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Interlaboratory Comparison Report
December 2011

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The mission of the JRC-IRMM is to promote a common and reliable European measurement system in support of EU policies.

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15th December 2011

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Summary

The Institute for Reference Materials and Measurements (IRMM) of the Joint Research Centre (JRC), a Directorate-General of the European Commission, operates the International Measurement Evaluation Programme® (IMEP). It organises interlaboratory comparisons (ILC's) in support to EU policies. This report presents the results of an ILC which focussed on the determination of total Cd and Pb in baby food in support of Commission Regulation (EC) No 1881/2006 of 19 December 2006 setting maximum levels for certain contaminants in foodstuffs.

The test material used in this exercise was baby food formula purchased in a local pharmacy and prepared by the Reference Materials Unit of the IRMM for this exercise. Each participant received one bottle containing approximately 15 g of test material. Sixty-six laboratories from 23 countries registered to the exercise and 61 of them reported results. Participants were asked to analyse the measurands in the powder and in the reconstituted form (powder diluted with water, 1:8 fold, to mimic the product as consumed).

The assigned value for total Cd was determined by LGC Ltd (UK) and IRMM using direct isotope dilution inductively coupled plasma mass spectrometry (ID-ICP-MS). The assigned value for total Pb was determined by IRMM using ID-ICP-MS. The standard deviation for proficiency assessment $\hat{\sigma}$ was set at 22 % of the assigned value based on the Thompson modified equation.

Laboratories were rated with z- and ζ-scores (zeta-scores) in accordance with ISO 13528. Most of the participants reported results together with the corresponding measurement uncertainty.

The outcome of this exercise is clearly influenced by the very low level of Cd and Pb content in the test material which triggered: - a high number of "less than" values; - overestimated values especially for lead very likely due to contamination; and - a visible method influence in the case of lead (methods based on atomic absorption were not sensitive enough to attain such low limits of detection). The results were also evaluated with regard to the reported limit of detection and some incoherencies were observed here as well.

IMEP support to EU policy

IMEP is owned by the JRC – IRMM and provides support to the European measurement infrastructure in the following ways:

- IMEP **distributes metrological traceability** from the highest level down to the routine laboratories. Laboratories can benchmark their measurement result against the IMEP reference value which is established according to metrological best practice.

- IMEP helps laboratories to assess their estimate of **measurement uncertainty**. Participants are invited to report the uncertainty on their measurement result. IMEP integrates the estimate into the scoring, and provides assistance for the interpretation.

IMEP supports EU policies by organising interlaboratory comparisons (ILC) in the frame of specific EU legislation, or on request of a specific Directorate-General. IMEP-33 provided specific support to the following stakeholders:

- To the European Co-operation for Accreditation (EA) in the frame of a formal collaboration on a number of metrological issues, including the organisation of interlaboratory comparisons. National accreditation bodies were invited to nominate a limited number of laboratories for free participation in IMEP-33. Mrs. Hanna Tugi from the Polish Centre for Accreditation (PAC) liaised between EA and IMEP for this ILC. This report does not discern the EA nominees from the other participants. Their results are however summarised in a separate report to EA.

- To the European Union Reference Laboratory for Heavy Metals in Feed and Food (EU-RL-HM) in the frame of the support to the National Reference Laboratories (NRLs). The exercise was announced to the network of NRLs and they were invited to distribute the information between control laboratories in their respective countries.

IMEP is accredited according to ISO Guide 43-1.

Contents

1 Introduction

The IMEP-33 exercise was carried out in collaboration with the European Union Reference Laboratory for Heavy Metals (EU-RL-HM), who organised in parallel the proficiency test (PT) IMEP-113 for its network of National Reference Laboratories (NRLs), using the same test material.

Both exercises were requested by the Directorate General for Health and Consumer Protection (DG SANCO) in view to reduce the maximum levels of Cd and Pb in the legislation.

According to the Scientific Opinion on Cadmium (Cd) in food of the European Food Safety Authority (EFSA) Panel on Contaminants in the Food Chain (CONTAM), the previously established Provisional Tolerable Weekly Intake (PTWI) for cadmium of 7 µg kg^{-1} body weight (b.w.) differs only marginally from the actual weekly intake of cadmium by the general population [1].

The CONTAM Panel established in 2009 a new TWI for Cd of 2.5 µg kg^{-1} b.w. However, subgroups such as vegetarians, children, smokers and people living in highly contaminated areas may exceed the TWI by a factor of 2. Exposure for toddlers and children appears to be higher than for adults, primarily due to the greater amount of food consumed in relation to body weight. Milk, dairy products and baby formulas are the main contributors of Cd intake for babies and toddlers, in particular soya milk substitutes, which have significantly higher Cd levels than the other products of this category [1], because vegetables are known to accumulate Cd.

The situation is similar for lead (Pb) where the CONTAM Panel concluded that the current PTWI of 25 µg kg^{-1} b.w. is no longer appropriate as there is no evidence for a threshold for critical lead-induced effects. Therefore, the Panel considered it more appropriate to calculate margins of exposure to support the risk characterisation. In pregnant women, children and infants the margins of exposures were such that the possibility of an adverse effect, particularly in children from 1-7 years of age, cannot be excluded [2].

The CONTAM Panel concluded that the current exposure to Cd should be reduced at the population level and that the maximum limits for Pb should be lowered as much as possible.

IMEP-33 was organized to check the analytical capabilities of European control laboratories to determine low concentrations of total Cd and Pb in soya-based baby formulas, in powder form and reconstituted (eight fold dilution).

2 Scope

The scope of this PT was to test the competence of the participating laboratories to determine the total content of Cd and Pb in baby food (milk formula) at a very low mass fraction level. Measurements were to be done on the powder and the reconstituted formula (eight fold dilution), because in principle the maximum limits in European legislation refer to the food commodities as consumed.

The exercise followed the administrative and logistics procedures of IMEP (IRMM). The PT was carried out in the frame of Commission Regulation (EC) No 1881/2006 of 19 December 2006 setting maximum levels for certain contaminants in foodstuffs [3].

3 Set-up of the exercise

An invitation letter for participation was sent to the EA coordinator (Annex 1) on 28 March 2011 for distribution to nominated and interested laboratories. The NRL network and other laboratories having shown interest in IMEP activities were informed on 30 March 2011 by email (Annex 2). NRLs were thus given the opportunity to invite control laboratories from their respective countries. Finally, a web announcement (Annex 3) was made for the exercise on the IMEP webpage on 04 April 2011 [4].

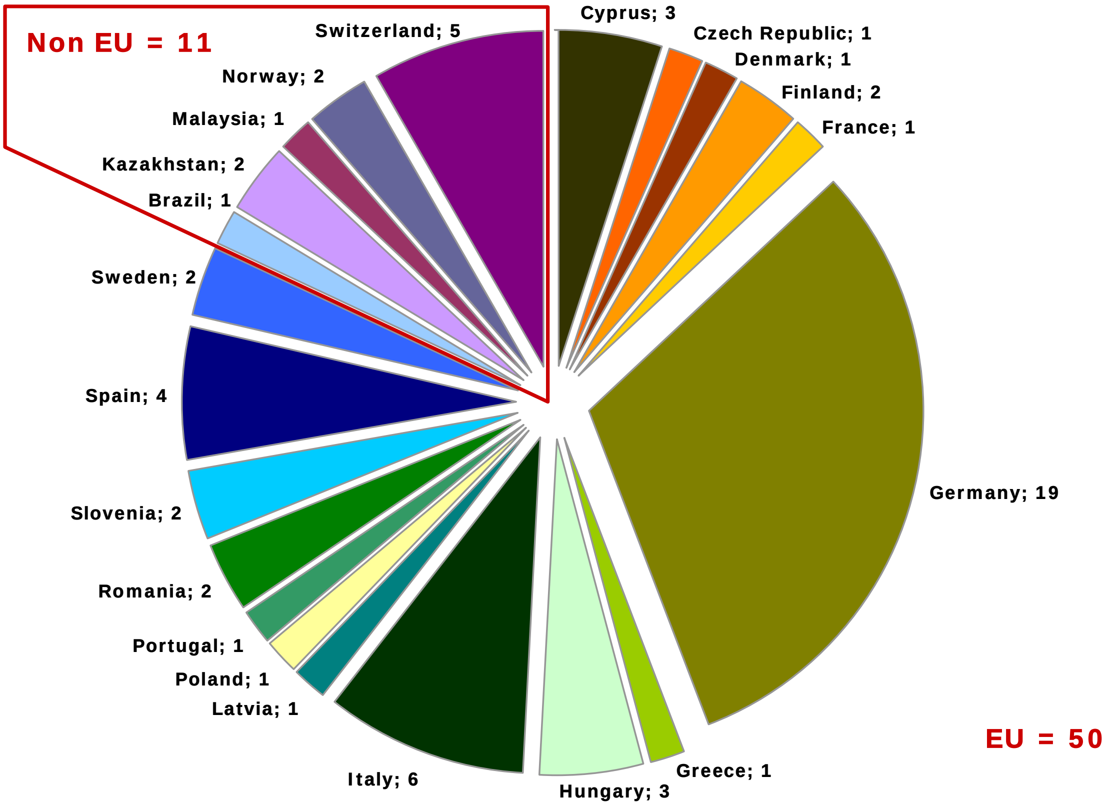
Laboratories could register until 15 May 2011. Samples were sent out to the participants on 17 May 2011. The reporting deadline was set at 24 June 2011 for all laboratories. It was extended by one week for one laboratory, because of the late reception of the sample by the participant.

Laboratory codes were given randomly after the registration deadline. Figure 1 shows the participating countries and the number of participants having reported results.

3.1 Confidentiality

EA was invited to nominate laboratories for participation. The following confidentiality statement was made to EA: "*Confidentiality of the participants and their results towards* *third parties is guaranteed. However, IMEP will disclose details of the participants that have been nominated by EA to the EA working group for ILCs in Testing. The EA accreditation bodies may wish to inform the nominees of this disclosure.*"

Fig. 1 – Country distribution in IMEP-33 based on number of participants having submitted results



3.2 Distribution

On 17 May 2011 IRMM dispatched to the participants parcels, each including:

- one bottle containing approximately 15 g of test material;
- an accompanying letter with instructions on measurands, sample storage conditions, protocol for the preparation of the reconstituted form, moisture determination, number of measurements, the individual access code for the result reporting website and the reporting deadline (Annex 4);
- a form for confirmation of arrival to be sent back to IMEP at reception of the test material (Annex 5);
- a summary questionnaire to be filled in when reporting results on line (Annex 6).

The status of delivery of parcels was monitored using the messenger's parcel tracking system on the internet except for one participant who wished to be sent the sample by post. In all but one cases, the sample was delivered within a week. One laboratory received the test material only in the week before the reporting deadline.

3.3 Procedure to apply

The measurands were defined as "total Cd and Pb in baby food, to be measured in the powder and in the reconstituted form". Laboratories were asked to perform two or three independent measurements and to report the mean of the results, the measurement uncertainty associated to the mean, the coverage factor and the technique that has been used to perform the measurements. The measurement results were to be corrected for recovery and moisture (moisture determination according to the specified procedure, Annex 4). Participants were asked to follow their routine procedures for analysis. The results were to be reported in the same manner (e.g. number of significant figures) as those normally reported to customers.

The results were to be reported in a dedicated on-line form for which each participant received an individual access code. After submitting their results the participants were asked to complete a detailed questionnaire, intended to provide further information on the measurements and the laboratories (Annex 7).

4 Test material

4.1 Preparation

Four boxes of soya based baby formula, 800 g each, were purchased in a local pharmacy in Belgium. The content of the 4 boxes was filled into an acid-washed and milli-Q rinsed 25 L drum and homogenised for 30 minutes in a three-dimensional mixer (WAB, Dynamix CM-200, Basel, Switzerland). The final mass of 3 kg was distributed in 15 g portions and fed into 100 ml acid-washed bottles.

4.2 Homogeneity and stability

The homogeneity and stability studies were performed by ALS Scandinavia AB (Sweden). Homogeneity was evaluated according to ISO 13528 [5]. The material proved to be homogeneous for total cadmium and lead. The contribution from homogeneity (u_{bb}) to the uncertainty of the reference value (u_{ref}) was calculated using SoftCRM [6].

The stability study was conducted following the isochronous approach [7-8]. The evaluation of the stability of the test item was made using the software SoftCRM [6]. The material proved to be stable for the five weeks that elapsed between the dispatch of the samples and the deadline for submission of results, for both total Cd and Pb.

The analytical results and statistical evaluation of the homogeneity and stability studies are provided in Annex 8.

5 Reference values and their uncertainties

5.1 Assigned value X_{ref}

The total Cd and Pb mass fractions were determined by LGC Ltd (UK) and IRMM using direct Isotope Dilution – Inductively Coupled Plasma – Mass Spectrometry (ID-ICP-MS). The assigned value for Cd was the mean of the results reported by the two certifiers. LGC had problems to determine total Pb with a reasonable low uncertainty due to contamination problems. Therefore, only the value reported by IRMM was used as assigned value for total Pb. The assigned value for the reconstituted formula was derived from formulation using the assigned value for the powder form (for each measurand) divided by the dilution factor of 8.

5.2 Associated uncertainty u_{ref}

The associated uncertainties (u_{ref}) of the assigned values in the powder were calculated combining the uncertainty of the characterization (u_{char}) with the contributions for homogeneity (u_{hom}) and stability (u_{st}):

$$\mathrm{u}_{\mathrm{ref}} = \sqrt{\mathrm{u}_{\mathrm{char}}^2 + \mathrm{u}_{\mathrm{hom}}^2 + u_{st}^2}$$

Where:

- u_{char} is the estimated uncertainty calculated according to the ISO Guide for the Expression of Uncertainty in Measurement (GUM) [9];
- u_{hom} is the standard uncertainty arising from the homogeneity study;
- u_{st} is the standard uncertainty arising from the stability study.

For total Cd u_{char} was estimated as:

$$u_{char} = \sqrt{u_{LGC}^2 + u_{IRMM}^2}$$

Where:

- u_{LGC} is the standard uncertainty reported by LGC
- u_{IRMM} is the standard uncertainty reported by IRMM

While for total Pb, $u_{char} = u_{IRMM}$.

In the reconstituted formula the associated uncertainty ($u_{ref\ reconst}$) of the assigned values were mathematically calculated combining the associated uncertainty of the assigned values of the powder with the uncertainty introduced by the gravimetric preparation of the reconstituted formula (u_{grav}) as:

$$u_{ref\ reconst} = \sqrt{\frac{u_{ref}^2}{8} + u_{grav}^2}$$

Where:

-$u_{ref\ reconst}$: is the associated uncertainty of the assigned value in the reconstituted formula

-u_{ref}: is the associated uncertainty of the assigned value in the powder

-u_{grav}: is the uncertainty introduced by the gravimetric preparation (8 fold dilution) of the reconstituted formula, calculated according to the ISO Guide for the Expression of Uncertainty in Measurement (GUM) [9].

$u_{ref\ reconst}$ does not reflect the difficulties introduced by the fact that the reconstituted formula is not a perfect solution but rather a suspension.

5.3 Target standard deviation $\hat{\sigma}$

The standard deviations for proficiency assessment $\hat{\sigma}$ (also called target standard deviations) were calculated applying the Thompson modified equation for both measurands and was set to 22 % of the respective assigned value.

An overview of all reference values (X_{ref}, u_{ref}, U_{ref}, $\hat{\sigma}$) is given in table 1.

Table 1 - Assigned values, their associated uncertainties and target standard deviations for the measurands of this ILC (all values in mg kg^{-1}).

Certifier	**Total Cd (X_n ± U_n)**		**Total Pb (X_n ± U_n)**	
	Powder	Reconst. Formula	Powder	Reconst. Formula
IRMM	0.01191 ± 0.00015		0.00650 ± 0.00031	
LGC	0.01160 ± 0.00030			
X_{ref}	0.01176	0.00147	0.00650	0.00081
u_{char}	0.00034		0.00031	
u_{bb}	0.00008		0.00022	
u_{st}	0.00009		0.00021	
u_{ref} ($u_{ref\ reconst}$)^{a}	0.00055	0.00007 ^{a}	0.00043	0.00005 ^{a}
U_{ref} (k=2)*	0.00109	0.00014	0.00087	0.00010
$\hat{\sigma}$	0.00260	0.00032	0.00143	0.00018

**X_{ref} is the reference value and U_{ref}= k·u_{ref} is the estimated associated expanded uncertainty; with a coverage factor k= 2 corresponding to a level of confidence of about 95 %.*

6 Evaluation of results

6.1 General observations

Of the 66 laboratories that registered for participation 61 submitted results and completed the associated questionnaire. From these results, those reporting "less than" and "0" values were not included in the evaluation (Table 2). However, reported "less than" values were compared with the corresponding X_{ref} – U_{ref} values. If the reported limit value is lower than the corresponding X_{ref} – U_{ref}, this is an incorrect statement, since the laboratory should have detected the respective element.

As for reported "0" values, it is generally recommended not to report any value when a measurand has not been detected, or to give a "less than" value.

Table 2 - Number of reported results and "less than" values per measurand

	Total Cd		***Total Pb***	
	Powder	Reconstituted	Powder	Reconstituted
N° *	54	38	36	25
"less than" ("0")	6 (1)	14	23	26

- N° – number of participants having reported results

6.2 Scores and evaluation criteria

Individual laboratory performance was expressed in terms of z- and ζ-scores in accordance with ISO 13528 [5]

$$z = \frac{x_{lab} - X_{ref}}{\hat{\sigma}} \qquad \text{and} \qquad \zeta = \frac{x_{lab} - X_{ref}}{\sqrt{u_{ref}^2 + u_{lab}^2}}$$

where:		
	x_{lab}	is the measurement result reported by a participant
	X_{ref}	is the 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 assigned reference values (X_{ref}), and their respective uncertainties are summarised in Table 1. The interpretation of the z- and ζ-score is done as follows:

$\lvert score\rvert \leq 2$	satisfactory result	(green in the tables of Annexes 9-12)
$2 < \lvert score\rvert \leq 3$	questionable result	(orange in the tables of Annexes 9-12)
$\lvert score\rvert > 3$	unsatisfactory result	(red in the tables of Annexes 9-12)

The ζ-score states if the laboratory result agrees with the assigned value within the respective uncertainty. The denominator is the combined uncertainty of the assigned value and the measurement uncertainty as stated by the laboratory. The ζ-score is therefore the most relevant evaluation parameter, as it includes all parts of a measurement result, namely the expected value (assigned value), its uncertainty and the unit of the result as well as the uncertainty of the reported values. An unsatisfactory ζ-score can either be caused by an inappropriate estimation of the concentration or of its uncertainty or both.

The standard uncertainty of the laboratory (u_{lab}) was estimated by dividing the reported expanded uncertainty by the reported coverage factor, k. When no uncertainty was reported, it was set to zero ($u_{lab} = 0$). 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 √3, as recommended by Eurachem and CITAC [10].

