ΣΧΗΜΑ ΑΞΙΟΛΟΓΗΣΗΣ ΧΗΜΙΚΩΝ ΜΕΤΡΗΣΕΩΝ

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SCHEME FOR CHEMICAL MEASUREMENT ASSESSMENT

REPORT

PROFICIENCY TESTING SCHEME

SCHEMA 30 10

Migration of Cd and Pb from ceramics

Athens, August 2019

SUMMARY

Fifty-two (52) laboratories [across Europe, America and Asia] registered to participate in the Proficiency Testing scheme (PTs) SCHEMA 30 10 - migration of Cd & Pb from ceramics (refer to Figure 1 for the countries of the participating laboratories). The samples for SCHEMA 30 10 were dispatched to the participants in the end of May 2019 (31.05.2019). Each laboratory received four (4) category II ceramic articles. Fifty-two (52) participants submitted their results.

The assigned value for Cd and Pb migration was calculated from the median of the mean values (after rejecting, by Cochran's test, one outlying value out of the four reported) of the results which were submitted by the participants.

The target-value of the standard deviation for the proficiency assessment was estimated on the basis of measurement uncertainty from sampling (according to the Eurachem guide) using robust methods of analysis (RANOVA) for the migration of Cd and Pb from the ceramic articles.

The target-value of standard deviation was used in conjunction to the assigned value to derive the z-scores for participants' results. z-scores are considered satisfactory if $|z| \leq 2$.

Results of this proficiency testing scheme are summarized in Table 1:

Table 1. Summary of the PTs SCHEMA 30 10

Parameter	Assigned value $\hat{X}$ (μg/L)	Target value σ_p (μg/L)	total number of submitted results	number of results with satisfactory z-score	satisfactory z-scores (%)
Cd	114.2	34.42	52	48	92
Pb	280.8	49.34	52	48	92

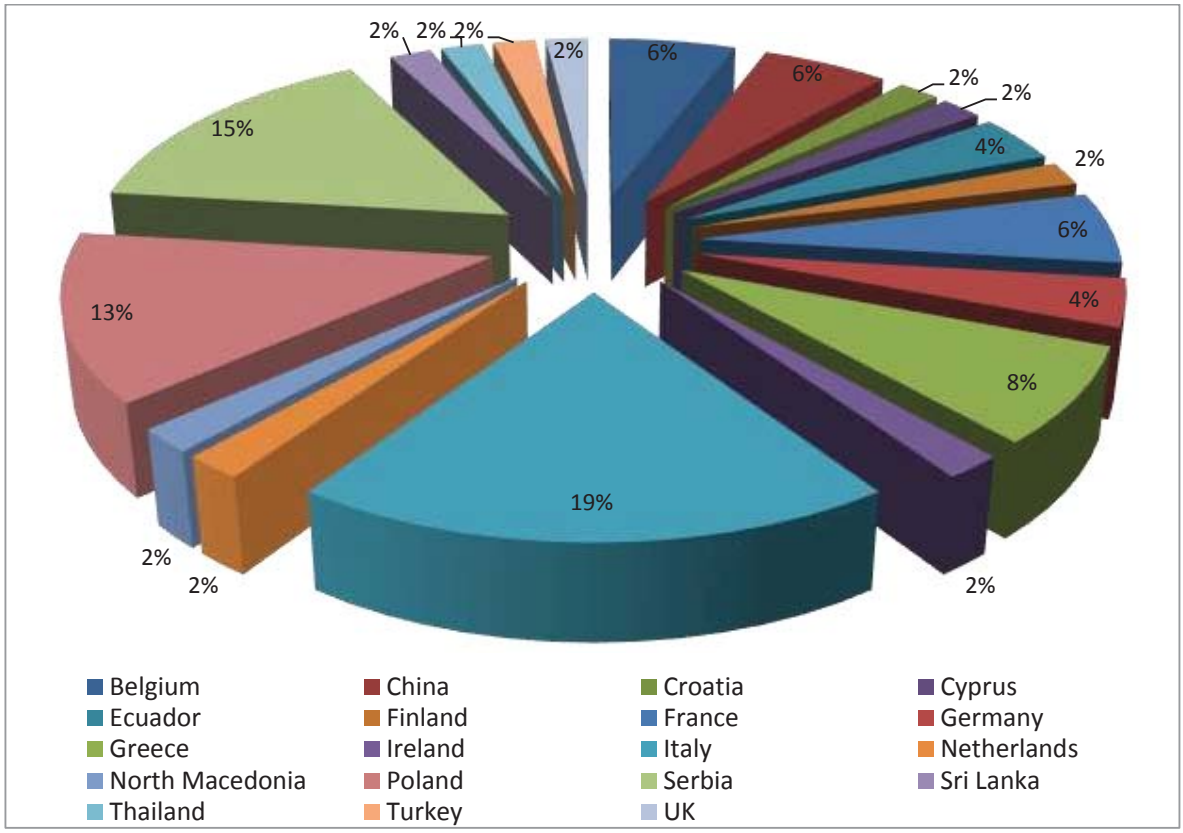

Figure 1. Participating laboratories per country for SCHEMA 30 10.

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CONTENTS

1 INTRODUCTION

1.1 Scope

Proficiency testing schemes constitute a key-point in the use of interlaboratory comparisons for the assessment of laboratory performance in specific methods or comparisons. Proficiency testing is a periodical independent assessment of laboratory performance and consequently an important tool to assure the validity and reliability of results. Its basic aim is to assist laboratories to have a continuous supervision on their results quality and in case of poor performance to undertake the required corrective actions, so as to improve the quality of their measurements and services.
Additionally, successful participation in proficiency testing schemes is a requirement for the accreditation of testing laboratories to the international standard ISO/IEC 17025. Therefore, together with method validation, participation in proficiency testing is an essential tool for laboratory quality assurance.
This proficiency testing scheme, SCHEMA 30 10, is organized in order to strengthen the technical competency of laboratories carrying out migration control studies from ceramic articles and to ensure the quality of goods as well as the protection of consumer's health.
Furthermore, SCHEMA 30 10 is organized at relative low migration levels for Cd and Pb in order to verify the suitability of the applied techniques used to assess the conformity of ceramics in contact with food according to the new EU proposed limits.

2 SAMPLES

2.1 Sample Selection

Preliminary experiments using ceramic articles with different Cd & Pb migration levels were conducted. A ceramic article, characterized by Cd & Pb migration levels similar to the new proposed limits was chosen as the substrate to be distributed. A set of four (4) ceramic articles was distributed to the participants.

2.2 Sample Preparation

The distributed ceramic articles were produced by a subcontractor under the supervision of the Chemical Metrology Service and were delivered in cardboard boxes.

2.3 Samples Homogeneity Testing

Homogeneity studies for the ceramic articles were carried out according to the IUPAC harmonized protocol. All measurements were performed by the Chemical Metrology Service. Ten (10) sets of four (4) ceramic articles were randomly selected and measured. The homogeneity testing results were evaluated by the Chemical Metrology Service using the target-value of the standard deviation for the proficiency testing scheme (Annex I). The data showed that the samples were homogeneous.

2.4 Sample Distribution

The samples were dispatched on 31st May 2019. Each participant received four (4) labeled, category II ceramic articles and by e-mail: a cover letter with instructions for the results' submission, a form for confirming samples' receipt, a results' reporting form in excel format and a questionnaire. The closing date for submitting results was the 5th of July 2019. Participants were asked to subject each ceramic item to

migration testing and provide the concentration of Cd and Pb in the simulant in μg/L for each ceramic article.

