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IMEP®

Summary

The Institute for Reference Materials and Measurements (IRMM) of the Joint Research Centre (JRC), a Directorate-General of the European Commission, operates the European Union Reference Laboratory for Heavy Metals in Feed and Food (EU-RL-HM) One of its core tasks is to organize interlaboratory comparisons (ILC's) among appointed National Reference laboratories (NRLs). This report presents the results of the thirteenth proficiency test (PT) organized by the EU-RL-HM, which focussed on the determination of total Cd and Pb in baby food in support to 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. Thirty five laboratories from 26 countries registered to the exercise and all 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 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 results together with the corresponding measurement uncertainty.

The outcome of this exercise is clearly influenced by the very low level content for both measurands in the test material which triggered: - a high number of "less than" values; - overestimated values especially for lead very likely due to contamination. Reported results were satisfactory for total cadmium in both forms, (powder and in the reconstituted formula).

Contents

1 Introduction

The IMEP-113 exercise was carried out by the European Union Reference Laboratory for Heavy metals (EU-RL-HM) for the network of National Reference Laboratories (NRLs) to assess their performance on the determination of total cadmium and lead in baby food formula. In parallel to the IMEP-113, another proficiency test (PT) exercise was organized, using the same test material, whereby food control laboratories were allowed to participate (IMEP-33).

Both exercises were requested by the Directorate General for Health and Consumers (DG SANCO) in view of the ongoing review of maximum levels for Cd and Pb.

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 mean dietary exposure for adults across EU countries is between 1.9 and 3.0 μg kg^{-1} body weight (b.w.) per week and high consumers have estimates in the range of 2.5 to 3.9 μg kg^{-1} b.w. per week. 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. Vegetarians have a higher dietary exposure calculated to be up 5.4 μg kg^{-1} b.w. per week [1].

The CONTAM Panel established in 2009 a new tolerable weekly intake (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 significant 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 provisional TWI 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 characterization. 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 exposure to Cd and Pb should be reduced. In case of lead EFSA didn't say we should reduce the MLs as this is risk management. What they recommended was: *"At the same time, work should continue to reduce exposure to lead, from both dietary and non-dietary sources."*

IMEP-113 was organized to check the analytical capabilities of National Reference Laboratories (NRLs) to determine low concentrations of total Cd and Pb in soya-based baby formulas, in the powder and reconstituted formula (eight fold dilution). For Pb maximum levels currently exist in Regulation (EC) N° 1881/2006 while this is not the case for cadmium.

2 Scope

As stated in Regulation N° 882/2004 of the European Parliament and the Council [3], one of the core duties of the EU-RL-HM is to organize interlaboratory comparisons for the benefit of staff from National Reference Laboratories. The scope of this proficiency test was to test the competence of the appointed NRLs to determine the total content of Cd and Pb in baby food (milk formula) at very low mass fraction level. Measurements were to be done on the powder and on the reconstituted formula (eight fold dilution) because in principle the maximum limits in the European legislation refer to the infant formula as consumed.

The exercise followed the administrative and logistics procedures of the International Measurement Evaluation Program (IMEP®) of the IRMM. IMEP is accredited according to ISO Guide 43.

The PT was carried out in the frame of Commission Regulation (EC) N° 1881/2006 of 19 December 2006 setting maximum levels for certain contaminants in foodstuffs European Commission [4]. The designation of this PT was IMEP-113.

3 Set-up of the exercise

This proficiency test was agreed upon by the National Reference Laboratories (NRLs) network at the fifth EU-RL-HM workshop held on 24 September 2010. Invitation letters for participation were sent to the participants (Annex 1) on 29 March 2011. A web

announcement (Annex 2) was made for the exercise on the IMEP webpage on 04 April 2011 [5].

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.

Laboratory codes were given randomly after the registration deadline.

3.1 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 3),
- a form for confirmation of arrival to be sent back to IMEP at reception of the test material (Annex 4).

The status of delivery of parcels was monitored using the messenger's parcel tracking system on the internet.

3.2 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 3). 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 5).

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 rinced 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 [6]. 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 [7].

The stability study was conducted following the isochronous approach [8-9]. The evaluation of the stability of the test item was made using the software SoftCRM [7]. 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 6.

5 Reference values and their uncertainties

5.1 Assigned value X_{ref}

The total Cd and total 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 total Cd was the mean of the results reported by the two

certifiers. LGC had problems to determine total Pb with a reasonable 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}):

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

Where:

- u_{char} is the estimated uncertainty calculated according to the ISO Guide for the Expression of Uncertainty in Measurement (GUM) [10]
- 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) [10].

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

The standard deviations for proficiency assessment $\hat{\sigma}$ (also called target standard deviation) were calculated applying the modified Horwitz 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 ($X_n \pm U_n$)		Total Pb ($X_n \pm U_n$)	
	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

All 35 laboratories that registered for participation submitted their 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. Hence, 2 out of the 3 and 6 out of the 16 reported "less than" values for total Cd and Pb, respectively, were identified as incorrect.

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,"less than" values and number of incorrect statements

	Total Cd		***Total Pb***	
	Powder	Reconstituted	Powder	Reconstituted
N°	31	13	15	4
"less than" ("0")	3 (0)	5 (1)	16 (2)	12 (1)
Incorrect statement "less than X" < (X_{ref}-U_{ref})	2		6	

N° – number of participants having reported evaluable results. X_{lab} = reported result, X_{ref} and U_{ref} as defined in Table 1.

6.2 Scores and evaluation criteria

Individual laboratory performance was expressed in terms of z- and ζ-scores in accordance with ISO 13528 [6].

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

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:

|score| ≤ 2	satisfactory result	(green in the tables of Annexes 7 - 10)
2 < |score| ≤ 3	questionable result	(orange in the tables of Annexes 7 - 10)
|score| > 3	unsatisfactory result	(red in the tables of Annexes 7 - 10)

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 [11].

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 organizer as the maximum acceptable standard uncertainty. Values for $\hat{\sigma}$ in IMEP-113 were set to 22 % of the respective assigned value, following the modified Horwitz equation.

6.3 Relevance of the limit of detection in the outcome of IMEP-113 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 immediate action of the European Commission is to reduce 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 total 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 total 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 5).

When evaluating the results together with the answers to the questionnaire one observes: (i) the 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 lower acceptance limit of the assigned values, X_{ref} (at approximately 95 % confidence level, expressed as $L_L = X_{ref} - U_{ref}$). They are shown in Table 3. The table explains why results for Cd are overall better than for Pb, as its mass fraction in the material is higher than that of Pb and the reported LoDs generally lower than those for Pb. For the latter, the mass fraction is clearly in the range of the reported LoDs, or even lower for the reconstituted formula.

The reported LoDs range from 0.000011 to 0.02 mg kg^{-1} for Cd and from 0.000016 to 0.2 mg kg^{-1} for Pb. The participants used 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 the reported results as "less than" a value X and the lower acceptance limit for the assigned value ($L_L = X_{ref} - U_{ref}$) revealed the incorrectness of some reported "less than" values (Table 3).

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.

Table 3 – Summary of incoherent situations when evaluating the submitted results, the LoD and the lower acceptance limit (L_L) for the reference value ($X_{ref} - U_{ref}$)

Situation	*Laboratory identification*			
	Cd Powder	*Cd Reconstituted*	*Pb Powder*	*Pb Reconstituted*
"Less than X" and $X \leq X_{ref} - U_{ref}$ (L_L)	L02, L28	L21	L03, L04, L08, L16, L17, L19	
"Less than X" and X > LoD	L02, L22, L28	L02, L06	L01, L02, L03, L08, L16, L17, L18, L22, L28, L34	L01, L02, L16, L17, L18,
"Less than X" and X = LoD		L04, L21	L04, L07, L09, L19, L25, L33	L04, L07, L13, L19, L21, L31

6.4 Evaluation of the ratio – powder / reconstituted formula

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. It appears that those ratios ranged from 1.0 to 16.0. The few participants for whom it was possible to calculate both ratios (for Cd and Pb), reported a similar ratio, thus these participants were consistent in their estimations.

