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Scoping investigations on the release of metals from crystalware

in support of the revision of the Ceramics Directive 84/500/EEC

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Abstract

In the present work, the release from 15 samples of crystalware was investigated with respect to migration of metals in different conditions from different samples. Three test regimes were compared. The first one, currently in use for ceramic, foresees the use of acetic acid 4% as simulant and the test conditions are 22°C for 24 hours. This procedure was repeated three times to better represent the repeated use regime. Two alternative approaches: 1) citric acid 0.5% for 2 hours at 70ºC, three consecutives migrations and 2) pre-conditioning of the ceramic with acetic acid 10% during 5 hours followed by a single migration for 24h at 22°C with acetic acid 4% were investigated to shorten the time of analysis. The release of metals was also studied into white wine as benchmark food.
For all samples included in the study a relevant release of Pb was observed. Only few other metals were found in leaching solutions: Zn, Sb, Ba and Ag. Both simulants presented higher migration respect to the white wine as a benchmark food. In general the release of metals seemed to be higher with citric acid than with the acetic acid in the first migration. Migration values obtained with pre conditioning step were above the third migration obtained with the conventional test with acetic acid.

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Summary

Materials and articles in contact with foods fall under a framework legislation at the EU level to ensure the safety of the consumer while facilitating trade.

For ceramics articles in contact with foods, European Directive 84/500/EEC stipulates specific limits on the release of lead (Pb) and cadmium (Cd) and basic rules for determining their migration [9].

The European Commission (EC) is now considering revising Directive 84/500/EEC to foresee reduction of limits for lead and cadmium, establishing limits for additional metals, and potentially extend the scope to other types of articles for example in particular crystalware. The Joint Research Centre was entrusted to provide scientific and technical supporting data on testing options in order to underpin the evaluation of technical means to ensure the feasibility of future measures and aid the decision making process for the EC, Member States and stakeholders.

This report focuses on crystalware. The overall aim of this study was investigate the release of lead from crystalware and experimental approaches for testing these articles. In the present work, the release of metals from 15 samples of crystalware was investigated under different conditions. Three methodologies were compared and optimised. The first one, currently in use for ceramic, foresees the use of acetic acid 4% (AA 4%) as simulant and test conditions of 24 hours at 22°C. This procedure was investigated for three successive migration tests to represent a repeated use regime. Two alternative methodologies: 1) citric acid 0.5% (CA0.5%) for 2 hours at 70°C, three consecutives migrations and 2) pre-conditioning of the ceramic with acetic acid 10% during 5 hours followed by a single migration for 24h at 22°C with acetic acid 4% were also investigated. These alternative testing regimes aimed to evaluate the ability of potential shortcuts to shorten the testing time. The release of metals was also studied into a relatively acidic white wine as benchmark food using worst foreseeable conditions of 24 hours at 22°C.

A relevant release of Pb was observed for all samples included in the study. Only very few other metals were found in leaching solutions: Zn, Sb, Ba and Ag. Both simulants generated higher release of lead from the articles under study compared to wine. In general the level of metal released was higher with the test using citric acid than with the test done with acetic acid especially in the first migration, and much higher compared to the most foreseeable test using an acidic wine.

Migration values obtained using a pre-conditioning step followed by a single migration with AA4% at 22°C for 24 hours were much higher than the third migration obtained with conventional test. Thus this accelerated approach did not reach its intended scope of getting more rapidly the articles in the same state that they would be at the end of the repeat use exposures. Further investigations will compare kinetics on both food (wine) and simulants to derive more appropriate testing approaches.

Introduction

In the European Union, labelling of "crystal glass" products is regulated by Council Directive 69/493/EEC [1]. This directive defines four categories of crystal depending on the chemical composition and properties of the material: 1) Superior crystal PbO ≥ 30%; 2) Lead crystal PbO ≥

24%; 3) Crystal glass superior or crystallin ZnO, BaO, PbO, K2O singly or together ≥ 10%; 4) Crystal glass BaO, PbO, K2O singly or together ≥ 10%..

While many studies have been conducted on the release of metals from ceramics, much fewer have investigated the release of heavy metals from crystal glass in contact with food or food simulants [2-8]. The leaching of metals from crystalware depends on several factors such as composition, pH, temperature, physical properties of the food and time of contact [8].

European Directive 84/500/EEC stipulates specific migration limits and basic rules for determining the migration of lead and cadmium for ceramic articles [9], but no harmonized European legislation exists for the glass or crystal sector. The European Commission (EC) is now considering a potential reduction of limits for lead and cadmium and limits for additional metals. It could also be considered to cover crystalware, as long technical means are developed to ensure the feasibility of future measures. The Joint Research Centre, as EURL-FCM, was entrusted to provide the underpinning scientific and technical supporting data and testing options in order to facilitate the decision taking at the EC, Member States and stakeholder levels.

The work included various sets of deliverables including scoping studies on the release of metals from such articles. This work has been started in 2014 and will be completed in 2017.

This report presents the preliminary investigations related to migration of metals from crystalware into representative worst case food and into simulants. The results are presented anonymously as this study is for scoping purposes only and relied on volunteer collaborations from stakeholders.

Materials and methods

The study included investigations on "repeated use" by conducting experiments under repeat use regime testing of three migrations.

White wine was taken as benchmark food to establish comparisons with liquids simulating foods. European Directive 84/500/EEC stipulates a conventional test using 4% acetic acid solution which is the conventional simulant for ceramics and 24 hours as 22 °C as time-temperature exposure. This test is also an ISO standard as well as a national standard in a large number of countries.

In this study, a reference worst foreseeable exposure using wine as benchmarch "food" was used, and repeat tests were conducted using the conventional test. In addition, since the conventional test under repeat use takes 3 times 24hr, an alternative testing was explored using a "pre-conditioning" of the test samples with acetic acid 10% during 5 hours followed by a single migration in 24h with acetic acid 4% [10]. Finally a third approach was also explored using an increase in testing temperature to reduce the time of exposure. In the case the nature of the acid was also changed as using acetic acid would cause implementation issues (fumes). The conditions were based on those established for the field of metals and alloys using 0.5% citric acid and 2 hours at 70°C.

Reagents

Acetic acid, 99-100% purity, Sigma-Aldrich; Citric acid, 99.5% purity, Fluka; Ultrapure Milli-Q water (≥18MΩ); Metal standards 1000 µg/mL (2% HNO3), Analytical technology, Milano

Benchmark foods

White wine "Tamburino" of pH 3.2 for drinkware.

Crystalware samples

The samples used in this study were supplied by the ceramic and glass project contributors to represent various types and geographical origins. The samples used for this study are reported in table 1. They are presented anonymously as this study is for scoping purposes.

Table 1 – Crystalware samples under study

Sample	Description and type of test performed	Sample	Description and type of test performed
	Lead crystal tumbler, PbO 28% AA4%; CA0.5%; white wine; Pre-conditioning		Lead crystal cup, AA4%; CA0.5%; white wine; Pre-conditioning
	Lead crystal plate, PbO 28% AA4%; CA0.5%; white wine; Pre-conditioning		Lead crystal cup, AA4%; white wine; Pre-conditioning
	Lead crystal flute cup, PbO 40% AA4%; CA0.5%; white wine; Pre-conditioning		Lead crystal cup, AA4%; white wine; Pre-conditioning
	Lead crystal cup, PbO 24% AA4%; CA0.5%; white wine; Pre-conditioning		Lead crystal cup, AA4%; white wine; Pre-conditioning
	Lead crystal cup, PbO 24% AA4%; CA0.5%; white wine; Pre-conditioning		Lead crystal cup, AA4%; white wine; Pre-conditioning
	Lead crystal plate, PbO AA4%; CA0.5%; white wine; Pre-conditioning		Lead crystal cup, AA4%; white wine; Pre-conditioning
	Lead crystal flute cup, AA4%; CA0.5%; white wine; Pre-conditioning.		Lead crystal cup, AA4%; CA0.5%; white wine; Pre-conditioning
	Lead crystal cup, AA4%; CA0.5%; white wine; Pre-conditioning		

Instrumentation

Inductively-coupled plasma mass spectrometer (ICP-MS)

The quadrupole inductively-coupled plasma mass spectrometer used in this study was a PerkinElmer NexIon 300D (figure 1), equipped with a concentric nebulizer Meinhard, a glass cyclonic spray chamber and a standard torch (2.5 mm i.d.)).

