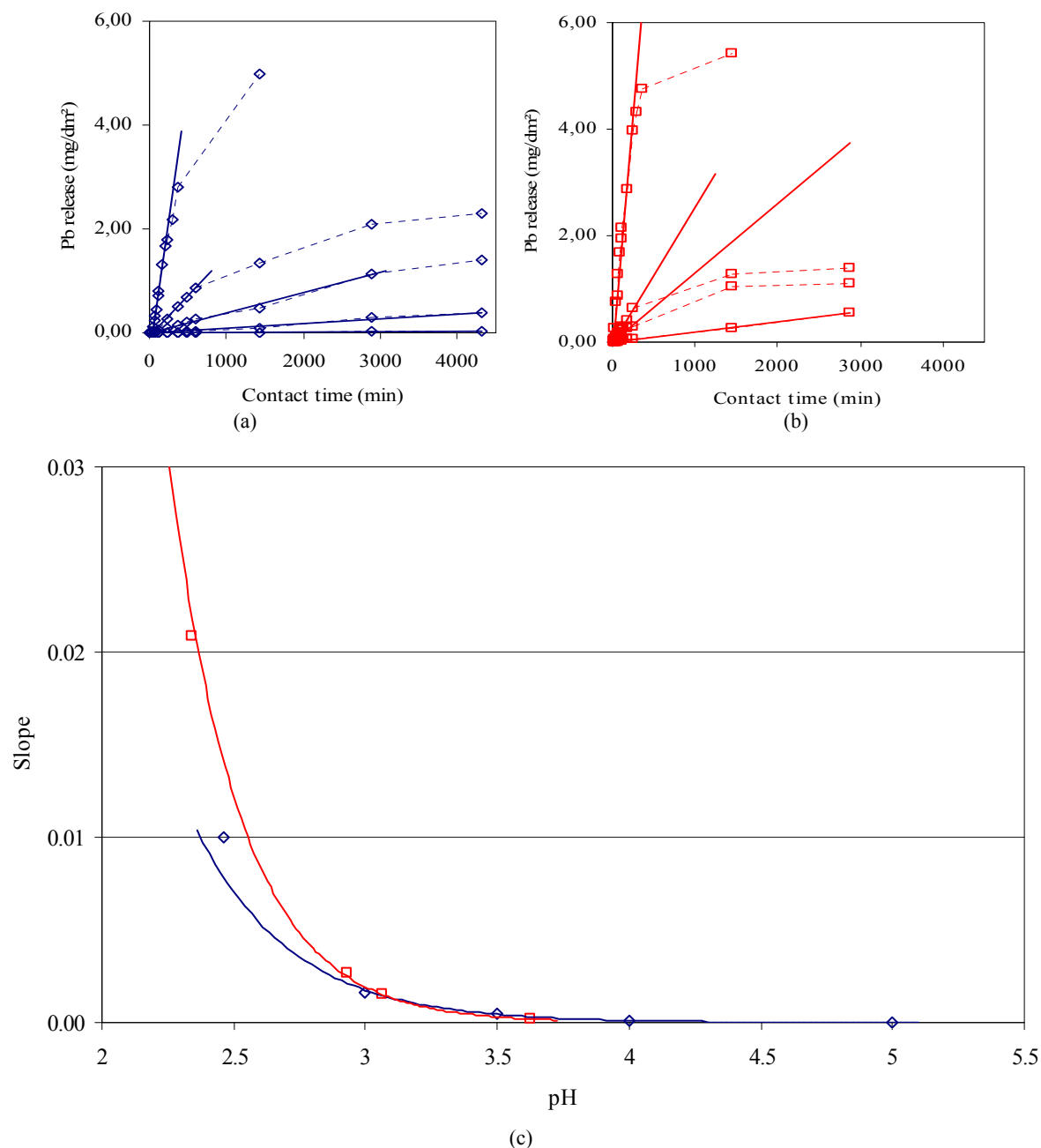
The glaze used is (a) 89329, (b) ZrO, (c) FeO, (d) SnO, (e) BaCrO, (f) CrO, (g) Bo, (h) SbO, and (i) AlCr. The points are connected for better visibility.



as effective as acetic acid ( $\diamond$  in Fig. 1). It is important to note that the variability due to the replicates on flatwares considered alike summarized in Table 5 goes from 14% to 46%, making it, in some case, difficult to draw a straightforward conclusion concerning the extraction strength of food simulants.

