European Commission

JRC SCIENCE AND POLICY REPORT

Scoping investigations on the release of metals from the rim area of decorated articles

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

Mercedes Ana Peltzer, Giorgia Beldi,

Natalia Jakubowska and Catherine Simoneau

2015

Report EUR 27178 EN

Joint Research Centre

European Commission
Joint Research Centre
Institute for Health and Consumer Protection

Contact information
Catherine Simoneau
Address: Joint Research Centre, xxx *(relevant complete address)*
E-mail: JRC-FCM@ec.europa.eu

JRC Science Hub
https://ec.europa.eu/jrc

JRC95336

EUR 27178 EN

ISBN 978-92-79-47228-2 (PDF)

ISSN 1831-9424 (online)

doi:10.2788/484454

Luxembourg: Publications Office of the European Union, 2015

Abstract

In the present work, the release of metals from 14 samples (9 industrial samples, 2 ad-hoc manufactured ceramic cups and 3 ad-hoc manufactured glasses) was investigated in order to provide underpinning data on migration of metals under different conditions from different samples. The rim area was tested using 2 different approaches (wine and a wine-simulating acidic liquid, i.e 4% aqueous acetic acid). The test using the simulant acetic acid 4% (AA4%) was further investigated using two different protocols (with and without the use of paraffin wax). The release of metals from glass samples were also studied into white wine as benchmark food.
All the samples tested in this study released Pb. It was also possible to detect limited release of Cd and other metals from the rim area of decorated articles. It was observed that the release of Pb, Cd and other metals generally decreased in successive migrations. Highly decorated articles with very bright colours led to a greater release of metals. The release of elements from test articles into white wine was always lower than that into acidic simulants. The testing using citric acid at higher temperature and shorter time was not significantly more severe than that using acetic acid 4% and depended on the metals considered and potential damage of the heterogeneous decoration of the articles during the exposure. Overglaze decorated samples were more sensitive to exposure to food simulants and released metals to a greater extent than test articles with underglaze decorations. The use of melted paraffin wax on the non-rim area may gave lower migration of metals into food simulants and could be more realistic, but might not be necessarily relevant when considering the standard deviation of the results..

Contents

1. 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 testing the release from the rim of articles. The overall aim of this study was investigate the release of various metals from the rim and on the experimental approaches for testing the release specific to the rim part of articles. In the present work, the release of metals from 14 samples (9 industrial samples, 2 ad-hoc manufactured ceramic cups and 3 ad-hoc manufactured glasses). The rim area was tested using 2 different approaches (wine and a wine-simulating acidic liquid, i.e 4% aqueous acetic acid). The test using the simulant acetic acid 4% (AA4%) was also investigated using two different protocols (with and without the use of paraffin wax). A testing mode using The testing using citric acid 0.5% at higher temperature and shorter time was also tested for comparison. The release of metals from test samples was also studied into benchmark food white wine.

All the samples tested in this study released Pb. It was also possible to detect limited release of Cd and other metals from the rim area of decorated articles. It was observed that the release of Pb, Cd and other metals generally decreased in successive migrations. Highly decorated articles with very bright colours led to a greater release of metals. The release of elements from test articles into white wine was always lower than that into acidic simulants. The testing using citric acid at higher temperature and shorter time was not significantly more severe than that using acetic acid 4% and depended on the metals considered and potential damage of the heterogeneous decoration of the articles during the exposure. Overglaze decorated samples were more sensitive to exposure to food simulants and released metals to a greater extent than test articles with underglaze decorations. The use of melted paraffin wax on the non-rim area may gave lower migration of metals into food simulants.

2. Introduction

The EU Directive 84/500/EEC has set limits for lead (Pb) and cadmium (Cd) [1]. Scientific data have shown the need to lower the current limits [2-5]. Limits on the release of other metals such as chromium, cobalt, copper, manganese, nickel, etc., are also under consideration [6-9].

It is important to have adequate methodologies for testing hollowware such as tableware and drinkware including the rim area. The drinking rim area is considered the portion of a glass tumbler or ceramic mug which extends 20 mm below the rim on the outside of the specimen.

Several standards for testing the drinking rim are available that contain test protocols:

- Standard EN 1388-2:1995 "Determination of the release of lead and cadmium from silicate surfaces other than ceramic ware" [10];
- ISO 4531-1/2:1998 "Vitreous and porcelain enamels-Release of lead and cadmium from enamelled ware in contact with food" [11];
- Standard ASTM C927-80 "Lead and Cadmium Extracted from the Lip and Rim area of Glass Tumblers Externally Decorated with Ceramic Glass Enamels" [12].
- Standard ISO 7086-1:2000 "Glass hollowware in contact with food-Release of lead and cadmium" [13];
- Standard ISO 6486-1:1999 "Ceramic ware, glass-ceramic ware and glass dinnerware in contact with food-release of lead and cadmium" [14];

The standards have generally the same scope, but may differ in methodology. The standard EN 1388-2:1995 and the ISO standards make use of melted paraffin wax to cover the zone that is not in contact with the simulant, while the ASTM standard does not. The testing conditions to carry out the migration test use for all standards acetic acid 4% as test liquid with an exposure of 24 ± 0.5 h. at 22 ± 2°C.

Several testing approaches were investigated as part of an overall umbrella covering ceramics, crystalware and rim. They included protocols based on the conventional test with acetic acid 4% for 24 hours at 22°C (three migrations) as well as an accelerated test using citric acid 0.5% for 2 hours at 70°C (three migrations). The conventional test AA4% was performed with and without the use of melted paraffin wax, and the results were compared. For decorated crystal articles the migration test was also performed in white wine as base for comparison.

3. Materials and methods

Migration tests were performed in acetic acid 4%, citric acid 0.5%, and white wine.

3.1 Reagents

Acetic acid, 99-100% purity, Sigma-Aldrich, Citric acid, 99.5% purity, Fluka, Ultra-pure Milli-Q water (≥18MΩ), Paraffin wax, m.p. 53-57°C

3.2 Benchmark food

White wine "Tamburino" of pH 3.2.

3.3 Samples

The samples used in this study were supplied by the ceramic and glass project contributors (via their European Associations – CERAM-Unie and ICF-EDG). Most of the tested samples were industrial samples decorated on the external part and the decoration was also present on the drinking rim area. In addition, samples manufactured ad-hoc for the project were also tested to evaluate better the differences stemming from the various testing modes under study. The samples used for this study are reported in table 2 and those produced ad hoc are presented in table 3. The samples and results are presented anonymously as this study is for scoping purposes only and relied on volunteer collaborations from stakeholders.

Table 2 – Industrial samples

Sample	Simulant volume [L]	Inner volume [L]	Description and type of test performed	Sample	Simulant volume [L]	Inner volume [L]	Description and type of test performed
	0.14	0.065	Cup decorated outside AA4% (Wax and no Wax); CA0.5%		0.10	0.075	Cup coloured outside AA4% (Wax and no Wax); CA0.5%
	0.12	0.055	Cup decorated outside AA4% ; CA0.5%		0.10	0.075	Cup coloured outside AA4% (Wax and no Wax); CA0.5%
	0.14	0.200	Cup decorated outside AA4% ; CA0.5%		0.10	0.075	Cup coloured outside AA4% (Wax and no Wax); CA0.5%
	0.09	0.260	Cup decorated outside AA4% ; CA0.5%		0.10	0.125	Crystal glass decorated outside AA4%; CA0.5%
	0.14	0.300	Cup decorated outside AA4% ; CA0.5%				

Table 3 - Ceramic and glass Samples manufactured ad-hoc

Sample	Simulant volume [L]	Inner volume [L]	Description and type of test performed
	0.11	0.050	Overglaze cup decorated inside and outside AA4% (Wax and no Wax); CA0.5%
	0.11	0.050	Underglaze cup decorated inside and outside AA4% (Wax and no Wax); CA0.5%
	0.08	0.320	Tumblers decorated outside with ceramic glass enamels; AA4% (Wax and no Wax); CA0.5%; White wine
	0.10	0.320	Tumblers decorated outside with ceramic glass enamels AA4% (Wax and no Wax); CA0.5%; White wine
	0.12	0.400	Tumblers decorated outside with ceramic glass enamels AA4% (Wax and no Wax); CA0.5%; White wine

3.4 Instrumentation

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

3.5 Migration methodologies in food simulants

3.5.1 Method (AA4%): Migration in acetic acid 4%, 22°C, 24 hours

Test liquid: 4% (v/v) acetic acid, in a freshly prepared aqueous solution.

Procedure based on ASTM C97-80: 4 identical units were taken and cleaned with non-acidic diluted detergent and tap water followed by Milli-Q water and dried. The internal volume of the article was recorded in mL by filling from a graduated cylinder to approximately 6 to 7 mm of overflowing. The external side of the article was marked, in a non-decorated area, 20 mm below the rim. The articles were inverted in a plastic beaker and the 4% (v/v) acetic acid solution was carefully added from a graduated cylinder to the 20-mm mark. The volume of simulant used was recorded. The beaker was covered with a plastic lid to prevent evaporation. The test was carried out at a temperature of 22 ± 2°C for 24 ± 0.5 hours using a temperature-controlled incubator. The final results were expressed in micrograms per litre (µg/L) extracted relative to the internal volume of the glass article.

Procedure based on EN1388-2:1995 and ISO standards: 4 identical units were taken and cleaned with non-acidic diluted detergent and tap water followed by Milli-Q water and dried. The area of the drinking rim was marked, i.e. a 20 mm wide section of the external surface of the drinking vessel measured downward from the upper edge along the wall of the vessel. The portion of the external surface of the article not to be tested was covered carefully with melted paraffin wax. The migration procedure was performed as in ASTM C97-80 by inverting the articles in a plastic beaker and filling carefully with the simulant. The results were expressed in micrograms per article (µg/article).

3.5.2 Method (CA0.5%): Migration in citric acid 0.5%, 70°C, 2 hours

The test liquid (simulant) was 0.5% (w/v) citric acid, in a freshly prepared aqueous solution. The simulant was pre-heated using a hot plate or an oven to 70°C. The article was inverted in a plastic beaker and equilibrated to 70°C in the oven. The beaker was filled with the hot simulant inside the oven in order to minimize a drop in temperature. The citric acid 0.5% was added to the 20-mm mark. The volume of simulant used was recorded. The beakers were covered with a Plexiglas lid to prevent evaporation. The exposure time was 70°C for 2 hours in the dark. The migration procedure for all methodologies was repeated three times and the lag time between consecutive migrations was no longer than one hour. After each migration, the test articles and plastic holding beakers were washed with distilled water followed by Milli-Q water and dried. The plastics holding beakers were refilled with fresh simulants and the test specimens incubated to carry out the second migration (II). The same procedure was followed to conduct the third migration experiment (III).

3.5.3 Sample treatment after migration with method AA4% and CA0.5%

Following the exposure to the simulant (4.5.1, 4.5.2), the samples were treated similarly before analysis by ICP-MS: 1 mL of simulant was added with 100 µL of internal standard solution at 1000 µg/L (185Re, 45Sc, 103Rh, 89Y) and filled up to 10 mL with Milli-Q water (dilution 1/10). The dilution depended from the concentration of each individual metal (it was sometimes necessary to dilute the samples by 100 before analysis). The internal standard concentration was kept constant independently from the dilution applied (10 µg/L). 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 standard 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 fill up to 10 mL with Milli-Q water. The calibration curve was built to cover the entire range of the concentrations 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 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.

3.6 Migration methodology in white wine

3.6.1 Method Wine: Migration in white wine at 22°C, 24 hours

White wine was chosen as worst case scenario for these articles due to its low pH. The pH of white wine used in the test was 3,2. Four identical units were taken and cleaned with non-acidic diluted detergent and tap water followed by Milli-Q water and dried. The internal volume of the article was recorded in mL by filling from graduated cylinder to approximately 6 to 7 mm of overflowing. The external side of the article was marked, in a non-decorated area, 20 mm below the rim. The articles were inverted in a plastic beaker and the white wine was carefully added from a graduated cylinder to the 20-mm mark. The volume of simulant used was recorded. The beaker was covered with a Plexiglas lid to prevent evaporation. The test was carried out at a temperature of 22 ± 2°C for 24 ± 0.5 hours using an incubator to maintain a controlled temperature. After the first migration (I), glass articles and the holding beakers were washed with distilled water followed by Milli-Q water and dried. The beakers (with the sample inside) were refilled with fresh white wine and incubated to carry out the second migration (II). The same procedure was followed to conduct the third migration experiment (III). The time between each successive migration was no more than one hour. The results were expressed in micrograms per litre (µg/L) relative to the internal volume of the article.