Uncertainty estimation is not trivial; therefore an additional assessment was provided to each laboratory reporting uncertainty, indicating how reasonable their uncertainty estimate is. The standard uncertainty from the laboratory (u_{lab}) is most likely to fall in a range between a minimum uncertainty (u_{min}), and a maximum allowed (u_{max}). u_{min} is set to the standard uncertainty of the reference value. It is unlikely that a laboratory carrying out the analysis on a routine basis would measure the measurand with a smaller uncertainty than the expert laboratories chosen to establish the assigned value. u_{max} is set to the target standard deviation ($\hat{\sigma}$) accepted for the PT. If u_{lab} is smaller than u_{min}, the laboratory may have underestimated its uncertainty. Such a statement has to be taken with care as each laboratory reported only measurement uncertainty, whereas the uncertainty of the reference value also includes contributions of homogeneity and stability. If those are large, measurement uncertainties smaller than u_{min} are possible and plausible. If $u_{lab} > u_{max}$, the laboratory may have overestimated the uncertainty. An evaluation of this statement can be made when looking at the difference of the reported value and the assigned value: if the difference is small and the uncertainty is large, then overestimation is likely. If, however, the deviation is large but is covered by the uncertainty, then the uncertainty is properly assessed but large. It should be pointed out that u_{max} is only a normative criterion if set down by legislation.

The z-score compares the participant's deviation from the reference value with the target standard deviation for proficiency assessment ($\hat{\sigma}$) used as common quality criterion. $\hat{\sigma}$ is defined by the PT organiser as the maximum acceptable standard uncertainty. Values for $\hat{\sigma}$ in IMEP-33 were set to 22 % of the respective assigned value, following the modified Thompson equation.

6.3 Relevance of the limit of detection in the outcome of IMEP-33 and its impact on the reported results

As indicated in the introduction, according to the scientific opinions of the EFSA CONTAM Panel on total Cd and Pb, there is an absolute need to reduce the weekly intake of those contaminants in food, mainly for some subpopulations such as babies and children. The remedial action of the European Commission is to revise the maximum levels for Cd and Pb in several food commodities in the European legislation on contaminants in food. Nevertheless, to do this in a sound way a number of issues related to the analytical capabilities of the European food control laboratories need to be clarified before hand.

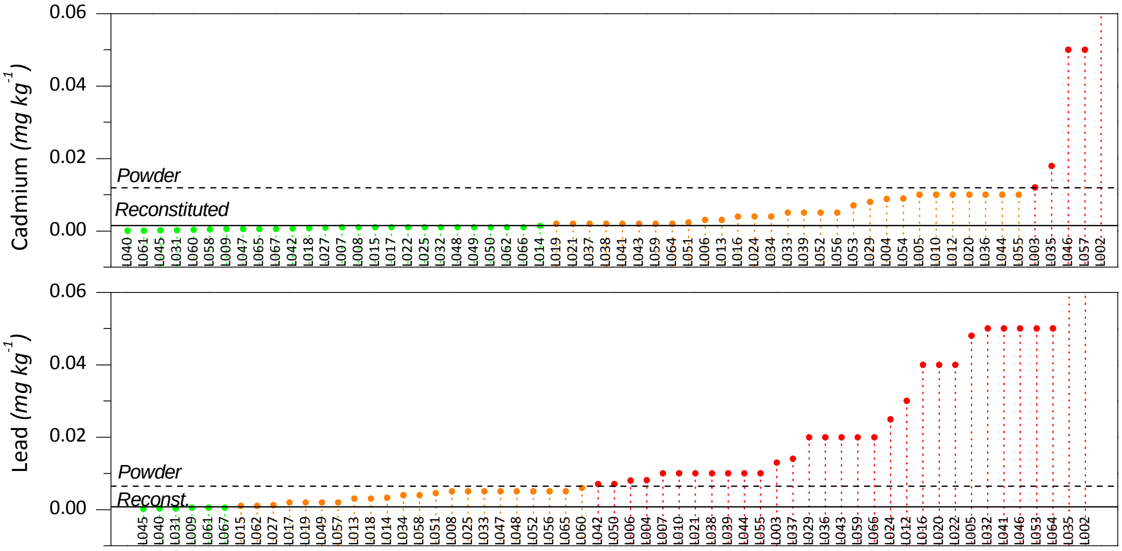
In that context the EU-RL-HM was asked by DG SANCO to provide a clear answer to the question: *"Are NRLs and European food control laboratories able to measure total Cd and Pb in infant soya-based formulas at the low µg kg^{-1} levels in which those elements are normally found in commercially available products, knowing that such low concentrations could be close to the limits of detection (LoD) of the methods used?"*

With this objective in mind the EU-RL-HM decided to organise IMEP-113 and IMEP-33 using as test material a soya-based formula commercially available in the European market without any further addition of Cd and Pb to it, being aware that the very low concentration of total Cd and Pb very likely to be found in the test material, would have an impact in the results reported by the laboratories. Furthermore, participants were asked to report in the questionnaire the LoD of their analytical methods and the approach used to calculate them (Annex 7).

When evaluating the results together with the answers to the questionnaire one observes: (i) a high number of "less than" values (Table 2) and (ii) a tendency to overestimate the mass fraction, particularly in the case of lead. Both observations can be linked to the low content of the measurands in the test material; the first one because mass fractions are close to many laboratories' limit of detection, while the second one maybe due to potential contamination, to be expected at such level of concentration.

The LoDs reported by the participants were compared to the assigned values (X_{ref}) (Fig. 2). In general, better results were reported for Cd than for Pb, as the Cd mass fraction is higher while the respective LoDs for Cd are lower. The mass fraction for Pb is clearly in the range of the reported LoDs, or even lower for the reconstituted form.

Fig. 2 - Reported LoDs plotted together with respective X_{ref} values



The reported LoDs range from 0.0001 to 0.08 mg kg^{-1} for Cd and from 0.0002 to 0.4 mg kg^{-1} for Pb. The participants used two different approaches to determine the LoD, but no connection was observed between the method and the LoD itself or the reported result. The comparison of LoDs with the reported results also revealed the presence of some incoherencies, as summarised in Table 3.

Table 3 - Summary of four identified incoherent situations when evaluating together the results and the LoDs reported by the participants.

Situation	**Participant**			
	Cd powder	**Cd reconst**	**Pb powder**	**Pb reconst**
X_{lab} < LoD	L046, L057	L019, L046, L054	L046	L015, L019, L046, L050, L059
X_{lab} = LoD	L029	L032, L041, L055, L062	L008, L021, L029	L062
"less than *X*" and *X* < LoD		L016, L020, L053		L016, L020, L022, L066
"less than *X*" and *X* >> LoD	L013		L013, L047	

The first three statements can be considered as incorrect, the last one is correct but questionable. It must be assumed that a mistake was made either at the reporting of the results, or of the LoD, or in the laboratory. The concerned participants are advised to verify the different points.

Two approaches were used by the participants to determine the standard deviation (S_0) at concentrations close to the LoD: i) extrapolating the calibration line to zero, or ii) performing replicate measurements on the blank.

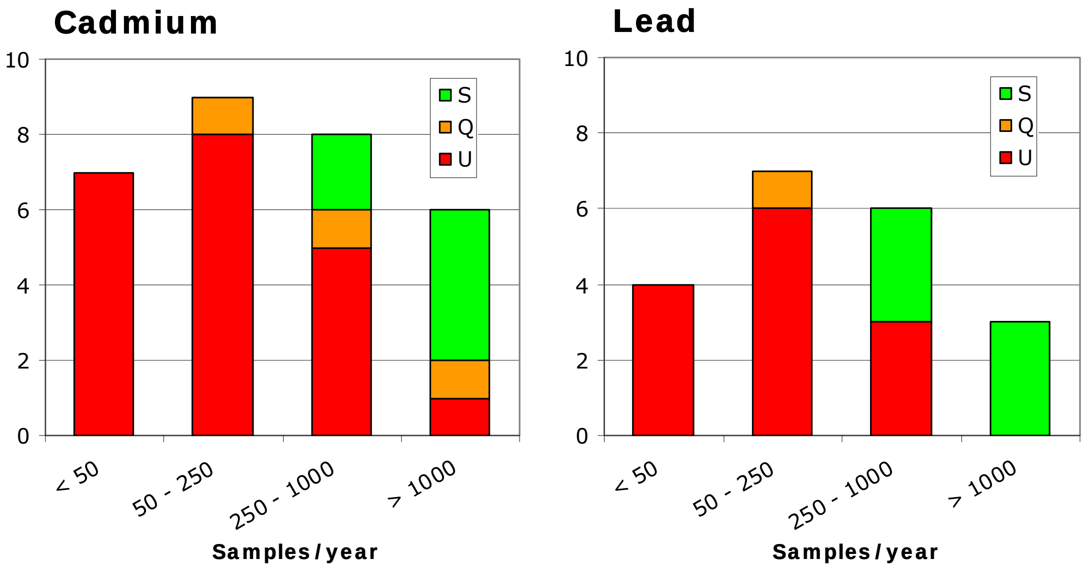
Having determined S_0, participants used two multiplication factors to derive their LoD:
i) LoD = 3 S_0 or ii) LoD = 6 S_0.
Few laboratories did not provide any information regarding LoD.

Finally, the question of the LoD led to evaluating the influence of: - the technique used by the participants; - their experience; and - whether an official method was applied or not. The first two factors appeared to make a difference in the results for Pb. For Cd no influence could be observed.

In the case of Pb, in both forms (powder and reconstituted), a relatively small number of satisfactory results was obtained, all obtained by participants using inductively coupled plasma - mass spectrometry (ICP-MS). In comparison, the other main technique used, electrothermal atomic absorption spectrometry (ETAAS), resulted in a higher proportion of "less than" values, as well as only unsatisfactory z-scores. This clearly indicates that for such low mass fraction ranges ETAAS is not sensitive enough. On the other hand, using ICP-MS does not guarantee good results, as shown by the rather high percentage (36 %, i.e., 9 out of 25) of the unsatisfactory results. Laboratories are advised to verify the method details of the more "successful" participants (Annex 14).

Together with the technique, experience also seems to have an impact on the quality of the results for Pb. This is visible when looking at the distribution of the scorings (z-score) by experience (Fig. 3), expressed by the number of samples analysed by the participants per year.

Fig. 3 – Scores by experience (Unsatisfactory, U, Questionable, Q, Satisfactory, S). Number of laboratories having scoring according to the above classification.



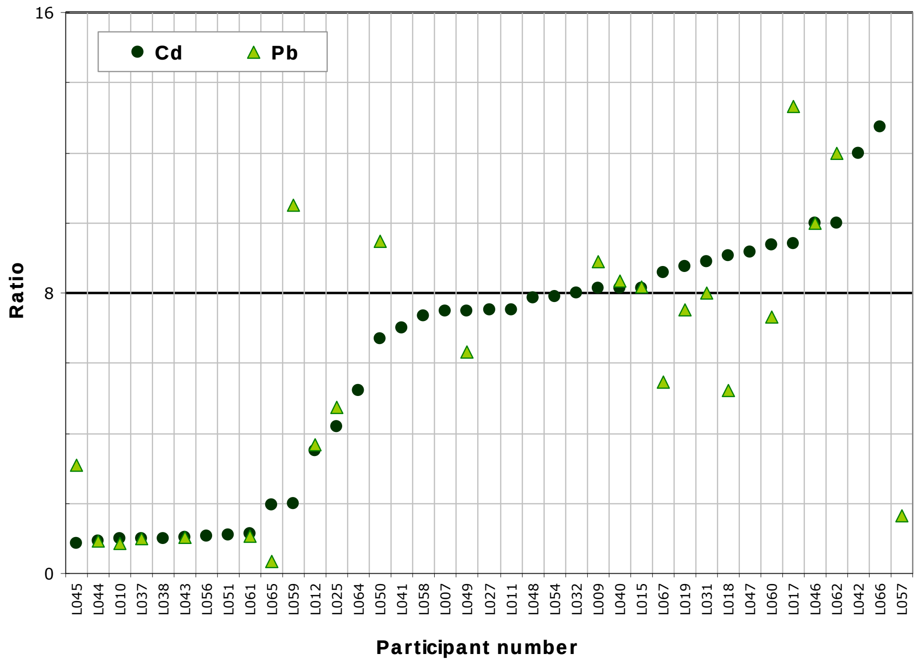
6.4 Evaluation of the ratio – powder / reconstituted

To evaluate the plausibility of the results reported for the reconstituted formula, which represented an additional difficulty from an analytical point of view, since the concentrations were closer to the LoDs, IMEP also investigated the effect of reconstituting the powder. According to the protocol given to the participants for the preparation of the reconstituted form, the dilution factor is 8. Where available, the ratio "result powder / result reconstituted" was calculated. Ideally, this ratio should be around 8. Figure 4 shows ratios ranging from 0.3 to 13.3. In addition, a number of laboratories reported inconsistent ratios for Cd and Pb. These ratios should be similar for the two measurands. Such inconsistencies indicate the presence of an error in the determination of one or the other measurand (or both) that was not identified/questioned by the laboratories themselves.

Although the ratio should be 8, ratios around "1" were not considered as incorrect. It can be assumed that the concerned participants have measured the reconstituted form, and have back calculated the obtained mass fraction to that of the powder. This identifies an ambiguity of the corresponding question.

It is unclear whether laboratories reporting values for total Cd and Pb in the reconstituted formula which are precisely eight times lower than those for the powder, actually determined them experimentally or simply dividing the results obtained in the powder by 8.

Fig. 4 – Ratios "result powder / result reconstituted" sorted by values for Cd



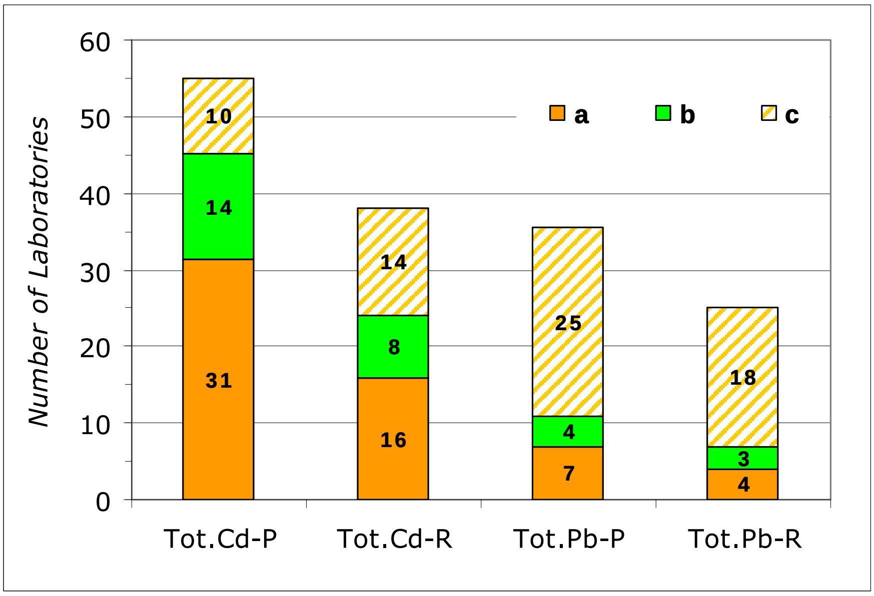
6.5 Uncertainty evaluation

Five out of the total 61 participants did not report an uncertainty associated to their results (~ 8 %), including one who has reported "0" as uncertainty. Another participant reported "0" as uncertainty, but only for the Cd results. Furthermore, 2 participants having reported uncertainties for the measurands in the powder form did not do so for the reconstituted form.

L010, L014 and L062 reported abnormally high measurement uncertainty values with their results. It looks as if they reported the uncertainty in percentage (not in mg kg^{-1}), as requested in the instructions (Annex 4).

Of the 56 participants who reported a measurement uncertainty, 4 (~ 7 %) did not give a value for the coverage factor. The coverage factor *k* is defined and explained in detail in the GUM [9]. Figure 5 gives an overview of the uncertainty evaluation. The share of participants in group (a), giving uncertainties within $u_{min}(=u_{ref})$ to $u_{max}(=\hat{\sigma})$, ranges between 16 % and 57 % only. Furthermore, it appears that participants tend to overestimate the uncertainty ($u_{lab} > u_{max}$ in Fig. 5), rather than to underestimate it ($u_{lab} < u_{min}$ in Fig. 5, note that this group also includes those who have not reported an uncertainty and for whom U was set to "0"). This is mostly true for total Pb in the powder and the reconstituted form. Despite this uncertainty overestimation the reported results did not overlap with the accepted range of results as reflected by the low number of laboratories that obtained satisfactory results (Annexes 11 and 12).

Fig. 5 – Uncertainty evaluation; a : $u_{min} \leq u_{lab} \leq u_{max}$; b : $u_{lab} < u_{min}$; and c : $u_{lab} > u_{max}$, xx-P refers to powder whereas xx-R refers to the reconstituted formula.



These findings together with the calculated ζ-scores indicate that laboratories have still difficulties in making a realistic estimation of the measurement uncertainty.

For uncertainty estimates, various combinations of one or more options were given. Four laboratories gave an additional method to base their uncertainty on (Annex 13). One of them gives the Commission Regulation (EC) 333/2007 as alternative, which is surprising, as no formula is given in that regulation [11] to calculate the actual measurement uncertainty of a laboratory, but a formula to benchmark the fit-for-purpose approach for analytical methods.

Participants who are not familiar with the concept of uncertainty are advised to read the GUM [9], the EURACHEM / CITAC Guide CG 4 [10] or to consult the informative web pages of the National Institute of Standards and Technology (NIST) on the subject of uncertainty evaluation [12].

6.6 Laboratory results and scorings

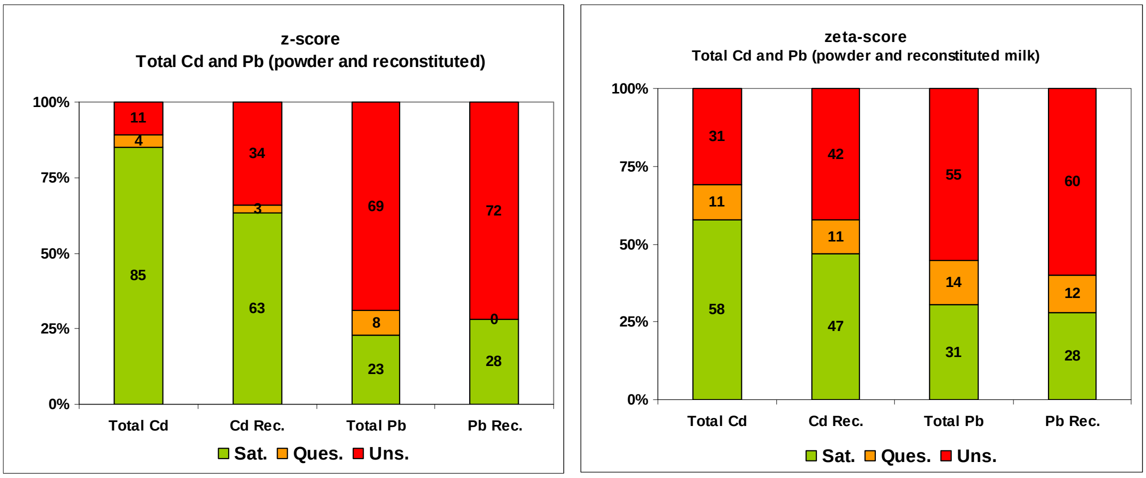
The results reported by the participants are listed in Annex 9 - 12. A table of the results and their graphical representation are provided. The tables also contain z-, ζ-scores and the evaluation of uncertainties. The Kernel density plots, included in the result graphs, are an alternative to histograms, useful to represent the overall structure of a data group and to highlight sub-populations. The software used to calculate Kernel densities was provided by the Statistical Subcommittee of the Analytical Methods Committee (AMC) of the Royal Society of Chemistry [13].