Ceramic flatwares were used to study and compare the kinetics of migration in acetic acid and in citric

acid. For this purpose, leachates of 5 mL were taken at regular contact times and then analysed according to experimental conditions summarized in Table 3. In Figs. 2(a)-(b), the Pb release is represented in function of the contact time for HAc ( $\diamond$ ) and HCit ( $\square$ ) respectively, as well as the fitted linear trendlines (full lines). Measured data points in Figs. 2(a)-(b) are connected with dotted lines for better visibility. Both



**Fig. 2** (a) Pb release in acetic acid and in (b) citric acid. (c) Migration kinetics of Pb in acetic acid ( $\diamond$ ) and citric acid ( $\square$ ). Full lines are fitted trendlines.

in Figs. 2(a)-(b), the steepest curves correspond to the experiments carried out at lowest pH and the flattest curve to experiments carried out at the highest pH. The sum-of-squares method was used to determine the model describing the most accurately the relationship between the contact time and amount of released lead. For each pH, before attending the plateau, a linear relationship between the contact time and the amount of released Pb was found. The same relationship was found by Gould et al. [26]. For each pH, the slope of the fitted linear model was calculated. This linear relationship is valid for shorter period at lower pH, 240 minutes for both acetic acid and citric acid at pH 2.37 and 2.34, respectively, and longer period at high pH, plateau still not reached after 2 days at pH 3.63 in citric acid, and 4 days at pH 5.0 in acetic acid. These findings are in agreement with Experiment 1. It reinforces the question of contact time to apply in conformity tests in case of ceramic food contact material intended for extended food storage. Migration kinetics is represented on Fig. 2(c). The slopes of the fitted trendlines, calculated from Fig. 2(a) and 2(b), are

plotted in function of the pH. The obtained curves allow concluding that the stronger migration kinetics of Pb is observed in citric acid below pH 3.0. This result agrees with the results of the previous set of experiments carried out on artisanal ceramic hollowware suggesting that the nature of the acid does not influence migration above pH 3.0-3.5 (Fig. 1.).

Fig. 3 represents the Pb release in function of the pH in acetic acid ( $\blacklozenge$ ). Trendline following an exponential curve was fitted to the datapoints ( $r^2 = 0.989$ ). The amount of Pb released in different foodstuffs, i.e. datapoints obtained in Experiment 1 for lemon juice, acetic acid 4%, white vinegar, and tomato juice, were plotted on Fig. 3. Lead migrations in lemon juice ( $\circ$ ), acetic acid 4% ( $\diamond$ ), and white vinegar ( $\square$ ) fit well with the results obtained in Experiment 4. Surprisingly, datapoint obtained for lead migration in tomato juice ( $\Delta$ ) sits well above the exponential curve. The observed lead migration in tomato juice exceeds 34 times lead migration in acetic acid at the same pH (4.1). In the tomato juice sample, the amount of lead was below LOQ.

