CODA –CERVA

Belgian National Reference Laboratory
for Trace Elements in Food and Feed

Final report on the 2011 Interlaboratory Comparison organised by the National Reference Laboratory for Trace Elements in Food and Feed

Trace elements in a food supplement of vegetable origin

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1 Summary

From the 1st of January 2008, the laboratory for Trace Elements in the Veterinary and Agrochemical Research Centre (CODA-CERVA), Tervuren, operates as National Reference Laboratory for Trace Elements in Feed and Food (NRL-TE). One of its core tasks is to organise interlaboratory comparisons (ILCs) among laboratories appointed by the Federal Agency for the Safety of the Food Chain. This report presents the results of the interlaboratory comparison organised by the NRL-TE which focused on the determination of trace elements in a food supplement of vegetable origin.

The results from the ILC were treated in CODA-CERVA, Tervuren.

The 2011 ILC was obligatory for all laboratories approved for the analysis of heavy metals in food, fruits and/or vegetables by the Federal Agency for the Safety of the Food Chain (FASFC). Ten laboratories, which were approved for these foodstuffs, registered for and participated in the exercise. Two other laboratories participated voluntarily.

The test material used in this exercise was an Asian algae food supplement prepared from 500 g of dried material. The material was mixed for 24 hours prior to be bottled. Each participant received approximately 6 g of test material.

Participants were invited to report the mean value and measurement uncertainty on their results for arsenic (As), cadmium (Cd), lead (Pb) and mercury (Hg). The assigned values (x_a) and their uncertainty ($u(x_a)$) were determined as the consensus of participant's results. Standard deviations for proficiency assessment were calculated using the modified Horwitz equation (Thompson, 2000).

Of the twelve laboratories that registered for participation, 11 submitted results for Cd, Pb and Hg, and all 12 submitted results for As. Of the 41 z-scores that were calculated, 90% was satisfactory, 2 % was questionable and 7% was unsatisfactory. Of the 41 zeta-scores, 81% was satisfactory, 7% was questionable and 12% was unsatisfactory.

2 Introduction

Trace elements occur in varying amounts as natural elements in soils, plants and animals, and consequentially in food and feed. High levels of lead, cadmium and mercury have been found in certain food supplements[1] 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 lead, cadmium and mercury. In order to protect human health, the Commission of the European Communities has laid down maximum levels for lead, cadmium and mercury in food supplements. Regarding food supplements of vegetable origin, these maximum levels are[1] 3.0 mg/kg for lead, 1.0 mg/kg for cadmium and 0.1 mg/kg for mercury.

[1] Commission Regulation (EC) No 629/2008 of 2 July 2008 amending Regulation (EC) No 1881/2006 setting maximum levels for certain contaminants in foodstuffs.

There is currently no European legislation regarding arsenic levels in food supplements. The Royal Decree of 14 June 2002 laying down maximum levels of contaminants including heavy metals in food supplements determined a maximum level of 1 mg/kg for arsenic.

The scope of this ILC was to test the competence of the participating laboratories to determine the total mass fraction of As, Cd, Pb and Hg in a food supplement of vegetable origin.

3 Time frame, test material and instructions to participants

Invitation letters to this ILC were sent to participants in February (Annex 1). The 2011 ILC was obligatory for all laboratories approved for the analysis of heavy metals in food, fruits and/or vegetables by the Federal Agency for the Safety of the Food Chain (FASFC). Ten laboratories, which were approved for these foodstuffs, registered for and participated in the exercise. Two other laboratories participated voluntarily. The samples were dispatched to the participants by end of June 2011. Reporting deadline was 1 September 2011.

This year the test sample was an algae food supplement from Asian origin. The material was received as dried material and was mixed for 24 hours. The homogeneity of the test material was tested following the recommended procedure according to IUPAC[2] (2006). All the trace elements appeared to be homogeneously distributed in the food supplement samples (Annex 2). Approximately 6 g of material was placed in a plastic bottle prior to dispatch to each participant. Each participant received one bottle of test material, an accompanying letter (Annex 3) with instructions on sample handling and reporting, and a form that had to be sent after receipt of the sample to confirm its arrival (Annex 4).

Participants were instructed to store the material in a dark place at room temperature until analysis. Before starting the analyses, the sample had to be re-homogenized by shaking for about 30 seconds. The procedure followed for the exercise, had to be as close as possible to the method used by the participant in routine sample analysis. Nevertheless participants were instructed to a) perform three independent measurements per parameter, b) correct the measurements for recovery, and c) to report measurement uncertainty.

A questionnaire was attached to the reporting form. The questionnaire was intended to provide further information on the measurements and the laboratories. A copy of the questionnaire is presented in Annex 5.

Laboratory codes were given randomly and communicated confidentially to the corresponding participant.

[2] IUPAC 2006. The International harmonized protocol for the proficiency testing of analytical chemistry laboratories. Pure Appl. Chem 78: 145-196.

4 Assigned values

The assigned values for the different trace elements in the food supplement sample were determined as the consensus of participant's results (IUPAC[2], 2006). The major advantages of consensus values are the straightforward calculation and the fact that none of the participants is accorded higher status. The disadvantages are that the consensus values are not independent of the participant's results and, especially in the current case with 12 participants, that the uncertainty on the consensus (identified as the standard error) may be high and the information content of the z-scores will be correspondingly reduced.

The robust statistic approach is a convenient modern method of handling results when they are expected to follow a near-normal distribution and it is suspected that they include a small proportion of outliers. There are many different robust estimators of mean and standard deviation (AMC[3], 2001). The median and MAD (median absolute difference) were chosen here as robust estimators.

The modified Horwitz equation was used to establish the standard deviation for proficiency testing (σ_p) (Thompson[4], 2000). It is an exponential relationship between the variability of chemical measurements and concentration. The Horwitz value is widely recognized as a fitness for purpose criterion in proficiency testing.

The Kernel density estimate gives a good estimate of the population density function without making any assumptions that it is a normal distribution. The Kernel distribution plots were obtained using a software tool developed by AMC[5].