In the cover letter, it was recommended to follow standard/official or other accredited methods of analysis. The analytical methods used by the participants are concisely presented in Annex III, where the participants' answers to the questionnaire are summarized.

3 STATISTICAL EVALUATION OF RESULTS

- The distributions of the homogeneity results for Cd and Pb migration from ceramics and the results submitted by the participants were statistically evaluated. Since statistically significant differences were not observed, the migration values from the homogeneity study describe the population of the participants' submitted results adequately. Therefore, the robust standard deviation arising from the Robust Analysis of Variance of the homogeneity study results was used to evaluate the performance of the participants.
- Schematic representations concerning the Cd and Pb migration results submitted by the participants are given in Figures 2 and 3, respectively.
- Kernel density plots for participants' migration results for Cd and Pb were constructed and qualitatively evaluated (Figures 4 and 5).
- Cochran's C test was applied in order to detect outlying values within the quartet of each participant's submitted results respectively. Only one value per participant (out of the four reported) can be rejected as an outlying value.
- The evaluation of laboratory performance was based on the mean value of the four reported results after the rejection of any outlying values (by Cochran's C test). For the calculation of the assigned value, the median (of the mean values calculated for the participating laboratories) was used, which constitutes a robust statistical parameter. For each parameter the median of the mean values is compared to A15 (robust statistics) - Table 2.
- Different tests were applied in order to detect outliers among the mean values. Outliers were evaluated by: (1) Grubbs tests, (2) Dixon Q test and (3) Hampel's test.
- After the rejection of the outliers, the normality was checked by the Kolmogorov-Smirnov test. The robust standard deviation $\hat{\sigma}$ (sMAD) was calculated for each parameter - Table 2.
- For each parameter, the target-value of the standard deviation for Proficiency Assessment σ_p was calculated, as well as the uncertainty of each assigned value (Annex I &Table 2).

The descriptive summary statistics are presented in Table 2.

3.1 Assigned Value $\widehat{X}$

The assigned value for Cd and Pb migration was calculated as the median of the mean values of all reported results (mean values after removing any outliers). The assigned value for each parameter is given in Table 2.

3.2 Target-value of standard deviation for proficiency assessment σ_p

The target-value of the standard deviation for the proficiency assessment σ_p of Cd and Pb migration from ceramic articles was determined on the basis of the uncertainty of measurement evaluation by estimating the interlaboratory reproducibility through a model of random sampling (according to the Eurachem guide "Measurement of the uncertainty from sampling"), using a Robust Analysis of Variance (the ROBAN v.1.01 software program from AMC - details see Annex I).

3.3 z-score calculation

Participants' z-scores were calculated as:

$$z = \frac{x - \hat{\hat{X}}}{\sigma_p}$$

where: x the result reported by the participant
$\hat{X}$ the assigned value
σ_p the target-value standard deviation for proficiency assessment

(a) Results with $|z| \leq 2$ are designated as acceptable or satisfactory,
(b) A result with $2 < |z| < 3$ shall be considered to give a 'warning signal' according to ISO 13528:2015 and is designated as questionable according to the IUPAC International Harmonized Protocol,
(c) A result with $|z| \geq 3$ shall be considered to give an 'action signal' according to ISO 13528:2015 and is designated as unacceptable or unsatisfactory according to the IUPAC International Harmonized Protocol.

For all parameters, the target-value of the standard deviation for Proficiency Assessment σ_p was compared to the robust standard deviation $\hat{\sigma}$ and the square value of the uncertainty of the assigned value u_x was compared to the square value of the target-value of the standard deviation for the proficiency assessment σ_p (Table 2).
The submitted results and participants' performance evaluation through z-scores are presented in Tables 3 and 4. Schematic representations of z-score and kernel density plots are shown in Figures 4 and 5.

4 RESULTS – CONCLUSIONS

4.1 Migration of Cd and Pb and from ceramic articles

Migration of Cd from ceramics: One outlier was detected in 52 submitted results for Cd migration from ceramic articles by both Grubbs and Hampel's tests. A small shoulder on the right side of the major peak, observed in the kernel density plot, is attributed to the outlying values (Figure 4).
Migration of Pb from ceramics: Three outliers were detected by Grubbs, Dixon's Q or Hampel's tests in 52 submitted results for Pb migration from ceramic articles. Two minor peaks, observed on both sides in the kernel density plot, are attributed to the outliers (Figure 5).

Conclusions

The performance of the participating laboratories was satisfactory. No correlation between the laboratory performance and the corresponding analytical technique could be established. Taking into account the new

discussion starting values (DSVs) for Cd and Pb migration from ceramic articles, the performance of the methods (Limit of Detection - as reported by the participants - (Table 5)) should be reconsidered.

5 REFERENCES

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- Council Directive 84/500/EEC of 15 October 1984 on the approximation of the laws of the Member States relating to ceramic articles intended to come into contact with foodstuffs.
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- Eurachem/CITAC Guide, Measurement uncertainty arising from sampling, 2007.
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- M. Peltzer, C. Simoneau, 'Preliminary investigations on the release of metals from ceramic and glassware in support to the revision of the ceramics Directive 84/500/EEC', JRC-Technical Report, Progress Report 2013.
- 2nd, 3rd and 6th Stakeholder workshop on ceramics. Revision of ceramics regulation. JRC-Ispra, 24.10.2013, 10.06.2014 & 25.10.2016.

Table 2. Descriptive Summary Statistics

	Migration from ceramics	
	Cd	**Pb**
Median value (µg/L)	114.2	280.8
Mean value (µg/L)	119.7	290.7
Number of results	52	52
Standard Deviation (µg/L)	41.87	71.35
Central Tendency Estimation A15 (µg/L)	113.3	286.0
Robust standard deviation $\hat{\sigma}$ (sMAD) (µg/L)	26.06	50.86
Target-value of standard deviation σ_p (µg/L)	34.42	49.34
$(u_x)^2/(\sigma_p)^2$	0.01	0.02
Assigned Value $\hat{X}$ (µg/L)	114.2	280.8

Table3. Migration of Cd from ceramics - Participants'submitted results, means of submitted results and z-scores