Figure 1– ICP-MS Perkin Elmer NexIon 300D

Migration methodologies in food simulants

Conventional test used in Directive 84/500/EEC (referred to as "AA4%")

Migration exposure: 4% (v/v) acetic acid, in a freshly prepared aqueous solution, 22ºC, 24 hours.

Procedure: 4 identical units were taken and cleaned with non-acidic diluted detergent and tap water at approximately 40 °C followed by Milli-Q water and dried. The articles were filled with the 4% (v/v) acetic acid solution to a level no more than 1 mm from the overflow point; the distance was measured from the upper rim of the sample. Samples with a flat or slightly sloping rim were filled so that the distance between the surface of the liquid and the overflow point was no more than 6 mm measured along the sloping rim. The test was carried out at a temperature of 22 ± 2°C for 24 ± 0.5 hours using an incubator to maintain the temperature controlled.

Accelerated trials (referred to as "pre-conditioning")

Migration exposure: pre-treatment with 10% (v/v) acetic acid aqueous solution, 5 hours 22ºC followed by migration in acetic acid 4% (v/v), 22ºC, 24 hours.

Procedure: 4 identical units were taken and cleaned with non-acidic diluted detergent and tap water at approximately 40 °C followed by Milli-Q water and dried. The articles were filled with a 10% (v/v) acetic acid solution to as close as possible to the edge (i.e. almost overflowing). This ensured that the area to be later put in contact with the subsequent 4% acetic acid solution was exposed[1].

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[1] Note: drinkware that is to test by immersion may simply be immersed after any areas not to be tested have been covered with a suitable paraffin wax (or similar). There is no specific volume/ratio required, but ware should be covered.

The test items were left covered in an incubator at a temperature of 22 ± 2°C for 5 hours ± 5 minutes. The drinkware was then removed and the acetic acid solution analysed. The drinkware was rinsed with Milli-Q water and allowed to dry. The items were then filled with a 4% (v/v) acetic acid solution and tested at a temperature of 22 ± 2°C for 24 ± 0.5 hours using an incubator[2].

Additional comparison (referred to as "CA0.5%")

Migration exposure: 0.5% (w/v) citric acid, in a freshly prepared aqueous solution, 70°C, 2 hours.

Procedure: The simulant was pre-heated using a hot plate or an oven to 70°C. The temperature of the oven was set so that the temperature of the simulant was 70°C during the migration test. Four identical units were taken and cleaned with non-acidic diluted detergent and tap water at approximately 40°C followed by Milli-Q water and dried. The ceramic test pieces were equilibrated to 70°C in the oven. The sample was filled inside the oven in order to minimize the drop in temperature. The article was filled with a 0.5% citric acid as described for the test with acetic acid. The test was carried out at a temperature of 70 ± 2°C for 2 hours ± 5 min using an incubator.

Repeat use

For all tests compared, the samples were exposed to the simulant three times. After the first migration (I), the samples were washed with Milli-Q water and dried. Afterwards, they were refilled with fresh simulant and incubated for the second migration (II). The same procedure was followed to conduct the third migration experiment (III).

Sample treatment after migration

Leachates obtained applying these methods were treated in the same manner before analysing them by ICP-MS: 100 µL of internal standard solution at 1000 µg/L (185Re, 45Sc, 103Rh, 89Y) was added to 1 mL of leachate, and filled up to 10 mL with Milli-Q water (dilution 1/10). The dilution depended strictly from the concentration of each individual metal. Sometimes it was necessary to dilute the samples 100 times before the analysis. The internal standard concentration was kept constant independently from the dilution applied (10 µg/L).

Preparation of the calibration curve

Calibration curves were prepared by using standard solutions of 1000 µg/mL of each metal and diluting with suitable percentage of acetic or citric acid in ultrapure water. These acids were added to the standards solutions in order to have the same matrix effect as in the sample during the measurements. Calibration curves were prepared as follows: 1 mL of acetic acid 4% (v/v) or citric acid 0.5% (w/v), 100 µL of Internal standards solution (1000 µg/L) of 185Re, 45Sc, 103Rh, 89Y to have a final concentration of 10 µg/L, the proper aliquot of metals stock solution to reach the concentration required and filled up to 10 mL with Milli-Q water. The calibration curve was built up to cover the entire range of the concentration of metals in the sample. Samples that required a dilution 1/100 were quantified using the calibration curve prepared as follows: 100 µL of acetic acid

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[2] Note: The laps of time between pre-treatment with acetic acid 10% (v/v) and the migration with acetic acid 4% (v/v) migrations should be no more than one hour.

4% (v/v) or citric acid 0.5% (w/v), 100 µL of internal standard solution (1000 µg/L), the proper aliquot of metals stock solution to reach the concentration required and fill up to 10 mL with Milli-Q water.

Migration methodologies in the benchmark food

Migration test in white wine at 22ºC, 24 hours

White wine was chosen as "worst case scenario" for crystalware due to its low pH. The pH of white wine used in the test was 3.2. The samples were filled with the white wine in the same manner as performed in method AA4% (using white wine instead of acetic acid 4%). The test was performed at 22°C during 24 hours following the same procedure of method AA4%.

Repeat use

The samples were exposed to three times. After the first migration (I), the samples were washed with Milli-Q water and dried. Afterwards, they were refilled with fresh wine and incubate to carry out the second migration (II). The same procedure was followed to conduct the third migration experiment[3] (III).

Sample treatment after migration in white wine

Sample extracts of white wine were treated in the same manner as that of food simulants before analysing them by ICP-MS: 100 µL of internal standard solution at 1000 µg/L (185Re, 45Sc, 103Rh, 89Y) was added to 1 mL of white wine and filled up to 10 mL with Milli-Q water (dilution 1/10). The dilution depended strictly from the concentration of each individual metal. The internal standard concentration was kept constant independently from the dilution applied (10 µg/L).

Preparation of calibration standards

Calibration curves were prepared in the matrix by using standard solutions of 1000 µg/mL of each metal and diluting with 1 mL of white wine (1/10 dilution) and ultrapure water up to 10 mL. Internal standards (185Re, 45Sc, 103Rh, 89Y) were added at a final concentration of 10 µg/L.

Results and discussion

This report presents the preliminary results on release of elements from drinkware. Due to the limited sample size, the release values were scattered, yet this scoping study could give a quick overview of the migration of metals from real samples. All results reported in the tables are average values and are presented with their corresponding standard deviations from four replicates obtained after the first (I), second (II) and third (III) migration. All results are expressed in µg/kg. Method detection limits (LOD) were calculated from the standard deviation of the blank. For the calculation of LOD, 10 determinations of the blank samples were analysed according to the same analytical method and their standard deviation was calculated. The LOD of the method was calculated as: LOD $=x_{bl} + 3\ sd_{bl,}$ where x_{bl} is the mean concentration calculated from the counts of the noise for the 10 determinations, sd_{bl} is the standard deviation of the analysis. The LODs are reported in table 2.

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[3] Note: The time between each successive migration should be as short as possible anyway no more than one hour.