The scheme that was followed to estimate the consensus and its uncertainty is outlined below:

a) Results that were identifiable invalid or extreme outliers (data outside the range mean ± 3 x stdev) were excluded (e.g. Pb – L02)
b) A visual presentation of the remaining results was examined. It was checked whether the distribution was apparently unimodal and roughly symmetric, possible outliers aside. If so ⇒ c) (As, Cd, Pb); else ⇒ d) (Hg).
c) The robust mean $\hat{\mu}_{rob}$ and standard deviation $\hat{\sigma}_{rob}$ of the n results were calculated as $\hat{\mu}_{rob}$ = median and $\hat{\sigma}_{rob}$ = 1.4826*MAD. If $\hat{\sigma}_{rob}$ was less than about $1.2\sigma_p$, then $\hat{\mu}_{rob}$ was used as the assigned value x_a and $\hat{\sigma}_{rob}/\sqrt{n}$ as its standard uncertainty $u(x_a)$ (As, Cd). If $\hat{\sigma}_{rob} > 1.2\sigma_p$ then ⇒ d) (Pb).
d) A Kernel density estimate of the distribution was made using normal kernels with a bandwith h of $0.75\sigma_p$. If this resulted in a unimodal and roughly symmetric kernel density, and the mode and median were nearly coincident, then $\hat{\mu}_{rob}$ was used as the assigned value and $\hat{\sigma}_{rob}/\sqrt{n}$ as its standard uncertainty; else ⇒ e) (Pb, Hg).

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[3] AMC technical brief. 2001. Robust statistics: a method of coping with outliers.
[4] Thompson, M. 2000. *Analyst*, 125: 385-386.
[5] AMC Technical Brief « Representing data distributions with Kernel density estimates.

e) If the minor mode could be safely attributed to an outlying result, then $\hat{\mu}_{rob}$ was still used as the assigned value and $\hat{\sigma}_{rob}/\sqrt{n}$ as its standard uncertainty (Pb, Hg); else no consensus value could be derived.

The consensus values, their standard uncertainty and some other statistical parameters are summarised in Table 1.

Table 1. Summary of statistical parameters for the test material.

	As mg/kg	**Cd µg/kg**	**Pb µg/kg**	**Hg µg/kg**
n	12	10	10[$]	8
Mean	58.0	616	912	29.2
SD	8.2	87	199	9.2
Robust mean (median)	58.7	609	930	26.0
Robust SD	3.0	104	189	4.8
Assigned value x_a	**58.7**	**609**	**930**	**26.0**
Standard uncertainty of the assigned value $u(x_a)$	**0.9**	**40**	**60**	**1.7**
σ_p	5.1	105	150	5.7

Assigned value (x_a): median of the reported results
σ_p: standard deviation for proficiency assessment
[$] Excluding the result of L02

5 Scores and evaluation criteria

Individual laboratory performances are expressed in terms of z-scores and zeta-scores in accordance with ISO 135283 and the International Harmonised Protocol (IUPAC, 2006).

$$z = \frac{x_{lab} - x_a}{\sigma_p}$$

$$zeta = \frac{x_{lab} - x_a}{\sqrt{u^2(x_a) + u^2(x_{lab})}}$$

where:

x_{lab} is the mean of the individual measurement results as reported by the participant
x_a is the assigned value
σ_p is the standard deviation for proficiency assessment
$u(x_a)$ is the standard uncertainty for the assigned value
$u(x_{lab})$ is the reported standard uncertainty in the reported value x_{lab}. When no uncertainty was reported by the laboratory, it was set to zero.

The z-score compares the participant's deviation from the reference value with the standard deviation accepted for the proficiency test, σ_p. Should participants feel that these σ values are not fit for their purpose they can recalculate their scorings with a standard deviation matching their requirements.

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 uncertainty claimed by this laboratory (taking due account of the uncertainty on the reference value itself). 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

Per trace element, a set of figures is provided. Each set includes (a) the Kernel density plot, (b) the individual mean values with their reported uncertainty, and (c) the z- and zeta-scores. The solid line represents the assigned value, the dashed lines delimit the reference interval ($x_a \pm 2u(x_a)$) and the dotted lines delimit the target interval ($x_a \pm 2\sigma_p$).

6 Results

6.1 Arsenic

X_a = 58.7 ± 1.8 mg/kg (k = 2)

Eleven out of 12 laboratories obtained satisfactory z-scores for arsenic against the standard deviation accepted for the proficiency test (Table 2; Fig 1a-c). One laboratory obtained an unsatisfactory z-score. Ten out of 12 laboratories obtained good zeta-scores against their stated measurement uncertainty, one laboratory obtained a questionable zeta-score and one laboratory obtained an unsatisfactory zeta-score.

Table 2: values reported for As by the participants and scores calculated by the organiser.

Lab code	Result 1 (mg kg^{-1})	Result 2 (mg kg^{-1})	Result 3 (mg kg^{-1})	Mean (mg kg^{-1})	Extended uncertainty (k = 2) (U_{lab}; mg kg^{-1})	z-scores	zeta-scores
L01	52.1	59.5	59.5	57.0	8.4	-0.3	-0.4
L02	31.94	34.76	33.05	33.3	0.19	-5.0	-28.1
L03	60	62	64	62	12.4	0.6	0.5
L04	63.26	61.84	58.11	61.07	18.32	0.5	0.3
L05	64.7	64.0	63.8	64.2	8.0	1.1	1.3
L06	59.3	57.5	57.2	58.0	3.1	-0.1	-0.4
L07	57.91	57.00	62.62	59.18	11.84	0.1	0.1
L08	54.7	56.1	61.5	57.4	19.1	-0.3	-0.1
L09	62.1	59.7	70.7	64.2	26.0	1.1	0.4
L10	64.5	62.5	64.1	63.7	3.0	1.0	2.9
L11	59.4	55.7	56.1	57.1	12.2	-0.3	-0.3
L12	69.9	52.4	52.5	58.3	16.0	-0.1	0.0

Figure 1a: kernel density plot for arsenic

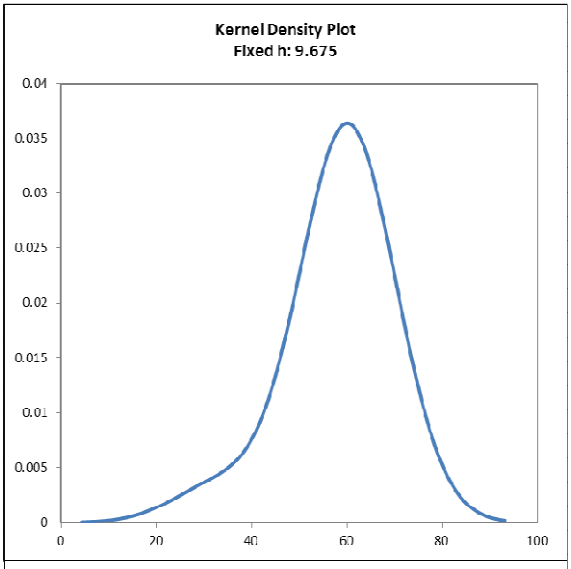


Figure 1b: Results and expanded uncertainty for As, as reported by the participants

x_a = 58.7 mg kg^{-1}
$u(x_a)$ = 0.9 mg kg^{-1}
σ_p = 5.1 mg kg^{-1}

(dashed lines: $x_a \pm 2\ u(x_a)$, dotted lines: $x_a \pm 2\ \sigma_p$)