Cd migration (µg/L) assigned value: 114.2							
Laboratory code	**Ceramic cup a**	**Ceramic cup b**	**Ceramic cup c**	**Ceramic cup d**	Mean Value of four submitted results	Mean Value excluding value rejected by Cochran's test	**z-score**
CER01	142.57	124.50	110.91	108.02	121.5	121.5	0.2
CER02	214.00	179.00	311.00*	223.00	231.8	205.3	**2.6**
CER03	91.99	94.92	92.06	103.61	95.6	95.6	-0.5
CER04	144.10	125.20	140.2	132.60	135.5	135.5	0.6
CER05	93.00	99.00	99.00	98.00	97.3	97.3	-0.5
CER06	106.00	114.00	116.00	116.00	113.0	113.0	0.0
CER07	106.80	122.20	113.80	109.40	113.1	113.1	0.0
CER08	125.60	123.40	122.90	114.50	121.6	121.6	0.2
CER09	131.83	120.02	124.65	103.82	120.1	120.1	0.2
CER10	86.40	80.39	84.61	84.34	83.9	83.9	-0.9
CER11	95	120	120	130	116.3	116.3	0.1
CER12	99.03	96.37	104.33	112.78	103.1	103.1	-0.3
CER13	86.00	80.00	94.00	72.00	83.0	83.0	-0.9
CER14	93.80	93.70	79.20	89.10	89.0	89.0	-0.7
CER15	68.00	64.00	75.00	66.00	68.3	68.3	-1.3
CER16	94	84	123	83	96.0	96.0	-0.5
CER17	150.30	160.5	176.60	169.10	164.1	164.1	1.5
CER18	104.50	99.70	120.80	129.60	113.7	113.7	0.0
CER19	103.88	117.51	103.42	97.13	105.5	105.5	-0.3
CER20	237.50	219.90	257.90*	183.10	224.6	213.5	**2.9**
CER21	193.00*	310.90	288.70	265.40	264.5	288.3[1,2,3]	**5.1**
CER22	122.65	98.00	134.17	115.35	117.5	117.5	0.1
CER23	85.98	89.86	108.95	108.16	98.2	98.2	-0.5
CER24	141.40	142.00	127.20	132.70	135.8	135.8	0.6
CER25	130.33	131.23	120.41	135.65	129.4	129.4	0.4
CER26	161.10	163.80	139.70	155.20	155.0	155.0	1.2

z-score values (|z|) > 2 are shown in bold, [1]Outlier- by Grubbs-test, [2]Outlier- by Dixon's Q-test, [3]Outlier- by Hampel test

* Outlying value by Cochran's test

Table 3(cont). Migration of Cd from ceramics - Participants' submitted results, means of submitted results and z-scores

Cd migration (µg/L) assigned value: 114.2							
Laboratory code	**Ceramic cup a**	**Ceramic cup b**	**Ceramic cup c**	**Ceramic cup d**	Mean Value of four submitted results	Mean Value excluding value rejected by Cochran's test	**z-score**
CER27	44.10	42.00	46.40	44.30	44.2	44.2	-2.0
CER28	157.00	159.00	158.00	161.00	158.8	158.8	1.3
CER29	146.00	152.00	143.00	125.00	141.5	141.5	0.8
CER30	77.40	79.30	91.20	78.00	81.5	81.5	-1.0
CER31	82.50	90.90	82.50	87.50	85.9	85.9	-0.8
CER32	101.00	109.00	101.00	102.00	103.3	103.3	-0.3
CER33	105.00	95.00	95.00	105.00	100.0	100.0	-0.4
CER34	130.00	110.00	120.00	110.00	117.5	117.5	0.1
CER35	92.00	87.10	79.40	92.60	87.8	87.8	-0.8
CER36	100.00	113.40	123.40	110.00	111.7	111.7	-0.1
CER37	122.044	124.986	117.252	115.154	119.9	119.9	0.2
CER38	45.8	43.8	55.4	58.8	51.0	51.0	-1.8
CER39	197.60	225.60	223.10	206.70	213.3	213.3	**2.9**
CER40	100.79	100.46	112.61	103.52	104.3	104.3	-0.3
CER41	144.05	130.71	150.05	146.05	142.7	142.7	0.8
CER42	147.40	150.80	160.80	170.60	157.4	157.4	1.3
CER43	118.40	109.50	144.50	135.10	126.9	126.9	0.4
CER44	110.00	126.00	128.00	95.00	114.8	114.8	0.0
CER45	111.80	94.90	94.10	100.60	100.4	100.4	-0.4
CER46	87.00	94.00	61.00	84.00	81.5	81.5	-1.0
CER47	100.89	104.63	94.00	94.70	98.6	98.6	-0.5
CER48	122.00	116.00	151.00	126.00	128.8	128.8	0.4
CER49	127.42	125.61	136.88	187.24	144.3	144.3	0.9
CER50	114.00	107.00	97.00	148.00	116.5	116.5	0.1
CER51	125.00	131.00	114.00	114.00	121.0	121.0	0.2
CER52	76.00	83.00	94.00	84.00	84.3	84.3	-0.9

z-score values (|z|) > 2 are shown in bold, [1]Outlier- by Grubbs-test, [2]Outlier- by Dixon's Q-test, [3]Outlier- by Hampel test

* Outlying value by Cochran's test

Table 4.Migration of Pb from ceramics - Participants' submitted results, means of submitted results and z-scores

Pb migration (µg/L) assigned value: 280.8							
Laboratory code	**Ceramic cup a**	**Ceramic cup b**	**Ceramic cup c**	**Ceramic cup d**	Mean Value of four submitted results	Mean Value excluding value rejected by Cochran's test	**z-score**
CER01	428.20	379.74	343.51	363.49	378.7	378.7	2.0
CER02	297.00	312.00	337.00	329.00	318.8	318.8	0.8
CER03	255.92	274.68	251.12	287.52	267.3	267.3	-0.3
CER04	279.60	260.20	292.60	275.20	276.9	276.9	-0.1
CER05	250.00	280.00	260.00	259.00	262.3	262.3	-0.4
CER06	290.00	284.00	322.00	296.00	298.0	298.0	0.3
CER07	466.52	410.71	496.76	371.82	436.5	436.5	**3.2**
CER08	258.20	235.30	241.10	241.20	244.0	244.0	-0.7
CER09	341.70	322.91	336.30	282.61	320.9	320.9	0.8
CER10	262.30	246.80	247.80	247.40	251.1	251.1	-0.6
CER11	260	330	320	350	315.0	315.0	0.7
CER12	296.31	281.64	298.97	331.28	302.1	302.1	0.4
CER13	247.00	224.00	298.00	222.00	247.8	247.8	-0.7
CER14	303.50	276.30	209.80	261.70	262.8	262.8	-0.4
CER15	220.00	200.00	210.00	210.00	210.0	210.0	-1.4
CER16	260	250	370	260	285.0	285.0	0.1
CER17	338.60	365.20	415.50	384.40	375.9	375.9	1.9
CER18	271.40	261.95	306.50	320.00	290.0	290.0	0.2
CER19	285.13	284.47	282.37	257.18	277.3	277.3	-0.1
CER20	356.40	338.20	365.00	332.60	348.1	348.1	1.4
CER21	320.20	372.30	397.70	228.10	329.6	329.6	1.0
CER22	264.39	220.89	284.50	238.75	252.1	252.1	-0.6
CER23	247.84	262.30	314.28	319.33	285.9	285.9	0.1
CER24	362.60	356.30	336.40	353.80	352.3	352.3	1.4
CER25	321.02	323.72	272.07	311.41	307.1	307.1	0.5
CER26	347.20	341.10	331.30	346.80	341.6	341.6	1.2

z-score values (|z|) > 2 are shown in bold, [1]Outlier- by Grubbs-test, [2]Outlier- by Dixon's Q-test, [3]Outlier- by Hampel test
*Outlying value by Cochran's test

Table 4 (cont). Migration of Pb from ceramics - Participants' submitted results, means of submitted results and z-scores

