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Report of the sixth interlaboratory comparison organised by the Community Reference Laboratory for Heavy Metals in Feed and Food

Total cadmium, lead, arsenic and mercury in food supplements

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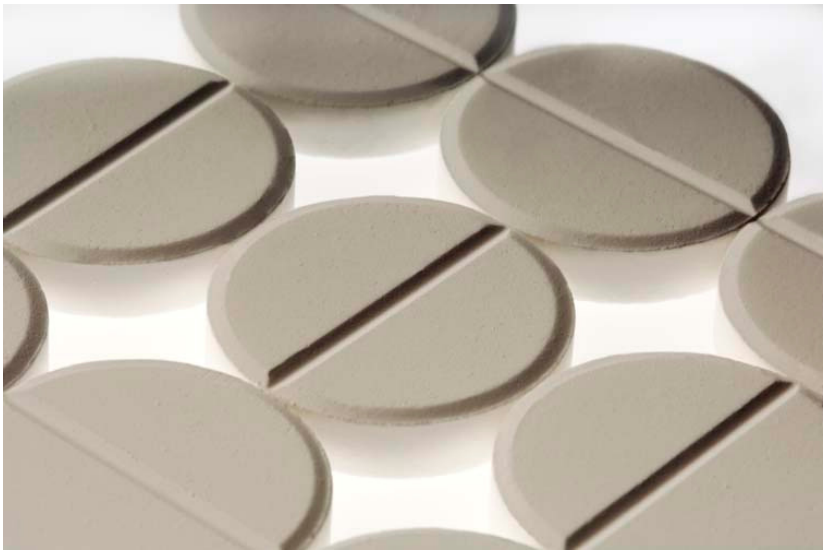

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Heavy Metals
in Feed and Food

Report of the sixth interlaboratory comparison

Total Cd, Pb and As, and Hg in food supplements

IMEP®

September 2009

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Table of contents

1 Summary

The Institute for Reference Materials and Measurements (IRMM) of the Joint Research Centre (JRC), a Directorate-General of the European Commission, operates the Community Reference Laboratory for Heavy Metals in Feed and Food (CRL-HM). One of its core tasks is to organise interlaboratory comparisons (ILCs) among appointed National Reference Laboratories (NRLs). This report presents the results of the sixth ILC of the CRL-HM which focused on the determination of total Cd, Pb, As and Hg, (related to dry mass) in food supplements.

The test material used in this exercise was the candidate standard reference material (SRM) SRM 3256, of the National Institute of Standards and Technology (NIST), the matrix being a green tea food supplement. The material was labeled at IRMM and dispatched to the participants the first week of June 2009. Each participant received two sachets containing approximately 2.5 g of test material each. Thirty-three participants from twenty-five countries registered to the exercise of which 32 sets of results were reported for total Cd and for total Pb, and 29 for total As and for total Hg. One laboratory reported two sets of values for total Cd, Pb, As and Hg obtained with two different techniques, respectively. The assigned values were the reference values as provided by NIST.

The uncertainties of the respective assigned values, u_{ref}, were also provided by NIST. Participants were invited to report the uncertainty on their measurements. This was done by the majority of laboratories taking part in this exercise.

Laboratory results were rated with z and zeta scores in accordance with ISO 13528[1]. Standard deviation for proficiency assessment (also called target standard deviation) was fixed to 15 % for total Cd, Pb and As by the advisory board of this ILC, on the basis of the outcome of previous ILC's organised by the CRL-HM for the same population. For total Hg the standard deviation for proficiency assessment was set to 22 % as derived by the modified Horwitz equation[2].

2 Introduction

According to Directive 2002/46/EC of the European Parliament and of the Council on the approximation of the laws of the Member States relating to food supplements, *"Food supplements means foodstuffs the purpose of which is to supplement the normal diet and which are concentrated sources of nutrients or other substances with a nutritional or physiological effect alone or in combination, marketed in dose form, namely forms such as capsules, pastilles, tablets, pills and other similar forms, sachets of powder, ampoules of liquids, drop dispensing bottles and other similar forms of liquids and powders designed to be taken in measured small unit quantities"*.

High levels of Pb, Cd and Hg have been found in certain food supplements and were notified through the Rapid Alert System for Food and Feed (RASFF). It has been shown that these food supplements can contribute significantly to human exposure to the mentioned metals. In order to protect public health, it was therefore considered appropriate to set maximum levels for Pb, Cd and Hg in the legislation. Maximum levels for Pb, Cd and Hg in food supplements have been introduced by Regulation (EC) No. 629/2008 of 2 July 2008 and are applicable since 1 July 2009. These maximum levels are the following: lead: 3.0 mg/kg for all food

supplements, cadmium: 1.0 mg/kg for all food supplements excluding supplements consisting exclusively or mainly of dried seaweed or of products derived from seaweed, for which a maximum level of 3.0 mg/kg applies. Mercury: 0.1 mg/kg for all food supplements. Some laboratories have also found As in food supplements at the level of several mg kg^{-1} (unpublished results). High levels of arsenic are frequently found in different food supplements and have been subject to Raid Alert Notifications in recent years. Products often notified are clays, mineral drinks, products on basis of seaweed and ayurvedic food supplements.

The Community Reference laboratory for Heavy Metals in Feed and Food has organised a proficiency test (PT) exercise for the network of appointed National Reference Laboratories (NRLs) to determine the total Cd, Pb, As and Hg in food supplements.

3 Scope

As stated in Regulation 882/2004 of the European Parliament and of the Council[3], one of the core duties of the CRL-HM is to organise interlaboratory comparisons for the benefit of staff from National Reference Laboratories. The scope of this ILC is to test the competence of the appointed NRLs to determine the total concentration of Cd, Pb, As and Hg in food supplements.

The assessment of the measurements results is undertaken on the basis of requirements laid down in legislation[4],[5] and follows the administrative and logistics procedures of IMEP, the International Measurement and Evaluation Programme, of IRMM. This programme is accredited according to ISO Guide 43-1. The designation of this ILC is IMEP-106.

4 Time frame

This interlaboratory comparison was agreed upon by the NRLs network at the third CRL-HM workshop held on 25-26 September 2008. Invitation letters were sent to the participants on 30th April 2009 (cf Annex 1). The samples were dispatched to the participants on 2nd June 2009. Reporting deadline was 3rd July 2009.

5 Material

5.1 Preparation

Processing of the test material used in this exercise was made by NIST. SRM 3256 is a blend of 4 different green tea-containing formulations obtained from commercial sources. The tablets were ground and capsules were opened, then the materials were sieved, and blended prior to packaging. The material was packed in portions of 2.6 g ± 0.1 g in heat-sealed 4 mil polyethylene bags. These bags were heat sealed in aluminized plastic bags along with 2 packs of silica gel.

NIST dispatched 386 sachets at room temperature by courier to IRMM.

5.2 Homogeneity and stability

The homogeneity tests were conducted by NIST. No short term stability test was performed because according to the experience of the SRM producer the measurands covered in this exercise are stable at room temperature in this type of matrix.

5.3 Distribution

The samples were dispatched to the participants by IRMM on 2nd June 2009. Each participant received: a) two sachets containing approximately 2.5 g of test material each, b) an accompanying letter with instructions on sample handling and reporting (cf. Annex 2) and c) a form that had to be sent after receipt of the test material to confirm its arrival (cf. Annex 3).

6 Instructions to participants

Details on this intercomparison were discussed with the NRLs at the third workshop organised by the CRL-HM, held in Geel on 25-26 September 2008. Concrete instructions were given to all participants in a letter that accompanied the test material. The measurands and matrix were defined as "total Cd, Pb, As and Hg in food supplements".

Laboratories were asked to perform two or three independent measurements and report them, together with the mean of the results and its associated uncertainties. The measurement results were to be corrected for moisture (following a procedure described in the accompanying letter which had been optimised at IRMM by the Reference Materials Unit) and recovery. Participants were asked to follow their routine procedures. The results were to be reported in the same manner (eg. number of significant figures) as those normally reported to the customer.

The results were to be reported in a special on-line form for which each participant received an individual access code. A specific questionnaire was attached to this on-line form. The questionnaire was intended to provide further information on the measurements and the laboratories. A copy of the questionnaire is presented in Annex 4.

7 Reference values and their uncertainties

NIST provided reference values for all the measurands included in this study. Certification of SRM 3526 was carried out in the same period of time that IMEP-106 was organised and conducted. The reference values as provided by NIST, obtained by inductively coupled plasma-mass spectrometry (ICP-MS) were used as assigned values (X_{ref}) for this ILC.

The uncertainty in the reference concentration values is expressed as an expanded uncertainty, U, and is calculated according to the method described in the ISO Guide 35. The expanded uncertainty is calculated as $U = ku_c$, where u_c is intended to represent, at the level of one standard deviation, the effect of within-laboratory components of uncertainty. The uncertainty for mercury incorporates an inhomogeneity component and is in the form of a prediction interval. The coverage factor, k, is determined from the Student's t-distribution corresponding to the appropriate associated degrees of freedom and 95 % confidence for each analyte.

The assigned values and their respective estimated uncertainties, expanded and not expanded, the degrees of freedom (df) and the expansion factors, are summarised in Table 1.

Table 1: Assigned values and their associated standard and associated uncertainties for the measurands of this ILC as provided by NIST, degrees of freedom and expansion factors.