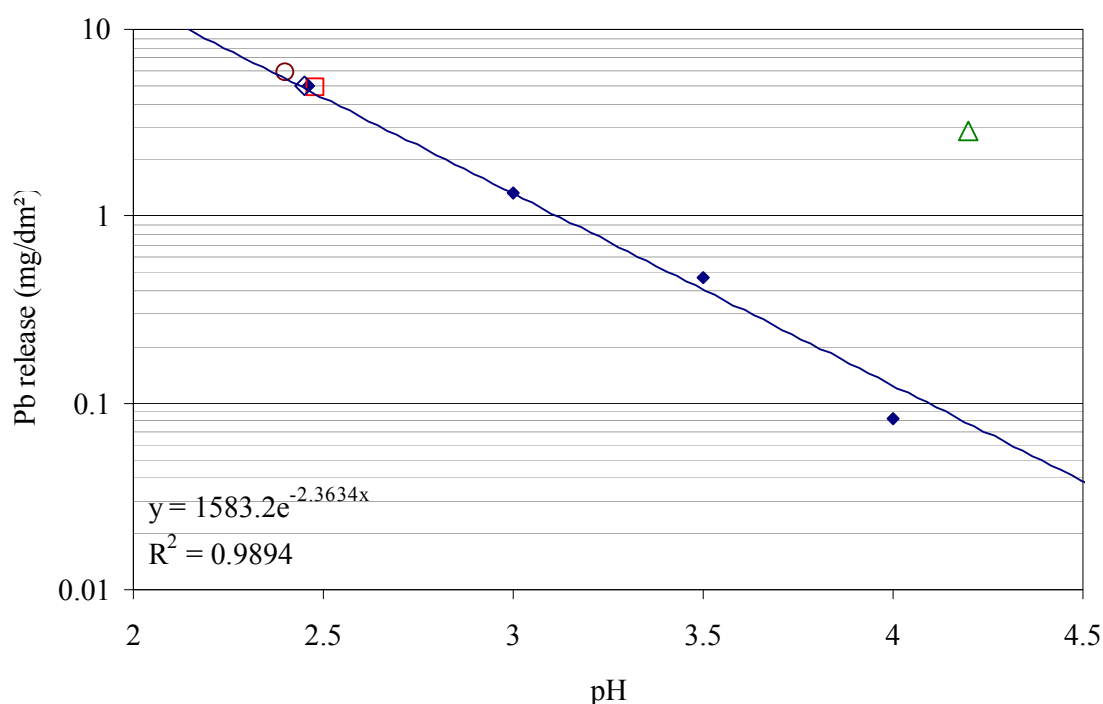


Fig. 3 Pb release in function of the pH in acetic acid ( $\blacklozenge$ ). The amount of extracted lead in lemon juice ( $\circ$ ), acetic acid 4% ( $\diamond$ ), white vinegar ( $\square$ ), and in tomato juice ( $\Delta$ ) are plotted on the graph.

These comparative tests show the importance of glazes applied to ceramicware. Moreover it highlights a trend suggesting that Pb migration above pH 3.0-3.5 at ambient temperature is similar in acetic acid, citric acid and malic acid. At low pH < 3.0, citric acid appears to be more effective than both acetic acid and malic acid. Migration kinetics below pH 3.5 in citric acid was stronger than migration kinetics in acetic acid. Citric acid may be, therefore, an interesting alternative food simulant to use for the standard test method in quantification of lead migration allowing either to shorten the time of the conformity test or setting stricter limits by keeping the same experimental conditions. It is, however, important to interpret the results with precaution considering the variability between ceramicwares sometimes as high as 46% (Table 5).

In Experiment 5, the influence of temperature was investigated using imported flatwares.

Fig. 4 shows the amount of Pb migrated in HAc 4% in function of time at different temperatures. At higher temperatures, Pb migration is more important. Between the mass transfer from ceramic material and the temperature, an exponential relationship was

observed, in this case, obeying to Fick's laws of diffusion [27]. It is interesting to note that at 90 °C, after 2 h, the plateau is reached and the amount of extracted Pb corresponds to 6.17 mg/dm<sup>2</sup>. It exceeds by 18% the amount of Pb extracted at 20 °C after 24 h (5.1 mg/dm<sup>2</sup> in Experiment 1). At 90 °C, after 10 minutes 50% of the extracted Pb (equals to 3.09 mg/dm<sup>2</sup>) in 120 min. At 20 °C, after 10 minutes, the Pb concentration is still below LOD. At 20 °C, it takes 400 minutes to release 3.09 mg/dm<sup>2</sup> Pb, 40 times more than at 90 °C.

As illustrated in Fig. 5, the time needed to extract 0.8 mg/dm<sup>2</sup> of Pb (limit set by ED 84/500/EEC for flatwares) is represented in function of the temperature. The exponential relationship is verified ( $r^2 = 0.991$ ). By extrapolating the fitted exponential trendline till 100 °C, it is possible to calculate that 0.8 mg/dm<sup>2</sup> Pb is extracted in only 1.42 min, whereas at 20 °C, it takes 102 min to pass the limit of 0.8 mg/dm<sup>2</sup> Pb, approximately 70 times more (illustrated on Fig. 5 with the dotted lines).