Pb migration (µg/L) assigned value: 280.8							
Laboratory code	**Ceramic cup a**	**Ceramic cup b**	**Ceramic cup c**	**Ceramic cup d**	Mean Value of four submitted results	Mean Value excluding value rejected by Cochran's test	**z-score**
CER27	102.10	101.40	104.80	102.90	102.8	102.8[1,2]	**-3.6**
CER27	355.00	364.00	361.00	347.00	356.8	356.8	1.5
CER29	365.00	370.00	390.00	358.00	370.8	370.8	1.8
CER30	235.00	262.00	257.90	248.80	250.9	250.9	-0.6
CER31	223.00	250.50	217.70	246.20	234.4	234.4	-0.9
CER32	273.00	296.00	244.00	303.00	279.0	279.0	0.0
CER33	290.00	240.00	270.00	260.00	265.0	265.0	-0.3
CER34	260.0	260.0	240.0	220.0	245.0	245.0	-0.7
CER35	286.20	272.90	251.60	279.30	272.5	272.5	-0.2
CER36	276.30	305.50	374.70	304.40	315.2	315.2	0.7
CER37	348.09	355.68	336.38	331.11	342.8	342.8	1.3
CER38	65.4	66.3	71.7	78.1	70.4	70.4[1,2,3]	**-4.3**
CER39	289.70	308.40	239.70	240.60	269.6	269.6	-0.2
CER40	238.97	254.18	260.49	231.95	246.4	246.4	-0.7
CER41	324.12	349.25	339.20	319.10	332.9	332.9	1.1
CER42	293.40	302.60	328.40	357.90	320.6	320.6	0.8
CER43	312.60	288.40	387.70	384.20	343.2	343.2	1.3
CER44	260	300	320	250	282.5	282.5	0.0
CER45	305.60	259.00	242.00	249.90	264.1	264.1	-0.3
CER46	274.00	272.00	181.00	234.00	240.3	240.3	-0.8
CER47	252.92	272.22	224.87	263.92	253.5	253.5	-0.6
CER48	250.00	230.00	310.00	300.00	272.5	272.5	-0.2
CER49	509.39	482.29	675.30	709.33*	594.1	555.7[1,2,3]	**5.6**
CER50	289.00	280.00	233.00	366.00	292.0	292.0	0.2
CER51	253.00	308.00	279.00	265.00	276.3	276.3	-0.1
CER52	201.00	224.00	250.00	231.00	226.5	226.5	-1.1

z-score values (|z|) > 2 are shown in bold, [1]Outlier- by Grubbs-test, [2]Outlier- by Dixon's Q-test, [3]Outlier- by Hampel test