Table 2 – LOD values in µg/kg for different methods

<table>
<tr><th colspan="11">Acetic Acid 4% [µg/kg]</th></tr>
<tr><td></td><td>Li</td><td>Al</td><td>Mn</td><td>Cu</td><td>Ti</td><td>Co</td><td>Zn</td><td>Cd</td><td>Ba</td><td>Pb</td></tr>
<tr><td>LOD</td><td>0.05</td><td>0.55</td><td>0.15</td><td>0.10</td><td>0.10</td><td>0.11</td><td>8.21</td><td>0.01</td><td>0.04</td><td>0.26</td></tr>
<tr><td></td><td>Zr</td><td>Fe</td><td>V</td><td>Ni</td><td>Cr</td><td>Ag</td><td>Sn</td><td>Sb</td><td>As</td><td></td></tr>
<tr><td>LOD</td><td>1.87</td><td>2.92</td><td>0.11</td><td>0.19</td><td>0.06</td><td>0.04</td><td>0.54</td><td>0.01</td><td>0.09</td><td></td></tr>
<tr><th colspan="11">White wine [µg/kg]</th></tr>
<tr><td></td><td>Li</td><td>Al</td><td>Mn</td><td>Cu</td><td>Ti</td><td>Co</td><td>Zn</td><td>Cd</td><td>Ba</td><td>Pb</td></tr>
<tr><td>LOD</td><td>-</td><td>15.83</td><td>15.90</td><td>2.28</td><td>65.03</td><td>0.11</td><td>15.34</td><td>0.07</td><td>7.13</td><td>0.31</td></tr>
<tr><td></td><td>Fe</td><td>V</td><td>Ni</td><td>Cr</td><td>Sn</td><td>Sb</td><td>As</td><td></td><td></td><td></td></tr>
<tr><td>LOD</td><td>41.65</td><td>1.75</td><td>0.53</td><td>1.38</td><td>0.05</td><td>0.03</td><td>0.23</td><td></td><td></td><td></td></tr>
</table>

Determination of metal background of the benchmark food

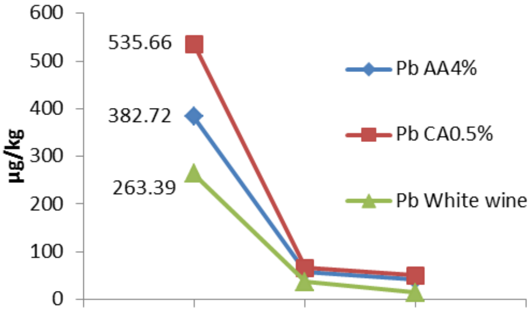
The background levels of metals present in the white wine were measured. Table 3 shows the concentrations of the metals identified and their relative standard deviation calculated on 10 replicates for white wine. The table indicated that it is possible to discriminate the amount of metals migrating from the crystalware from those already present in the matrix if the level of metals migrating is relevant enough.

Table 3 - Metals background in white wine

Metal	Concentration (µg/kg)	RSD (%)
Cd	0.2	3.4
Pb	6.6	0.9
Li	3.3	1.8
Al	650.3	1.7
Ti	922.0	4.2
V	24.1	1.4
Cr	12.3	2.7
Ni	12.5	1.4
Cu	97.8	1.3
Zn	341.5	1.3
Sn	3.0	9.5
Ba	103.3	1.2
Mn	456.6	1.9
Fe	1016.0	0.9
Co	3.4	1.5
As	3.6	2.5

Release of Pb from Crystal Glass

Figure 3-5 show the gradual decrease of Pb leached after successive migrations, into food and food simulants. Studies have indicated that lead released from silicate surfaces dramatically decreased after repeated contact at the same temperature, due to the formation of a silica surface layer acting as a barrier against progressive diffusion from the inner layers [4, 6]. It was demonstrated that at 20°C the amount of lead leached out from the glass in the first 15 minutes is higher than that released in the following 24 h [4]. Acetic acid 4% is a more severe extractant than drinks such as white wine [6]. The amount of Pb leached was always higher into food simulants than into white wine showing that food simulants represented the worst case scenario (figure 2). For this type of articles, the CA0.5% test was more aggressive than the AA4% test especially in the first migration. The results could suggest that the AA4% may represent more adequately the worst foreseeable behaviour with white wine. It should be noted that the result for sample (f) with the CA0.5% method should not be considered reliable due to small volume of simulant and evaporation issues and small volume of simulant to test the migration. In this work the release of Cd from lead crystal articles was under the LOD level (and its presence to impurities from the raw materials).



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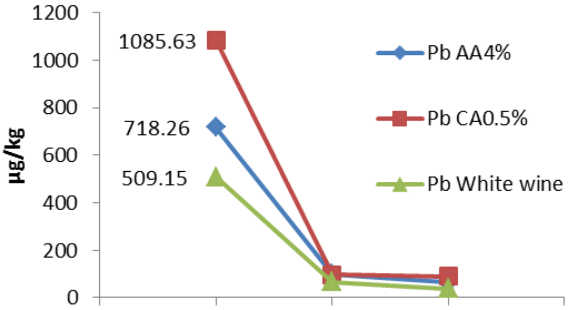

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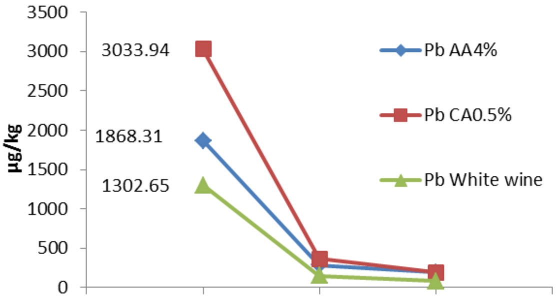

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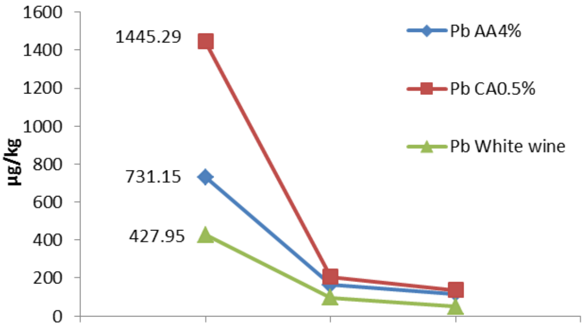

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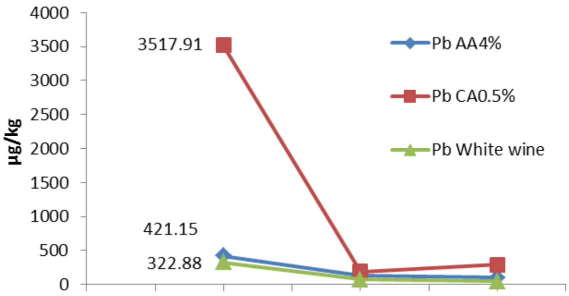

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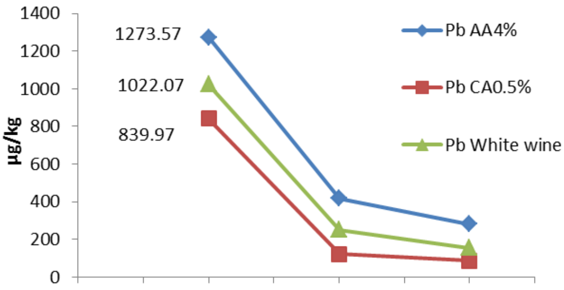

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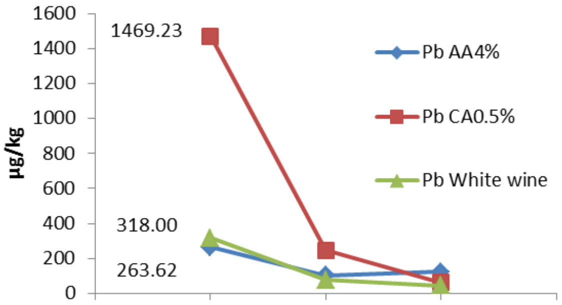
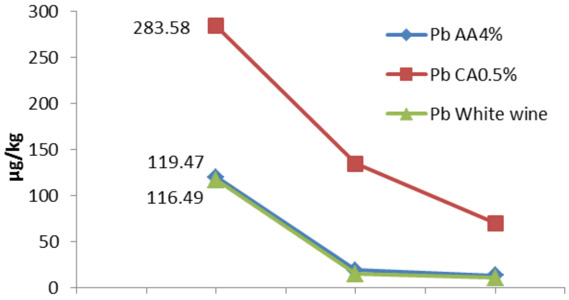
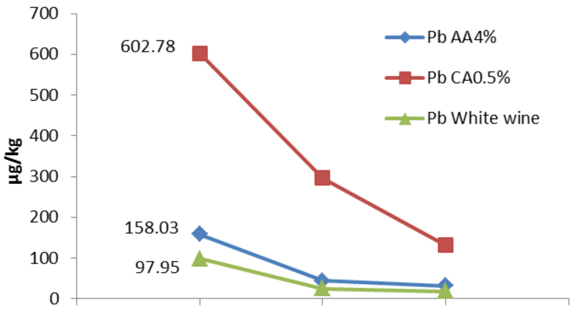