Figure 6 presents an overview of the z- and ζ-scores. The laboratories' performances appear to be good for total Cd in the powder form with 85 % of the participants reporting satisfactory z-scores. The percentage of laboratories obtaining a satisfactory z-score for total Cd in the reconstituted formula decreased to 63 % probably due to the fact that the concentration in the sample was too close to their limit of detection and/or problems related to the reconstitution process.

The number of satisfactory z-scores is significantly lower for total Pb, with 23 and 28 % of laboratories scoring satisfactory for the powder and the reconstituted formula, respectively.

Concerning the ζ-scores, 58 % of the population obtained a satisfactory score for total Cd in the powdered formula, for the other measurands, the percentage of satisfactory scores ranged between 28 % and 47 %. Furthermore, the percentage of participants having both satisfying z- and ζ-scores was between 14 % and 58 % for total Pb and Cd in the powder and 20 % and 42 %, for Pb and Cd in the reconstituted formula, respectively.

Fig. 6 - Overview of scores (in %)



6.7 Further information extracted from the questionnaire

Additional information was gathered from the questionnaire that participants were asked to fill in (Annex 7). Some of the answers are summarised in Annex 13 & 14 (recovery factors, uncertainty related questions, moisture, method related questions, experience and purpose of use of reference materials), or is otherwise highlighted in the following paragraphs.

Fifty-four participants reported recovery factors R, and their distribution range is shown in Annex 13. How R was determined is summarised in Table 4 below.

Table 4 – Determination of the recovery factors

Recovery factor R determined by:	**Number of participants**
a) adding a known amount of the same analyte to be measured (spiking)	12
b) using a certified reference material	30
c) other	3
a) & b)	8
b) & c)	1

Reported as "Others":
- Using another PT material (known value of same analyte from PT report)
- Aqueous standards
- In-house reference materials
- Mix with Standard Solution

An overview of the reported moisture content is shown in Annex 13. Eight participants did not correct for moisture content, among which four gave the reasons listed in the Annex. Nine have reported moisture contents above 90 %, which is very probably a reporting mistake (dry matter instead of water content).

All participants but one has a quality system in place. Two of the 60 are not accredited.

Around 80 % of the participants do regularly participate in ILC schemes for both measurands.

Most of the participants work according to the quality related requirements set by ISO 17025 (50 laboratories), seven participants follow ISO 17025 and ISO 9000 series and other 2 participants follow ISO 17025, ISO 9000 and ISO 14001 series.

Table 5 summarises the reference materials (RM) used for this type of analysis as reported by the participants, and final comments made by participants are listed in Table 6.

Table 5 – Reference materials used by the participants as reported in the questionnaire

Part Nr	Which reference material?
L003	whole milk powder 8435 NIST
L005	SLV, IMEP, FAPAS, PROFEA, BAM
L006	Reference material from other interlaboratory comparisons
L007	Tort-2, oyster tissue, bovine liver
L008	BCRs
L009	leftovers from the above mentioned ILC *(FAPAS, LVU)*
L010	other different materials, proficiency test materials
L011	We used some interlaboratory samples left overs during validation and the aquous NIST1643e solution for routine control together with the calibration standards traceable to NIST.
L012	CRM from National Research Council Canada
L013	BCR/ERM
L014	NIST, FAPAS, BCR
L015	NIST 2976, FAPAS-LVU Material Cheese
L016	Bovine Liver, Tort-1 an others
L017	BCR-450 (BROWN BREAD), internal reference material (milk powder, infant cereal)
L019	NIST 8414, NIST 1547, NIST NIST1567a, NIST 1549
L020	Soya Flour Test Material (FAPAS Proficiency Test 07130)
L021	SRM 1549 - Non-Fat Milk Powder
L022	BRC
L024	BCR 185 R
L027	NBS NIST 1567a Wheat Flour, NBS NIST 1571 Orchard Leaves and others
L029	our lab usually used the governmental standard
L031	NIST 1548a
L032	BCR-191
L033	NIST 1515
L034	peach leaves, rice flour
L037	IRMM 804; SRM 1643e
L038	CNRC TORT2 Lobster Hepatopancreas
L039	NCS ZC73012
L040	BCR 151 Spiked Skim Milk Powder
L041	wheat flour
L042	In-house and commercial references
L044	FAPAS reference material (cacao, coffee, meat)
L046	Various commercial
L047	CRM simulate diet D (Livesmedels Verket)
L048	MERCK cadmium, lead standard solution
L049	NIST 1548a Typical Diet, samples of previous FAPAS Scheme
L050	different plant and animal materials (e.g. BCR 151, LGC 7162)
L052	BCR 679 and DORM-3
L054	LGC 7162 (Strawberry leaves), BCR 191 (Brown Bread)
L055	FAPAS T07117, FAPAS 07148 (FY 2011)
L056	BCR 150, BCR 63R
L057	BCR 151
L058	IRMM 804 (Rice Flour)
L059	FAPAS
L060	IMEP 30 and reference material of nrl
L061	NIST SRM1549
L062	Usually BCR
L064	Merck 1.70309.0100; Merck 1.70328.0100; Ultra Scientific IQC-026; own reference material to control mineralisation step
L066	BCR 150 - Spiked skim milk powder, SRM NIST 1549 - Milk powder
L067	BCR 150, milk powder

Table 6 – Comments as taken from the questionnaire

Part Nr	**Comments**
L004	first time we performed this kind of analysis
L005	We thank you very much for your help.
L006	We unfortunately did not make the measurands in the reconstituted form of the testmaterial.
L011	Lead content in this sample was too low and for next tests of Lead in milk sample it could prepared with a Pb content a bit higher, for example half of the maximum allowed limit
L027	The LoD depends on the sample weight and the dilution of the digested sample. The LoD's told above refer to the reconstituted sample. The LoD for Cd referring to the dry powder is 0,0045 mg/kg, for Pb 0,006 mg/kg.
L034	determination of dry mass: drying for 4h instead of 1h; sample amount not enough => no determination of Pb and Cd in the reconstituted sample
L036	the Recovery not determined In the GSRK 51301-2005
L041	Since our ICP-MS is not working at the moment, we couldn't provide a better limit of detection for lead.
L042	Pb results were not good, but we had to report them, because this page would not let us continue without results
L044	The bottle of IMEP-33 not contain 20g of the test material (11-12g)
L046	The results are below our routinemethods detection limits and are submitted in part of validating for lower detction limits
L050	LoD for powder submitted; the lead seems to be not very homogen in the powder and esp. in the Reconstituted near the LoD
L055	No recovery test performed because we need more sample (near 30g - only to perform one test, one recovery test, one moisture analisys and reconstitution)
L062	1ppb is usually our LOQ for milk and honey. For other matrices the LOQ is 5 ppb

7 Conclusion

The IMEP-33 exercise was run in parallel to the IMEP-113, open for NRLs only. The aim was to verify laboratories' capacity to analyse low levels of Cd and Pb in view of a possible reduction of the maximum limits in legislation.

The results for Cd were generally satisfactory for the powdered infant formula, and slightly worse for the reconstituted form. A tendency for overestimation was observed, which is to be expected at this low mass fraction level, but no other factor of influence could be determined.

Lead appeared to be more problematic than Cd, one reason certainly being that it was present at a lower mass fraction. Already the results for the powdered form show a high number of "less than" values and unsatisfactory scores, and these are increasing for the reconstituted form. Apart from the low mass fraction, other factors of influence appeared to be the technique used and the experience of the participant.

Another important outcome of this exercise was the observation of incoherent ratios between the results from the reconstituted form and the powder form. Eighteen out of 39 participants reported values resulting in inappropriate ratios and/or in different ratios for Cd and Pb. This was rather unexpected as it implies a mistake at some stage of the analytical procedure going unnoticed by the laboratory, despite the reporting and involved verification of results. Another reason might be that laboratories were measuring at the limit of their capabilities and that errors were enhanced.

So far, the maximum limits (MLs) in the European legislation on contaminants, applies to the product as consumed. Due to the very low concentration level to be expected for total Cd and Pb in the reconstituted formula and to problems associated to reconstitute the powder, which result in a suspension and not on a perfect solution, the EU-RL-HM advices to introduce MLs in the legislation which refer to the powder and not to the reconstituted formula.

8 Acknowledgements

C. Contreras and P. Connely from the Reference Materials Unit of IRMM are acknowledged for their support for setting-up the short-term stability study of the test material and in checking the drying method against Karl-Fisher titration. R. Hearn and H. Goenaga (LGC Ltd) are acknowledged for the certified value for total cadmium. Franz Ulberth is thanked for revising the manuscript.

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

Organisation	**Country**
Food Technology Institute	Brazil
GEMANALYSIS LABORATORY	Cyprus
PANCHRIS ANIMAL PREMIX LTD	Cyprus
ARISTOS LOUCAIDES CHEMICAL LABORATORY LTD	Cyprus
Statni veterinarni ustav Praha	Czech Republic
Danish Veterinary and Food Administration, Region West	Denmark
MTTAgrifood research Finland	Finland
MetropoliLab Oy	Finland
Laboratoire Nestlé France	France
LAVES	Germany
CVUA-OWL	Germany
Landesbetrieb Hessisches Landeslabor	Germany
Chemisches Untersuchungsamt der Stadt Hamm	Germany
CVUA Freiburg	Germany
HiPP-Werk Georg Hipp OHG	Germany
Bay. Landesamt für Gesundheit und Lebensmittelsicherheit	Germany
GLU mbH	Germany
IGV GmbH	Germany
Landeslabor Schleswig-Holstein	Germany
Lebensmittelinstitut Oldenburg	Germany
TLLV Bad Langensalza	Germany
Landeslabor Berlin-Brandenburg	Germany
Staatliches Veterinäruntersuchungsamt	Germany
Kreis Mettmann	Germany
Chemisches und Veterinäruntersuchungsamt Sigmaringen	Germany
LAVES Veterinary Institute Hannover	Germany

Organisation	**Country**
LAV Sachsen-Anhalt	Germany
Institut fuer Hygiene und Umwelt	Germany
Laboratory of analytical chemistry, department of chemistry university of Athens	Greece
Food Analytica Ltd.	Hungary
Corvinus University of Budapest	Hungary
Hungarian Authority for Consumer Protection	Hungary
Epta Nord srl	Italy
Istituto Zooprofilattico Sperimentale - Puglia e Basilicata	Italy
IZSLER - Istituto Zooprofilattico Sperimentale della Lombardia e dell'Emilia-Romagna	Italy
Istituto zooprofilattico sperimentale LER	Italy
Istituto Zooprofilattico Sp.le Umbria-Marche	Italy
ENEA	Italy
Republican State State-owned Enterprise	Kazakhstan
LTD	Kazakhstan
LATSERT Latvian Certification Centre Ltd	Latvia
MINISTRY OF HEALTH	Malaysia
Trondheim kommune	Norway
NIFES- National Institute of Nutrition and Seafood Research	Norway
JS HAMILTON POLAND Ltd. Sp. z o.o.	Poland
Silliker Portugal, S.A.	Portugal
Sanitary Veterinary and Food Safety Directorate	Romania
Sanitary Veterinary and Food Safety Directorate Cluj	Romania
Zavod za zdravstveno varstvo Maribor	Slovenia
Institut of Public Health	Slovenia
Laboratory of the Public Health Agency of Barcelona	Spain
Silliker Ibérica	Spain
SANIDAD Y CONSUMO GOBIERNO VASCO	Spain
CENTRO DE SALUD PUBLICA DE ALICANTE	Spain
ALS Scandinavia AB	Sweden
Eurofins Environment AB	Sweden
Kantonale Lebensmittelkontrolle Solothurn	Switzerland
SQTS	Switzerland
Service de la consommation et des affaires vétérinaires	Switzerland
Kantonales Labor Zürich	Switzerland
UFAG LABORATORIEN AG	Switzerland

Abbreviations

AMC	Analytical Methods Committee of the Royal Society of Chemistry
APLAC	Asia Pacific Laboratory Accreditation Cooperation
BIPM	Bureau International des Poids et Mesures
CITAC	Co-operation for International Traceability in Analytical Chemistry
CONTAM	Panel on Contaminants in the Food Chain
DG SANCO	Directorate General for Health and Consumer Protection
EA	European Co-operation for Accreditation
EFSA	European Food Safety Authority
ETAAS	Electrothermal atomic absorption spectrometry
EU	European Union
EURACHEM	A focus for Analytical Chemistry in Europe
EU-RL-HM	European Union Reference Laboratory for Heavy Metals in Feed and Food
GUM	Guide for the Expression of Uncertainty in Measurement
ID-ICP-MS	Isotope dilution - inductively coupled plasma - mass spectrometry
ILC	Interlaboratory Comparison
IMEP	International Measurement Evaluation Programme
IRMM	Institute for Reference Materials and Measurements
JRC	Joint Research Centre
LoD	Limit of detection
NIST	National Institute of Standards and Technology
NRL	National Reference Laboratory
PAC	Polish Centre for Accreditation
PT	Proficiency Test
PTWI	Provisional Tolerable Weekly Intake
RM	Reference material

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[3] Commission Regulation (EC) No 1881/2006 of 19 December 2006 setting maximum levels for certain contaminants in foodstuffs, issued by European Commission, Official Journal of the European Union, L 364/5.

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[9] "Evaluation of measurement data - Guide to the Expression of Uncertainty in Measurement" (GUM 1995 with minor corrections) (2008). Joint Committee for Guides in Metrology (JCGM/WG 1 - BIPM, IEC, IFCC, ILAC, ISO, IUPAC, IUPAP and OIML).

[10] Eurachem/CITAC (2000) "Quantifying Uncertainty in Analytical Measurement", http://www.eurachem.org.

[11] 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 (2007), issued by European Commission, Official Journal of the European Union, L 88/29.

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[13] AMC/RSC (2006), "Representing data distributions with Kernel density estimates", Issued by the Statistical Subcommittee of the Analytical Methods Committee (AMC) of the Royal Society of Chemistry (RSC), AMC Technical Brief.

Annexes

Annex 1 : Invitation to EA to nominate laboratories

EUROPEAN COMMISSION
JOINT RESEARCH CENTRE
Institute for Reference Materials and Measurements

Geel, 28 March 2011
JRC.DG.D6/IB/mdr/ARES(2011)/337019

Mrs Hanna Tugi
Polish Centre for Accreditation PCA
ul. Szczotkarska 42
01-382 Warszawa
POLAND

Dear Hanna,

Intercomparison for cadmium and lead in baby food

The Institute for Reference Materials and Measurements (IRMM) organises an interlaboratory comparison for the **"Determination of the total cadmium and lead in baby food"**.

In the frame of the EA-IRMM collaboration agreement, IRMM kindly invites EA to nominate laboratories for free participation. They should hold (or be in the process of obtaining) an accreditation for this type of measurement.

I suggest that you forward this invitation to the national EA accreditation bodies for their consideration. The number of nominees should not exceed 2-3 laboratories per country.

Confidentiality of the participants and their results towards third parties is guaranteed. However, IMEP will disclose details of the participants that have been nominated by EA to the EA working group for ILCs in Testing. The EA accreditation bodies may wish to inform the nominees of this disclosure.

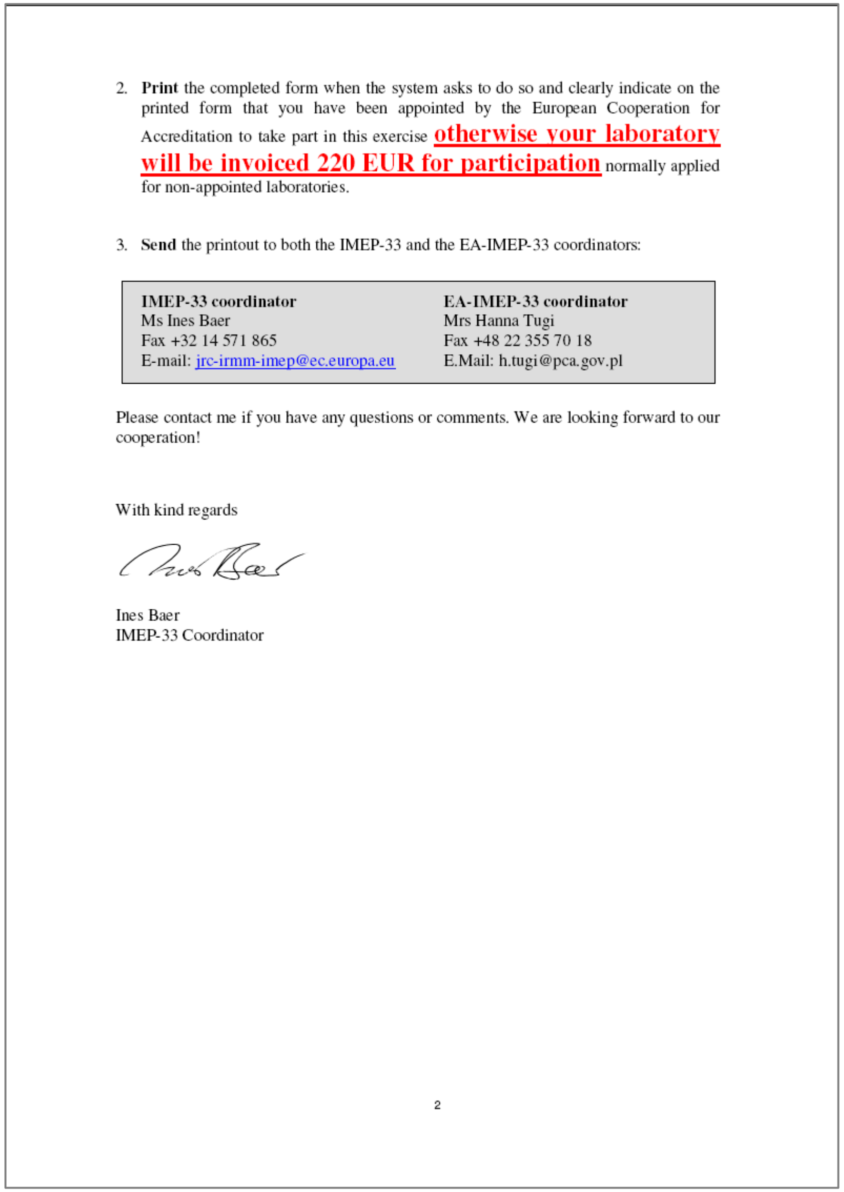
Registration of participants is open until **13 May 2011**. Distribution of the samples is foreseen for the second half of May 2011, and the foreseen registration deadline is **17 June 2011**.

In order to register, laboratories must:

1. **Enter** their details online:

https://irmm.jrc.ec.europa.eu/ilc/ilcRegistration.do?selComparison=680

Retieseweg 111, B-2440 Geel - Belgium. Telephone: (32-14) 571 211. http://irmm.jrc.ec.europa.eu
Telephone: direct line (32-14) 571 715. Fax: (32-14) 571 865.
E-mail: jrc-irmm-imep@ec.europa.eu



2. **Print** the completed form when the system asks to do so and clearly indicate on the printed form that you have been appointed by the European Cooperation for Accreditation to take part in this exercise **otherwise your laboratory will be invoiced 220 EUR for participation** normally applied for non-appointed laboratories.