* Outlying value by Cochran's test

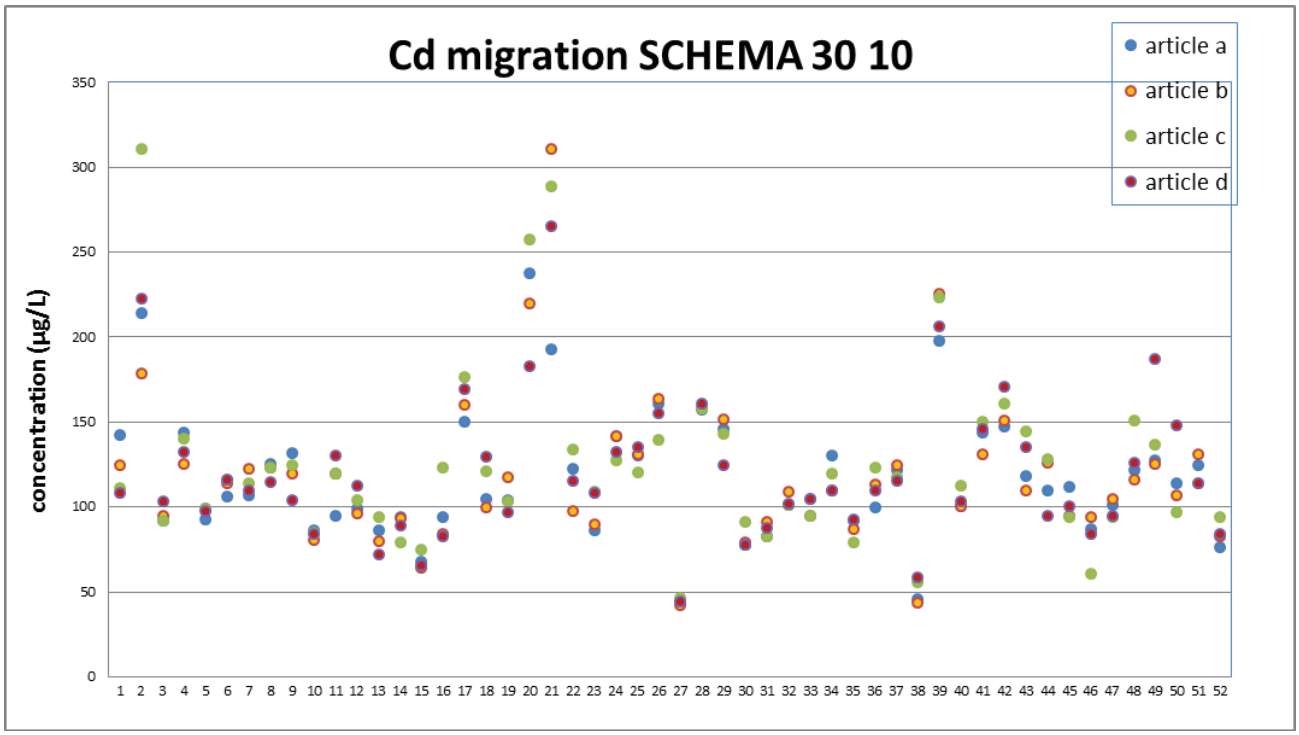


Figure 2. Cd migration from ceramics - participants' results

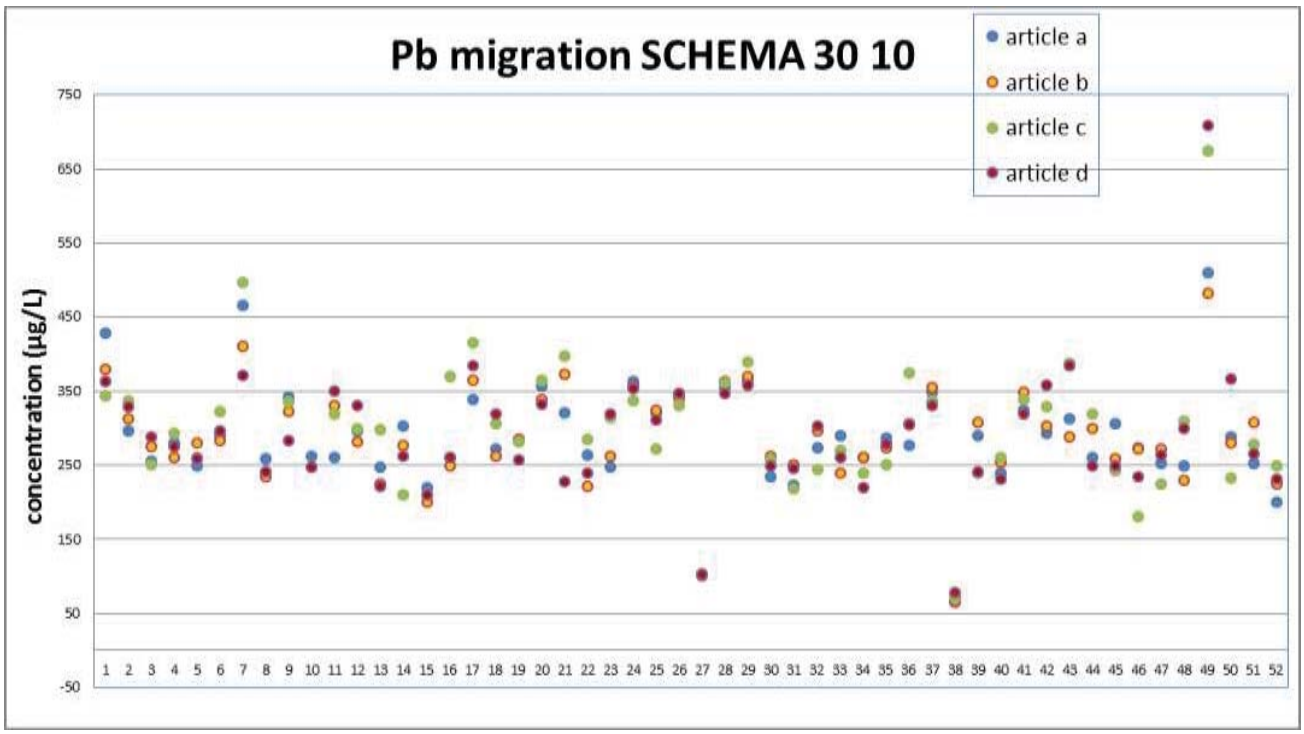


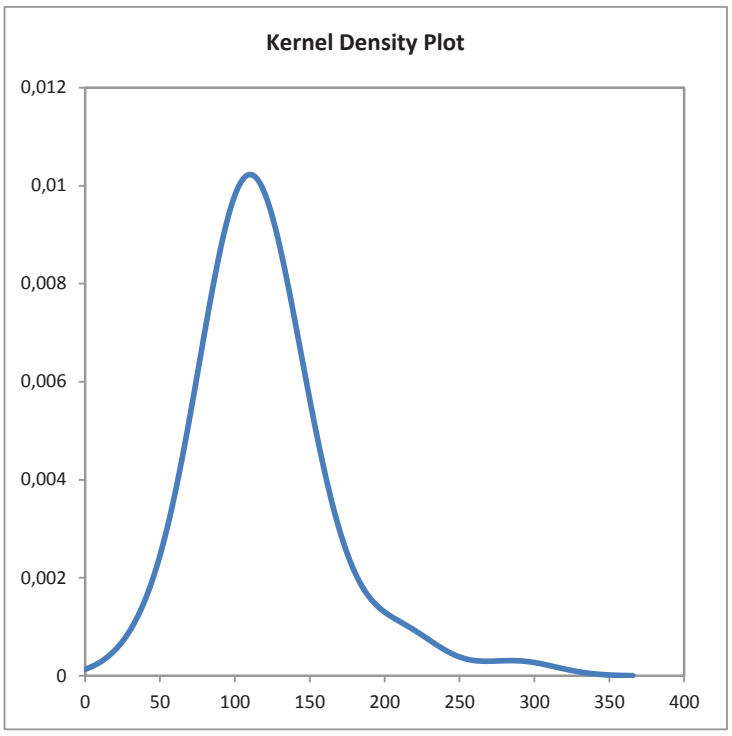
Figure 3. Pb migration from ceramics - participants' results

Table 5.Migration of Cd and Pb - participants' method details (LOD)

Laboratory code	Cd	Pb		Laboratory code	Cd	Pb
	LOD (µg/L)	LOD (µg/L)			LOD (µg/L)	LOD (µg/L)
CER01	20	200		**CER27**	0.10	1.00
CER02	0.01	0.02		**CER28**	4.80	5.40
CER03	1.00	10.0		**CER29**	5.00	50.0
CER04	30.0	33.0		**CER30**	10.0	100.0
CER05	8.00	24.0		**CER31**	5.0	20.0
CER06	0.17	1.09		**CER32**	6.0	21.0
CER07	25.0	5.0		**CER33**	20.0	20.0
CER08	10	20		**CER34**	10.0	100.0
CER09	0.06	0.03		**CER35**	10.0	50.0
CER10	2	5		**CER36**	20.0	200.0
CER11	12.5	100		**CER37**	10.0	100.0
CER12	20.0	100.0		**CER38**	0.1	0.1
CER13	2.0	14.0		**CER39**	10.0	40.0
CER14	3.0	3.0		**CER40**	0.70	0.40
CER15	6.0	60.0		**CER41**	1.80	49.10
CER16	1.4	16		**CER42**	10.0	100.00
CER17	5.0	100.0		**CER43**	5.0	5.0
CER18	10.0	10.0		**CER44**	70.00	100.00
CER19	1.00	10.0		**CER45**	10.0	100.0
CER20	0.40	6.10		**CER46**	0.03	0.25
CER21	0.40	6.10		**CER47**	0.16	0.64
CER22	<0.5	<5.0		**CER48**	8.00	40.00
CER23	1.00	1.00		**CER49**	15.0	15.0
CER24	10.0	80.0		**CER50**	3.0	3.0
CER25	10.00	100.0		**CER51**	10.0	100.0
CER26	5.0	10.0		**CER52**	3.0	10.0

Table 6. Filling volumes used for the migration analysis (mL)

Lab code	Filling Volume (mL) of ceramic				Lab code	Filling Volume (mL) of ceramic			
	cup a	**cup b**	**cup c**	**cup d**		**cup a**	**cup b**	**cup c**	**cup d**
CER01	56.0	55.5	56.0	56.0	**CER28**	38.74	38.14	38.22	39.10
CER02	40.0	40.0	40.0	40.0	**CER29**	37.1	35.4	37.2	37.1
CER03	45.0	45.0	45.0	45.0	**CER30**	50.0	50.0	50.0	50.0
CER04	42.0	41.0	42.0	42.0	**CER31**	50.0	50.0	50.0	50.0
CER05	45.0	45.0	45.0	45.0	**CER32**	45.0	45.0	45.0	45.0
CER06	44.0	44.0	43.5	44.5	**CER33**	45.0	45.0	47.0	47.0
CER07	42.5	42.0	42.1	43.5	**CER34**	48.0	48.0	48.0	48.0
CER08	40.0	40.0	40.0	40.0	**CER35**	46.0	46.0	46.0	46.0
CER09	45.0	45.0	45.0	45.0	**CER36**	46.0	46.0	46.0	46.0
CER10	48.0	50.0	50.0	49.0	**CER37**	40.1	40.0	40.6	40.5
CER11	44.0	44.0	44.0	44.0	**CER38**	45.0	45.0	45.0	45.0
CER12	47.0	47.0	47.0	47.0	**CER39**	43.0	43.0	43.0	43.0
CER13	45.0	45.0	45.0	45.0	**CER40**	47.0	47.0	47.0	48.0
CER14	45.0	45.0	45.0	45.0	**CER41**	36.0	36.0	36.0	36.0
CER15	47.0	47.0	46.0	47.0	**CER42**	40.0	40.0	40.0	40.0
CER16	45	45	45	45	**CER43**	40.0	40.0	40.0	40.0
CER17	45.0	45.0	45.0	45.0	**CER44**	50.0	50.0	50.0	50.0
CER18	46.0	46.0	46.0	46.0	**CER45**	42.0	42.0	41.0	42.0
CER19	45.0	45.0	45.0	45.0	**CER46**	44.3	44.5	44.8	44.2
CER20	40.0	40.0	40.0	40.0	**CER47**	42.0	42.0	43.0	43.0
CER21	40.0	40.0	40.0	40.0	**CER48**	44.0	43.0	43.0	44.0
CER22	40.0	40.0	40.0	40.0	**CER49**	2.0	2.0	2.0	2.0
CER23	45.0	45.0	45.0	45.0	**CER50**	38.0	38.0	38.0	38.0
CER24	39.5	39.5	36.5	38.5	**CER51**	46.0	46.0	46.0	46.0
CER25	44.0	44.0	44.0	44.0	**CER52**	50.0	50.0	50.0	50.0
CER26	38.93	37.56	37.47	38.03					
CER27	45.0	45.0	45.0	45.0					