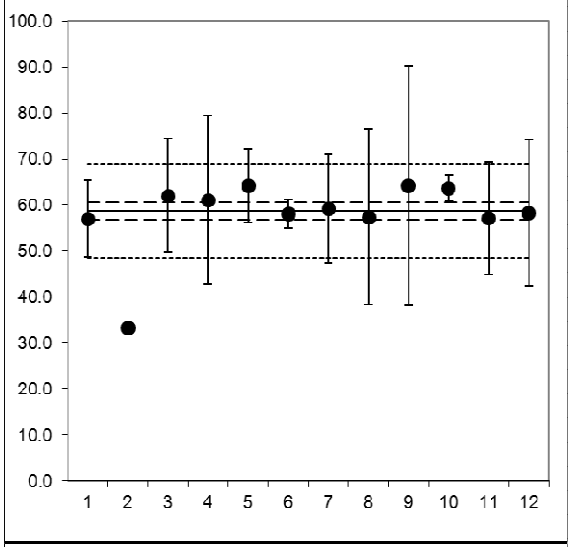
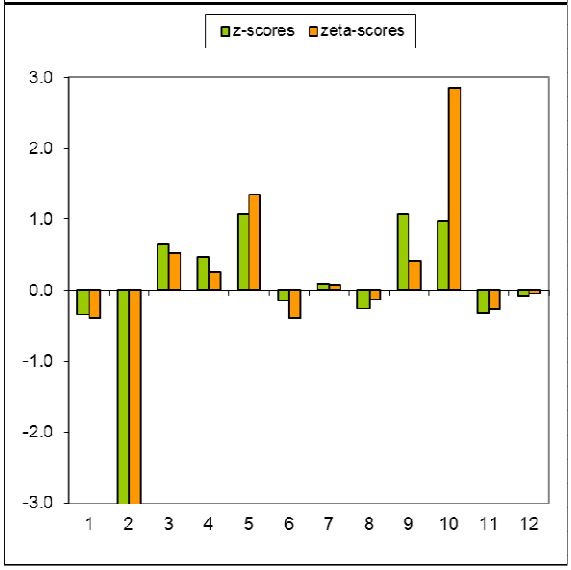


Figure 1c: z- and zeta-scores
$z = (x_{lab} - x_a) / \sigma_p$

$$\text{zeta} = \frac{x_{lab} - x_a}{\sqrt{u^2(x_a) + u^2(x_{lab})}}$$



6.2 Cadmium

X_a = 609 ± 80 µg/kg (k = 2)

All laboratories that submitted results other than “less than” (n = 10) obtained satisfactory z-scores for cadmium against the standard deviation accepted for the proficiency test (Table 3; Fig 2a-c). All but one laboratory obtained satisfactory zeta-scores against their stated measurement uncertainty. One laboratory obtained an unsatisfactory zeta-score. One laboratory did not provide results.

Table 3: values reported for Cd by the participants and scores calculated by the organiser.

Lab code	Result 1 (µg kg^{-1})	Result 2 (µg kg^{-1})	Result 3 (µg kg^{-1})	Mean (µg kg^{-1})	Extended uncertainty (k = 2) (U_{lab}; µg kg^{-1})	z-scores	zeta-scores
L01	512	540	514	522	53	-0.8	-1.8
L02	<500	<500	<500	<500	1.526	-	-
L03	594	582	594	590	118	-0.2	-0.3
L04	628	608	622	619	186	0.1	0.1
L05	782	802	820	801	58	1.8	3.9
L06	523	525	525	524	34.6	-0.8	-2.0
L07	600	600	594	598	126	-0.1	-0.1
L08	672	685	686	681	227	0.7	0.6
L09	660.5	654.9	712.7	676.0	123.4	0.6	0.9
L10							
L11	643	596	623	621	141	0.1	0.1
L12	531	528	529	529	151	-0.8	-0.9

Figure 2a: kernel density plot for cadmium

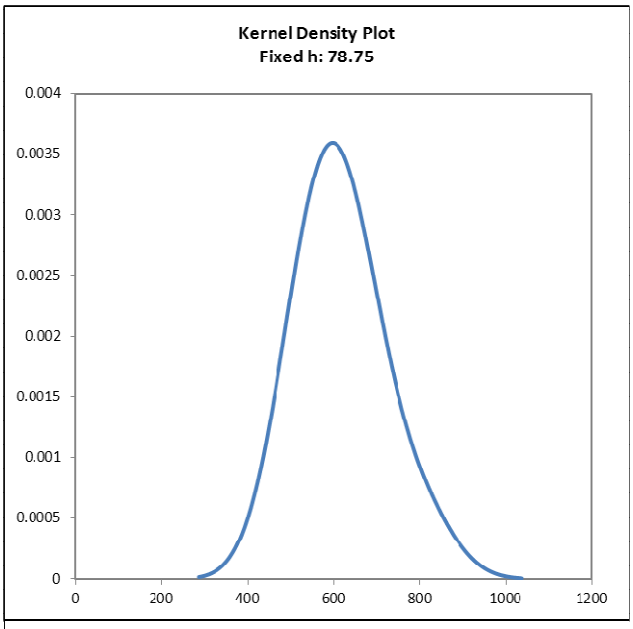


Figure 2b: Results and expanded uncertainty for Cd, as reported by the participants

x_a = 609 µg kg^{-1}
$u(x_a)$ = 40 µg kg^{-1}
σ_p = 105 µg kg^{-1}

(dashed lines: $x_a \pm 2\ u(x_a)$, dotted lines: $x_a \pm 2\ \sigma_p$)