3. **Send** the printout to both the IMEP-33 and the EA-IMEP-33 coordinators:

IMEP-33 coordinator Ms Ines Baer Fax +32 14 571 865 E-mail: jrc-irmm-imep@ec.europa.eu	**EA-IMEP-33 coordinator** Mrs Hanna Tugi Fax +48 22 355 70 18 E.Mail: h.tugi@pca.gov.pl

Please contact me if you have any questions or comments. We are looking forward to our cooperation!

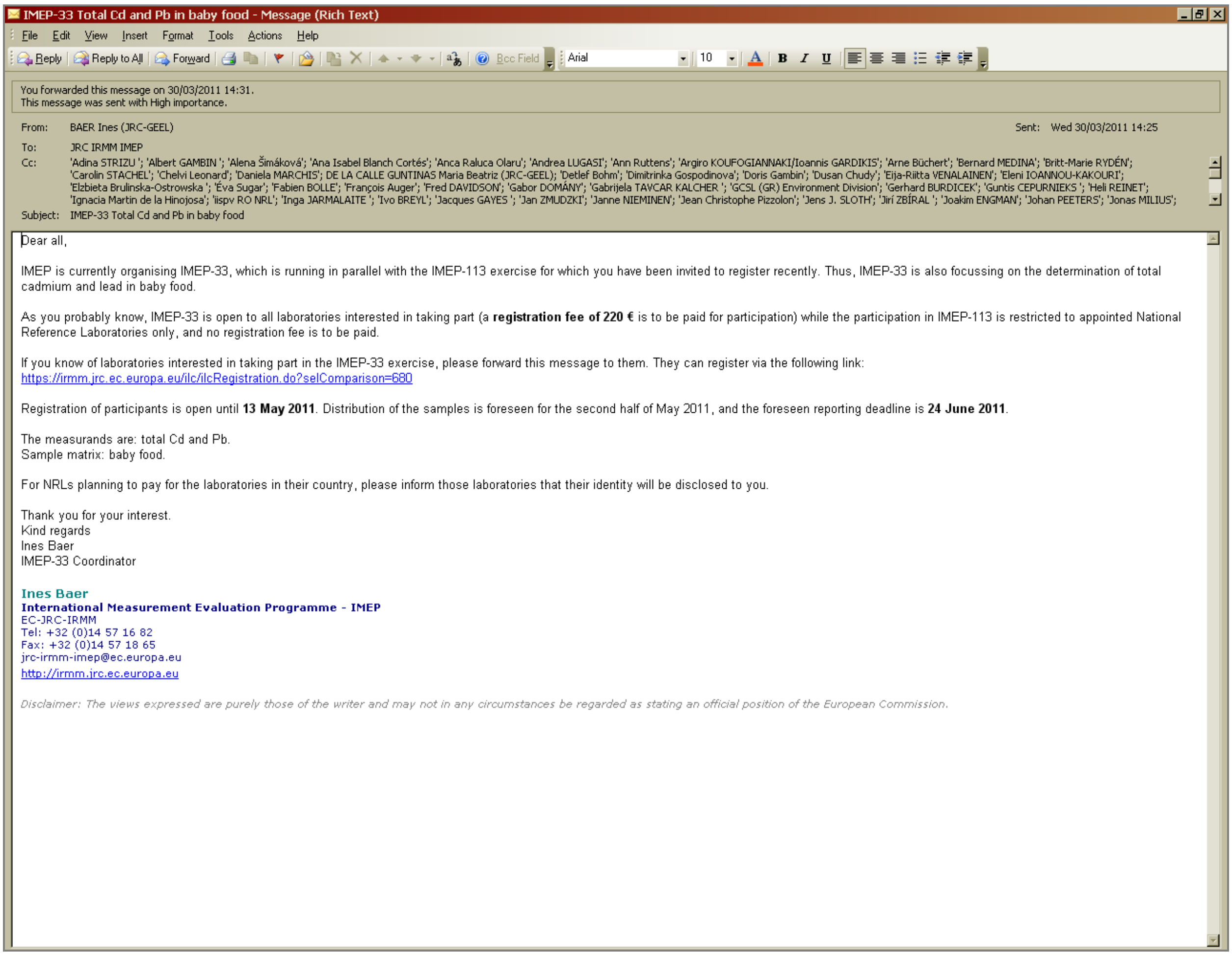
With kind regards

Ines Baer

Ines Baer
IMEP-33 Coordinator

2

Annex 2 : Invitation sent to NRLs



You forwarded this message on 30/03/2011 14:31.
This message was sent with High importance.

From: BAER Ines (JRC-GEEL)
Sent: Wed 30/03/2011 14:25
To: JRC IRMM IMEP
Cc: 'Adina STRIZU '; 'Albert GAMBIN '; 'Alena Šimáková'; 'Ana Isabel Blanch Cortés'; 'Anca Raluca Olaru'; 'Andrea LUGASI'; 'Ann Ruttens'; 'Argiro KOUFOGIANNAKI/Ioannis GARDIKIS'; 'Arne Büchert'; 'Bernard MEDINA'; 'Britt-Marie RYDÉN'; 'Carolin STACHEL'; 'Chelvi Leonard'; 'Daniela MARCHIS'; DE LA CALLE GUNTINAS Maria Beatriz (JRC-GEEL); 'Detlef Bohm'; 'Dimitrinka Gospodinova'; 'Doris Gambin'; 'Dusan Chudy'; 'Eija-Riitta VENALAINEN'; 'Eleni IOANNOU-KAKOURI'; 'Elzbieta Brulinska-Ostrowska '; 'Éva Sugar'; 'Fabien BOLLE'; 'François Auger'; 'Fred DAVIDSON'; 'Gabor DOMÁNY'; 'Gabrijela TAVCAR KALCHER '; 'GCSL (GR) Environment Division'; 'Gerhard BURDICEK'; 'Guntis CEPURNIEKS '; 'Heli REINET'; 'Ignacia Martin de la Hinojosa'; 'iispv RO NRL'; 'Inga JARMALAITE '; 'Ivo BREYL'; 'Jacques GAYES '; 'Jan ZMUDZKI'; 'Janne NIEMINEN'; 'Jean Christophe Pizzolon'; 'Jens J. SLOTH'; 'Jirí ZBÍRAL '; 'Joakim ENGMAN'; 'Johan PEETERS'; 'Jonas MILIUS';
Subject: IMEP-33 Total Cd and Pb in baby food

Dear all,

IMEP is currently organising IMEP-33, which is running in parallel with the IMEP-113 exercise for which you have been invited to register recently. Thus, IMEP-33 is also focussing on the determination of total cadmium and lead in baby food.

As you probably know, IMEP-33 is open to all laboratories interested in taking part (a **registration fee of 220 €** is to be paid for participation) while the participation in IMEP-113 is restricted to appointed National Reference Laboratories only, and no registration fee is to be paid.

If you know of laboratories interested in taking part in the IMEP-33 exercise, please forward this message to them. They can register via the following link:
https://irmm.jrc.ec.europa.eu/ilc/ilcRegistration.do?selComparison=680

Registration of participants is open until **13 May 2011**. Distribution of the samples is foreseen for the second half of May 2011, and the foreseen reporting deadline is **24 June 2011**.

The measurands are: total Cd and Pb.
Sample matrix: baby food.

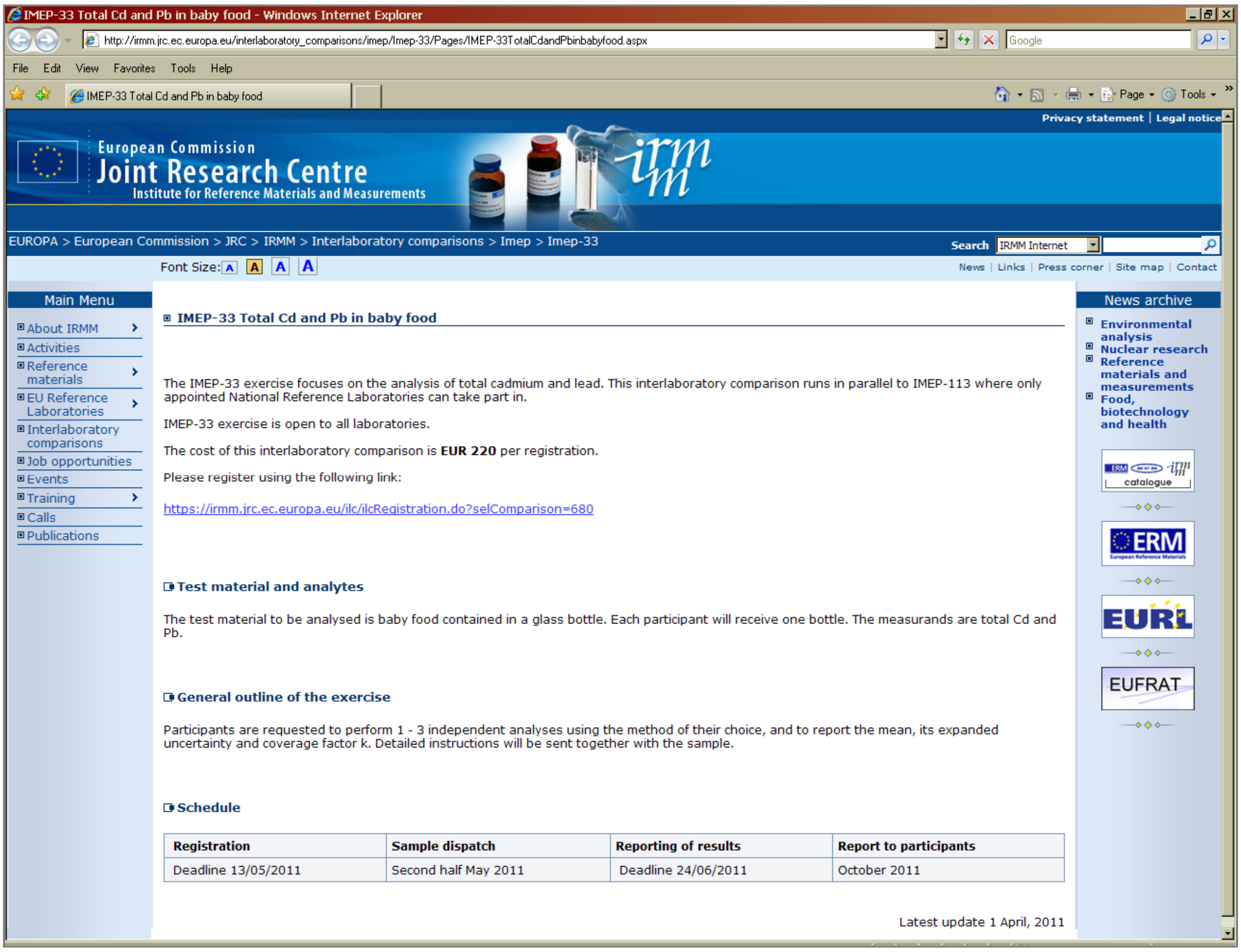
For NRLs planning to pay for the laboratories in their country, please inform those laboratories that their identity will be disclosed to you.

Thank you for your interest.
Kind regards
Ines Baer
IMEP-33 Coordinator

Ines Baer
International Measurement Evaluation Programme - IMEP
EC-JRC-IRMM
Tel: +32 (0)14 57 16 82
Fax: +32 (0)14 57 18 65
jrc-irmm-imep@ec.europa.eu
http://irmm.jrc.ec.europa.eu

Disclaimer: The views expressed are purely those of the writer and may not in any circumstances be regarded as stating an official position of the European Commission.

Annex 3 : Announcement on IRMM - IMEP website



IMEP-33 Total Cd and Pb in baby food

The IMEP-33 exercise focuses on the analysis of total cadmium and lead. This interlaboratory comparison runs in parallel to IMEP-113 where only appointed National Reference Laboratories can take part in.

IMEP-33 exercise is open to all laboratories.

The cost of this interlaboratory comparison is **EUR 220** per registration.

Please register using the following link:

https://irmm.jrc.ec.europa.eu/ilc/ilcRegistration.do?selComparison=680

Test material and analytes

The test material to be analysed is baby food contained in a glass bottle. Each participant will receive one bottle. The measurands are total Cd and Pb.

General outline of the exercise

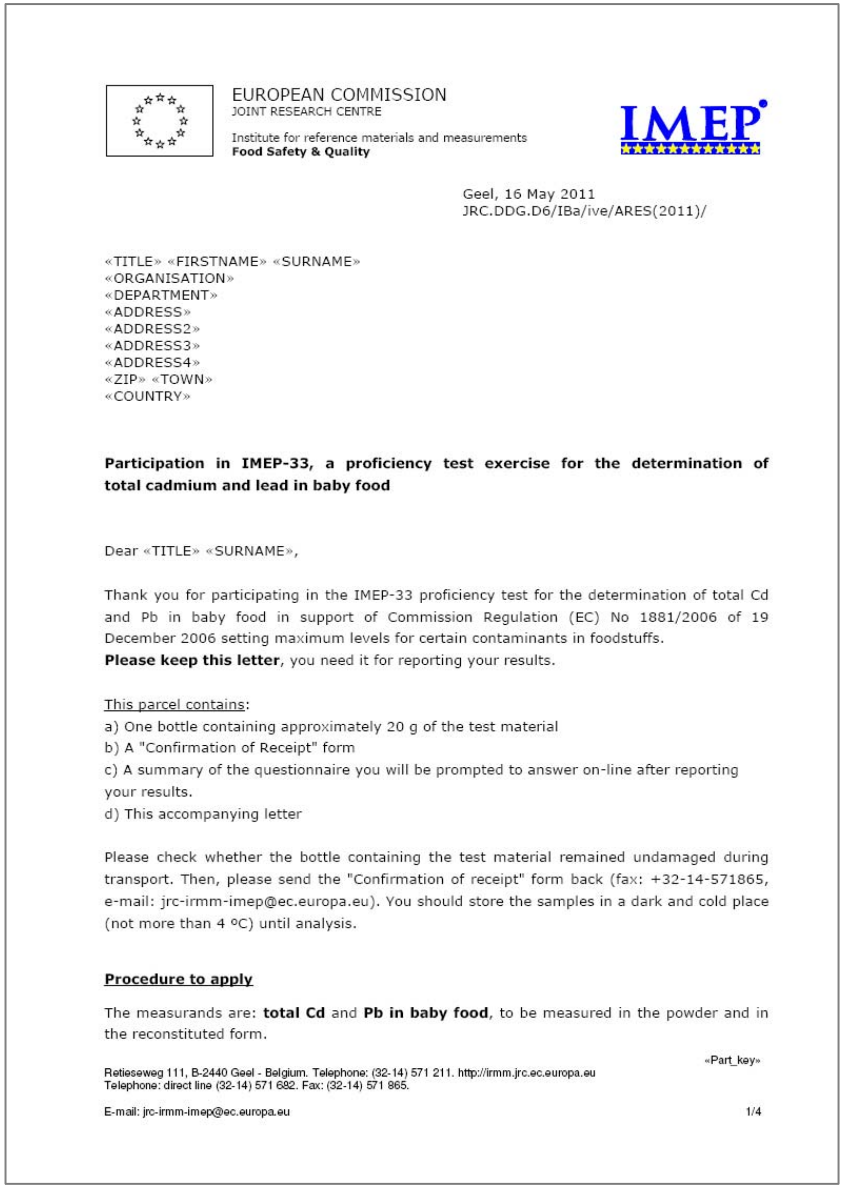
Participants are requested to perform 1 - 3 independent analyses using the method of their choice, and to report the mean, its expanded uncertainty and coverage factor k. Detailed instructions will be sent together with the sample.

Schedule

Registration	Sample dispatch	Reporting of results	Report to participants
Deadline 13/05/2011	Second half May 2011	Deadline 24/06/2011	October 2011

Latest update 1 April, 2011

Annex 4 : Sample accompanying letter



EUROPEAN COMMISSION
JOINT RESEARCH CENTRE
Institute for reference materials and measurements
Food Safety & Quality

Geel, 16 May 2011
JRC.DDG.D6/IBa/ive/ARES(2011)/

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

Participation in IMEP-33, a proficiency test exercise for the determination of total cadmium and lead in baby food

Dear «TITLE» «SURNAME»,

Thank you for participating in the IMEP-33 proficiency test for the determination of total Cd and Pb in baby food in support of Commission Regulation (EC) No 1881/2006 of 19 December 2006 setting maximum levels for certain contaminants in foodstuffs.
Please keep this letter, you need it for reporting your results.

This parcel contains:
a) One bottle containing approximately 20 g of the test material
b) A "Confirmation of Receipt" form
c) A summary of the questionnaire you will be prompted to answer on-line after reporting your results.
d) This accompanying letter

Please check whether the bottle containing the test material remained undamaged during transport. Then, please send the "Confirmation of receipt" form back (fax: +32-14-571865, e-mail: jrc-irmm-imep@ec.europa.eu). You should store the samples in a dark and cold place (not more than 4 ºC) until analysis.

Procedure to apply

The measurands are: **total Cd** and **Pb in baby food**, to be measured in the powder and in the reconstituted form.

«Part_key»

Retieseweg 111, B-2440 Geel - Belgium. Telephone: (32-14) 571 211. http://irmm.jrc.ec.europa.eu
Telephone: direct line (32-14) 571 682. Fax: (32-14) 571 865.

E-mail: jrc-irmm-imep@ec.europa.eu 1/4

a) For the determination of the measurands in the **powder**, the procedure used for the analyses should resemble as closely as possible the one that you use in routine sample analysis.

b) The results in the powder 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:

→ *Weigh 1.5 g of test material and dry it at 120 ± 1 ºC for 1 hour in triplicate.*

c) For the determination of the measurand in the **reconstituted form**, please apply the following procedure:

→ *Weigh 0.5 g of test material and add de-ionised water up to 4.0 g. Shake until all solid is dissolved (if needed sonicate the sample till the solid is totally dissolved).*

Perform the measurements as you use to in routine sample analysis. The concentrations are to be reported referring to the reconstituted sample.

Reporting of results

Please perform two or three independent measurements per measurand. Correct the measurement results for recovery, and report on the reporting website:
- **the corrected mean**,
- the associated expanded **uncertainty**,
- the **coverage factor** and
- the **technique** you used.

The results should be reported in the same form (e.g. number of significant figures) as those normally reported to the customer. Mean and uncertainty are to be reported in the same unit.

The reporting website is https://irmm.jrc.ec.europa.eu/ilc/ilcReporting.do
To access this webpage you need a personal password key, which is: **«Part_key»**. The system will guide you through the reporting procedure. **Check your results carefully** for any errors before submission, since your results cannot be changed after we have received them.

Please also complete the relating online-questionnaire. A summary of the questions was sent with this letter. Do not forget to save and submit when required.

For final submission please:
- press "Confirm results and questionnaire"
- **print** the completed report form
- **sign** the paper version and
- **send** it to IRMM by fax or by e-mail.

2/4 «Part_key»

The **deadline** for submission of results is **24/06/2011**.

The reporting website will be unavailable due to maintenance on 2 and 3 June 2011.

