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IMEP-111: Total cadmium, lead, arsenic, mercury and copper and extractable cadmium and lead in mineral feed

Report of the eleventh interlaboratory comparison organised by the European Union Reference Laboratory for Heavy Metals in Feed and Food

M.B. de la Calle, A. Krata, B. Ari, C. Quétel, H. Emteborg, P. Robouch, I.Verbist

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Contact information
Address: European Commission, Joint Research Centre, Institute for Reference Materials and Measurements, Retieseweg 111, 2440 Geel, Belgium.
E-mail: maria.de-la-calle@ec.europa.eu
Tel.: +32 (0) 14 571252
Fax: +32 (0) 14 571865

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

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IMEP-111: Total cadmium, lead, arsenic, mercury and copper and extractable cadmium and lead in mineral feed.

Report of the eleventh interlaboratory comparison of the EU-RL-HM

IMEP

February 2011

María Beatriz de la Calle
Agnieszka Krata
Betül Ari
Christophe Quétel
Håkan Emteborg
Piotr Robouch
Inge Verbist

Table of contents

1 Summary

The Institute for Reference Materials and Measurements (IRMM) of the Joint Research Centre, a Directorate General of the European Commission, operates the European Union Reference Laboratory for Heavy Metals in Feed and Food (EU-RL-HM). One of its core tasks is to organize interlaboratory comparisons (ILCs) among appointed National Reference Laboratories. This report presents the results of the eleventh proficiency test (PT) of the EU-RL-HM which focused on the determination of total Cd, Pb, As, Hg and Cu and 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. The material was relabelled to prevent identification by the participants and was dispatched the second half of October 2010. Each participant received one bottle containing approximately 100 g of test material. Thirty-one laboratories from 26 countries registered to the exercise of which 28 reported results for total Cd and total Pb, 25 for total Hg and total Cu, 23 for total As and for extractable Cd and extractable Pb. The assigned values (X_{ref}) for total Cd, As and Cu are the indicative values taken from the BCR-032 certificate. The assigned values (X_{ref}) for total Pb, total Hg and for extractable Cd and Pb were provided by IRMM using isotope dilution-inductively coupled plasma-mass spectrometry (ID-ICP-MS).

For total Cd, As, Hg and Cu and for extractable Cd, the uncertainty of the assigned values (u_{ref}) was calculated by combining the uncertainty of the characterization (u_{char}) and a contribution for between-bottle homogeneity (u_{bb}) (which was calculated from the certification report). For total and extractable 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} included a contribution for the homogeneity. For total Cd, As and Cu, u_{char} were taken from the CRM certificate as indicated by the producer. For extractable Cd the same u_{char} as for total Cd was used. For total Pb and Hg and for extractable Pb, u_{char} was calculated according to the ISO Guide for the Expression of Uncertainty in Measurement (GUM) [2]. Participants were invited to report the uncertainties of their measurements. This was done by the majority of the laboratories taking part in this exercise.

Laboratory results were rated using z- and ζ-scores (zeta-scores) in accordance with ISO 13528 [3]. The standard deviation for proficiency assessment ($\hat{\sigma}$), also called target standard deviation, were calculated applying the modified Horwitz equation for total Cd, As and Cu and for extractable Cd. However, for total Hg, $\hat{\sigma}$ was set to 15 % on the basis of previous experience of the EU-RL-HM with this network of laboratories. For total Pb, $\hat{\sigma}$ was set at 25 % due to micro-inhomogeneity observed

when small aliquots were taken for analysis. For extractable Pb we used the same criteria as for total Pb to score the participants ($\hat{\sigma}$ = 25 %).

Between 70 and 80 % of the laboratories reported satisfactory results for all measurands but Hg. For the latter, only 57 % of the laboratories submitted satisfactory results. All the questionable and unsatisfactory results for Hg were obtained using direct thermal decomposition-based methods.

2 Introduction

In the second half of 2008 the EU-RL-HM organized a proficiency test (PT) IMEP-105 [4] for the 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. Using reference materials that do not match the type of the test material used in a PT or in the daily control activities, can introduce a significant bias in the determination of some of the measurands, as it was the case of total Pb in IMEP-105.

Another PT was organised by the EU-RL-HM for determination of heavy metals in mineral feed, IMEP-111, to check the effectiviness of the corrective actions to be implemented after the IMEP-105 exercise.

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, and the EU-RL-HM (former CRL-HM) network has been built up to ensure quality and comparability in official controls throughout the European Union [5]. In March 2006 a footnote was introduced in Directive 2002/32/EC stating 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"*.

Several proficiency tests have been organised by the EU-RL-HM for the determination of heavy metals in different types of feed (IMEP-103 [6], -105 [4] and -108 [7]) in which the results obtained for total Cd and Pb were compared with those obtained with a method compliant with the footnote of Directive 2002/32/EC, mentioned above. IMEP-111 included extractable Cd and Pb to broaden the applicability of the procedure agreed upon by the EU-RL-HM and the network of NRLs, which is in agreement with the requirements laid down in Directive 2002/32/EC, to a broaden variety of matrices. This report summarises the outcome of IMEP-111.