3.6.2 Sample treatment after migration in white wine

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

4. Results and discussion

This report presents the raw results of release of elements from ceramic, glassware or crystalware drinking rim areas. The concentration values were sometimes very low and close to the detection limit. Standard deviations were often relatively high mainly due to the samples heterogeneity. Yet, these results can give an overview of the migration of metals from real samples. All results reported in the tables were average values and are presented with their corresponding standard deviation from four replicates obtained after first (I), second (II) and third (III) migration. All results for Pb and Cd were expressed in µg/L and in µg/article, for other metals the results were reported in µg/L. 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 overall method was calculated as: LOD= $x_{bl} + 3sd_{bl}$, where x_{bl} is the means concentration calculated from the counts of the noise peak for the 10 determinations, sd_{bl} is the standard deviation of the analysis. The LODs are reported in table 4.

Table 4 – LOD values in µg/kg for different methods

Acetic Acid 4% [µg/kg]										
	Li	**Al**	**Mn**	**Cu**	**Ti**	**Co**	**Zn**	**Cd**	**Ba**	**Pb**
LOD	0.05	0.55	0.15	0.10	0.10	0.11	8.21	0.01	0.04	0.26
	Zr	**Fe**	**V**	**Ni**	**Cr**	**Ag**	**Sn**	**Sb**	**As**	
LOD	1.87	2.92	0.11	0.19	0.06	0.04	0.54	0.01	0.09	
Citric Acid 0.5% [µg/kg]										
	Li	**Al**	**Mn**	**Cu**	**Ti**	**Co**	**Zn**	**Cd**	**Ba**	**Pb**
LOD	0.01	2.07	0.27	0.29	0.24	0.05	6.83	0.03	0.16	0.20
	Zr	**Fe**	**V**	**Ni**	**Cr**	**Ag**	**Sn**	**Sb**	**As**	
LOD	0.11	0.42	0.04	0.12	0.26	0.06	0.10	0.01	0.16	
White wine [µg/kg]										
	Li	**Al**	**Mn**	**Cu**	**Ti**	**Co**	**Zn**	**Cd**	**Ba**	**Pb**
LOD	-	15.83	15.90	2.28	65.03	0.11	15.34	0.07	7.13	0.31
	Fe	**V**	**Ni**	**Cr**	**Sn**	**Sb**	**As**			
LOD	41.65	1.75	0.53	1.38	0.05	0.03	0.23			

4.1 Migration of metals from market articles in simulants

The simplest approach to test the drinking-rim area was to follow the ASTM Standard (without the use of melted paraffin wax), where the samples are immersed in the simulant upside-down into a beaker as shown in figure 2.

Figure 2 – Drinking-rim testing method ASTM Standard C927-80

Samples 213C01, 213C03 and 213C10 exhibited low releases of Pb and Cd and no significant difference was observed across simulants. Sample 413C10 and 613C09 presented a higher release of these two metals and again AA4% and CA0.5% showed similar behaviour (table 5). Table 6 presents the results for samples 413C12, 413C14 and 413C16 (i.e. same cups for different colours, yellow, green and red). The results suggested an influence of the colour on the release of Pb and Cd, with the red samples releasing more Pb and Cd than the green and yellow one. Other metals such as Al, Mn, Fe, Co, Cu, Ni, Zn, Ba than Pb and Cd were quantified in the leachate solution, and the full results are presented in table 7. The highest release was observed for sample 413C10 especially for Co probably due to a blue brilliant colour. The method using CA0.5% was more severe for this element. Metals released from samples 413C12, 413C14 and 413C16 are reported in table 8. The results again suggested an influence of the colour with the red sample releasing more than the green and yellow samples. No significant difference was observed between the different methodologies. The only industrial lead crystal glass sample externally decorated 314G08 was tested with both simulants and white wine. It was observed a high release of several metals such as Pb, Cd, Al, Ti, Fe and Zn. Also other metals were detected in lesser amount such as Zr, Sb, Ba and Cr. The full results are reported in table 9.

Table 5- Release of Pb/Cd from industrial samples: 213C01, 213C03, 213C10, 413C10 and 613C09

Results corrected for			AA 4%		CA 0.5%		AA 4%		CA 0.5%	
Simulant			**(µg/L)**	**(µg/article)**	**(µg/L)**	**(µg/article)**	**(µg/L)**	**(µg/article)**	**(µg/L)**	**(µg/article)**
213C01	I	**Av**	**6.51**	**1.30**	**2.40**	**0.48**	**0.04**	**0.01**	**0.03**	**0.005**
		std	11.65	2.33	0.65	0.13	0.06	0.01	0.02	0.003
	II	**Av**	**<LOD**	**<LOD**	**0.39**	**0.08**	**<LOD**	**<LOD**	**<LOD**	**<LOD**
		std			0.09	0.02				
	III	**Av**	**0.24**	**0.05**	**0.51**	**0.10**	**0.032**	**0.006**	**0.073**	**0.0145**
		std	0.07	0.01	0.06	0.01	0.004	0.001	0.002	0.0004
213C03	I	**Av**	**0.29**	**0.08**	**0.40**	**0.10**	**0.05**	**0.014**	**0.05**	**0.014**
		std	0.04	0.01	0.11	0.03	0.01	0.002	0.01	0.003
	II	**Av**	**0.21**	**0.05**	**0.18**	**0.05**	**0.02**	**0.005**	**0.04**	**0.011**
		std	0.05	0.01	0.11	0.03	0.01	0.002	0.01	0.003
	III	**Av**	**0.13**	**0.033**	**0.14**	**0.04**	**0.032**	**0.008**	**0.06**	**0.016**
		std	0.01	0.003	0.03	0.01	0.003	0.001	0.01	0.002
213C10	I	**Av**	**0.68**	**0.20**	**1.40**	**0.42**	**<LOD**	**<LOD**	**<LOD**	**<LOD**
		std	0.14	0.04	0.29	0.09				
	II	**Av**	**0.16**	**0.05**	**0.27**	**0.08**	**<LOD**	**<LOD**	**<LOD**	**<LOD**
		std	0.11	0.03	0.05	0.01				
	III	**Av**	**<LOD**	**<LOD**	**0.56**	**0.17**	**<LOD**	**<LOD**	**<LOD**	**<LOD**
		std			0.21	0.06				
413C10	I	**Av**	**109.44**	**7.11**	**105.54**	**6.86**	**0.28**	**0.018**	**0.34**	**0.022**
		std	12.01	0.78	8.63	0.56	0.05	0.003	0.08	0.005
	II	**Av**	**13.65**	**0.89**	**28.52**	**1.85**	**0.10**	**0.006**	**0.15**	**0.010**
		std	1.23	0.08	10.34	0.67	0.08	0.005	0.07	0.005
	III	**Av**	**8.70**	**0.57**	**23.18**	**1.51**	**0.12**	**0.008**	**0.28**	**0.018**
		std	2.36	0.15	6.24	0.41	0.01	0.001	0.03	0.002
613C09	I	**Av**	**66.18**	**3.64**	**71.58**	**3.94**	**0.71**	**0.04**	**0.57**	**0.03**
		std	41.47	2.28	18.58	1.02	0.42	0.02	0.30	0.02
	II	**Av**	**9.65**	**0.53**	**15.94**	**0.88**	**1.41**	**0.08**	**0.21**	**0.01**
		std	4.92	0.27	13.28	0.73	1.67	0.09	0.24	0.01
	III	**Av**	**5.36**	**0.29**	**12.51**	**0.69**	**0.20**	**0.011**	**0.30**	**0.016**
		std	1.68	0.09	3.42	0.19	0.04	0.002	0.05	0.003

Table 6 – Release of Pb and Cd from industrial samples: 413C12, 413C14 and 413C16

Results corrected for Internal volume (µg/L)			Pb				Cd			
			AA 4%		CA 0.5%		AA 4%		CA 0.5%	
Simulant			(µg/L)	(µg/article)	(µg/L)	(µg/article)	(µg/L)	(µg/article)	(µg/L)	(µg/article)
413C12	I	**Av**	**2.08**	**0.28**	**1.80**	**0.14**	**0.10**	**0.008**	**0.13**	**0.010**
		std	0.32	0.25	0.32	0.02	0.03	0.002	0.09	0.007
	II	**Av**	**0.91**	**0.26**	**0.60**	**0.04**	**0.03**	**0.003**	**0.04**	**0.003**
		std	0.25	0.38	0.12	0.01	0.03	0.002	0.03	0.002
	III	**Av**	**0.88**	**0.066**	**0.74**	**0.06**	**0.07**	**0.0052**	**0.15**	**0.011**
		std	0.03	0.002	0.15	0.01	0.01	0.0005	0.02	0.001
413C14	I	**Av**	**374.03**	**28.05**	**547.37**	**41.05**	**52.13**	**3.78**	**75.78**	**5.68**
		std	44.08	3.31	92.72	6.95	6.30	0.48	10.85	0.81
	II	**Av**	**100.40**	**7.53**	**541.05**	**40.58**	**19.15**	**1.46**	**78.73**	**5.90**
		std	6.79	0.51	121.40	9.11	1.29	0.11	13.56	1.02
	III	**Av**	**71.96**	**5.40**	**296.52**	**22.24**	**12.70**	**0.97**	**47.03**	**3.53**
		std	9.32	0.70	51.92	3.89	1.46	0.13	8.18	0.61
413C16	I	**Av**	**905.57**	**67.92**	**1038.60**	**77.90**	**607.71**	**45.58**	**361.94**	**27.15**
		std	114.80	8.61	226.55	16.99	75.08	5.63	83.12	6.23
	II	**Av**	**184.87**	**13.87**	**531.46**	**39.86**	**254.80**	**19.11**	**190.71**	**14.30**
		std	10.47	0.79	61.79	4.63	23.24	1.74	21.18	1.59
	III	**Av**	**120.23**	**9.02**	**437.32**	**32.80**	**134.78**	**10.11**	**211.39**	**15.85**
		std	5.14	0.39	79.43	5.96	15.59	1.17	34.78	2.61

Table 7- Concentration values of other metals released from samples: 213C01, 213C03, 213C10, 413C10 and 613C09