Measurand	X_{ref} (mg kg $^{-1}$)	U_{ref} (mg kg^{-1})	df	*k*	u_{ref} (mg kg^{-1})
Total Cd	0.0264	0.0012	5.07	2.56	0.0005
Total Pb	0.314	0.069	5	2.57	0.027
Total As	0.278	0.022	5.02	2.57	0.009
Total Hg	0.0129	0.0026	6.6	2.39	0.0011

X_{ref} is the reference value and u_{ref} is the corresponding associated standard uncertainty; U_{ref} is the estimated associated expanded uncertainty; with a coverage factor k, corresponding to a level of confidence of about 95 %.

8 Evaluation of results

8.1 General observations

Thirty-three participants from 25 countries registered to this exercise of which 32 sets of results were reported for Cd (4 out of the 32 reported "less than") and for Pb (2 out of the 32 reported "less than"), and 29 for total As (1 out of the 20 reported "less than") and for Hg (7 out of the 29 reported "less than"). All the laboratories that submitted results reported uncertainties for total Cd and for total Pb, while for As and Hg uncertainties were submitted by all participants but one.

8.2 Scores and evaluation criteria

Individual laboratory performance is expressed in terms of z and zeta scores in accordance with ISO 13528[6] and the International Harmonised Protocol[7].

$$z = \frac{x_{lab} - X_{ref}}{\hat{\sigma}} \qquad \text{Eq. 2}$$

$$zeta = \frac{x_{lab} - X_{ref}}{\sqrt{u^2_{ref} + u^2_{lab}}} \qquad \text{Eq. 3}$$

where:

x_{lab} is the measurement result reported by a participant
X_{ref} is the reference reference value (assigned value)
u_{ref} is the standard uncertainty of the reference value
u_{lab} is the standard uncertainty reported by a participant
$\hat{\sigma}$ is the standard deviation for proficiency assessment

The z score compares the participant's deviation from the reference value with the standard deviation accepted for the proficiency test, $\hat{\sigma}$. In this exercise $\hat{\sigma}$ was fixed to 15 % for total Cd, Pb and As by the advisory board of this ILC, on the basis of the outcome of previous ILC's organised by the CRL-HM for the same population. For Hg the standard deviation accepted for the PT was 22 %, as derived from the Horwtiz equation, due to the low concentration of Hg in the test material.

Should participants feel that these $\hat{\sigma}$ values are not fit for their purpose they can recalculate their scorings with a standard deviation matching their requirements. x_{lab} is the mean of the individual measurement results calculated by the ILC organiser. If sigma-hat is regarded as satisfactory, the z-score can be interpreted as:

$\|z\| \leq 2$	satisfactory result
$2 < \|z\| \leq 3$	questionable result
$\|z\| > 3$	unsatisfactory result

The zeta score states if the laboratory result agrees with the assigned value within the respective uncertainties. The interpretation of the zeta score is similar to the interpretation of the z-score:

$\|zeta\| \leq 2$	satisfactory result
$2 < \|zeta\| \leq 3$	questionable result
$\|zeta\| > 3$	unsatisfactory result

An unsatisfactory zeta-score might be due to an underestimation of the uncertainty, or to a large error causing a large deviation from the reference value, or to a combination of the two factors. A laboratory with an unsatisfactory zeta-score has an estimation of the uncertainty of its measurements which is not consistent with the laboratory's deviation from the reference value.

The standard uncertainty of the laboratory (u_{lab}) was calculated by dividing the reported expanded uncertainty by the reported coverage factor (k). When k was not specified, the reported expanded uncertainty was considered as the half-width of a rectangular distribution; u_{lab} was then calculated by dividing this half-width by $\sqrt{3}$, as recommended by Eurachem and CITAC[8]. When a laboratory did not report any uncertainty, u_{lab} was set to zero.

8.3 Laboratory results and scorings

The results as reported by the participants are summarised in Table 2 a-d for total Cd, total Pb, total As and total Hg, respectively, together with the z- and zeta scores. Laboratory codes were given randomly.

Three sets of figures are provided for Cd, Pb, As and Hg (Figure 1-4). Each set includes (a) the Kernel density plot, (b) the individual mean value and associated expanded uncertainty, (c) the z- and zeta scores. The solid line represents the assigned value, the dashed lines delimit the reference interval ($X_{ref} \pm 2\ u_{ref}$) and the dotted lines delimit the target interval ($X_{ref} \pm 2\ \hat{\sigma}$). The Kernel plots were obtained using a software tool developed by AMC[9].

Regarding the z and zeta scores, the results for total Cd, Pb, As and Hg are summarised in Table 3. In general, the laboratories participating in this exercise performed well when taking into consideration the z score. For all measurands, with the exception of Hg, between 70 and 80 % of the laboratories obtained a satisfactory z score.

As indicated by the z-score, about 50 % of the participants seem to have problems in the estimation of their uncertainties. For Pb 90 % of the participants obtained a satisfactory zeta-score because the u_{ref} provided by NIST is larger than the u_{ref} for Cd, As and Hg. For Hg most results with $|z| \leq 2$ also have a $|zeta| \leq 2$. In the same way a high percentage of the results with an unsatisfactory zeta score also have an unsatisfactory z score. This is not the case for Cd and As, in which several laboratories obtained a satisfactory z score and an unsatisfactory zeta score. However, as can be seen in Figure 4a, a group of laboratories reported results for Hg which are positively biased, probably due to a contamination problem, to the presence of interferences or to problems in calibration at low concentrations.

No scorings z or zeta were given to L08 for total Cd, Pb and As because apparently the results were reported with the wrong unit.

Additional information was gathered from the questionnaire that participants were asked to fill in (Annex 4). For uncertainty estimates, various combinations of one or more options (question 3 of the questionnaire shown in Annex 4) were given. Fourteen laboratories use the uncertainty as calculated during the in-house validation of the method, eleven laboratories use the uncertainty obtained by measuring replicates (i.e. precision). Six laboratories made use of intercomparison data. Three participants applied the ISO-GUM. Two laboratories used the known uncertainty of the standard method and one used the expert guesstimate (which corresponds to "estimation based on judgment", as defined in the Eurachem/CITAC guide on Quantifying Uncertainty in Analytical Measurements[8]). One laboratory calculated the uncertainty according to ISO 5725 and another one used the expanded uncertainty following Regulation (EC) No 333/2007. Nineteen laboratories provide an uncertainty statement to their customers and thirteen do not.

All participants but two corrected their results for the water content. One of the two had dried the sample before the analysis. The way in which the moisture content of the test material was to be calculated was described in detail in the accompanying letter.

Nineteen laboratories analysed the test material following an official method. One participant did not answer to this question. The information reported by the remaining laboratories about their method of analysis is summarised in Annex 5.

Twenty-eight participants carry out this type of analysis (as regards the measurands, matrix and methods) on a routine basis, four do not and one did not answer this question.

All participants but one have a quality system in place, based on ISO 17025. Seven laboratories are not accredited for the determination of Cd, six for the determination of Pb, eleven for the determination of As (two did not provide information about their accreditation status regarding As determination), and six for the determination of Hg.

Twenty-eight laboratories participate regularly in ILC's for this type of analysis, five do not. This question might have been misinterpreted because four out of the five answering

No, have been participating since 2006, at least once per year (and in some cases twice per year) in the PT's organised by the CRL-HM.

Twenty-eight participants use a reference material for this type of analysis: twenty-five use it for the validation procedure and eight for calibration of the instrument.

The comments made by the participants are summarised in Table 4. As it can be seen, several laboratories indicated that the amount of test material distributed was too small. According to the International Harmonised Protocol for Proficiency Testing of Analytical Chemistry Laboratories[7] *"The quantity of material in a distribution unit must be sufficient for the analysis required, including any reanalysis where permitted by the scheme protocol"*. In the case of IMEP-106 the material was distributed as produced by the SRM producer in sachets containing about 2.5 g of test material. Being aware that this amount was not enough for the 2 to 3 replicates required plus the material needed for the moisture content determination (1.5 g in total), two sachets were sent to every participant. Every participant received then around 5 g of test material which was enough for three replicates (assuming an average sample intake for every replicate of 0.5 g) and the moisture determination. About 2 g would still remain for further replicates in case accidental spillage occur. Furthermore, extra material was sent to the participants when requested if a reasonable justification was given, for instance laboratories that used dry ashing for sample digestion used aliquots of 5 to 10 g for every replicate.