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-imep@ec.europa.eu

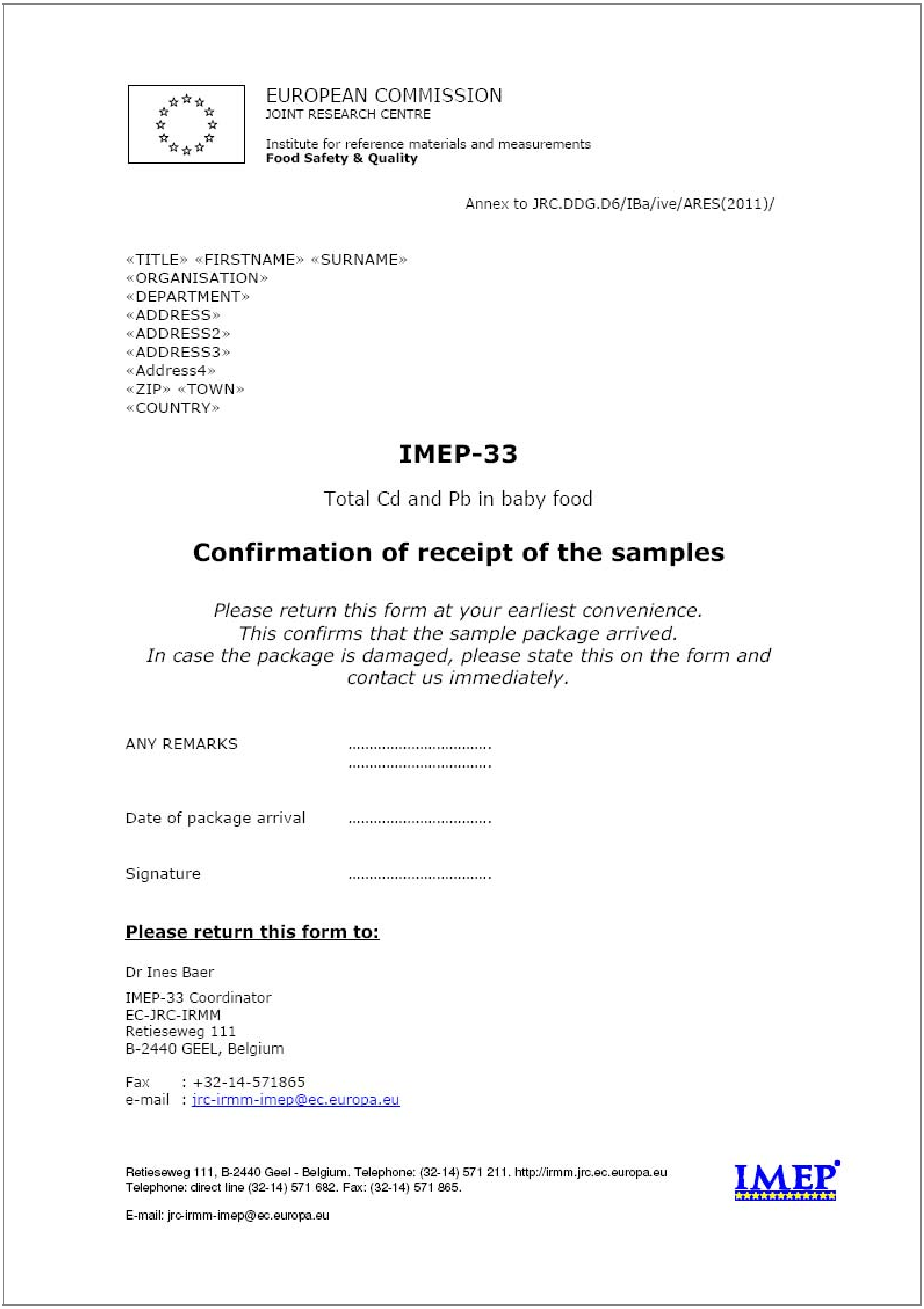
With kind regards

Dr. Ines Baer
IMEP-33 Co-ordinator

Enclosures: 1) one bottle containing the test material; 2) confirmation of receipt form; 3) Summary IMEP-33 questionnaire; 4) Accompanying letter.

Cc: F. Ulberth

Annex 5 : 'Confirmation of receipt' form



EUROPEAN COMMISSION
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Institute for reference materials and measurements
Food Safety & Quality

Annex to JRC.DDG.D6/IBa/ive/ARES(2011)/

«TITLE» «FIRSTNAME» «SURNAME»
«ORGANISATION»
«DEPARTMENT»
«ADDRESS»
«ADDRESS2»
«ADDRESS3»
«Address4»
«ZIP» «TOWN»
«COUNTRY»

IMEP-33

Total Cd and Pb in baby food

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 ....

Please return this form to:

Dr Ines Baer

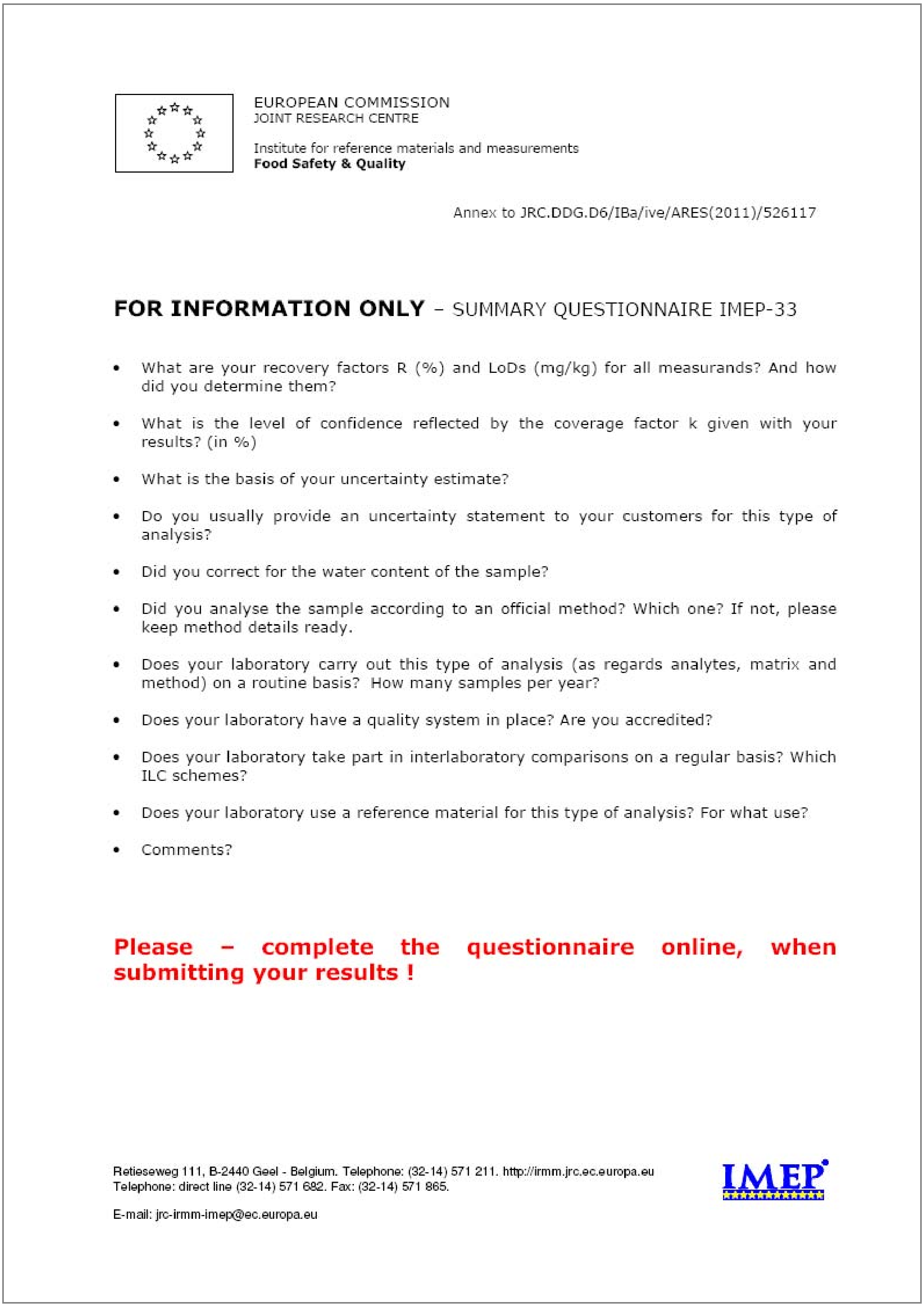
IMEP-33 Coordinator
EC-JRC-IRMM
Retieseweg 111
B-2440 GEEL, Belgium

Fax : +32-14-571865
e-mail : jrc-irmm-imep@ec.europa.eu

Retieseweg 111, B-2440 Geel - Belgium. Telephone: (32-14) 571 211. http://irmm.jrc.ec.europa.eu
Telephone: direct line (32-14) 571 682. Fax: (32-14) 571 865.

E-mail: jrc-irmm-imep@ec.europa.eu

Annex 6 : Summary questionnaire sent with sample



EUROPEAN COMMISSION
JOINT RESEARCH CENTRE

Institute for reference materials and measurements
Food Safety & Quality

Annex to JRC.DDG.D6/IBa/ive/ARES(2011)/526117

FOR INFORMATION ONLY – SUMMARY QUESTIONNAIRE IMEP-33

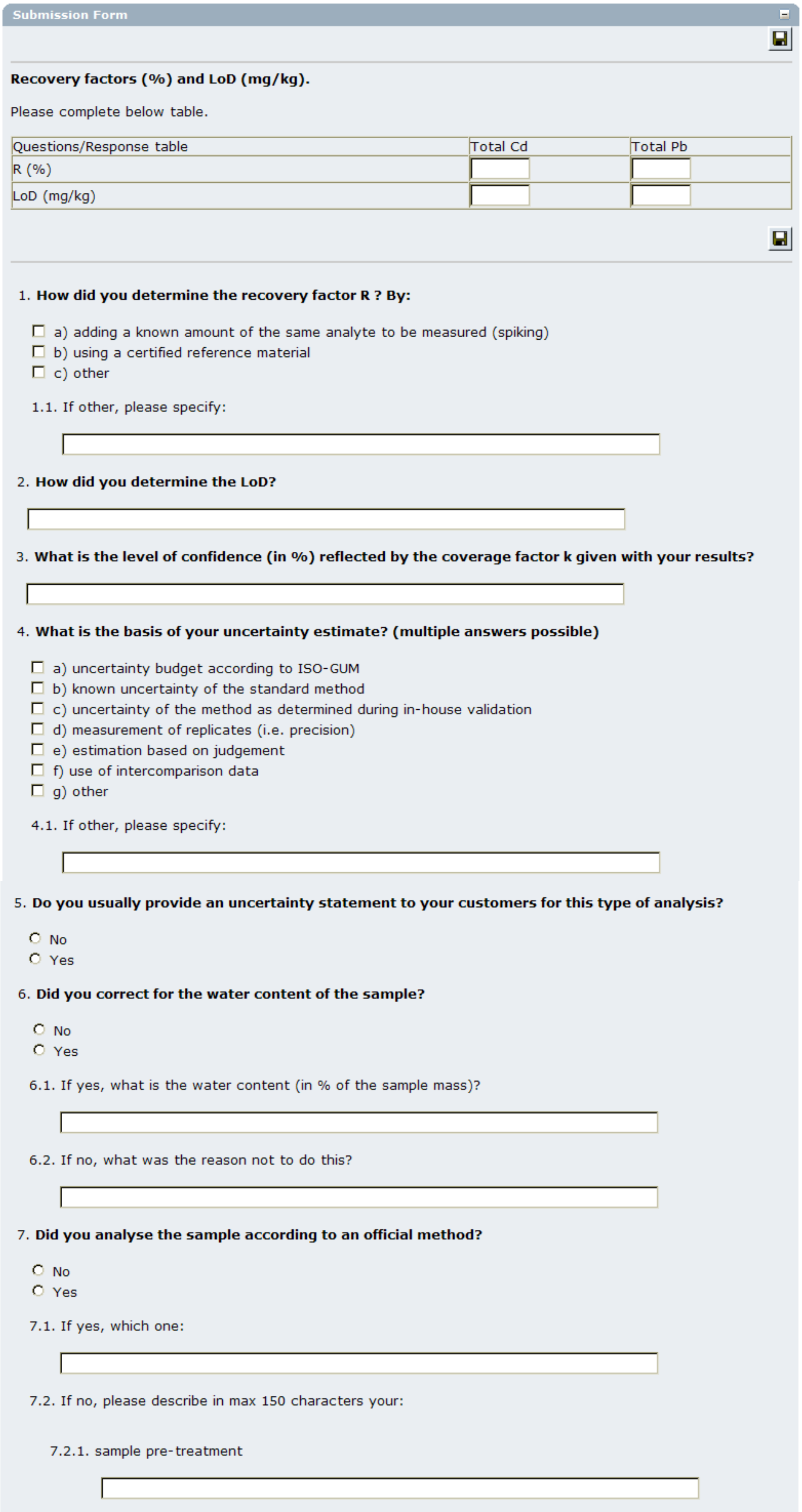
- What are your recovery factors R (%) and LoDs (mg/kg) for all measurands? And how did you determine them?
- What is the level of confidence reflected by the coverage factor k given with your results? (in %)
- What is the basis of your uncertainty estimate?
- Do you usually provide an uncertainty statement to your customers for this type of analysis?
- Did you correct for the water content of the sample?
- Did you analyse the sample according to an official method? Which one? If not, please keep method details ready.
- Does your laboratory carry out this type of analysis (as regards analytes, matrix and method) on a routine basis? How many samples per year?
- Does your laboratory have a quality system in place? Are you accredited?
- Does your laboratory take part in interlaboratory comparisons on a regular basis? Which ILC schemes?
- Does your laboratory use a reference material for this type of analysis? For what use?
- Comments?

Please – complete the questionnaire online, when submitting your results !

Retieseweg 111, B-2440 Geel - Belgium. Telephone: (32-14) 571 211. http://irmm.jrc.ec.europa.eu
Telephone: direct line (32-14) 571 682. Fax: (32-14) 571 865.

E-mail: jrc-irmm-imep@ec.europa.eu

Annex 7 : Online Questionnaire



Submission Form

Recovery factors (%) and LoD (mg/kg).

Please complete below table.

Questions/Response table	Total Cd	Total Pb
R (%)		
LoD (mg/kg)		

1. **How did you determine the recovery factor R ? By:**

☐ a) adding a known amount of the same analyte to be measured (spiking)
☐ b) using a certified reference material
☐ c) other

1.1. If other, please specify:

2. **How did you determine the LoD?**

3. **What is the level of confidence (in %) reflected by the coverage factor k given with your results?**

4. **What is the basis of your uncertainty estimate? (multiple answers possible)**

☐ a) uncertainty budget according to ISO-GUM
☐ b) known uncertainty of the standard method
☐ c) uncertainty of the method as determined during in-house validation
☐ d) measurement of replicates (i.e. precision)
☐ e) estimation based on judgement
☐ f) use of intercomparison data
☐ g) other

4.1. If other, please specify:

5. **Do you usually provide an uncertainty statement to your customers for this type of analysis?**

○ No
○ Yes

6. **Did you correct for the water content of the sample?**

○ No
○ Yes

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

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

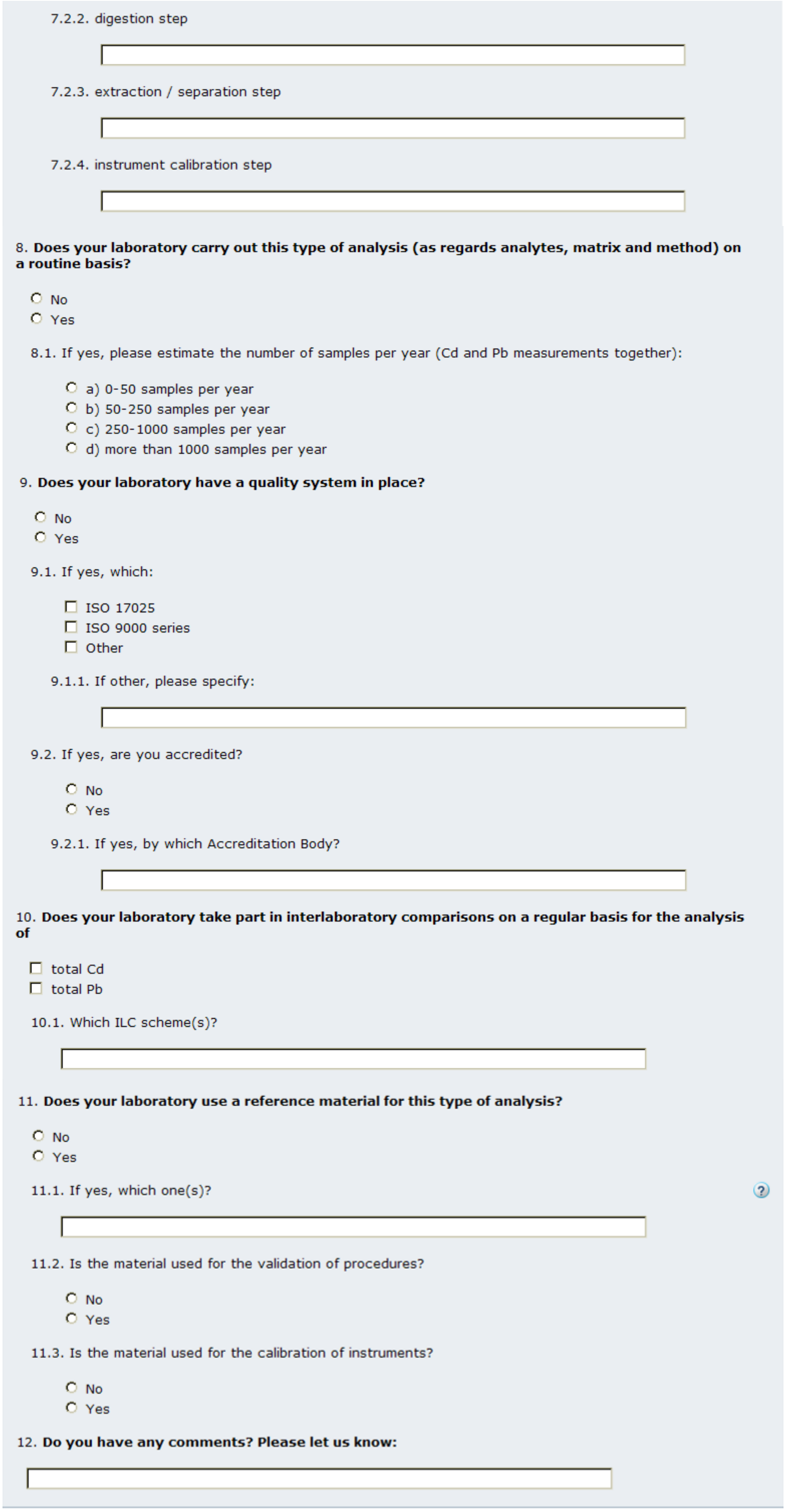
7. **Did you analyse the sample according to an official method?**