Results corrected for internal vol. (µg/L)			Al		Mn		Fe		Co		Cu		Ni		Zn		Ba	
			AA4%	CA0.5%	AA4%	CA0.5%	AA4%	CA0.5%	AA4%	CA0.5%	AA4%	CA0.5%	AA4%	CA0.5%	AA4%	CA0.5%	AA4%	CA0.5%
213C01	I	**Av**	**12.29**	**19.13**	**0.40**	**0.94**	**11.71**	**36.10**	**1.60**	**3.40**	**2.83**	**3.75**	**0.88**	**0.33**	**48.81**	**57.10**	**5.32**	**0.37**
		std	1.48	3.27	0.28	0.26	2.62	4.20	0.16	0.23	1.62	1.14	0.08	0.04	6.24	5.23	6.13	0.07
	II	**Av**	**2.53**	**<LOD**	**0.11**	**<LOD**	**2.38**	**5.28**	**0.31**	**0.77**	**0.36**	**0.98**	**0.17**	**0.10**	**11.12**	**40.20**	**0.73**	**0.16**
		std	0.35		0.02		0.88	1.76	0.08	0.15	0.30	0.24	0.05	0.03	0.37	1.00	0.54	0.14
	III	**Av**	**5.95**	**11.04**	**0.14**	**<LOD**	**1.79**	**4.66**	**0.37**	**1.22**	**0.41**	**0.37**	**0.24**	**0.12**	**348.89**	**100.56**	**0.30**	**0.51**
		std	2.99	5.27	0.06		0.37	1.53	0.01	0.21	0.07	0.10	0.31	0.01	2.28	0.43	0.10	0.42
213C03	I	**Av**	**6.70**	**11.75**	**0.31**	**0.66**	**6.87**	**14.39**	**0.43**	**0.92**	**0.90**	**0.60**	**0.38**	**0.07**	**22.75**	**21.37**	**1.81**	**0.97**
		std	1.06	1.95	0.05	0.15	1.18	3.78	0.20	0.43	0.17	0.06	0.01	0.01	0.85	8.72	0.53	0.09
	II	**Av**	**3.01**	**5.61**	**0.09**	**<LOD**	**3.71**	**3.87**	**0.23**	**0.82**	**0.36**	**0.27**	**0.13**	**0.16**	**7.34**	**21.25**	**0.49**	**0.56**
		std	0.77	1.75	0.03		1.74	0.60	0.13	0.38	0.39	0.04	0.08	0.04	1.23	0.67	0.10	0.22
	III	**Av**	**3.32**	**5.44**	**0.07**	**<LOD**	**1.83**	**2.54**	**0.25**	**0.83**	**0.51**	**<LOD**	**0.10**	**<LOD**	**174.61**	**51.42**	**0.29**	**0.65**
		std	1.41	2.09	0.02		0.27	1.14	0.08	0.34	0.62		0.12		2.73	0.54	0.09	0.20
213C10	I	**Av**	**22.07**	**11.39**	**0.39**	**0.43**	**8.07**	**23.48**	**0.16**	**0.20**	**1.49**	**2.07**	**0.69**	**0.19**	**37.63**	**33.91**	**1.60**	**0.15**
		std	17.90	2.55	0.14	0.16	1.03	7.47	0.02	0.04	0.58	0.51	0.24	0.06	7.36	2.68	0.30	0.05
	II	**Av**	**2.01**	**2.14**	**0.11**	**<LOD**	**2.00**	**4.15**	**<LOD**	**0.12**	**0.42**	**0.56**	**0.18**	**<LOD**	**11.88**	**25.94**	**0.33**	**0.10**
		std	1.29	2.85	0.05		0.85	1.03		0.03	0.16	0.09	0.06		5.80	0.93	0.04	0.08
	III	**Av**	**2.10**	**8.33**	**<LOD**	**<LOD**	**1.37**	**3.04**	**<LOD**	**0.21**	**<LOD**	**<LOD**	**<LOD**	**0.06**	**22.54**	**66.86**	**0.10**	**0.18**
		std	1.94	1.43			1.80	0.73		0.06				0.02	1.12	0.35	0.06	0.09
413C10	I	**Av**	**75.50**	**93.94**	**20.56**	**23.93**	**147.82**	**52.23**	**104.80**	**611.60**	**13.06**	**2.29**	**3.51**	**2.40**	**165.30**	**130.52**	**7.46**	**2.96**
		std	9.26	5.18	4.10	0.61	43.69	7.58	10.26	73.29	5.46	0.31	0.25	0.11	8.54	5.05	0.60	1.69
	II	**Av**	**16.20**	**67.35**	**4.38**	**13.00**	**18.96**	**24.37**	**55.48**	**654.94**	**16.93**	**1.99**	**0.92**	**2.13**	**52.03**	**124.01**	**2.65**	**1.42**
		std	4.85	63.02	0.76	5.85	5.34	7.36	9.55	126.02	5.22	0.37	0.08	0.43	5.45	7.77	0.62	0.61
	III	**Av**	**21.41**	**19.02**	**3.07**	**12.89**	**15.40**	**17.27**	**47.36**	**568.54**	**1.22**		**0.44**	**1.80**	**1072.21**	**308.71**	**1.35**	**1.44**
		std	10.50	11.35	1.51	4.62	9.68	5.02	9.49	91.69	0.33		0.14	0.36	4.77	2.69	0.40	0.75
613C09	I	**Av**	**43.50**	**70.18**	**1.29**	**2.85**	**35.76**	**67.93**	**2.76**	**6.41**	**3.86**	**5.40**	**1.03**	**1.00**	**55.03**	**138.16**	**1.96**	**1.56**
		std	14.37	13.26	0.34	2.24	4.47	42.70	0.94	0.70	1.41	2.62	0.08	0.96	6.54	83.68	0.32	0.27
	II	**Av**	**18.23**	**19.75**	**0.79**	**<LOD**	**17.92**	**17.64**	**4.35**	**3.46**	**4.16**	**2.14**	**0.71**	**<LOD**	**4436.68**	**122.80**	**1.95**	**3.42**
		std	5.91	12.52	0.03		4.93	6.93	3.26	1.57	1.97	0.55	0.15		327.80	4.78	0.13	4.46
	III	**Av**	**20.25**	**<LOD**	**0.49**	**<LOD**	**13.10**	**7.59**	**1.01**	**2.89**	**1.02**	**<LOD**	**<LOD**	**<LOD**	**1096.77**	**311.16**	**0.88**	**1.03**
		std	8.93		0.08		4.85	5.10	0.13	1.24	0.19				24.04	6.19	0.25	0.33

Table 8 – Concentration values of other metals released from samples: 413C12, 413C14 and 413C16

Results corrected for internal vol. (µg/L)			Li		Al		Cr		Mn		Fe		Co		Cu		Ni		Zn		Ba	
			AA 4%	CA 0.5%	AA 4%	CA 0.5%	AA 4%	CA 0.5%	AA 4%	CA 0.5%	AA 4%	CA 0.5%	AA 4%	CA 0.5%	AA 4%	CA 0.5%	AA 4%	CA 0.5%	AA 4%	CA 0.5%	AA 4%	CA 0.5%
413C12	I	Av	<LOD	<LOD	16.50	20.01	<LOD		1.08	1.60	25.13	32.66	<LOD	<LOD	7.95	2.20	1.54	0.25	88.67	54.95	4.41	0.58
		std			1.64	7.10			0.12	0.74	2.86	10.09			7.48	0.21	0.10	0.04	9.72	14.91	0.22	0.10
	II	Av	<LOD	<LOD	11.92	18.01	<LOD		0.41	<LOD	9.99	11.63	<LOD	<LOD	1.04	1.06	0.42	0.20	31.92	73.64	1.42	0.50
		std			6.76	2.14			0.14		3.10	1.96			0.46	0.17	0.25	0.11	11.77	2.94	0.29	0.11
	III	Av	<LOD	<LOD	15.43	6.04	<LOD	0.50	0.32	<LOD	8.23	5.33	0.31	0.13	1.12	<LOD	<LOD	0.51	667.96	197.53	0.85	0.75
		std			2.24	10.29		0.66	0.09		3.71	5.03	0.01	0.05	0.36			0.81	2.18	13.99	0.33	0.69
413C14	I	Av	4.03	7.92	98.50	133.05	1.84	0.93	1.31	2.01	66.19	42.47	1.15	1.71	9.38	2.40	0.79	0.33	72.78	112.23	3.77	2.75
		std	0.38	0.89	10.76	18.83	2.73	0.12	0.61	0.78	22.22	7.31	0.12	0.26	6.38	0.07	0.30	0.07	31.97	16.23	1.34	0.23
	II	Av	0.61	5.09	33.72	59.02	<LOD	0.43	0.84	<LOD	17.69	10.68	1.53	0.93	1.55	1.34	0.47	0.51	2624.18	102.35	1.48	0.86
		std	0.12	1.10	9.14	9.66		0.02	0.48		5.13	1.92	0.05	0.15	0.79	0.11	0.13	0.46	44.62	7.25	0.20	0.16
	III	Av	0.22	9.27	25.50	89.31	<LOD	0.41	0.41	<LOD	19.19	7.38	0.56	1.52	0.78	0.63	<LOD	<LOD	667.01	229.35	1.41	1.35
		std	0.18	1.58	2.62	14.78		0.02	0.08		12.11	1.84	0.02	0.23	0.16	0.07			5.82	5.52	1.06	0.28
413C16	I	Av	11.34	12.61	237.23	259.62	0.47	1.29	1.37	1.38	73.67	40.22	<LOD	11.22	7.46	4.77	1.64	0.43	142.08	119.56	352.05	285.84
		std	1.44	1.70	38.21	26.66	0.20	0.47	0.14	0.23	36.66	11.04		10.00	1.89	1.22	0.08	0.10	10.08	5.32	33.51	100.63
	II	Av	0.89	5.54	42.15	81.13	<LOD	0.57	0.39	<LOD	15.85	14.21	<LOD	0.16	1.04	1.77	0.43	0.18	34.70	103.24	56.54	64.36
		std	0.05	0.38	2.94	9.18		0.09	0.15		8.25	1.59		0.14	0.39	0.24	0.04	0.01	1.79	7.10	15.78	14.85
	III	Av	0.14	5.33	31.89	88.56	<LOD	0.39	0.32	<LOD	10.07	7.05	0.34	0.13	1.68	<LOD	0.30	<LOD	670.30	221.38	25.82	69.03
		std	0.06	0.65	9.41	17.81		0.11	0.08		5.50	4.31	0.07	0.01	1.15		0.30		10.33	12.53	2.37	5.11

Table 9 – Concentration values of metals released from sample 314G08

Results corrected for Internal volume (µg/L) and per article (µg/article)			Pb						Cd					
			Wine		AA 4%		CA 0.5%		Wine		AA 4%		CA 0.5%	
Simulant			(µg/L)	(µg/article)	(µg/L)	(µg/article)	(µg/L)	(µg/article)	(µg/L)	(µg/article)	(µg/L)	(µg/article)	(µg/L)	(µg/article)
314G08	**I**	**Av**	**20382.63**	**2547.83**	**17954.27**	**2244.28**	**19032.91**	**2379.11**	**177.11**	**22.14**	**189.86**	**23.73**	**139.20**	**17.40**
		std	3093.28	386.66	12080.90	1510.11	2453.24	306.65	25.49	3.19	31.13	3.89	16.63	2.08
	II	**Av**	**881.45**	**110.18**	**213.13**	**26.64**	**1048.02**	**131.00**	**8.97**	**1.12**	**0.66**	**0.08**	**6.68**	**0.84**
		std	648.44	81.06	196.19	24.52	782.36	97.79	7.67	0.96	0.88	0.11	7.15	0.89
	III	**Av**	**440.31**	**55.04**	**57.87**	**7.23**	**627.47**	**66.21**	**6.60**	**0.82**	**0.09**	**0.01**	**4.13**	**0.41**
		std	439.31	54.91	12.56	1.57	619.57	67.80	3.14	0.39	0.04	0.01	3.64	0.43

			Al		Ti		Fe		Zn	
			AA 4%	CA 0.5%	AA 4%	CA 0.5%	AA 4%	CA 0.5%	AA 4%	CA 0.5%
			(µg/L)	(µg/L)	(µg/L)	(µg/L)	(µg/L)	(µg/L)	(µg/L)	(µg/L)
	I	**Av**	**196.42**	**194.99**	**39.00**	**41.32**	**22.59**	**21.82**	**27.23**	**8.50**
		std	37.26	14.50	4.61	3.04	4.01	3.10	32.80	2.30
	II	**Av**	**13.51**	**<LOD**	**2.06**	**1.69**	**1.21**	**6.75**	**38.04**	**56.50**
		std	8.74		0.50	1.61	1.11	1.93	68.47	20.98
	III	**Av**	**5.78**	**<LOD**	**0.86**	**0.63**	**0.23**	**<LOD**	**<LOD**	**<LOD**
		std	1.84		0.41	0.81	0.86			

			Zr		Sb		Ba		Cr	
			AA 4%	CA 0.5%	AA 4%	CA 0.5%	AA 4%	CA 0.5%	AA 4%	CA 0.5%
			(µg/L)	(µg/L)	(µg/L)	(µg/L)	(µg/L)	(µg/L)	(µg/L)	(µg/L)
	I	**Av**	**9.96**	**9.24**	**2.71**	**4.12**	**1.40**	**3.34**	**0.12**	**0.27**
		std	6.81	0.67	0.63	1.21	0.38	0.66	0.19	0.02
	II	**Av**	**<LOD**	**<LOD**	**0.30**	**2.68**	**0.20**	**2.68**	**< LOD**	**<LOD**
		std			0.06	0.51	0.13	0.14		
	III	**Av**	**<LOD**	**<LOD**	**0.16**	**1.83**	**0.11**	**3.11**	**< LOD**	**<LOD**
		std			0.01	0.22	0.02	2.00		

With regards to the comparison with the use of melted paraffin, standard EN 1388-2:1995 and the ISO standards make use of melted paraffin wax to cover the zone that is not in contact with the simulant, while the ASTM standard does not. During the study a comparison of these two approaches was performed. The test was done only with AA4% method, as is described in the standards. The test with melted paraffin wax was carried out only on samples (ceramic and glass) that presented a greater release of metals, in order to have data amenable for comparison. The samples were covered with melted paraffin wax in the non-drinking-rim area before the exposure to acetic acid 4% as shown in figure 3.