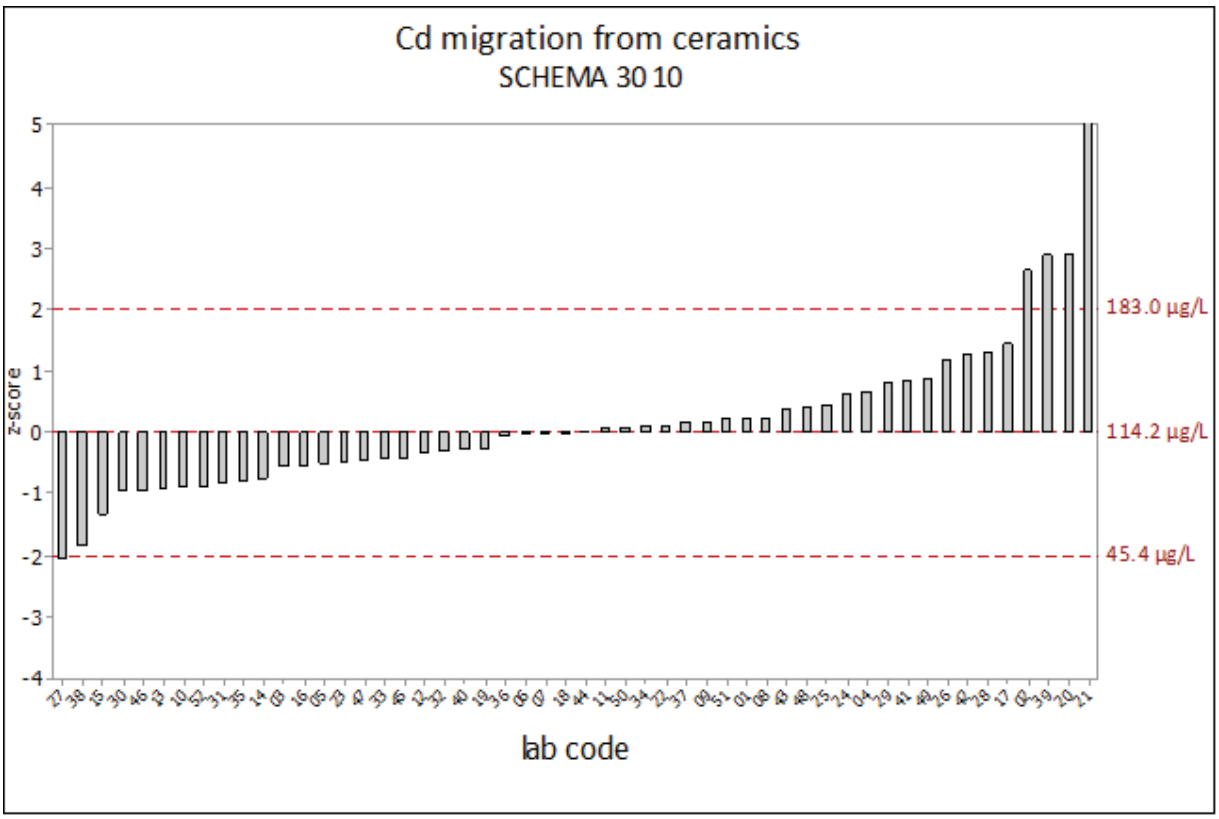
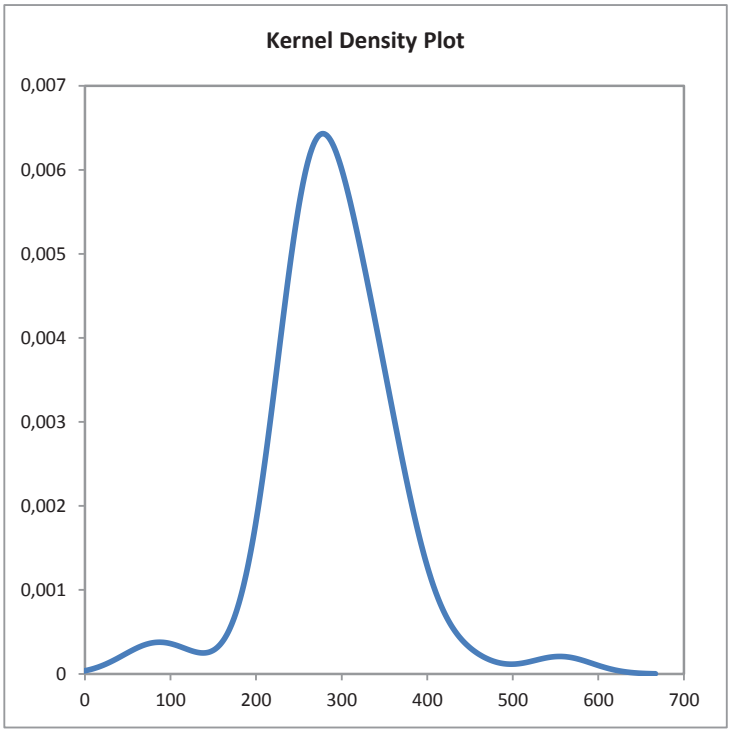