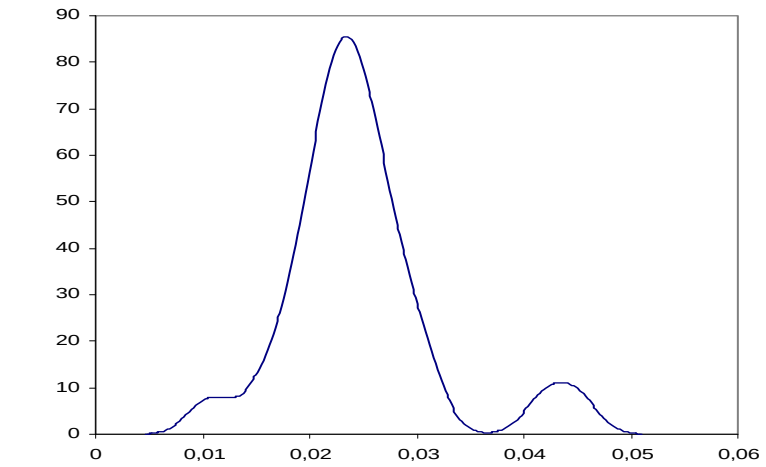


Figure 1a
Total Cd in food supplements
Kernel density,
all results

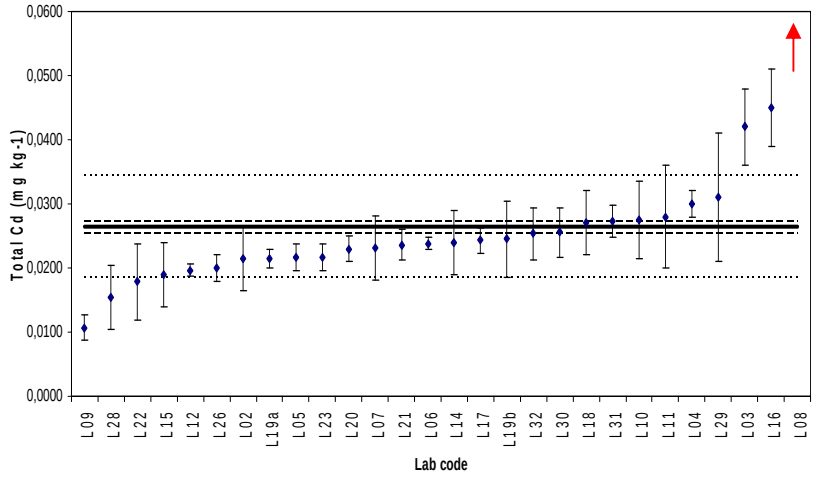


Figure 1b
Reported results and corresponding expanded uncertainties

X_{ref} = 0.0264
u_{ref} = 0.0005
$\hat{\sigma}$ = 0.0039 (15 %)
in mg kg^{-1}

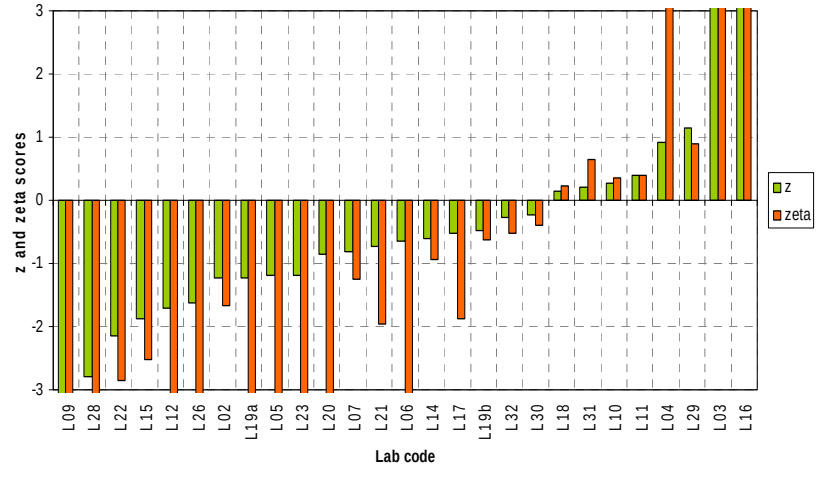


Figure 1c
Performance evaluation
$z = (x_{lab}-X_{ref})/ \hat{\sigma}$
$zeta = (x_{lab}-X_{ref})/ \sqrt{(u_{lab}^2+u_{ref}^2)}$

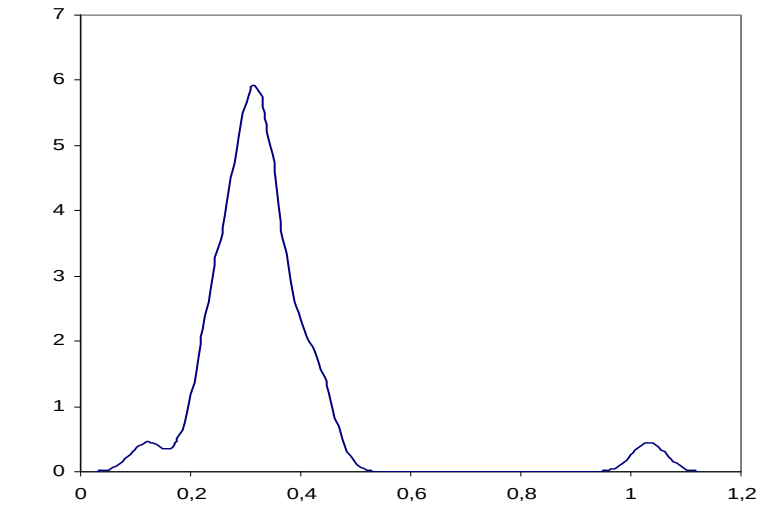


Figure 2a
Total Pb in food supplements
Kernel density,
all results

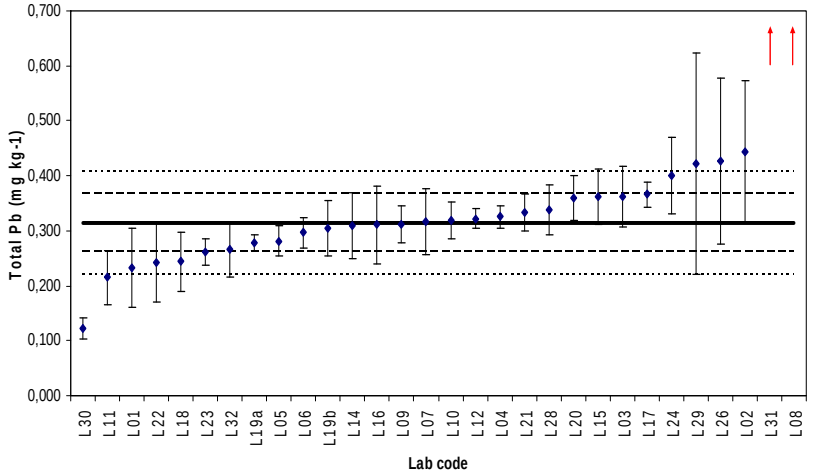


Figure 2b
Reported results and corresponding expanded uncertainties

$X_{ref} = 0.314$
$u_{ref} = 0.027$
$\hat{\sigma} = 0.047$ (15 %)
in mg kg^{-1}

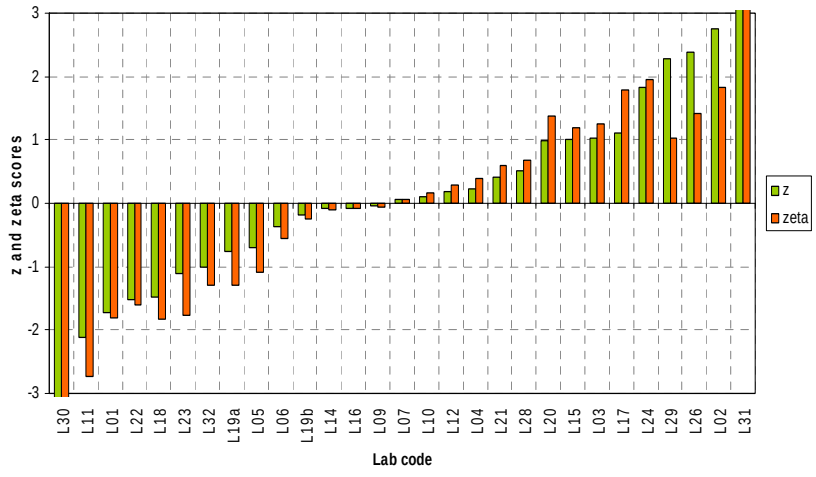


Figure 2c
Performance evaluation
$z = (x_{lab}-X_{ref})/ \hat{\sigma}$
$zeta = (x_{lab}-X_{ref})/ \sqrt{(u_{lab}^2+u_{ref}^2)}$