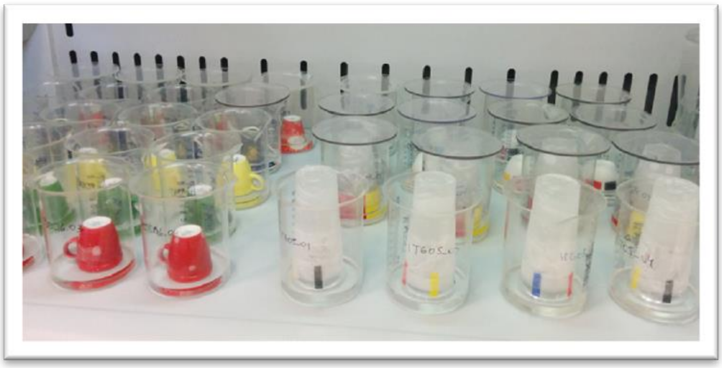


Figure 3 – Drinking-rim testing method with melted paraffin wax

The method with paraffin wax was generally slightly less severe than the method without, likely due to the fact that the area not in contact with the simulant was protected from the acidic vapour that could condense on the article surface and extract additional amounts of metals. However If we consider the standard deviation reported in the graphs this difference between the two methodologies is not so evident. The full results of this comparison are presented in the following figures 4-8.