Figure4.z-score and kernel density plot for Cd migration from ceramics



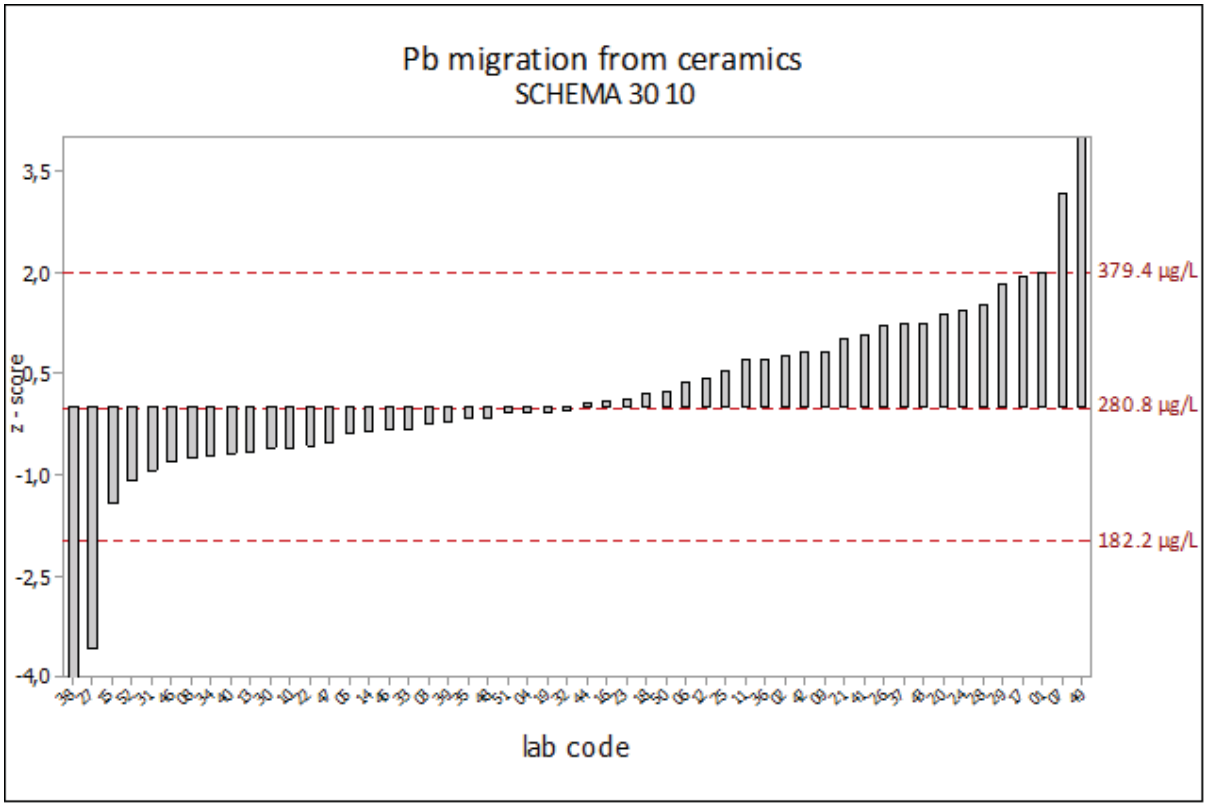


Figure 5. z-score and kernel density plot for Pb migration from ceramics

Annex I.

Determination of target-value of standard deviation for proficiency assessment, σ_p

The empirical 'top-down' approach was used for the determination of the target-value of standard deviation for the proficiency assessment concerning migration of Cd and Pb from ceramic articles. The methodology used in SCHEMA 30 10 is based on the duplicate method described in the Eurachem guide 'Uncertainty of measurement arising from sampling', which uses the branched model of sampling - Figure 6. This method uses repeated measurements in order to estimate the sampling and the analysis contribution to the uncertainty of measurement. Random constituents of uncertainty can be appreciated by Analysis Of Variance, ANOVA.

$$s^2_{measurament} = s^2_{sampling} + s^2_{analysis}$$

In the presence of outliers, robust models of statistical processing are used, as they minimize the contribution of outliers. In this Proficiency Testing scheme Robust Analysis of Variance was applied, by using ROBAN v.1.01 software program of AMC (Analytical Methods Committee).

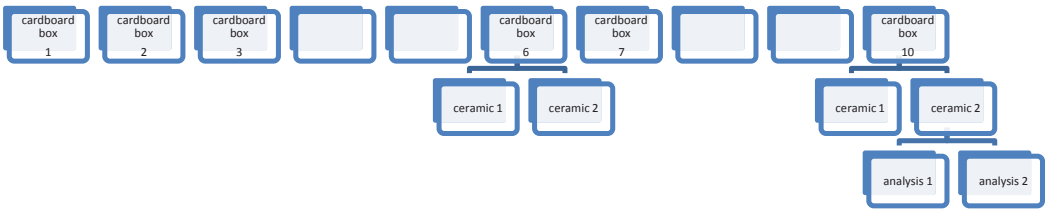


Figure 6. Duplicate 'top-down' sampling approach.

Twelve (12) sets of four (4) ceramic articles (per set) were randomly selected; from these sets two ceramic articles were taken and each article was measured twice. The results from the Classical ANOVA and the Robust ANOVA model of statistical processing are shown in the following Table.

Cd			***Pb***	
Classical ANOVA results				
mean	133.3		*mean*	281.2
SD	32.81		***SD***	47.34
ROBust ANova results (ROBAN results)				
mean	132.9		*mean*	278.6
SD	***34.42***		***SD***	***49.34***

According to the results above, the uncertainty from sampling, which contains the selection of random articles as well as the sources related to the migration experiment (temperature, migration time, concentration of acid etc.) constitutes the main component of the uncertainty of measurement compared to the component arising from the repeatability of the instrument. Therefore, the overall estimation of uncertainty is a satisfactory estimation of the interlaboratory reproducibility.

For PTs SCHEMA 30 10 the target-value of standard deviation for proficiency assessment σ_p is defined as the standard deviation of measurement, as calculated by the robust analysis of variation (ROBAN AMC).

Annex II. Results of homogeneity testing

Table A.1.Results of homogeneity testing for the migration of Cd from ceramics

Sample code	Ceramic cup a/b	ceramic cup c/d
30 10 02	132.5	168.5
30 10 03	125.5	174.8
30 10 19	125.0	127.0
30 10 27	102.0	152.8
30 10 38	120.9	142.3
30 10 39	122.3	118.5
30 10 41	105.8	115.8
30 10 61	143.0	105.3
30 10 73	141.8	185.5
30 10 75	124.0	115.8

general average (µg/L)	132.4
within-sample standard deviation, s_{an}^2	513.9
allowable sampling variance σ_{all}^2	106.6
between-samples standard deviation, s_{sam}^2	23.2
Target standard deviation, $\boldsymbol{\sigma_p}$ Originates: ROBAN sampling-Annex I	34.42
Accepted homogeneity if $s_{sam}^2 \leq c$: critical value for the homogeneity assessment	YES (c=719.5)

Table A.2.Results of homogeneity testing for the migration of Pb from ceramics

Sample code	Ceramic cup a/b	ceramic cup c/d
30 10 02	310.7	306.5
30 10 03	232.4	296.9
30 10 19	356.1	372.0
30 10 27	330.4	309.1
30 10 38	281.1	331.4
30 10 39	312.0	247.6
30 10 41	277.8	241.9
30 10 61	247.9	248.6
30 10 73	253.8	261.9
30 10 75	301.2	274.5

general average (µg/L)	289.7
within-sample standard deviation. s_{an}^2	681.2
allowable sampling variance σ_{all}^2	219.1
between-samples standard deviation. s_{sam}^2	927.9
Target standard deviation, $\boldsymbol{\sigma_p}$ Originates: ROBAN sampling-Annex I	49.34
Accepted homogeneity if $s_{sam}^2 \leq c$: critical value for the homogeneity assessment	YES (c=1099.9)

Annex III. Methods used by participants

Method description:

