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IMEP-31: Total arsenic, cadmium, copper, lead and mercury, as well as extractable cadmium and lead in mineral feed

Interlaboratory Comparison Report

Ines Baer, Beatriz de la Calle, Inge Verbist, Betül Ari, Agnieszka Krata, Christophe Quétel, Piotr Robouch

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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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April 2011

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Contents

1 Summary

The Institute for Reference Materials and Measurements (IRMM) of the Joint Research Centre (JRC), a Directorate-General of the European Commission, operates the 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 As, Cd, Cu, Pb, and Hg, as well as extractable Cd and Pb in mineral feed according to Directive 2002/32/EC [1] of the European Parliament and of the Council on undesirable substances in animal feed.

The test material used in this exercise was the Certified Reference Material (CRM) BCR-032 (Moroccan phosphate rock) from the IRMM. The material was relabelled and each participant received one bottle containing approximately 100 g of test material. Fifty-six laboratories from 26 countries registered to the exercise and 51 of them reported results.

Total As, Cd, Cu and Hg were certified in BCR-032 in 1979. The material was re-analysed by two expert laboratories and As an Cd values could be confirmed. Copper could not be analysed in time by an expert laboratory, and thus it was decided to use the indicative value from the certificate as assigned value. The assigned values for total Hg and total Pb were determined at IRMM by a primary method. The same method was used to determine extractable Cd and Pb, whose mass fractions appeared to be identical to the respective total mass fractions and thus the same assigned values were used.

The standard deviation for proficiency assessment $\hat{\sigma}$ was set at 11 % for total As, 10 % for total and extractable Cd, 9 % for total Cu, and at 15 % for total Hg based on the modified Horwitz equation and/or the outcome of previous ILCs organised by IMEP. For total and extractable Pb, $\hat{\sigma}$ was set at 25 %.

The majority of the laboratories reported uncertainties with their results and were rated with z- and ζ-scores (zeta-scores) in accordance with ISO 13528 [2]. Performances appear to be good for total & extractable Cd and total & extractable Pb, the percentage of satisfying z-scores ranging between 85 % and 89 %. Share of satisfactory z-scores are significantly lower for total As (61 %), Cu (67 %) and in particular for Hg (47 %). No distinct reason could be given, but it seems altogether that the analytical methods were not always adjusted to the inorganic test material, reflected by some influence of applied technique and inappropriate choice of reference material.

2 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. These laboratories can benchmark their measurement result against the IMEP reference value. This value is established according to metrological best practice.

- IMEP helps laboratories to assess their estimate of **measurement uncertainty**. The 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 intercomparisons in the frame of specific EU legislation, or on request of a specific Directorate-General. IMEP-31 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 intercomparisons. National accreditation bodies were invited to nominate a limited number of laboratories for free participation in IMEP-31. Mrs. Alexandra Morazzo from the Instituto Português de Acreditação (IPAC) liaised between EA and IMEP for this intercomparison. 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 Asia Pacific Laboratory Accreditation Cooperation (APLAC), in the frame of the collaboration with EA. The chair of the APLAC Proficiency Testing Committee, Mr. Dan Tholen, was invited to register a limited number of laboratories for this collaboration.

- 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.

3 Introduction

The IMEP-31 exercise was carried out in collaboration with the EU-RL-HM. The latter has organised a proficiency test (PT) IMEP-105 [3] in 2008 for its network of National Reference Laboratories (NRLs) to determine total Cd, Pb and As and extractable Cd and Pb in mineral feed. The main outcome of that exercise was that the correct selection of the reference material used to evaluate the recovery and/or to validate the method of analysis is of paramount importance.

A follow-up exercise, IMEP-111, was organised by the EU-RL-HM for the NRLs in order to verify if corrective actions have been taken since 2008. In parallel, the IMEP-31 was set up to see how other control laboratories handle this type of sample and if similar problems would appear.

To overcome problems associated with a high metal content in feed, maximum levels for trace elements in different types of feed have been laid down in Directive 2002/32/EC [1], and a network has been built up to ensure quality and comparability in official controls throughout the European Union [4]. In March 2006 a footnote was introduced in Directive 2002/32/EC in which it is stated that "*Maximum levels refer to an analytical determination of lead and cadmium whereby extraction is performed in nitric acid 5 % (w/w) for 30 minutes at boiling temperature*". From there derives the term extractable amounts of cadmium and lead and a procedure was agreed upon by the EU-RL-HM and the network of NRLs for their determination, as asked for in this exercise.

Several proficiency tests have been organised by the EU-RL-HM and IMEP for the determination of heavy metals in different types of feed (IMEP-27, -29 and IMEP-103, -105, -108 [3]) in which the results obtained for total Cd and Pb were compared with those obtained for extractable Cd and Pb. With the aim of expanding the previously mentioned studies to a wider variety of feed matrices, extractable Cd and Pb were also included as measurands in IMEP-31.

4 Scope

The scope of this PT is to test the competence of the participating laboratories to determine the total mass fractions of As, Cd, Cu, Pb, and Hg, as well as those of extractable Cd and Pb. The exercise follows the administrative and logistics procedures of IMEP (IRMM).

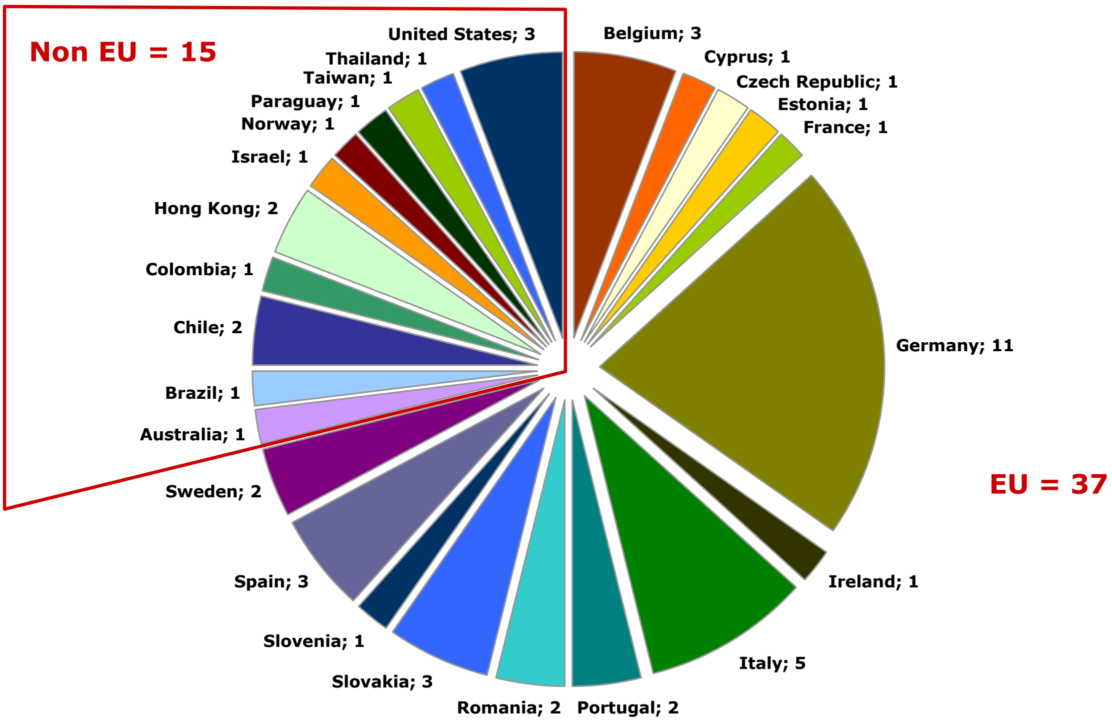
5 Set-up of the exercise

An invitation letter for participation was sent to the EA coordinator (Annex 1) and APLAC responsible (Annex 2) on 13 October 2010 for distribution to nominated and interested laboratories. A web announcement (Annex 3) was made for the exercise on the IMEP webpage on 16 October 2010 [3]. Finally, the NRL network and other laboratories having shown interest in IMEP activities were informed on 18 October 2010 by email (Annex 4). NRLs were thus given the opportunity to invite control laboratories from their respective countries.

Laboratories could register until 29 November 2010. Samples were sent out to the participants on 1 – 2 December 2010. The reporting deadline was set at 28 January 2011 for all laboratories.

Laboratory codes were given randomly after the registration deadline. The participants who submitted results received the reference values one week after the reporting interface was closed. Fig 1 shows the participating countries and the number of participants having reported results.

Fig 1 – Country distribution in IMEP-31 based on number of participants having submitted results



5.1 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.*"

5.2 Distribution

On 1 – 2 December 2010 IRMM dispatched to the participants a parcel containing

- one bottle containing approximately 100 g of test material,
- an accompanying letter with instructions on measurands, sample storage conditions, protocol for the determination of extractable Cd and Pb, water content determination, measurements, the individual access code for the result reporting website and the reporting deadline (Annex 5)
- a form that had to be sent back to IMEP after receipt of the test material to confirm its arrival (Annex 6)
- a sum-up of the questionnaire they would have to fill in when reporting their results (Annex 7).

The dispatch was followed by the messenger's parcel tracking system on the internet and in almost all cases the sample was delivered within a week. For one laboratory (L044) the shipment took exceptionally long and arrived only 2 weeks before reporting deadline (reasons are still unclear).

5.3 Procedure to apply

The measurands and matrix were defined as "Total As, Cd, Cu, Pb, and Hg, as well as extractable Cd and Pb". Laboratories were asked to perform two or three independent measurements and to report the mean of the results, the 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 for water content (following a procedure based on the test material's certificate). Participants were asked to follow their routine procedures. 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 8).

6 Test material

6.1 Preparation

The commercially available CRM BCR-032 (Moroccan phosphate rock) was used for this PT, as it is similar to mineral feed from an analytical point of view. The material was relabelled to avoid identification by the participants as an existing CRM. Comprehensive information on the preparation of the CRM can be found in the certification report which is available on the IRMM website [5].

6.2 Homogeneity and stability

Information on the homogeneity and stability of the test material was gathered from the certification report of the CRM [5]. Homogeneity was considered sufficient for this intercomparison. Furthermore, the material was considered stable for the duration of the exercise, as the indicative values from the certificate (determined in 1979) and the newly measured values agreed within their uncertainties.

7 Reference values and their uncertainties

7.1 Assigned value X_{ref}

The total content of As, Cd, Cu and Hg were certified in BCR-032. However, since BCR-032 is an old CRM (1st certificate issued in November 1979) the CRM producer decided in 2007 to provide the concentration of total As, Cd, Cu, and Hg only as indicative values. In order to verify if these indicative values could be used as assigned values in IMEP-31, two laboratories expert in the field were asked to analyse the material before the start of the exercise. Both laboratories have proven their measurement capabilities by successful participation in the Comité Consultative de la Quantité de Matière (CCQM) key comparisons.

Pb was also analysed in the certification process in the 1970's and is included under Additional Material Information in the certificate. However, the standard deviation was large and could not be explained at the time of the certification, which is why it was only included as informative value in the certificate. It was therefore decided to have the assigned value determined by an expert laboratory as well (IRMM).

The mass fraction for total and extractable Cd and Pb, and for total Hg were determined at IRMM using Isotope Dilution – Inductively Coupled Plasma – Mass Spectrometry (ID-ICP-MS). For total an extractable Pb, the obtained results by ID-ICP-MS were used as assigned value. The value obtained for total Cd agreed with the indicative value from the certificate within its uncertainty and hence was used as assigned value in IMEP-31. The value obtained for total Hg also agreed with the indicative value within its uncertainty, but since the applied techniques 30 years ago did not reflect the current state-of-the-art and methods for Hg analysis have greatly improved since then, it was decided to use the recent IRMM result as assigned value for this exercise. The indicative value for total As in BCR-032 was confirmed by the Studiecentrum voor Kernenergie (SCK) using neutron activation analysis and could thus be used as assigned value in IMEP-31.

Initially, copper was not considered as a measurand for this exercise and was included after request by some NRLs. Consequently, IMEP could not obtain in time an external confirmation of the indicative value given in the certificate. Thus, it was decided to use the indicative value from the certificate as assigned value, which was not contradicted by participants' results.

7.2 Associated uncertainty u_{ref}

The associated uncertainties (u_{ref}) of the assigned values were calculated as follows: for total As, Cd, Cu, Hg, and for extractable Cd, the uncertainty of the characterization (u_{char}) was combined with a contribution for homogeneity (u_{hom}) according to:

$$u_{ref} = \sqrt{u_{char}^2 + u_{hom}^2} \qquad \text{Eq. 1}$$

Where:

- U_{hom} is the contribution for homogeneity. In the certification report it is indicated that "*at least down to the 0.1 g level a possible inhomogeneity for all the trace elements tested is less than 5 %*". Thus, the contribution for homogeneity was set to 5 % of the assigned value.

- u_{char} are the uncertainties from the indicative values for total As, Cd and Cu in the certificate. For extractable Cd, the same u_{char} as for total Cd was used. For total Hg, u_{char} was calculated according to the ISO Guide for the Expression of Uncertainty in Measurement (GUM) [6].

For total Pb the number of replicates performed to establish the assigned value was higher (11 replicates) than for the other measurands (6 replicates). Since the aliquots were taken from different bottles, it was assumed that u_{char} contained a contribution for the homogeneity and u_{char} was set as u_{ref}. It was calculated according to the ISO GUM [6]. In analogy to Cd, the same u_{ref} was set for total and extractable Pb.

No contribution for stability was added to the associated uncertainties as the material has proven to be stable since the certification took place.

7.3 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 total As, Cd, Cu and for extractable Cd. For total Hg, $\hat{\sigma}$ was set to 15 % (and not to 22 % as obtained with the modified Horwitz equation) on the basis of the outcome of previous ILCs organised by IMEP. For total Pb, $\hat{\sigma}$ was set to 25 % due to some lack of homogeneity observed when small aliquots were taken for analysis. The same $\hat{\sigma}$ was used for extractable Pb to apply the same criteria as for total Pb to score the participants. An overview of all reference values is given in Table 1.

Table 1 - Assigned values, their associated uncertainties and target standard deviations for the measurands of this ILC.

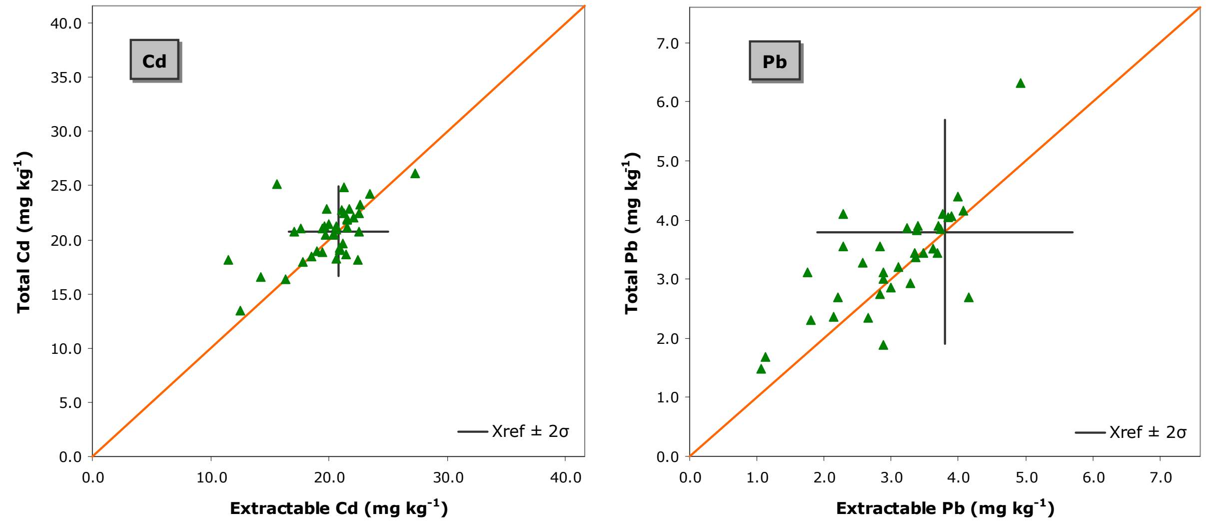
Measurand	**X_{ref} (mg kg^{-1})**	**U_{ref} (mg kg^{-1})**	**$\hat{\sigma}$ (mg kg^{-1})**	**$\hat{\sigma}$ (%)**
Total As	9.5	1.1	1.0	11
Total & Extractable Cd	20.8	2.2	2.1	10
Total Cu	33.7	3.7	3.0	9
Total & Extractable Pb	3.8	0.5	1.0	25
Total Hg	0.044	0.006	0.007	15

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

7.4 Youden plots

The same assigned values were attributed for extractable and total Cd and Pb (Table 1), because the extractable amounts were expected to be identical to the total mass fractions. These findings are confirmed by the experimental data shown in the Youden plots (Fig 2), reporting the total mass fractions versus reported extractable mass fractions. For both elements, most of the points are close to the diagonal axis Extractable = Total mass fraction, and thus confirm our assumption.

Fig 2 – Youden plots for reported Cd and Pb results



8 Evaluation of results

8.1 General observations

Of the 56 laboratories that registered for participation 51 submitted results and completed the associated questionnaire. Of these 51 participants, 50 gave results for total Cd, 49 for total Cu and Pb, 46 for total Hg, 44 for total As, 39 for extractable Cd and 38 for extractable Pb.

From these results, those reporting "less than" and "0" values were not included in the evaluation. This was the case for 3 laboratories for total Pb, Hg and extractable Pb. However, reported "less than" values were compared with the corresponding $X_{ref} - U_{ref}$ values. If the reported value was found to be lower than the corresponding $X_{ref} - U_{ref}$, this is an incorrect statement, since the laboratory should have detected the respective element. This was the case for participant L034 for total and extractable Pb, for L036 in the case of extractable Pb and for L041 for total Pb.

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.

8.2 Uncertainties and coverage factor

Seven out of the total 51 participants did not report an uncertainty associated to their results (~ 14 %). Furthermore, 4 participants having reported uncertainties for the total mass fractions did not do so for the extractable mass fractions.

Of the 44 participants who reported a measurement uncertainty 2 (~ 5 %) did not give a value for the coverage factor. Two participants mixed up the coverage factor *k* and the recovery factor R. One participant informed us in the questionnaire that they were not familiar with the term "*coverage factor k*". The coverage factor *k* is defined and explained in detail in the GUM [6], which can be downloaded from the website of the Bureau International des Poids et Mesures (BIPM) [7]. The value of the coverage factor *k* is chosen on the basis of the level of confidence required of the interval $y - U$ to $y + U$ (where $U = ku_c$, and y the measurement result). When the distribution is close to normal and the uncertainty $u_c(y)$ is a reliable estimate of the measurement, it can be assumed that $k = 2$ produces an interval with a level of confidence of approximately 95 percent, and $k = 3$ produces an interval with a level of confidence of approximately 99 percent.

Participants who are not familiar with this term are advised to read the GUM [6], the EURACHEM / CITAC Guide CG 4 [8] or to consult the informative web pages of National Institute of Standards and Technology (NIST) on the subject of uncertainty evaluation [9].

8.3 Scores and evaluation criteria

Individual laboratory performance is expressed in terms of z- and ζ-scores in accordance with ISO 13528 [2].

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

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

Both scores can be interpreted as: satisfactory result for |score| ≤ 2, questionable result for 2 < |score| ≤ 3 and unsatisfactory result for |score| > 3.

z-score

The z-score compares the participant's deviation from the reference value with the target standard deviation for the proficiency assessment $\hat{\sigma}$, used as common quality criterion. $\hat{\sigma}$ is defined by the PT organiser as the maximum acceptable standard uncertainty and is based on feedback from experts, on the state-of-the-art and on discussions among the members of the advisory board of this PT. Values for $\hat{\sigma}$ of this exercise are listed in Table 1 (Chapter 7.3).

Should participants consider that these $\hat{\sigma}$ values are not fit for their purpose they can recalculate their scorings with a standard deviation matching their requirements.

ζ-score

The ζ-score states if the laboratory result agrees with the assigned value within the respective uncertainties. The denominator of its equation 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 the measurement result, the expected value (assigned value), its uncertainty as well as the uncertainty of the reported values. An unsatisfactory ζ-score can either be caused by an inappropriate measurement result or of its uncertainty.

Uncertainty evaluation

It is a well-established fact that uncertainty estimation is not trivial. Therefore an additional assessment was given as an indication of the plausibility of its uncertainty estimate for each laboratory providing an uncertainty. The standard uncertainty (u_{lab}) is most likely to fall in a range between a minimum uncertainty (u_{min}), and maximum allowed uncertainty (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 accepted for the PT, $\hat{\sigma}$. If u_{lab} is smaller than u_{min}, the laboratory might have underestimated its uncertainty. However, 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 might 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 it is covered by the uncertainty, then the uncertainty is properly assessed even if large. It should be pointed out that u_{max} is not a normative criterion. It is up to the customer of the respective result to decide which uncertainty is acceptable for a certain measurement.

The standard uncertainty of the laboratory (u_{lab}) was calculated by dividing the reported expanded uncertainty by the reported coverage factor (k). When k was not specified, the reported expanded uncertainty was considered as the half-width of a rectangular distribution; u_{lab} was then calculated by dividing this half-width by $\sqrt{3}$, as recommended by Eurachem / CITAC [8]. When no uncertainty was reported, it was set to zero ($u_{lab} = 0$).

8.4 Laboratory results and scorings

The results reported by the participants are listed in Annex 9 - 15. 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, shown on the result graph, are an alternative to histograms and a useful method 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 [10].