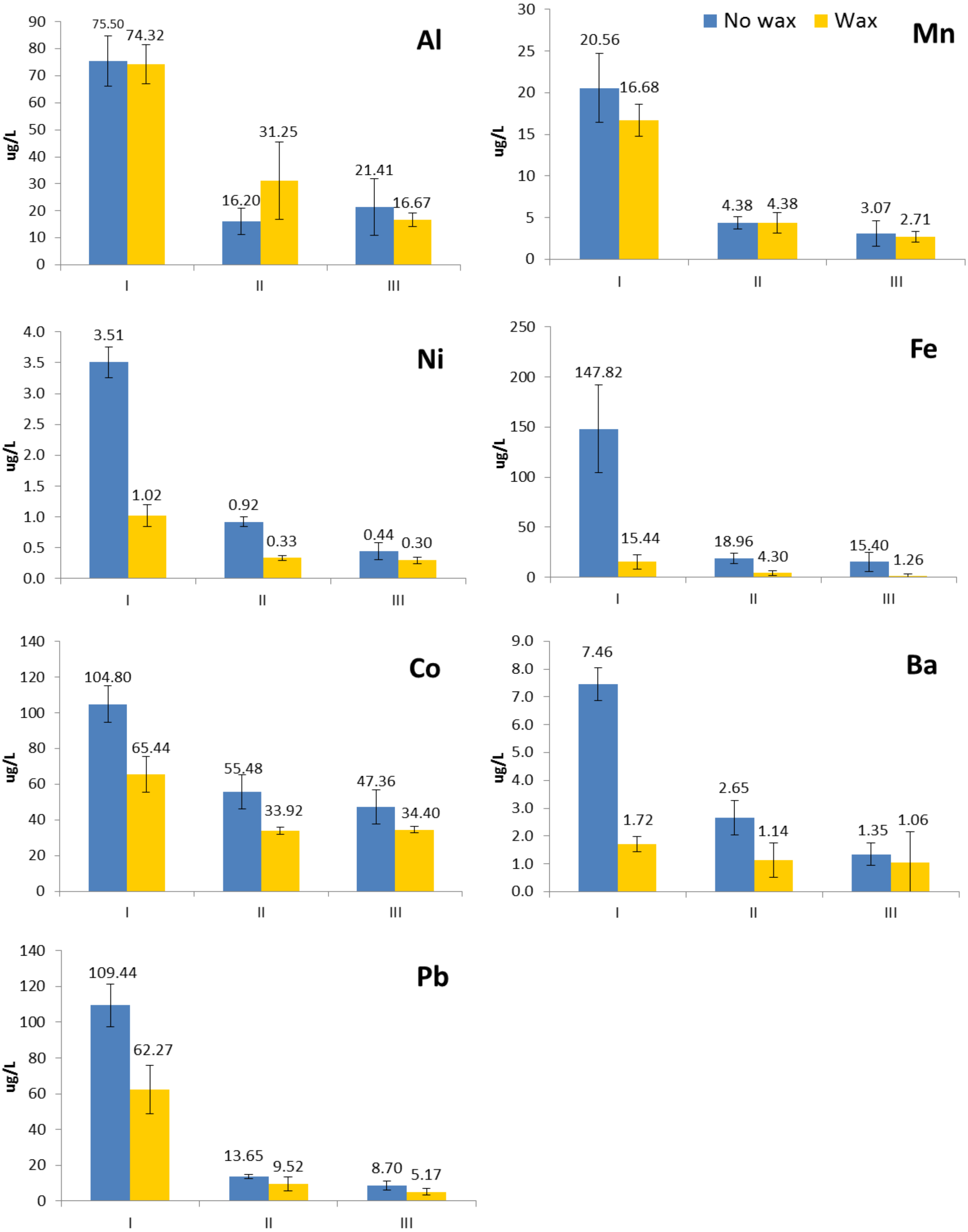


Figure 4 – Metals release from sample 413C10 with and without paraffin wax

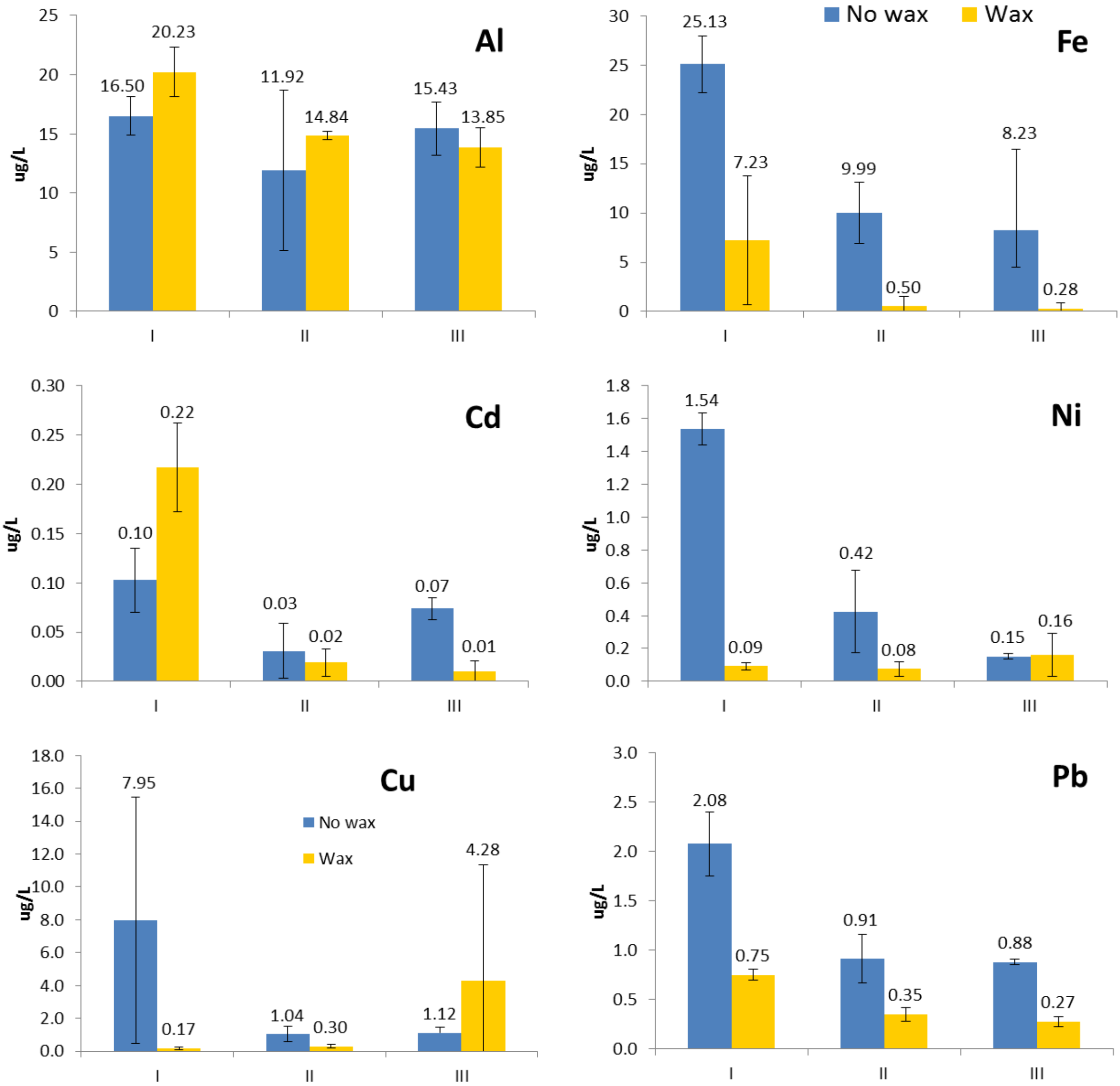


Figure 5 – Metals release from sample 413C12 with and without paraffin wax

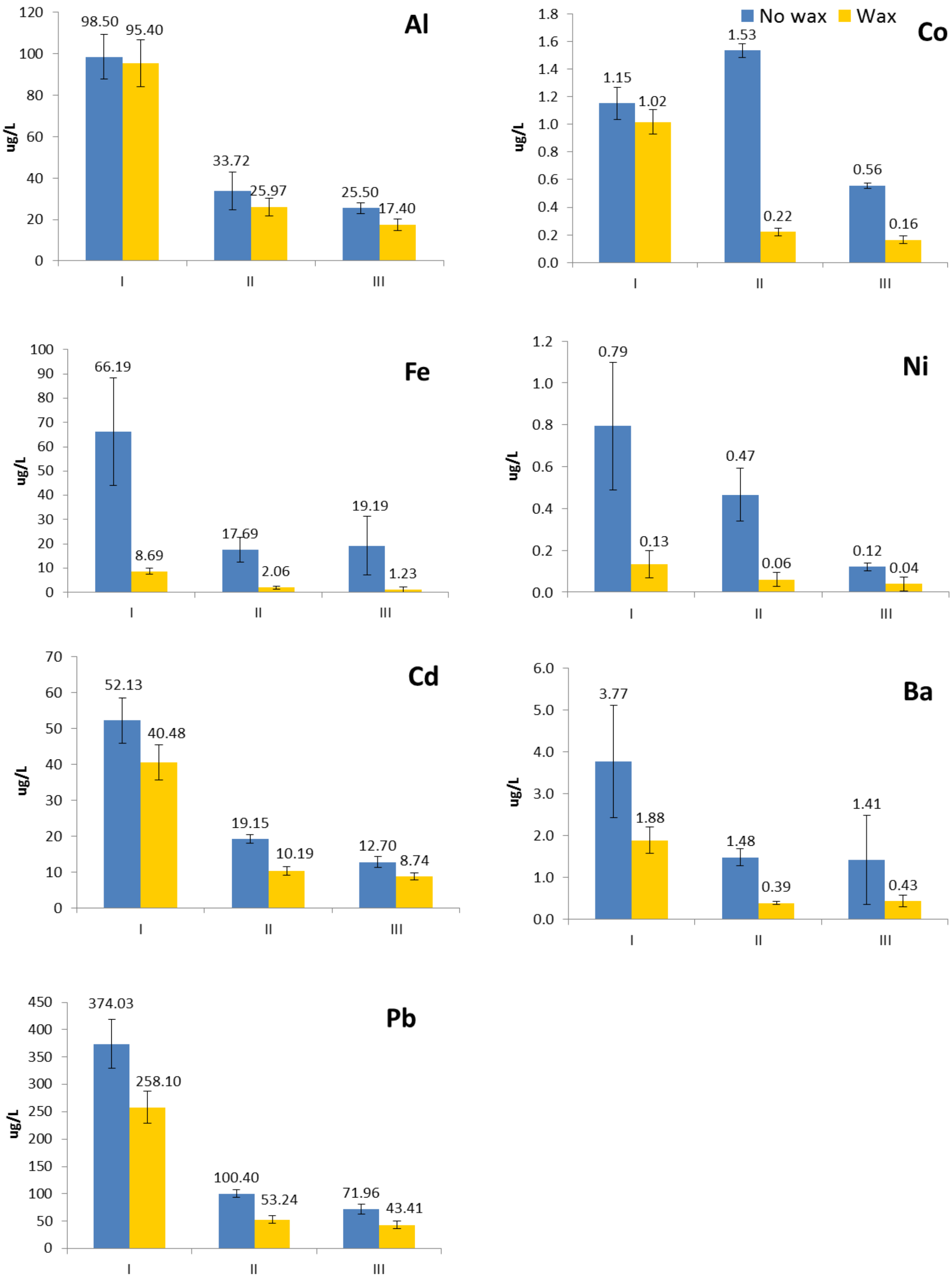


Figure 6 – Metals release from sample 413C14 with and without paraffin wax

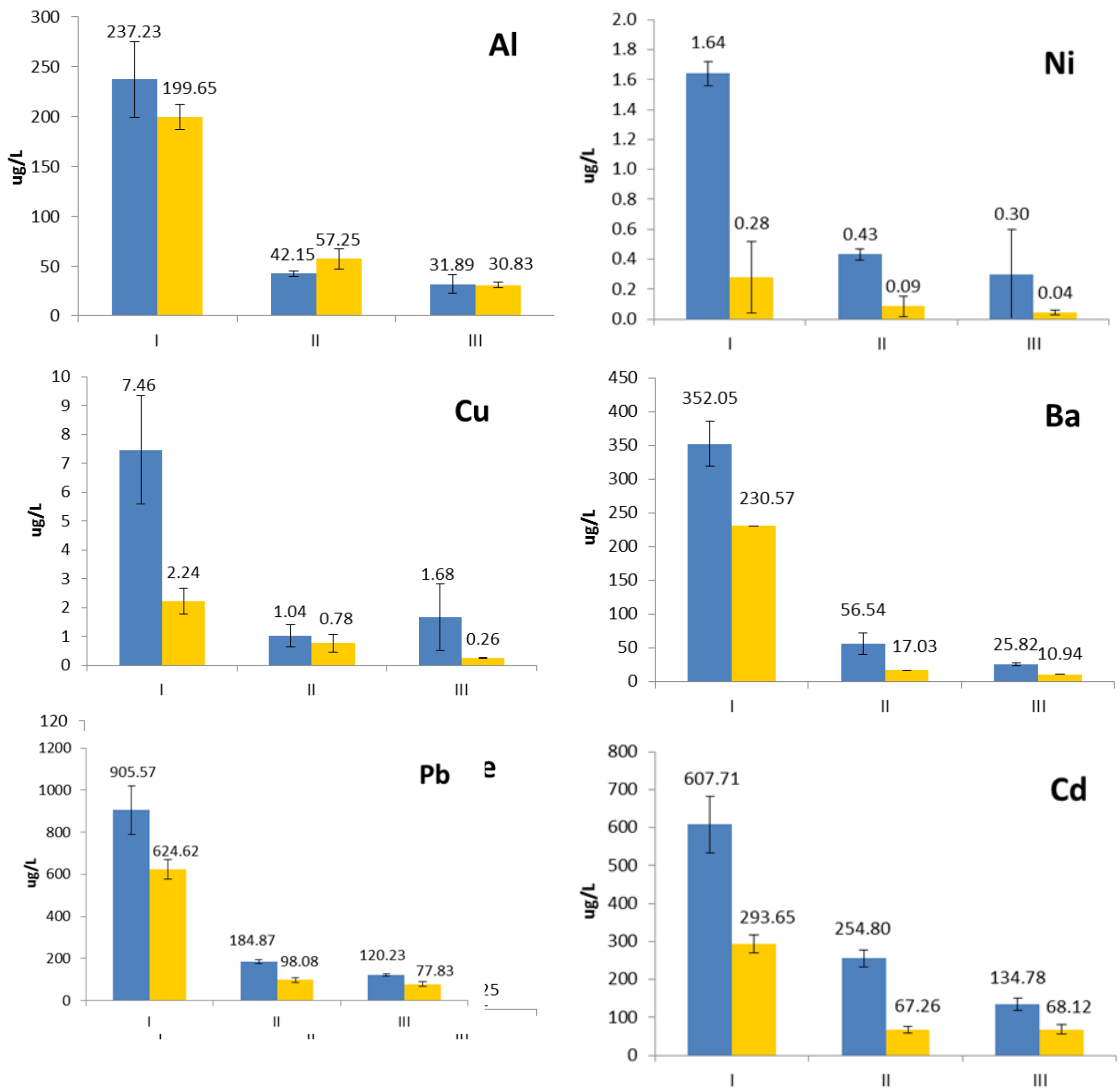


Figure 7 – Metals release from sample 413C16 with and without paraffin wax

4.2 Migration of metals from ad hoc manufactured samples in food and food simulants

Five samples decorated on the rim area were manufactured ad hoc in order to compare migration methodologies. Three tumblers decorated on the outside and two ceramic coffee cups with an overglaze and underglaze decorations in the rim area were tested with the simulants. The glass samples were also exposed to white wine. The metal background of white wine was also measured in order to take into account the composition of the matrix. It is important to know which metals are naturally present in the food itself to compare to that migrating from the articles themselves. Table 10 presents the metals concentrations for white wine and their relative standard deviation calculated on 10 replicates. The decoration of the glass samples after the exposition to acidic simulant were partially removed as shown in figure 8. This resulted in a high and heterogeneous release of metals.

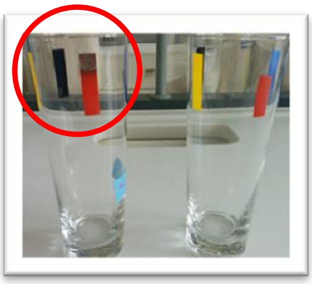


Figure 8 - Samples decoration after exposure with acetic acid 4%

Table 10 - Metals background in the white wine

Metal	Concentration (µg/L)	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

Figure 9 shows the release of Pb and Cd in AA4%, CA0.5% and white wine from glass samples. The results suggested that the release of Pb and Cd generally decreased in successive migrations. The test using CA0.5% was not always more severe than the one using AA4% but always higher with respect to the white wine. The concentrations of the leachates are reported in table 10. The release of Pb and Cd from samples 613C03 was much higher than in sample 613C06 due to the overglaze decoration more sensible to the acidic attack (see table 11). In tables 12-13, the results for other elements are reported. it was difficult to establish clear trends regarding the relative severities of the two simulants compared because the decoration on the glass surface was damaged differently across the exposed articles.