1600
1400
1200
1000
800
600
400
200
0
µg/kg
1469.23
318.00
263.62
Pb AA4%
Pb CA0.5%
Pb White wine

g)


300
250
200
150
100
50
0
µg/kg
283.58
119.47
116.49
Pb AA4%
Pb CA0.5%
Pb White wine

h)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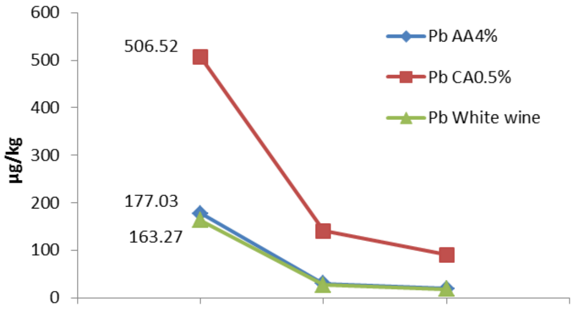
600
500
400
300
200
100
0
µg/kg
602.78
158.03
97.95
Pb AA4%
Pb CA0.5%
Pb White wine

i)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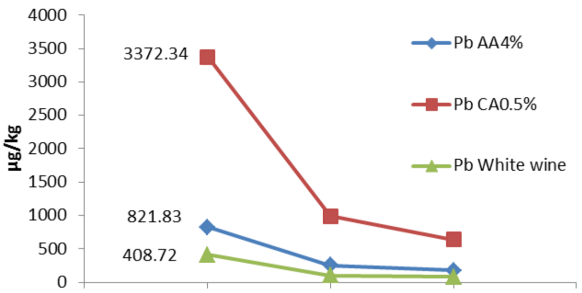
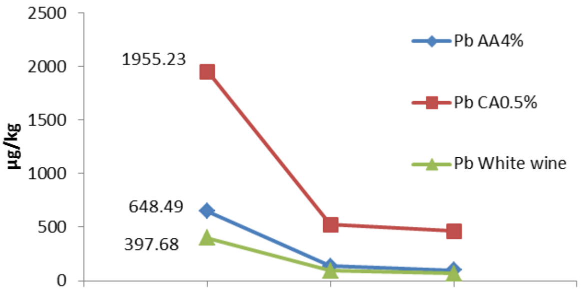
500
400
300
200
100
0
µg/kg
506.52
177.03
163.27
Pb AA4%
Pb CA0.5%
Pb White wine

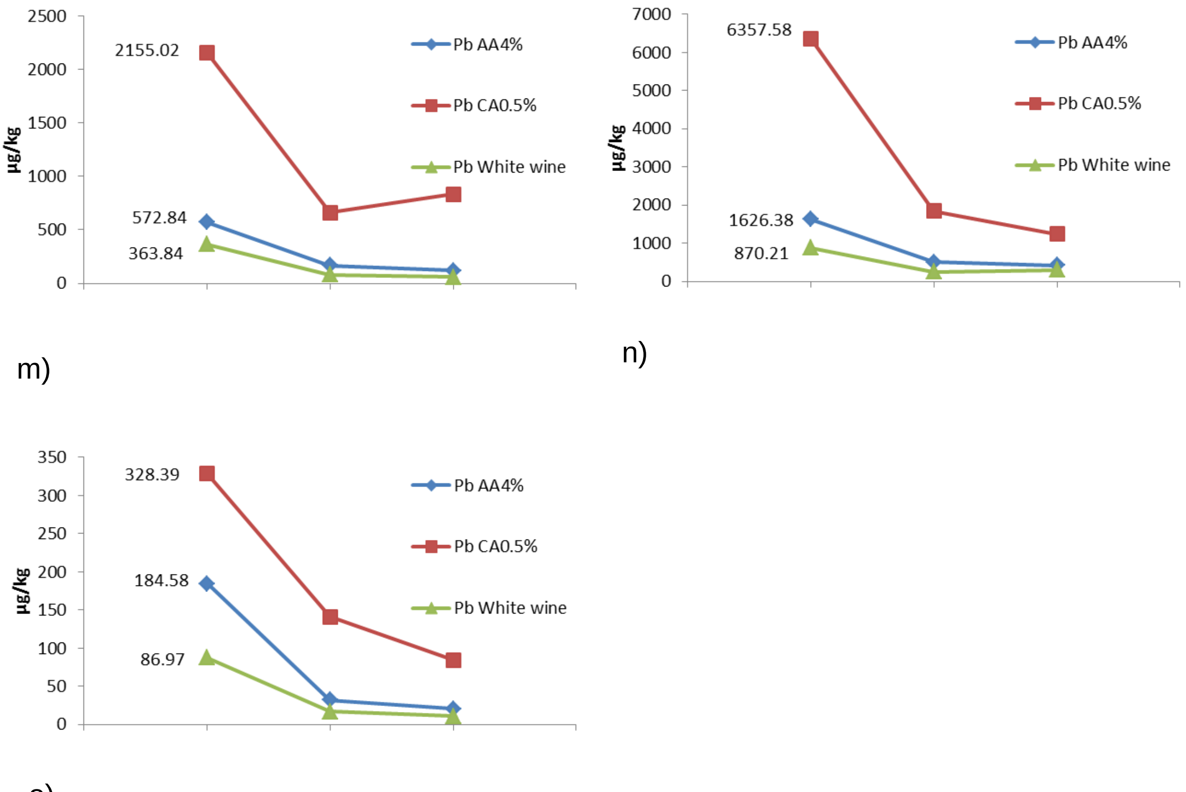
j)


4000
3500
3000
2500
2000
1500
1000
500
0
µg/kg
3372.34
821.83
408.72
Pb AA4%
Pb CA0.5%
Pb White wine

k)


2500
2000
1500
1000
500
0
µg/kg
1955.23
648.49
397.68
Pb AA4%
Pb CA0.5%
Pb White wine

l)



m)

n)

o)

Figure 2 - Pb leached in AA4%, CA0.5% and white wine in the three consecutives migration for samples : a) 613G01, b) 613G02, c) 813G01, d) 813G02, e) 313G01, f) 313G02, g) 513G01, h) 414G01, i) 313G03, j) 813G03, k) 314G04, l) 314G05 m) 314G06, n) 314G07 and o) 314G08.

Table 4 shows the third migration values that could be considered in compliance for repeat use testing regime. In all crystal glass samples analysed in the study the lead release in the third migration was above the discussion starting values (DSV). However, we must consider that the tests are done both with wine and acetic acid for 24 hours, which is not necessarily representative of actual use. In addition, crystalware maybe used only occasionally, thus their contribution to a daily lead intake could be minor. It should be also noted that recommendations for these types of articles often include washing before use, which reduces the successive lead release [11].

Only few elements other than Pb such as Zn, Sb and Ba were detected in the samples studied. For these other metals no significant differences were observed between the different tests applied (AA vs. CA). The results are reported in tables 5-7. One sample released detectable amount of Ag in the first migration due to its type of decoration and the concentrations are presented in table 8. Trace of iron and chromium were detected in two coloured samples.