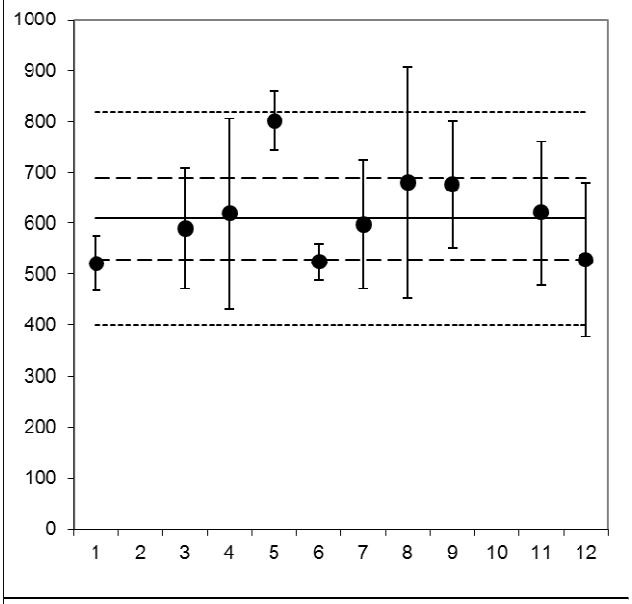
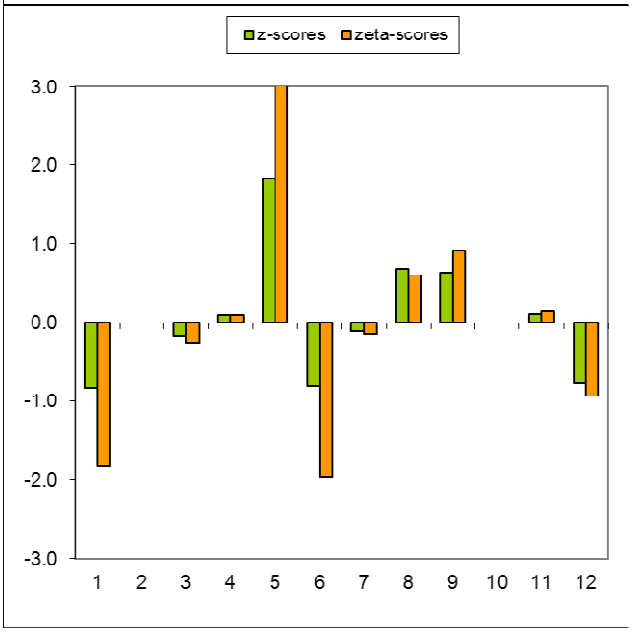


Figure 2c: z- and zeta-scores

$z = (x_{lab} - x_a) / \sigma_p$

$$\text{zeta} = \frac{x_{lab} - x_a}{\sqrt{u^2(x_a) + u^2(x_{lab})}}$$



6.3 Lead

X_a = 930 ± 120 µg/kg (k = 2)

Nine of the laboratories that submitted results (n = 11) obtained satisfactory z-scores for lead against the standard deviation accepted for the proficiency test (Table 4; Fig 3a-c). Two laboratories obtained unsatisfactory z-scores. One of those two laboratories (L02) submitted a mean result that was larger than any of its three replicate values. Furthermore the submitted result was about 8-fold larger than the median of the results of all participants. Therefore the result of L02 was considered as an erroneous result and it was not taken into account in the calculation of the consensus value. Eight laboratories obtained satisfactory zeta-scores against their stated measurement uncertainty. One laboratory obtained a questionable zeta-score, two laboratories obtained an unsatisfactory zeta-score. One laboratory did not provide results.

Table 4: values reported for Pb by the participants.

Lab code	Result 1 (µg kg^{-1})	Result 2 (µg kg^{-1})	Result 3 (µg kg^{-1})	Mean (µg kg^{-1})	Extended uncertainty (k = 2) (U_{lab}; µg kg^{-1})	z-scores	zeta-scores
L01	829	736	795	787	289	-1.0	-0.9
L02	7440	6320	7200	7700[$]	0.196	45	113
L03	983	986	994	988	247	0.4	0.4
L04	880	872	843	865	260	-0.4	-0.5
L05	1062	1012	968	1014	86	0.6	1.1
L06	1140	1112	1079	1110	98	1.2	2.3
L07	863	828	922	871	139	-0.4	-0.6
L08	450	432	492	458	153	-3.1	-4.9
L09	1149.4	1194.6	1052.5	1132.2	375.8	1.3	1.0
L10							
L11	1079	1008	1083	1057	182	0.8	1.2
L12	829	845	830	835	391	-0.6	-0.5

[$] The mean reported by the participant does not correspond to the calculated mean of the three replicates (6987 µg/kg).

Figure 3a: kernel density plot for lead

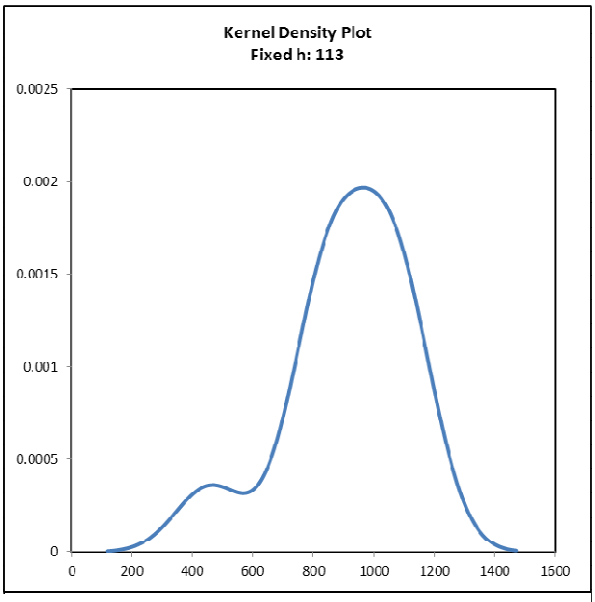


Figure 3b: Results and expanded uncertainty for Cd, as reported by the participants

x_a = 930 µg kg^{-1}
$u(x_a)$ = 60 µg kg^{-1}
σ_p = 150 µg kg^{-1}

(dashed lines: $x_a \pm 2\ u(x_a)$, dotted lines: $x_a \pm 2\ \sigma_p$)