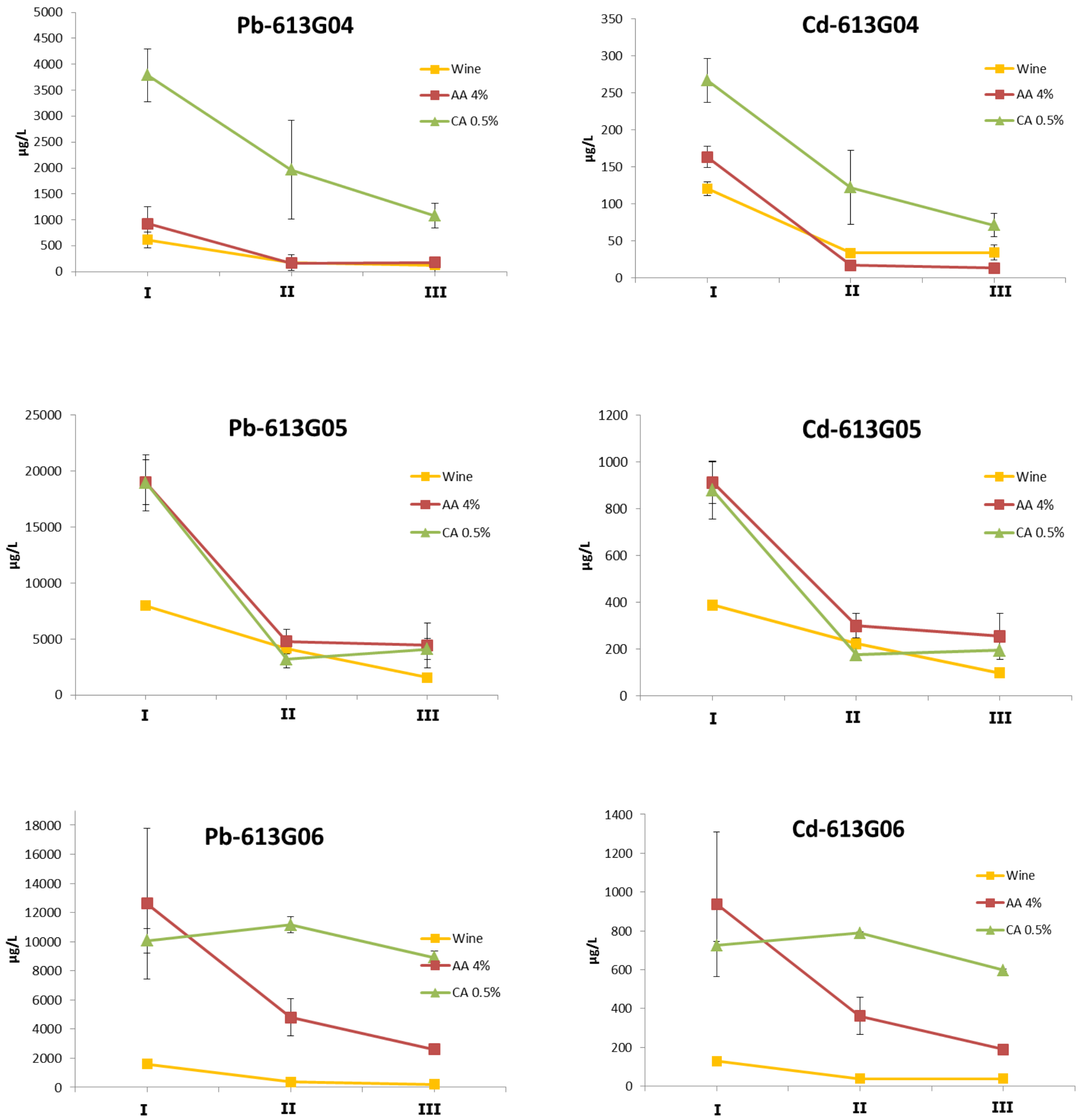


Figure 9 – Release of Pb and Cd from the rim area in decorated glass samples

Table 11 – Pb and Cd released from samples manufactured ad hoc

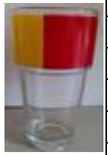
Results corrected for Internal volume (µg/L) and per article (µg/article)			Pb						Cd					
			WINE		AA 4%		CA 0.5%		WINE		AA 4%		CA 0.5%	
Simulant			(µg/L)	(µg/article)	(µg/L)	(µg/article)	(µg/L)	(µg/article)	(µg/L)	(µg/article)	(µg/L)	(µg/article)	(µg/L)	(µg/article)
613G04 	I	**Av**	**613.25**	**196.24**	**929.83**	**297.55**	**3787.44**	**1211.98**	**120.65**	**38.61**	**163.34**	**52.27**	**267.10**	**85.47**
		std	126.73	40.55	322.10	103.07	510.23	163.27	9.14	2.92	14.25	4.56	29.70	9.50
	II	**Av**	**175.06**	**56.02**	**168.63**	**53.96**	**1967.46**	**629.59**	**33.75**	**10.80**	**16.99**	**5.44**	**122.15**	**39.09**
		std	27.33	8.75	31.84	10.19	954.15	305.33	5.86	1.88	5.58	1.79	50.15	16.05
Sim Vol: 80 mL	III	**Av**	**124.06**	**39.70**	**178.98**	**57.27**	**1081.26**	**346.00**	**34.06**	**10.90**	**13.51**	**4.32**	**71.35**	**22.83**
		std	21.60	6.91	41.33	13.23	238.39	76.28	10.18	3.26	4.15	1.33	15.77	5.04
613G05 	I	**Av**	**7963.29**	**2548.25**	**18973.54**	**6071.53**	**18937.04**	**6059.85**	**387.17**	**123.90**	**910.68**	**291.42**	**877.44**	**280.78**
		std	311.81	99.78	2006.20	641.98	2517.99	805.76	13.87	4.44	89.28	28.57	124.14	39.72
	II	**Av**	**4146.50**	**1326.88**	**4768.00**	**1525.76**	**3171.53**	**1014.89**	**221.31**	**70.82**	**297.57**	**95.22**	**173.67**	**55.58**
		std	58.65	18.77	1082.86	346.52	739.55	236.66	3.30	1.06	52.46	16.79	26.64	8.52
Sim Vol: 100 mL	III	**Av**	**1559.63**	**499.08**	**4438.60**	**1420.35**	**4096.29**	**1310.81**	**95.39**	**30.53**	**252.64**	**80.84**	**192.74**	**61.68**
		std	146.65	46.93	1995.99	638.72	914.06	292.50	10.62	3.40	99.09	31.71	39.91	12.77
613G06 	I	**Av**	**1593.27**	**669.17**	**12616.67**	**5046.67**	**10065.43**	**4026.17**	**129.16**	**54.25**	**937.86**	**375.14**	**724.25**	**289.70**
		std	251.28	105.54	5171.52	2068.61	831.92	332.77	21.91	9.20	372.34	148.94	61.41	24.56
	II	**Av**	**357.63**	**150.20**	**4798.21**	**1919.28**	**11155.80**	**4462.32**	**37.59**	**15.79**	**361.59**	**144.63**	**788.95**	**315.58**
		std	68.99	28.98	1278.19	511.28	572.14	228.86	7.41	3.11	96.60	38.64	47.50	19.00
Sim Vol: 120 mL	III	**Av**	**196.20**	**82.40**	**2598.52**	**1039.41**	**8906.57**	**4324.38**	**37.64**	**15.81**	**188.25**	**75.30**	**596.93**	**320.08**
		std	21.86	9.18	326.34	130.54	439.45	1530.25	6.11	2.57	27.15	10.86	31.66	162.95
613C03 	I	**Av**	not performed (coffee cup)		**24733.59**	**1236.68**	**28094.55**	**1404.73**	not performed (coffee cup)		**657.91**	**32.90**	**762.13**	**38.11**
		std			7006.84	350.34	6241.43	312.07			188.12	9.41	132.37	6.62
	II	**Av**			**11811.51**	**590.58**	**12402.81**	**620.14**			**314.51**	**15.73**	**343.39**	**17.17**
		std			2761.73	138.09	2810.84	140.54			70.49	3.52	59.33	2.97
(overglaze)	III	**Av**			**6669.68**	**333.48**	**8365.48**	**418.27**			**183.13**	**9.16**	**253.31**	**12.67**
		std			1260.18	63.01	1689.44	84.47			33.85	1.69	35.33	1.77
613C06 	I	**Av**	not performed (coffee cup)		**44.60**	**2.23**	**54.67**	**2.73**	not performed (coffee cup)		**0.33**	**0.02**	**0.23**	**0.012**
		std			12.32	0.62	17.66	0.88			0.21	0.01	0.06	0.003
	II	**Av**			**7.28**	**0.36**	**6.75**	**0.34**			**0.09**	**0.004**	**<LOD**	**<LOD**
		std			1.56	0.08	0.74	0.04			0.06	0.003		
(under glaze)	III	**Av**			**4.30**	**0.21**	**7.89**	**0.39**			**0.12**	**0.006**	**0.26**	**0.013**
		std			0.98	0.05	1.10	0.06			0.02	0.001	0.06	0.003

Table 12 – Other elements released from samples manufactured ad hoc glass

Results corrected for internal vol. (µg/L)			Li			Ti			Cr			Co			Zn			Zr			Ba		
			WINE	AA4%	CA 0.5%	WINE	AA4%	CA 0.5%	WINE	AA4%	CA 0.5%	WINE	AA4%	CA 0.5%	WINE	AA4%	CA 0.5%	WINE	AA4%	CA 0.5%	WINE	AA4%	CA 0.5%
 613G04	I	Av	**2.97**	**3.69**	**12.89**	<LOD	**4.17**	**13.76**	**1.05**	**0.82**	**1.50**	**23.37**	**64.18**	**188.75**	**25.43**	<LOD	**26.92**	**0.92**	<LOD	**1.07**	<LOD	**3.71**	**13.12**
		std	0.72	0.57	2.63		0.41	1.98	0.33	0.24	0.25	3.15	34.77	35.68	1.92		4.65	0.03		0.16		1.68	1.68
	II	Av	**0.71**	**0.58**	**6.08**	<LOD	**0.90**	**13.13**	**0.26**	<LOD	**0.25**	**5.48**	**7.59**	**52.98**	**12.08**	<LOD	**43.89**	**0.56**	<LOD	**1.69**	<LOD	<LOD	**10.67**
		std	0.11	0.10	1.39		0.33	4.98	0.07		0.17	0.92	1.90	16.81	2.11		65.37	0.05		2.04			9.51
	III	Av	**0.46**	**0.62**	**4.01**	**16.61**	**0.88**	**8.99**	**0.10**	<LOD	**0.17**	**3.12**	**9.28**	**29.24**	**13.84**	<LOD	**6.09**	**0.56**	<LOD	**0.48**	<LOD	<LOD	**9.25**
		std	0.15	0.14	1.15	2.57	0.29	3.03	0.08		0.13	0.43	3.91	4.91	2.60		2.85	0.04		0.28			3.11
 613G05	I	Av	**1.64**	**5.38**	**7.73**	<LOD	**4.66**	**4.82**	**0.38**	<LOD	**0.42**	**81.09**	**123.71**	**121.94**	**235.14**	**378.87**	**346.67**	**1.00**	**0.81**	**0.80**	**10.52**	**45.51**	**68.61**
		std	0.07	0.95	1.04		0.75	2.54	0.04		0.18	2.68	23.06	13.06	5.67	68.45	29.30	0.06	0.09	0.47	1.31	4.60	12.98
	II	Av	**0.46**	**1.15**	**7.32**	**27.83**	**5.49**	**12.64**	**0.20**	<LOD	**0.15**	**7.53**	**20.90**	**76.89**	**71.70**	**55.74**	**137.09**	**0.80**	<LOD	**2.22**	**7.97**	**6.14**	**28.85**
		std	0.04	0.19	0.50	1.74	1.27	2.78	0.08		0.15	3.65	7.73	6.19	7.42	32.65	91.98	0.07		1.22	0.15	2.93	13.47
	III	Av	**0.30**	**0.93**	**8.88**	**28.70**	**4.80**	**10.06**	**0.21**	<LOD	**0.22**	**5.55**	**25.15**	**91.83**	**49.66**	**55.31**	**181.60**	**0.86**	<LOD	**2.06**	**4.70**	**3.87**	**46.18**
		std	0.04	0.25	1.22	2.29	1.17	4.27	0.08		0.07	2.20	7.81	8.28	6.14	43.61	17.75	0.03		2.02	0.95	2.41	11.29
 613G06	I	Av	**10.80**	**64.59**	**46.42**	**20.69**	**1.95**	**13.00**	**1.19**	**1.08**	**2.90**	**0.64**	**2.25**	**3.91**	<LOD	<LOD	**10.98**	**0.77**	<LOD	<LOD	<LOD	**0.50**	**1.89**
		std	1.98	25.71	4.19	1.83	1.38	1.80	0.12	0.51	0.44	0.21	0.53	0.62			5.28	0.06				0.32	0.76
	II	Av	**2.81**	**26.00**	**54.46**	**20.22**	**2.95**	**28.14**	**0.16**	<LOD	**2.03**	**0.17**	**2.18**	**2.62**	<LOD	<LOD	**11.62**	**0.64**	<LOD	**0.23**	<LOD	<LOD	**2.44**
		std	1.05	6.71	4.03	4.44	2.60	5.08	0.15		0.45	0.02	3.07	0.66			3.87	0.08		0.16			0.68
	III	Av	**2.78**	**12.73**	**43.98**	<LOD	**1.92**	**30.80**	**0.13**	<LOD	**1.47**	**0.22**	**0.52**	**3.12**	<LOD	<LOD	**11.25**	**0.66**	<LOD	**0.98**	<LOD	<LOD	**0.86**
		std	1.23	1.31	5.64		1.36	3.09	0.08		0.34	0.14	0.46	1.61			5.12	0.04		1.21			0.36

Table 13 - Other elements released from ceramic samples manufactured ad hoc

Results corrected for internal vol. (µg/L)			Li		Al		Cr		Mn		Fe	
			AA4%	CA 0.5%	AA4%	CA 0.5%	AA4%	CA 0.5%	AA4%	CA 0.5%	AA4%	CA 0.5%
 613C03	I	Av	**203.15**	**23.35**	**2494.47**	**2564.74**	<LOD	**8.73**	**3.94**	**0.80**	**180.40**	**105.17**
		std	78.19	4.79	712.70	594.21		1.12	1.88	1.51	61.64	35.80
	II	Av	**79.72**	**9.97**	**1163.36**	**1054.35**	<LOD	**4.99**	**1.34**	<LOD	**38.72**	**103.58**
		std	25.55	1.91	270.76	245.38		0.38	0.62		26.06	22.58
	III	Av	**38.37**	**6.99**	**662.77**	**730.89**	<LOD	**4.03**	**0.61**	**0.36**	**12.56**	**88.56**
		std	11.64	0.98	122.01	150.82		0.44	0.28	1.80	5.15	34.21
 613C06	I	Av	<LOD	<LOD	**157.40**	**212.06**	<LOD	**0.48**	**2.96**	**3.10**	**53.49**	**64.28**
		std			25.90	61.87		0.17	0.76	1.69	8.49	31.12
	II	Av	<LOD	<LOD	**41.87**	**32.33**	<LOD	**0.26**	**0.50**	**0.18**	**17.16**	**12.87**
		std			6.47	24.26		0.07	0.14	0.21	13.42	3.94
	III	Av	<LOD	<LOD	**49.80**	**45.75**	<LOD	**0.29**	**0.51**	<LOD	**15.15**	**7.30**
		std			7.43	11.82		0.07	0.17		9.44	7.02

Results corrected for internal vol. (µg/L)			Co		Ni		Cu		Zn		Ba	
			AA4%	CA 0.5%	AA4%	CA 0.5%	AA4%	CA 0.5%	AA4%	CA 0.5%	AA4%	CA 0.5%
 613C03	I	Av	**5.99**	**8.50**	**13.38**	**4.82**	**23.07**	**19.13**	**1649.32**	**1480.14**	**47.80**	**35.00**
		std	2.28	4.15	4.72	6.24	4.42	10.91	414.15	327.53	6.48	6.37
	II	Av	**3.66**	**4.87**	<LOD	**5.49**	<LOD	**21.42**	**618.27**	**1892.41**	**18.72**	**26.00**
		std	1.01	2.62		7.26		2.73	136.72	92.85	9.72	8.69
	III	Av	**2.82**	**4.51**	<LOD	**1.46**	**69.02**	**3.39**	**339.15**	**425.50**	**8.92**	**28.64**
		std	0.96	2.53		0.47	58.20	2.91	53.16	47.97	1.87	27.11
 613C06	I	Av	**7117.76**	**4968.35**	**3.79**	**1.14**	**9.44**	**2.09**	**10103.60**	**8424.36**	**9.04**	**4.12**
		std	1948.32	2298.03	0.95	0.31	5.09	0.65	6131.78	3692.04	0.34	1.05
	II	Av	**50.72**	**250.78**	**0.66**	**0.29**	**1.23**	**1.82**	**122.35**	**542.18**	**2.19**	**1.01**
		std	40.47	231.89	0.11	0.12	0.64	0.56	69.41	407.67	0.36	0.32
	III	Av	**125.88**	**114.57**	<LOD	<LOD	**1.50**	<LOD	**1388.97**	**451.43**	**4.25**	**1.73**
		std	131.85	58.99			0.84		240.77	97.31	5.50	0.50

4.2.1 Comparison with the use of melted paraffin

The ad hoc manufactured samples were also tested after application of a melted paraffin wax layer as in the EN 1388-2:1995 and ISO standards in order to cover the area not exposed to the simulant before performing the migration test (Figure 10).

Figure 10 - Application of the melted paraffin wax on the non-exposed area of glass decorated samples

Figures 11-15 illustrate the release of different metals from ad hoc manufactured samples either using or not using the covering of melted paraffin wax. Samples not covered with melted paraffin wax presented generally slightly higher release of metals but if the differences were not necessarily relevant when considering the dispersion of results (e.g. from the standard deviation).