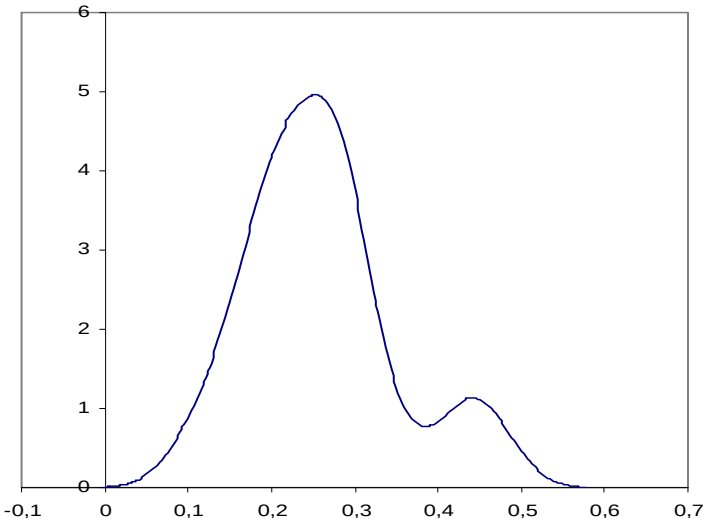


Figure 3a
Total As in food supplements
Kernel density,
all results

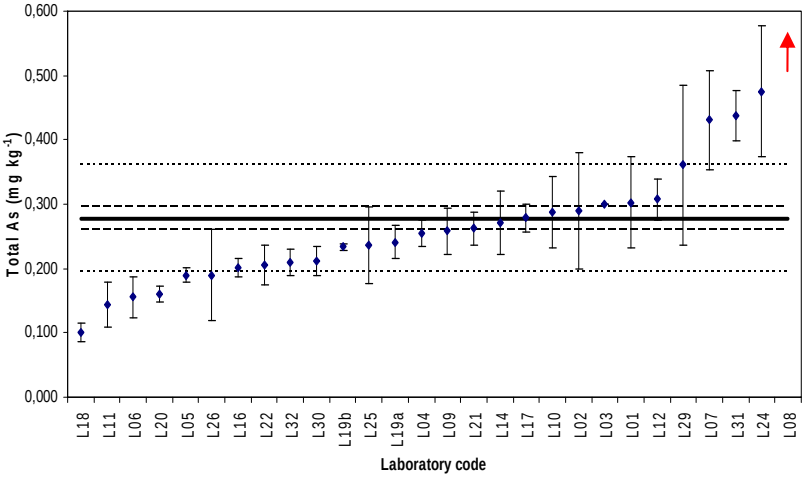


Figure 3b
Reported results and corresponding expanded uncertainties

$X_{ref} = 0.278$
$u_{ref} = 0.009$
$\hat{\sigma} = 0.042$ (15 %)
in mg kg^{-1}

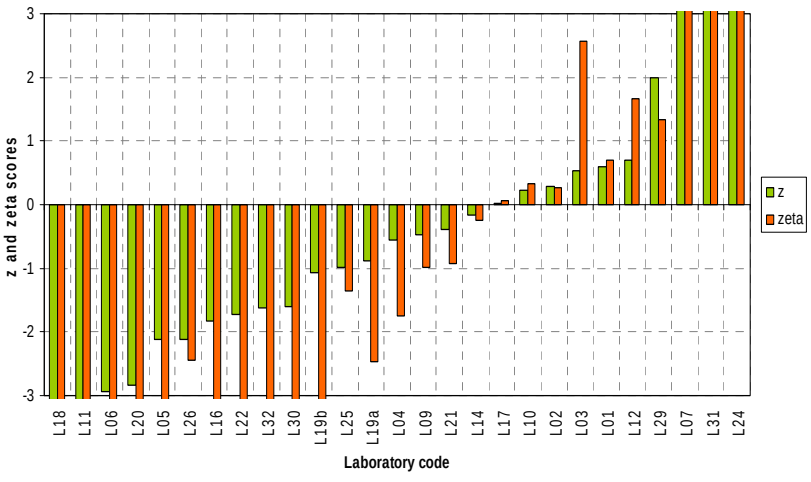


Figure 3c
Performance evaluation
$z = (x_{lab}-X_{ref})/ \hat{\sigma}$
$zeta = (x_{lab}-X_{ref})/ \sqrt{(u_{lab}^2+u_{ref}^2)}$

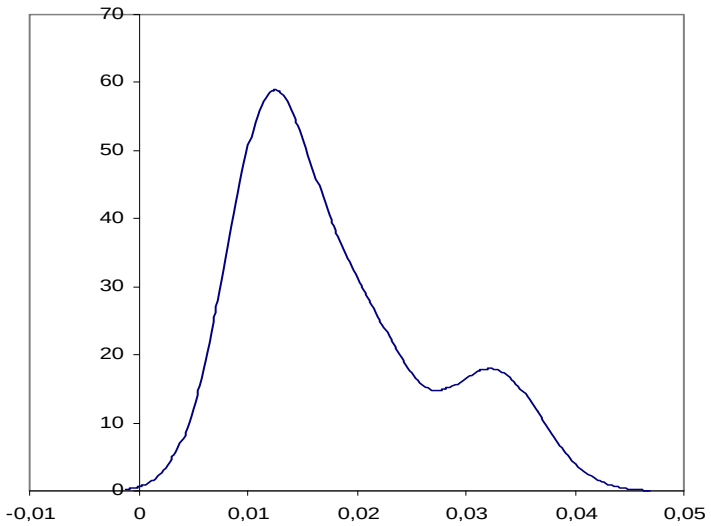


Figure 4a
Total Hg in food supplements
Kernel density,
all results

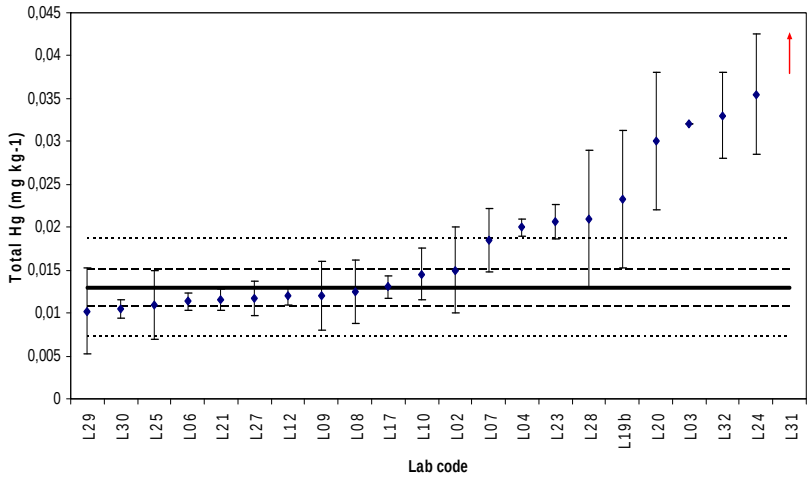


Figure 4b
Reported results and corresponding expanded uncertainties

$X_{ref} = 0.0129$
$u_{ref} = 0.0011$
$\hat{\sigma} = 0.0028$ (22 %)
in mg kg^{-1}

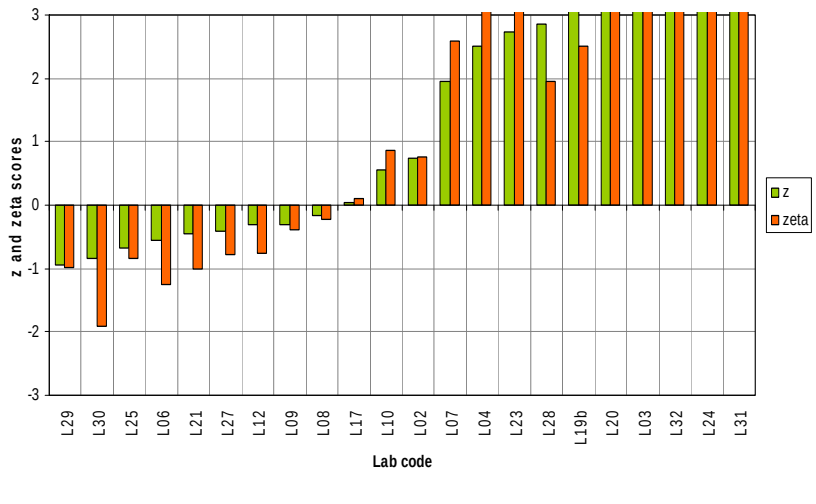


Figure 4c
Performance evaluation
$z = (x_{lab}-X_{ref})/ \hat{\sigma}$
$zeta = (x_{lab}-X_{ref})/ \sqrt{(u_{lab}^2+u_{ref}^2)}$

Table 2a: Total Cd, quantitative information reported by the participants and laboratory scorings provided by the organiser.

Total Cd content: 0.0264 ± 0.0012 mg kg^{-1}

Lab code	x1	x2	x3	x4	Ulab	*k*	Mean-calc	Technique	z	zeta
L01	<0,05	<0,05					<0,05	ICP-MS		
L02	0,023	0,020			0,005	**a**	0,022	ET-AAS	-1,2	-1,7
L03	0,048	0,036			0,006	2	0,042	ET-AAS	3,9	5,1
L04	0,030	0,030			0,002	2	0,030	ICP-MS	0,9	3,3
L05	0,022	0,023	0,020		0,002	2	0,022	ICP-MS	-1,2	-4,3
L06	0,0235	0,0242			0,0010	**a**	0,0239	ET-AAS	-0,6	-3,4
L07	0,0236	0,0228			0,0050	2	0,0232	ET-AAS	-0,8	-1,3
L08	17,4	11,6	14,6	13,5	4,29	2	14,3	ET-AAS		
L09	0,01096	0,0097	0,0113		0,002	2	0,0107	ICP-MS	-4,0	-14,3
L10	0,027	0,028			0,006	2	0,028	ICP-MS	0,3	0,4
L11	0,030	0,026			0,008	2	0,028	ET-AAS	0,4	0,4
L12	0,019	0,021	0,019		0,001	2	0,020	ICP-MS	-1,7	-9,8
L13	<0,25	<0,25	<0,25	0,25			<0,25	ZET-AAS		
L14	0,024	0,024			0,005	2	0,024	ICP-MS	-0,6	-0,9
L15	0,018	0,022	0,017		0,005	**a**	0,019	ET-AAS	-1,9	-2,5
L16	0,046	0,044			0,006	2	0,045	ICP-MS	4,7	6,1
L17	0,024	0,024	0,025		0,002	2	0,024	ICP-MS	-0,5	-1,9
L18	0,031	0,027	0,023		0,005	2	0,027	ET-AAS	0,2	0,2
L19a	0,0215				0,0014	2,2	0,0215	ICP-MS	-1,2	-6,2
L19b	0,024	0,025			0,006	2	0,025	FAAS	-0,5	-0,6
L20	0,023	0,023			0,002	2	0,023	ET-AAS	-0,9	-3,1
L21	0,0231	0,0240			0,0024	**a**	0,0236	ICP-MS	-0,7	-1,9
L22	0,0185	0,0182	0,0169		0,00589	2	0,0179	ICP-MS	-2,2	-2,9
L23	0,022	0,021	0,022		0,002	2	0,022	AAS	-1,2	-4,3
L24	<0,025	<0,025					<0,025	ICP-MS		
L25	<0,025	<0,025	<0,025				<0,025	ET-AAS		
L26	0,02	0,02	0,02		0,002	2	0,02	ET-AAS	-1,6	-5,8

Lab code	x1	x2	x3	x4	Ulab	*k*	Mean-calc	Technique	z	zeta
L28	0,015	0,016	0,015		0,005	2	0,015	ET-AAS	-2,8	-4,4
L29	0,0310	0,0312	0,0305	0,0311	0,010	2	0,0310	ICP-MS	1,1	0,9
L30	0,0263	0,0244	0,0259		0,0038	**a**	0,02553	ICP-MS	-0,2	-0,4
L31	0,029	0,027	0,028	0,025	0,0025	2	0,027	ET-AAS	0,2	0,6
L32	0,022	0,028	0,026		0,004	2	0,025	ET-AAS	-0,3	-0,5

All results expressed in mg kg-1

a) k not reported; k= √3

Satisfactory

Questionable

Unsatisfactory

Table 2b: Total Pb, quantitative information reported by the participants and laboratory scorings provided by the organiser.