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.

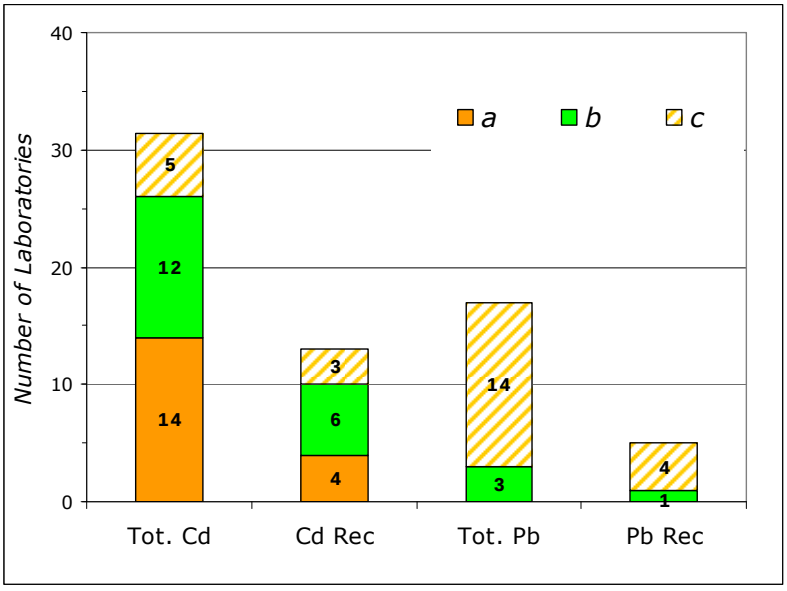
6.5 Uncertainty evaluation

Figure 1 gives an overview of the uncertainty evaluation. The percentage of participants in group "a", giving uncertainties within u_{min} (= u_{ref}) to u_{max} (= $\hat{\sigma}$), ranges between 0 % and 45 %. Furthermore, it appears that participants tend to overestimate the uncertainty ("c" in Fig. 1), rather than to underestimate it ("b" in Fig. 1). These findings were mostly true for total Pb. Group "b" also includes those who have not reported an uncertainty and for whom u was set to "0". Despite this uncertainty overestimation the reported results did not overlap with the accepted range of results as reflected by the low number of participants that obtained satisfactory scores for total Pb (see below and Annex 8 and 10).

This outcome together with the calculated ζ-scores indicates that laboratories have still difficulties in making a realistic estimation of the measurement uncertainty.

Participants who are not familiar with the concept of uncertainty are advised to read the GUM [10], the EURACHEM / CITAC Guide CG 4 [11] or to consult the informative web pages of the National Institute of Standards and Technology (NIST) on the subject of uncertainty evaluation [12].

Fig. 1 – Uncertainty evaluation: a = $u_{min} \leq u_{lab} \leq u_{max}$; b = $u_{lab} < u_{min}$; c = $u_{lab} > u_{max}$



Where: Cd Rec and Pb Rec refers to total Cd and total Pb in the reconstituted formula, respectively.

6.6 Laboratory results and scorings

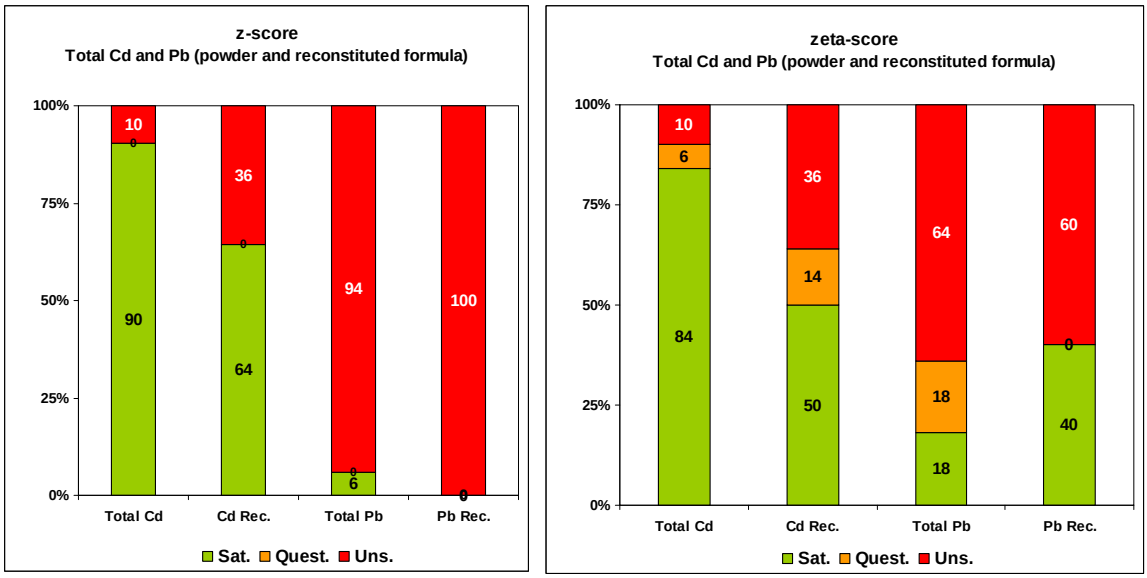
The results reported by the participants are listed in Annexes 7 to 10. A table of the results and their graphical representation are provided. The tables also contain z-, ζ-scores and the evaluation of uncertainties. The Kernel density plots, included in the result graphs, are an alternative to histograms, 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 2 presents an overview of the z- and ζ-scores. The laboratories' performances appear to be good for total Cd in the powder formula with a percentage of satisfying z-scores of 90 %. For the reconstituted formula this percentage decreased to 64 %, hence less satisfactory, probably due to the fact that the concentration level 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 6 % and 0 % performing satisfactory for the powder and for the reconstituted formula, respectively.

Concerning the ζ-scores, only total Cd in powder formula presented a percentage of satisfactory scores above 80 %. For the reconstituted formula half of the participants (50 %) got a satisfactory score. For total lead the percentage of satisfactory scores ranged between 18 % and 40 % (for the powder and reconstituted formula, respectively).
The percentage of satisfactory ζ-scores for total Pb emphasize the fact that when taking account of the uncertainties of both results (the reference and the participant's reported value) a significant improvement in the overall performance of the participants could be observed (from 0 %, if expressed as a z-score to 40 % if expressed as a ζ-score, and from 6 to 18 % for the reconstituted formula and for the powder, respectively).

Fig. 2 - Overview of scores (in %)



The question of the participant's LoD led to the estimation of all the potentially influential factors on their reported values. This was achieved by establishing a multivariate linear relationship between their reported z-score values and all the answers from the questionnaire. Partial least squares-regression (PLS-R) was used (The Unscrambler X 10.1, Camo, Norway). Due to the reduced number of participants who reported a value for total Pb no model was attempted for this element. The total Cd PLS-R model captured 77 % of the total variance (using the first three components) with a model error significantly lower than the observed variability (expressed as a standard deviation of all reported calculated z-scores for this measurand).

Figure 3 show the PLS-R plots (scores; "A" and loadings; "B") for the total Cd z-score value as Y-variable and all the answers from the questionnaire as X-variables.

Among all the influencing factors, some quality assurance related issues have been identified as mostly relevant (being positively correlated with participants who got satisfactory z-scores):

i) the experience on analysing identical test samples (analysing between 250-1000 or more than 1000 test samples per year),
ii) the fact that the laboratory is following an official method (question 7, Q7),
iii) the use of reference materials (Q11) for validation purposes (RM Val),
iv) having a quality system in place (Q9)

When comparing with the overview of all the reported results (Annex 7) one can see all the participants who have answered affirmatively to the previous questions have also reported a value which gave a correct z-score value (all laboratories projected in the upper left side of Figure 3 (PLS score plot, left side of "A")). Inversely, for the majority of the participants for which their combinations of answers to the questionnaire (and their reported result) resulted in being projected on the upper right side of the PLS score plot (right side of "A" in Fig. 3), a higher z-score value was computed (compare with Annex 7). The reasons for that could be explained by inversing the above mentioned quality system related issues, (i.e., an official method was not followed; no RM used for calibration purposes and lower expertise in identical test samples (only 0-50 samples per year)).