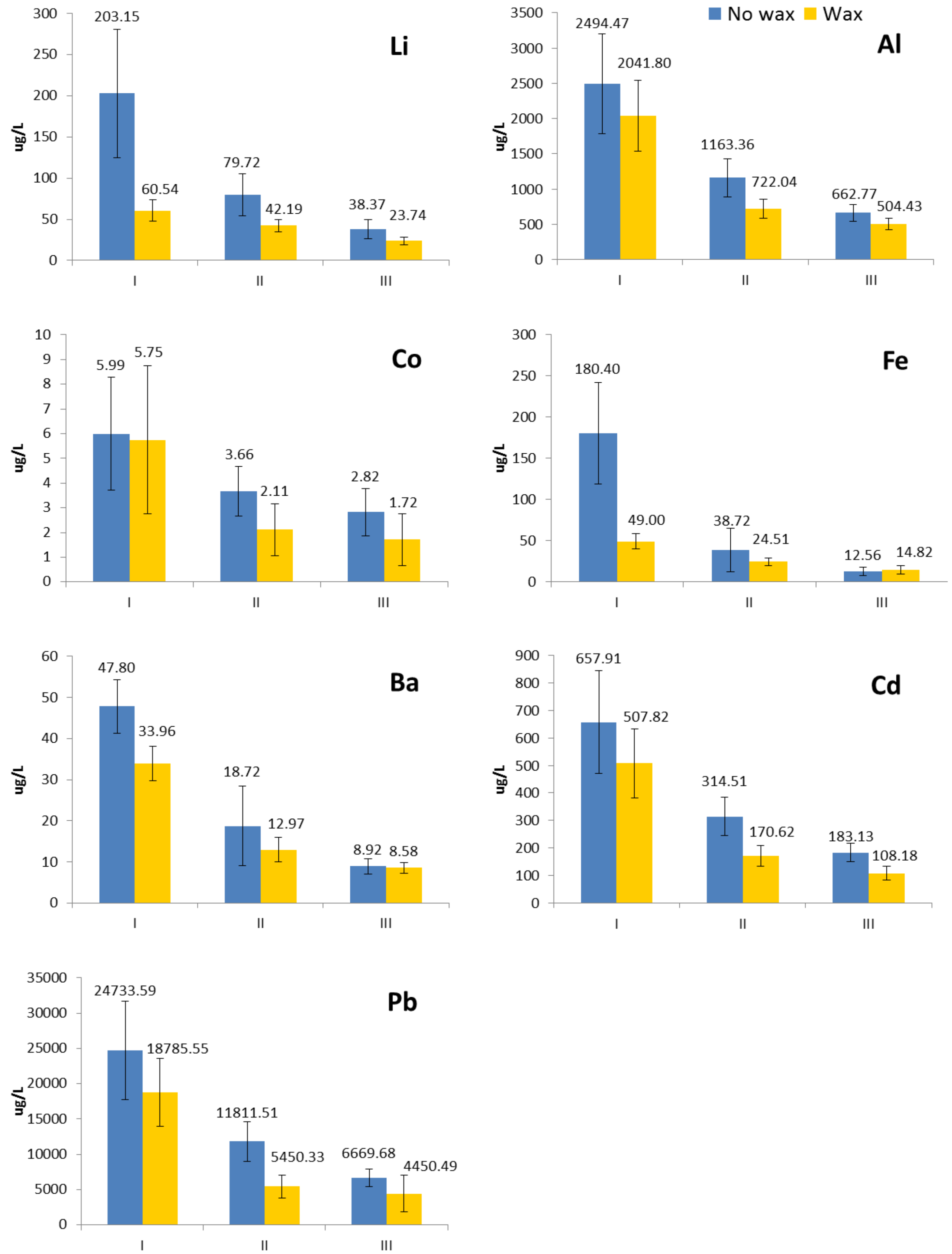


Figure 11 – Test of sample 613C03 rim area with and without paraffin wax

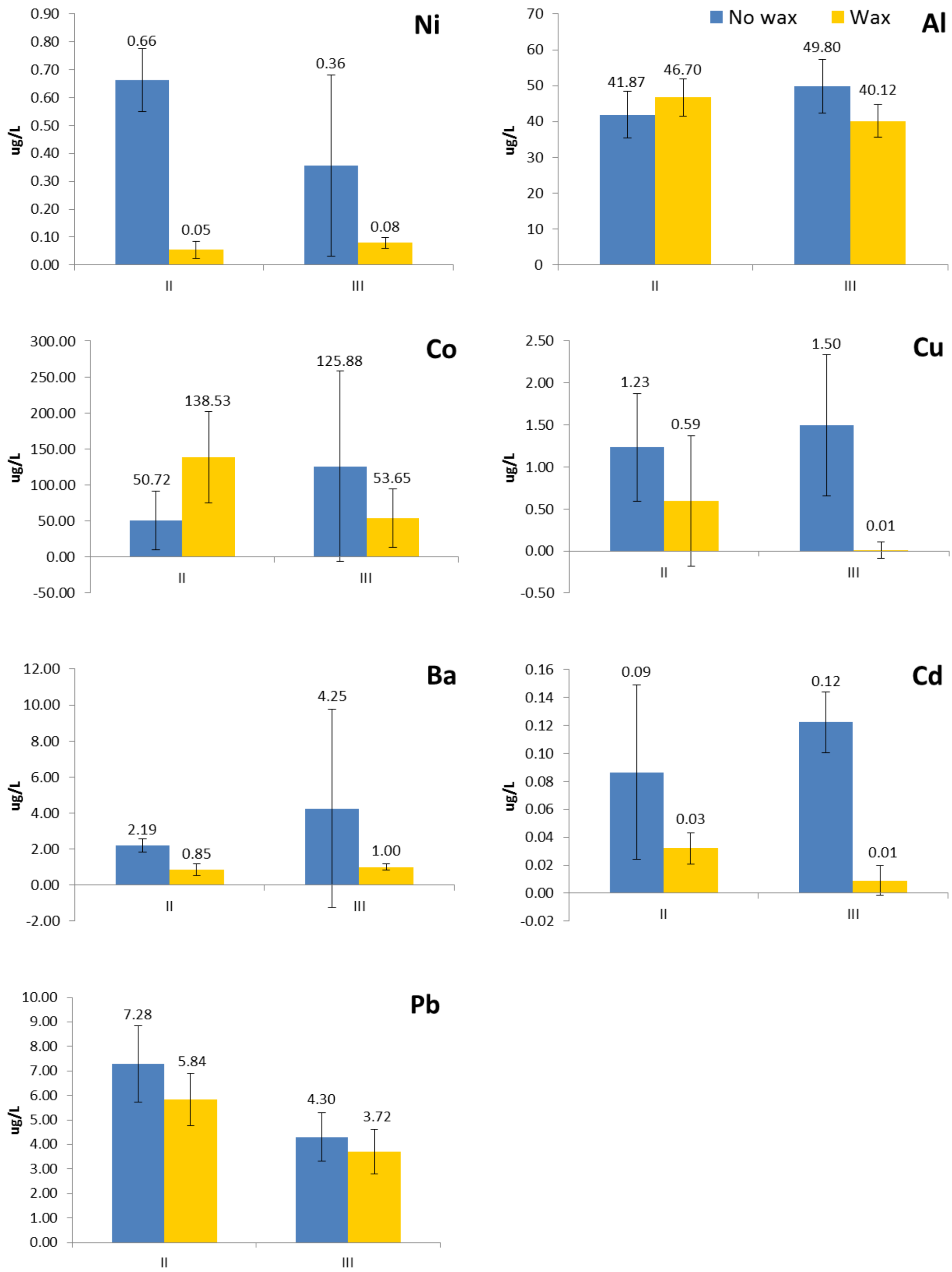


Figure 12 – Test of sample 613C06 rim area with and without paraffin wax

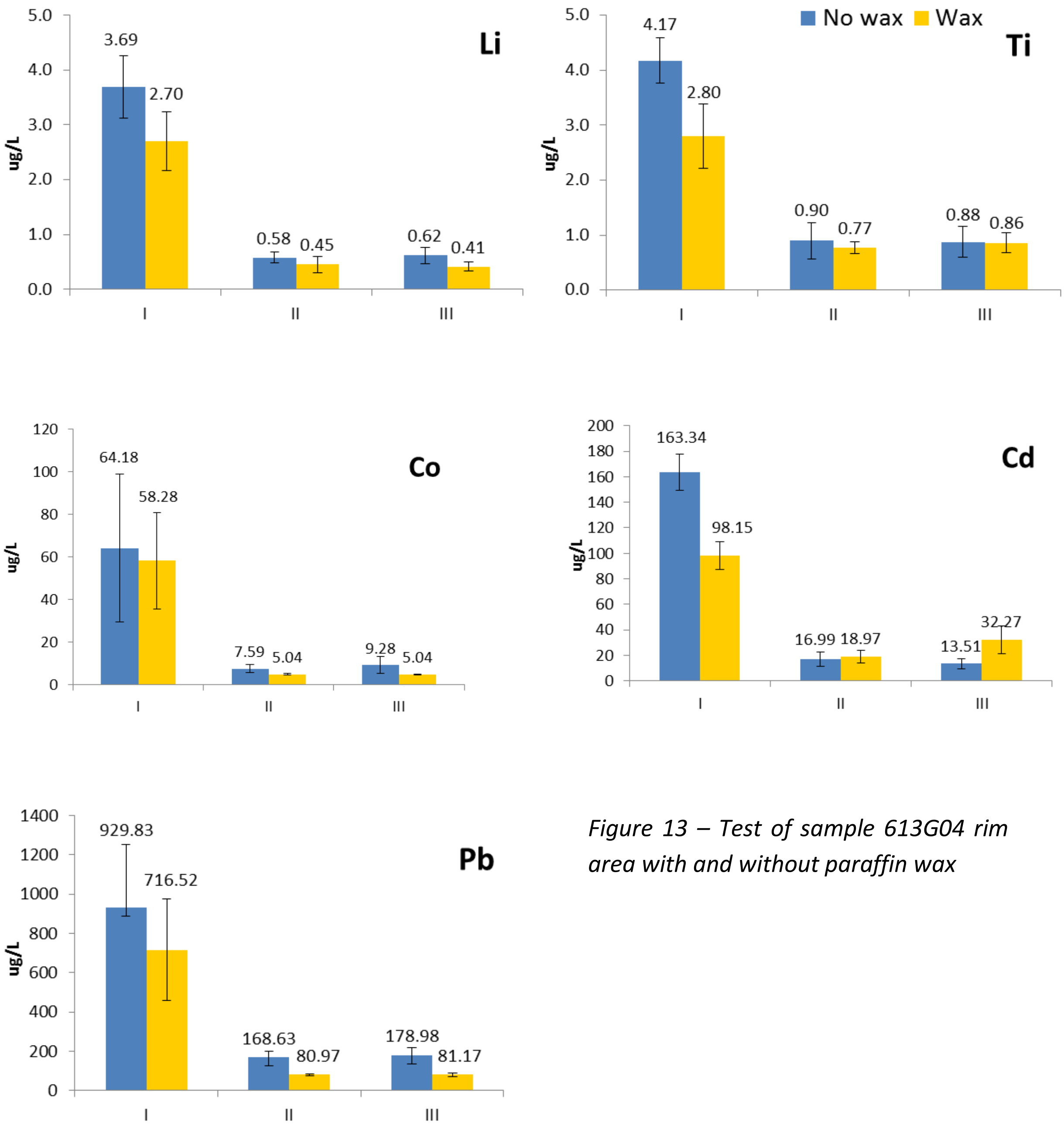


Figure 13 – Test of sample 613G04 rim area with and without paraffin wax

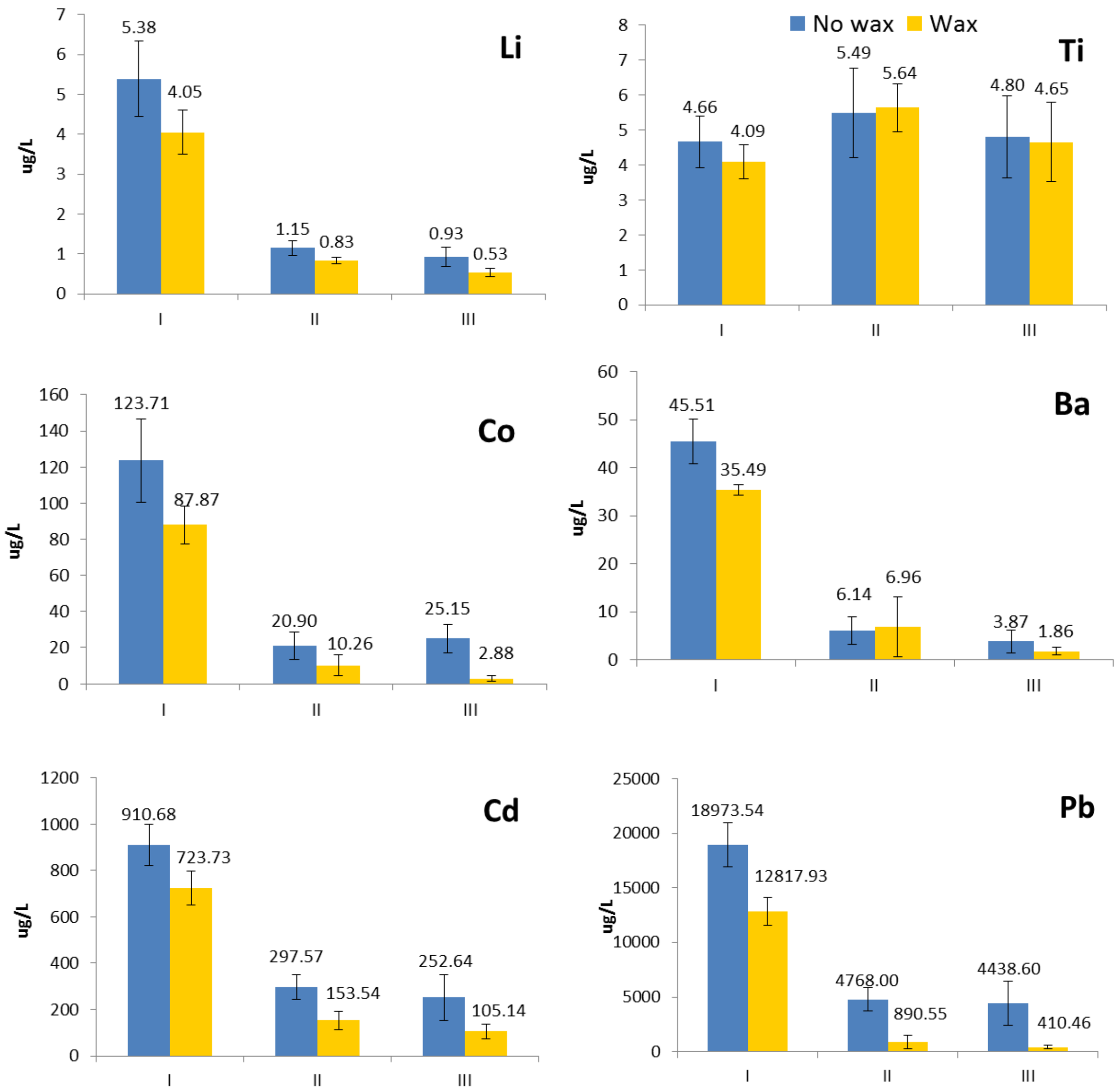


Figure 14 – Test of sample 613G05 rim area with and without paraffin wax

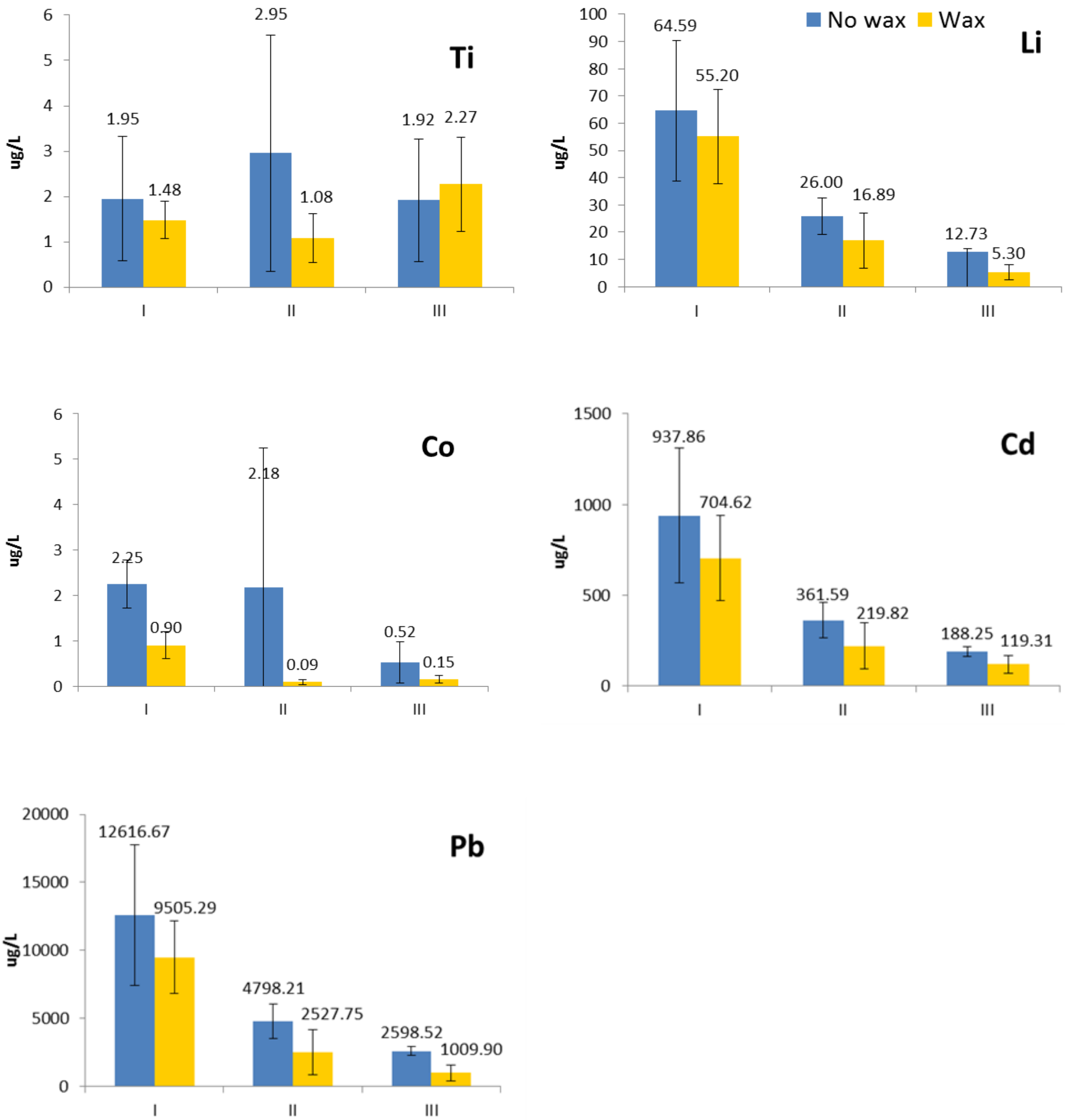


Figure 15 – Test of sample 613G06 rim area with and without paraffin wax

5. Conclusions

In this study 14 samples (8 industrial ceramic samples,1 crystal glass cup, 2 ad-hoc manufactured ceramic cups and 3 ad-hoc manufactured glasses) were tested. The results obtained using acetic acid 4%, citric acid 0.5% as well as white wine for the glass sample were compared. In addition, the AA4% methodology was investigated with and without the use of paraffin wax.

All the samples included in this study released Pb. some articles exhibited limited release of Cd and other metals from the drinking-rim area. It was observed that the release of Pb, Cd and other metals generally decreased in successive migrations. Highly decorated articles with very bright colours, released appreciably greater amounts of metals. The overglaze decorated samples were more sensitive to the food simulants and released more metals than the samples with underglaze decorations. The release of the elements from the glass samples into white wine was always lower than into acidic simulants. The differences in testing modes between using citric acid 0.5% 2hr 70°C and acetic acid 4% 24hr 22°C were apparently not significant. When a difference was observed, it depended highly on the elements considered. It also depended on the heterogeneous decoration damage of the samples. The use of melted paraffin wax on the non-exposed parts of the drinking-rim area before performing the exposure might reduce the release of metals into food simulants, but the difference between the two methodologies with or without the use of melted paraffin wax was not necessarily relevant when considering the standard deviation of the results.

6. Acknowledgements

We would like to thank all the contributors for this project, for supplying samples and sharing knowledge on the ceramic and glass field.

Alfareria Corzana Martines S.A.
Alfareria La Navà S.L. (Museo de Alfareria Agost)
Asociacion de ceramicas/ Ceramicques Aparicio
Asociacion Valenciana de Ceramica
Ayuntament Marraxti
Baccarat
BHS Table Top
Ceramica Meridiano
Chrystian Seltman GmbH
d'Ancap
The Denby Pottery Company Ltd
Demeyere FEC
Fiskars Home
IPA – Industria Porcellane S.p.A
LUCIDEON
Peter Titulaer GmbH
Portmerion Group
RCR
Riedel-Glasses
Riess Kelomat GmBh
Rogaska
Rosenthal
Royal Stafford
Sargadelos
Saint-Luis
Saturnia, Porcellane da Tavola
Steelite International
SSV
Villeroy & Boch
Waterford

Wedgwood

8. References

[1] ED 84/500/EEC, Council Directive of 15 Oct. 1984 on the approximation of the laws of the Member States relating to ceramic articles intended to come into contact with foodstuffs