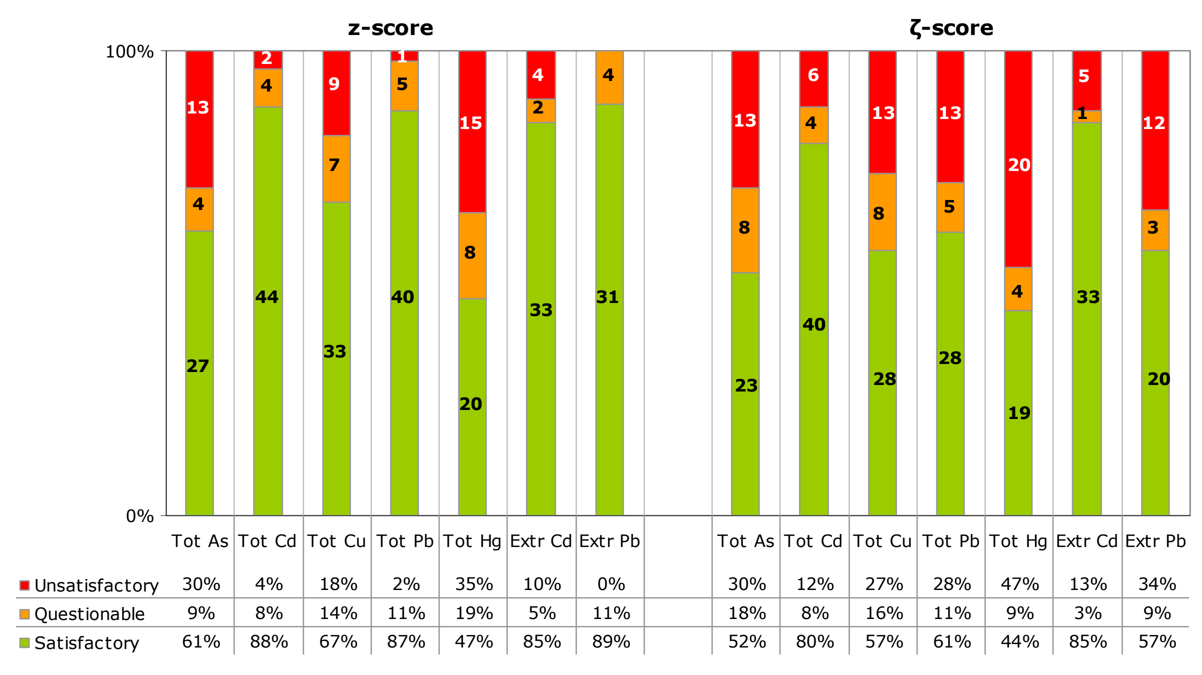
8.4.1 Scorings

Fig 3 presents an overview of the z- and ζ-scores. The laboratories' performances appear to be good for total & extractable Cd and total & extractable Pb, the percentage of satisfying z-scores ranging between 85 % and 89 %. Share of satisfactory z-scores are significantly lower for total As (61 %), Cu (67 %) and in particular for Hg (47 %).

It must be pointed out that in the case of Pb the good z-scores are due to the high $\hat{\sigma}$ value and thus might give a wrong impression of unproblematic determination of Pb. It can be seen in the results' graphs for total and extractable Pb, that there is an underestimation of the mass fraction.

Concerning the ζ-scores, only total & extractable Cd present shares of satisfactory scores ≥ 80 %. For the other measurands, the shares of satisfactory scores range between 44 % and 61 %. Furthermore, the share of participants having a satisfying z- <u>and</u> ζ-score is between 42 % and 85 %, standing for total Hg and extractable Cd, respectively.

Fig 3 - Overview of scores



	z-score								ζ-score						
	Tot As	Tot Cd	Tot Cu	Tot Pb	Tot Hg	Extr Cd	Extr Pb		Tot As	Tot Cd	Tot Cu	Tot Pb	Tot Hg	Extr Cd	Extr Pb
🟥 Unsatisfactory	30%	4%	18%	2%	35%	10%	0%		30%	12%	27%	28%	47%	13%	34%
🟧 Questionable	9%	8%	14%	11%	19%	5%	11%		18%	8%	16%	11%	9%	3%	9%
🟩 Satisfactory	61%	88%	67%	87%	47%	85%	89%		52%	80%	57%	61%	44%	85%	57%

8.4.2 Discussion of the scorings

Considering the low percentage of satisfactory results for total As, Cu and Hg, their results were carefully scrutinised. The results for As and Hg were compared to those reported in former ILCs IMEP-28 and IMEP-29 [3]. Poor performances in those ILCs generally consisted in an overestimation of the respective mass fractions.

For total Hg, the mass fractions in IMEP-28 and -29 were of the same order of magnitude than in IMEP-31. In IMEP-28 and -29, it was thought that the overestimation was most likely due to contamination issues which could be significant at those low concentration levels. However, this hypothesis does not explain the observed tendency to underestimate.

For total As, results in IMEP-28 were satisfactory, while in IMEP-29 laboratories also tended to overestimate the mass fraction. The mass fraction of total As in IMEP-29 was much lower than in IMEP-31 ($0.042\ \mathrm{mg\ kg^{-1}}$ and $9.6\ \mathrm{mg\ kg^{-1}}$, respectively) and overestimation was explained by contamination from the reagents used for the analysis. Such a contamination problem would have a high impact considering the relatively low concentration of As in the test material. However, the impact of contamination is certainly less at the mass fraction range of As in the IMEP-31 exercise and thus cannot be considered as sole contributor.

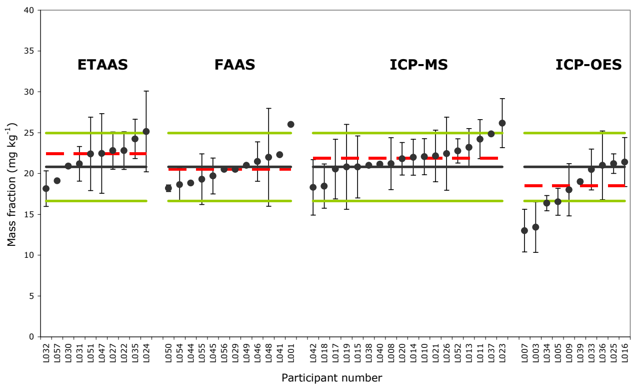
Copper was only analysed in one former IMEP exercise, IMEP-21 (sewage sludge) using a very different matrix from mineral feed. Furthermore, the results in IMEP-21 were satisfactory, so that no further information can be drawn from there.

As no satisfying explanation for these deviating results could be found, additional information obtained from the participants was evaluated, such as: application of a recovery factor, correction for water content, use of an official method, type of reference materials used, and the applied instrumental technique. Only the instrumental technique applied appears to have an influence and was thus verified in detail.

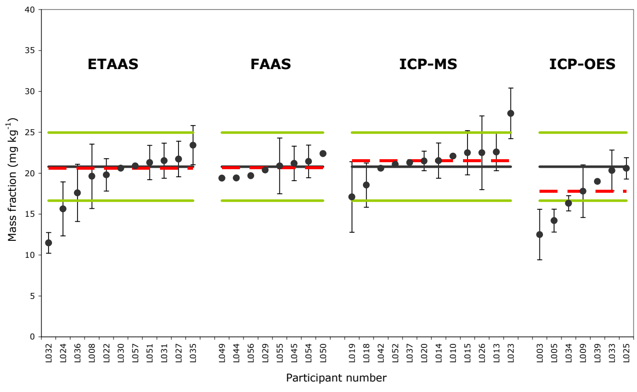
Some tendencies were observed throughout all measurands, even those with satisfactory results, when plotting the results in function of the applied techniques. Sometimes the results of one technique are widely spread, sometimes they tend to group at a lower/higher range than X_{ref}, or both. As illustrated in Fig 4, results obtained with ICP-MS have a nice distribution around X_{ref} for nearly all measurands and thus resulted in a high number of satisfactory z-scores over the whole exercise. The other techniques show a high number of negatively biased questionable and unsatisfactory results. The exception is Hydride generation-atomic absorption spectrometry (HG-AAS) where the reported results tend to be above X_{ref} and which is typically the technique mostly applied for As detection, the only measurand showing a slight overestimation of mass fraction.

TDA refers to methods based on solid sampling-amalgamation, such as direct mercury analyzer (DMA), thermal desorption – atomic absorption spectroscopy (TD-AAS), advanced mercury analyzer (AMA) and were applied uniquely for Hg detection. When looking closely at these, it was observed that all five laboratories applying this type of

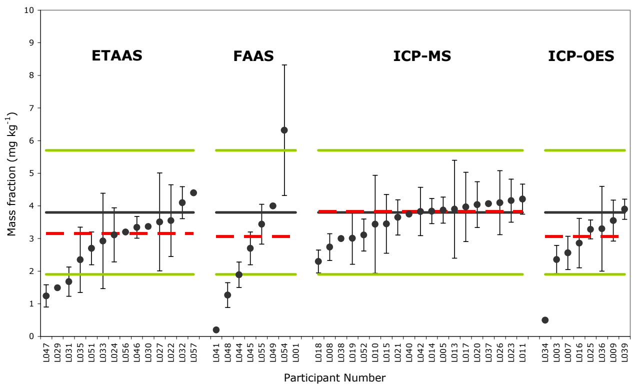
Fig 4 – Influence of applied technique for all measurands



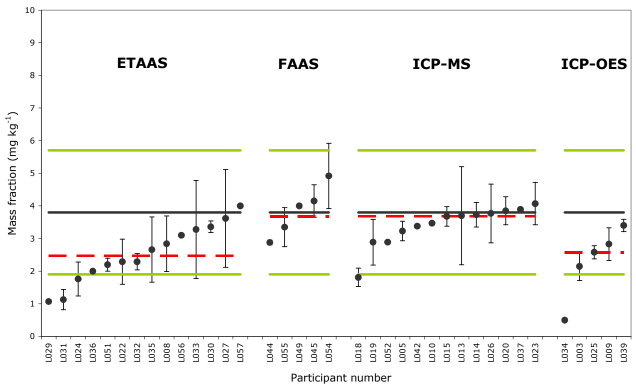
Total Cd



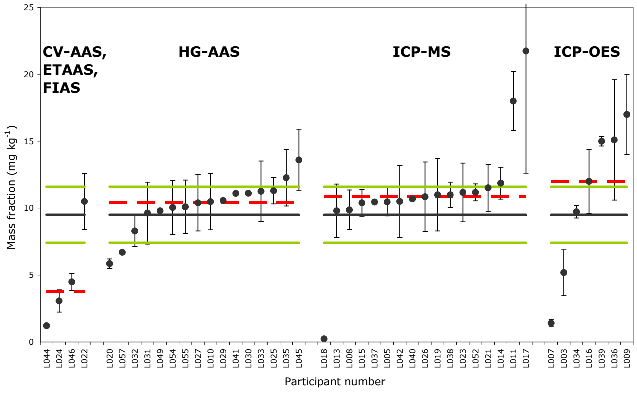
Extractable Cd



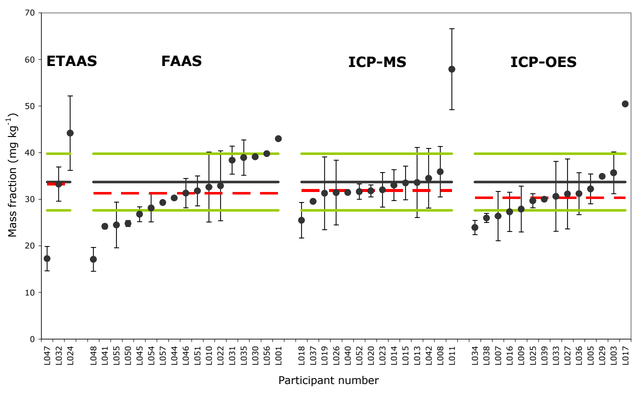
Total Pb



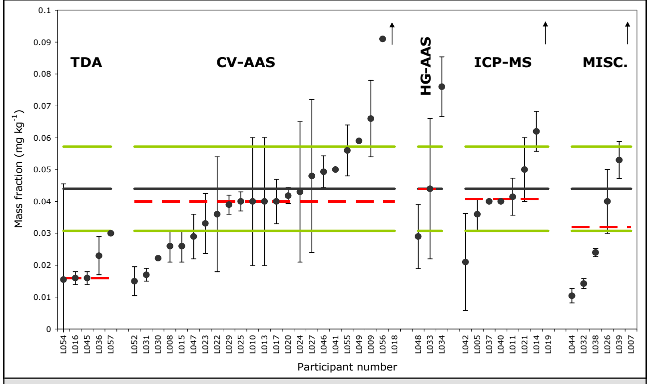
Extractable Pb



Total As



Total Cu



Total Hg

Legend

Xref

Median

Xref ± 2σ

For explanation see Ch. 8.4.2

technique received unsatisfactory z-scores. This is surprising as this finding enters in contradiction with the outcome of IMEP-106 and -28 [11] (both exercises dealt with the determination of heavy metals in food supplements but only NRLs could take part in the former while the latter was open for all laboratories that wished to register), where participants using solid sampling-amalgamation performed particularly well, with all of them reporting satisfactory results. However, according to US EPA method 7473, when Hg can be bound in silicates or other matrices that may not thermally decompose, validation of direct analysis should be confirmed with total decomposition with an appropriate method [12]. It is worth mentioning that in IMEP-111 all unsatisfactory results for total Hg were obtained with TDA methods [3].

Thus, an explanation for the outcome of this exercise could be that the mineral matrix used as test material was difficult to totally decompose, introducing a negative bias in the results (low recovery). This hypothesis should be confirmed by additional experimental evidence.

8.4.3 Uncertainty evaluation

Table 2 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 20 % and 46 % only. One possible reason might be a high uncertainty of the reference value resulting in a rather narrow range $u_{min} - u_{max}$. Furthermore, it appears that participants tend to underestimate the uncertainty (b in Table 2), rather than to overestimate it (c in Table 2). It is also noticeable that, although Pb has a higher $\hat{\sigma}$ than the other measurands while keeping a comparable u_{ref} and thus resulting in a larger range (a), its reported uncertainties are not significantly better.

Table 2 – Uncertainty evaluation where a = $u_{min} \leq u_{lab} \leq u_{max}$, b = $u_{lab} < u_{min}$ and c = $u_{lab} > u_{max}$

		$u_{min} \leq u_{lab} \leq u_{max}$	$u_{lab} < u_{min}$	$u_{lab} > u_{max}$
	n	**a (%)**	**b (%)**	**c (%)**
Tot As	44	20%	45%	34%
Tot Cd	50	40%	44%	16%
Tot Cu	49	22%	57%	20%
Tot Pb	46	46%	50%	4%
Tot Hg	43	26%	51%	23%
Extr Cd	39	33%	62%	5%
Extr Pb	35	40%	60%	0%

n – total number of laboratories having submitted results, # - number of laboratories

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

8.5 Further information extracted from the questionnaire

Additional information was gathered from the questionnaire that participants were asked to fill in (Annex 8). Some of the answers are summarised in Annex 16 & 17 (recovery factors, uncertainty related questions, water content, method related questions, experience and use of reference material), or is otherwise highlighted in the following paragraphs.

Forty-one participants reported recovery factors R, and their distribution range is shown in Annex 16. All of them but one declared how R was determined and the answers are summarised in Table 3 below. Of the 11 participants who did not report recovery factors 6 gave specifications about how R was determined and are thus included in Table 3. It can only be assumed that they actually applied recovery factors and simply omitted reporting them.

Table 3 – 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)	14
b) using a certified reference material	19
c) other	9*
a) & b)	4
b) & c)	1
a) & c)	0
Reported as "Others": - According to VDLUFA agreement for determination of inorganic parameters - 100 % digestion is assumed for total content; confirmation via reference materials - We spiked a sample of salad before mineralisation - Via interlaboratory test material (own mean value of test vs. mean value of all participants multiplied wit 100) - VDLUFA analytical latitudes - Samples - QC Sample	

* 2 of these laboratories specified later that they did not determine a recovery factor

Participants were asked to report the limits of detection (LoD) and of quantification (LoQ) of the methods used for the determination of the different measurands covered in this exercise. Table 4 shows the ranges for LoD and LoQ as reported by the participants in IMEP-31 for the different measurands.

Table 4 – Range of LoD and LoQ reported by the participants for the different measurands.

Measurand	LoD (mg kg^{-1})	LoQ (mg kg^{-1})
Total As	0.00031 to 0.5	0.00093 to 1.25
Total Cd	0.00015 to 4	0.00046 to 10
Total Cu	0.002 to 3	0.004 to 10
Total Pb	0.00069 to 3.5	0.0021 to 10
Total Hg	0.00003 to 0.2	0.0001 to 0.5

The huge spread of the reported LoD and LoQ values (up to five orders of magnitude for some elements) could be due to the use of different approaches to calculate them or to actual differences in the methods used. A deeper investigation on this issue will be performed in future IMEP exercises.

For uncertainty estimates, various combinations of one or more options were given. Ten laboratories gave an additional method to base their uncertainty on. Details are shown in Annex 16.

Seven participants did not correct for the water content, among which 6 gave the reasons listed in Table 5. Of the other 44 participant, most gave a water content below 2 %. The way in which the water content of the test material was to be determined was described in detail in the sample accompanying letter.

Table 5 – Reasons for not applying water correction as reported in the questionnaire

Part Nr	Reasons
L001	The sample was dried prior to analysis, but no correction factors were applied.
L019	Measured moisture content was less than 1% and not significant to results
L035	-1.0%
L040	it is not a laboratory practise
L044	We tested dry and natural samples, and we found no significant diferences in results.
L053	Not requested

Two participants declared having modified the procedure given for the partial digestion, a) "*According to our in house method*" and, b) by using 67% HNO_3 instead of the 5 % solution. Annex 17 gives information reported by the laboratories about their method of analysis.

All 51 participants have a quality system in place based on ISO 17025, among which five have it combined with ISO 9000. All laboratories but 3 are accredited and between 71 % and 81 % of them regularly participate in ILC schemes depending on the measurand.

Table 6 summarises the reference materials (RM) used for this type of analysis as reported by the participants. In the cases where the RM could be identified (and not just the producer), only two participants used an inorganic RM and all others an organic RM. This is striking as the test material was clearly identified as mineral feed and the use of an organic RM must be considered as inappropriate. For analyses dealing with determination of heavy metals in mineral feed it is advisable to use mineral RMs, such as soils.

Final comments made by participants are listed in Table 7.

Table 6 – Reference materials used by the participants as reported in the questionnaire

Part Nr	**Which reference material?**
L001	NIST (used for Calibration, calibration checks, and method checks (blanks and reference materials carried through all steps of the method))
L002	canned fish
L003	FAPAS, IMEP, SLV, BAM PROFEA
L008	Tomato leaves, citrus leaves, DOLT4
L009	Tort
L010	different, IPE-materials, materials from Bonner enquete
L013	ILC testing material, BCR-482
L014	CRM
L015	NIST 1573a
L016	AAFCO, FAPAS
L017	IRMM 804 Rice; NIST 1570a spinach leaves
L018	Wheat
L019	NIST SRM 2976 Mussel Tissue
L020	several CRM, SRM, local RM
L022	Rice flour NIST 1568a; Milk powder BCR No 151; VDLUFA Bonner Enquete 346 Qc
L023	material from Bonner Enquete
L025	AFFCO (Association of American Feed Control Officials)
L027	VDLUFA, IPE-Wageningen
L029	GBW 07605
L030	Material from former interlaboratory tests with known contents
L031	NCS DC73351-tea
L032	NCS ZC73012, NCS ZC73016
L033	Material from ILC
L035	ALFALFA, protein, white cadbage
L036	Bipea, CEN validation test samples
L038	INCT-MPH-2, NCS ZC73012
L040	FAPAS MRC for each matrix
L041	TORT 2 - DORD
L042	NIST 1547
L046	CRM LGC6187 River sediment, IMEP-30 Seafood
L047	IRMM
L048	CRM
L049	BCR-032
L050	heavy metals standards 1 ppm Merck certied
L054	internal
L057	FAPAS

Table 7 – Comments as taken from the questionnaire

Part Nr	**Comments**
L001	IMEP-31 was analyzed by the method used for soils as the sample most closely resembled a soil in form/texture. Annual MDL study results and statistical data is available as needed.
L003	We thank you very much for your help
L005	Very difficult matrix in comparison of our routine samples, high dissolved solids in sample extract
L008	Mention the use of
L010	The questionnaire and the form for results should be simplified.
L014	Lead is calculated as sum of isotope 204Pb, 206Pb, 207Pb, 208Pb
L015	The submitted Hg-content was received by partial digestion. The Hg-content we have received by total digestion was 0.026 mg/kg (uncertainty: 0.005 mg/kg).
L019	Samples required dilution due to interference with internal standard (Tb) from sample matrix.
L022	We use one of the reference materials for the control of every measurement.
L025	Sample high interferences.
L030	Question 10: Both treatments are used and accredited; Other: In our opinion methods for the estimation of extractable contents (Hg; As; Pb; Cd) are against the published european norms and such one being currently in normation. This should be cleared by the European commission!
L031	Our laboratory does not use partial digestion for the sample treatment
L036	We are shifting from AAS GF analysis towards ICP-OES since we have a new ICP-OES since recently. We are accredited for Cu ICP-OES, Cd and Pb AAS GF, Hg AMA and are validating ICP-OES analysis.
L044	We use spiked samples with a different AA standard that the one used for the calibration curve

9 Conclusion

In the IMEP-31 exercise 56 laboratories registered and 51 of them submitted results. The outcome was satisfying for total and extractable Cd and Pb, where the share of satisfactory z-scores ranged between 85 and 89 %. This was not the case for the remaining measurands, total As, Cu and Hg, where significantly lower shares of satisfactory z-scores were obtained. As for the ζ-scores, only total and extractable Cd still presented ~80 % satisfactory scores. This indicates that a number of participants have problems making an appropriate estimate of the uncertainty, and the situation can be improved.

Possible explanations for the unsatisfactory results could be related to the test material. Mineral feed is an inorganic material and more complex to analyse than organic material e.g.; special attention has to be paid to sample decomposition and appropriate choice of reference material for validation of procedures. This was reflected by a detected influence of the applied technique on all measurands.

It is crucial that the reference material should resemble as much as possible the sample to analyse. Thus, for mineral feed a reference material such as soil could be considered. A similar approach applies to the method which should take into account that inorganic material might not decompose totally, where organic material does, and conditions should be adjusted. Applying analytical procedures for the analysis of soils may be advised.

Finally, it could be observed that the concentrations of total and extractable Pb and total and extractable Cd are identical. Although this finding strictly applies to the test material used in IMEP-31 and might be different in another material, it confirms a tendency observed already in former IMEP exercises.

10 Acknowledgements

The Reference Materials Unit of IRMM is acknowledged for relabeling the test material. The IMEP-group and Franz Ulberth are thanked for revising the manuscript.