Table 4 – Pb leached in AA4%, CA0.5% and white wine in the 3rd migration

Third Migration		**Pb (µg/kg)**		
		White wine	**AA4%**	**CA0.5%**
313G01	**Av**	**45.06**	**100.72**	**294.59**
	std	7.04	9.32	77.53
	RSD (%)	15.6	9.3	26.3
313G02	**Av**	**154.90**	**280.07**	**84.92**
	std	12.03	10.60	11.96
	RSD (%)	7.8	3.8	14.1
513G01	**Av**	**45.30**	**122.37**	**62.82**
	std	2.70	0.90	3.93
	RSD (%)	6.0	0.7	6.3
613G01	**Av**	**14.63**	**41.61**	**50.08**
	std	0.40	16.63	3.24
	RSD (%)	2.7	40.0	6.5
613G02	**Av**	**38.22**	**64.35**	**88.04**
	std	5.52	1.52	7.17
	RSD (%)	14.4	2.4	8.1
813G01	**Av**	**80.15**	**187.65**	**188.37**
	std	6.26	15.95	17.68
	RSD (%)	7.8	8.5	9.4
813G02	**Av**	**49.41**	**114.84**	**136.58**
	std	3.46	8.17	22.76
	RSD (%)	7.0	7.1	16.7
414G01	**Av**	**10.21**	**12.70**	**69.64**
	std	0.52	0.28	7.65
	RSD (%)	5.0	2.2	11.0
314G03	**Av**	**17.93**	**31.08**	**130.76**
	std	3.74	3.21	12.29
	RSD (%)	20.9	10.3	9.4
314G04	**Av**	**80.02**	**178.97**	**638.50**
	std	12.65	29.27	176.88
	RSD (%)	15.8	16.4	27.7
314G05	**Av**	**65.68**	**98.49**	**464.15**
	std	7.40	12.96	85.66
	RSD (%)	11.3	13.2	18.5
314G06	**Av**	**57.32**	**120.38**	**833.18**
	std	11.10	18.81	170.28
	RSD (%)	19.4	15.6	20.4
314G07	**Av**	**291.61**	**415.35**	**1236.04**
	std	121.79	143.76	266.58
	RSD (%)	41.8	34.6	21.6
314G08	**Av**	**10.37**	**20.33**	**84.00**
	std	3.26	4.33	41.21
	RSD (%)	31.4	21.3	49.1
814G03	**Av**	**18.03**	**19.54**	**90.29**
	std	0.53	0.62	4.53
	RSD (%)	3.0	3.2	5.0

Table 5 – Metals leached in AA4%, CA0.5% and white wine from different samples under study

			Zn (µg/Kg)			**Sb (µg/Kg)**			**Ba (µg/Kg)**		
			White wine	**AA4%**	**CA0.5%**	**White wine**	**AA4%**	**CA0.5%**	**White wine**	**AA4%**	**CA0.5%**
313G01	**I**	**Av**	<LOD	<LOD	**408.50**	**0.46**	**1.15**	<LOD	<LOD	**0.48**	**1.65**
		std			190.83	0.06	0.32			0.31	0.76
		RSD (%)			46.7	13.5	27.5			65.2	46.0
	II	**Av**			**24.06**	**0.03**	**0.23**			**0.29**	**0.36**
		std			26.02	0.02	0.05			0.29	0.25
		RSD (%)			108.1	75.1	23.1			98.6	69.7
	III	**Av**			**7.79**	<LOD	**0.16**			**1.33**	**0.25**
		std			1.86		0.01			1.23	0.14
		RSD (%)			23.9		8.1			92.5	56.7
313G02	**I**	**Av**	<LOD	**13.91**	**7.78**	**4.72**	**8.26**	<LOD	<LOD	**0.36**	**0.26**
		std		3.34	1.30	1.85	2.37			0.20	0.10
		RSD (%)		24.0	16.8	39.1	28.7			54.4	38.8
	II	**Av**		**10.22**	**7.82**	**0.63**	**1.07**			**1.31**	**0.16**
		std		3.02	2.84	0.25	0.21			1.90	0.02
		RSD (%)		29.6	36.4	39.3	19.6			145.1	14.8
	III	**Av**		<LOD	<LOD	**0.32**	**0.67**			**0.07**	**0.12**
		std				0.14	0.17			0.03	0.30
		RSD (%)				42.3	25.0			47.4	254.8
513G01	**I**	**Av**	<LOD			<LOD			<LOD	<LOD	**17.80**
		std									7.07
		RSD (%)									39.7
	II	**Av**									**18.95**
		std									19.12
		RSD (%)									100.9
	III	**Av**									**10.18**
		std									8.05
		RSD (%)									79.1
613G01	**I**	**Av**	<LOD	**10.50**	**22.06**	**0.04**	**0.93**	<LOD	<LOD	**0.79**	**0.98**
		std		0.61	3.27	0.02	0.10			0.19	0.29
		RSD (%)		5.8	14.8	63.0	10.8			24.5	29.6
	II	**Av**		<LOD	<LOD	**0.16**	**0.24**			**0.12**	**0.26**
		std				0.16	0.02			0.04	0.29
		RSD (%)				102.7	8.7			34.0	110.3
	III	**Av**		<LOD	<LOD	<LOD	**0.15**			**0.09**	**0.16**
		std					0.03			0.02	0.11
		RSD (%)					21.4			21.3	70.4
613G02	**I**	**Av**	<LOD	**42.50**	**30.47**	**0.21**	**1.60**	<LOD	<LOD	**14.71**	**0.34**
		std		6.83	1.53	0.02	0.05			2.97	0.16
		RSD (%)		16.1	5.0	9.8	3.4			20.2	46.6
	II	**Av**		<LOD	<LOD	<LOD	**0.15**			**0.17**	**0.21**
		std					0.03			0.10	0.20
		RSD (%)					20.4			60.4	94.7
	III	**Av**		<LOD	<LOD	<LOD	**0.11**			**0.09**	**0.25**
		std					0.05			0.07	0.27
		RSD (%)					47.7			80.4	108.7

Table 6 – Metals leached in AA4%, CA0.5% and white wine from various samples under study

			Zn (µg/Kg)			Sb (µg/Kg)			Ba (µg/Kg)		
			White wine	AA4%	CA0.5%	White wine	AA4%	CA0.5%	White wine	AA4%	CA0.5%
813G01	**I**	**Av**	<LOD	**465.50**	**33.97**	**2.03**	**4.95**	<LOD	<LOD	**13.42**	**28.19**
		std		515.99	3.75	0.99	1.87			2.08	2.36
		RSD (%)		110.8	11.0	48.7	37.7			15.5	8.4
	II	**Av**		**97.15**	**75.23**	**0.32**	**1.45**			**2.70**	**2.24**
		std		109.07	102.54	0.08	0.34			0.42	0.26
		RSD (%)		112.3	136.3	23.8	23.1			15.7	11.8
	III	**Av**		**423.94**	**9.09**	**0.17**	**0.86**			**2.17**	**1.51**
		std		550.03	0.20	0.03	0.18			0.53	0.45
		RSD (%)		129.7	2.2	17.8	20.9			24.4	29.8
813G02	**I**	**Av**	<LOD	**42.71**	**65.89**	**0.79**	**1.54**	<LOD	<LOD	**14.51**	**33.90**
		std		6.9	6.05	0.19	0.07			2.62	6.74
		RSD (%)		16.4	9.2	24.0	4.2			18.0	19.9
	II	**Av**		<LOD	**10.04**	**0.03**	**0.27**			**4.12**	**6.83**
		std			1.38	0.02	0.01			1.20	1.06
		RSD (%)			13.8	81.3	5.2			29.1	15.5
	III	**Av**		<LOD	**9.08**	<LOD	**0.17**			**3.39**	**3.26**
		std			1.48		0.02			1.34	1.07
		RSD (%)			16.3		13.9			39.4	32.8
414G01	**I**	**Av**	<LOD			<LOD			<LOD	<LOD	**5.82**
		std									0.59
		RSD (%)									10.2
	II	**Av**									**0.13**
		std									0.10
		RSD (%)									79.1
	III	**Av**									**5.03**
		std									0.87
		RSD (%)									17.4
314G03	**I**	**Av**	<LOD			**0.24**	**1.02**	**1.62**	<LOD	<LOD	<LOD
		std				0.01	0.53	0.16			
		RSD (%)				4.1	51.3	9.7			
	II	**Av**				<LOD	**0.16**	**0.19**			
		std					0.12	0.09			
		RSD (%)					76.2	50.4			
	III	**Av**				<LOD	**0.08**	**0.11**			
		std					0.03	0.03			
		RSD (%)					41.4	30.4			
814G03	**I**	**Av**	<LOD			**0.24**	**0.38**	**0.84**	<LOD	**4.96**	**15.75**
		std				0.09	0.07	0.04		0.54	0.09
		RSD (%)				39.0	19.1	4.3		10.9	0.6
	II	**Av**				<LOD	<LOD	**0.09**		**1.09**	**5.07**
		std						0.05		0.05	1.00
		RSD (%)						52.4		4.3	19.7
	III	**Av**				<LOD	<LOD	**0.06**		**0.68**	**2.81**
		std						0.07		0.02	0.24
		RSD (%)						107.2		3.6	8.5