If we assume that cooking food with low pH (e.g. lemon sauce) in the above studied ceramicware ( $S = 2.92 \text{ dm}^2$ ) for 30 minutes at 90 °C extracts as much Pb

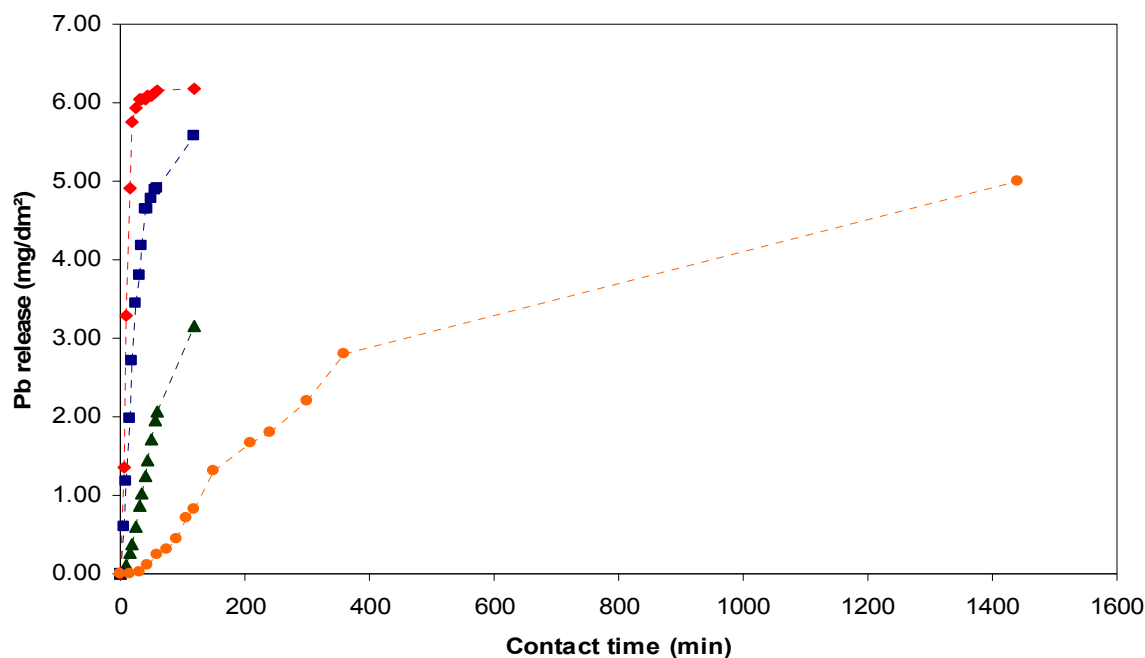


Fig. 4 Pb migration at 90°C (♦), 70°C (■), 40°C (▲), and 20°C (●). Consecutive data points are connected with dotted lines.

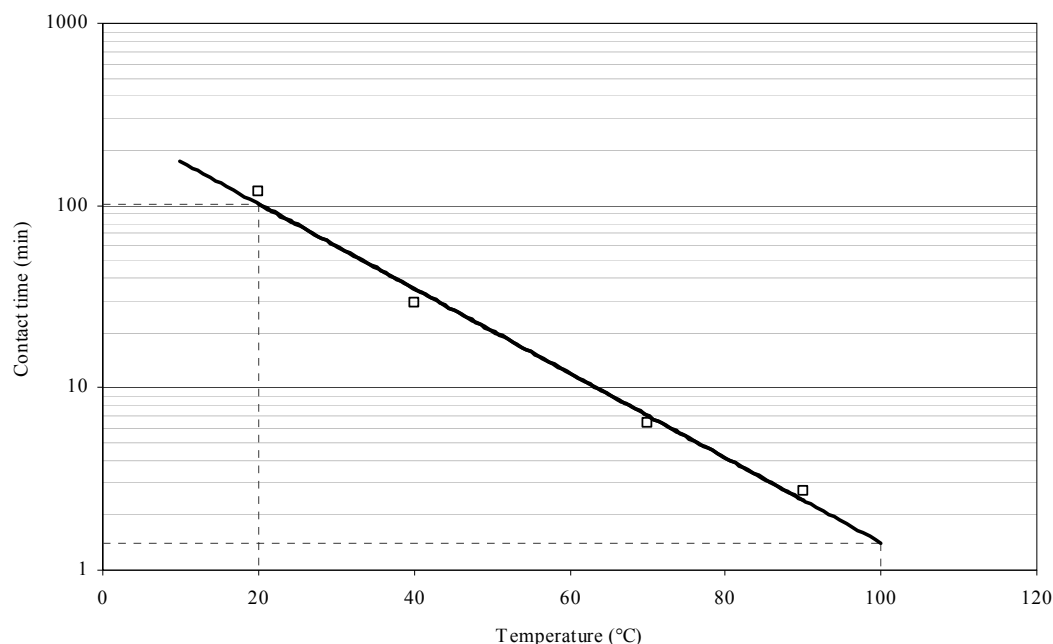


Fig. 5 Time needed to extract 0.8 mg/dm<sup>2</sup> of Pb in function of temperature.