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

Organisation	Country
Symbio Alliance	Australia
Eurofins Belgium	Belgium
Provincie West-Vlaanderen	Belgium
FAVV	Belgium
M.Cassab Ind & Com Ltda	Brazil
Comercial Analab Chile S.A.	Chile
Gestión de Calidad y Laboratorio	Chile
QUIMIA LTDA	Colombia
Panchris Animal Premix LTD	Cyprus
MVDr. Pavel Mikulas	Czech Republic
Tallinn University of Technology	Estonia
Laboratoire PHYTOCONTROL	France
Landesbetrieb Hessisches Landeslabor	Germany
Chemisches und Veterinäruntersuchungsamt Ostwestfalen-Lippe CVUA-OWL	Germany
Thüringer Landesanstalt für Landwirtschaft	Germany
BfUL Leipzig	Germany
Landeslabor Berlin-Brandenburg	Germany
LTZ Augustenberg	Germany
Staatliches Veterinäruntersuchungsamt	Germany
Nds. Landesamt für Verbraucherschutz und Lebensmittelsicherheit (LAVES)	Germany
Bavarian Health and Food Safety Autority	Germany
Institut für Hygiene und Umwelt	Germany
LUFA Speyer	Germany
SGS Hong Kong Limited	Hong Kong
ALS Technichem (HK) Pty Ltd	Hong Kong
Dairygold Feed Laboratory	Ireland
Milouda Laboratories	Israel
NEOTRON S.p.A.	Italy
Istituto Zooprofilattico Sperimentale - Puglia e Basilicata	Italy
CHELAB SRL	Italy
Istituto Zooprofilattico Sperimentale Lazio e Toscana	Italy
Trondheim kommune	Norway

Organisation	**Country**
CEMIT – DGICT – UNA	Paraguay
ISQ - Instituto de Soldadura e Qualidade	Portugal
Controlvet Segurança Alimentar SA	Portugal
D.S.V.S.A Iasi	Romania
DSVSA Calarasi	Romania
Mikrolab, s.r.o.	Slovakia
Ustredny kontrolny a skusobny ustav polnohospodarsky	Slovakia
Statny veterinarny a potravinovy ustav	Slovakia
Kmetijski Institut Slovenije	Slovenia
Laboratorio Agroalimentario y de Sanidad Animal	Spain
Navarra de Servivios S.A	Spain
Trouw Nutrition Spain	Spain
Eurofins Environment Sweden AB	Sweden
ALS Scandinavia AB	Sweden
National Animal Industry Foundation	Taiwan
ALS Laboratory Group (Thailand) Co.,Ltd.	Thailand
Consumer Product Laboratories	United States
K Prime APLAC nominee from ACLASS	United States
Michelson Laboratories, Inc.	United States

Abbreviations

AMC	Analytical Methods Committee of the Royal Society of Chemistry
APLAC	Asia Pacific Laboratory Accreditation Cooperation
BIPM	Bureau International des Poids et Mesures
CCQM	Comité Consultative de la Quantité de Matière
CITAC	Co-operation for International Traceability in Analytical Chemistry
CRM	Certified Reference Material
CV-AAS	Cold Vapor Atomic Absorption Spectrometry
EA	European Co-operation for Accreditation
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
HG-AAS	Hydride generation-atomic absorption spectrometry
ID-ICP-MS	Isotope dilution - inductively coupled plasma - mass spectrometry
ILC	Interlaboratory Comparison
IMEP	International Measurement Evaluation Programme
IPAC	Instituto Português de Acreditação
IRMM	Institute for Reference Materials and Measurements
ISO	International Organisation for Standardisation
JRC	Joint Research Centre
LoD	Limit of detection
LoQ	Limit of quantification
NIST	National Institute of Standards and Technology
NRL	National Reference Laboratory
PT	Proficiency Test
RM	Reference material
SCK	Studiecentrum voor Kernenergie
TDA	Thermal desorption amalgamation
US EPA	Unired State's Environment Protection Agency

References

[1] Directive 2002/32/EC of the European Parliament and of the Council of 7 May 2002 on undesirable substances in animal feed (2002), issued by European Commission, Official Journal of the European Union, L 140/10.

[2] ISO 13528 - Statistical Methods for Use in Proficiency Testing by Interlaboratory Comparisons, issued by ISO-Geneva (CH), International Organization for Standardization.

[3] http://irmm.jrc.ec.europa.eu/interlaboratory_comparisons/imep/Pages/index.aspx. Accessed at date of submission.

[4] 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 (2004), issued by European Commission, Official Journal of the European Union, L 165/6.

[5] BCR-032, https://irmm.jrc.ec.europa.eu/refmat_pdf/BCR-032_report.pdf, 2nd part, pp. 1-64.

[6] 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).

[7] http://www.bipm.org/en/publications/guides/. Accessed at date of submission.

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

[9] http://physics.nist.gov/cuu/Uncertainty/index.html. Accessed at date of submission.

[10] 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.

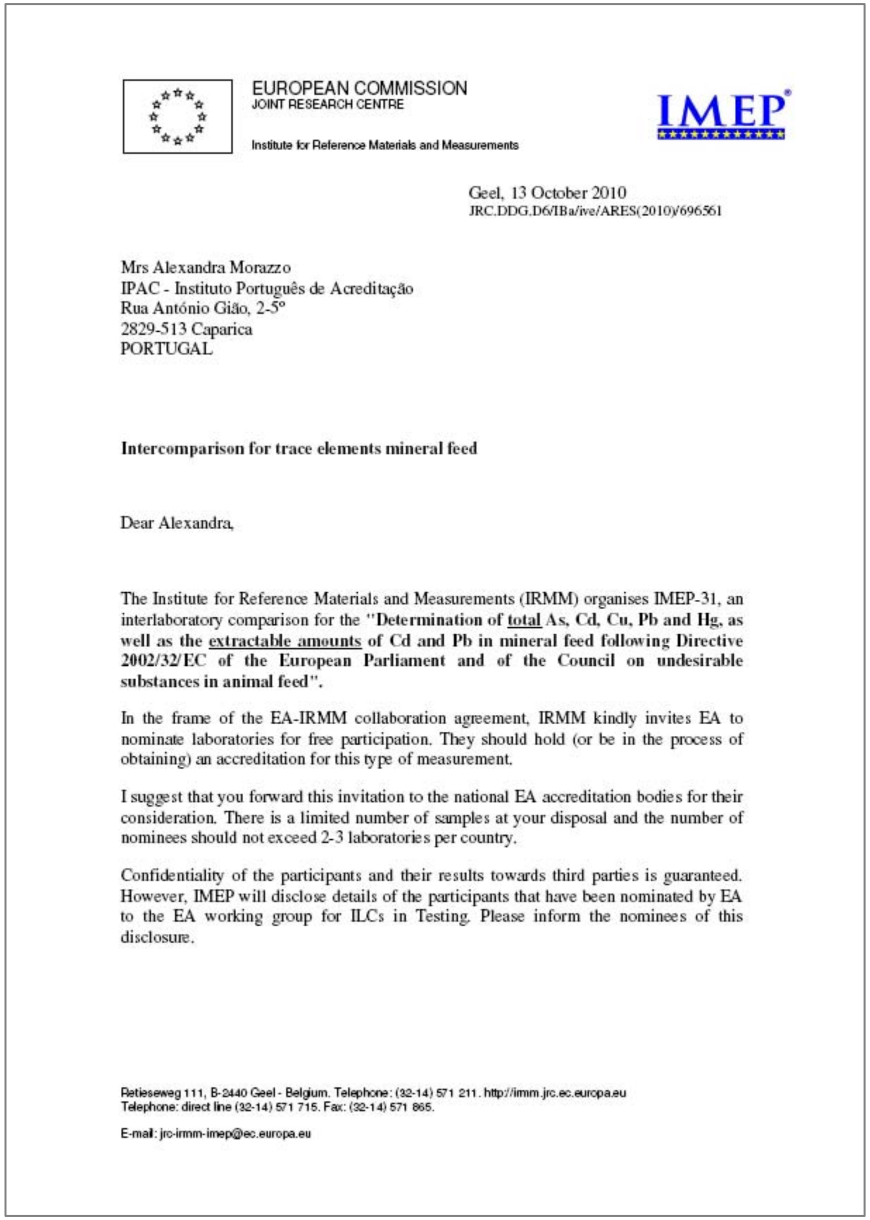
[11] Baer I., Emteborg H., de la Calle B. (2011) Results from two interlaboratory comparisons on the measurement of trace element contents in food supplements -

State of the art of control laboratories in Europe. Food Chemistry 126(3): 1498-1504.

[12] US-EPA (2007) Method 7473 - Mercury in Solids and Solutions by Thermal Decomposition, Amalgamation, and Atomic Absorption Spectrophotometry. U.S. Environmental Protection Agency, http://www.epa.gov/osw/hazard/testmethods/sw846/online/index.htm.

Annexes

Annex 1 : Invitation to EA to nominate laboratories



EUROPEAN COMMISSION
JOINT RESEARCH CENTRE
Institute for Reference Materials and Measurements

IMEP®

Geel, 13 October 2010
JRC.DDG.D6/IBa/ive/ARES(2010)/696561

Mrs Alexandra Morazzo
IPAC - Instituto Português de Acreditação
Rua António Gião, 2-5°
2829-513 Caparica
PORTUGAL

Intercomparison for trace elements mineral feed

Dear Alexandra,

The Institute for Reference Materials and Measurements (IRMM) organises IMEP-31, an interlaboratory comparison for the "**Determination of <u>total</u> As, Cd, Cu, Pb and Hg, as well as the <u>extractable amounts</u> of Cd and Pb in mineral feed following Directive 2002/32/EC of the European Parliament and of the Council on undesirable substances in animal feed**".

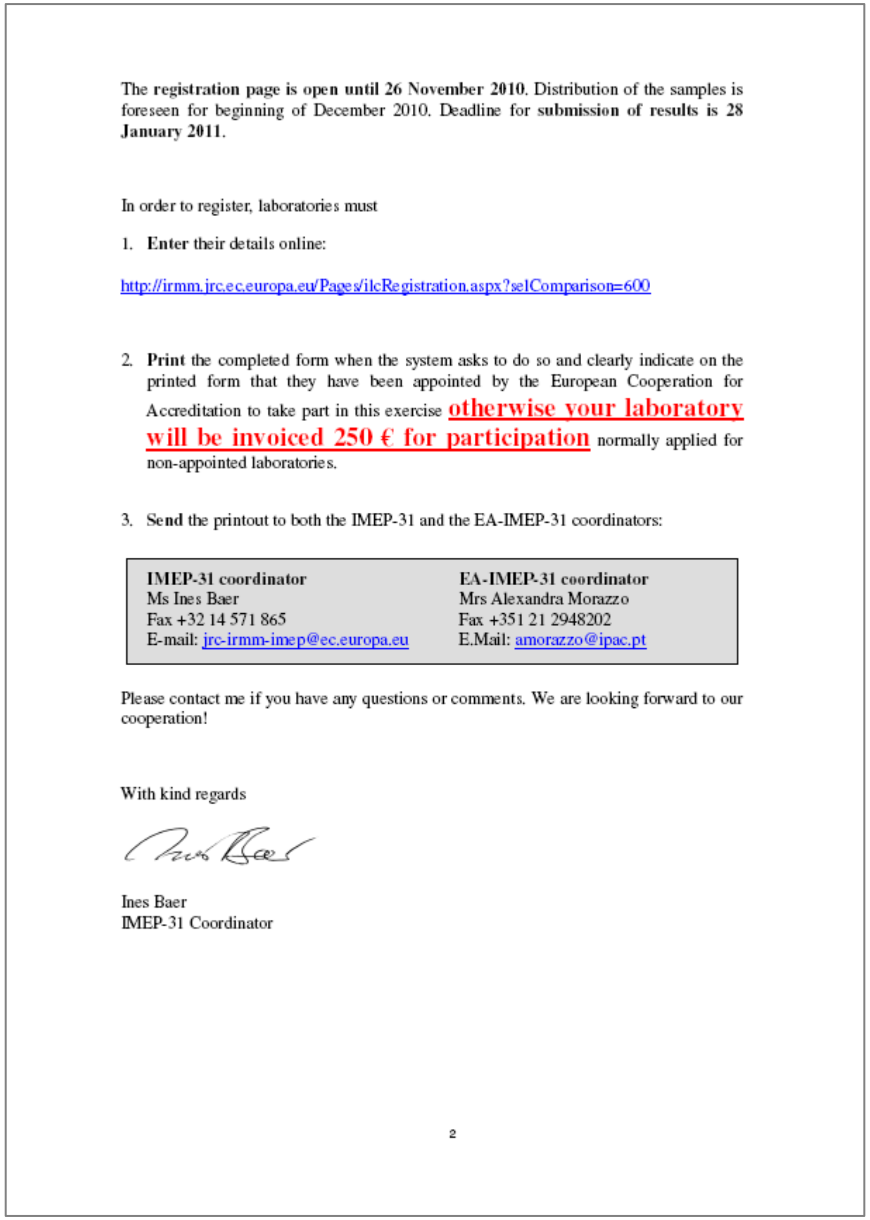
In the frame of the EA-IRMM collaboration agreement, IRMM kindly invites EA to nominate laboratories for free participation. They should hold (or be in the process of obtaining) an accreditation for this type of measurement.

I suggest that you forward this invitation to the national EA accreditation bodies for their consideration. There is a limited number of samples at your disposal and 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. Please inform the nominees of this disclosure.

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



The **registration page is open until 26 November 2010**. Distribution of the samples is foreseen for beginning of December 2010. Deadline for **submission of results** is **28 January 2011**.

In order to register, laboratories must

1. **Enter** their details online:

http://irmm.jrc.ec.europa.eu/Pages/ilcRegistration.aspx?selComparison=600

2. **Print** the completed form when the system asks to do so and clearly indicate on the printed form that they have been appointed by the European Cooperation for Accreditation to take part in this exercise **<u>otherwise your laboratory will be invoiced 250 € for participation</u>** normally applied for non-appointed laboratories.

3. **Send** the printout to both the IMEP-31 and the EA-IMEP-31 coordinators:

IMEP-31 coordinator Ms Ines Baer Fax +32 14 571 865 E-mail: jrc-irmm-imep@ec.europa.eu	**EA-IMEP-31 coordinator** Mrs Alexandra Morazzo Fax +351 21 2948202 E.Mail: amorazzo@ipac.pt

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

With kind regards

Ines Baer
IMEP-31 Coordinator

Annex 2 : Invitation to APLAC to nominate laboratories

EUROPEAN COMMISSION
JOINT RESEARCH CENTRE
Institute for Reference Materials and Measurements

IMEP®

Geel, 13 October 2010
JRC.DDG.D6/IBa/ive/ARES(2010)/696574

Mr Daniel Tholen
Chairman, APLAC PT Committee

Intercomparison for trace elements mineral feed

Dear Daniel,

The Institute for Reference Materials and Measurements (IRMM) organises IMEP-31, an interlaboratory comparison for the "**Determination of total As, Cd, Cu, Pb and Hg, as well as the extractable amounts of Cd and Pb in mineral feed following Directive 2002/32/EC of the European Parliament and of the Council on undesirable substances in animal feed**".

IRMM kindly invites APLAC to nominate 10 laboratories for free participation. However, 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 a selection of specialised laboratories in this area.

In addition to the 10 laboratories above mentioned, other laboratories may take part in IMEP-31 paying a registration fee of 250 €.

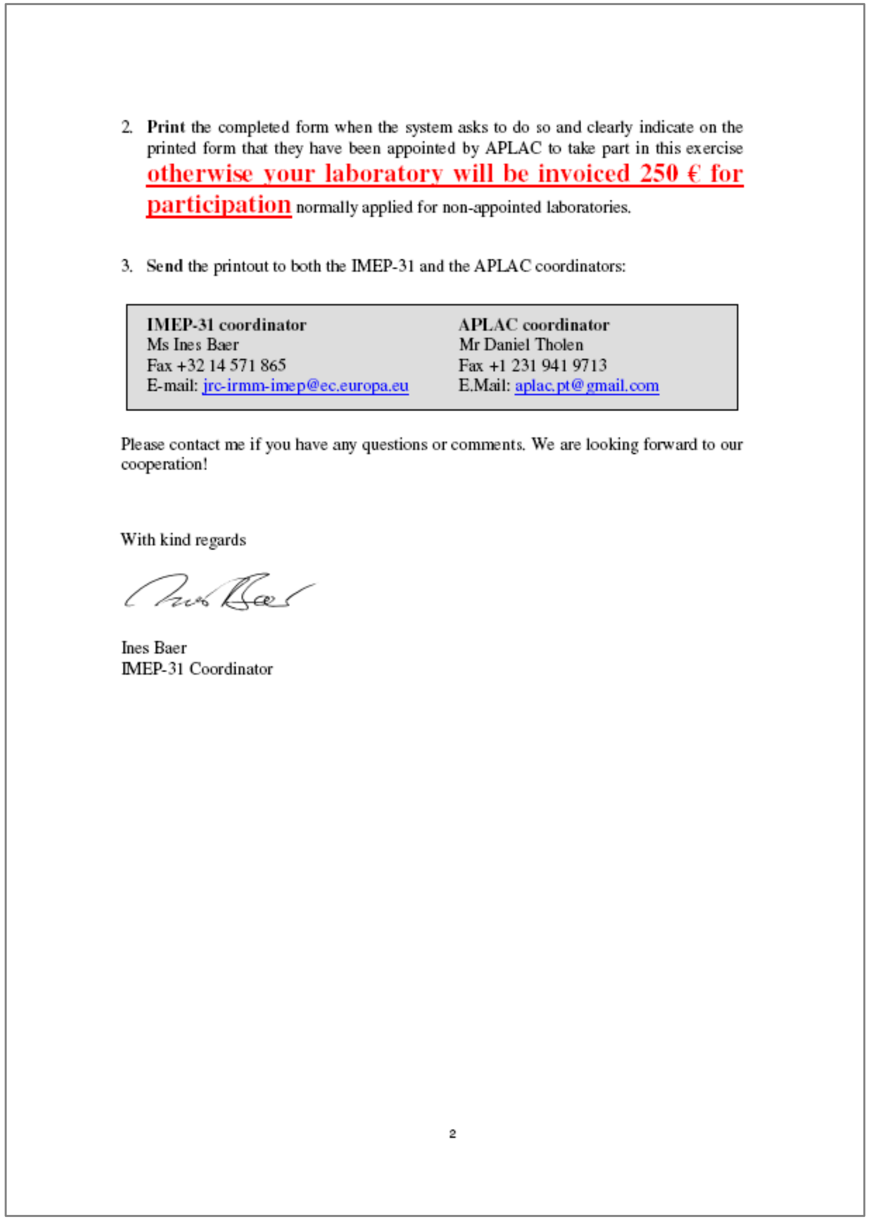
Confidentiality of the participants and their results towards third parties is guaranteed.

The **registration page is open until 26 November 2010**. Distribution of the samples is foreseen for beginning of December 2010. Deadline for **submission of results is 28 January 2011**.

In order to register, laboratories must

1. **Enter** their details online:

http://irmm.jrc.ec.europa.eu/Pages/ilcRegistration.aspx?selComparison=600



2. **Print** the completed form when the system asks to do so and clearly indicate on the printed form that they have been appointed by APLAC to take part in this exercise **otherwise your laboratory will be invoiced 250 € for participation** normally applied for non-appointed laboratories.

3. **Send** the printout to both the IMEP-31 and the APLAC coordinators:

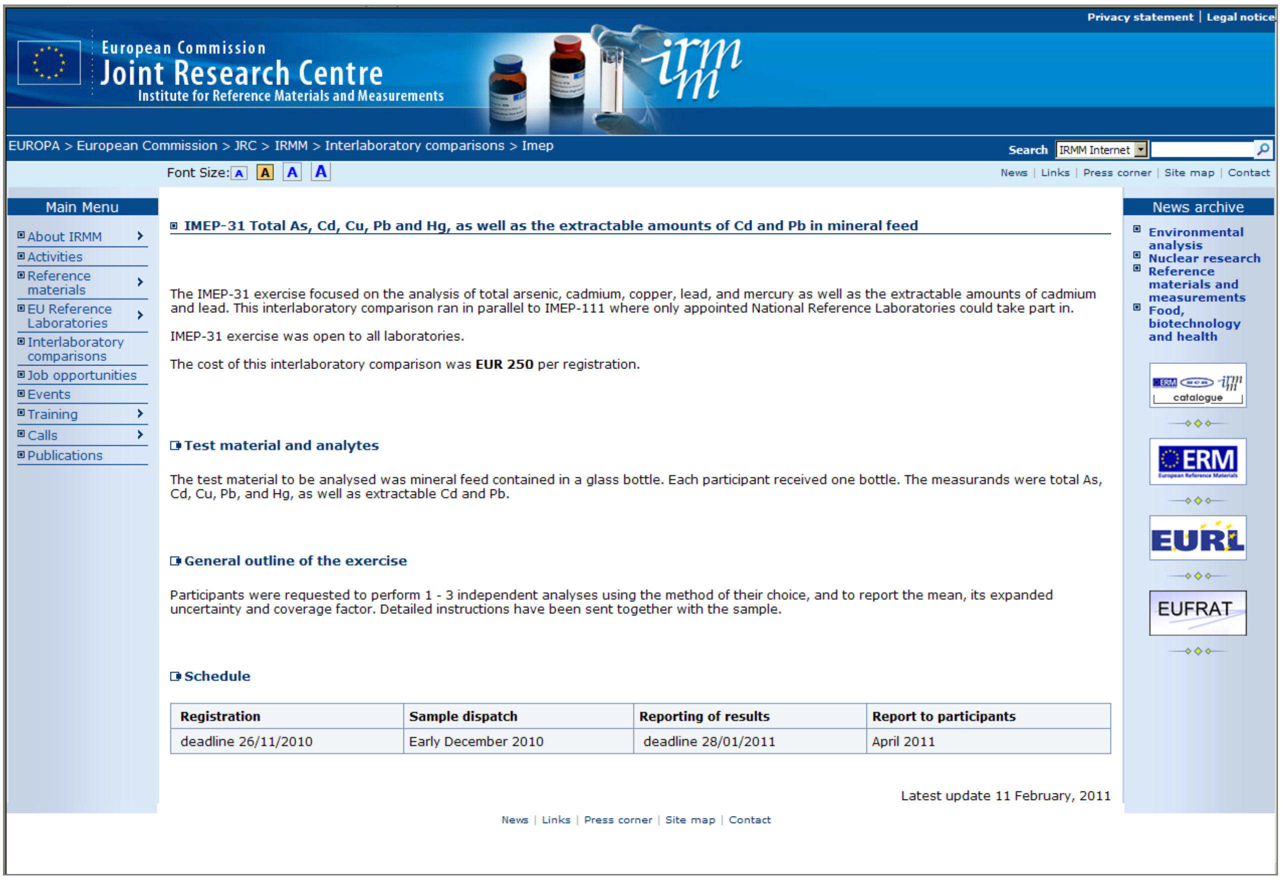
IMEP-31 coordinator Ms Ines Baer Fax +32 14 571 865 E-mail: jrc-irmm-imep@ec.europa.eu	**APLAC coordinator** Mr Daniel Tholen Fax +1 231 941 9713 E.Mail: aplac.pt@gmail.com

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

With kind regards

Ines Baer
IMEP-31 Coordinator

Annex 3 : Announcement on IRMM - IMEP website



IMEP-31 Total As, Cd, Cu, Pb and Hg, as well as the extractable amounts of Cd and Pb in mineral feed

The IMEP-31 exercise focused on the analysis of total arsenic, cadmium, copper, lead, and mercury as well as the extractable amounts of cadmium and lead. This interlaboratory comparison ran in parallel to IMEP-111 where only appointed National Reference Laboratories could take part in.