3 Scope

As stated in Regulation No 882/2004 of the European Parliament and the Council [5], one of the core duties of the EU-RL-HM is to organise interlaboratory comparisons for the benefit of staff from National

Reference Laboratories. The scope of this proficiency test is to test the competence of the appointed NRLs to determine the total concentration of Cd, Pb, As, Cu and Hg and of extractable Cd and Pb in mineral feed.

The assessment of the measurement results is undertaken on the basis of requirements laid down in legislation [1], and follows the administrative and logistic procedures of the International Measurement Evaluation Program (IMEP) of the IRMM of the European Commission Directorate Joint Research Centre. IMEP is accredited according to ISO Guide 43. The designation of this PT is IMEP-111.

4 Time Frame

The proficiency test was agreed upon by the EU-RL-HM and the Directorate General for Health and Consumers (DG SANCO) when preparing the work program of the EU-RL-HM for 2010. Invitation letters were sent to the participants on 4th October 2010 (cf. Annex 1). The samples were dispatched to the participants on 26th October 2010. The reporting deadline was 30th November 2010.

5 Test material

5.1 Preparation

The commercially available CRM BCR-032 (Moroccan phosphate rock), which from an analytical point of view is similar to mineral feed, was used for this PT. 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 available at the IRMM website [8].

5.2 Homogeneity and stability

According to the certification report the material is homogeneous [8]. Homogeneity was considered sufficient for this intercomparison.

As the certified values given in the certificate of the material (November 1979) were confirmed experimentally in the frame of the project (see Chapter 7). For this reason the material was considered sufficiently stable.

5.3 Distribution

All samples were dispatched to the participants by IRMM on 26th October 2010. Each participant received:

a) One bottle containing approximately 100 g of test material,

b) An accompanying letter with instructions for sample handling and reporting (cf. Annex 2) and

c) A "Confirmation of receipt" form to be sent back to IRMM after receipt of the test material (cf. Annex 3).

6 Instructions to participants

Concrete instructions were given to all participants in a letter accompanying the test material. The measurands and matrix were defined as “Total Cd, Pb, As, Hg and Cu and extractable 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”.

Laboratories were asked to perform two or three independent measurements and to report the mean, the associated uncertainty, the coverage factor of the associated uncertainty and the technique used to perform the measurements. The measurement results were to be corrected for (i) recovery and (ii) moisture, following the procedure described in BCR-032 certificate. Participants were asked to follow their routine procedures for the analysis. Laboratories were asked to report results in the same way (eg. number of significant figures) as they would report to their customers.

The results were to be reported in a special on-line form for which each participant received an individual access code. A questionnaire was attached to this on-line form (Annex 4).

The laboratory codes were given randomly and communicated to the participants in a confidential letter that was sent to each participant by e-mail and by courier post.

7 Reference values and their uncertainties

The total content of Cd, As, Hg and Cu were certified in BCR-032. However, since BCR-032 is an old CRM (1st certificate issued in November 1979) the CRM producer decided in to include the concentration of total Cd, As, Hg and Cu only as indicative values and as such they appear in the last revision of the certificate (March 2010), Annex 5. To ascertain whether the indicative values could be used as assigned values for IMEP-111, the total content of Cd and Hg were determined at IRMM for the purpose of this exercise using ID-ICP-MS. The values obtained by ID-ICP-MS agreed with the

indicative values within their respective uncertainties for total Cd and hence the indicative value was used as assigned value in IMEP-111.

The indicative value for total As in BCR-032 was confirmed to the EU-RL-HM by the Studiecentrum voor Kernenergie (SCK-CEN) using neutron activation analysis.

For total Hg there was a discrepancy between the indicative values on the certificate and the values found at IRMM. After carefully checking the certification report it was observed that not all the techniques used during the certification of the CRM reflect the current state-of-the-art of mercury analysis and for this reason, the value obtained at IRMM by ID-ICP-MS was taken as assigned value for IMEP-111.

The assigned values for total Pb and extractable Cd and Pb were determined at IRMM by ID-ICP-MS.

IRMM and SCK have proven its measurement capabilities by successful participation in the Comité Consultative de la Quantité de Matière (CCQM) key comparisons.

Copper was not included as measurand when the exercise was planned and it was only included after request by some NRLs during the fifth workshop organised by the EU-RL-HM on 24th September 2010. The EU-RL-HM could not obtain a confirmation of the indicative value given in the certificate. The indicative value was used as assigned value and it was not contradicted by the participants results.