The technique used seems not to influence significantly the performance of the participants. From the five participants having scored a questionable or unsatisfactory result ($z > 2$) for total Cd, two have used ICP-MS, other two electrothermal atomic absorption spectrometry (ET-AAS) and one graphite furnace atomic absorption spectrometry (GF-AAS).

In the case of total Pb (in powder), only one participant got a satisfactory result, obtained using inductively coupled plasma - mass spectrometry (ICP-MS). Out of the 15 participants who have not reported a "less than" value (45.5 % of the total) 6 used ICP-MS, 7 used GF-AAS and 2 used ET-AAS. Similarly, out of the 16 participants (55.5 % of the total) who have reported a "less than" value, 11 used ICP-MS, where only five used AAS techniques (GF-AAS, Zeeman-AAS or ET-AAS).

ICP-MS does not guarantee a good result, as is proven by a 35.7 % of unsatisfactory results, and laboratories are advised to verify the method details of the more "successful" participants.

Annex 11 summarises all answers related to the analytical method used by the participants.

Fig. 3 – Score (A) and loading (B) plot for the PLS-R model establishing a multivariate relationship between the Cd z-score and all the answers from the questionnaire. The model identifies which X-variables (questions from the questionnaire) are mostly influencing this relationship.

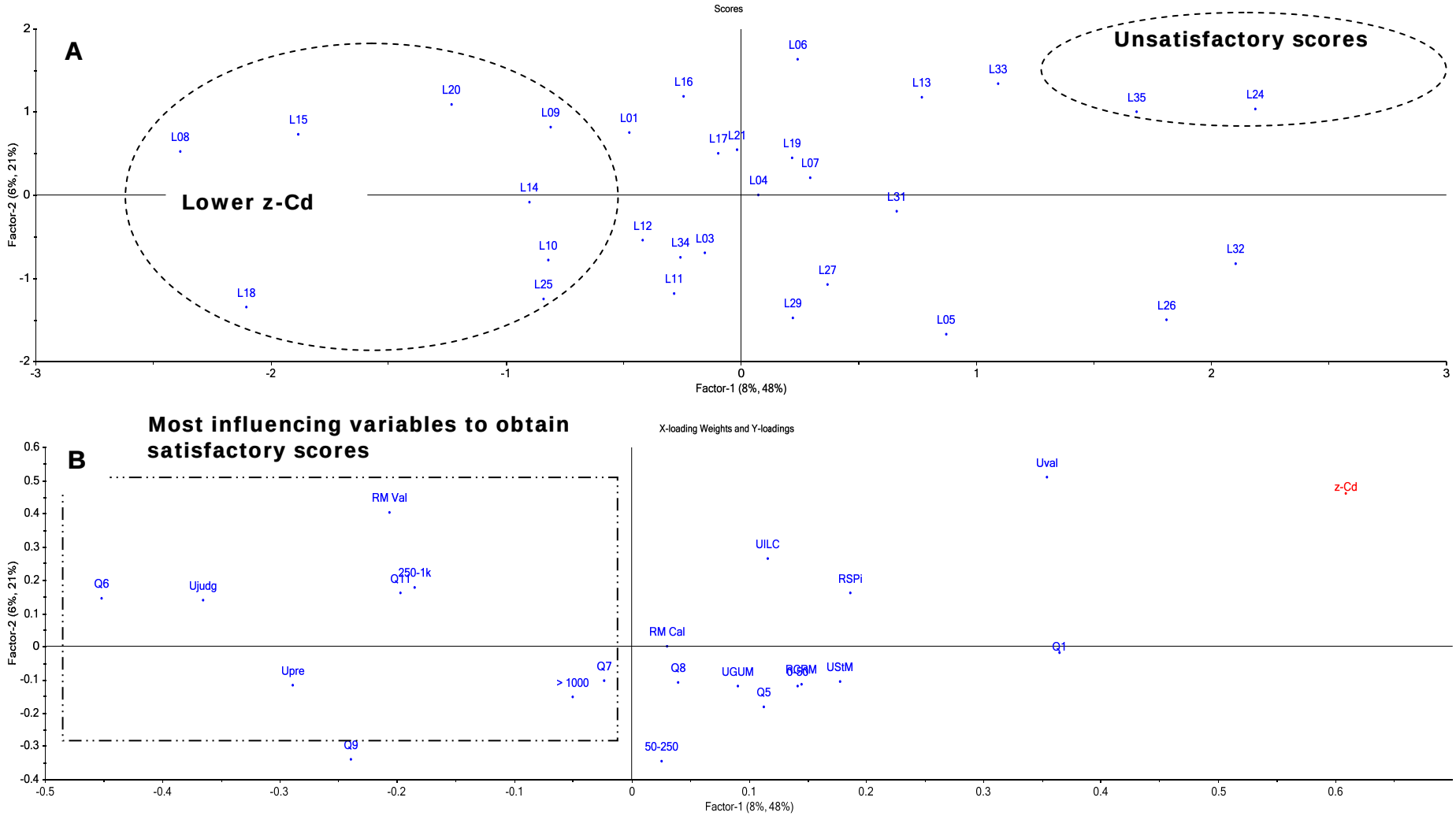


Table 4 lists all the reference materials used by the participants. Table 5 lists the comments from the participants regarding the present PT.

Table 4 – Reference materials used by the participants as reported in the questionnaire

Lab ID	Which reference material?
L01	BCR 150, BCR 063R
L02	LGC 7162 Strawberry Leaves
L03	Wheat Flour NIST 1567a
L04	
L05	T0784; BCR 151
L06	rest of PT test materials
L07	
L08	NIST 1547
L09	BCR 191, NCS ZC 73009
L10	Rice 1568A
L11	NIST1549 non-fat milk powder
L12	BCR-150, BCR-151
L13	
L14	Previous PT round surplus material and NIST reference material if available
L15	IMEP-110 and BCR-191
L16	BCR-191
L17	IRMM-804 & BCR-150
L18	IAEA-155, T-10
L19	Various including BCR 150, NIST 8436, NIST 1547, NIST 1548a
L20	BCR, NIST
L21	Cd, Pb standard solutions; PT materials
L22	bovine leaver NIST1577b; tea GBW10016 MC China
L23	BCR 279, NIST 1570a
L24	BCR 151
L25	
L26	
L27	EU-RL-CEFAO, spiked samples
L28	
L29	
L30	
L31	NIST 1548, 1568, 1566, 1515, 1570; BCR 150, 66, 422, CTA-OTL-1; other
L32	
L33	CPAchem 1000 g/l
L34	High -Purity Standards
L35	

Table 5 – Comments as taken from the questionnaire

Lab ID	Comments
L07	The sample was not stored at the cold place (it was store at room temperature)
L08	Out of a mistake we didn´t have enough Sample for the Reconstitution
L12	Bottle contained approximately 15 g of the test material.
L14	Unfortunatly the sample size submitted was not enough to proceed to the analysis of the sample in the reconstituted form. Also repeated testing and recoveries were limited by the sample size.
L15	Total lead and reconstituted form not tested due to technical problems of the instrument
L16	Our limits of quantification (LOQ): Pb 0.005 mg/kg, Cd 0.001 mg/kg.
L21	Cd, Pb standard solutions are always used for the calibrations and PT materials for QC and validation.
L26	specific method for the determination of Cd and Pb in Babyfood is not operational in our lab, however we dor have a flex-scope accreditation for the determination of elements using ICP-MS
L27	We didn't report results for Pb for any of the samples because of the low amount of Pb (close to our LoD)
L28	Our institute do not provide official control of food and because of this analysis of food as well.