Total Pb content: 0.314 ± 0.069 mg kg^{-1}

Lab code	x1	x2	x3	x4	Ulab	*k*	Mean-calc	Technique	z	zeta
L01	0,231	0,235			0,072	2	0,233	ICP-MS	-1,7	-1,8
L02	0,42	0,43	0,48		0,13	2	0,44	ET-AAS	2,7	1,8
L03	0,382	0,342			0,054	2	0,362	ET-AAS	1,0	1,3
L04	0,34	0,31			0,02	2	0,33	ICP-MS	0,2	0,4
L05	0,279	0,283	0,281		0,028	2	0,281	ICP-MS	-0,7	-1,1
L06	0,306	0,287			0,027	**a**	0,297	ET-AAS	-0,4	-0,6
L07	0,308	0,325			0,060	2	0,317	ET-AAS	0,1	0,1
L08	225	216	249	213	67,7	2	226	ET-AAS		
L09	0,316	0,323	0,298		0,034	2	0,312	ICP-MS	0,0	-0,1
L10	0,323	0,315			0,034	2	0,319	ICP-MS	0,1	0,2
L11	0,153	0,242	0,249		0,049	2	0,215	ET-AAS	-2,1	-2,7
L12	0,294	0,346	0,327		0.019	2	0,322	ICP-MS	0,2	0,3
L13	<1,8	<1,8	<1,8	<1,8				ZET-AAS		
L14	0,308	0,312			0,060	2	0,310	ICP-MS	-0,1	-0,1
L15	0,385	0,335	0,364		0,050	**a**	0,361	ET-AAS	1,0	1,2
L16	0,320	0,301			0,07	2	0,31	ICP-MS	-0,1	-0,1
L17	0,345	0,384	0,369		0,022	2	0,366	ICP-MS	1,1	1,8
L18	0,263	0,247	0,222		0,054	2	0,244	ET-AAS	-1,5	-1,8
L19a	0,278				0,014	2,1	0,278	ICP-MS	-0,8	-1,3
L19b	0,29	0,32			0,05	2	0,31	FAAS	-0,2	-0,2
L20	0,34	0,38			0,04	2	0,36	ET-AAS	1,0	1,4
L21	0,340	0,327			0,033	**a**	0,334	ICP-MS	0,4	0,6
L22	0,222	0,254	0,250		0,0727	2	0,242	ICP-MS	-1,5	-1,6
L23	0,264	0,272	0,250		0,024	2	0,262	AAS	-1,1	-1,8
L24	0,41	0,39			0,070	2	0,40	ICP-MS	1,8	1,9
L25	<0,25	<0,25	<0,25					ET-AAS		
L26	0,36	0,50	0,42		0,15	2	0,43	ET-AAS	2,4	1,4

Lab code	x1	x2	x3	x4	Ulab	*k*	Mean-calc	Technique	z	zeta
L28	0,344	0,344	0,327		0,046	2	0,338	ET-AAS	0,5	0,7
L29	0,407	0,437	0,420		0,201	2	0,421	ICP-MS	2,3	1,0
L30	0,125	0,117	0,122		0,0194	**a**	0,121	ICP-MS	-4,1	-6,6
L31	0,994	1,170	1,020	0,948	0,14	2	1,033	ET-AAS	15,3	9,6
L32	0,27	0,25	0,28		0,05	2	0,27	ET-AAS	-1,0	-1,3

All results expressed in mg kg-1

a) k not reported; k= √3

Satisfactory

Questionable

Unsatisfactory

Table 2c: Total As, quantitative information reported by the participants and laboratory scorings provided by the organiser.

Total As content: 0.278 ± 0.022 mg kg^{-1}

Lab code	x1	x2	x3	x4	Ulab	*k*	Mean-calc	Technique	z	zeta
L01	0,286	0,320			0,070	2	0,3030	ICP-MS	0,6	0,7
L02	0,28	0,30			0,09	2	0,29	ET-AAS	0,3	0,3
L03	0,29	0,31			0	**a**	0,30	ET-AAS	0,5	2,6
L04	0,25	0,26			0,02	2	0,26	ICP-MS	-0,6	-1,7
L05	0,192	0,188			0,012	2	0,190	HG-AAS	-2,1	-8,4
L06	0,144	0,167			0,032	**a**	0,156	ET-AAS	-2,9	-6,0
L07	0,415	0,446			0,078	2	0,431	HG-AAS	3,7	3,8
L08	1824	1708	1704	1836	530	2	1768	ET-AAS		
L09	0,262	0,259	0,254		0,036	2	0,258	ICP-MS	-0,5	-1,0
L10	0,292	0,283			0,056	2	0,288	ICP-MS	0,2	0,3
L11	0,168	0,148	0,113		0,035	2	0,143	ET-AAS	-3,2	-6,9
L12	0,296	0,297	0,329		0,031	2	0,307	ICP-MS	0,7	1,7
L13	<0,85	<0,85	<0,85	<0,85				ZET-AAS		
L14	0,269	0,274			0,050	2	0,272	ICP-MS	-0,2	-0,2
L16	0,197	0,207			0,014	2	0,20	ICP-MS	-1,8	-6,9
L17	0,270	0,293	0,274		0,022	2	0,279	ICP-MS	0,0	0,1
L18	0,119	0,101	0,081		0,015	2	0,100	ET-AAS	-4,3	-15,6
L19a	0,241				0,026	2,1	0,241	ICP-MS	-0,9	-2,5
L19b	0,227	0,237	0,236		0,006	2	0,233	HG-AAS	-1,1	-4,9
L20	0,18	0,14			0,012	2	0,16	HG-AAS	-2,8	-11,3
L21	0,266	0,258			0,026	**a**	0,262	ICP-MS	-0,4	-0,9
L22	0,211	0,204	0,204		0,0309	2	0,206	ICP-MS	-1,7	-4,1
L24	0,47	0,48			0,102	2	0,48	ICP-MS	4,7	3,8
L25	0,235	0,238			0,059	2	0,237	HG-AAS	-1,0	-1,4
L26	0,21	0,18	0,18		0,07	2	0,19	HG-AAS	-2,1	-2,4
L29	0,370	0,357	0,356		0,124	2	0,361	ICP-MS	2,0	1,3
L30	0,208	0,212	0,214		0,023	**a**	0,211	ICP-MS	-1,6	-4,2

Lab code	x1	x2	x3	x4	Ulab	*k*	Mean-calc	Technique	z	zeta
L31	0,435	0,44	0,464	0,408	0,039	2	0,437	HG-AAS	3,8	7,5
L32	0,19	0,21	0,23		0,02	2	0,21	HG-AAS	-1,6	-5,2

All results expressed in mg kg-1

a) k not reported; k= √3

Satisfactory

Questionable

Unsatisfactory

Table 2d: Total Hg, quantitative information reported by the participants and laboratory scorings provided by the organiser.

Total Hg content: 0.0129 ± 0.0026 mg kg^{-1}

Lab code	x1	x2	x3	x4	Ulab	*k*	Mean-calc	Technique	z	zeta
L01	<0,05	<0,05	<0,05					ICP-MS		
L02	0,013	0,016	0,016		0,005	2	0,015	Atomic fluorescence	0,7	0,8
L03	0,041	0,023			0	**a**	0,032	CV-AAS	6,7	17,6
L04	0,018	0,022			0,001	2	0,020	ICP-MS	2,5	5,9
L05	<0,01	<0,01	<0,01	<0,01				ICP-MS		
L06	0,0110	0,0117			0,0010	**a**	0,0114	CV-AAS	-0,5	-1,3
L07	0,0199	0,0170			0,0037	2	0,0185	CV-AFS	2,0	2,6
L08	0,0176	0,0122	0,01	0,0099	0,0037	2	0,0124	AA by amalgamation	-0,2	-0,2
L09	0,0119	0,0138	0,0103		0,004	2	0,0120	AMA	-0,3	-0,4
L10	0,016	0,013			0,003	2	0,015	ICP-MS	0,6	0,9
L12	0,012	0,012	0,012	0,012	0,001	2	0,012	AMA-254	-0,3	-0,8
L13	<0,034	<0,034	<0,034	<0,034				TDA-AAS		
L16	<0,1	<0,1						ICP-MS		
L17	0,0134	0,0122	0,0135		0,0013	2	0,0130	CV-AAS	0,0	0,1
L18	<0,01	<0,01	<0,01	<0,01				CV-AAS		
L19b	0,022	0,028	0,021	0,022	0,008	2	0,023	CV-AAS	3,6	2,5
L20	0,03	0,03			0,008	**a**	0,03	CV	6,0	3,6
L21	0,0118	0,0114			0,0012	**a**	0,0116	CV-AAS	-0,5	-1,0
L22	<0,04	<0,04	<0,04	<0,04			<0,04	ICP-MS		
L23	0,020	0,021	0,021		0,002	2	0,021	HG-AAS	2,7	5,3
L24	0,036	0,035			0,007	2	0,036	ICP-MS	8,0	6,2
L25	0,009	0,01	0,014		0,004	2	0,011	Automated mercury analyser	-0,7	-0,8
L26	<0,1	<0,1	<0,1					CV-AAS		