Validated Method	Laboratory code (CER)
NO	12 17 38 46 47 52
YES	01 02 03 04 05 06 07 08 09 10 11 13 14 15 16 18 19 20 21 22 23 24 25 26 27 28 30 31 32 33 34 35 36 37 39 40 41 42 43 44 45 48 49 50 51
Cd migration from ceramics	01 02 03 04 05 06 07 08 09 10 11 13 14 15 16 18 19 20 21 22 23 24 25 26 27 28 30 31 32 33 34 35 36 37 39 40 41 42 43 45 48 49 50 51
Pb migration from ceramics	01 02 03 04 05 06 08 09 10 11 13 14 15 16 18 19 20 21 22 23 24 25 26 27 28 30 31 32 33 34 35 36 37 39 40 41 42 43 45 48 49 50 51
Accredited Method	**Laboratory code (CER)**
NO	05 07 20 21 40 46 47 52
YES	01 02 03 04 06 08 09 10 11 12 13 14 15 16 17 18 19 22 23 24 25 26 27 28 30 31 32 33 34 35 36 37 38 39 41 42 43 44 45 48 49 50 51
Cd migration from ceramics	01 02 03 04 06 08 09 10 11 12 13 14 15 16 17 18 19 22 23 24 25 26 27 28 30 31 32 33 34 35 36 37 38 39 41 42 43 45 48 49 50 51
Pb migration from ceramics	01 02 03 04 06 08 09 10 11 12 13 14 15 16 17 18 19 22 23 24 25 26 27 28 30 31 32 34 35 36 37 38 39 41 42 43 45 48 49 50 51
Reference	**Laboratory code (CER)**
EN ISO/IEC 17025	02 34 48 50
COFRAC no1-0194	03
ISO 6486	04 37 43 49
Directive 1984/500/EEC	06
Directive 2005/31/EC	06
DM-020	08
Belac	09 10 11
Polish Centre for Accreditation	13 30
PCA no AB 515	14
AB 492	15
EN 1388	18 25 32 51
DM01/02/2007 GU N.66	22
Official gazette SFRJ 26/83	24
VMK 052	26
Method based on ISO 13695	27
A2LA	35
AB-539	31
BS 6748	37
FINAS	42
DAkkS	39
METH 12 KE 01	45
Accredia	23
Official Method	
YES	01 02 03 04 05 06 07 09 10 11 12 13 14 15 16 17 18 19 20 21 22 23 25 26 28 30 31 32 33 34 35 36 37 38 39 41 42 43 44 45 46 47 48 50 51 52
NO	24 27 40 49

Please specify	
DM04/04/1985 GU98	01 02 17 19
DM01/02/2007 GU66	01 02 17 22
UNI EN ISO 17294-2:2016	02 38
EN 1388	03 05 13 14 15 16 18 20 21 25 30 31 32 34 35 38 39 44 51
ISO 6486	04 07 12 23 28 41 43
Directive 1984/500/EEC	09 10 11 33 45 47
Japan Food Sanitation Law, Pat 3, Section D-1	36
BS 6748	37
Dir 2005/31/EC	42 47
ISO 7086 & Greek Food Code (art.25)	48 52
Directive 84/500 EEC	45
Directive 2005/32/EC	50

Experimental section:

Extraction solution used	Laboratory code (CER)
Acetic acid 4% v/v	01 02 03 04 05 06 07 08 09 10 11 12 13 14 15 16 17 18 19 20 21 22 23 24 25 26 28 30 31 32 33 34 35 36 37 38 39 40 41 42 43 44 45 47 48 49 50 51 52
3%CH3COOH/3%C4H6O6	27
Time (simulant prep-sample analysis), days	**Laboratory code (CER)**
0, same day	02 03 05 08 13 16 19 27 30 31 33 36 37 42 43
1 day	01 04 06 07 09 12 14 15 17 18 22 23 24 25 28 32 34 35 39 40 45 46 47 48 49 50 51 52
2 days	09 20 21 26 41 44
14 days	10
6 days	38
Temperature, (°C)	**Laboratory code (CER)**
22 ± 2	01 02 03 04 05 06 07 09 10 11 12 13 14 15 16 17 18 19 20 21 22 23 31 32 33 34 36 37 38 41 43 44 45 47 48 49 50 51
22 ± 4	08
20 ± 1	24 26
22 ± 1	25 30
22 ± 0.5	52
20 ± 2	27 28
22	30 39 40
21 ± 2	35 42
20	46
Duration, h	**Laboratory code (CER)**
24h ± 30min	03 11 19 44 45
24h	01 02 04 05 06 07 08 09 10 12 13 14 15 16 17 18 20 21 22 23 24 25 26 27 28 30 31 32 33 34 35 36 37 38 39 40 41 42 43 46 47 48 49 50 51 52
pretreatment	**Laboratory code (CER)**
YES	01 02 03 14 15 17 19 23 25 33 34 35 38 39 40 44 48 50
NO	04 05 06 07 08 09 10 11 12 13 16 18 20 21 22 24 26 27 28 30 31 32 36 37 41 42 43 45 46 47 49 51 52
If YES please specify	**Laboratory code (CER)**
wash with warm water, detergent/distilled water	01 39 40
Washing	02 44

According to EN 1388	03 38
Water/cleaning agent	14 15 19
Surface cleaning	17
Distilled water	25 33 35 50
Washing at 40°C	34 40 48
Cd determination, technique followed	Laboratory code (CER)
AAS-ETA/ GF-AAS	06 22 46 49
FAAS	04 07 12 13 15 24 25 26 30 32 44 48
ICP/OES	01 05 08 10 17 18 19 20 21 27 28 36 37 39 42 45 52
ICP-MS	02 03 09 11 23 33 38 40 43 50
EN-1388	14
AAS	16 31 35 47 51
SAAF	34
Lab_GYE-ME-577, based on ISO 6486-1, 7086-1	41
Pb determination, technique followed	Laboratory code (CER)
AAS-ETA/ GF-AAS	06 07 22 46 49
FAAS	04 12 13 15 24 25 26 30 32 44 48
ICP/OES	01 05 08 10 17 18 19 20 21 27 28 36 37 39 42 45 52
ICP-MS	02 03 09 11 23 33 38 40 43 50
EN-1388	14
AAS	16 31 35 47 51
SAAF	34
Lab_GYE-ME-577, based on ISO 6486-1, 7086-1	41
Cd determination wavelength, nm	Laboratory code (CER)
228.8	04 05 06 07 10 13 14 15 16 17 22 24 25 26 27 28 30 31 32 34 35 36 37 41 44 45 46 47 48 51
214.4	01 18 20 21 39 52
228	12
226.6	08 19 42
Pb determination wavelength, nm	Laboratory code (CER)
283.3	04 06 07 22 26 30 37 41 46 47 51
217	12 13 14 15 16 19 24 25 31 32 34 35 44 48
220.3	01 05 08 10 17 18 20 21 27 28 36 39 42 45 52
Analysis used on a routine basis	Laboratory code (CER)
YES	01 02 03 04 05 06 07 08 09 10 12 13 14 15 16 17 18 19 20 21 22 23 24 25 26 27 28 30 31 32 33 34 35 36 37 38 39 40 41 42 43 45 48 49 50 51
NO	11 46 47 52
Analyzed samples per year	Laboratory code (CER)
0-30	02 04 05 14 22 24 25 26 35 37 40 41 43 48 49 50
30-100	01 06 09 13 15 16 17 19 28 31 33 45
100-250	10 12 18 20 21 27 30 34 39 52
>250	03 07 08 23 32 36 38 42 44 51

Comments

Problems with analysis	Laboratory code (CER)
YES	18

NO	01 02 03 04 05 06 07 09 10 11 12 13 14 15 16 17 19 20 21 22 23 24 25 26 27 28 30 31 32 33 34 35 36 37 38 39 40 41 42 43 44 45 46 47 48 49 50 51 52
Other comments-observations	Laboratory code (CER)
Sample indicated with 'cup C & D' are significantly different from the 'cup A & B'	18

-end of report-