7 Conclusion

The IMEP-113 exercise was run in parallel to the IMEP-33, open to all food control laboratories. The aim was to verify the capability of National Reference Laboratories to analyse low levels of Cd and Pb in view of the ongoing review of Regulation (EC) N° 1881/2006 as regards Cd and Pb.

The results for Cd were quite satisfying for the powder (90 % of the total reported values got a satisfying z-score), but less satisfactory for the reconstituted formula (64 % satisfying z-score). If taking account of the uncertainties in both the reported values by the participant and the one associated with the assigned value (ζ-score), these values were 84 % and 50 %, for the powder and reconstituted formula, respectively.
The main influencing factors for these good scoring were related with the experience and the use of quality assurance tools by the participants. No other significant 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 powder form show a high number of "less than" values (54.5 %) and unsatisfactory z-scores (94 %), and these are increasing for the reconstituted formula (76.5 % of "less than" and 100 % for unsatisfactory z-scores, respectively). Due to the very low amount of participants obtaining satisfactory scores for the total Pb determination, both in the powder and in the reconstituted formula, it was not possible to make a sound study on the estimation of the influencing factors on the reported results.

So far, the maximum limit (ML) in the European legislation for lead in infant formula applies to the product as consumed. For cadmium, a maximum level has not been established yet. 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 results in a suspension and not on a perfect solution, the EU-RL-HM advises to introduce MLs in the legislation which refers 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
AGES GmbH	AUSTRIA
CODA-CERVA	BELGIUM
Scientific Institute of Public Health	BELGIUM
CLVCE	BULGARIA
State General Laboratory	CYPRUS
CISTA(ÚKZÚZ)	CZECH REPUBLIC
State Veterinary Institute Olomouc	CZECH REPUBLIC
DTU Food	DENMARK
AGRICULTURAL RESEARCH CENTRE	ESTONIA
Veterinary and Food Laboratory	ESTONIA
Finnish Customs Laboratory	FINLAND
Finnish Food Safety Authority Evira	FINLAND
ANSES	FRANCE
Federal Office of Consumer Protection and Food Safety (BVL)	GERMANY
GENERAL CHEMICAL STATE LABORATORY	GREECE
REGIONAL CENTER OF PLANT PROTECTION AND QUALITY CONTROL OF MAGNISIA	GREECE
Central Agricultural Office	HUNGARY
Central Agricultural Office	HUNGARY
Central Agricultural Office, Food and Feed Safety Directorate	HUNGARY
Health Service Executive	IRELAND
Istituto Superiore di Sanità	ITALY
Istituto Zooprofilattico Sperimentale del Piemonte Liguria e Valle d'Aosta	ITALY
Institute of Food Safety,Animal Health and Environment	LATVIA
National food and veterinary risk assessment institute	LITHUANIA
Public Health Laboratory	MALTA
Food and Consumer Product Safety Authority	NETHERLANDS
RIKILT	NETHERLANDS
NIFES - National Institute of Nutrition and Seafood Research	NORWAY
National Institute of Public Health-National Institute of Hygiene	POLAND
Hygiene Institute of Veterinary Public Health	ROMANIA
State veterinary and food institute - Kosice	SLOVAKIA
National Veterinary Institute	SLOVENIA
Laboratorio Arbitral Agroalimentario	SPAIN
National Food Administration	SWEDEN
Food and Environment Research Agency (Fera)	UNITED KINGDOM

Abbreviations

AMC	Analytical Methods Committee of the Royal Society of Chemistry
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
GF-AAS	Graphite furnace atomic absorption spectrometry
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
NRL	National Reference Laboratory
PT	Proficiency Test
PTWI	Provisional Tolerable Weekly Intake
RM	Reference material

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[3] Commission Regulation (EC) No 882/2004 of the European Parliament and of the Council of 29 April 2004 on official controls performed to ensure the verification of compliance with feed and food law, animal health and animal welfare rules.

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Annexes

Annex 1 : Invitation letter sent to NRLs

EUROPEAN COMMISSION
JOINT RESEARCH CENTRE

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

European Union Reference Laboratory
Heavy Metals in Feed and Food

Geel, 29 March 2011
JRC.DG.D6/IBa/mdr/ARES(2011) 346581

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

Dear Madam / Sir,

Inter-laboratory comparison for EU-RL Heavy Metals in Feed and Food

On behalf of the EU-RL Heavy Metals in Feed and Food, I would like to invite you to participate in the Proficiency Test [IMEP-113] for the **"Determination of total Cd and Pb in baby food"**.
I would like to remind you that - according to Regulation (EC) No 882/2004 - you have the duty as NRL to participate in PTs organised by the EU-RL-HM if you hold a mandate for the type of matrix investigated.
Please register electronically for this interlaboratory comparison using the following link:

https://irmm.jrc.ec.europa.eu/ilc/ilcRegistration.do?selComparison=681

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

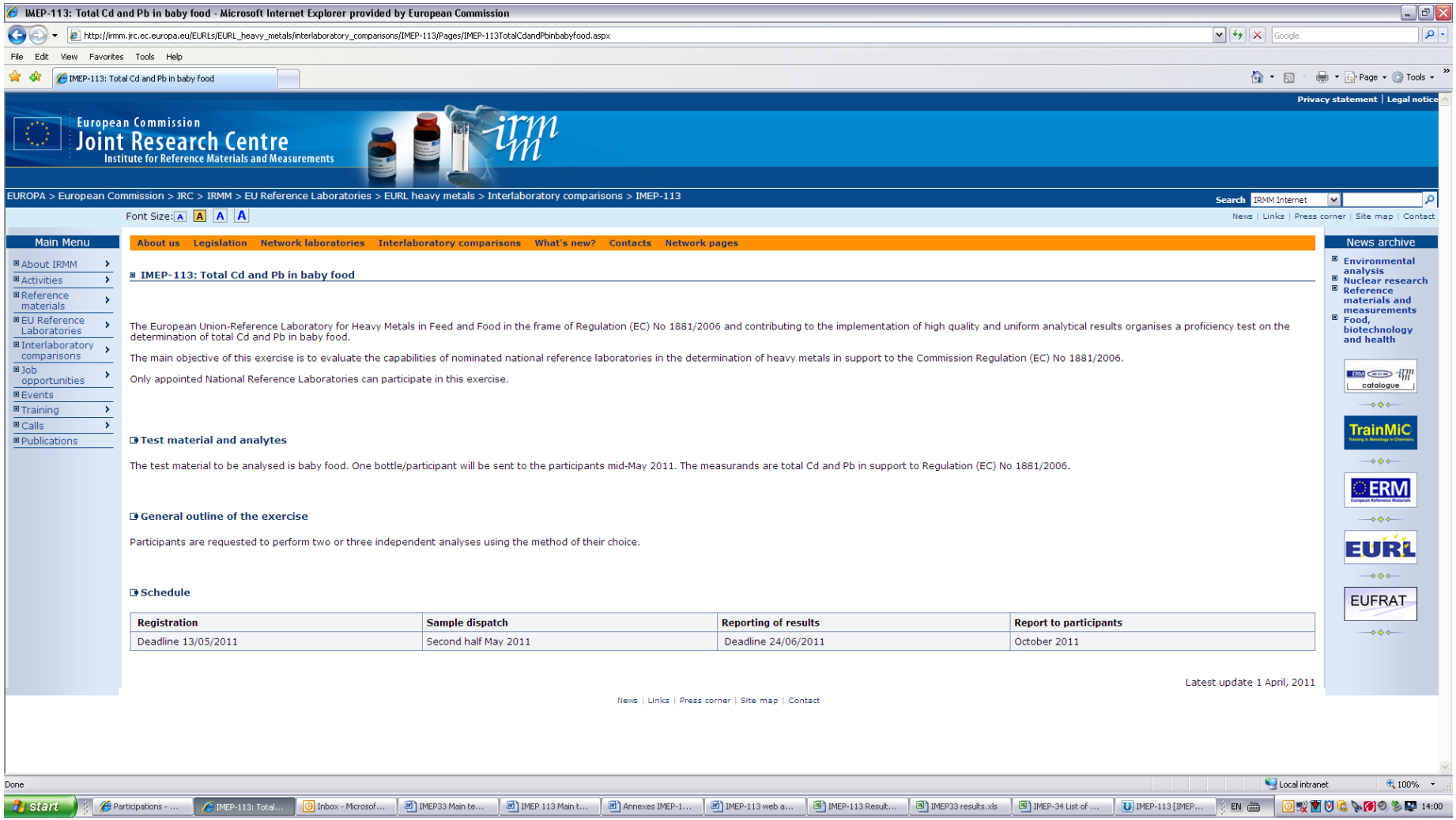
The **deadline for registration is 13 May 2011**. Samples will be sent to participants during the second half of May. The deadline for submission of results is 24 June 2011.
I am the project leader for this interlaboratory comparison. In case of questions/doubts, do not hesitate to contact me at fernando.cordeiro-raposo@ec.europa.eu .