Lab code	x1	x2	x3	x4	Ulab	*k*	Mean-calc	Technique	z	zeta
L27	0,012	0,012	0,011	0,012	0,002	2	0,012	TDA-AAS	-0,4	-0,8
L28	0,021	0,019	0,023		0,008	2	0,021	CV-AAS	2,9	2,0
L29	0,0102	0,0102	0,0102		0,005	2	0,0102	AMA	-1,0	-1,0
L30	0,0103	0,0108	0,0104		0,00109	**a**	0,0105	AMA	-0,8	-1,9
L31	0,318	0,255	0,270	0,265	0,041	2	0,277	CV-AAS	93,1	12,9
L32	0,030	0,034	0,035		0,005	2	0,033	CV-AAS	7,1	7,4

All results expressed in mg kg-1

a) k not reported; k= √3

Satisfactory

Questionable

Unsatisfactory

Table 3: Number and percentage of laboratories reporting results not *"< than"* with satisfactory, questionable and unsatisfactory scores.

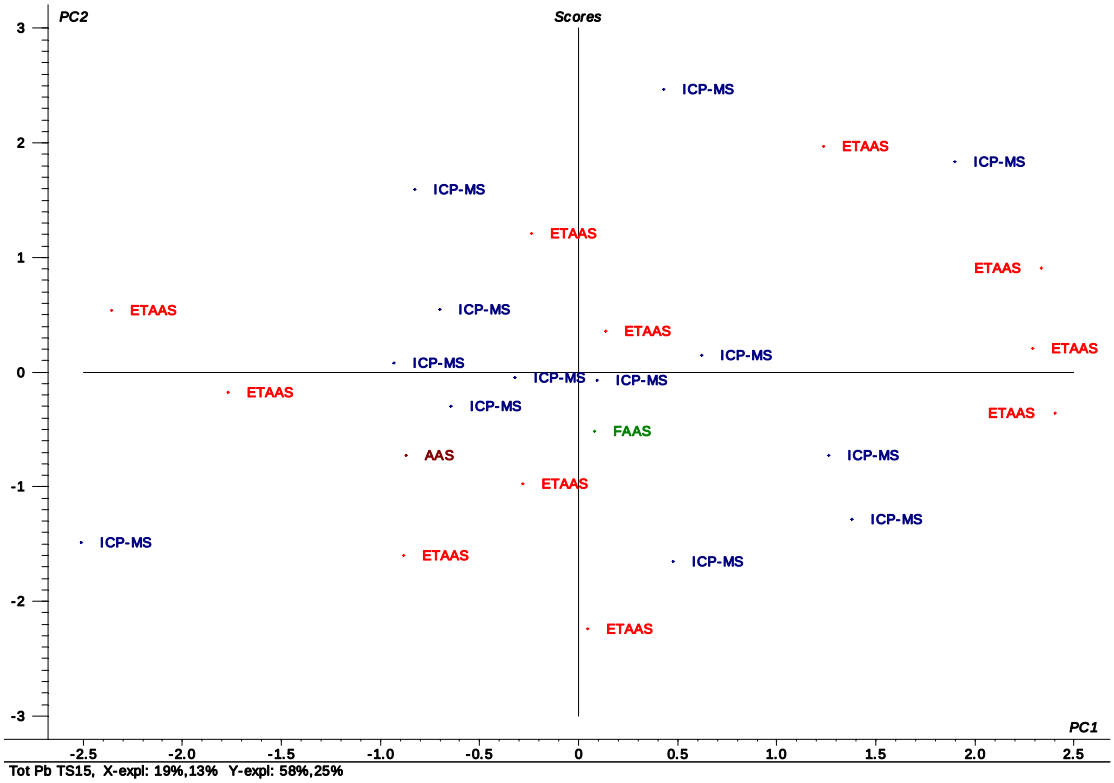
	Total Cd		Total Pb		Total As		Total Hg	
	Num. Labs.	%	Num. Labs.	%	Num. Labs.	%	Num. Labs.	%
z								
Satisf.	22	82	23	79	18	67	13	59
Quest.	2	7	4	14	4	15	3	14
Unsatisf.	3	11	2	7	5	18	6	27
zeta								
Satisf.	13	48	26	90	11	40	13	59
Quest.	1	4	1	3	3	11	2	9
Unsatisf.	13	48	2	7	13	48	7	32

Table 4: Comments submitted by the participants to this exercise.

Lab code	Comments
L09	We are accredited for the analysis of Cd, Pb and Hg but not in food supplements
L10	It would be easier if the test boxes could display all text for easier checking.
L15	Not enough material for determination 4 metals
L19a	The amount of test material was really few.
L19b	The sample mass was few
L20	A technical problem was experienced during the mercury analysis and results will be available on Monday 7th July
L21	The Amount of material was very small.
L25	The amount of test material was too small
L28	We don't analyse very often food supplements but we analyse usually foodstuffs
L31	We analized this matrix, for this test, but officially we are not responsible for this specific matrix.

No cluster of results was observed as function of the technique used to perform the analysis for total Pb, As and Hg, Figure 5a shows the results obtained for total Pb. In the case of total Cd, it was observed that the results obtained using atomic absorption spectrometry were randomly distributed showing no particular correlation, with total Cd concentration, while results obtained by ICP-MS were clustered in the right zone of the graphic, Figure 5b, indicating that the values obtained by ICP-MS were slightly higher than the mean.

a)



b)

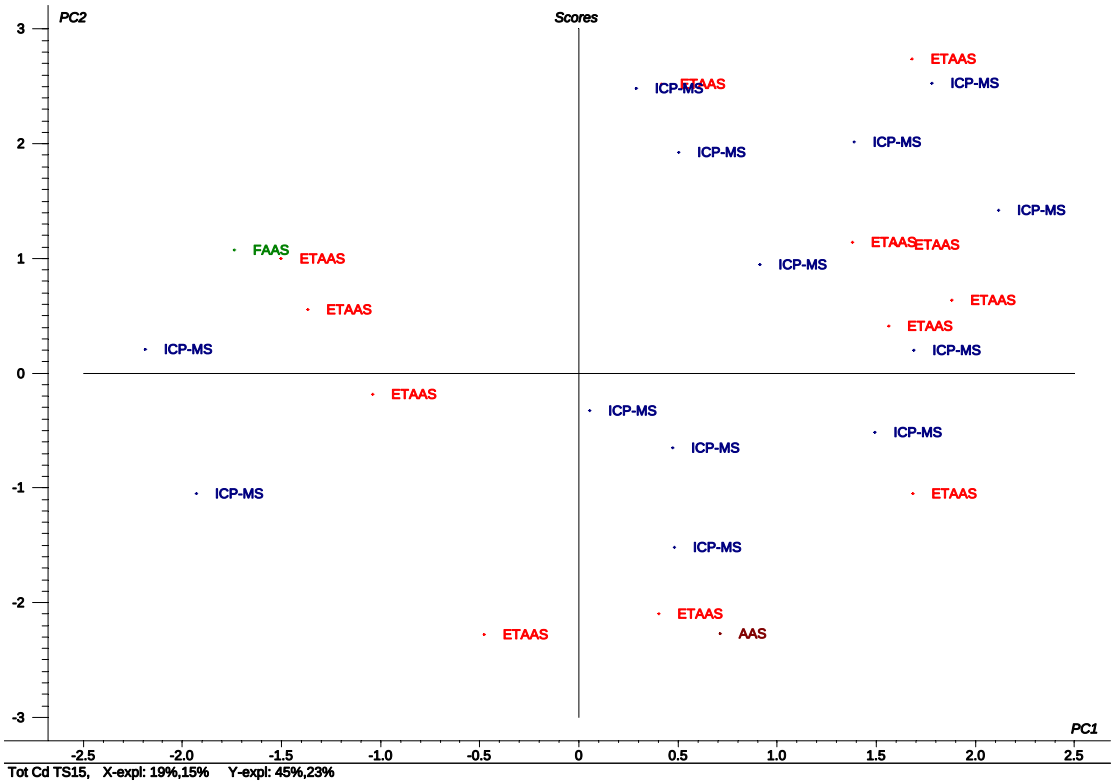


Figure 5: Distribution of results for: a) total Pb and b) total Cd in function of the technique used as derived from multivariant analysis.

9 Conclusions

The main conclusion that can be drawn from this exercise is that the capabilities of the network of NRLs to analyse Hg have improved considerably since 2006, when the first PT organised by the CRL-HM, IMEP-101, was conducted. On that occasion only eight laboratories reported results. In the present exercise twenty-two participants reported values, 60 % of them with satisfactory scores, even at the very low concentration that was present in the test material.
An extra effort is still needed in the evaluation of the uncertainties associated to the results. laboratories must take into account that the uncertainty of a measurement frequently depends on the concentration range, so that when analysing trace elements present at low concentrations, as it was the case of Cd in this exercise, the uncertainty is higher.