IMEP-31 exercise was open to all laboratories.

The cost of this interlaboratory comparison was **EUR 250** per registration.

Test material and analytes

The test material to be analysed was mineral feed contained in a glass bottle. Each participant received one bottle. The measurands were total As, Cd, Cu, Pb, and Hg, as well as extractable Cd and Pb.

General outline of the exercise

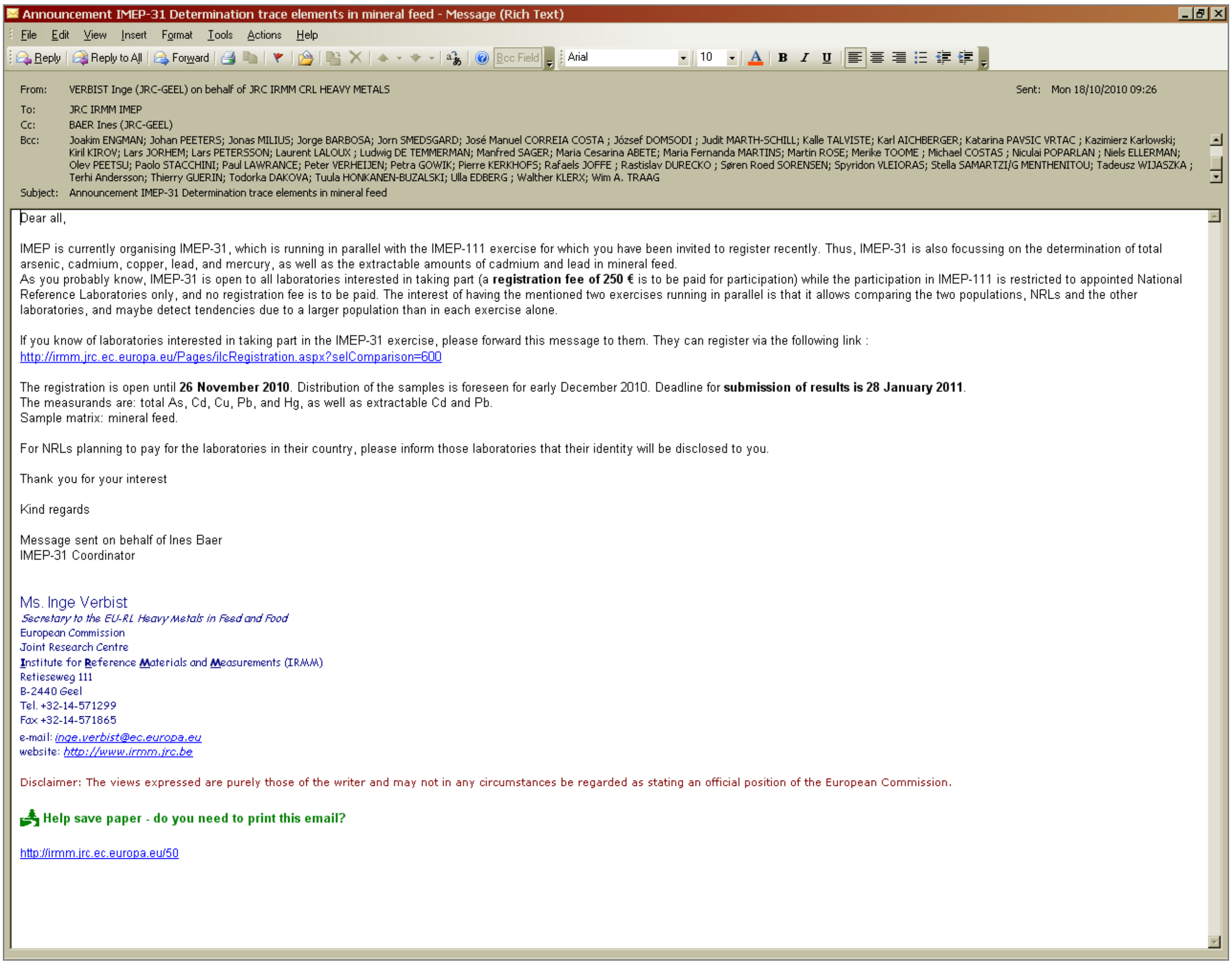
Participants were requested to perform 1 - 3 independent analyses using the method of their choice, and to report the mean, its expanded uncertainty and coverage factor. Detailed instructions have been sent together with the sample.

Schedule

Registration	Sample dispatch	Reporting of results	Report to participants
deadline 26/11/2010	Early December 2010	deadline 28/01/2011	April 2011

Latest update 11 February, 2011

Annex 4 : Invitation sent to NRLs



From: VERBIST Inge (JRC-GEEL) on behalf of JRC IRMM CRL HEAVY METALS
Sent: Mon 18/10/2010 09:26
To: JRC IRMM IMEP
Cc: BAER Ines (JRC-GEEL)
Bcc: Joakim ENGMAN; Johan PEETERS; Jonas MILIUS; Jorge BARBOSA; Jorn SMEDSGARD; José Manuel CORREIA COSTA ; József DOMSODI ; Judit MARTH-SCHILL; Kalle TALVISTE; Karl AICHBERGER; Katarina PAVSIC VRTAC ; Kazimierz Karlowski; Kiril KIROV; Lars JORHEM; Lars PETERSSON; Laurent LALOUX ; Ludwig DE TEMMERMAN; Manfred SAGER; Maria Cesarina ABETE; Maria Fernanda MARTINS; Martin ROSE; Merike TOOME ; Michael COSTAS ; Niculai POPARLAN ; Niels ELLERMAN; Olev PEETSU; Paolo STACCHINI; Paul LAWRANCE; Peter VERHEIJEN; Petra GOWIK; Pierre KERKHOFS; Rafaels JOFFE ; Rastislav DURECKO ; Søren Roed SORENSEN; Spyridon VLEIORAS; Stella SAMARTZI/G MENTHENITOU; Tadeusz WIJASZKA ; Terhi Andersson; Thierry GUERIN; Todorka DAKOVA; Tuula HONKANEN-BUZALSKI; Ulla EDBERG ; Walther KLERX; Wim A. TRAAG
Subject: Announcement IMEP-31 Determination trace elements in mineral feed

Dear all,

IMEP is currently organising IMEP-31, which is running in parallel with the IMEP-111 exercise for which you have been invited to register recently. Thus, IMEP-31 is also focussing on the determination of total arsenic, cadmium, copper, lead, and mercury, as well as the extractable amounts of cadmium and lead in mineral feed.
As you probably know, IMEP-31 is open to all laboratories interested in taking part (a **registration fee of 250 €** is to be paid for participation) while the participation in IMEP-111 is restricted to appointed National Reference Laboratories only, and no registration fee is to be paid. The interest of having the mentioned two exercises running in parallel is that it allows comparing the two populations, NRLs and the other laboratories, and maybe detect tendencies due to a larger population than in each exercise alone.

If you know of laboratories interested in taking part in the IMEP-31 exercise, please forward this message to them. They can register via the following link :
http://irmm.jrc.ec.europa.eu/Pages/ilcRegistration.aspx?selComparison=600

The registration is open until **26 November 2010**. Distribution of the samples is foreseen for early December 2010. Deadline for **submission of results is 28 January 2011**.
The measurands are: total As, Cd, Cu, Pb, and Hg, as well as extractable Cd and Pb.
Sample matrix: mineral feed.

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

Message sent on behalf of Ines Baer
IMEP-31 Coordinator

Ms. Inge Verbist
Secretary to the EU-RL Heavy Metals in Feed and Food
European Commission
Joint Research Centre
Institute for Reference Materials and Measurements (IRMM)
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B-2440 Geel
Tel. +32-14-571299
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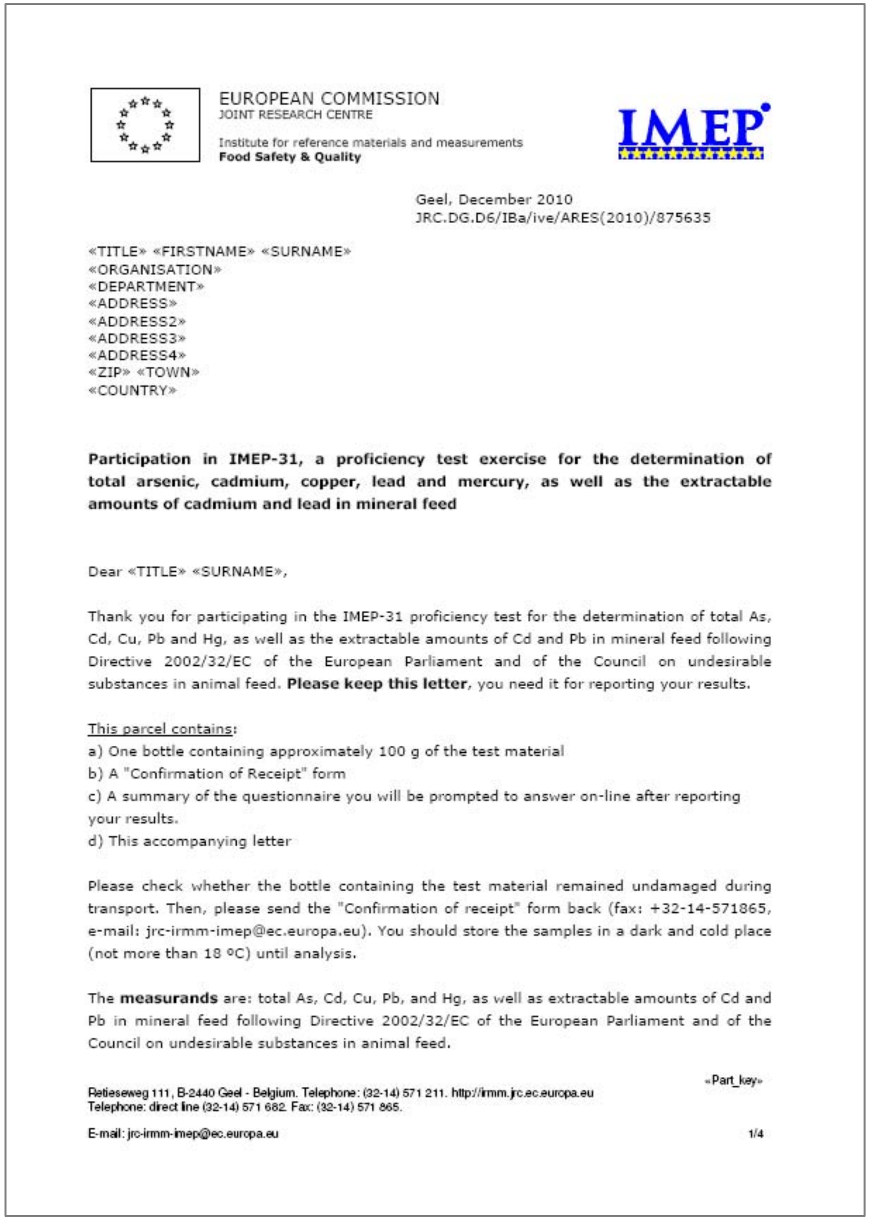
e-mail: *inge.verbist@ec.europa.eu*
website: *http://www.irmm.jrc.be*

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.

Help save paper - do you need to print this email?

http://irmm.jrc.ec.europa.eu/50

Annex 5 : Sample accompanying letter



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

Geel, December 2010
JRC.DG.D6/IBa/ive/ARES(2010)/875635

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

Participation in IMEP-31, a proficiency test exercise for the determination of total arsenic, cadmium, copper, lead and mercury, as well as the extractable amounts of cadmium and lead in mineral feed

Dear «TITLE» «SURNAME»,

Thank you for participating in the IMEP-31 proficiency test for the determination of total As, Cd, Cu, Pb and Hg, as well as the extractable amounts of Cd and Pb in mineral feed following Directive 2002/32/EC of the European Parliament and of the Council on undesirable substances in animal feed. **Please keep this letter**, you need it for reporting your results.

This parcel contains:
a) One bottle containing approximately 100 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 18 ºC) until analysis.

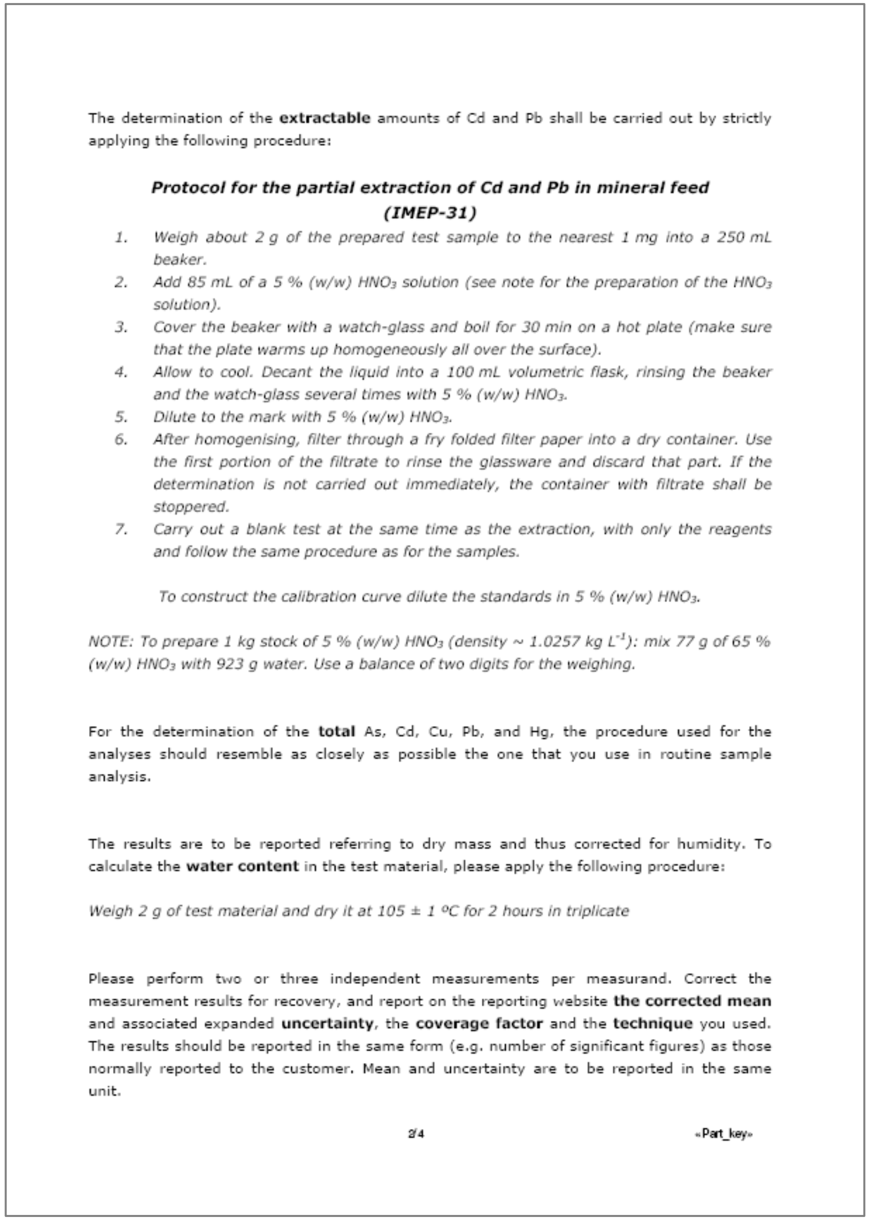
The **measurands** are: total As, Cd, Cu, Pb, and Hg, as well as extractable amounts of Cd and Pb in mineral feed following Directive 2002/32/EC of the European Parliament and of the Council on undesirable substances in animal feed.

«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



The determination of the **extractable** amounts of Cd and Pb shall be carried out by strictly applying the following procedure:

Protocol for the partial extraction of Cd and Pb in mineral feed (IMEP-31)

1. *Weigh about 2 g of the prepared test sample to the nearest 1 mg into a 250 mL beaker.*
2. *Add 85 mL of a 5 % (w/w) HNO_3 solution (see note for the preparation of the HNO_3 solution).*
3. *Cover the beaker with a watch-glass and boil for 30 min on a hot plate (make sure that the plate warms up homogeneously all over the surface).*
4. *Allow to cool. Decant the liquid into a 100 mL volumetric flask, rinsing the beaker and the watch-glass several times with 5 % (w/w) HNO_3.*
5. *Dilute to the mark with 5 % (w/w) HNO_3.*
6. *After homogenising, filter through a fry folded filter paper into a dry container. Use the first portion of the filtrate to rinse the glassware and discard that part. If the determination is not carried out immediately, the container with filtrate shall be stoppered.*
7. *Carry out a blank test at the same time as the extraction, with only the reagents and follow the same procedure as for the samples.*

To construct the calibration curve dilute the standards in 5 % (w/w) HNO_3.

NOTE: To prepare 1 kg stock of 5 % (w/w) HNO_3 (density ~ 1.0257 kg L^{-1}): mix 77 g of 65 % (w/w) HNO_3 with 923 g water. Use a balance of two digits for the weighing.

For the determination of the **total** As, Cd, Cu, Pb, and Hg, the procedure used for the analyses should resemble as closely as possible the one that you use in routine sample analysis.

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

Weigh 2 g of test material and dry it at 105 ± 1 ºC for 2 hours in triplicate

Please perform two or three independent measurements per measurand. Correct the measurement results for recovery, and report on the reporting website **the corrected mean** and 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.

2/4 «Part_key»

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.

After entering all results, please also complete the relating online-questionnaire. A summary of the latter was sent with this letter. Do not forget to save and submit when required. **For final submission please press "Confirm results and questionnaire"**. Check your results carefully for any errors before submission, since this is your definitive confirmation. You will then be prompted to **print the completed report form**. Please do so, **sign the paper version and return it to IRMM by fax or by e-mail.**

The deadline for submission of results is 28/01/2011.

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

Ines Baer

Dr. Ines Baer
IMEP-31 Co-ordinator

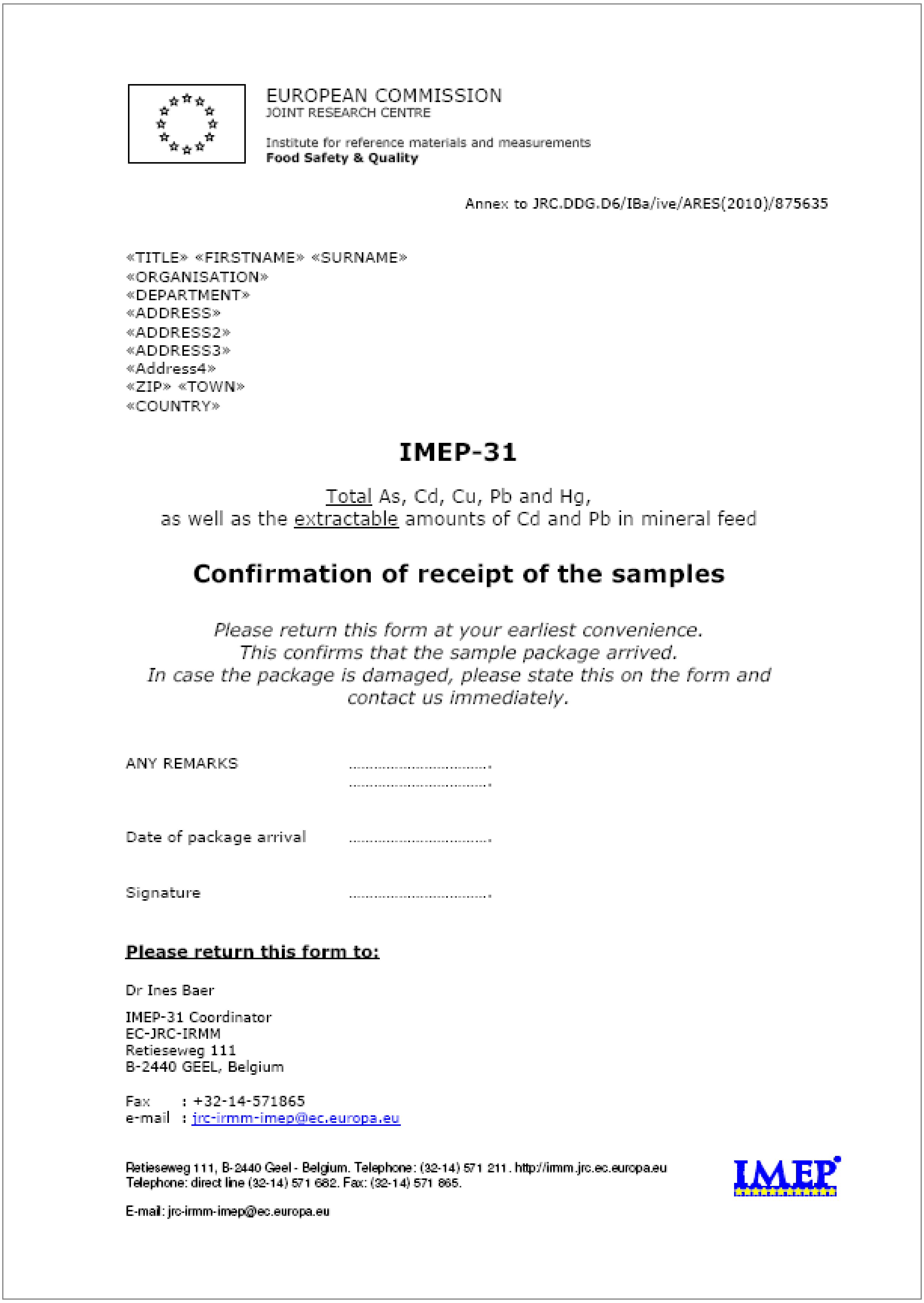
Enclosures: 1) one bottle containing the test material; 2) confirmation of receipt form; 3) Summary IMEP-31 questionnaire; 4) Accompanying letter.