Yours sincerely

Dr. F. Cordeiro Raposo
Project Co-ordinator

Cc: Franz Ulberth

Annex 2 : IRMM – IMEP web announcement



Annex 3 : Accompanying letter

EUROPEAN COMMISSION
JOINT RESEARCH CENTRE

Institute for reference materials and measurements
Food Safety & Quality

European Union Reference Laboratory
Heavy Metals in Feed and Food

Geel, 16 May 2011
JRC.DDG.D6/FCo/ive/ARES(2011)/527591

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

Participation in IMEP-113, 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-113 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.

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.

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

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. Fernando Cordeiro
IMEP-113 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 4 : Acknowledgment of receipt form

EUROPEAN COMMISSION
JOINT RESEARCH CENTRE

Institute for reference materials and measurements
Food Safety & Quality

European Union Reference Laboratory
Heavy Metals in Feed and Food

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

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

IMEP-113

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 Fernando Cordeiro

IMEP-113 Coordinator
EC-JRC-IRMM
Retieseweg 111
B-2440 GEEL, Belgium

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

Annex 5 : Questionnaire

Submission Form

Recovery factor R (%) and LoD (mg/kg)

Please complete below table.

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

1. **Did you apply a recovery factor to correct your measurements?**

- ○ No
- ○ Yes

1.1. If yes, did you determine R by:

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

1.1.1. If other, please specify:

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

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 6 : Homogeneity and stability studies

6.1 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]		
$0.3\,\hat{\sigma}$	0.697	
S_x	0.096	
S_w	0.081	
S_s	0.077	
$S_s \leq 0.3\ \hat{\sigma}$?	Yes	
Test result	Passed	

6.2 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

6.3 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]		
$0.3\,\hat{\sigma}$	0.356	
S_x	0.311	
S_w	0.316	
S_s	0.216	
$S_s \leq 0.3\ \hat{\sigma}$?	Yes	
Test result	Passed	

6.4 Stability study for total lead

Stability Study – Total lead

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 7: Results for Total Cadmium – Powder

Assigned range: X_{ref} = 0.01176, U (k = 2) = 0.00109 (all values in mg kg^{-1})

Lab ID	Mean (X_{lab})	Unc.	k[a]	u_{lab}	Technique	z-score[b]	ζ-score[b]	Unc [c]
L01	0.016	0.002	2	0.001	ICP-MS	1.64	2.05	**b**
L02	< 0.01				FAAS			
L03	0.0119	0.0031	2	0.00155	GF-AAS	0.05	0.04	**a**
L04	0.012	0.003	2	0.0015	GF-AAS	0.09	0.08	**a**
L05	0.012	0.003	2	0.0015	ICP-MS	0.09	0.08	**a**
L06	0.016	0.005	2	0.0025	GF-AAS	1.64	0.84	**a**
L07	0.0131	0.0013	2	0.00065	ETAAS	0.52	0.95	**b**
L08	0.0095	0.0024	2	0.0012	ICP-MS	-0.87	-0.92	**a**
L09	0.013	0.006	2	0.003	GF-AAS	0.48	0.21	**c**
L10	0.0114	0.0021	2	0.00105	GF-AAS	-0.14	-0.17	**b**
L11	0.012	0.001	2	0.0005	ICP-MS	0.09	0.21	**b**
L12	0.012	0.002	2	0.001	GF-AAS	0.09	0.12	**b**
L13	0.014	0.0028	√3	0.00162	GF-AAS	0.87	0.79	**a**
L14	0.009	0.002	2	0.001	ICP-MS	-1.07	-1.33	**b**
L15	0.0112	0.0024	2	0.0012	ICP-MS	-0.22	-0.23	**a**
L16	0.0142	0.0058	2	0.0029	ETAAS	0.94	0.42	**c**
L17	0.014	0.003	2	0.0015	ICP-MS	0.87	0.73	**a**
L18	0.0091	0.0007	2	0.00035	ICP-MS	-1.03	-3.00	**b**
L19	0.014	0.0026	2	0.0013	ICP-MS	0.87	0.84	**a**
L20	0.014	0.003	2	0.0015	ICP-MS	0.87	0.73	**a**
L21	0.0137	0.0033	2	0.00165	ICP-MS	0.75	0.58	**a**
L22	< 0.04				ICP-MS			
L24	0.021	0.0019	2	0.00095	GF-AAS	3.57	4.67	**b**
L25	0.012	0.0015	2	0.00075	ICP-MS	0.09	0.15	**b**
L26	0.0123	0.0026	2	0.0013	ICP-MS	0.21	0.20	**a**
L27	0.014	0.0062	2	0.0031	ZETA-AAS	0.87	0.36	**c**
L28	< 0.02				ETAAS			
L29	0.014	0.002	2	0.001	ETAAS	0.87	1.08	**b**
L30	0.053	0.011	2	0.0055	ICP-MS	15.94	3.74	**c**
L31	0.012	0.002	2	0.001	GF-AAS	0.09	0.12	**b**
L32	0.0156	0.0019	√3	0.00110	GF-AAS	1.48	1.94	**a**
L33	0.0152	0.006	2	0.003	ICP-MS	1.33	0.57	**c**
L34	0.0133	0.0021	3.2	0.0006563	ICP-MS	0.60	0.71	**b**
L35	0.02	0.003	2	0.0015	ICP-MS	3.18	2.70	**a**