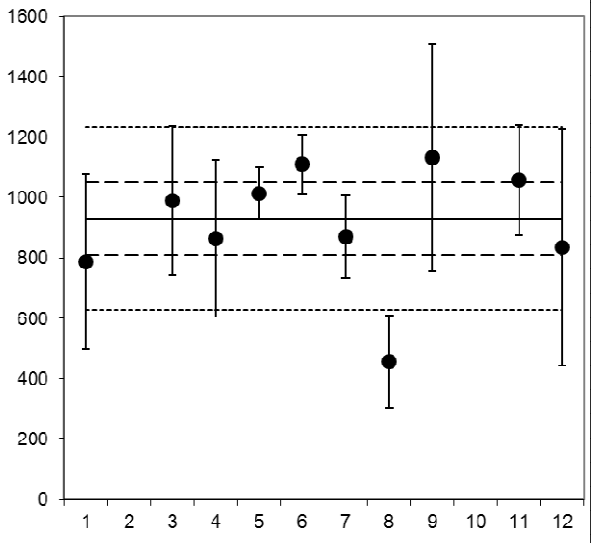
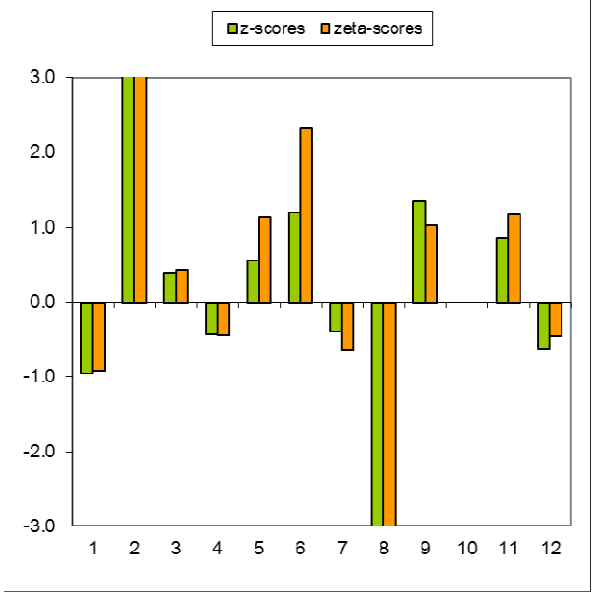


Figure 3c: z- and zeta-scores

$z = (x_{lab} - x_a) / \sigma_p$

$$\text{zeta} = \frac{x_{lab} - x_a}{\sqrt{u^2(x_a) + u^2(x_{lab})}}$$



6.4 Mercury

X_a = 26.0 ± 3.4 µg/kg (k = 2)

Seven of the laboratories that submitted results other than "less than" (n = 8; L04 participated twice with two different techniques) obtained satisfactory z-scores for mercury against the standard deviation accepted for the proficiency test (Table 5; Fig 4a-c). One laboratory obtained an unsatisfactory z-score. Six laboratories obtained satisfactory zeta-scores against their stated measurement uncertainty. One laboratory obtained a questionable zeta-score and one laboratory obtained an unsatisfactory zeta-score. Three laboratories could not produce results above their limit of quantification. Two laboratories did not submit results.

Table 5: values reported for Hg by the participants and scores calculated by the organiser.

Lab code	Result 1 (µg kg^{-1})	Result 2 (µg kg^{-1})	Result 3 (µg kg^{-1})	Mean (µg kg^{-1})	Extended uncertainty (k = 2) (U_{lab}; µg kg^{-1})	z-scores	zeta-scores
L01	56.2	44.6	47.1	49.3	12	4.1	3.7
L02	21.4	22.7	21.5	21.9	0.0107	-0.7	-2.4
L03	25	23	24	24	4	-0.3	-0.8
L04a	25.2	26.4	28.0	27	11	0.2	0.2
L04b	41	33	33	36	13	1.7	1.5
L05							
L06	<20	<20	<20	<20			
L07	<50	<50	<50	<50			
L08	<100	<100	<100	<100			
L09	20.7	24.5	25.3	23.5	7.3	-0.4	-0.6
L10							
L11	28.4	24.7	26.1	26.4	5.6	0.1	0.1
L12	25.4	25.3	25.7	25.5	13	-0.1	-0.1

Figure 4a: kernel density plot for mercury

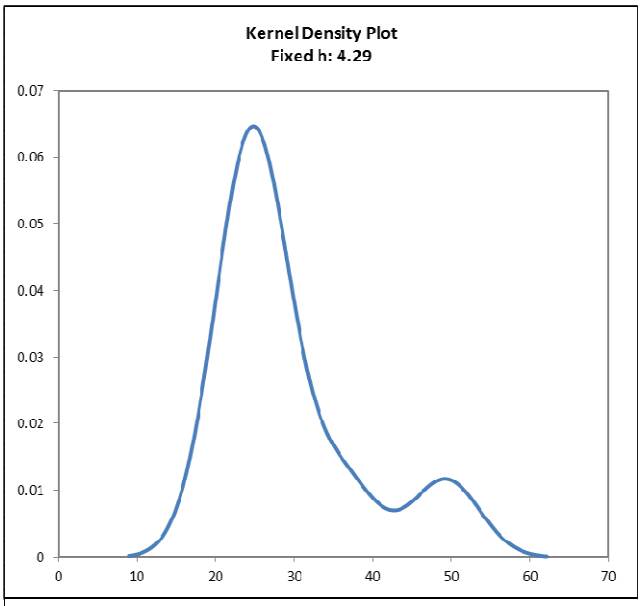


Figure 4a: Results and expanded uncertainty for Hg, as reported by the participants

x_a = 26.0 µg kg^{-1}
$u(x_a)$ = 1.7 µg kg^{-1}
σ_p = 5.7 µg kg^{-1}

(dashed lines: $x_a \pm 2\ u(x_a)$, dotted lines: $x_a \pm 2\ \sigma_p$)