Cc: **F. Ulberth**

3/4

«Part_key»

Annex 6 : '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(2010)/875635

«TITLE» «FIRSTNAME» «SURNAME»
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«ADDRESS3»
«Address4»
«ZIP» «TOWN»
«COUNTRY»

IMEP-31

Total As, Cd, Cu, Pb and Hg,
as well as the extractable amounts of Cd and Pb in mineral feed

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

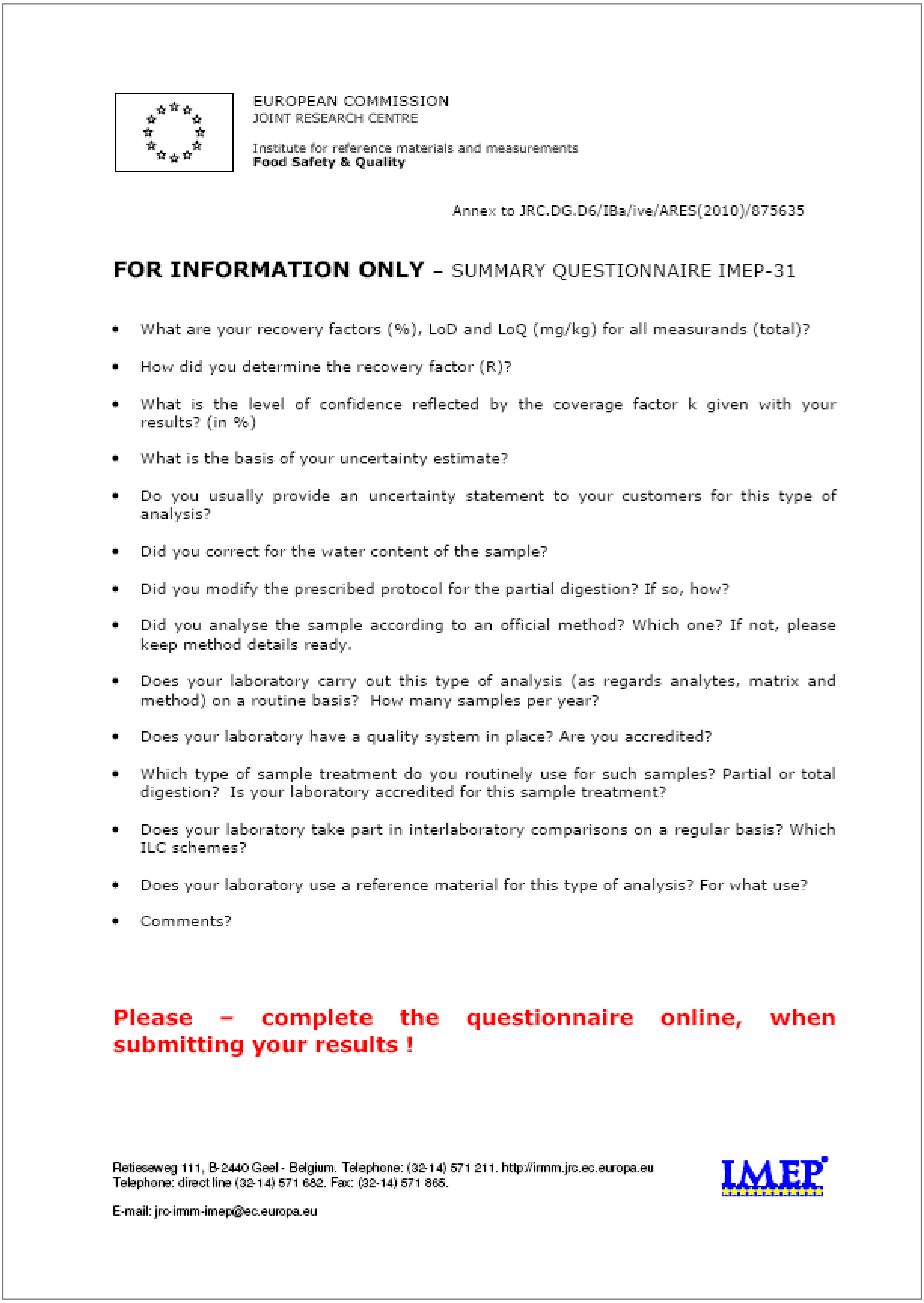
IMEP-31 Coordinator
EC-JRC-IRMM
Retieseweg 111
B-2440 GEEL, Belgium

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 7 : Summary questionnaire sent with sample



EUROPEAN COMMISSION
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Food Safety & Quality

Annex to JRC.DG.D6/IBa/ive/ARES(2010)/875635

FOR INFORMATION ONLY – SUMMARY QUESTIONNAIRE IMEP-31

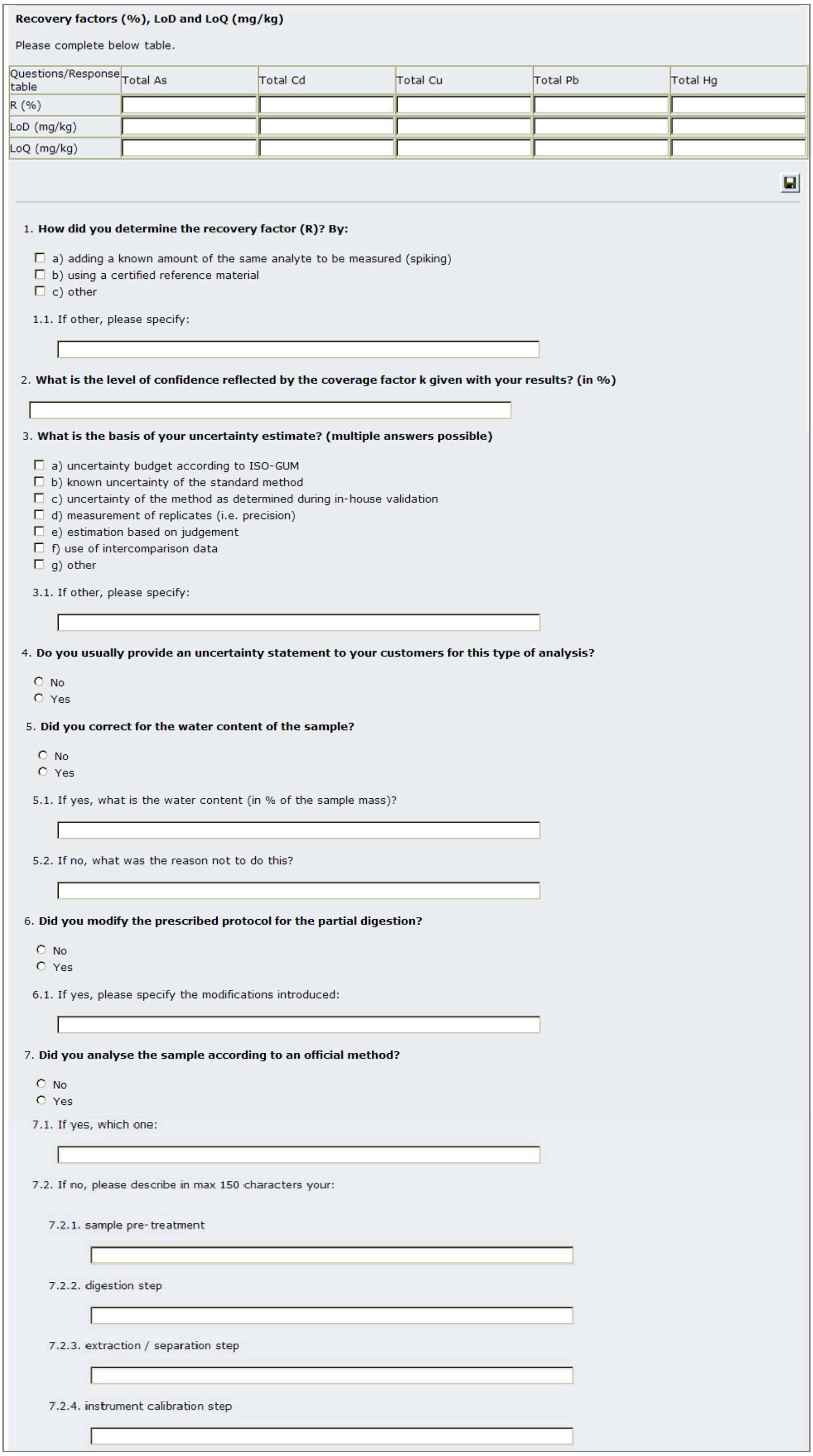
- What are your recovery factors (%), LoD and LoQ (mg/kg) for all measurands (total)?
- How did you determine the recovery factor (R)?
- What is the level of confidence reflected by the coverage factor k given with your results? (in %)
- What is the basis of your uncertainty estimate?
- Do you usually provide an uncertainty statement to your customers for this type of analysis?
- Did you correct for the water content of the sample?
- Did you modify the prescribed protocol for the partial digestion? If so, how?
- 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?
- Which type of sample treatment do you routinely use for such samples? Partial or total digestion? Is your laboratory accredited for this sample treatment?
- 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 8 : Online Questionnaire



Recovery factors (%), LoD and LoQ (mg/kg)

Please complete below table.

Questions/Response table	Total As	Total Cd	Total Cu	Total Pb	Total Hg
R (%)					
LoD (mg/kg)					
LoQ (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. **What is the level of confidence reflected by the coverage factor k given with your results? (in %)**

3. **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

3.1. If other, please specify:

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

○ No
○ Yes

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

○ No
○ Yes

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

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

6. **Did you modify the prescribed protocol for the partial digestion?**

○ No
○ Yes

6.1. If yes, please specify the modifications introduced:

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

○ No
○ Yes

7.1. If yes, which one:

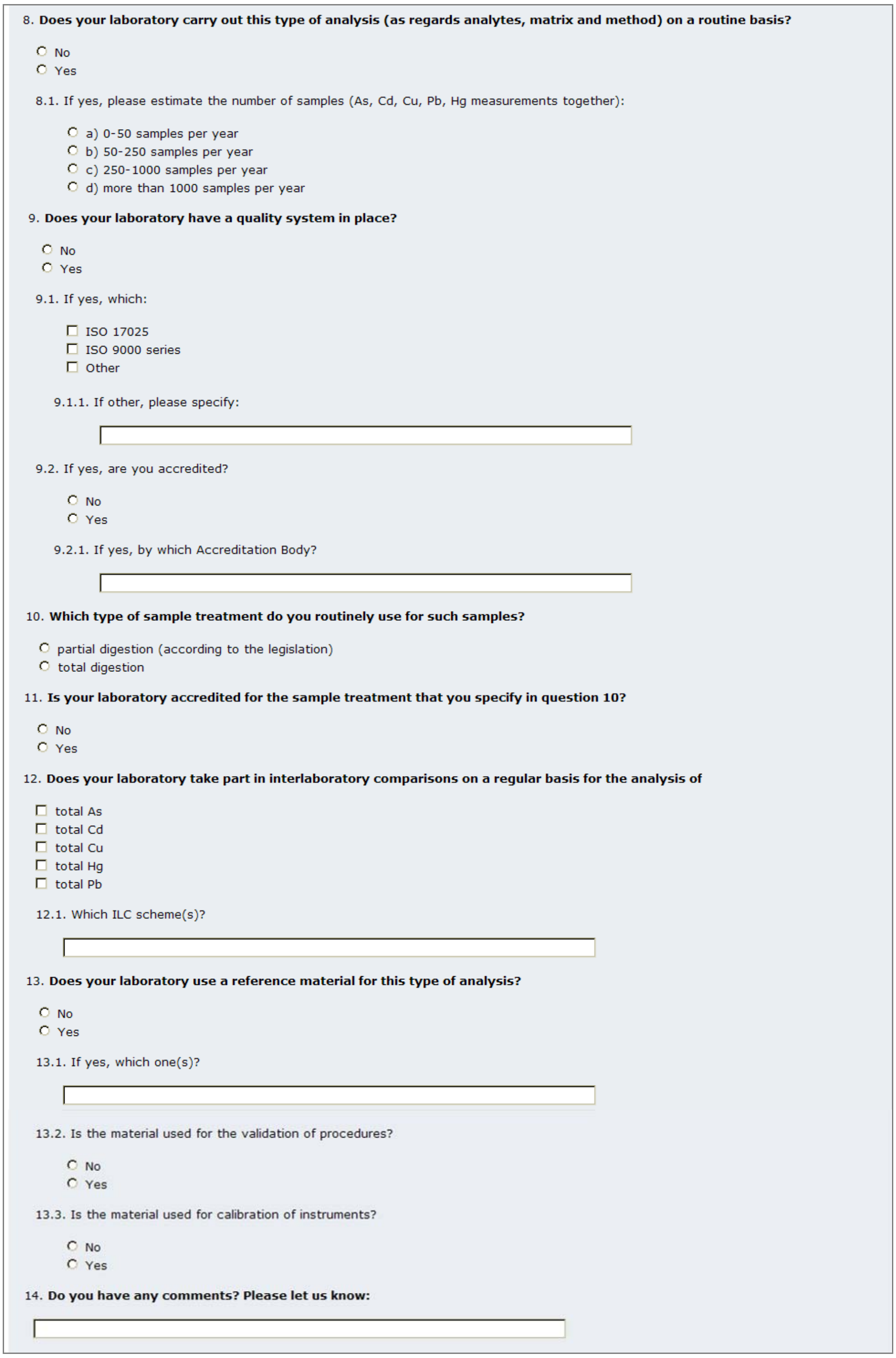
7.2. If no, please describe in max 150 characters your:

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 (As, Cd, Cu, Pb, Hg 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. **Which type of sample treatment do you routinely use for such samples?**

○ partial digestion (according to the legislation)
○ total digestion

11. **Is your laboratory accredited for the sample treatment that you specify in question 10?**

○ No
○ Yes

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

☐ total As
☐ total Cd
☐ total Cu
☐ total Hg
☐ total Pb

12.1. Which ILC scheme(s)?

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

○ No
○ Yes

13.1. If yes, which one(s)?

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

○ No
○ Yes

13.3. Is the material used for calibration of instruments?

○ No
○ Yes

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

Annex 9 : Results for Total Arsenic

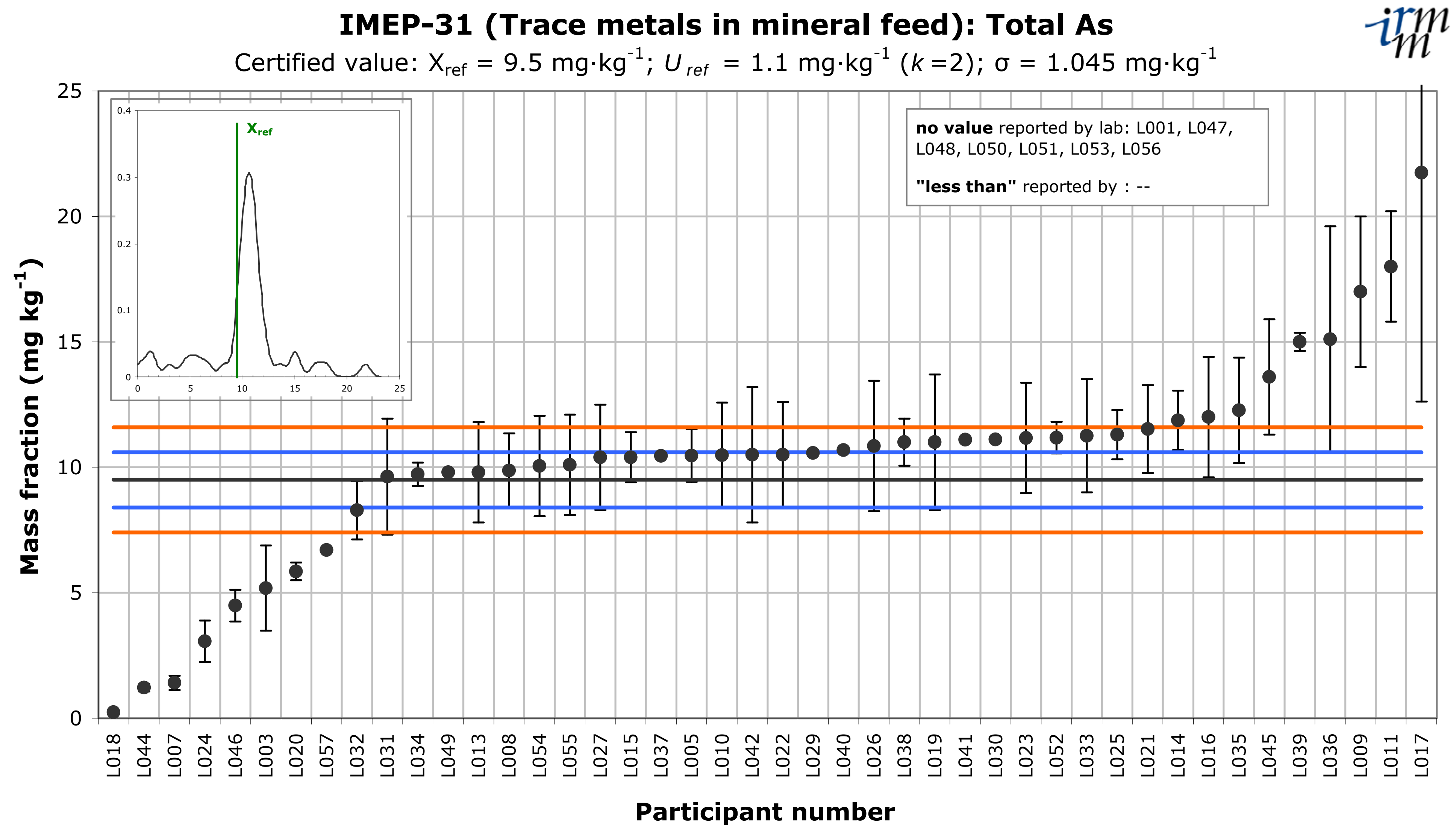
X_{ref} = 9.5 and U_{ref} = 1.1; all values are given in (mg kg^{-1})

Part Nr	Mean (xlab)	***Ulab***	***k*** [a]	***ulab***	Technique	z [b]	zeta [b]	Unc [c]
L003	5.187	1.7	2	0.9	ICP-OES	-4.1	-4.3	a
L005	10.47	1.05	2	0.53	ICP-MS	0.9	1.3	b
L007	1.41	0.28	2	0.14	ICP-OES	-7.7	-14.3	b
L008	9.87	1.48	2	0.74	ICP-MS	0.4	0.4	a
L009	17.0	3.0	2	1.5	ICP-OES	7.2	4.7	c
L010	10.48	2.1	1	2.1	HG-AAS	0.9	0.5	c
L011	18.0	2.2	2	1.1	ICP-MS	8.1	6.9	c
L013	9.8	2.0	2	1.0	ICP-MS	0.3	0.3	a
L014	11.87	1.187	2	0.594	ICP-MS	2.3	2.9	a
L015	10.4	1.0	2.35	0.4	HR-ICP-MS	0.9	1.3	b
L016	12.0	2.4	2	1.2	ICP-OES	2.4	1.9	c
L017	21.74	9.12	95	0.10	ICP-MS	11.7	21.9	b
L018	0.237	0.07	2	0.04	ICP-MS	-8.9	-16.8	b
L019	11.0	2.7	2	1.35	ICP-MS	1.4	1.0	c
L020	5.85	0.35	2	0.18	HG-AAS	-3.5	-6.3	b
L021	11.52	1.75	2	0.88	ICP-MS	1.9	2.0	a
L022	10.5	2.1	2	1.1	FIAS Furnace	1.0	0.8	c
L023	11.17	2.2	2	1.1	ICP-MS	1.6	1.4	c
L024	3.068	0.83	2	0.42	ETAAS	-6.2	-9.3	b
L025	11.3	0.98	2	0.49	HG-AAS	1.7	2.4	b
L026	10.85	2.60	2	1.30	ICP-MS	1.3	1.0	c
L027	10.4	2.1	2	1.1	HG-AAS	0.9	0.8	c
L029	10.57	0.09	1	0.09	HG-AAS	1.0	1.9	b
L030	11.11	0.07	95	0.00	HG-AAS	1.5	2.9	b
L031	9.63	2.31	2	1.16	HG-AAS	0.1	0.1	c
L032	8.29	1.16	√3	0.67	HG-AAS	-1.2	-1.4	a
L033	11.259	2.26	√3	1.30	HG-AAS	1.7	1.2	c
L034	9.728	0.463	2	0.232	ICP-OES	0.2	0.4	b
L035	12.27	2.1	2	1.1	HG-AAS	2.7	2.3	c
L036	15.1	4.5	2	2.3	ICP-OES	5.4	2.4	c
L037	10.46	0	√3	0	ICP-MS	0.9	1.7	b
L038	11	0.94	1	0.94	ICP-MS	1.4	1.4	a
L039	15	0.36	2	0.18	ICP-OES	5.3	9.5	b
L040	10.69	0	√3	0	ICP-MS	1.1	2.2	b
L041	11.1	0.1	2	0.1	HG-AAS	1.5	2.9	b
L042	10.5	2.7	2	1.4	ICP-MS	1.0	0.7	c
L044	1.22	0.15	2	0.08	CV-AAS	-7.9	-14.9	b
L045	13.6	2.3	2	1.2	HG-AAS	3.9	3.2	c
L046	4.489	0.628	2	0.314	ETAAS	-4.8	-7.9	b
L049	9.8	0	√3	0	HG-AAS	0.3	0.5	b
L052	11.18	0.63	2	0.32	ICP-MS	1.6	2.7	b
L054	10.05	2	2	1	HG-AAS	0.5	0.5	a
L055	10.1	2.0	2	1.0	HG-AAS	0.6	0.5	a
L057	6.7	0	√3	0	HG-AAS	-2.7	-5.1	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. 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-31 (Trace metals in mineral feed): Total As

Certified value: X_{ref} = 9.5 mg·kg^{-1}; U_{ref} = 1.1 mg·kg^{-1} (k=2); σ = 1.045 mg·kg^{-1}

no value reported by lab: L001, L047, L048, L050, L051, L053, L056

"less than" reported by : --

This graph displays all revised 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} ± 2u_{ref}**), and the orange lines that of the target interval (**X_{ref} ± 2σ**).