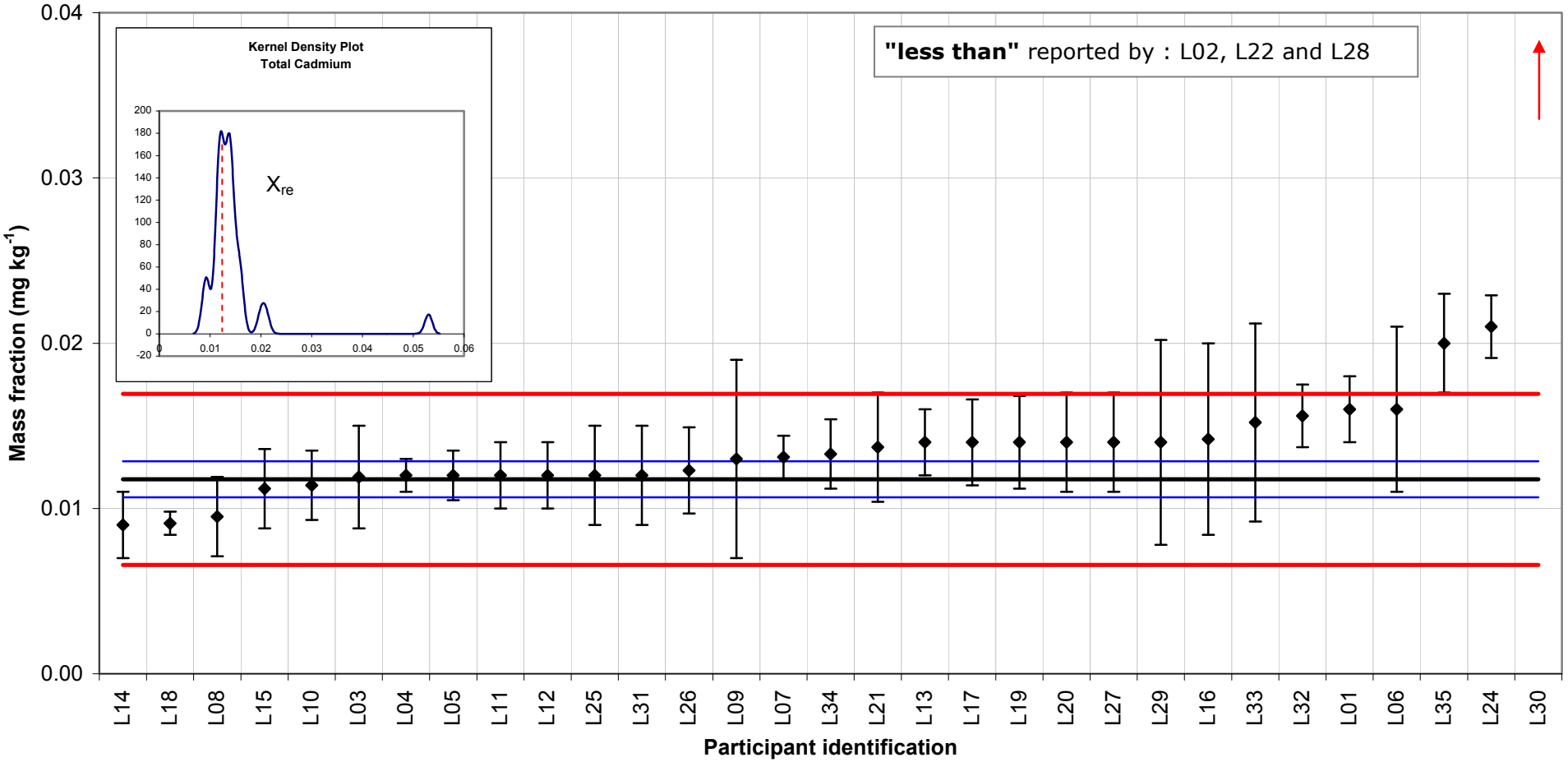
[a] √3 is set by the ILC coordinator when no expansion factor *k* is reported. The reported uncertainty was assumed to have a rectangular distribution with $k=\sqrt{3}$.

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

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

IMEP-113 (Total Cd and Pb in baby food): Total Cd in powder

Certified value: X_{ref} = 0.01176 mg·kg^{-1}; U_{ref} = 0.00109 mg·kg^{-1} (k=2); σ = 0.00260 mg·kg^{-1}



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

Annex 8: Results for Total Lead – Powder

Assigned range: X_{ref} = 0.00650, U (k = 2) = 0.00087 (all values in mg kg^{-1})

Lab ID	Mean (X_{lab})	Unc.	k[a]	u_{lab}	Technique	z-score[b]	ζ-score[b]	Unc [c]
L01	< 0.014				ICP-MS			
L02	< 0.12				ICP-MS			
L03	< 0.008				ICP-MS			
L04	< 0.006				ICP-MS			
L06	0.029	0.01	2	0.005	GF-AAS	15.73	2.25	c
L07	< 0.04				GF-AAS			
L08	< 0.0075				ICP-MS			
L09	< 0.05				ICP-MS			
L10	0.0476	0.01	2	0.005	GF-AAS	28.74	4.11	c
L11	0	0	0	0		-4.55	-14.94	b
L12	0.022	0.006	2	0.003	GF-AAS	10.84	2.58	c
L13	0.014	0.0035	√3	0.00202	ICP-MS	5.24	2.13	c
L14	0.026	0.005	2	0.0025	GF-AAS	13.64	3.89	c
L15	0	0	0	0		-4.55	-14.94	b
L16	< 0.005				ICP-MS			
L17	< 0.006				ICP-MS			
L18	< 0.048				GF-AAS			
L19	< 0.005				ICP-MS			
L20	0.011	0.004	2	0.002	ICP-MS	3.15	1.12	c
L21	0.0053	0.0007	2	0.00035	ICP-MS	-0.84	-1.46	b
L22	< 0.08				ZETA-AAS			
L23	0.182	57	2	28.5	GF-AAS	122.73	0.00	c
L24	0.15	0.02	2	0.01	ETAAS	100.35	7.17	c
L25	< 0.05				ETAAS			
L26	0.0204	0.0045	2	0.00225	ICP-MS	9.72	3.07	c
L28	< 0.3				ICP-MS			
L29	0.145	0.02	2	0.01	GF-AAS	96.85	6.92	c
L30	0.083	0.022	2	0.011	ICP-MS	53.50	3.48	c
L31	0.022	0.005	2	0.0025	GF-AAS	10.84	3.09	c
L32	0.1096	0.0118	√3	0.00681	ICP-MS	72.10	8.73	c
L33	< 0.05				FAAS			
L34	< 0.02				ICP-MS			
L35	0.032	0.004	2	0.002	ETAAS	17.83	6.34	c

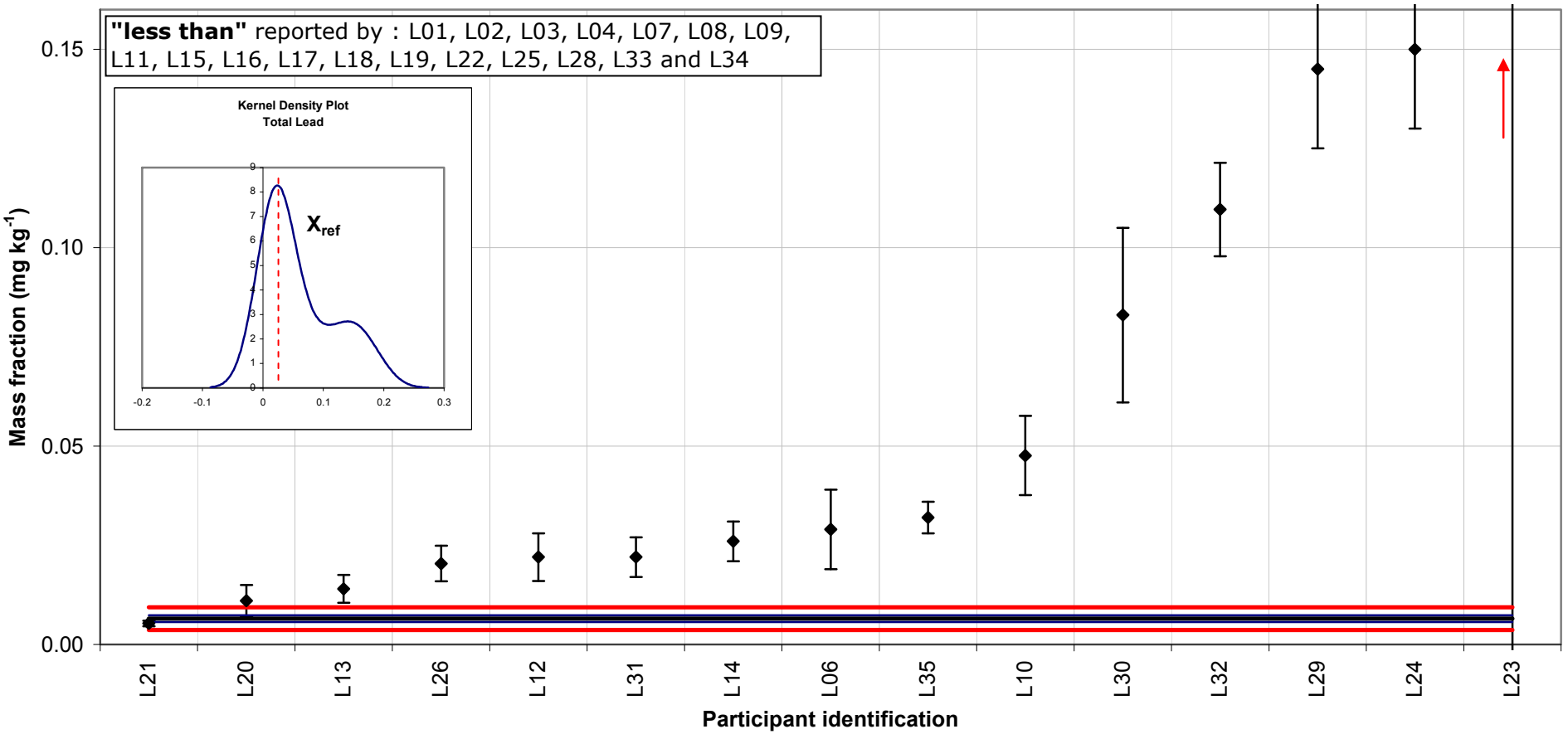
[a] √3 is set by the ILC coordinator when no expansion factor *k* is reported. The reported uncertainty was assumed to have a rectangular distribution with $k=\sqrt{3}$.