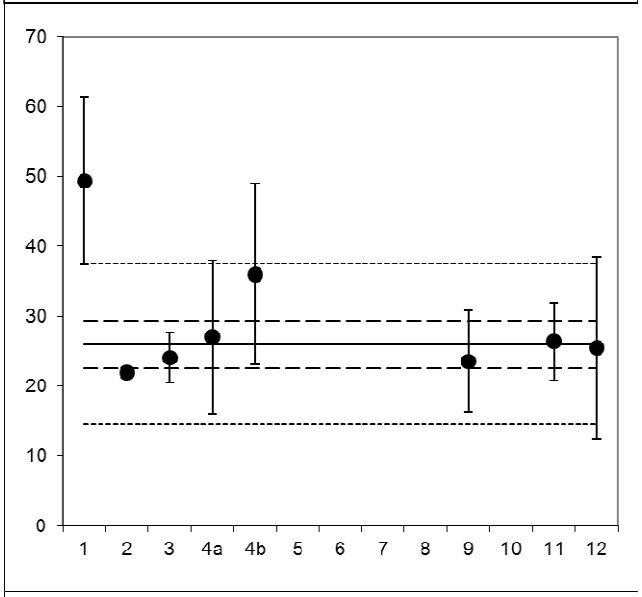
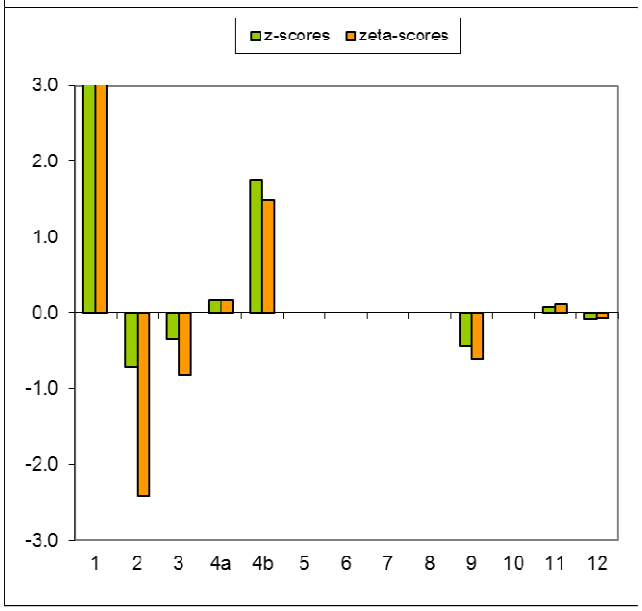


Figure 4b: z- and zeta-scores

$z = (x_{lab} - x_a) / \sigma_p$

$$\text{zeta} = \frac{x_{lab} - x_a}{\sqrt{u^2(x_a) + u^2(x_{lab})}}$$



6.5 Discussion

Of the twelve laboratories that registered for participation, 11 submitted results for Cd, Pb and Hg, and all 12 submitted results for As. From these results, values reported as "less than" were not included in the evaluation. This was the case for one laboratory for Cd and three laboratories for Hg. It should be noted that L06 reported for Hg "< 20 µg/kg" which is lower than the corresponding x_a - 3 $u(x_a)$ value (20.9 µg/kg). Hence this should be considered as an incorrect statement. Laboratory L02 reported for Cd "< 500 µg/kg" which is lower than the corresponding x_a - 2 $u(x_a)$ (529 µg/kg) but larger than x_a - 3 $u(x_a)$ (489 µg/kg). Hence the statement can be considered as questionable.

Of the 41 z-scores that were calculated, 90% was satisfactory, 2 % was questionable and 7% was unsatisfactory. For Cd all the results other than "less than" were satisfactory. Of the 41 zeta-scores, 81% was satisfactory, 7% was questionable and 12% was unsatisfactory.

Different techniques are used for analysing trace element concentrations in the test samples, whereby ICP-MS was the most commonly used technique. The number of participants per technique was too small to make inferences on the performance of the different techniques.

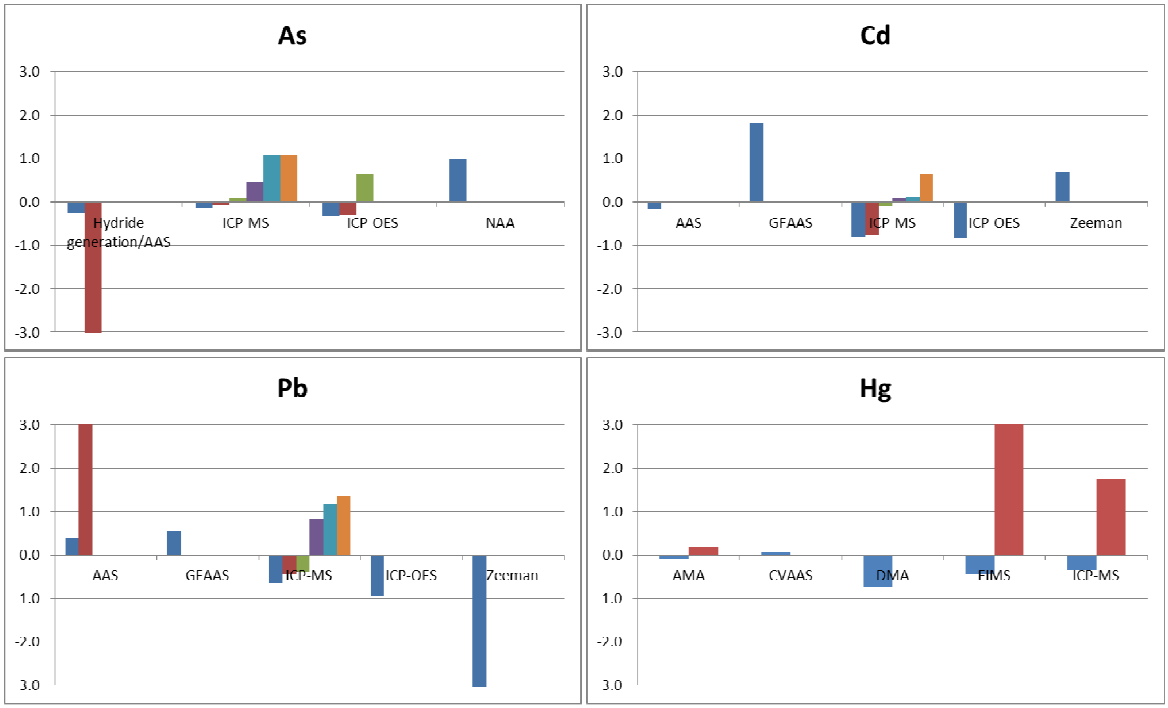


Figure 5. Z-scores obtained by the participants, ordered per element and per technique. The z-scores are topped-off at -3 and +3.

Additional information was gathered from the questionnaire that participants were asked to fill in. All the laboratories have a quality system in place (ISO 17025). Two out of 12 participating laboratories did not carry out this type of analysis on a routine basis.

Five laboratories usually provide an uncertainty statement to their customers for this type of analysis, 7 laboratories usually do not. One of the latter specified they only provide an uncertainty estimate for non-compliant samples. For uncertainty estimation, 6 laboratories used one of the methods prescribed by the FASFC (Fig 6). The other laboratories based their uncertainty estimations on calculations according to ISO-GUM (n = 2), results of proficiency tests (n = 2), in-house validation (n = 1) or control charts (n = 1). One laboratory did an expert estimate to determine its measurement uncertainty for As.