Annex 10 : Results for Total Cadmium

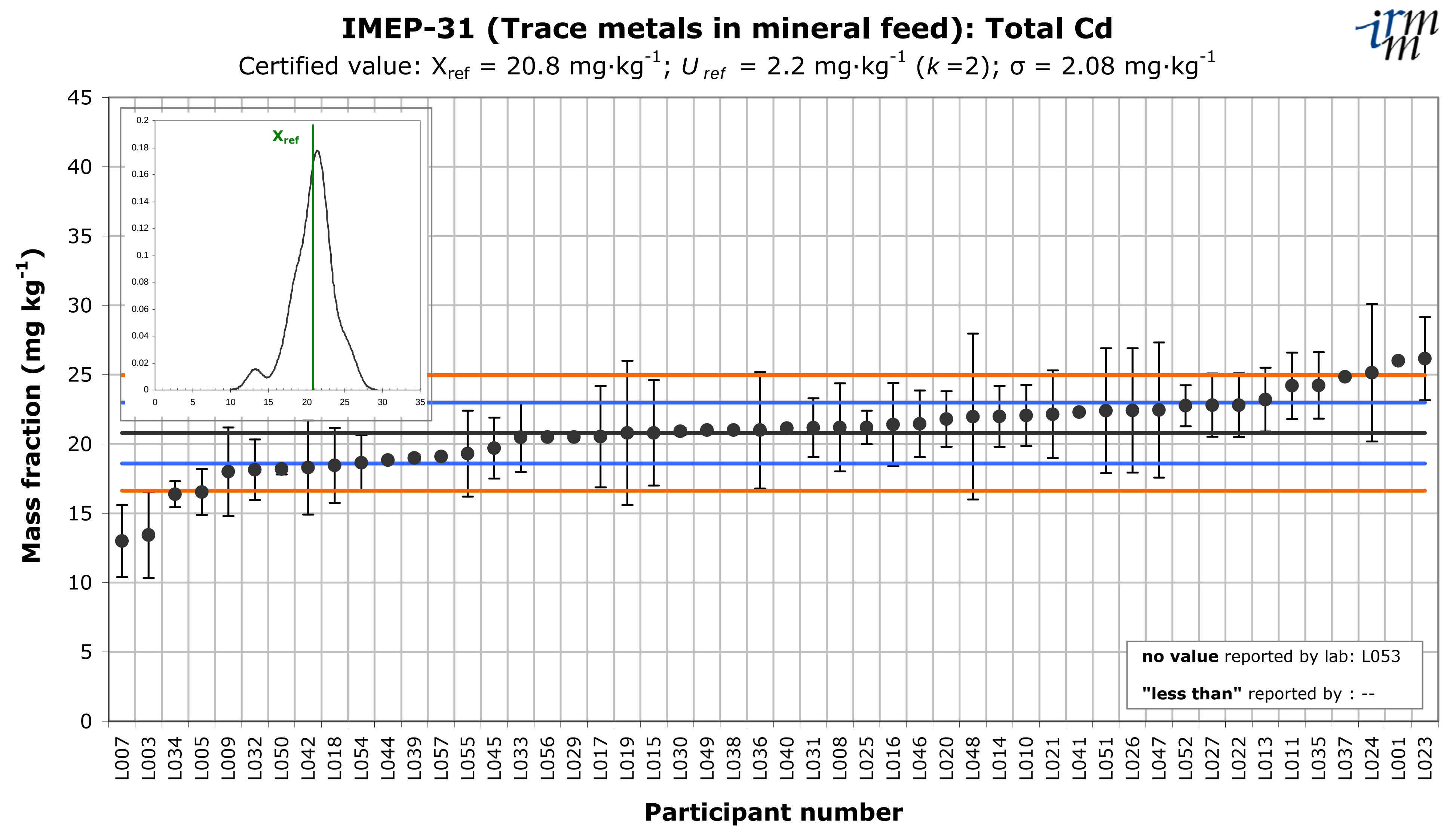
X_{ref} = 20.8 and U_{ref} = 2.2; all values are given in (mg kg^{-1})

Part Nr	Mean (xlab)	*Ulab*	*k*[a]	*ulab*	Technique	z[b]	zeta[b]	Unc[c]
L001	26.0	0	√3	0	FAAS	2.5	4.7	b
L003	13.43	3.09	2	1.55	ICP-OES	-3.5	-3.9	a
L005	16.54	1.65	2	0.83	ICP-OES	-2.0	-3.1	b
L007	13.0	2.6	2	1.3	ICP-OES	-3.8	-4.6	a
L008	21.20	3.18	2	1.59	ICP-MS	0.2	0.2	a
L009	18.0	3.2	2	1.6	ICP-OES	-1.3	-1.4	a
L010	22.06	2.2	1	2.2	ICP-MS	0.6	0.5	c
L011	24.2	2.4	2	1.2	ICP-MS	1.6	2.1	a
L013	23.2	2.3	2	1.2	ICP-MS	1.2	1.5	a
L014	21.99	2.199	2	1.100	ICP-MS	0.6	0.8	b
L015	20.8	3.8	2.35	1.6	ICP-MS	0.0	0.0	a
L016	21.4	3.0	2	1.5	ICP-OES	0.3	0.3	a
L017	20.54	3.65	95	0.04	ICP-MS	-0.1	-0.2	b
L018	18.45	2.7	2	1.4	ICP-MS	-1.1	-1.3	a
L019	20.8	5.2	2	2.6	ICP-MS	0.0	0.0	c
L020	21.8	2.0	2	1.0	ICP-MS	0.5	0.7	b
L021	22.15	3.16	2	1.58	ICP-MS	0.6	0.7	a
L022	22.8	2.3	2	1.2	ETAAS	1.0	1.3	a
L023	26.16	3.0	2	1.5	ICP-MS	2.6	2.9	a
L024	25.141	4.95	2	2.48	ETAAS	2.1	1.6	c
L025	21.2	1.2	2	0.6	ICP-OES	0.2	0.3	b
L026	22.42	4.48	2	2.24	ICP-MS	0.8	0.6	c
L027	22.8	2.28	2	1.14	ETAAS	1.0	1.3	a
L029	20.5	0.22	1	0.22	FAAS	-0.1	-0.3	b
L030	20.91	0.26	95	0.00	ETAAS	0.1	0.1	b
L031	21.18	2.12	2	1.06	ETAAS	0.2	0.2	b
L032	18.15	2.18	√3	1.26	ETAAS	-1.3	-1.6	a
L033	20.489	2.50	√3	1.44	ICP-OES	-0.1	-0.2	a
L034	16.372	0.936	2	0.468	ICP-OES	-2.1	-3.7	b
L035	24.23	2.4	2	1.2	GF AAS zeeman correction	1.6	2.1	a
L036	21.0	4.2	2	2.1	ICP-OES	0.1	0.1	c
L037	24.84	0	√3	0	ICP-MS	1.9	3.7	b
L038	21	0.083	1	0.083	ICP-MS	0.1	0.2	b
L039	19	0.26	2	0.13	ICP-OES	-0.9	-1.6	b
L040	21.14	0	√3	0	ICP-MS	0.2	0.3	b
L041	22.3	0.05	2	0.03	FAAS	0.7	1.4	b
L042	18.3	3.4	2	1.7	ICP-MS	-1.2	-1.2	a
L044	18.83	0.13	2	0.07	FAAS	-0.9	-1.8	b
L045	19.7	2.2	2	1.1	FAAS	-0.5	-0.7	a
L046	21.461	2.403	2	1.202	FAAS	0.3	0.4	a
L047	22.45	4.87	2	2.44	ETAAS	0.8	0.6	c
L048	21.98	5.99	2	3.00	FAAS	0.6	0.4	c
L049	21.0	0	√3	0	FAAS	0.1	0.2	b
L050	18.2	0.404	2	0.202	FAAS	-1.3	-2.3	b
L051	22.4	4.5	2	2.3	ETAAS	0.8	0.6	c
L052	22.76	1.48	2	0.74	ICP-MS	0.9	1.5	b
L054	18.64	2	2	1	FAAS	-1.0	-1.5	b
L055	19.3	3.1	2	1.6	FAAS	-0.7	-0.8	a
L056	20.5	0	√3	0	FAAS	-0.1	-0.3	b
L057	19.1	0	√3	0	ETAAS	-0.8	-1.5	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. 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** : $u_{lab} > u_{max}$



This graph displays all revised 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} ± $2u_{ref}$), and the orange lines that of the target interval (X_{ref} ± 2σ).

Annex 11 : Results for Total Copper

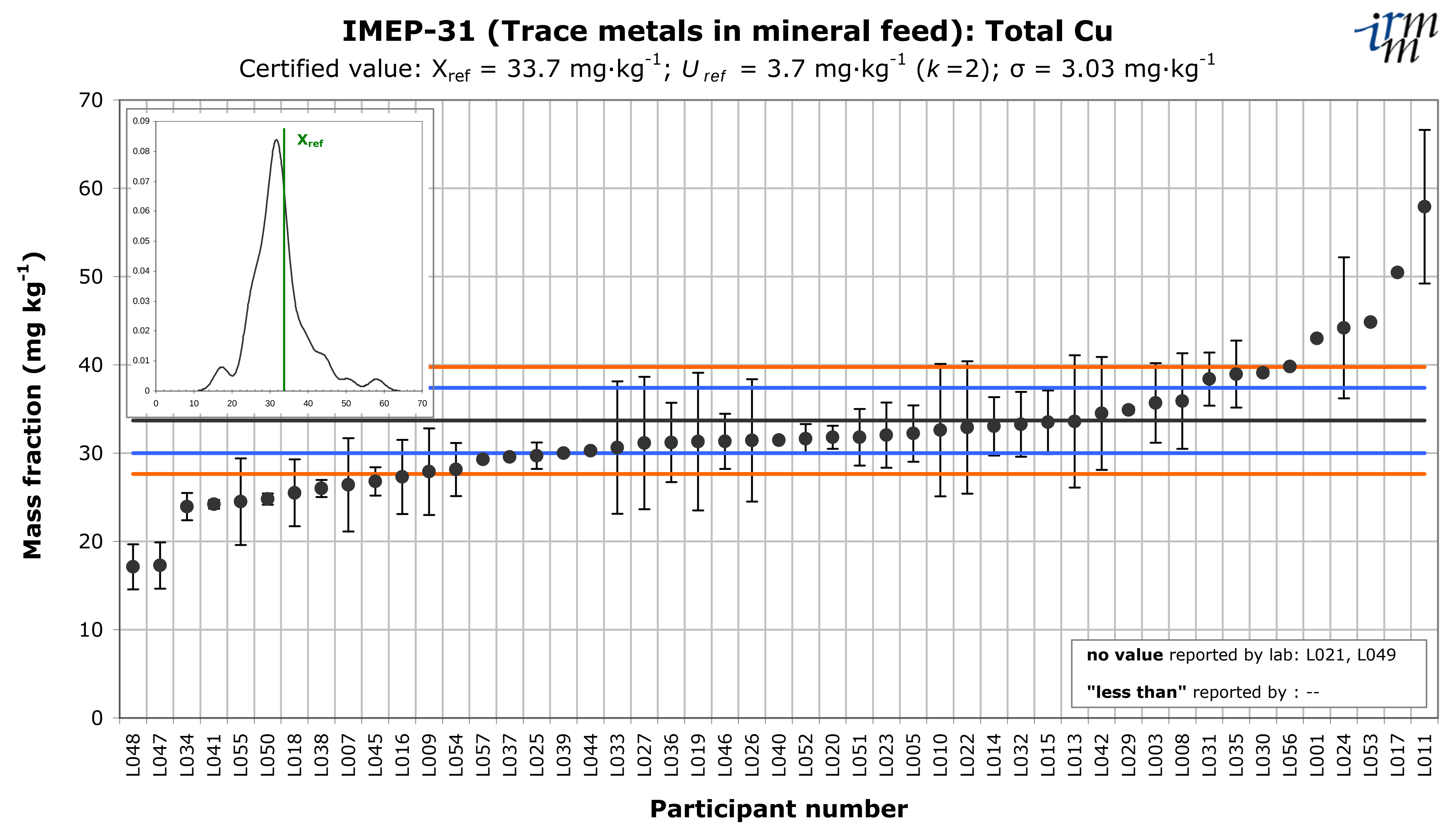
X_{ref} = 33.7 and U_{ref} = 3.7; all values are given in (mg kg^{-1})

Part Nr	Mean (xlab)	*Ulab*	*k*[a]	*ulab*	Technique	z[b]	zeta[b]	Unc[c]
L001	43.0	0	√3	0	FAAS	3.1	5.0	b
L003	35.68	4.50	2	2.25	ICP-OES	0.7	0.7	a
L005	32.22	3.2	2	1.6	ICP-OES	-0.5	-0.6	b
L007	26.4	5.28	2	2.64	ICP-OES	-2.4	-2.3	a
L008	35.9	5.4	2	2.7	ICP-MS	0.7	0.7	a
L009	27.9	4.9	2	2.5	ICP-OES	-1.9	-1.9	a
L010	32.62	7.5	1	7.5	FAAS	-0.4	-0.1	c
L011	57.9	8.7	2	4.4	ICP-MS	8.0	5.1	c
L013	33.6	7.5	2	3.8	ICP-MS	0.0	0.0	c
L014	33.03	3.303	2	1.652	ICP-MS	-0.2	-0.3	b
L015	33.5	3.6	2.35	1.5	ICP-MS	-0.1	-0.1	b
L016	27.3	4.2	2	2.1	ICP-OES	-2.1	-2.3	a
L017	50.46	0	95	0	ICP-OES	5.5	9.1	b
L018	25.50	3.8	2	1.9	ICP-MS	-2.7	-3.1	a
L019	31.3	7.8	2	3.9	ICP-MS	-0.8	-0.6	c
L020	31.8	1.3	2	0.7	ICP-MS	-0.6	-1.0	b
L022	32.9	7.5	2	3.8	FAAS	-0.3	-0.2	c
L023	32.03	3.7	2	1.9	ICP-MS	-0.6	-0.6	a
L024	44.188	7.99	2	4.00	ETAAS	3.5	2.4	c
L025	29.7	1.5	2	0.8	ICP-OES	-1.3	-2.0	b
L026	31.44	6.92	2	3.46	ICP-MS	-0.7	-0.6	c
L027	31.15	7.5	2	3.8	ICP-OES	-0.8	-0.6	c
L029	34.9	0.34	1	0.34	ICP-OES	0.4	0.6	b
L030	39.11	0.35	95	0.00	FAAS	1.8	2.9	b
L031	38.39	3.00	2	1.50	FAAS	1.5	2.0	b
L032	33.26	3.66	√3	2.11	ETAAS	-0.1	-0.2	a
L033	30.629	7.5	√3	4.3	ICP-OES	-1.0	-0.7	c
L034	23.937	1.54	2	0.77	ICP-OES	-3.2	-4.9	b
L035	38.95	3.8	2	1.9	FAAS	1.7	2.0	a
L036	31.2	4.5	2	2.3	ICP-OES	-0.8	-0.9	a
L037	29.56	0	√3	0	ICP-MS	-1.4	-2.2	b
L038	26	0.97	1	0.97	ICP-OES	-2.5	-3.7	b
L039	30	0.25	2	0.13	ICP-OES	-1.2	-2.0	b
L040	31.46	0	√3	0	ICP-MS	-0.7	-1.2	b
L041	24.2	0.5	2	0.3	FAAS	-3.1	-5.1	b
L042	34.5	6.4	2	3.2	ICP-MS	0.3	0.2	c
L044	30.27	0.09	2	0.05	FAAS	-1.1	-1.9	b
L045	26.8	1.6	2	0.8	FAAS	-2.3	-3.4	b
L046	31.325	3.132	2	1.566	FAAS	-0.8	-1.0	b
L047	17.27	2.62	2	1.31	ETAAS	-5.4	-7.2	b
L048	17.12	2.56	2	1.28	FAAS	-5.5	-7.4	b
L050	24.8	0.647	2	0.324	FAAS	-2.9	-4.7	b
L051	31.8	3.2	2	1.6	FAAS	-0.6	-0.8	b
L052	31.64	1.65	2	0.83	ICP-MS	-0.7	-1.0	b
L053	44.84	0	√3	0		3.7	6.0	b
L054	28.14	3	2	2	FAAS	-1.8	-2.3	b
L055	24.5	4.9	2	2.5	FAAS	-3.0	-3.0	a
L056	39.8	0	√3	0	FAAS	2.0	3.3	b
L057	29.3	0	√3	0	FAAS	-1.5	-2.4	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. 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** : $u_{lab} > u_{max}$



This graph displays all revised 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} ± 2u_{ref}**), and the orange lines that of the target interval (**X_{ref} ± 2σ**).

Annex 12 : Results for Total Lead

X_{ref} = 3.8 and U_{ref} = 0.5; all values are given in (mg kg^{-1})

Part Nr	Mean (xlab)	*Ulab*	*k*[a]	*ulab*	Technique	z[b]	zeta[b]	Unc[c]
L001	43.0	0	√3	0	FAAS	41.3	156.8	b
L003	2.357	0.43	2	0.22	ICP-OES	-1.5	-4.4	b
L005	3.87	0.4	2	0.2	ICP-MS	0.1	0.2	b
L007	2.56	0.51	2	0.26	ICP-OES	-1.3	-3.5	a
L008	2.74	0.41	2	0.21	ICP-MS	-1.1	-3.3	b
L009	3.55	0.63	2	0.32	ICP-OES	-0.3	-0.6	a
L010	3.44	1.5	1	1.5	ICP-MS	-0.4	-0.2	c
L011	4.21	0.46	2	0.23	ICP-MS	0.4	1.2	b
L013	3.9	1.5	2	0.8	ICP-MS	0.1	0.1	a
L014	3.84	0.384	2	0.192	ICP-MS	0.0	0.1	b
L015	3.45	0.9	2.35	0.4	ICP-MS	-0.4	-0.8	a
L016	2.86	0.76	2	0.38	ICP-OES	-1.0	-2.1	a
L017	3.97	1.06	95	0.01	ICP-MS	0.2	0.7	b
L018	2.30	0.35	2	0.18	ICP-MS	-1.6	-4.9	b
L019	3.01	0.8	2	0.4	ICP-MS	-0.8	-1.7	a
L020	4.04	0.70	2	0.35	ICP-MS	0.3	0.6	a
L021	3.65	0.54	2	0.27	ICP-MS	-0.2	-0.4	a
L022	3.55	1.1	2	0.6	ETAAS	-0.3	-0.4	a
L023	4.162	0.66	2	0.33	ICP-MS	0.4	0.9	a
L024	3.112	0.83	2	0.42	ETAAS	-0.7	-1.4	a
L025	3.28	0.29	2	0.15	ICP-OES	-0.5	-1.8	b
L026	4.10	0.98	2	0.49	ICP-MS	0.3	0.5	a
L027	3.51	1.5	2	0.8	ETAAS	-0.3	-0.4	a
L029	1.49	0.03	1	0.03	ETAAS	-2.4	-9.2	b
L030	3.37	0.03	95	0.00	ETAAS	-0.5	-1.7	b
L031	1.68	0.45	2	0.23	ETAAS	-2.2	-6.3	b
L032	4.10	0.49	√3	0.28	ETAAS	0.3	0.8	a
L033	2.926	1.46	√3	0.84	ETAAS	-0.9	-1.0	a
L034	<0.500				ICP-OES			
L035	2.35	1.0	2	0.5	GF AAS zeeman correction	-1.5	-2.6	a
L036	3.3	1.3	2	0.7	ICP-OES	-0.5	-0.7	a
L037	4.07	0	√3	0	ICP-MS	0.3	1.1	b
L038	3.0	0.058	1	0.058	ICP-MS	-0.8	-3.1	b
L039	3.9	0.31	2	0.16	ICP-OES	0.1	0.3	b
L040	3.75	0	√3	0	ICP-MS	-0.1	-0.2	b
L041	<0.2				FAAS			
L042	3.83	0.74	2	0.37	ICP-MS	0.0	0.1	a
L044	1.89	0.39	2	0.20	FAAS	-2.0	-6.0	b
L045	2.7	0.5	2	0.3	FAAS	-1.2	-3.1	a
L046	3.342	0.334	2	0.167	ETAAS	-0.5	-1.5	b
L047	1.242	0.342	2	0.171	ETAAS	-2.7	-8.4	b
L048	1.267	0.38	2	0.19	FAAS	-2.7	-8.1	b
L049	<4				FAAS			
L051	2.7	0.5	2	0.3	ETAAS	-1.2	-3.1	a
L052	3.11	0.49	2	0.25	ICP-MS	-0.7	-2.0	b
L054	6.32	2	2	1	FAAS	2.7	2.4	c
L055	3.44	0.61	2	0.31	FAAS	-0.4	-0.9	a
L056	3.2	0	√3	0	ETAAS	-0.6	-2.4	b
L057	4.4	0	√3	0	ETAAS	0.6	2.4	b

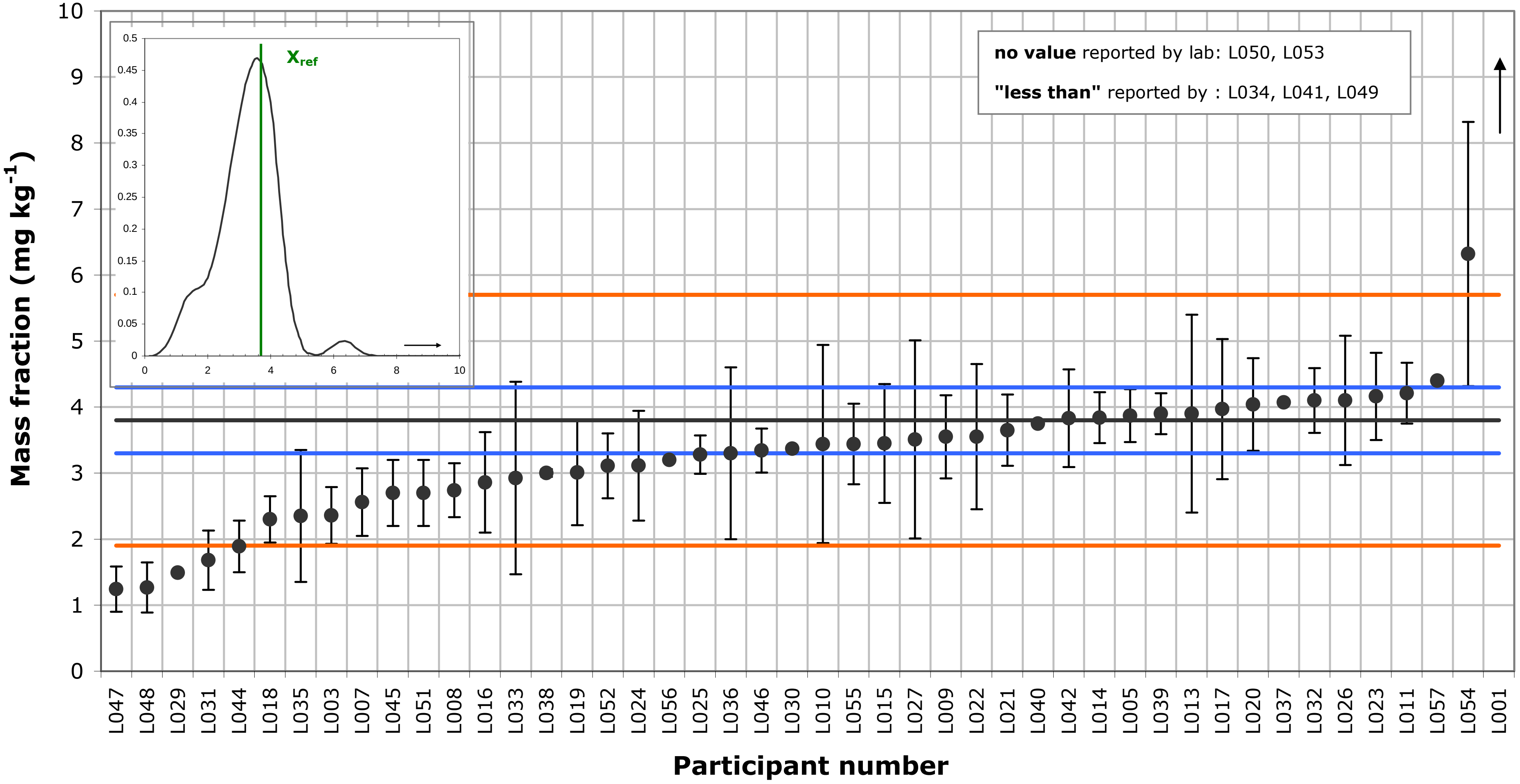
[a] √3 is set by the ILC coordinator when no expansion factor *k* is reported. The reported uncertainty was assumed to have a rectangular distribution with *k*=√3. For explanation see Ch 9.3

[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-31 (Trace metals in mineral feed): Total Pb

Certified value: X_{ref} = 3.8 mg·kg^{-1}; U_{ref} = 0.5 mg·kg^{-1} (k =2); σ = 0.95 mg·kg^{-1}



This graph displays all revised 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} ± $2u_{ref}$**), and the orange lines that of the target interval (**X_{ref} ± 2σ**).