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

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

IMEP-113 (Total Cd and Pb in baby food): Total Pb in powder

Certified value: X_{ref} = 0.00650 mg·kg^{-1}; U_{ref} = 0.00087 mg·kg^{-1} (k=2); σ = 0.00143 mg·kg^{-1}



This graph displays all 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 the target interval ($\mathbf{X_{ref} \pm 2\sigma}$)

Annex 9: Results for Total Camium – Reconstituted formula

Assigned range: X_{ref} = 0.00147, U (k = 2) = 0.00014 (all values in mg kg^{-1})

Lab ID	Mean (X_{lab})	Unc.	k[a]	u_{lab}	Technique	z-score[b]	ζ-score[b]	Unc [c]
L01	0.001	0.0002	2	0.0001	ICP-MS	-1.45	-2.22	b
L02	< 0.01				ICP-MS			
L04	< 0.005				ICP-MS			
L05	0.0014	0.0003	2	0.00015	GF-AAS	-0.22	-0.23	a
L06	< 0.003				GF-AAS			
L07	0.0136	0.0013	2	0.00065	GF-AAS	37.51	9.32	c
L11	0.012	0.001	2	0.0005	ICP-MS	32.56	10.50	c
L13	0.001	0.0002	√3	0.00012	ICP-MS	-1.45	-2.22	b
L15	0	0	√3	0		-4.55	-21.00	b
L16	0.00184	0.00075	2	0.000375	ICP-MS	1.14	0.49	c
L17	0.0018	0.0004	2	0.0002	ICP-MS	1.02	0.81	a
L18	0.0011	0.0002	2	0.0001	GF-AAS	-1.14	-1.75	b
L19	0.001	0.0003	2	0.00015	ICP-MS	-1.45	-1.53	a
L20	< 0.01				ICP-MS			
L21	< 0.0002							
L24	0.0026	0.00025	2	0.000125	ETAAS	3.49	4.35	b
L27	0.0016	0.00038	2	0.00019	GF-AAS	0.40	0.34	a
L29	0.009	0.001	2	0.0005	GF-AAS	23.28	7.51	c
L31	0.0014	0.0002	2	0.0001	GF-AAS	-0.22	-0.33	b

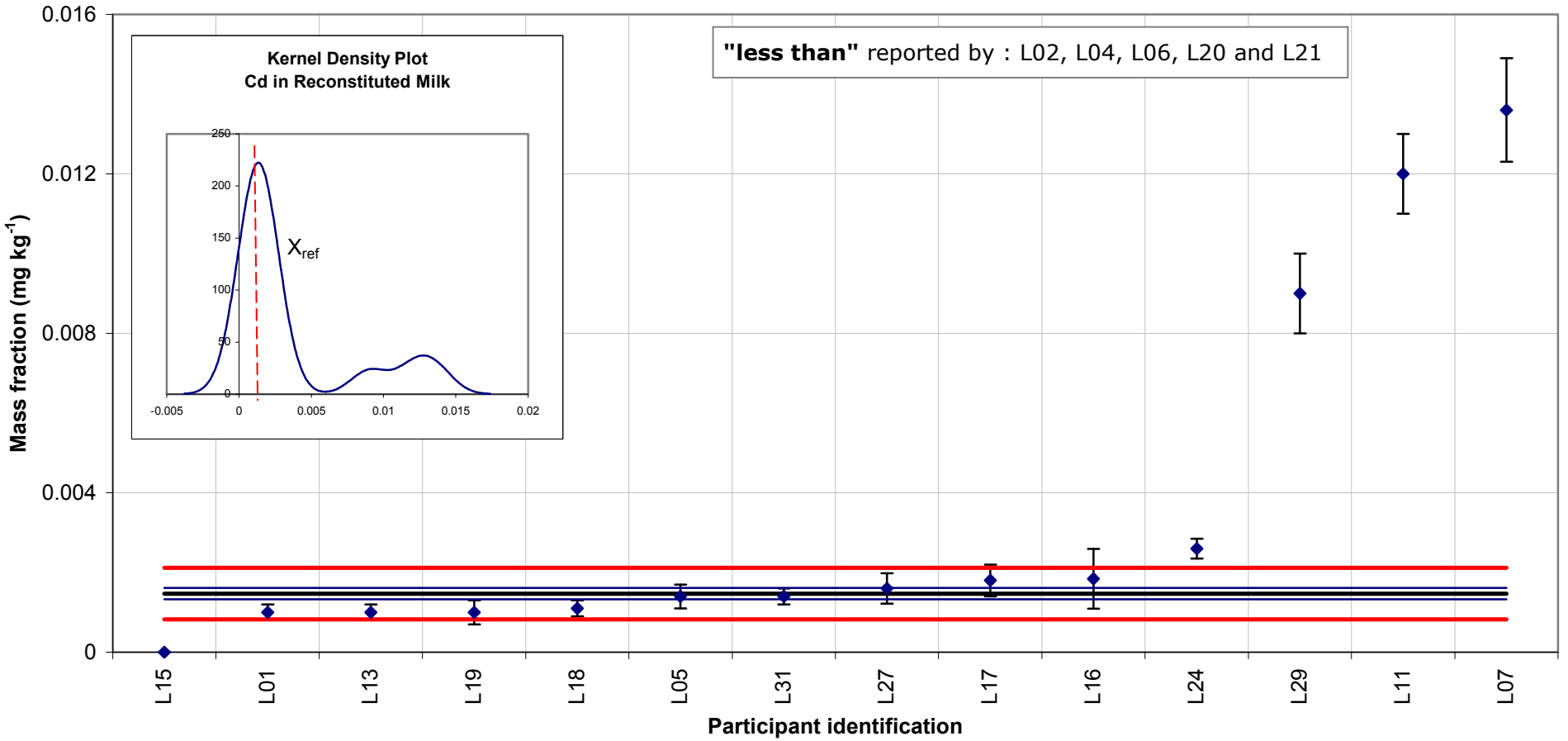
[a] √3 is set by the ILC coordinator when no expansion factor *k* is reported. The reported uncertainty was assumed to have a rectangular distribution with k=√3.