as HAc 4%, the dietary Pb intake would increase by 17.64 mg. The absorption rate of Pb when taken with a meal varies from 3% to 21% with an average of 8% [28-32]. The amount of absorbed lead would correspond to 94.1 µg/kg bw (body weight) in children and 23 µg/kg bw in adults. It has been reported by Carlisle and Wade [33] that an increase in Pb intake by 1 µg a day through diet and/or water increase the blood Pb level (B-Pb) by 1.6 µg/L in children and 0.4 µg/L in adults, corresponding, in the present example, to 150.5 µg/L and 9.4 µg/L increase in B-Pb in children and adults, respectively (considering a simplified linear relationship between the adsorbed dose and the absorbed Pb). Studies in rats and nonhuman primates have demonstrated deficits in learning associated with B-Pb concentrations between 100 and 150 µg/L, a range that is comparable to those reported in epidemiological studies, in which learning deficits were found in children [34]. If the above mentioned ceramicware is used only irregularly from time to time, the ingested lead does not pose any health problem. Indeed, lead has been described as a classic chronic poison meaning that health effects are generally not

observed after a single exposure. In everyday life, however, ceramicwares are not used as disposables in an average household but on a regular basis leading to possible affectation of behaviours such as learning abilities of children.

#### 4. Conclusion

Imported flatwares, available in local retail store were tested non-conforming according to ED 84/500/EEC. Even though the product was recalled, the customer who purchased the product before it was recalled from the market is exposed to, in the present case, lead concentrations that may cause neurological, haematological and growth problems. The doses are especially dangerous to children. It is therefore suggested that as far as possible products should be tested before arriving to the market in order to fully protect the consumer.

Parameters such as pH, nature of food simulants, ceramicware glaze, acid beverages, temperature, and contact time were investigated in order to test the capacity of ED 84/500/EEC. Both non-conforming flatwares and artisanal hollowwares were used to carry out the experiments. It was concluded that the

pH, temperature and nature of the acid present in foodstuff in contact with ceramicware influenced the lead migration. Besides, it was observed that 20% more lead was released after 48 h than after 24 h. After 48 h, at pH 2.37, 3.0, 3.5, 4.0, and 5.0, the amount of the extracted lead is 42%, 36%, 58%, 71%, and 53% more important than after 24 hours suggesting that ceramicware intended to store food for longer periods should be tested under more restricted conditions, or conform to stricter norm values to provide a good protection of the consumer.

The nature of the food simulant seems to play a role in lead extraction, especially in the low pH range. In higher pH though, its importance disappears. Below pH 3.0, it was shown that citric acid is a more efficient extractant than acetic acid. It also displays stronger migration kinetics. In addition, citric acid occurs in abundance naturally in food and frequently used as a food additive (E330). Hence, citric acid (5 mg/L) is proposed as an alternative to acetic acid 4% in standard migration tests.

The applied glaze is also an important factor in lead release. Among the nine studied glazes six of them release appreciatively two times more Pb than the three other ones.

Moreover, it was shown that the temperature had an important impact on lead migration. The exponential relationship was proved, as expected from Fick's laws of diffusion. The lead extracted in acetic acid 4% after 2 h at 90 °C exceeded by 18% the amount of lead extracted at 20 °C after 24 h in acetic acid 4%. It is of particular interest because ceramicwares are often used cooking at high temperatures.

Considering these results, it may be interesting to reconsider some of the conditions laid down by ED 84/500/EEC with special remark on the temperature and the nature of food simulant. Moreover, we conclude that the concentration limits for leachable lead from ceramicware set by ED 84/500/EEC are not strict enough compared to concentration limits of Pb in food. In order to protect the consumer, stricter

standards and protocols are necessary to face the real hazard one occurs.

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