Table 7 – Metals leached in AA4%, CA0.5% and white wine from various samples under study

			Zn (µg/Kg)			**Sb (µg/Kg)**			**Ba (µg/Kg)**		
			White wine	**AA4%**	**CA0.5%**	**White wine**	**AA4%**	**CA0.5%**	**White wine**	**AA4%**	**CA0.5%**
313G04	**I**	**Av**	**<LOD**	**61.58**	**27.79**	**2.00**	**4.27**	**11.72**	**<LOD**	**2.34**	**6.82**
		std		17.23	1.97	0.14	0.63	0.31		0.13	0.83
		RSD (%)		28.0	7.1	6.9	14.7	2.6		5.5	12.2
	II	**Av**		**<LOD**	**<LOD**	**0.59**	**1.08**	**4.44**		**0.63**	**1.90**
		std				0.11	0.17	0.28		0.39	0.65
		RSD (%)				18.7	16.0	6.3		62.2	34.3
	III	**Av**		**<LOD**	**<LOD**	**0.41**	**0.79**	**3.33**		**0.30**	**0.74**
		std				0.07	0.11	0.49		0.06	0.30
		RSD (%)				16.1	13.5	14.8		20.9	40.3
313G05	**I**	**Av**	**<LOD**	**22.93**	**20.86**	**2.05**	**1.91**	**8.91**	**<LOD**	**1.65**	**3.55**
		std		13.78	2.41	1.08	0.17	1.99		0.35	0.35
		RSD (%)		60.1	11.5	52.6	9.0	22.4		20.9	9.8
	II	**Av**		**<LOD**	**<LOD**	**0.49**	**0.46**	**2.63**		**0.21**	**0.44**
		std				0.10	0.11	0.64		0.03	0.25
		RSD (%)				19.5	24.9	24.4		14.1	56.4
	III	**Av**		**<LOD**	**<LOD**	**0.33**	**0.30**	**2.24**		**0.26**	**0.36**
		std				0.04	0.08	0.70		0.19	0.17
		RSD (%)				10.8	27.3	31.4		74.1	47.1
313G06	**I**	**Av**	**<LOD**	**21.55**	**30.25**	**1.51**	**3.29**	**9.82**	**<LOD**	**2.53**	**5.53**
		std		2.80	10.88	0.29	0.50	1.78		0.82	0.82
		RSD (%)		13.0	36.0	19.2	15.3	18.1		32.4	14.8
	II	**Av**		**<LOD**	**<LOD**	**0.39**	**0.85**	**2.44**		**0.49**	**0.77**
		std				0.06	0.22	0.23		0.14	0.13
		RSD (%)				15.2	26.5	9.4		27.7	17.1
	III	**Av**		**<LOD**	**<LOD**	**0.27**	**0.57**	**3.31**		**0.40**	**1.11**
		std				0.06	0.16	0.64		0.12	0.32
		RSD (%)				22.1	28.9	19.3		30.9	29.0
313G07	**I**	**Av**	**<LOD**	**21.93**	**21.22**	**1.45**	**3.56**	**6.50**	**<LOD**	**0.90**	**6.99**
		std		6.30	2.91	0.37	1.39	2.27		1.24	4.33
		RSD (%)		28.7	13.7	25.8	39.0	34.9		137.3	61.9
	II	**Av**		**<LOD**	**<LOD**	**0.32**	**0.33**	**0.37**		**<LOD**	**3.86**
		std				0.06	0.11	0.11			0.58
		RSD (%)				20.0	32.6	30.5			15.0
	III	**Av**		**<LOD**	**13.00**	**0.64**	**0.18**	**0.26**		**<LOD**	**2.89**
		std			20.58	0.41	0.05	0.07			0.31
		RSD (%)			158.3	63.2	27.3	26.9			10.7
313G08	**I**	**Av**	**<LOD**	**<LOD**	**<LOD**	**0.20**	**0.53**	**1.02**	**<LOD**	**0.09**	**0.15**
		std				0.21	0.06	0.10		0.03	0.15
		RSD (%)				105.8	11.7	9.9		29.5	100.8
	II	**Av**				**0.11**	**0.10**	**0.29**		**<LOD**	**<LOD**
		std				0.01	0.01	0.15			
		RSD (%)				11.2	12.0	51.7			
	III	**Av**				**0.08**	**0.06**	**0.20**		**<LOD**	**<LOD**
		std				0.01	0.01	0.03			
		RSD (%)				4.2	25.1	14.8			

Table 8 – Ag leached in AA4%, CA0.5% and white wine from sample 813G01

			Ag (µg/kg)		
			White wine	**AA4%**	**CA0.5%**
813G01	**I**	**Av**	**0.83**	**0.52**	**<LOD**
		std	0.15	0.10	
		RSD (%)	18.4	19.1	
	II	**Av**	**0.18**	**<LOD**	
		std	0.02		
		RSD (%)	12.6		
	III	**Av**	**<LOD**	**<LOD**	
		std			
		RSD (%)			

Preconditioning

One of the drawbacks of repeat testing is the time needed to obtain results: the conventional test under repeat use amounts to three days of exposure plus the analysis. One way of minimizing this testing time without resorting to accelerated leaching at elevated temperatures could be to pre-condition the drinkware to an equivalent state using the same acetic acid at higher concentration, after which a normal, AA4%, 22°C, 24 h extraction is carried out. The release of Cd and Pb and other metals were compared for this accelerated test vs. the conventional one. The aim of the pre-conditioning was to accelerate the leaching process and achieve values of migration similar to those of the third migration of the traditional test AA4%.

The results showed that in all the samples compared, pre-conditioning of the articles with acetic acid 10% for 5 hours at 22°C followed by a single migration in acetic acid 4% for 24 hours at 22°C resulted in higher concentration values than those obtained in the third migration with AA4% (current migration test 84/500/EEC). Thus the pre-treatment with AA10% for 5 hours to get the articles in the same state that they would be at the end of the second exposure, i.e. ready to do the third exposure but much more quickly did not achieve this. In figures 3-5 the values of Pb released applying a single migration at 22°C for 24 hours after the preconditioning step is marked as a red square and was plotted against the values obtained applying the method AA4% that foresee three successive migrations (I, II, III) marked in blue. In the same graphs are also reported the migration values of Pb obtained in acetic acid 10% after 5 hours (red triangle). The preliminary results indicated that the conditions applied in this pilot trial could not be considered fit for purpose. Further work should be carried out to determine a more appropriate means of pre-conditioning the sample to achieve this. However, the amount of data to be able to provide a generalised conclusion is likely not cost effective.