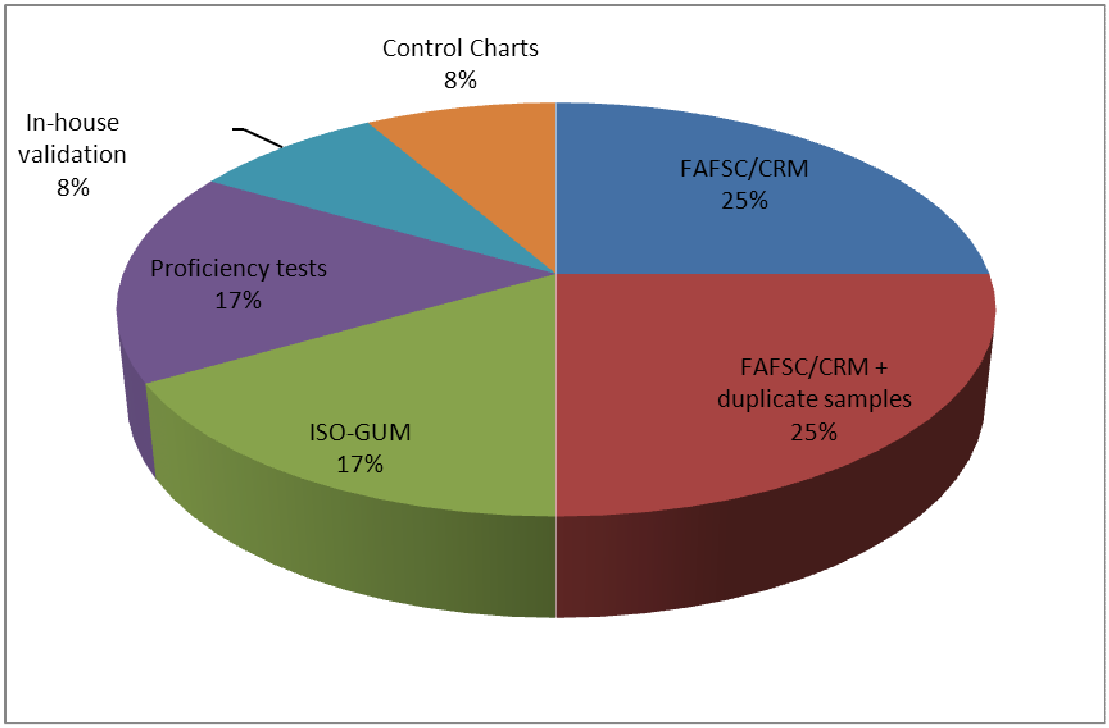


Figure 6. Different approaches used by the participants to estimate the uncertainty of their measurements.

7 Conclusion

Of the twelve laboratories that registered for participation, 11 submitted results for Cd, Pb and Hg, and all 12 submitted results for As. Of the 41 z-scores that were calculated, 90% was satisfactory, 2 % was questionable and 7% was unsatisfactory. Of the 41 zeta-scores, 81% was satisfactory, 7% was questionable and 12% was unsatisfactory.

Annexes

Annex 1: Invitation letter to laboratories

Dear colleague,

It is my pleasure to invite you to participate in the proficiency tests (PT) for the detection of trace elements and/or mycotoxins organized by the National Reference Laboratories (NRL) of the Operational Direction "Chemical Safety of the Food chain" (OD-CFC). The goal of the PT is to determine the performance of individual laboratories for specific tests. The PTs are organised according to the ISO/IEC 17043 norm: 2010 Conformity assessment – General requirements for proficiency testing.

The following PTs will be organized by the OD-CFC in 2011 for the labs involved in the official control program of the FASFC.:

- 1) **PT-2011-NRL-TE-FASFC** "Determination of As, Cd, Pb and Hg in food supplements"
- 2) **PT-2011-NRL-Mycotoxin-FASFC** "Determination of T-2 and HT-2 in cereals"

The time schedule for the PTs is as follows:

• Closing date for the application:	31 March 2011
• Shipment of the samples:	Week 23, 1th of June 2011
• Submission of the test results:	Week 36, 1th of September 2011
• Draft report:	Week 45, 1th of November 2011
• Final report:	Week 49, 1th of December 2011

If your lab is accredited for trace element in foodstuffs, participation to the PT-2011-NRL-TE-FASFC "Determination of As, Cd, Pb and Hg in food supplements" is mandatory for all accredited elements

If your lab is accredited for T-2 and/or HT-2 in cereals, participation to the PT-2011-NRL-mycotoxin-FASFC "Determination of T-2 and HT-2 in cereals" is mandatory for the accredited toxins

The costs for PT-2011-NRL-TE-FASFC and PT-2011-NRL-Mycotoxin-FASFC will be billed directly by the Federal Agency for the Safety of the Food Chain (FASFC).

You can receive more information about our PT programme by contacting directly Ludwig De Temmerman (ludet@var.fgov.be) and/or Jean-Christophe Pizzolon (jepiz@var.fgov.be) for the PT concerning trace elements and Alfons Callebaut (alcal@var.fgov.be) and/or Philippe Debongnie (phdeb@var.fgov.be) for the PTs concerning mycotoxins

We hope you will find this a useful tool to support your laboratory's Quality Assurance system and look forward to receiving your application before **the 31th of March 2011.**

If you are not the correct contact person for this message or if you know other colleagues that might be interested, please feel free to forward this invitation to your own colleagues or colleagues from other institutes.
If you would no longer like to receive this email, please send us a reply and we will remove you from our mailing list.

Kind regards,

Dr ir Luc PUSSEMIER
CODA-CERVA
Operational Director « Chemical Safety of the Food chain »
Lupus@var.fgov.be
www@var.fgov.be

Annex 2: Results of the homogeneity studies

	As	Cd	Pb	Hg
Cochran test for variance outliers				
Cochran test statistic	0.310	0.709	0.524	0.624
Critical (95%)	0.602	0.602	0.602	0.602
Cochran < critical?	accept	accept[(1)]	accept	accept[(1)]
Test for sufficient homogeneity				
$\mathbf{S_{an}^2}$	494455	210	1446	1.5
$\mathbf{S_{sam}^2}$	640610	88	501	1.1
$\mathbf{\sigma_{all}^2}$	2394593	953	2291	3
F1	1.88	1.88	1.88	1.88
F2	1.01	1.01	1.01	1.01
Critical	5001234	2003	5768	6.9
$\mathbf{S_{sam}^2}$ **< critical?**	accept	accept	accept	accept

[(1)] The Cochran's test statistic value was still below the critical value at the 99% level (0.718), therefore there was no exclusion of one of the tested pairs.