○ No
○ Yes

7.1. If yes, which one:

7.2. If no, please describe in max 150 characters your:

7.2.1. sample pre-treatment



7.2.2. digestion step

7.2.3. extraction / separation step

7.2.4. instrument calibration step

8. **Does your laboratory carry out this type of analysis (as regards analytes, matrix and method) on a routine basis?**

○ No
○ Yes

8.1. If yes, please estimate the number of samples per year (Cd and 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

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

○ No
○ Yes

9.1. If yes, which:

☐ ISO 17025
☐ ISO 9000 series
☐ Other

9.1.1. If other, please specify:

9.2. If yes, are you accredited?

○ No
○ Yes

9.2.1. If yes, by which Accreditation Body?

10. **Does your laboratory take part in interlaboratory comparisons on a regular basis for the analysis of**

☐ total Cd
☐ total Pb

10.1. Which ILC scheme(s)?

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

○ No
○ Yes

11.1. If yes, which one(s)?

11.2. Is the material used for the validation of procedures?

○ No
○ Yes

11.3. Is the material used for the calibration of instruments?

○ No
○ Yes

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

Annex 8 : Homogeneity and stability studies

8.1 Homogeneity study for total cadmium

	Total cadmium (µg kg^{-1})	
Bottle ID	**Replicate 1**	**Replicate 2**
9	10.6	10.6
70	10.7	10.8
20	10.5	10.6
152	10.5	10.6
119	10.7	10.6
95	10.5	10.5
37	10.6	10.4
33	10.5	10.6
53	10.6	10.4
132	10.4	10.4
Mean of 20 results	10.56	
$\hat{\sigma}$	22 %	
Homogeneity test according to ISO 13528 [5]		
$0.3\hat{\sigma}$	0.69663	
S_x	0.095597536	
S_w	0.080622577	
S_s	0.076739096	
$S_s \leq 0.3\ \hat{\sigma}$?	Yes	
Test result	Passed	

8.2 Stability study for total cadmium

Stability Study – Total cadmium

TEMPERATURE = 18°C

Meas.Unit: µg kg^{-1}

Time in Weeks

samples		0	3	5	8
	1	10.6	10.5	10.5	10.5
	2	10.3	10.5	10.8	10.6

CALCULATION OF U_{lts} for given X_{shelf}

Given X_{shelf} = 5 Weeks

U_{lts} = 0.085 µg kg^{-1}

U_{lts}[%] = 0.8%

REGRESSION LINE PARAMETERS

Slope = 0.016

SE Slope = 0.017

Intercept = 10.473

SE Intercept = 0.085

Correlation Coefficient =0.128

Slope of the linear regression significantly <> 0 (95%) :No

Slope of the linear regression significantly <> 0 (99%) :No

8.3 Homogeneity study for total lead

	Total lead (µg kg^{-1})	
Bottle ID	**Replicate 1**	**Replicate 2**
9	5	5.1
70	5	5.1
20	5.4	5.2
152	5.4	5
119	6	5.3
95	6.2	6
37	5.3	5.3
33	5.9	5.1
53	5.2	5.7
132	5.1	5.7
Mean of 20 results	5.4	
$\hat{\sigma}$	22 %	
Homogeneity test according to ISO 13528 [5]		
$0.3\hat{\sigma}$	0.3564	
S_x	0.310912635	
S_w	0.316227766	
S_s	0.21602469	
$S_s \leq 0.3\ \hat{\sigma}$?	Yes	
Test result	Passed	

8.4 Stability study for total lead

<u>Stability Study – Total lead</u>

TEMPERATURE = 18°C

Meas.Unit: µg kg^{-1}

		Time in Weeks			
samples		0	3	5	8
	1	4.5	4.7	5.7	5.7
	2	4.9	4.6	5.3	5.2

CALCULATION OF U_{lts} for given X_{shelf}

Given X_{shelf} = 5 Weeks

U_{lts} = 0.208 µg kg^{-1}

U_{lts}[%] = 4.1%

REGRESSION LINE PARAMETERS

Slope = 0.113

SE Slope = 0.042

Intercept = 4.622

SE Intercept = 0.205

Correlation Coefficient =0.554

Slope of the linear regression significantly <> 0 (95%) :No

Slope of the linear regression significantly <> 0 (99%) :No

Annex 9 : Results for Total Cadmium - Powder

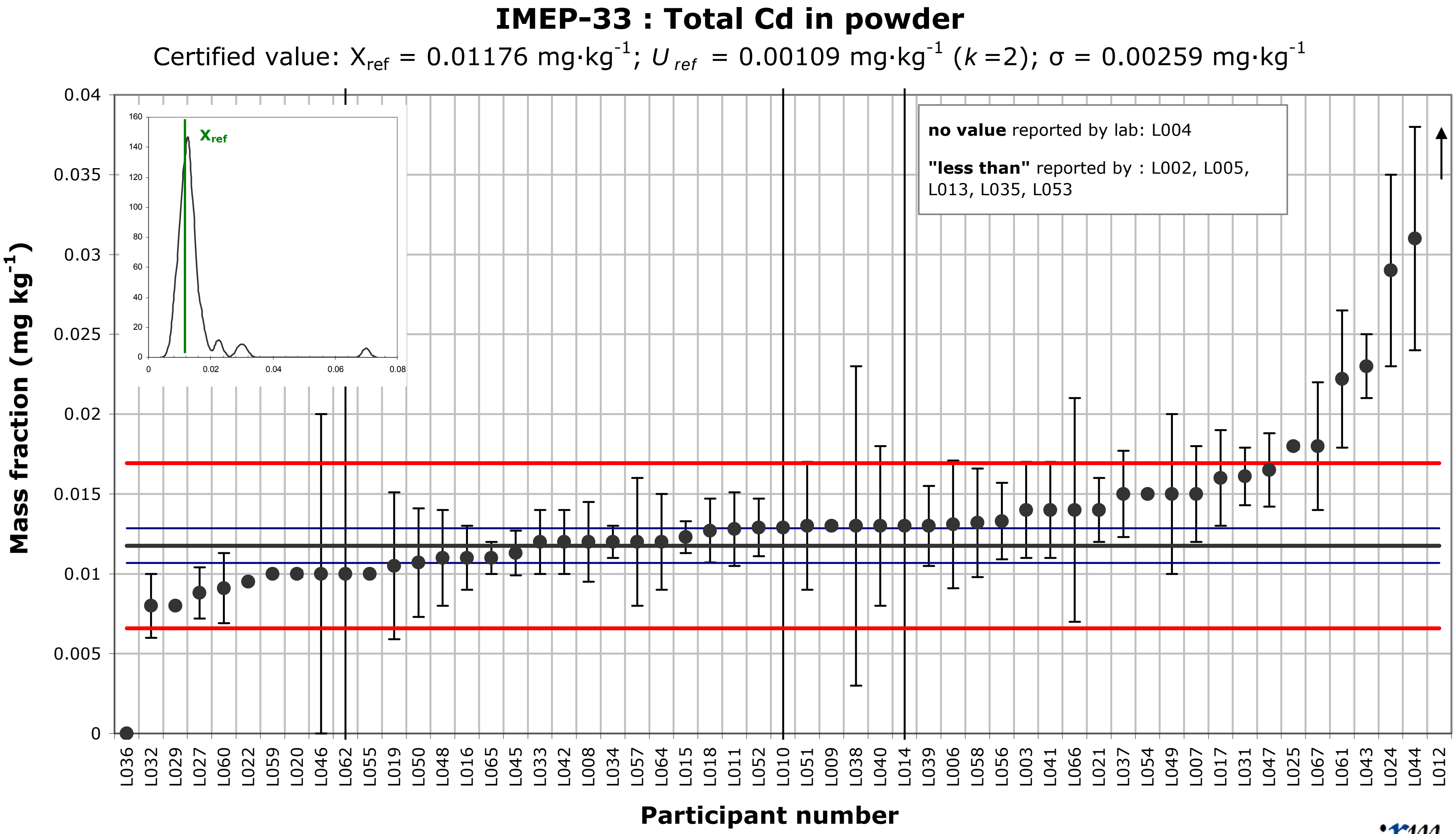
X_{ref} = 0.01176 and U_{ref} = 0.00109; all values are given in (mg kg^{-1})

Lab ID	Mean (xlab)	U_{lab}	k [a]	u_{lab}	Technique	z [b]	zeta [b]	Unc [c]
L002	< 0.08							
L003	0.014	0.003	2	0.002	ICP-OES	0.9	1.4	a
L005	< 0.010							
L006	0.0131	0.004	2	0.002	ICP-MS	0.5	0.6	a
L007	0.015	0.003	√3	0.000	ICP-MS	1.3	5.9	b
L008	0.012	0.0025	2	0.0013	ICP-MS	0.1	0.2	a
L009	0.013	0.0002	2	0.0001	ICP-MS	0.5	2.2	b
L010	0.0129	15	2	8	ICP-MS	0.4	0.0	c
L011	0.0128	0.0023	2	0.0012	ICP-MS	0.4	0.8	a
L012	0.07	0.00	2	0.00	ICP-MS	22.5	106.9	b
L013	< 0.050							
L014	0.013	7	2	4	ICP-MS	0.5	0.0	c
L015	0.0123	0.001	2.3	0.000	ICP-MS	0.2	0.8	b
L016	0.011	0.002	√3	0.000	ETAAS	-0.3	-1.4	b
L017	0.016	0.003	2	0.002	ICP-MS	1.6	2.7	a
L018	0.0127	0.002	3	0.001	ICP-MS	0.4	1.1	a
L019	0.0105	0.0046	2	0.0023	ICP-MS	-0.5	-0.5	a
L020	0.010	0.0002	2	0.0001	GF-AAS	-0.7	-3.2	b
L021	0.014	0.002	2	0.001	ICP-MS	0.9	2.0	a
L022	0.0095	0	√3	0	GF-AAS	-0.9	-4.1	b
L024	0.029	0.006	2	0.003	FAAS	6.7	5.7	c
L025	0.0180	0.0002	0.22	0.0009	GF-AAS	2.4	5.9	a
L027	0.0088	0.0016	2	0.0008	ICP-OES	-1.1	-3.1	a
L029	0.008	0	0.00	0.00	FAAS	-1.5	-6.9	b
L031	0.0161	0.0018	2	0.0009	ICP-MS	1.7	4.1	a
L032	0.008	0.002	2	0.001	GF-AAS	-1.5	-3.3	a
L033	0.012	0.002	2	0.001	ICP-MS	0.1	0.2	a
L034	0.012	0.001	2	0.001	ICP-MS	0.1	0.3	a
L035	< 0.018							
L036	0	0	√3	0		-4.5	-21.6	b
L037	0.015	0.0027	2	0.0014	GF-AAS	1.3	2.2	a
L038	0.013	0.01	2	0.01	GF-AAS	0.5	0.2	c
L039	0.013	0.0025	2	0.0013	ICP-MS	0.5	0.9	a
L040	0.013	0.005	2	0.003	GF-AAS	0.5	0.5	c
L041	0.014	0.003	1.008	0.003	GF-AAS	0.9	0.7	c
L042	0.012	0.002	2	0.001	ICP-MS	0.1	0.2	a
L043	0.023	0.002	2	0.001	GF-AAS	4.3	9.9	a
L044	0.031	0.007	2	0.004	ICP-OES	7.4	5.4	c
L045	0.0113	0.0014	1	0.0014	ICP-MS	-0.2	-0.3	a
L046	0.01	0.01	2	0.005	ICP-MS	-0.7	-0.3	c
L047	0.0165	0.0023	2	0.0012	GF-AAS	1.8	3.7	a
L048	0.011	0.003	2	0.002	GF-AAS	-0.3	-0.5	a
L049	0.015	0.005	2.365	0.002	ICP-MS	1.3	1.5	a
L050	0.0107	0.0034	2	0.0017	GF-AAS	-0.4	-0.6	a
L051	0.013	0.004	2	0.002	ICP-MS	0.5	0.6	a
L052	0.0129	0.0018	2	0.0009	ICP-MS	0.4	1.1	a
L053	< 0.008							
L054	0.015	0	√3	0	GF-AAS	1.3	5.9	b
L055	0.01	0	√3	0	GF-AAS	-0.7	-3.2	b
L056	0.0133	0.0024	2	0.0012	ICP-MS	0.6	1.2	a
L057	0.012	0.004	√3	0.000	GF-AAS	0.1	0.4	b
L058	0.0132	0.0034	1.96	0.0017	ETAAS	0.6	0.8	a
L059	0.010	0	√3	0	GF-AAS	-0.7	-3.2	b
L060	0.0091	0.0022	2	0.0011	GF-AAS	-1.0	-2.2	a
L061	0.0222	0.0043	1.96	0.0022	ETAAS	4.0	4.6	a
L062	0.010	20	2	10	ICP-MS	-0.7	0.0	c
L064	0.012	0.003	2	0.002	ICP-OES	0.1	0.2	a
L065	0.011	0.001	√3	0.000	GF-AAS	-0.3	-1.4	b
L066	0.014	0.007	2	0.004	GF-AAS	0.9	0.6	c
L067	0.018	0.004	2	0.002	ICP-MS	2.4	3.0	a

[a] √3 is set by the ILC coordinator when no expansion factor *k* is reported. The reported uncertainty was assumed to have a rectangular distribution with *k*=√3. For explanation see Ch 9.3

[b] **Satisfactory**, **Questionable**, **Unsatisfactory**

[c] Where: **a** = $u_{min} \le u_{lab} \le u_{max}$, **b** : $u_{lab} < u_{min}$, and **c** : $u_{lab} > u_{max}$



This graph displays all revised measurement results and their associated uncertainties. The uncertainties are shown as reported.
The thick black line corresponds to $\mathbf{X_{ref}}$, the orange lines mark the boundary of the reference interval ($\mathbf{X_{ref} \pm 2u_{ref}}$), and the red lines that of the target interval ($\mathbf{X_{ref} \pm 2\sigma}$).

Annex 10 : Results for Total Cadmium - Reconstituted

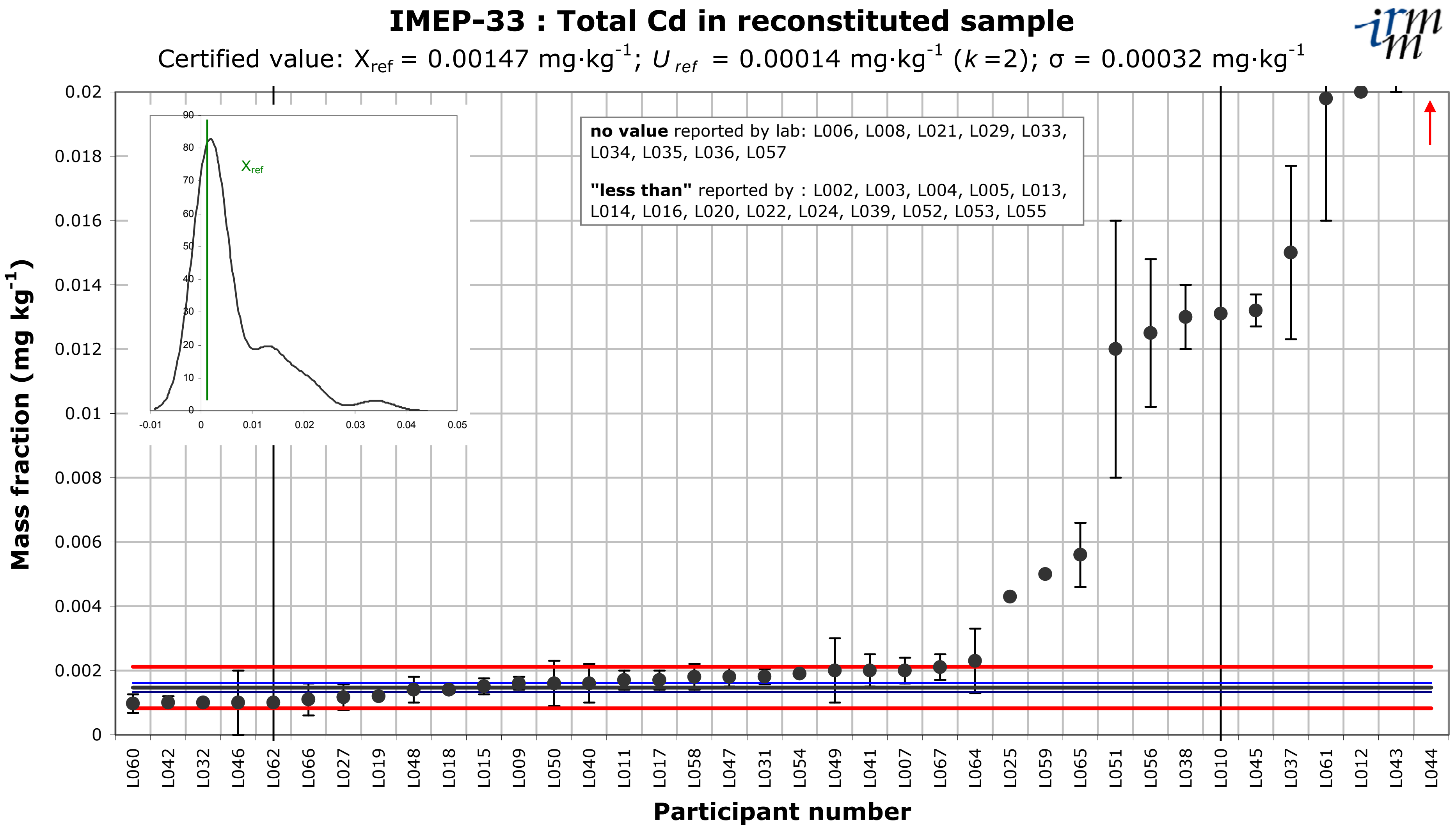
X_{ref} = 0.00147 and U_{ref} = 0.00014; all values are given in (mg kg^{-1})