10 Acknowledgements

The organiser of the IMEP-106 thanks NIST for the provision of the candidate Standard Reference Material used as test material in this exercise. The Reference Material Unit of IRMM is acknowledged for their support in the optimisation of a method for the determination of the moisture content of the material. P. Robouch is acknowledged for his comments and discussion on the manuscript. Anne-Mette Jensen is thanked for revising the manuscript.

The NRLs participating in this exercise, listed below are kindly acknowledged.

Organisation	Country
AGES	Austria
AGES	Austria
CODA-CERVA	Belgium
State General Laboratory	Cyprus
Central Institute for Supervising and Testing in Agriculture	Czech Republic
State Veterinary Institute Olomouc	Czech Republic
National Food Institute	Denmark
Estonian Veterinary and Food Laboratory	Estonia
Agricultural Research Centre	Estonia
Finnish Customs Laboratory	Finland
Evira	Finland
laboratoire SCL	France
Federal Office of Consumer Protection and Food Safety (BVL)	Germany
General Chemical State Laboratory	Greece
Central Agricultural Office, Food and Feed Safety Directorate	Hungary
Central Agricultural Office, Food and Feed Safety Directorate	Hungary
Health Service Executive	Ireland
Istituto Zooprofilattico Sperimentale Del Piemonte, Liguria E Valle D'aosta	Italy
National Diagnostic Centre	Latvia
National Food and Veterinary Risk Assessment Institute	Lithuania
Scientific Institute of Public Health	Luxemburg

Organisation	Country
Public Health Laboratory	Malta
Food and Consumer Product Safety Authority (VWA)	Netherlands
INRB, I.P./L-IPIMAR	Portugal
State Veterinary and Food Institute	Slovakia
National Veterinary Institute	Slovenia
Laboratorio Arbitral Agroalimentario	Spain
National Food Administration	Sweden
The Food and Environment Research Agency (Fera)	United Kingdom

Countries not appearing on the above list did not reported results to this ILC.

11 References

[1] ISO 13528:2005; Statistical Methods for Use in Proficiency Testing by Interlaboratory Comparisons.
[2] M. Thompson, *Analyst*, (2002), **125**, 385-386.
[3] Regulation (EC) No 882/2004 of the European Parliament and of the Council of 29 April 2004 on official controls performed to ensure the verification of compliance with feed and food law, animal health and animal welfare rules.
[4] Commission Regulation (EC) No 333/2007 of 28 March 2007 laying down the methods of sampling and analysis for the official control of the levels of lead, cadmium, mercury, inorganic tin, 3-MCPD and benzo(a)pyrene in foodstuffs.
[5] Commission Regulation (EC) No 1881/2006 of 19 December 2006 setting maximum levels for certain contaminants in foodstuffs.
[6] ISO 13528:2005; Statistical Methods for Use in Proficiency Testing by Interlaboratory Comparisons.
[7] M. Thompson, S.L.R. Ellison, R. Wood, *Pure Appl. Chem.*, (2006), **78(1)**, 145-196.
[8] Eurachem/CITAC guide "Quantifying Uncertainty in Analytical Measurements" (2000), see www.eurachem.ul.pt
[9] The software to calculate Kernel densities is provided by the Statistical Subcommittee of the Analytical Methods Committee (AMC) of the Royal Society of Chemistry and described in the AMC Technical Brief "Representing data distributions with Kernel density estimates" (2006), see www.rsc.org/amc

Annexes

Annex 1: Invitation letter to laboratories

EUROPEAN COMMISSION
JOINT RESEARCH CENTRE

Institute for reference materials and measurements
Community reference laboratory for heavy metals in feed and food

CRL Heavy Metals in Feed and Food

Geel, 30 April 2009
JRC.D04/BCa/ive/ARES(2009)83296

«Title» «M_1st_name» «last_name»
«Institute»
«Department»
«Address»
«DHL_delivery_address»
«ZIP» «City»
«COUNTRY»

Inter-laboratory comparison for CRL Heavy Metals in Feed and Food

Dear Madam / Sir,

On behalf of the CRL Heavy Metals in Feed and Food, I would like to invite you to participate in the Proficiency Test [IMEP-106] for the determination of "**total Cd, Pb, As and Hg in food supplements**".

I would like to remind you that – according to Regulation (EC) No 882/2004 - you have the duty as NRL to participate in PTs organised by the CRL if you hold a mandate for the type of matrix investigated.

Please register electronically for this inter-laboratory comparison using the following link: https://irmm.jrc.ec.europa.eu/ilc/ilcRegistration.do?selComparison=279

Your participation is free of charge.

Once you have submitted your registration electronically, please follow the procedure indicated: a) print your registration form; b) sign it; and c) fax it to us. **Your fax is the confirmation of your participation.**

The **deadline for registration is 29th May 2009**. Samples will be sent to participants during the first half of June. The deadline for submission of results is 3rd July 2009.

Retieseweg 111, B-2440 Geel - Belgium. Telephone: (32-14) 571 211. http://irmm.jrc.ec.europa.eu
Telephone: direct line (32-14) 571 299. Fax: (32-14) 571 865.

E-mail: jrc-irmm-crl-heavy-metals@ec.europa.eu

I am the project leader for this inter-laboratory comparison. In case of questions/doubts, do not hesitate to contact me.

Yours sincerely

Dr. M.B. de la Calle
Deputy-Operating Manger CRL-HM

Cc: Philip Taylor

2

Annex 2: Accompanying letter

EUROPEAN COMMISSION
JOINT RESEARCH CENTRE

Institute for reference materials and measurements
Community reference laboratory for heavy metals in feed and food

CRL Heavy Metals in Feed and Food

Geel, 2 June 2009
JRC.D04/BCa/ive/ARES(2009)/115107

«TITLE» «FIRSTNAME» «SURNAME»
«ORGANISATION»
«DEPARTMENT»
«ADDRESS»
«ADDRESS2»
«ADDRESS3»
«ADDRESS4»
«ZIP» «TOWN»
«COUNTRY»

Participation in IMEP-106, a proficiency test exercise for the determination of <u>total</u> Cd, Pb, As, and Hg in food supplements.

Dear «TITLE» «SURNAME»,

Thank you for participating in the IMEP-106 intercomparison for the determination of **<u>total</u>** Cd, Pb, As, and Hg in food supplements. This exercise takes place in the frame of the CRL Heavy Metals in Feed and Food.

<u>This parcel contains</u>:
a) Two sachettes containing approximately 2.5 g each of the test material
b) A "Confirmation of Receipt" form
c) This accompanying letter

Please check whether the sachettes containing the test material remained undamaged during transport. Then fax (at +32-14-571865) or send the "Confirmation of receipt" form back. You should store the samples in a dark place and cool place (not more than 18 °C) until analysis.

The measurands are: **<u>total</u>** Cd, Pb, As, and Hg in food supplements. The procedure used for the analyses should resemble as closely as possible the one that you use in routine sample analysis.

Please perform two or three independent measurements per measurand. Correct the measurement results for recovery and water content (following the procedure as described hereafter), and report the corrected values, plus their mean on the reporting website. The results should be reported in the same way (e.g., number of significant figures) as normally reported to the customer.

«PARTKEY»

Retieseweg 111, B-2440 Geel - Belgium. Telephone: (32-14) 571 211. http://irmm.jrc.ec.europa.eu
Telephone: direct line (32-14) 571 252. Fax: (32-14) 571 865.

E-mail: jrc-irmm-crl-heavy-metals@ec.europa.eu

The results are to be reported referring to dry mass and thus corrected for humidity. To calculate the water content in the test material, please apply the following procedure:

1. *Weigh accurately 0.5 g of test material in a glass container of 5-7 cm diameter, Preferably with a lid because when the prescribed drying time has passed, the glass container must cool down about 30 minutes in a desiccator before weighing.*
2. *Place it in an oven for 120 ± 5 min at 80 ± 2 °C.*
3. *Place the glass container covered with a lid in a desiccator and wait 30 min before weighing the test material again.*

Note 1: perform the measurements of the water content in triplicate.
Note 2: ***do not use for the heavy metal determinations the aliquots of test material that you have used for the water content determination!***

You can find the reporting website at https://irmm.jrc.ec.europa.eu/ilc/ilcReporting.do To access this webpage you need a personal password key, which is: «PARTKEY». The system will guide you through the reporting procedure. Please enter for each parameter the two or three measurement results plus the technique you used, but do not report the uncertainty for each individual measurement. In addition, please report the mean of the results with technique and with uncertainty information in the allocated space for "measurement 4". After entering all results, please also complete the relating questionnaire. **Do not forget to submit and confirm always when required**.

Directly after submitting your results and the questionnaire information online, you will be prompted to print the completed report form. Please do so, **sign the paper version and return it to IRMM by fax (at +32-14-571-865) or by e-mail**. Check your results carefully for any errors before submission, since this is your definitive confirmation.

The deadline for submission of results is 03/07/2009.

Please keep in mind that collusion is contrary to professional scientific conduct and serves only to nullify the benefits of proficiency tests to customers, accreditation bodies and analysts alike.

Your participation in this project is greatly appreciated. If you have any remaining questions, please contact me by e-mail:
JRC-IRMM-CRL-HEAVY-METALS@ec.europa.eu

With kind regards

Dr. M.B. de la Calle
IMEP-106 Co-ordinator

Enclosures: 1) two sachettes containing the test material; 2) confirmation of receipt form; 3) accompanying letter.