[2] Bolle F. et al., Lead migration from ceramic ware in contact with foodstuff: effect of glaze, temperature, pH and food. Journal of Food Science and Engineering 2, 301-313,(2012)

[3] U.S. Food and Drug Administration, CPG Sec. 545.450 Pottery (Ceramics), Import and Domestic-Lead Contamination http://www.fda.gov

[4] European Food Safety Agency, Scientific Opinion on Lead in Food, EFSA Journal (2010) 1-147.

[5] Belgiad, J.E. Release of heavy metals from Tunisian traditional ceramic ware. Food chemical Toxicology, 71, 2033, 95-98.

[6] Demont et.al, Migration of 18 trace metals from ceramic food contact material: influence of pigment, pH, nature of acid and temperature, Food and Chemical Toxicology 50 (2013) 734-743.

[7] Cubadda F. et al., Determination of cadmium, lead, iron, nickel and chromium in selected food matrices by plasma spectrometric techniques, Microchemical Journal, 79, 91-96 (2005)

[8] Sun D.-H. et al., Determination of Thirteen Common Elements in Food Samples by Inductively Coupled Plasma Atomic Emission Spectrometry: Comparison of five Digestion Methods, Journal of AOAC International, 83 (5), 1218-1224 (2000)

[9] Bressy F.C. et al., Determination of trace element concentrations in tomato samples at different stages of maturation by ICP OES and ICP-MS following microwave-assisted digestion, Microchemical Journal, 109, 145-149 (2013)

[10] DIN EN 1388-2: Silicate surfaces in contact with foodstuffs. Determination of the release of lead and cadmium from silicate surfaces other than ceramic ware (1995)

[11] ISO 4531-1/2: Vitreous and porcelain enamels – Release of lead and cadmium from enamelled ware in contact with food (1998)

[12] ASTM C927-80: Standard Test Method for Lead and Cadmium Extracted from the Lip and Rim Area of Glass Tumblers Externally Decorated with Ceramic Glass Enamels

[13] ISO 7086-1:2000 "Glass hollowware in contact with food-Release of lead and cadmium"

[14] ISO 6486-1:1999 "Ceramic ware, glass-ceramic ware and glass dinnerware in contact with food-release of lead and cadmium"

European Commission
EUR 27178 EN – Joint Research Centre – Institute for Health and Consumer Protection

Title: **Scoping investigations on the release of metals from the rim area of decorated articles (in support of the revision of Ceramic Directive 84/500/EEC)**

Author(s): Mercedes Ana Peltzer, Giorgia Beldì, Natalia Jakubowska and Catherine Simoneau

Luxembourg: Publications Office of the European Union

2015 – 34 pp. – 21.0 x 29.7 cm

EUR – Scientific and Technical Research series – ISSN 1831-9424 (online)

ISBN 978-92-79-47228-2 (PDF)

doi:10.2788/484454

LB-NA-27178-EN-N

JRC Mission

As the Commission's in-house science service, the Joint Research Centre's mission is to provide EU policies with independent, evidence-based scientific and technical support throughout the whole policy cycle.

Working in close cooperation with policy Directorates-General, the JRC addresses key societal challenges while stimulating innovation through developing new methods, tools and standards, and sharing its know-how with the Member States, the scientific community and international partners.

Serving society
Stimulating innovation
Supporting legislation

doi:10.2788/484454

ISBN 978-92-79-47228-2

Publications Office