Lab ID	Mean (xlab)	U_{lab}	k [a]	u_{lab}	Technique	z [b]	zeta [b]	Unc [c]
L002	< 0.65				ICP-OES			
L003	< 0.012				ICP-OES			
L004	< 0.0292				ICP-MS			
L005	< 0.010				ICP-OES			
L007	0.002	0.0004	1.73205081	0.0002	ICP-MS	1.6	2.2	a
L009	0.0016	0.0002	2	0.0001	ICP-MS	0.4	1.1	a
L010	0.0131	15	2	8	ICP-MS	36.0	0.0	c
L011	0.0017	0.0003	2	0.0002	ICP-MS	0.7	1.4	a
L012	0.02	0.00	2	0.00	ICP-MS	57.3	264.7	b
L013	< 0.010				GF-AAS			
L014	< 0.0014				ICP-MS			
L015	0.00151	0.00025	2.3	0.00011	ICP-MS	0.1	0.3	a
L016	< 0.002				ETAAS			
L017	0.0017	0.0003	2	0.0002	ICP-MS	0.7	1.4	a
L018	0.0014	0.0001	3	0.0000	ICP-MS	-0.2	-0.9	b
L019	0.0012	0	1.73205081	0	ICP-MS	-0.8	-3.9	b
L020	< 0.001				GF-AAS			
L022	< 0.002				GF-AAS			
L024	< 0.004				FAAS			
L025	0.0043	0.00004	0.032	0.00125	GF-AAS	8.8	2.3	c
L027	0.00117	0.0004	2	0.0002	ICP-OES	-0.9	-1.4	a
L031	0.00181	0.00024	2	0.00012	ICP-MS	1.1	2.4	a
L032	0.001	0.000	2	0.000	GF-AAS	-1.5	-6.7	b
L037	0.015	0.0027	2	0.0014	GF-AAS	41.8	10.0	c
L038	0.013	0.001	2	0.001	GF-AAS	35.7	22.8	c
L039	< 0.005				ICP-MS			
L040	0.0016	0.0006	2	0.0003	GF-AAS	0.4	0.4	a
L041	0.002	0.0005	1.074	0.0005	GF-AAS	1.6	1.1	c
L042	0.001	0.0002	2	0.0001	ICP-MS	-1.5	-3.9	a
L043	0.022	0.002	2	0.001	GF-AAS	63.5	20.5	c
L044	0.034	0.008	2	0.004	ICP-OES	100.6	8.1	c
L045	0.0132	0.0005	1	0.0005	ICP-MS	36.3	23.2	c
L046	0.001	0.001	2	0.001	ICP-MS	-1.5	-0.9	a
L047	0.0018	0.0003	2	0.0002	GF-AAS	1.0	2.0	a
L048	0.0014	0.0004	2	0.0002	GF-AAS	-0.2	-0.3	a
L049	0.002	0.001	2.365	0.000	ICP-MS	1.6	1.2	b
L050	0.0016	0.0007	2	0.0004	GF-AAS	0.4	0.4	c
L051	0.012	0.004	2	0.002	ICP-MS	32.6	5.3	c
L052	< 0.01				ICP-MS			
L053	< 0.001				GF-AAS			
L054	0.0019	0	1.73205081	0	GF-AAS	1.3	6.1	b
L055	< 0.01				GF-AAS			
L056	0.0125	0.0023	2	0.0012	ICP-MS	34.1	9.6	c
L058	0.0018	0.0004	1.96	0.0002	ETAAS	1.0	1.5	a
L059	0.005	0	1.73205081	0	GF-AAS	10.9	50.4	b
L060	0.00097	0.00029	2	0.00015	GF-AAS	-1.5	-3.1	a
L061	0.0198	0.0038	1.96	0.0019	ETAAS	56.7	9.4	c
L062	0.001	30	2	15	ICP-MS	-1.5	0.0	c
L064	0.0023	0.0010	2	0.0005	ICP-OES	2.6	1.6	c
L065	0.0056	0.001	1.73205081	0	GF-AAS	12.8	7.1	b
L066	0.0011	0.0005	2	0.0003	GF-AAS	-1.1	-1.4	a
L067	0.0021	0.0004	2	0.0002	ICP-MS	1.9	3.0	a

[a] √3 is set by the ILC coordinator when no expansion factor *k* is reported. The reported uncertainty was assumed to have a rectangular distribution with *k*=√3. For explanation see Ch 9.3

[b] **Satisfactory**, **Questionable**, **Unsatisfactory**

[c] Where: **a** = $u_{min} \leq u_{lab} \leq u_{max}$, **b** : $u_{lab} < u_{min}$, and **c** : $u_{lab} > u_{max}$



no value reported by lab: L006, L008, L021, L029, L033, L034, L035, L036, L057

"less than" reported by : L002, L003, L004, L005, L013, L014, L016, L020, L022, L024, L039, L052, L053, L055

This graph displays all revised measurement results and their associated uncertainties. The uncertainties are shown as reported.
The thick black line corresponds to $\mathbf{X_{ref}}$, the blue lines the reference interval ($\mathbf{X_{ref} \pm 2u_{ref}}$) the red lines that of the target interval ($\mathbf{X_{ref} \pm 2\sigma}$).

Annex 11 : Results for Total Lead - Powder

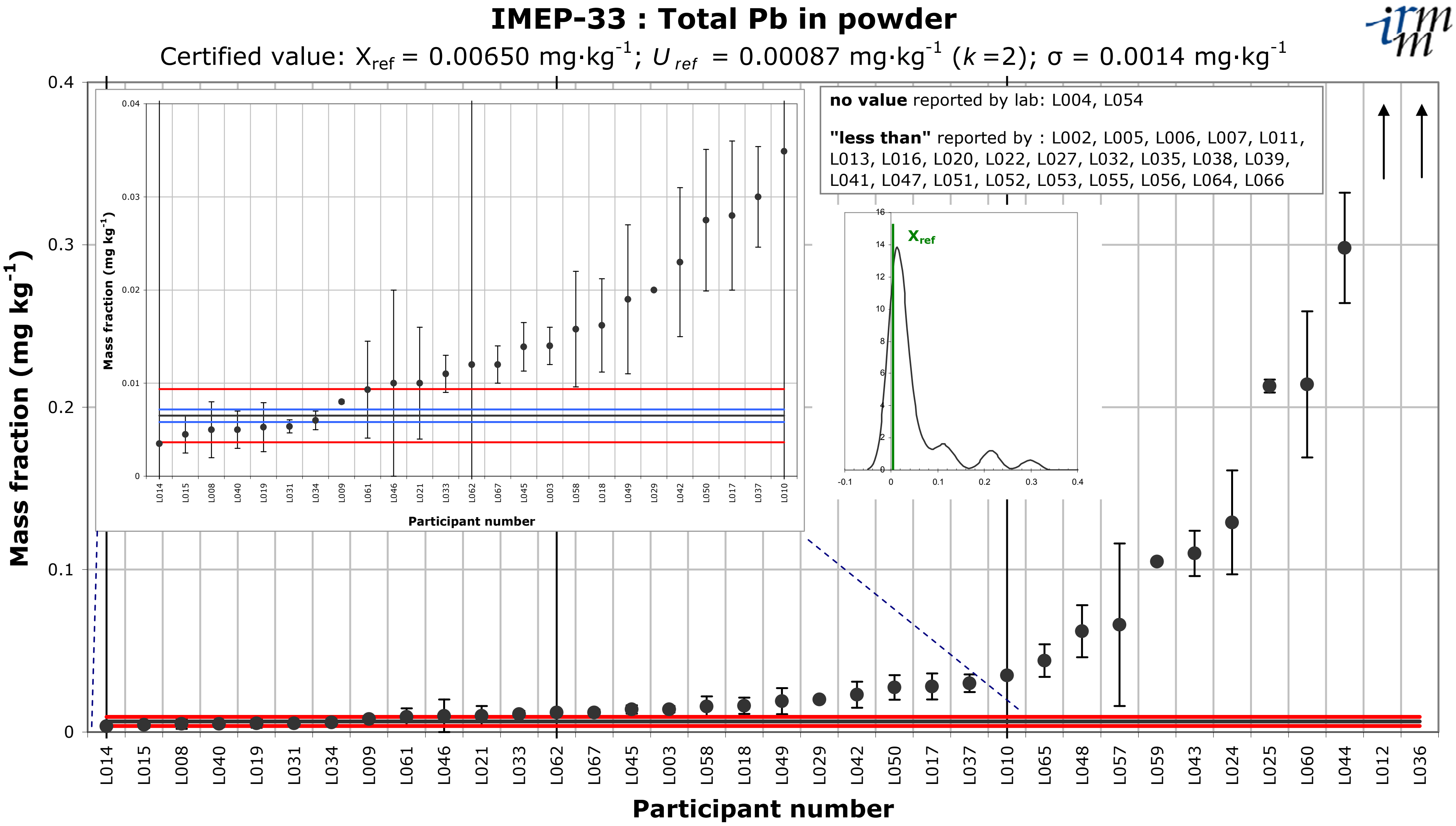
X_{ref} = 0.00650 and U_{ref} = 0.00087; all values are given in (mg kg^{-1})

Lab ID	Mean (x_{lab})	U_{lab}	k [a]	u_{lab}	Technique	z [b]	zeta [b]	Unc [c]
L002	< 0.4				ICP-OES			
L003	0.014	0.002	2	0.001	ICP-OES	5.2	6.9	**a**
L005	< 0.048				ICP-OES			
L006	< 0.015				ICP-MS			
L007	< 0.03				ICP-MS			
L008	0.005	0.003	2	0.002	ICP-MS	-1.0	-1.0	**c**
L009	0.008	0.0002	2	0.0001	ICP-MS	1.0	3.4	**b**
L010	0.0349	15	2	8	ICP-MS	19.9	0.0	**c**
L011	< 0.010				ICP-MS			
L012	1.32	0.52	2	0.26	GF-AAS	918.5	5.1	**c**
L013	< 0.050				GF-AAS			
L014	0.0035	10	2	5	ICP-MS	-2.1	0.0	**c**
L015	0.0045	0.002	2.3	0.001	ICP-MS	-1.4	-2.1	**a**
L016	< 0.04				ETAAS			
L017	0.028	0.008	2	0.004	ICP-MS	15.0	5.3	**c**
L018	0.0162	0.005	2	0.003	ICP-MS	6.8	3.8	**c**
L019	0.00527	0.00263	2	0.00132	ICP-MS	-0.9	-0.9	**a**
L020	< 0.040				GF-AAS			
L021	0.010	0.006	2	0.003	ICP-MS	2.4	0.7	**c**
L022	< 0.04				GF-AAS			
L024	0.129	0.032	2	0.016	FAAS	85.7	7.7	**c**
L025	0.213	0.004	0.032	0.125	GF-AAS	144.4	1.7	**c**
L027	< 0.02				GF-AAS			
L029	0.02	0	0.00	0	FAAS	9.4	31.0	**b**
L031	0.00535	0.00070	2	0.00035	ICP-MS	-0.8	-2.1	**b**
L032	< 0.050				GF-AAS			
L033	0.011	0.002	2	0.001	ICP-MS	3.1	4.1	**a**
L034	0.006	0.001	2	0.001	ICP-MS	-0.3	-0.8	**a**
L035	< 0.125				GF-AAS			
L036	3.08	1.50	2	0.75	AS Voltametry	2149.3	4.1	**c**
L037	0.03	0.0054	2	0.0027	GF-AAS	16.4	8.6	**c**
L038	< 0.010				GF-AAS			
L039	< 0.01				ICP-MS			
L040	0.005	0.002	2	0.001	ICP-MS	-1.0	-1.4	**a**
L041	< 0.05				GF-AAS			
L042	0.023	0.008	2	0.004	ICP-MS	11.5	4.1	**c**
L043	0.110	0.014	2	0.007	GF-AAS	72.4	14.8	**c**
L044	0.298	0.034	2	0.017	ICP-OES	203.8	17.1	**c**
L045	0.0139	0.0026	1	0.0026	ICP-MS	5.2	2.8	**c**
L046	0.01	0.01	2	0.01	ICP-MS	2.4	1.2	**c**
L047	< 0.04				GF-AAS			
L048	0.062	0.016	2	0.008	GF-AAS	38.8	6.9	**c**
L049	0.019	0.008	2.776	0.003	ICP-MS	8.7	4.3	**c**
L050	0.0275	0.0076	2	0.0038	GF-AAS	14.7	5.5	**c**
L051	< 0.0092				ICP-MS			
L052	< 0.01				ICP-MS			
L053	< 0.05				GF-AAS			
L055	< 0.01				GF-AAS			
L056	< 0.010				ICP-MS			
L057	0.066	0.05	1.73205081	0.03	GF-AAS	41.6	2.1	**c**
L058	0.0158	0.0062	1.96	0.0032	ETAAS	6.5	2.9	**c**
L059	0.105	0	√3	0	GF-AAS	68.9	226.4	**b**
L060	0.214	0.045	2	0.023	GF-AAS	145.1	9.2	**c**
L061	0.0093	0.0052	1.96	0.0027	ETAAS	2.0	1.0	**c**
L062	0.012	20	2	10	ICP-MS	3.8	0.0	**c**
L064	< 0.05				ICP-OES			
L065	0.044	0.01	1.73205081	0.01	GF-AAS	26.2	6.5	**c**
L066	< 0.05				GF-AAS			
L067	0.012	0.002	2	0.001	ICP-MS	3.8	5.0	**a**

[a] √3 is set by the ILC coordinator when no expansion factor *k* is reported. The reported uncertainty was assumed to have a rectangular distribution with *k*=√3. For explanation see Ch 9.3

[b] **Satisfactory**, **Questionable**, **Unsatisfactory**

[c] Where: **a** = $u_{min} \leq u_{lab} \leq u_{max}$, **b** : $u_{lab} < u_{min}$, and **c** : $u_{lab} > u_{max}$



IMEP-33 : Total Pb in powder

Certified value: X_{ref} = 0.00650 mg·kg^{-1}; U_{ref} = 0.00087 mg·kg^{-1} (k =2); σ = 0.0014 mg·kg^{-1}

no value reported by lab: L004, L054

"less than" reported by : L002, L005, L006, L007, L011, L013, L016, L020, L022, L027, L032, L035, L038, L039, L041, L047, L051, L052, L053, L055, L056, L064, L066

This graph displays all revised measurement results and their associated uncertainties. The uncertainties are shown as reported.
The thick black line corresponds to $\mathbf{X_{ref}}$, the blue lines to the boundary of the reference interval ($\mathbf{X_{ref} \pm 2u_{ref}}$) the red lines that of the target interval ($\mathbf{X_{ref} \pm 2\sigma}$).

Annex 12 : Results for Total Lead - Reconstituted

X_{ref} = 0.00081 and U_{ref} = 0.00010; all values are given in (mg kg^{-1})

Lab ID	Mean (x_{lab})	U_{lab}	k [a]	u_{lab}	Technique	z [b]	zeta [b]	Unc [c]
L002	< 3.66				ICP-OES			
L003	< 0.013				ICP-OES			
L004	0.128	0.0128	2	0.0064	ICP-MS	713.7	19.9	c
L005	< 0.048				ICP-OES			
L007	< 0.01				ICP-MS			
L009	0.0009	0.0002	2	0.0001	ICP-MS	0.5	0.8	a
L010	0.0412	15	2	8	ICP-MS	226.7	0.0	c
L011	< 0.003				ICP-MS			
L012	0.36	0.52	2	0.26	GF-AAS	2015.7	1.4	c
L013	< 0.008				GF-AAS			
L014	< 0.0033				ICP-MS			
L015	0.00055	0.0002	2.3	0.0001	ICP-MS	-1.5	-2.7	a
L016	< 0.02				ETAAS			
L017	0.0021	0.0006	2	0.0003	ICP-MS	7.2	4.3	c
L018	0.0031	0.0006	2	0.0003	ICP-MS	12.9	7.6	c
L019	0.0007	0	√3	0	ICP-MS	-0.6	-2.8	b
L020	< 0.004				GF-AAS			
L022	< 0.01				GF-AAS			
L024	< 0.025				FAAS			
L025	0.0449	0.0009	0.22	0.0041	GF-AAS	247.4	10.8	c
L027	< 0.003				GF-AAS			
L031	0.00067	0.00010	2	0.00005	ICP-MS	-0.8	-2.2	a
L032	< 0.050				GF-AAS			
L037	0.03	0.0054	2	0.0027	GF-AAS	163.8	10.8	c
L038	< 0.010				GF-AAS			
L039	< 0.01				ICP-MS			
L040	0.0006	0.0002	2	0.0001	ICP-MS	-1.2	-1.9	a
L041	< 0.05				GF-AAS			
L043	0.107	0.014	2	0.007	GF-AAS	595.9	15.2	c
L044	0.326	0.039	2	0.020	ICP-OES	1824.9	16.7	c
L045	0.0045	0.0015	1	0.0015	ICP-MS	20.7	2.5	c
L046	0.001	0.001	2	0.001	ICP-MS	1.1	0.4	c
L047	< 0.005				GF-AAS			
L048	< 0.01				GF-AAS			
L049	0.003	0.001	2.776	0.0004	ICP-MS	12.3	6.0	c
L050	0.0029	0.0011	2	0.0006	GF-AAS	11.7	3.8	c
L051	< 0.0092				ICP-MS			
L052	< 0.01				ICP-MS			
L053	< 0.007				GF-AAS			
L055	< 0.01				GF-AAS			
L056	< 0.010				ICP-MS			
L057	0.04	0	√3	0		219.9	979.8	b
L058	< 0.004				ETAAS			
L059	0.010	0	√3	0	GF-AAS	51.6	229.8	b
L060	0.0293	0.0083	2	0.0042	GF-AAS	159.9	6.9	c
L061	0.0088	0.0049	1.96	0.0025	ETAAS	44.8	3.2	c
L062	0.001	30	2	15	ICP-MS	1.1	0.0	c
L064	< 0.05				ICP-OES			
L065	0.133	0.010	√3	0.006	GF-AAS	741.8	22.9	c
L066	< 0.004				GF-AAS			
L067	0.0022	0.0004	2	0.0002	ICP-MS	7.8	6.8	c

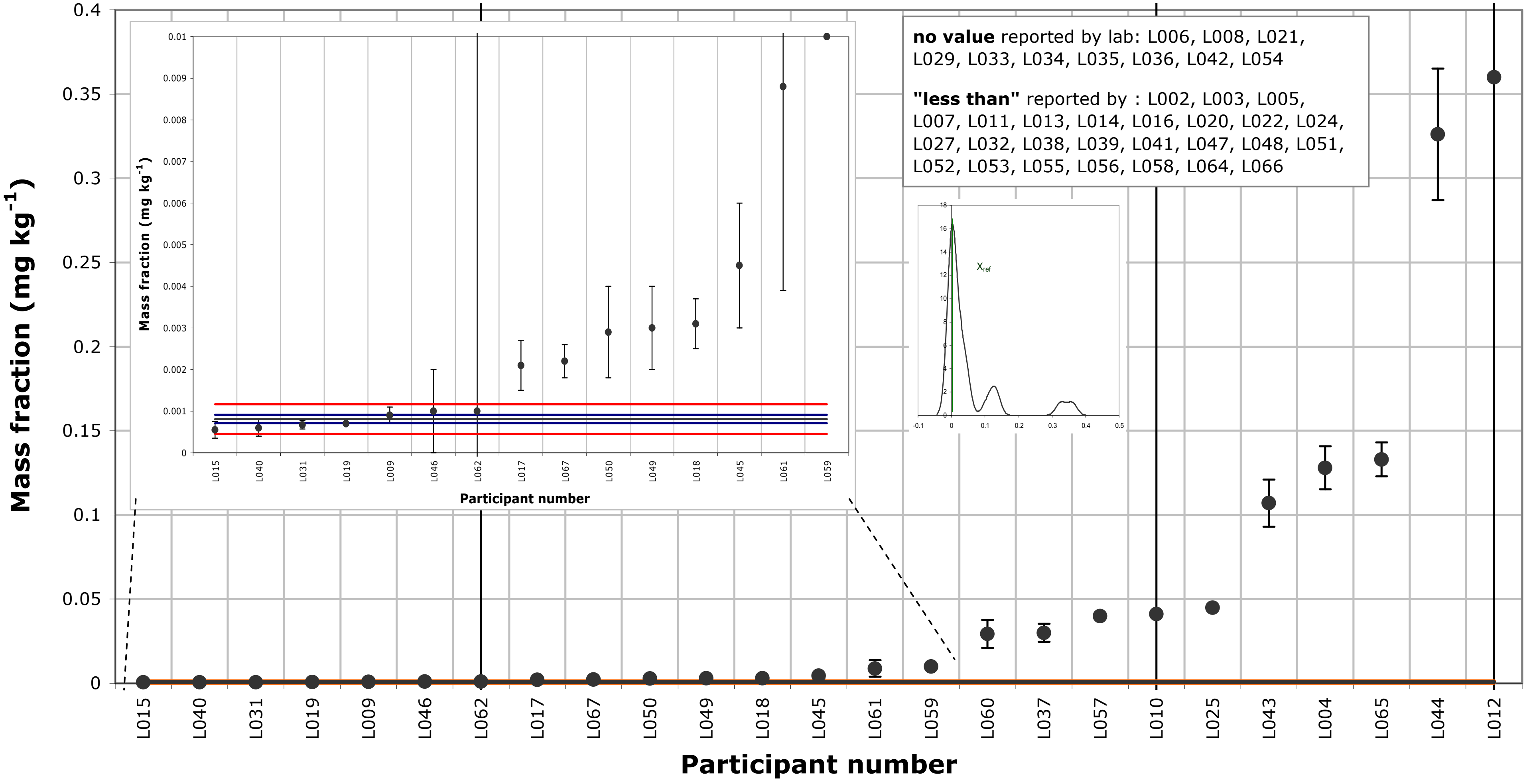
[a] √3 is set by the ILC coordinator when no expansion factor *k* is reported. The reported uncertainty was assumed to have a rectangular distribution with *k*=√3. For explanation see Ch 9.3