Annex 13 : Results for Total Mercury

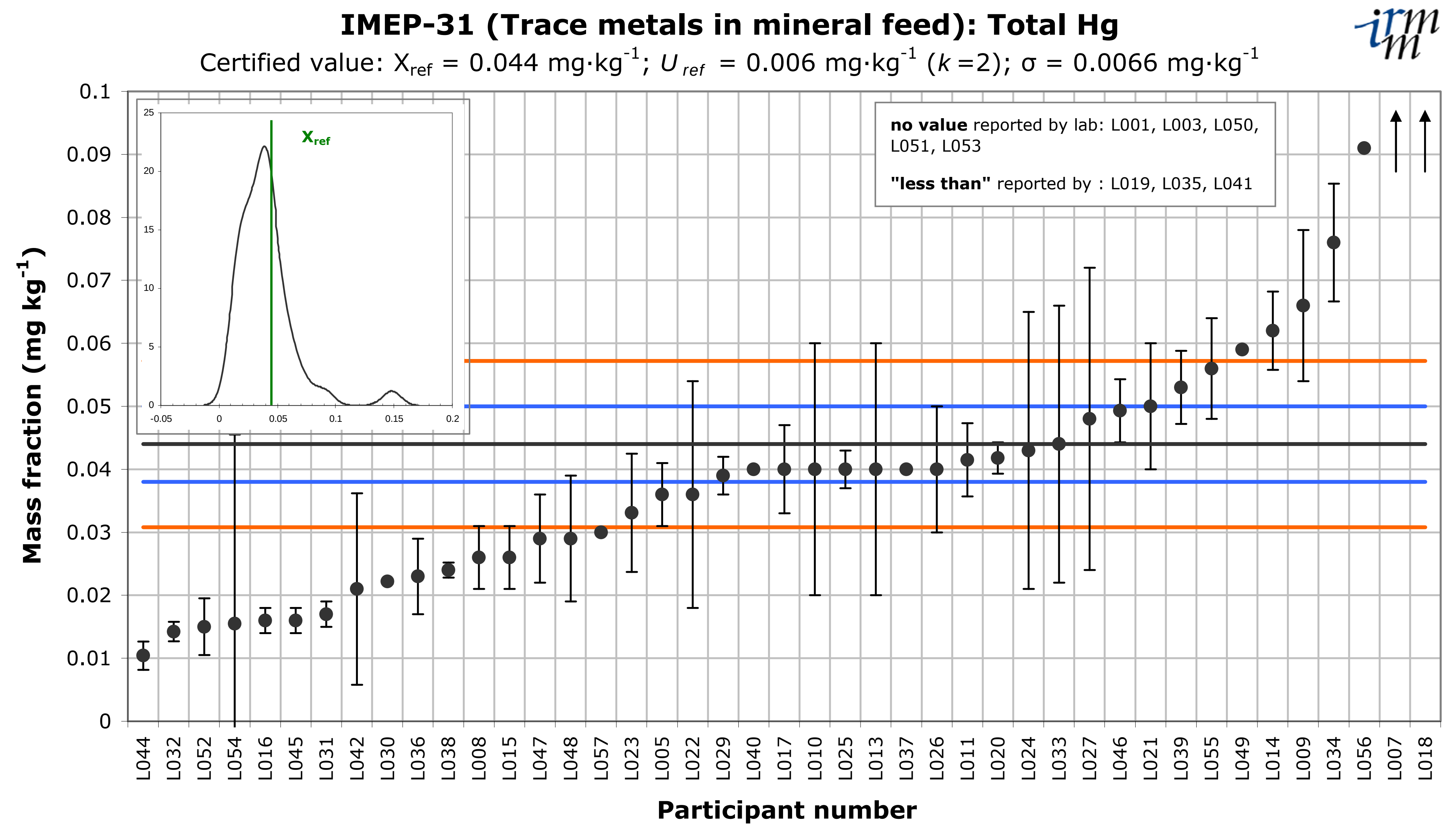
X_{ref} = 0.044 and U_{ref} = 0.006; all values are given in (mg kg^{-1})

Part Nr	Mean (xlab)	*Ulab*	*k*[a]	*ulab*	Technique	z[b]	zeta[b]	Unc[c]
L005	0.036	0.005	2	0.003	ICP-MS	-1.2	-2.0	b
L007	0.148	0.03	2	0.02	ICP-OES	15.8	6.8	c
L008	0.026	0.005	2	0.003	CV-AAS	-2.7	-4.6	b
L009	0.066	0.012	2	0.006	CV-AAS	3.3	3.3	a
L010	0.04	0.02	1	0.02	CV-AAS	-0.6	-0.2	c
L011	0.0415	0.0058	2	0.0029	ICP-MS	-0.4	-0.6	b
L013	0.04	0.02	2	0.01	CV-AAS	-0.6	-0.4	c
L014	0.062	0.0062	2	0.0031	ICP-MS	2.7	4.2	a
L015	0.026	0.005	2.35	0.002	CV-AAS	-2.7	-4.9	b
L016	0.016	0.002	2	0.001	DMA	-4.2	-8.9	b
L017	0.040	0.007	95	0.000	CV-AAS	-0.6	-1.3	b
L018	26.31	4.8	2	2.4	CV-AAS	3979.7	10.9	c
L019	<0.20				ICP-MS			
L020	0.0418	0.0025	2	0.0013	CV-AAS	-0.3	-0.7	b
L021	0.05	0.01	2	0.01	ICP-MS	0.9	1.0	a
L022	0.036	0.018	2	0.009	CV-AAS	-1.2	-0.8	c
L023	0.0331	0.0094	2	0.0047	CV-AFS	-1.7	-2.0	a
L024	0.043	0.022	2	0.011	CV-AAS	-0.2	-0.1	c
L025	0.04	0.003	2	0.002	CV-AFS	-0.6	-1.2	b
L026	0.04	0.01	2	0.01	FIMS	-0.6	-0.7	a
L027	0.048	0.024	2	0.012	CV-AAS	0.6	0.3	c
L029	0.039	0.003	1	0.003	CV-AAS	-0.8	-1.2	a
L030	0.0222	0.0004	95	0.0000	CV-AAS	-3.3	-7.3	b
L031	0.017	0.002	2	0.001	CV-AAS	-4.1	-8.5	b
L032	0.01424	0.00156	√3	0.00090	ETAAS	-4.5	-9.5	b
L033	0.044	0.022	√3	0.013	HG-AAS	0.0	0.0	c
L034	0.076	0.00937	2	0.00469	HG-AAS	4.8	5.8	a
L035	0.0							
L036	0.023	0.006	2	0.003	AMA254	-3.2	-4.9	a
L037	0.04	0	√3	0	ICP-MS	-0.6	-1.3	b
L038	0.024	0.0012	1	0.0012	AFS	-3.0	-6.2	b
L039	0.053	0.0058	2	0.0029	ICP-OES	1.4	2.2	b
L040	0.04	0	√3	0	ICP-MS	-0.6	-1.3	b
L041	<0.05				CV-AAS			
L042	0.021	0.0152	2	0.0076	ICP-MS	-3.5	-2.8	c
L044	0.01042	0.00225	2	0.00113	FAAS	-5.1	-10.5	b
L045	0.016	0.002	2	0.001	TD-AAS	-4.2	-8.9	b
L046	0.0493	0.005	2	0.003	CV-AAS	0.8	1.4	b
L047	0.029	0.007	2	0.004	CV-AAS	-2.3	-3.3	a
L048	0.029	0.01	2	0.01	HG-AAS	-2.3	-2.6	a
L049	0.059	0	√3	0	CV-AAS	2.3	5.0	b
L052	0.015	0.0045	2.37	0.0019	CV-AAS	-4.4	-8.2	b
L054	0.0155	0.03	2	0.02	AMA254	-4.3	-1.9	c
L055	0.056	0.008	2	0.004	CV-AAS	1.8	2.4	a
L056	0.091	0	√3	0	CV-AAS	7.1	15.7	b
L057	0.03	0	√3	0	AMA	-2.1	-4.7	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. 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 X_{ref}, the blue lines mark the boundary of the reference interval ($X_{ref} \pm 2u_{ref}$), and the orange lines that of the target interval ($X_{ref} \pm 2\sigma$).

Annex 14 : Results for Extractable Cadmium

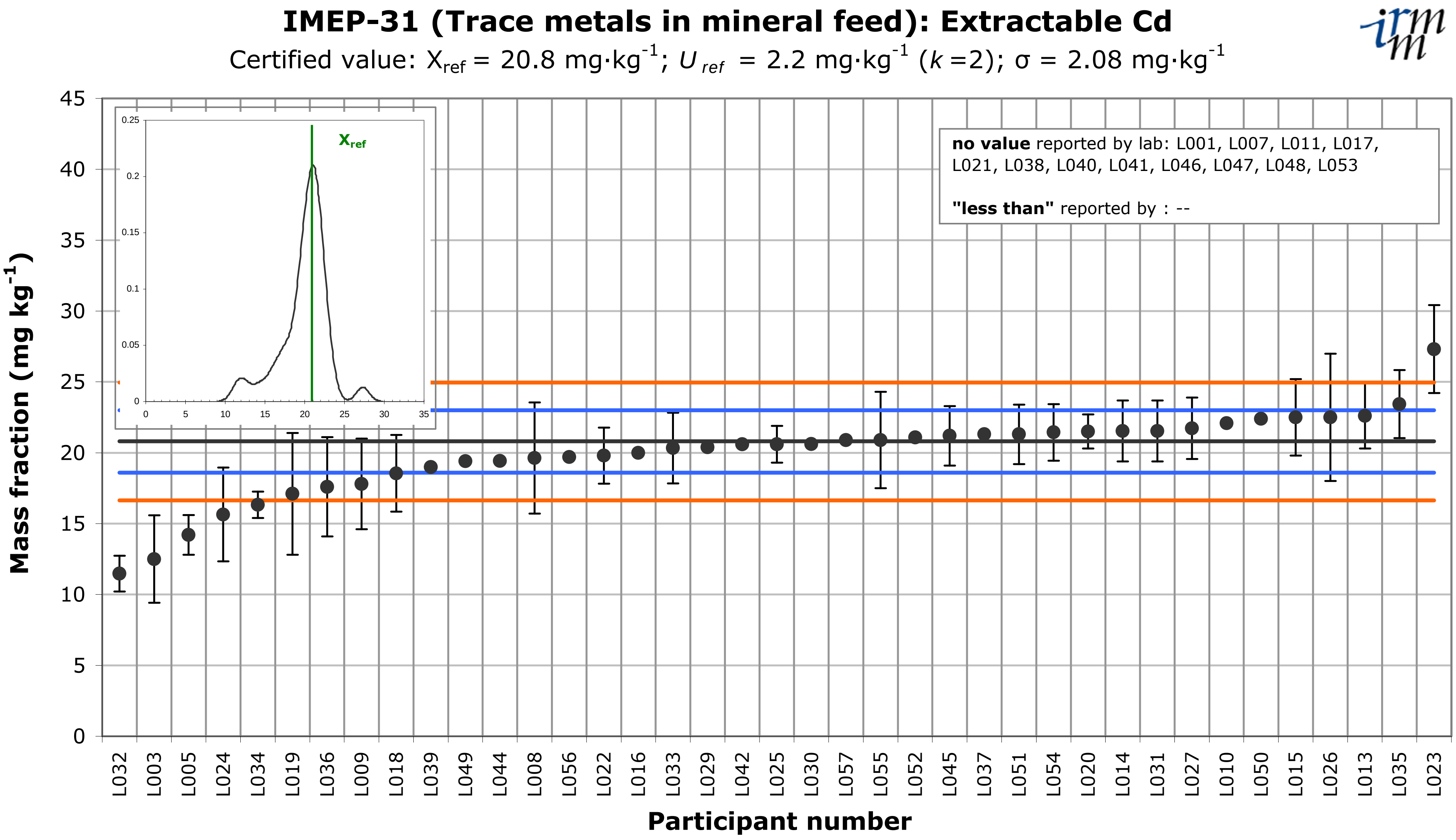
X_{ref} = 20.8 and U_{ref} = 2.2; all values are given in (mg kg^{-1})

Part Nr	Mean (xlab)	*Ulab*	*k*[a]	*ulab*	Technique	z[b]	zeta[b]	Unc[c]
L003	12.50	3.09	2	1.55	ICP-OES	-4.0	-4.4	a
L005	14.21	1.4	2	0.7	ICP-OES	-3.2	-5.1	b
L008	19.63	3.93	2	1.97	ETAAS	-0.6	-0.5	a
L009	17.8	3.2	2	1.6	ICP-OES	-1.4	-1.5	a
L010	22.09	0	√3	0	ICP-MS	0.6	1.2	b
L013	22.6	2.3	2	1.2	ICP-MS	0.9	1.1	a
L014	21.54	2.154	2	1.077	ICP-MS	0.4	0.5	b
L015	22.5	2.7	2.35	1.1	ICP-MS	0.8	1.1	a
L016	20.0	0	√3	0	IMEP-31 Protocol	-0.4	-0.7	b
L018	18.55	2.7	2	1.4	ICP-MS	-1.1	-1.3	a
L019	17.1	4.3	2	2.2	ICP-MS	-1.8	-1.5	c
L020	21.5	1.2	2	0.6	ICP-MS	0.3	0.6	b
L022	19.8	1.98	2	0.99	ETAAS	-0.5	-0.7	b
L023	27.31	3.1	2	1.6	ICP-MS	3.1	3.4	a
L024	15.641	3.31	2	1.66	ETAAS	-2.5	-2.6	a
L025	20.6	1.3	2	0.7	ICP-OES	-0.1	-0.2	b
L026	22.50	4.50	2	2.25	ICP-MS	0.8	0.7	c
L027	21.73	2.17	2	1.09	ETAAS	0.4	0.6	b
L029	20.4	0.19	1	0.19	FAAS	-0.2	-0.4	b
L030	20.61	0.17	95	0.00	ETAAS	-0.1	-0.2	b
L031	21.54	2.15	√3	1.24	ETAAS	0.4	0.4	a
L032	11.48	1.26	√3	0.73	ETAAS	-4.5	-7.1	b
L033	20.333	2.50	√3	1.44	ICP-OES	-0.2	-0.3	a
L034	16.324	0.933	2	0.467	ICP-OES	-2.2	-3.7	b
L035	23.43	2.4	2	1.2	GF AAS zeeman correction	1.3	1.6	a
L036	17.6	3.5	2	1.8	ETAAS	-1.5	-1.5	a
L037	21.30	0	√3	0	ICP-MS	0.2	0.5	b
L039	19	0.12	2	0.06	ICP-OES	-0.9	-1.6	b
L042	20.6	0	√3	0	ICP-MS	-0.1	-0.2	b
L044	19.42	0.13	2	0.07	FAAS	-0.7	-1.3	b
L045	21.2	2.1	2	1.1	FAAS	0.2	0.3	b
L049	19.4	0	√3	0	FAAS	-0.7	-1.3	b
L050	22.4	0.118	2	0.059	FAAS	0.8	1.5	b
L051	21.3	2.1	2	1.1	ETAAS	0.2	0.3	b
L052	21.08	0	√3	0	ICP-MS	0.1	0.3	b
L054	21.44	2	2	1	FAAS	0.3	0.4	b
L055	20.9	3.4	2	1.7	FAAS	0.0	0.0	a
L056	19.7	0	√3	0	FAAS	-0.5	-1.0	b
L057	20.9	0	√3	0	ETAAS	0.0	0.1	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. 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: L001, L007, L011, L017, L021, L038, L040, L041, L046, L047, L048, L053

"less than" reported by : --

This graph displays all revised 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} ± $2u_{ref}$**), and the orange lines that of the target interval (**X_{ref} ± 2σ**).

Annex 15 : Results for Extractable Lead

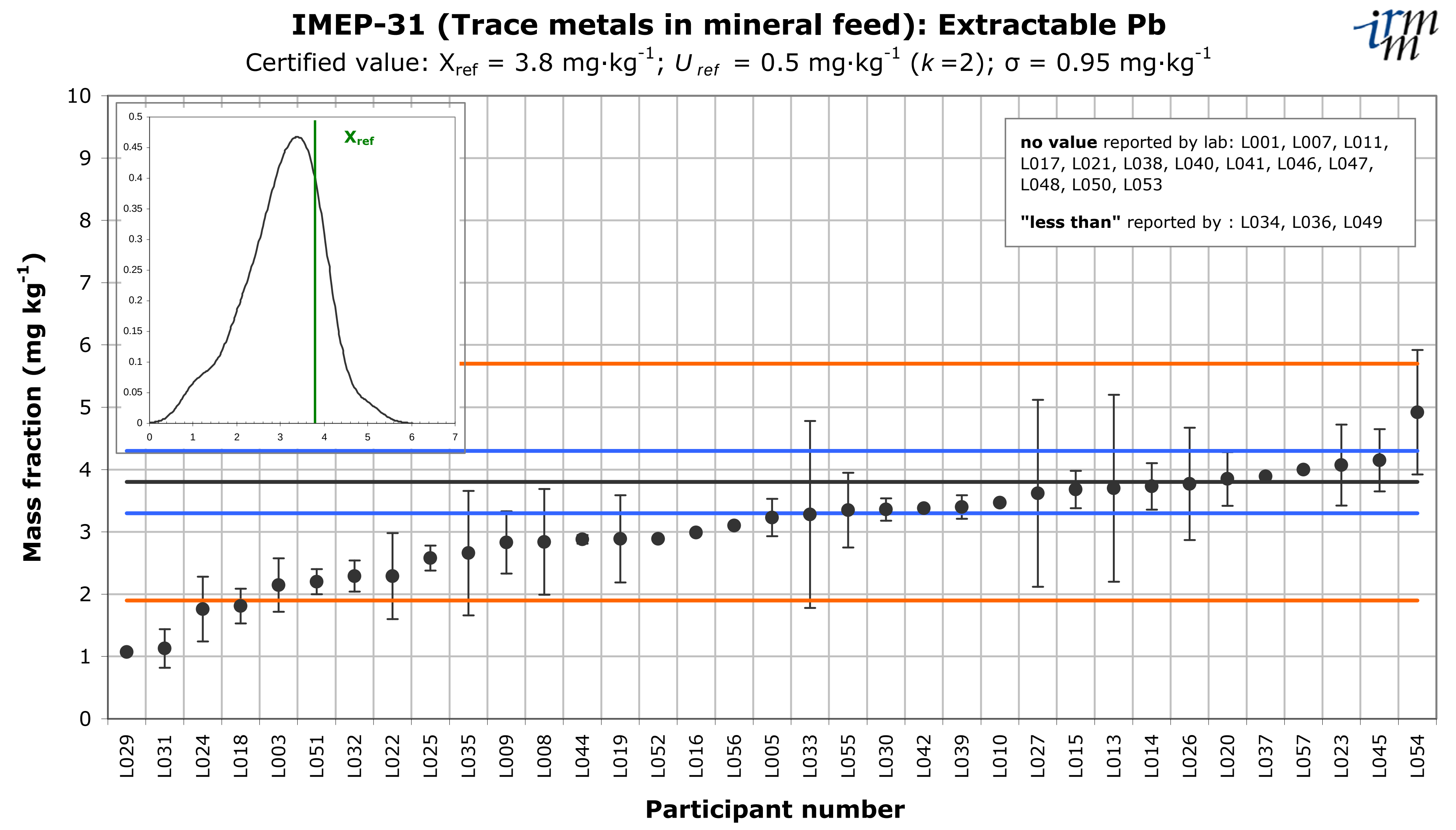
X_{ref} = 3.8 and U_{ref} = 0.5; all values are given in (mg kg^{-1})