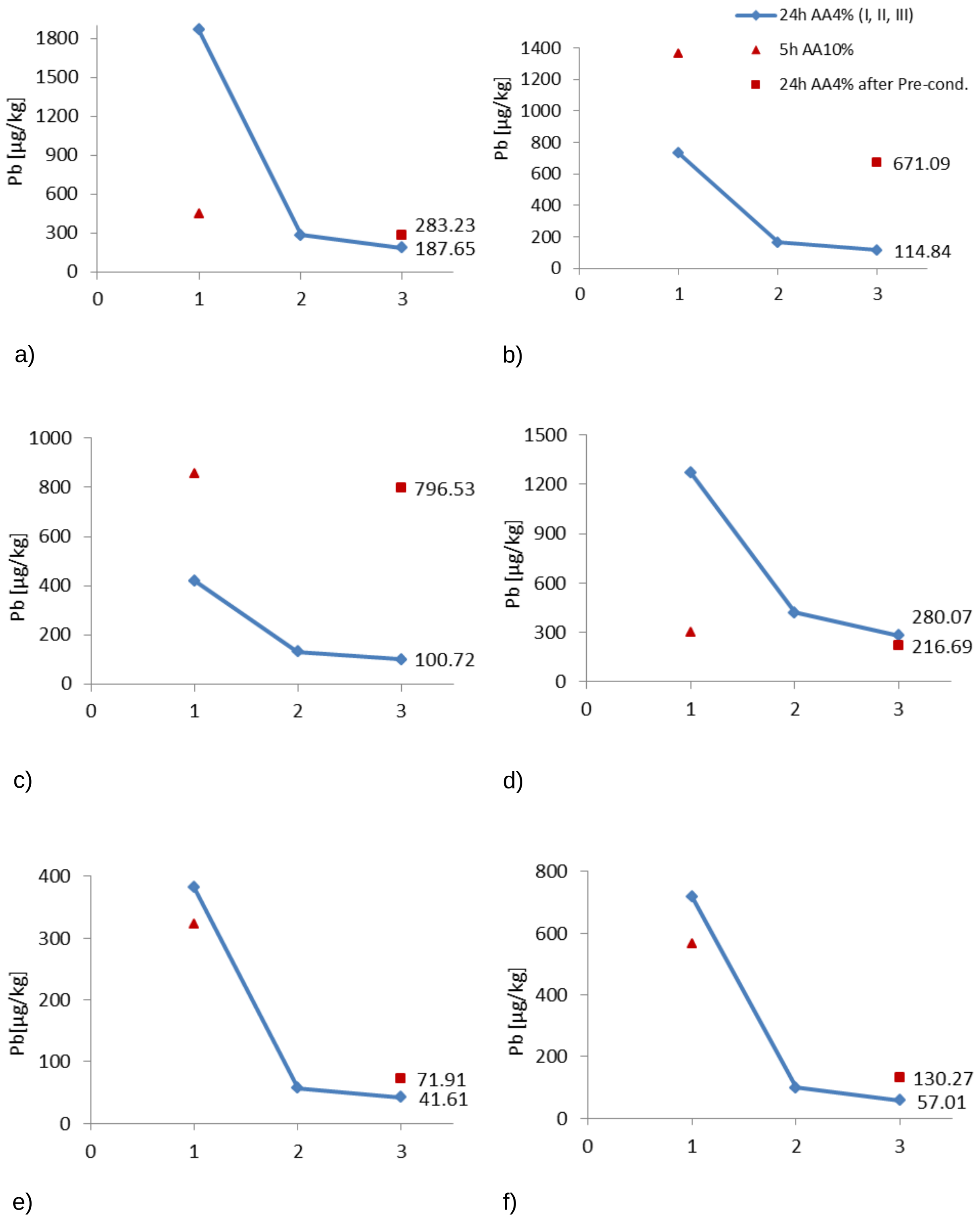


Figure 3 – Pb release from Lead crystal by method AA4% vs method using preconditioning for various samples: a) 813G01, b) 813G02, c) 313G01, d) 313G02, e) 613G01 and f) 613G02.

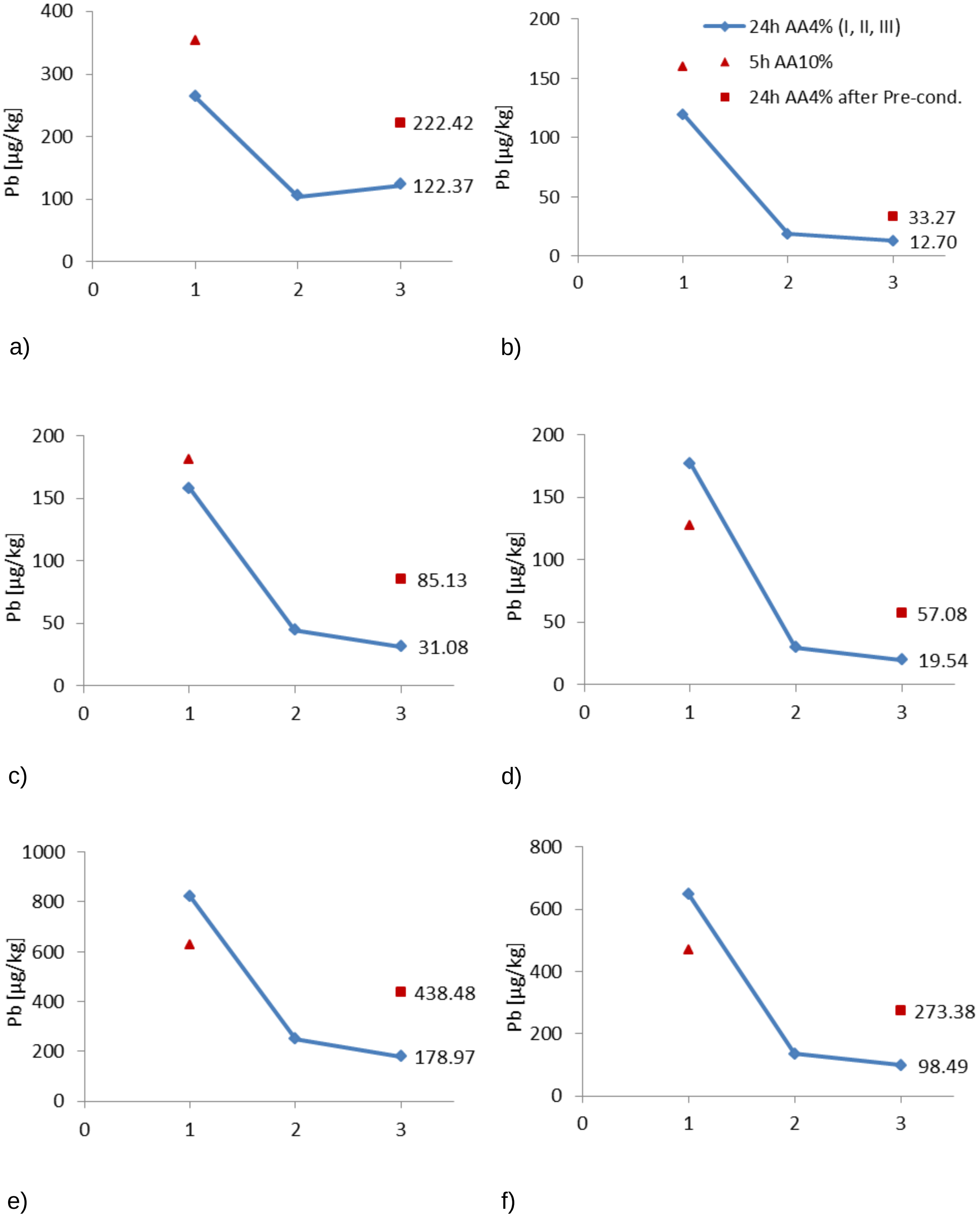
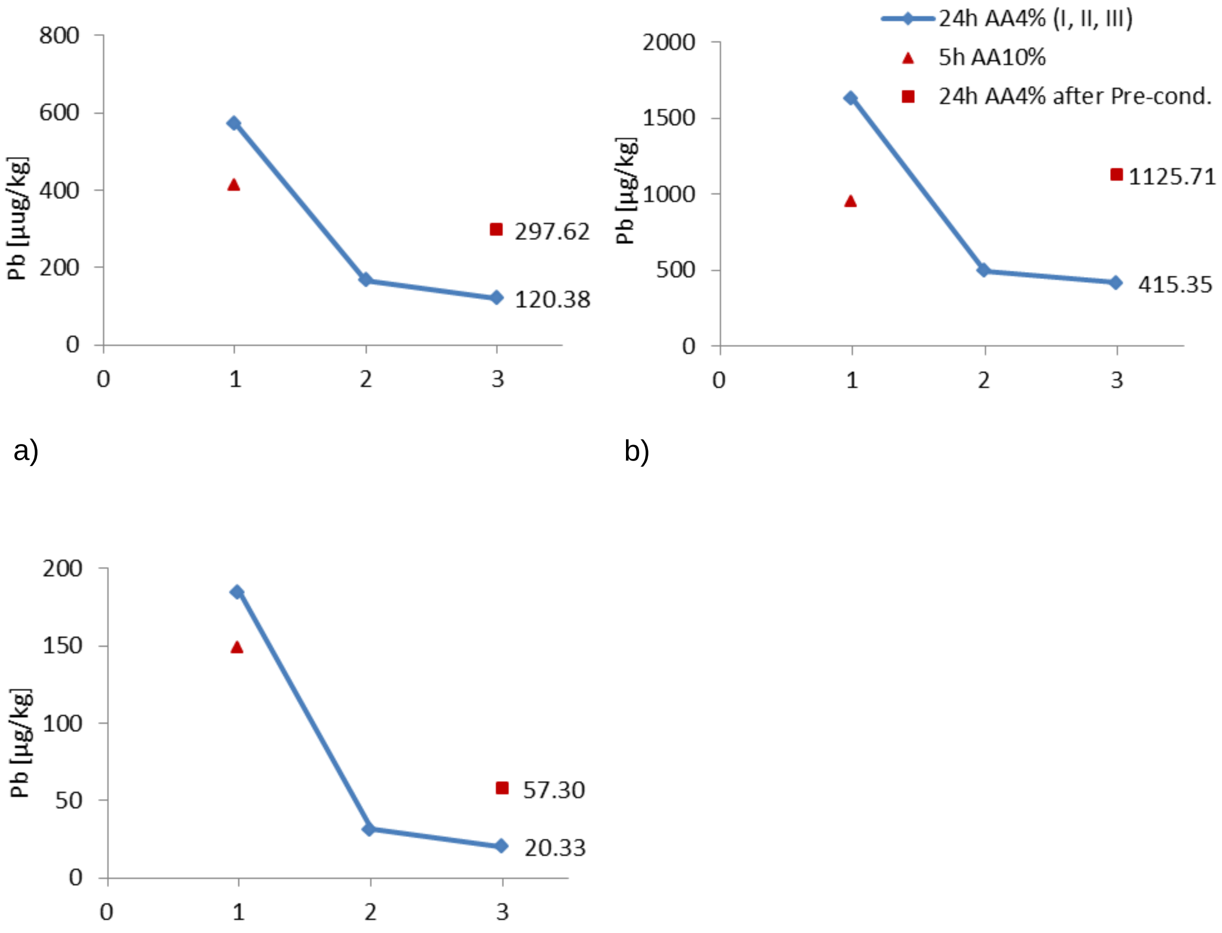