[b] **Satisfactory**, **Questionable**, **Unsatisfactory**

[c] Where: **a** = $u_{min} \leq u_{lab} \leq u_{max}$; **b** : $u_{lab} < u_{min}$; and **c** : $u_{lab} > u_{max}$

IMEP-33 : Total Pb in reconstituted sample

Certified value: X_{ref} = 0.00081 mg·kg^{-1}; U_{ref} = 0.00010 mg·kg^{-1} (k =2); σ = 0.00018 mg·kg^{-1}

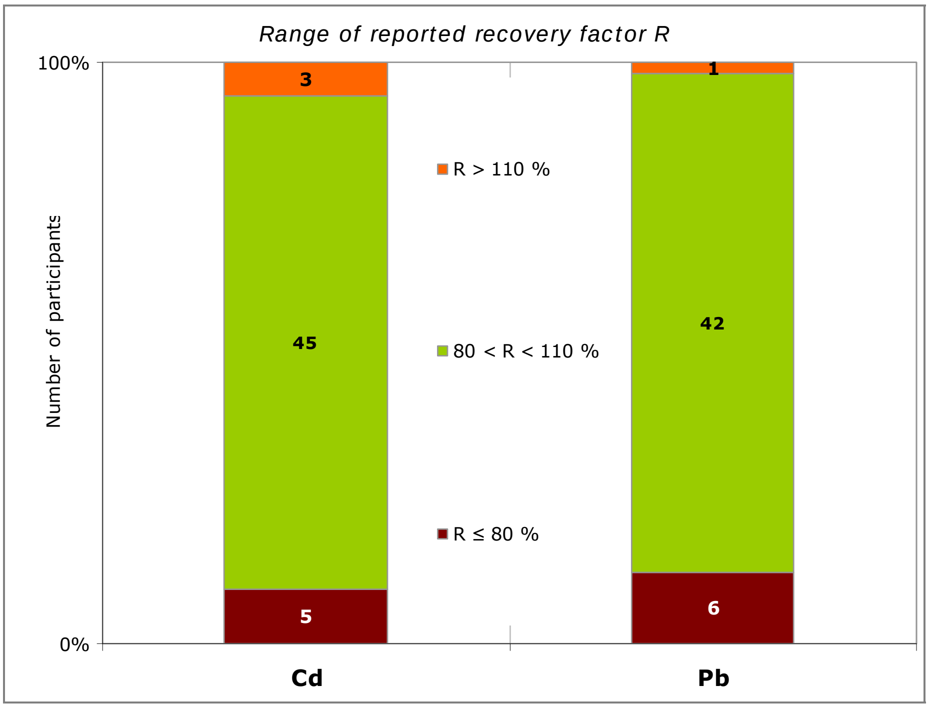


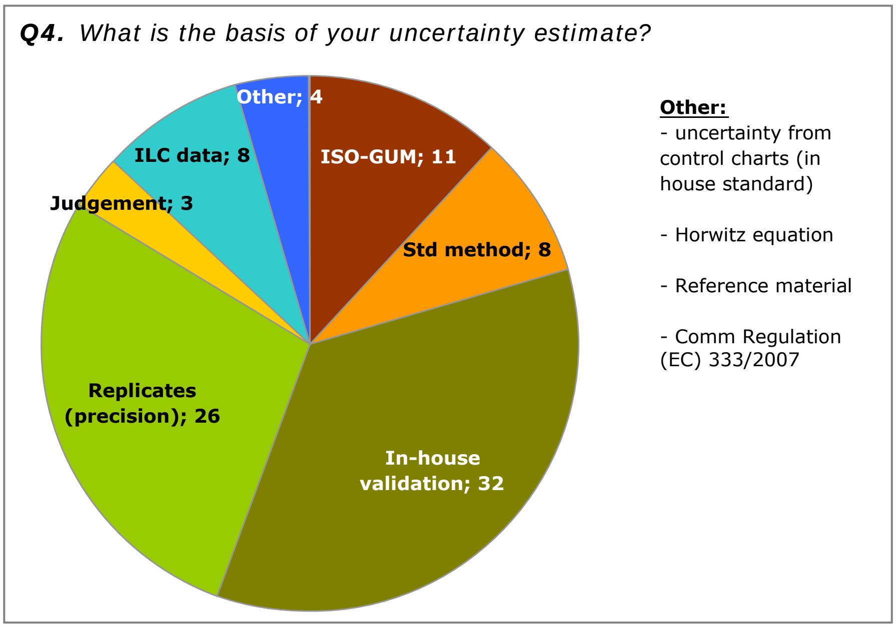
no value reported by lab: L006, L008, L021, L029, L033, L034, L035, L036, L042, L054

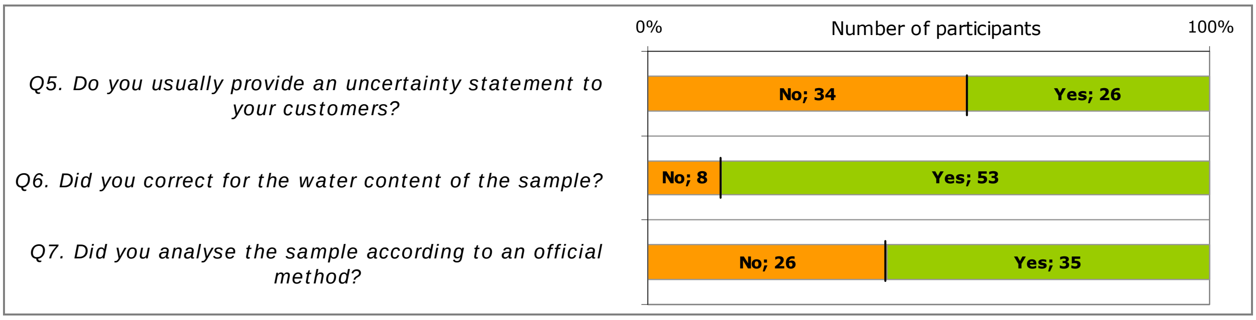
"less than" reported by : L002, L003, L005, L007, L011, L013, L014, L016, L020, L022, L024, L027, L032, L038, L039, L041, L047, L048, L051, L052, L053, L055, L056, L058, L064, L066

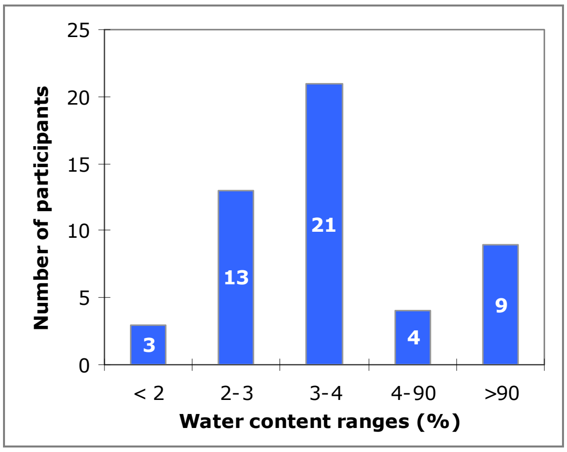
This graph displays all revised measurement results and their associated uncertainties. The uncertainties are shown as reported.
The thick black line corresponds to $\mathbf{X_{ref}}$, the blue lines mark the boundary of the reference interval ($\mathbf{X_{ref} \pm 2u_{ref}}$), and the red lines that of the target interval ($\mathbf{X_{ref} \pm 2\sigma}$).

Annex 13 : Evaluation of questionnaire





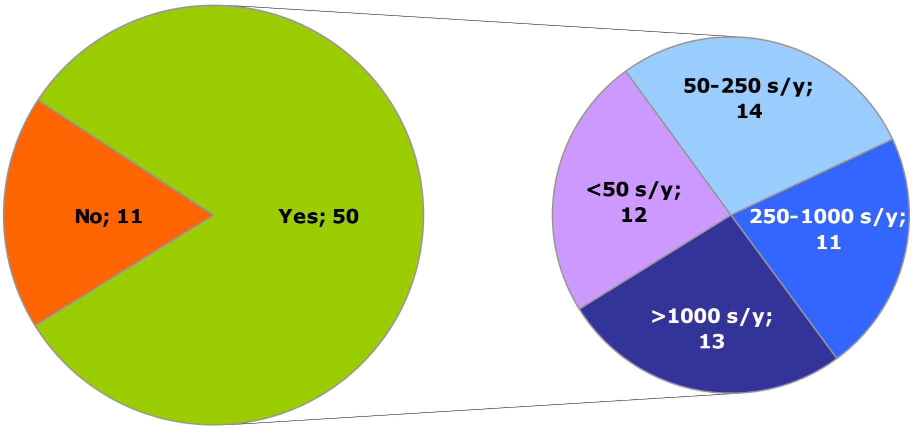




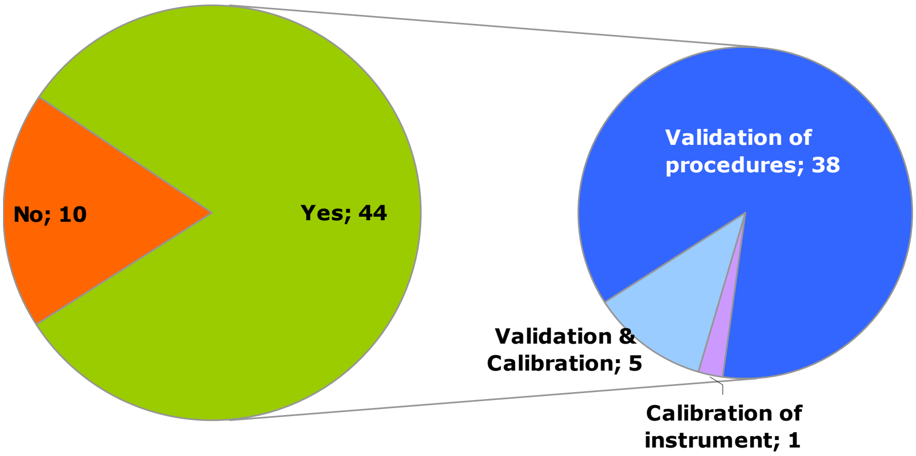
Part Nr	Reasons for not determining water content
L005	measurements<LOD
L013	usually not required by the customer
L016	Very low content of Pb and Cd, very low content of water in the sample
L053	LoD values were reached and these values are rough estimations

Q8. *Does your laboratory carry out this type of analysis on a regular basis?*

If yes, please estimate the number of samples per year.



Q13. *Does your laboratory use a reference material for this type of analysis?*



Annex 14 : Experimental details (Q7, Annex 7)

Part Nr	Official method	Sample pre-treatment	Digestion	Extraction / separation	Instrument calibration
L002		as received	microwave digestion		ICP-OES
L003	AOAC				
L004		0.5g of sample are weighed and deionised water is added up to 4.0g. sample is weighed in duplicate and spiked	Weighed test portion is digested twice on hotplate at 180 C with 10ml of conc. HNO_3 until evaporation to dryness.	After evaporation to dryness, sample is diluted with 1% HNO_3 in a 10ml volumetric flask.	Calibration with 6 standards, calibration range 0.5-200ppb
L005	EPA 5240, 6010C				
L006	EN 13805 and EN 15763				
L007	NMKL procedure nr.186; 2007				
L008			Digestion por via seca. Cenizas. 450ºC		ICP/MS
L009	§ 64 LFGB BVL L 00.00-135 (=DIN EN 15763:2010)				
L010	DIN EN 15763				
L011		none	microwave digestion of 0,5 g of powder or 1,5 g of liquid sample, + 8 mL of HNO_3 20 % + 1 mL of H_2O_2 conc		ICP-MS with internal std (Rh for Cd111 and Bi for Pb206+207+208). First STD for Cd = 0,065 ppb and for Pb= 0,02 ppb
L012		Weigh 0.5g sample. Then add 8ml HNO_3 and 2ml H_2O_2.	Microwave digestion.	Make up the sample to 50ml in the volumetric flask.	5 points calibration by using ICP-MS for Cadmium & GFAAS for Plumbum.
L013		homogeneization/agitation of the sample. reconstitution if required	Microwave digestion (Nitric + H_2O_2), high temp and pressure	dilution with diluted nitric	external calibration curve
L014	Methods from the Danish Veterinary and Food Administration				
L015	DIN EN 15763:2009				
L016	§ 64 LFGB				
L017		Homogeneization	Microwave digestion with nitric acid	No	External calibration using internal standards
L018	according to DIN EN ISO 17294 (E 36 + E 29), modified				
L019	EPA 200.8 (ICP-MS)				

Part Nr	Official method	Sample pre-treatment	Digestion	Extraction / separation	Instrument calibration
L020	DIN EN 13805, DIN EN 14083				
L021	DIN EN ISO 11885				
L022	SLMB				
L024	SR RN 14082/2003				
L025	§64 LFGB L 00.00-19/E 3				
L027	Pb: ASU §64 LFGB L00.00-19/3; Cd: DIN EN ISO 11885; Digestion: ASU §64 LFGB L00.00-19/1				
L029	Governnetal Standart 30178-96, atomic-absorptional method of determination of toxic elements				
L031		No pre-treatment step	Microwave assisted mineralization with 6 ml of HNO_3 and 2 ml of H_2O_2. running time about 1 h	No extraction/separation step	Standard additivation on mineralized sample. Additions: 100 ng/l; 200 ng/l; 500 ng/l
L032	§64 LFGB 00.00-19/1				
L033	E 29				
L034		-	microwave digestion with HNO_3/H_2O_2	-	ICP-MS: daily calibration with external standard solutions; Rh as internal standard
L035	NS-EN ISO 15586 1.utg 10.12.2003, NS 4780 1.utg 1.6.1988				
L036	GSRK 51301-2005				
L037	SR EN 14082		using dry ashing		calibration in five points
L038			Microwave with $HNO_3/H_2O_2/H_2O$		external calibration
L039	NMKL 161 1998				
L040	Cd: § 64 LFGB 00.00 19/1 and § 64 LFGB 00.00 19/3; Pb: § 64 LFGB 00.00 19/1 and ICP-MS				
L041	DIN, §64 LFGB				
L042		According to the instructions	Open acid digestion with conc. nitric acid		External calibration, standards 0-100 µg/l in nitric acid
L043		Homogeneization	Microwave digestion with nitric acid	No extraction	Calibration curve with analyte solutions at known

Part Nr	Official method	Sample pre-treatment	Digestion	Extraction / separation	Instrument calibration
					concentrations
L044		NA	Yes with nitric acid and H_2O_2 in microwave instrument	Dilution of sample digested with water	Calibration 5-100mg/Kg before the session of analysis
L045			microwave		
L046	NMKL 161 & ISO 17294-2				
L047	SIST EN 14083:2003				
L048	EN 14084:2003				
L049			microwave digestion with HNO_3 and H_2O_2		standard addition
L050	§ 64 LFGB: L 00.00 19/3				
L051		HNO_3 2 mL	HPA digestion		external calibration
L052		hand-shake homogenization of the bottle after thawing	0.5 g sample + 5.0 ml HNO_3 + 3.0 ml H_2O_2, digestion at 250 psi for 20 min, then evaporation and reconstitution in 1.0 ml HNO_3, after made up to 5.0 ml with deionized water	-	standard addition + Rh as the internal standard
L053			H_2O_2 and HNO_3 1:2 microwave		five-point calibrations
L054		HNO_3	Microwave	No	Yes
L055		None	Dry ashed at 450ºC	None	External standard
L056	SIST EN 15763				
L057	-	shake	microwave	acid	standard addition
L058			0.5 g were digested with (5+1 mL) HNO_3-H_2O_2 in microwave oven. Final dilution in 10 mL with ultrapure water.		matrix matched calibration
L059	MSZ EN 14084:2003				
L060	LMGB 00.00-19/3		microwave	HNO_3	external standards and recovery
L061			High pressure microwave digestion in quartz insert		standard addition starting from FLUKA traceCERT SI traceable Standard Solution
L062		Omogenization	Nitric acid mineralization in Digi-Prep instrument (open vials) 65°C 950 min.	//	in house calibration curve (solvent)
L064	EN 14082:2003/ICP-OES				
L065	§64-LFBG-Methode				
L066		0.5g of homogenised sample	microwave digestion using HNO_3+H_2O_2	none	calibration based on standard solutions
L067		sample weight (200 mg) in quartz glass, addition of water (0.5 ml)	addition of HNO_3 (5 ml) and H_2O_2 (0.5 ml), microwave digestion at 120°C for 30 min	dilution 1:2	5 calibration points, Rh as Internal Standard

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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 International Measurement Evaluation Programme® (IMEP). It organises interlaboratory comparisons (ILC's) in support to EU policies. This report presents the results of an ILC which focussed on the determination of total Cd and Pb in baby food in support of Commission Regulation (EC) No 1881/2006 of 19 December 2006 setting maximum levels for certain contaminants in foodstuffs.

The test material used in this exercise was baby food formula purchased in a local pharmacy and prepared by the Reference Material Unit of the IRMM for this exercise. Each participant received one bottle containing approximately 15 g of test material. Sixty-six laboratories from 23 countries registered to the exercise and 61 of them reported results. Participants were asked to analyse the measurands in the powder and in the reconstituted form.

The assigned value for total Cd was determined by LGC Ltd (UK) and IRMM using direct isotope dilution inductively coupled plasma mass spectrometry. The assigned value for total Pb was determined at IRMM using the same technique as for Cd. The standard deviation for proficiency assessment $\hat{\sigma}$ was set at 22 % of the assigned value based on the modified Horwitz equation.

Laboratories were rated with z- and ζ-scores (zeta-scores) in accordance with ISO 13528.
Most of the participants reported uncertainties with their results.
The outcome of this exercise is clearly characterised by the very low level of Cd and Pb content in the test material which triggered a high number of "less than" values, overestimation especially for lead very likely due to contamination, and a visible method influence in the case of lead. The results were also evaluated with regard to the reported limit of detection and some incoherencies were observed here as well.

Finally, the dilution factor between the reconstituted form and the powder, which should be 8, was investigated.

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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