Annex 3: Letter accompanying the sample

PRO/2.5/06/DOC03/V02 : INSTRUCTIONS TO THE PARTICIPANTS
PRO/2.5/06/DOC03/V02 : INSTRUCTIES AAN DE DEELNEMERS
PRO/2.5/06/DOC03/V02 : INSTRUCTIONS AUX PARTICIPANTS

Type of proficiency test / Type proficiency test / Type d'essai d'aptitude :
PT-2011-NRL-Trace Elements-FASFC / As, Cd, Pb and Hg / food supplements of vegetable origin / June-August 2011

Analyte(s) / Analyt(en) / Analyte(s) :
As, Cd, Pb and Hg

Matrix(-ces) / Matrix(-ces) / Matrice(s) :
Food supplement of vegetable origin

Number of materials sent / Aantal verstuurde materialen / Nombre de matériaux envoyés :
1 bottle

Storage method / Wijze van bewaring / Mode de conservation :
Store in a dark place at room temperature until analysis

Data to be sent and to whom / Gegevens die moeten opgestuurd worden en aan wie / Données à envoyer et à qui :
Data have to be filled in in the template which will be sent by e-mail to the contact person indicated on your registration form. The template has to be send by e-mail to Jean-Christophe Pizzolon (JeanChristophe.Pizzolon@var.fgov.be).

Deadline for sending the results to the OD-CSF / Datum (deadline) waarop de resultaten moeten opgestuurd worden naar de OD-CVV / Date (deadline) à laquelle les résultats doivent être envoyés à la DO-SCA :
September 1th, 2011

Specific instructions / Specifieke Intructies / Instructions spécifiques :

1° Receiving the sample:

a) This parcel contains:
- one plastic container with approximately 6 g of homogenised sample
- a sample receipt confirmation form

b) Please check whether the sample remained undamaged during the transport and send us as fast as possible the sample receipt confirmation form (scan and mail it to JeanChristophe.Pizzolon@var.fgov.be).

c) Before starting an analysis, re-homogenise the sample by shaking for ±30 sec.

2° Reporting results:

The procedure you will follow for this exercise should be as close as possible to the method you use in routine sample analysis.

a) Three independent measurements per parameter are needed.
b) **Correct** the measurements results for **recovery**
c) Report measurement uncertainty.

Your participation is greatly appreciated. If you have any remaining questions, please feel free to contact me.

Best regards,
Jean-Christophe Pizzolon

Reminder : for the Belgian official control labs, the results are communicated to the FASFC (FAVV-AFSCA)
Herinnering : Voor de belgische erkende labo's worden de resultaten aan het FAVV meegedeeld
Rappel : Pour les laboratoires belges agréés, les résultats sont communiqués à l'AFSCA

Annex 4: Sample receipt confirmation form

PRO/2.5/06/DOC04/V02:

PROFICIENCY TESTING MATERIALS RECEIPT FORM
FORMULIER VAN BEVESTIGING VAN ONTVANGST VAN HET MATERIAAL
FORMULAIRE DE CONFIRMATION DE RÉCEPTION DU MATÉRIEL

NAME ORGANISATION (LAB) / NAAM ORGANISATIE (LABO) / NOM ORGANISATION (LABO) :

CONTACT PERSON / CONTACTPERSOON / PERSONNE DE CONTACT :

TEL : FAX :

E-MAIL :

DATE OF THE RECEIPT / DATUM ONTVANGST VAN HET MATERIAAL / DATE DE RECEPTION DU MATERIEL :

STATE OF MATERIALS RECEIVED / STAAT BIJ ONTVANGST / ETAT A LA RECEPTION :

O GOOD / GOED / BON

O OPEN / OPEN / OUVERT

O BAD (specify) / SLECHT (specificeren) / MAUVAIS (à préciser) :

REMARKS / OPMERKINGEN / REMARQUES :

DATE / DATUM / DATE : SIGNATURE / HANDTEKENING / SIGNATURE :

Annex 5: Reporting form and questionnaire

CERVA

CENTRE D'ETUDE ET DE RECHERCHES VÉTÉRINAIRES ET AGROCHIMIQUES

LEUVENSESTEENWEG 17 – B 3080 TERVUREN

May 30th 2011

CODA-CERVA

National Reference Laboratory for Trace Elements in Food and Feed

Results Reporting Form
Trace elements in a food supplement of vegetable origin
June-August 2011

Lab Code: ……

Element	**Technique used**	**Units**	**Replicate 1**	**Replicate 2**	**Replicate 3**	**Mean value**	**Extended uncertainty (k=2)**
As		mg/kg					
Cd		µg/kg					
Pb		µg/kg					
Hg		µg/kg					

1) What is the basis of your measurement uncertainty estimate?

O Uncertainty calculation according to ISO-GUM
O Uncertainty of the method as determined during in-house validation
O FASFC method:
    O Based on CRM
    O Based on CRM + duplicate samples
    O Based on proficiency tests
O Uncertainty based on proficiency tests
O Other (please specify):

2) Do you usually provide an uncertainty statement to your customers for this type of analysis?

O Yes
O No

3) Does your laboratory carry out this type of analysis (as regards the parameters, matrix and methods) on a routine basis?

O Yes
O No

4) Does your laboratory have a quality system in place?

O Yes*
O No

*If yes please specify:
    O ISO 17025
    O ISO 9000 series
    O Other (please specify):

Annex 6: Participating Laboratories:

Chemiphar N.V., Belgium
CODA-CERVA, Belgium
Dr. A. Verwey, Silliker Netherlands, The Netherlands
Eurofins WEJ Contaminants GmbH, Germany
FAVV – FLVVG, Belgium
Institut Ernest Malvoz – Laboratoire Santé et Cadre de Vie, Belgium
Institut Scientifique de Santé Publique (ISP), Belgium
Laboratorium Ecca NV, Belgium
Lovap NV, Belgium
POVLT Laboratorium, Belgium
SCK•CEN, Belgium
SGS Belgium NV, Division IAC, Belgium