Part Nr	Mean (xlab)	*Ulab*	*k*[a]	*ulab*	Technique	z[b]	zeta[b]	Unc[c]
L003	2.147	0.43	2	0.22	ICP-OES	-1.7	-5.0	b
L005	3.23	0.3	2	0.2	ICP-MS	-0.6	-2.0	b
L008	2.84	0.85	2	0.43	ETAAS	-1.0	-1.9	a
L009	2.83	0.50	2	0.25	ICP-OES	-1.0	-2.7	a
L010	3.47	0	√3	0	ICP-MS	-0.3	-1.3	b
L013	3.7	1.5	2	0.8	ICP-MS	-0.1	-0.1	a
L014	3.73	0.373	2	0.187	ICP-MS	-0.1	-0.2	b
L015	3.68	0.3	2.35	0.1	ICP-MS	-0.1	-0.4	b
L016	2.99	0	√3	0	IMEP-31 Protocol	-0.9	-3.2	b
L018	1.81	0.28	2	0.14	ICP-MS	-2.1	-6.9	b
L019	2.89	0.7	2	0.4	ICP-MS	-1.0	-2.1	a
L020	3.85	0.43	2	0.22	ICP-MS	0.1	0.2	b
L022	2.29	0.69	2	0.35	ETAAS	-1.6	-3.5	a
L023	4.071	0.65	2	0.33	ICP-MS	0.3	0.7	a
L024	1.761	0.52	2	0.26	ETAAS	-2.1	-5.7	a
L025	2.58	0.2	2	0.1	ICP-OES	-1.3	-4.5	b
L026	3.77	0.90	2	0.45	ICP-MS	0.0	-0.1	a
L027	3.62	1.5	2	0.8	ETAAS	-0.2	-0.2	a
L029	1.07	0.03	1	0.03	ETAAS	-2.9	-10.8	b
L030	3.36	0.18	95	0.00	ETAAS	-0.5	-1.8	b
L031	1.13	0.31	√3	0.18	ETAAS	-2.8	-8.7	b
L032	2.29	0.25	√3	0.14	ETAAS	-1.6	-5.2	b
L033	3.278	1.50	√3	0.87	ETAAS	-0.5	-0.6	a
L034	<0.500				ICP-OES			
L035	2.66	1.0	2	0.5	GF AAS zeeman correction	-1.2	-2.0	a
L036	<2				ETAAS			
L037	3.89	0	√3	0	ICP-MS	0.1	0.4	b
L039	3.4	0.19	2	0.10	ICP-OES	-0.4	-1.5	b
L042	3.38	0	√3	0	ICP-MS	-0.4	-1.7	b
L044	2.88	0.07	2	0.04	FAAS	-1.0	-3.6	b
L045	4.15	0.5	2	0.3	FAAS	0.4	1.0	a
L049	<4				FAAS			
L051	2.2	0.2	2	0.1	ETAAS	-1.7	-5.9	b
L052	2.89	0	√3	0	ICP-MS	-1.0	-3.6	b
L054	4.92	1	2	1	FAAS	1.2	2.0	a
L055	3.35	0.60	2	0.30	FAAS	-0.5	-1.2	a
L056	3.1	0	√3	0	ETAAS	-0.7	-2.8	b
L057	4.0	0	√3	0	ETAAS	0.2	0.8	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. For explanation see Ch 9.3

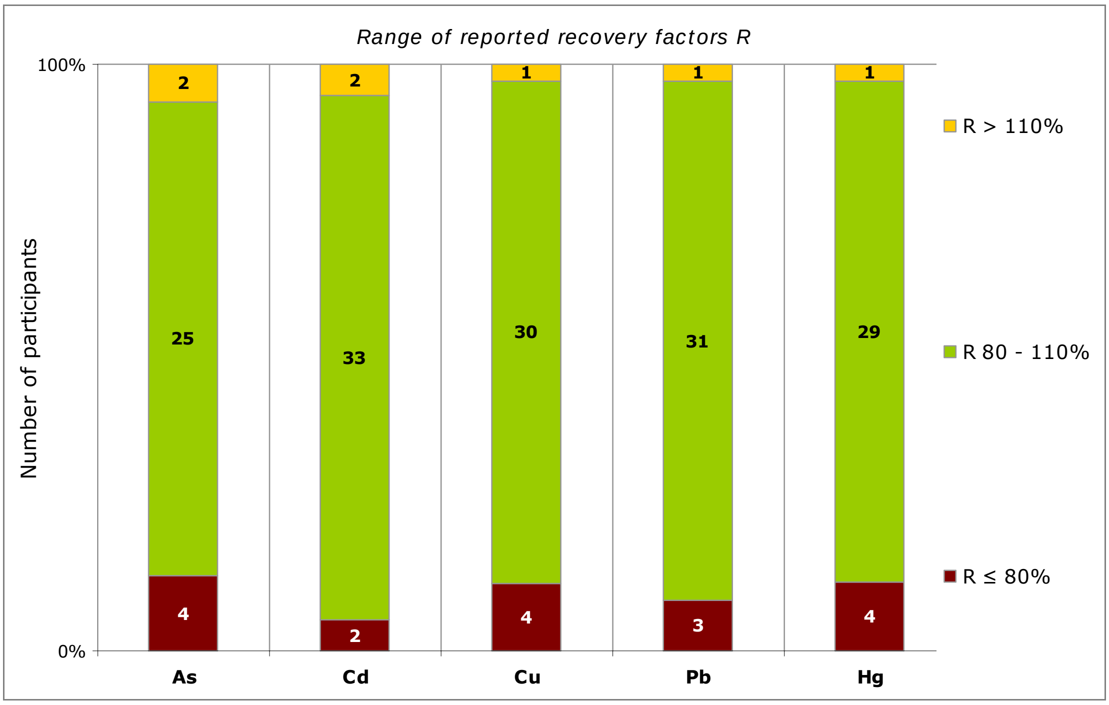
[b] **Satisfactory**, **Questionable**, **Unsatisfactory**

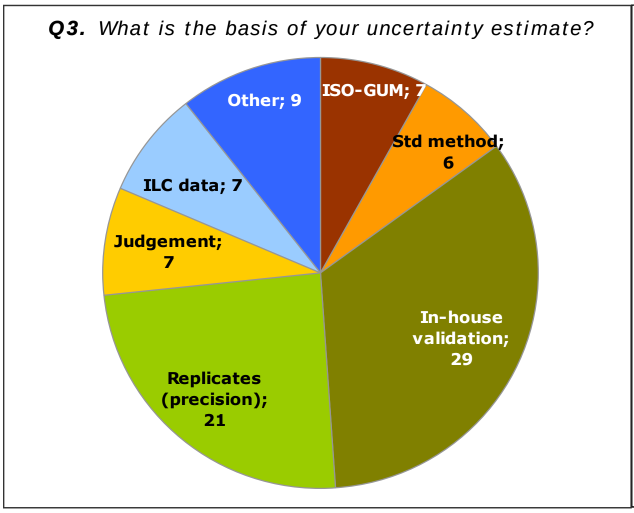
[c] Where: **a** = $u_{min} \leq u_{lab} \leq u_{max}$, **b** : $u_{lab} < u_{min}$, and **c** : $u_{lab} > u_{max}$



This graph displays all revised 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} ± $2u_{ref}$), and the orange lines that of the target interval (X_{ref} ± 2σ).

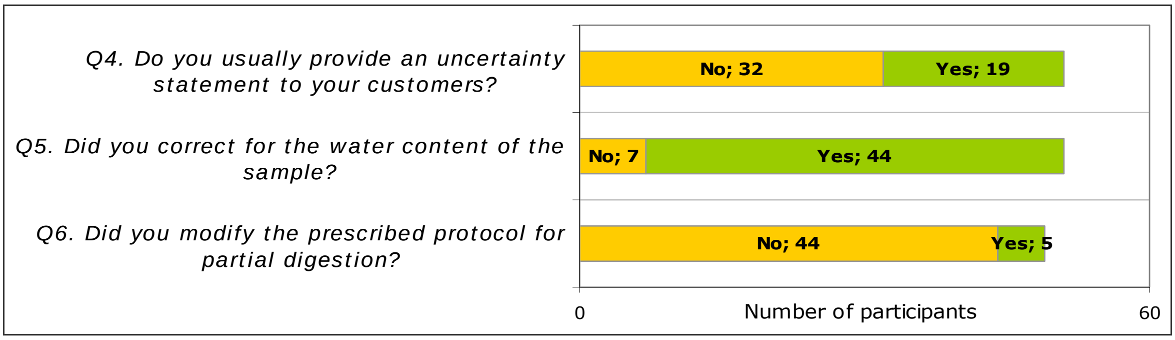
Annex 16 : Evaluation of questionnaire

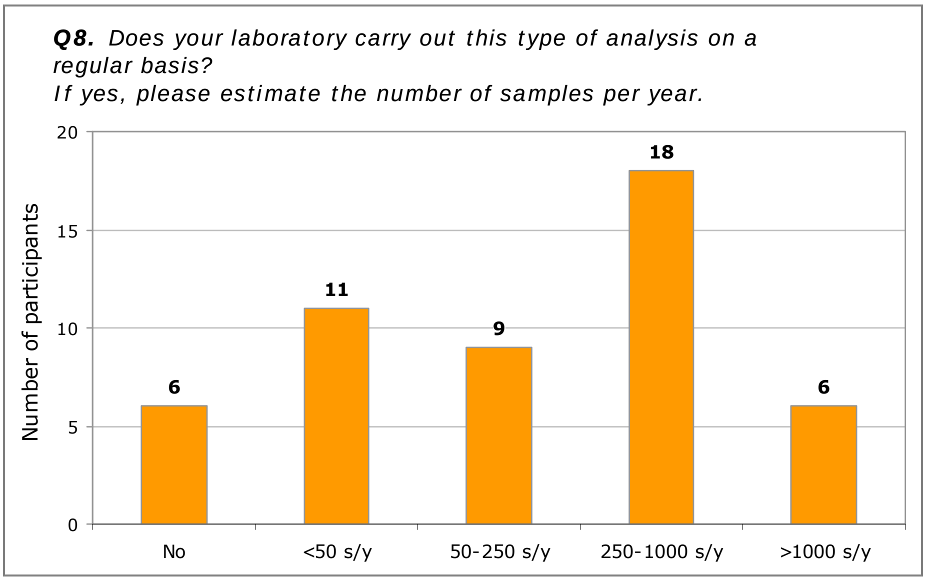


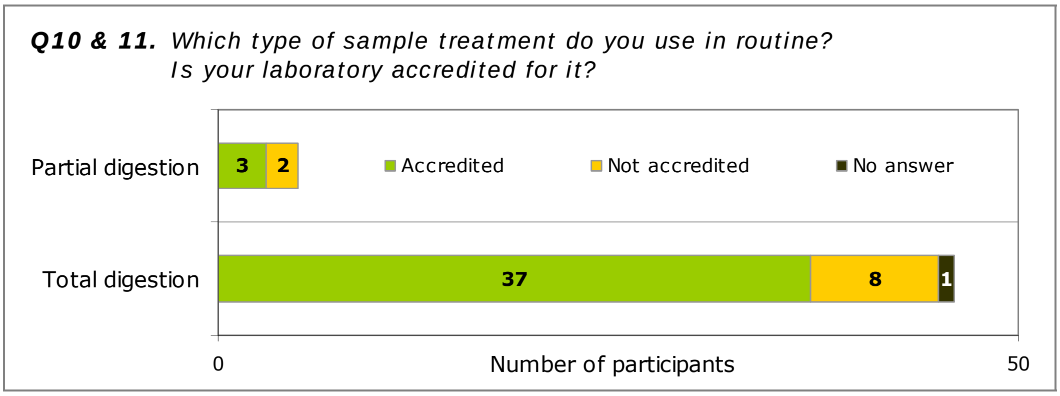


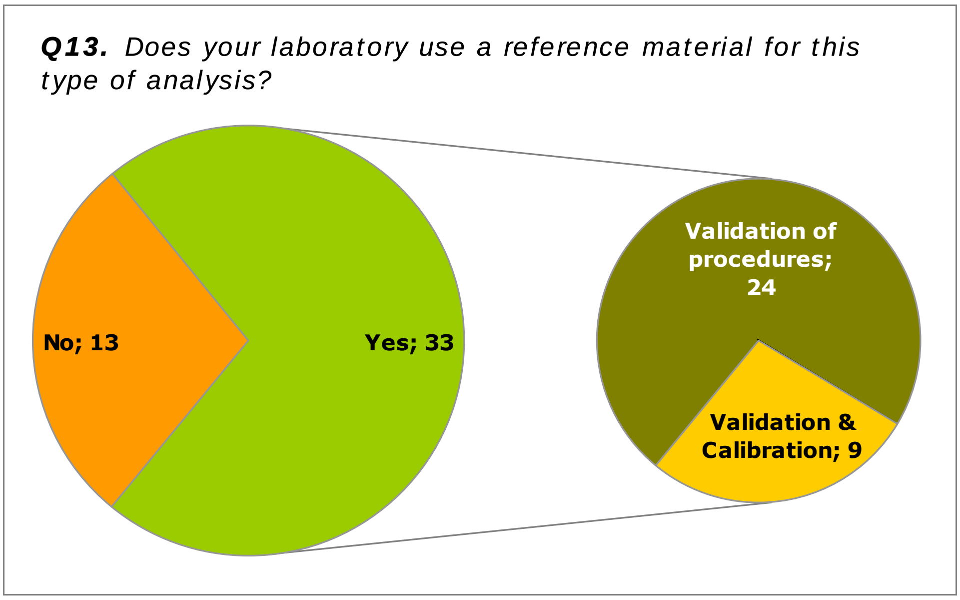
g) Other :

- We follow the EA-4/02, Expression of the Uncertainty of Measurement in Calibration, December 1999 as the basis for uncertainty estimate.
- According to the german VDLUFA agreement the uncertainty is expressed as the "Analysenspielraum (ASR)". The ASR is the doubled standard deviation of reproducibility, which is determined in ring analyses. It depends on the concentration of the analyte.
- Analytical margins published by VDLUFA for elemental determination in feeding stuffs
- Calculation of expanded uncertainty
- Analysenspielraum VDLUFA: Schönherr, Peterhänsel; Feed Magazine/Kraftfutter, 7-8/08, 20-27
- Horwitz formula
- VDLUFA analytical latitudes
- Control Charts
- Reproducibility + bias determined on (certified) reference material




Q8. *Does your laboratory carry out this type of analysis on a regular basis?*
If yes, please estimate the number of samples per year.


Q10 & 11. *Which type of sample treatment do you use in routine?*
Is your laboratory accredited for it?


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

Annex 17 : Experimental details (Q7, Annex 7)

Part Nr	Off Method	Sample pre-treatment	Digestion	Extraction/separation	Instrument calibration
L001	method based upon EPA SW846 3050				
L002					
L003	EN15510:2011	No	wet digestion WITH 4 ml HNO3+2 ml H2O2 microwave	5% HNO3 2g sample as per your instructions	blank +4-Standard calibration
L005		None	nitric acid digestion in hot block at 85 degree C for 4h	further dilution as appropiate	icp-oes and icp-ms
L007					
L008		Drying according to your described procedure	Microwave oven, internal procedure	Partial digestio: According to your demands	Exsternal standards, internal procedures
L009		no one pre-treatment	HNO3 microwave	no one	multilevel external calibration
L010	VDLUFA-methods-book vol. 7				
L011		Pre-digestion in mix of HNO3+H2O2+HF at atmospheric pressure for 120 minutes	mix (6 ml HNO3 + 2 ml H2O2 + 0.1 ml HF ultrapure) in MicroWave oven (cycle of 70 minutes)	diluition to 50.0 ml with Ultrapure Water - diluition of 10 times in order to get into the calibration range	5 calibration standard (external aqueous calibration) different for each element - Rodium & Bismut as Internal Standards
L013			microwave assisted pressure digestion		external calibration with internal standard and acid matching
L014	DIRECTIVE 2002/32/EC				
L015	DIN EN 15763:2009				
L016		No	Microwave acid nitric/H2O2	No	Standards in nitric acid
L017	NBN En 13805//NEN-En 15763// CMA/2/I/A.6.1// CMA/2/I/B.1//CMA/2/I/B.3				
L018			microwave 200°C / 80 bar, 0,25g sample, 10 ml HNO3 (1ml H2O2)		external standards
L019	USEPA 3050/6020A				
L020	§ 64 of the German Food and Feed Code (LFGB)				
L021		acid digestion	microwave digestion		ICP/MS
L022	As: DIN/EN 14546- Cu: §12 FPAV 8. RL- Hg: VDLUFA Bd. VII Nr. 2.2.2.9- Pb + Cd: VDLUFA Bd. VII Nr. 2.2.2.8				
L023	VDLUFA MB VII 2.2.2.5 for As, Cd, Cu, Pb; VDLUFA MB VII 2.2.2.9 for Hg				

Part Nr	Off Method	Sample pre-treatment	Digestion	Extraction/separation	Instrument calibration
L024			0.5g sample + 2 ml H2O2 + 5ml HNO3 (ramp of T° until aprox 180°C)		4 points of calibrant + blank
L025	AOAC 2005, 984.27				
L026			microwave acid digestion by using HNO3 + H2O2		
L027	VDLUFA				
L029	many				
L030	Pb and Cd: DIN EN 15550; As: VDLUFA, III, N2. 2.2.2.10 (= CEN Protocol); Hg: VDLUFA, III, N2. 2.2.2.9 (= CEN Protocol)				
L031	analytical method for spectroscopy				
L032	STN EN 14082				
L033	DIN EN 15510, DIN EN 15550				
L034	AOAC 984.27MOD, EPA 245.1 MOD.				
L035	EN 15550; EN				
L036	ICP-OES: according to EN15510				
L037					
L038	NMKL 161, 1998 (As, Cd, Cu, Pb), NMKL 170, 2002 (Hg)				
L039	ICP AES after acid destruction				
L040		no pre treatment	microwave digestion	all the sample digested is analysed	and read in ICP-MS
L041	AOAC				
L042	EN 13805 mod.				
L044	EPA Standard Methods 21 st edition,2005 -Metals/AOAC 18 Edition,2005 Ch3,9,25,33				
L045	BS EN 14084:2003				
L046		Pretreatment with HNO3 and H2O2	Microwave digestion		external standard calibration
L047	SR EN ISO 6869/2002				
L048	SREN ISO 14082:2003				

Part Nr	Off Method	Sample pre-treatment	Digestion	Extraction/separation	Instrument calibration
L049		No pre-treatment	Microwave Digestion. 0.5 g Sample / 10 Hydrocloric Acid 50%. Several Steps Temperature Program up to 195ºC	No extraction/separation	External Calibration
L050	AOAC 15 edition 940.25				
L051		0.250 g of sample was weighed into a teflon vessel. 5 ml of HNO3 (Suprapur) and 1 ml of H2O2 (Suprapur) was added.	Vessels were closed and the microwave program was conducted (max.T 210 deg.C, total time 30 minutes).	Vessels were cooled and digested samples were quantiutatively transferred to 10ml plastic tubes.	GFAAS was calibrated with 4 stds; for Cd 1.00; 2.00; 3.00 and 4.00 ppb, for Pb 25.0; 50.0; 75.0 and 100.0 ppb). FAAS was calibrated with 5 stds: 0.200; 0.400; 0.600; 0.800 and 1.000 ppm). Linear calibration curves were applied.
L052			Acid digestion with HNO3 and H2O2		ICPMS
L053	S I no 289 of 1999 (78/633/EEC)				
L054	EN ISO 5961 CSN 560065				
L055					
L056		The pre-teatment of the sample is carried out ashing the sample with Mg(NO3)2 50% (P/V).	The ashes are treated with aqua regia and it is completed to volume with HNO3 5% (P/P).		The calibration of the instrument is carry out with premixed standards prepared by dilution of AA standards (1000mg/L). The standards are prepared in Mg(NO3)2/HNO3 solution.
L057					

European Commission

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Abstract

The Institute for Reference Materials and Measurements (IRMM) of the Joint Research Centre (JRC), a Directorate-General of the European Commission, operates the 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 As, Cd, Cu, Pb, and Hg, as well as extractable Cd and Pb in mineral feed according to Directive 2002/32/EC of the European Parliament and of the Council on undesirable substances in animal feed.

The test material used in this exercise was the Certified Reference Material (CRM) BCR-032 (Moroccan phosphate rock) from the IRMM. The material was relabelled and each participant received one bottle containing approximately 100 g of test material. Fifty-six laboratories from 26 countries registered to the exercise and 51 of them reported results.

Total As, Cd, Cu and Hg were certified in BCR-032 in 1979. The material was re-analysed by two expert laboratories and As an Cd values could be confirmed. Copper could not be analysed in time by an expert laboratory, and thus it was decided to use the indicative value from the certificate as assigned value. The assigned values for total Hg and total Pb were determined at IRMM by a primary method. The same method was used to determine extractable Cd and Pb, whose mass fractions appeared to be identical to the respective total mass fractions and thus the same assigned values were used.

The standard deviation for proficiency assessment was set at 11 % for total As, 10 % for total and extractable Cd, 9 % for total Cu, and at 15 % for total Hg based on the modified Horwitz equation and/or the outcome of previous ILCs organised by IMEP. For total and extractable Pb, was set at 25 %.

The majority of the laboratories reported uncertainties with their results and were rated with z- and ζ-scores (zeta-scores) in accordance with ISO 13528. Performances appear to be good for total & extractable Cd and total & extractable Pb, the percentage of satisfying z-scores ranging between 85 % and 89 %. Share of satisfactory z-scores are significantly lower for total As (61 %), Cu (67 %) and in particular for Hg (47 %). No distinct reason could be given, but it seems altogether that the analytical methods were not always adjusted to the inorganic test material, reflected by some influence of applied technique and inappropriate choice of reference material.

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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