Cc: P. Taylor

Annex 3: Acknowledgement of receipt form

EUROPEAN COMMISSION
JOINT RESEARCH CENTRE

Institute for reference materials and measurements
Community reference laboratory for heavy metals in feed and food

CRL Heavy Metals in Feed and Food

Annex to JRC.D04/BCa/ive/ARES(2009)/115107

«TITLE» «FIRSTNAME» «SURNAME»
«ORGANISATION»
«DEPARTMENT»
«ADDRESS»
«ADDRESS2»
«ADDRESS3»
«ZIP» «TOWN»
«COUNTRY»

CRL-HM-06 / IMEP-106

<u>total</u> Cd, Pb, As, and Hg in food supplements

Confirmation of receipt of the samples

Please return this form at your earliest convenience.
This confirms that the sample package arrived.
In case the package is damaged,
please state this on the form and contact us immediately.

ANY REMARKS ……
……

Date of package arrival ……

Signature ……

<u>Please return this form to:</u>
Dr Beatriz de la Calle

IMEP-106 Coordinator
EC-JRC-IRMM
Retieseweg 111
B-2440 GEEL, Belgium

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IMEP

Annex 4: Questionnaire

Comparison for IMEP-106

This questionnaire is offline

Please fill in the questionnaire.

Submission Form

1. **Did you apply a recovery factor to correct your measurement results?**
   - ○ no
   - ○ yes

   1.1. If Yes, what are the recovery factors (R, in %) you used:

   1.1.1. for Cd (in %)

   1.1.2. for Pb (in %)

   1.1.3. for As (in %)

   1.1.4. for Hg (in %)

   1.2. If Yes, did you determine R by:

   - ☐ 1. adding a known amount of the same analyte to the sample
   - ☐ 2. using a certified reference material
   - ☐ 3. other

   1.2.1. If other, please specify

2. **What is the level of confidence reflected by the coverage (k) factors stated above? (in %)**

3. **What is the basis of your uncertainty estimate (multiple answers are possible)?**
   - ☐ 1. uncertainty budget calculated according to iso-gum
   - ☐ 2. known uncertainty of the standard method
   - ☐ 3. uncertainty of the method as determined in-house validation
   - ☐ 4. measurement of replicates (i.e. precision)
   - ☐ 5. expert guestimate
   - ☐ 6. use of intercomparison data
   - ☐ 7. other

   3.1. If other, please specify

4. **Do you usually provide an uncertainty statement to your custumers for this type of analysis?**
   - ○ no
   - ○ yes

5. **Did you correct for the water content of the sample?**
   - ○ no
   - ○ yes

   5.1. If Yes, what is the water content (in % of the sample mass)?

   5.2. If no, what was the reason not to do this?

6. **Did you analyse the sample according to an official method?**
   - ○ no
   - ○ yes

   6.1. If no, please describe (in max 150 characters for each reply) your:

   6.1.1. sample pre-treatment

   6.1.2. digestion step

   6.1.3. extraction / separation step

   6.1.4. instrument calibration step

   6.2. If yes, which:

7. **Does your laboratory carry out this type of analysis (as regards the measurands, matrix and methods) on a routine basis?**

- ○ no
- ○ yes

7.1. If Yes, please estimate the number of samples (Cd, Hg, Pb measurements together):

- ○ a) 0-50 samples per year
- ○ b) 50-250 samples per year
- ○ c) 250- 1000 samples per year
- ○ d) more than 1000 samples per year

8. **Does your laboratory have a quality system in place?**

- ○ no
- ○ yes

8.1. If yes, which:

- ☐ iso 9000 series
- ☐ iso/iec 17025
- ☐ other

8.1.1. If other, please specify

9. **Is your laboratory accredited for this type of analysis?**

Questions/Response table	**No**	**Yes**	*Info*
Total Cd	○	○	
Total Pb	○	○	
Total As	○	○	
Total Hg	○	○	

10. **If you are accredited, by which Accreditation Body?**

11. **Does your laboratory take part in an interlaboratory comparison for this type of analysis on a regular basis?**

- ○ no
- ○ yes

11.1. If yes, which one(s):

12. **Does your laboratory use a reference material for this type of analysis?**

- ○ no
- ○ yes

12.1. If yes, is the material used for the validation of procedures?

- ○ no
- ○ yes

12.2. If yes, is the material used for calibration of instrument?

- ○ no
- ○ yes

12.3. If yes, which one(s):

13. **Do you have any comments? Please let us know: ...**

Annex 5: Experimental details.

Lab code	SOP?	If yes, which:	Sample pre-treatment	Digestion step	Extraction / separation step	Instrument calibration step
L01	No		Weighing out sample (0.50g)	Acid digestion (microwave system), HNO_3, H_2O_2, H_2O	None	ICP-MS, Calibration Standard (As, Cd, Hg, Pb), In Internal Standard
L02	Yes	EN 13805:2002				
L03	Yes	NMKL-161				
L04	No		Mixing of sample	High pressure microwave oven with conc. Nitric acid		
L05	No		High pressure Microwave digestion	Nitric acid and perhydrol	No	0.1/0.5 /1.0/2.0/5.0/10.0/20.0
L06	Yes	For Cd and Pb LST EN 14084:2003; for Hg ASU L 00.00-19/4				
L07	Yes					
L08	No			Nitric acid	Filtration	2,6 ;5 ;10
L09	No		No	HNO_3 +H_2O_2	No	External calibration ICP-MS

Lab code	SOP?	If yes, which:	Sample pre-treatment	Digestion step	Extraction / separation step	Instrument calibration step
L10	No		None	0.5 g digested in 5 ml conc nitric acid using high pressure quartz vessels and microwave heating. Made up to 10 ml with high purity water.	None	Simple dilution prior to measurement with dilute nitric acid containing indium and rhodium as internal standards. Instrument calibrated with acid matched standards.
L11	Yes	AOAC official Method 999.10, AOAC Official Methods of analysis, 2000, Chapter 9, p16-19.				
L12	No					ICP-MS measurement with octopole reaction system and internal standard calibration
L13	No		None	Pb,Cd.As: microwave high pressure digestion with H_2O_2(30%) and HNO_3 conc.		ADD. METHOD; STD SOLUTION Cd: 2ppb; Pb: 50ppb; As 20 ppb; Hg: linearity calibration from 25 ppb to 5 ppm
L14	No	External standard calibration	No	Microwave		Yes
L15	Yes	AOAC 999.11				
L16	No			Microwave digestion	Dilution	External standards

Lab code	SOP?	If yes, which:	Sample pre-treatment	Digestion step	Extraction / separation step	Instrument calibration step
L17	Yes	AOAC				
L18	Yes					
L19a	Yes	MSZ EN ISo 13805, MSZ EN ISO 17294-1.2				
L19b	Yes	EN 14082:2003, EN14546:2005				
L20	No		N.A.	Nitric acid digestion for lead, cadmium and mercury	n.a..	External calibration
L21	Yes	EN 14084 (Digestion), ICP-MS and CV-AAS for Hg				
L22	Yes	NMKL Trace Elements-As, Cd, Hg, Pb and other elements. No. 186, 2007.				
L23	No		Add 2 ml 65% HNO3	Microwave	Dilution	4 steps
L24	No		Homogenise	Microwave digestion	n.a.	Calibration using certified standard solutions
L25	Yes	EN 15550(2007)				
L26	Yes	National Feed Codex				

Lab code	SOP?	If yes, which:	Sample pre-treatment	Digestion step	Extraction / separation step	Instrument calibration step
L27		Test method 7473, EPA 2007				
L28	Yes	AOAC 999.10 (2005)				
L29	Yes	External linear	Mixing	Micro wave assisted	Nitric acid	Yes
L30	Yes	ICP-MS				
L31	Yes	SR EN 13806:2003;SR EN 14084:2003; AOAC Method - 986.15				
L32	Yes					

European Commission

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Abstract
The Institute for Reference Materials and Measurements (IRMM) of the Joint Research Centre (JRC), a Directorate-General of the European Commission, operates the Community Reference Laboratory for Heavy Metals in Feed and Food (CRL-HM). One of its core tasks is to organise interlaboratory comparisons (ILCs) among appointed National Reference Laboratories (NRLs). This report presents the results of the sixth ILC o the CRL-HM which focused on the determination of total Cd, Pb, As and Hg, (related to dry mass) in food supplements.

The test material used in this exercise was the standard reference material (SRM) SRM 3256, of the National Institute of Standards and Technology (NIST), the matrix being green tea of Chinese origin. The material was labelled at IRMM and dispatched to the participants on the first week of June 2009. Each participant received two sachets containing approximately 2.5 g of test material each. Thirty-three participants from twenty-five countries registered to the exercise of which 32 sets of results were reported for total Cd and for total Pb, and 29 for total As and for total Hg. One laboratory reported two sets of values for total Cd, Pb, As and Hg obtained with two different techniques, respectively. The assigned values were the certified values as provided by NIST.

The uncertainties of the respective assigned values, u_{ref}, were also provided by NIST. Participants were invited to report the uncertainty on their measurements. This was done by the majority of laboratories taking part in this exercise.

Laboratory results were rated with z and zeta scores in accordance with ISO 13528. Standard deviation for proficiency assessment (also called target standard deviation) was fixed to 15 % for total Cd, Pb and As by the advisory board of this ILC, on the basis of the outcome of previous ILC's organised by the CRL-HM for the same population. For total Hg the standard deviation for proficiency assessment was set to 22 % as derived by the modified Horwitz equation.

The mission of the JRC is to provide customer-driven scientific and technical support for the conception, development, implementation and monitoring of EU policies. As a service of the European Commission, the JRC functions as a reference centre of science and technology for the Union. Close to the policy-making process, it serves the common interest of the Member States, while being independent of special interests, whether private or national.

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