Figure 4 – Pb release from Lead crystal by method AA4% vs method using preconditioning for various samples: a) 513G01, b) 414G01, c) 314G03, d) 814G03, e) 314G04 and f) 314G05.



a) b)

c)

Figure 5 – Pb release from Lead crystal by method AA4% vs method using preconditioning for various samples: a) 314G06, b) 314G07 and c) 314G08.

The difference between the Pb migration values (in %) obtained applying the preconditioning methodology (AA4% at 22°C for 24h after pretreatment with AA10% at 22°C for 5h) and values obtained in the third migration of consecutive tests with AA4% at 22°C for 24h are shown In figure 6. The values reported in figure 6 are calculated as follow:

$$\frac{(\text{24h AA4\% after pretreatment 5h AA10\%}) - \text{AA4\% III}}{\text{AA4\% III}} \text{*100 [\%]}$$

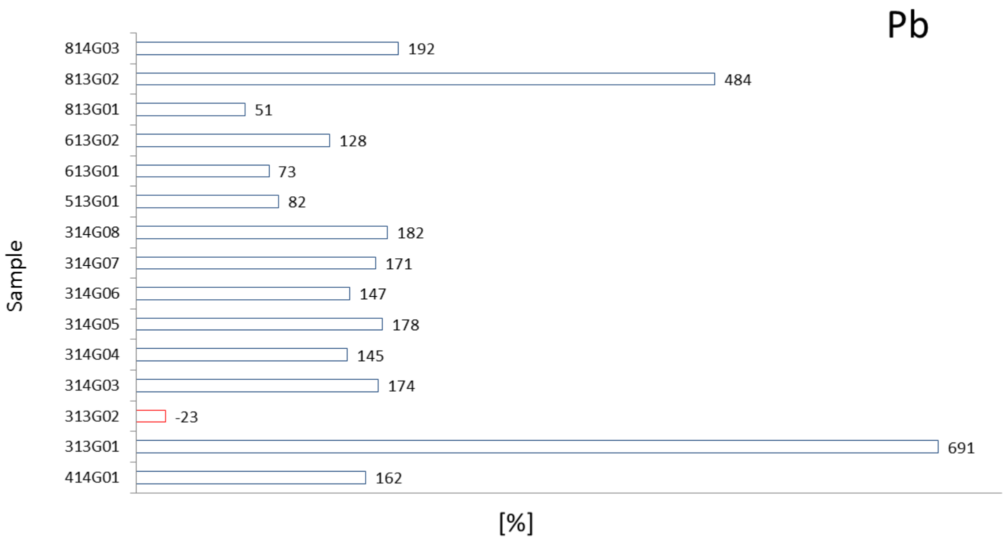


Figure 6 – Difference in percentage between Pb release from Lead crystal by method AA4% (III migration) vs method Preconditioning

Relationship between third and first migration

Previous work [12] refers to a potential relation between the results of a third migration and that of the first migration, where the third migration should be approximately 10% of the first one. For ceramics, it was discussed whether for example 100 µg/L of Pb in the first migration would give less than 10 µg/L in the third migration hence complying with the proposed limit. This relation should be demonstrated and in this work it was also considered for the limited sets of samples tested for crystalware. Table 9 shows the percentage of the third migration respect to the first one for Pb leached from 9 samples in both food simulants. These values are obtained dividing the concentration of the Pb in the migration III solution by the concentration of Pb from the migration I solution and presented in %. In contrast to ceramic, the relationship between the third and the first migration of Pb in crystal glass seemed to be more constant and generally in the range of 10-25%.

Table 9. 3rd migration as % of 1st migration for Pb in crystalware

Samples	Method AA 0.4% [%]	Method CA 0.5% [%]
313G01 (28% Pb)	24	8
313G02 (28% Pb)	22	10
513G01 (40% Pb)	46	4
613G01 (24% Pb)	11	9
613G02 (24% Pb)	9	8
813G01	10	6
813G02	16	9
414G01	11	25
314G03	20	22
314G04	22	19
314G05	15	24
314G06	21	39
314G07	26	19
314G08	11	26
814G03	11	18

Conclusions

For all samples included in the study a relevant release of Pb was observed. The release of Pb seemed to be higher with CA0.5% than with AA4% test especially in the first migration, probably also due to the temperature that plays an important role in the leaching process. Aside from Pb only few other elements such as Zn, Sb and Ba were detected in the samples studied. For these other metals no clear trend was observed with respect to a potential difference between testing with CA0.5% and with AA4%. Both simulants presented higher migration respect to the white wine for all metals. The migration profile in the test with AA4% was worst but more similar to white wine meaning that this simulants represents well this benchmark food. The relationship between the 3rd and the 1st migration for crystalware was more constant than for ceramic and the third migration was generally between 10-25% of the first one. Migration values obtained with a single migration in AA4% for 24 hours at 22°C after a pre-conditioning step were always above the third migration obtained with the method AA4%. Thus the pre-treatment with AA10% for 5 hours as an accelerated test was not adequate.

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