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

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

IMEP-113: Total Cd and Pb in baby food: Total Cd in reconstituted formula

Certified value: X_{ref} = 0.00147 mg·kg^{-1}; U_{ref} = 0.00014 mg·kg^{-1} (k=2); σ = 0.00032 mg·kg^{-1}



This graph displays all 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 the target interval ($\mathbf{X_{ref} \pm 2\sigma}$)

Annex 10: Results for Total Lead – Reconstituted formula

Assigned range: X_{ref} = 0.00081, U (k = 2) = 0.00010 (all values in mg kg^{-1})

Lab ID	Mean (X_{lab})	Unc.	k[a]	u_{lab}	Technique	z-score[b]	ζ-score[b]	Unc [c]
L01	< 0.004				ICP-MS			
L02	< 0.12				ICP-MS			
L04	< 0.006				ICP-MS			
L06	0.004	0.002	2	0.001	GF-AAS	17.83	1.59	c
L07	< 0.04				GF-AAS			
L13	< 0.01				ICP-MS			
L15	0	0	√3	0		-4.55	-16.20	b
L16	< 0.005				ICP-MS			
L17	< 0.002				ICP-MS			
L18	< 0.006				GF-AAS			
L19	< 0.001				ICP-MS			
L20	< 0.01				ICP-MS			
L21	< 0.002							
L23	0.023	0.1	2	0.05	GF-AAS	124.13	0.22	c
L24	0.019	0.0026	2	0.0013	ETAAS	101.75	6.99	c
L29	0.065	0.01	2	0.005	GF-AAS	359.09	6.42	c
L31	< 0.02				GF-AAS			

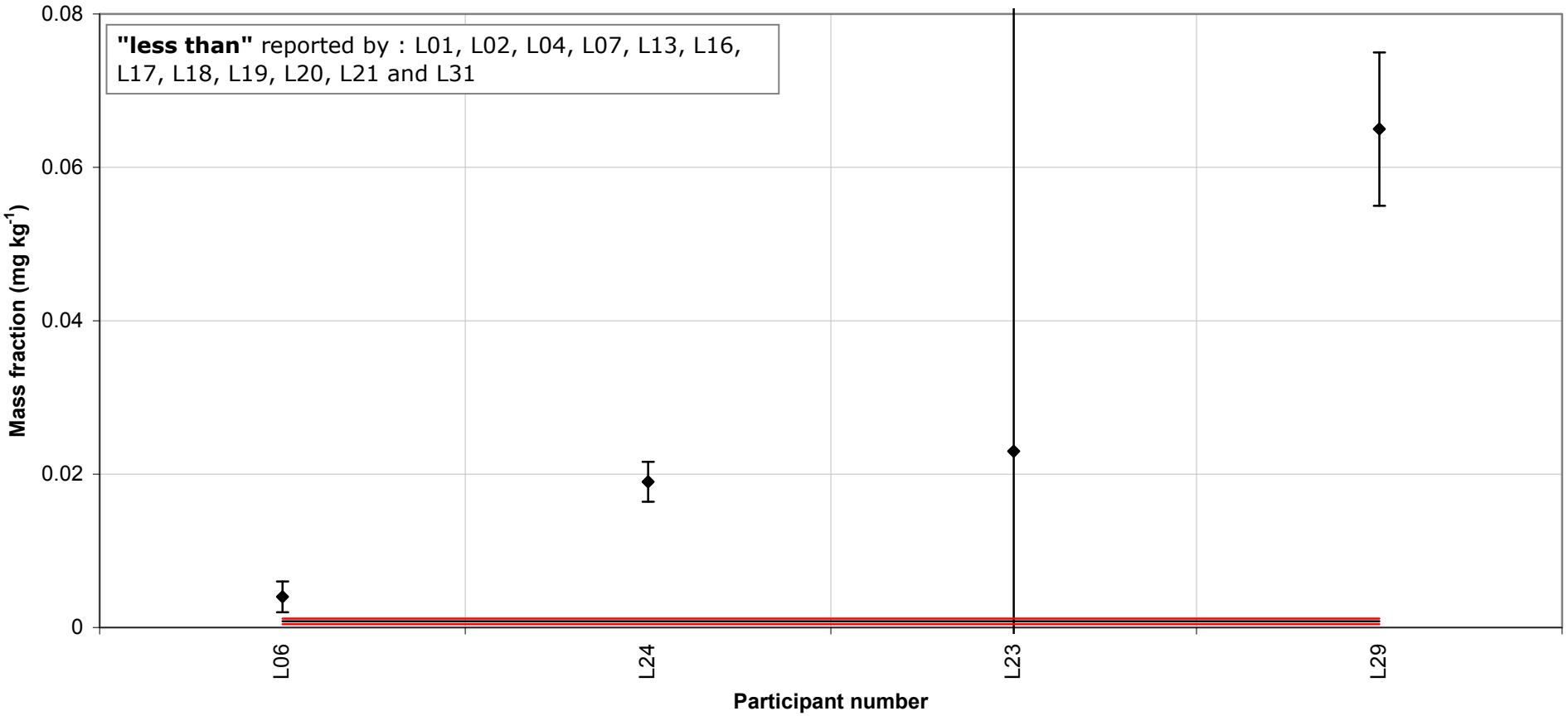
[a] √3 is set by the ILC coordinator when no expansion factor *k* is reported. The reported uncertainty was assumed to have a rectangular distribution with $k=\sqrt{3}$.

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

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

IMEP-113 (Cd and Pb in baby food): Total Pb in reconstituted milk

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



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

Annex 11: Experimental details (Annex 5, Question 7)

Lab ID	Official method?	Sample pre-treatment	Digestion	Extraction / separation	Instrument calibration
L01	No	None	Microwave		External calibration
L02	No	Addition of nitric acid, hydrogen peroxide and water	Microwave digestion	Dilution of digetsate with water to 100 ml.	7 Calibration standards (0 - 20 µg/L for both Cd & Pb)
L03	Yes				
L04	No	no	Microwave with Nitric Acid		
L05	Yes				
L06	Yes				
L07	No	Wet acid digestion: HNO_3 after evaporation then H_2O_2	Wet	No	ETA-AAS, external calibration
L08	Yes				
L09	Yes				
L10	Yes				
L11	No		µ-wave digestion with conc HNO_3 in high-pressure quartz vessels		Addition calibration with internal standardisation
L12	Yes				
L13	Yes				
L14	No	Drying	Ashing		
L15	No		Nitric acid, microwave digestion		Standard additions and preconcentration of sample in the graphite furnace
L16	Yes				
L17	No		Microwave assisted acid destruction		External linear
L18	Yes				
L19	No		Aliquots [0.5 g (dry) or 4 g (wet)] of test sample were digested in nitric acid using a high pressure microwave digestion system	Digests were diluted 100 fold with internal standard (Rh), ready for analysis	Calibration standards were prepared by serial dilution to match acid and internal standard concentrations in the sample solutions. NIST-traceable standard solutions used.
L20	No		Microwave digestion with nitric acid and hydrogen peroxide		Measurements were carried out with direct comparison by standard solution. Rh used as internal standard.
L21	No	Homogenization,	Microwave assisted acid digestion (3ml HNO_3 + 1 ml H_2O_2);	no	External calibration with aqueous solutions (0,1-10 µg/kg); Internal Standard Rh 2 µg/kg

Lab ID	Official method?	Sample pre-treatment	Digestion	Extraction / separation	Instrument calibration
L22	No	no	Microwave digestion high pressure	no	Method of addition Cd: 1,2 ppb; Pb: 25,50 ppb
L23	Yes				
L24	Yes				
L25	Yes				
L26	No	Homogenise	Microwave digestion	n. a.	Calibration using certified standard solutions
L27	Yes				
L28	Yes				
L29	Yes				
L30	No	Addition of nitric acid and hydrogen peroxide, let it stand for 1 hour	Microwave	Dilution	Matrix matched calibration
L31	Yes				
L32	Yes				
L33	Yes				
L34	Yes				
L35	No				

European Commission

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Abstract
This report presents the results of the thirteen proficiency test (PT) which focussed on the determination of total Cd and Pb in baby food according to 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. Thirty five laboratories from 26 countries registered to the exercise and all 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. 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.
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. Reported results were satisfactory for total cadmium in both forms, (powder and in the reconstituted formula).

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