For total Cd, As, Hg and Cu and for extractable Cd, the uncertainty of the assigned values (u_{ref}) was calculated by combining the uncertainty of the characterization (u_{char}) and a contribution for between-bottle homogeneity (u_{bb}):

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

Where:

u_{bb}: Homogeneity uncertainty contribution. 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}: For total Cd, As and Cu, u_{char} was taken from the certificate of analysis, for extractable Cd the same u_{char} as for total Cd was used. For total Hg, u_{char} was calculated at IRMM according to the ISO Guide for the Expression of Uncertainty in Measurement (GUM) [2].

For total and extractable 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} included u_{bb} and therefore is set as u_{ref}.

For total Pb and extractable Pb, u_{char} was calculated according to the ISO Guide for the Expression of Uncertainty in Measurement (GUM) [2].

The material has proven to be stable and thus no contribution for stability was added to the associated uncertainties.

The assigned reference values (X_{ref}) for all the measurands, and their respective uncertainties (u_{ref}, U_{ref}) are summarised in Table 1.

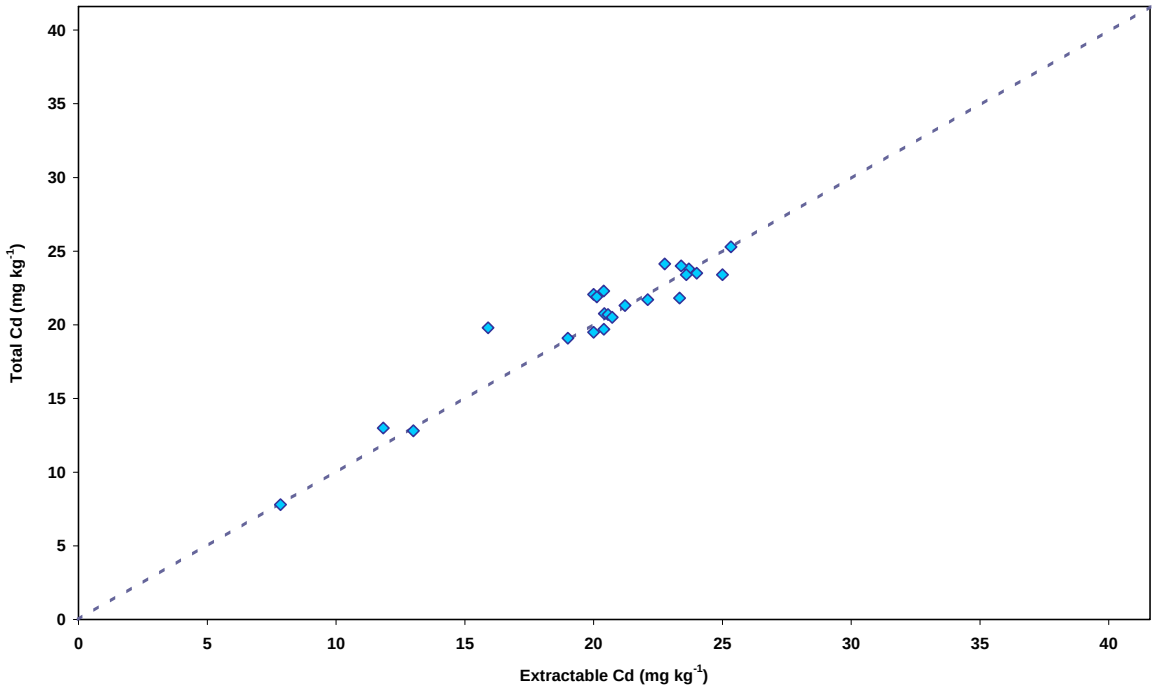
Table 1: *Assigned values and their associated standard uncertainties for the measurands of this proficiency test.*

Measurand	X_{ref} (mg kg^{-1})	u_{ref} (mg kg^{-1})	U_{ref} (mg kg^{-1})	$\hat{\sigma}$ (mg kg^{-1})
Total Cd	20.8	1.1	2.2	2.1
Extractable Cd				
Total Pb	3.8	0.3	0.5	1.0
Extractable Pb				
Total As	9.5	0.6	1.1	1.0
Total Hg	0.044	0.003	0.006	0.007
Total Cu	33.7	1.9	3.7	3.0

X_{ref} = assigned value, U_{ref} = expanded standard uncertainty, u_{ref} = standard uncertainty calculated from U_{ref} using a coverage factor k=2, $\hat{\sigma}$ = standard deviation for proficiency assessment .

As summarised in Table 1, total digestion and partial extraction of the test material, following the procedure described in the accompanying letter, provided identical Cd and Pb concentrations. These findings are supported by the Youden plots, Fig. 1.a and b, constructed with the results provided by the participants in this exercise for Cd and Pb, respectively. One cloud of points is observed on both axes around the reference value, when total vs the extractable contents are plotted. Most results are aligned along the diagonal which indicates that the majority of the laboratories have not found a significant difference between the total and extractable Cd and Pb respectively.

a)



b)

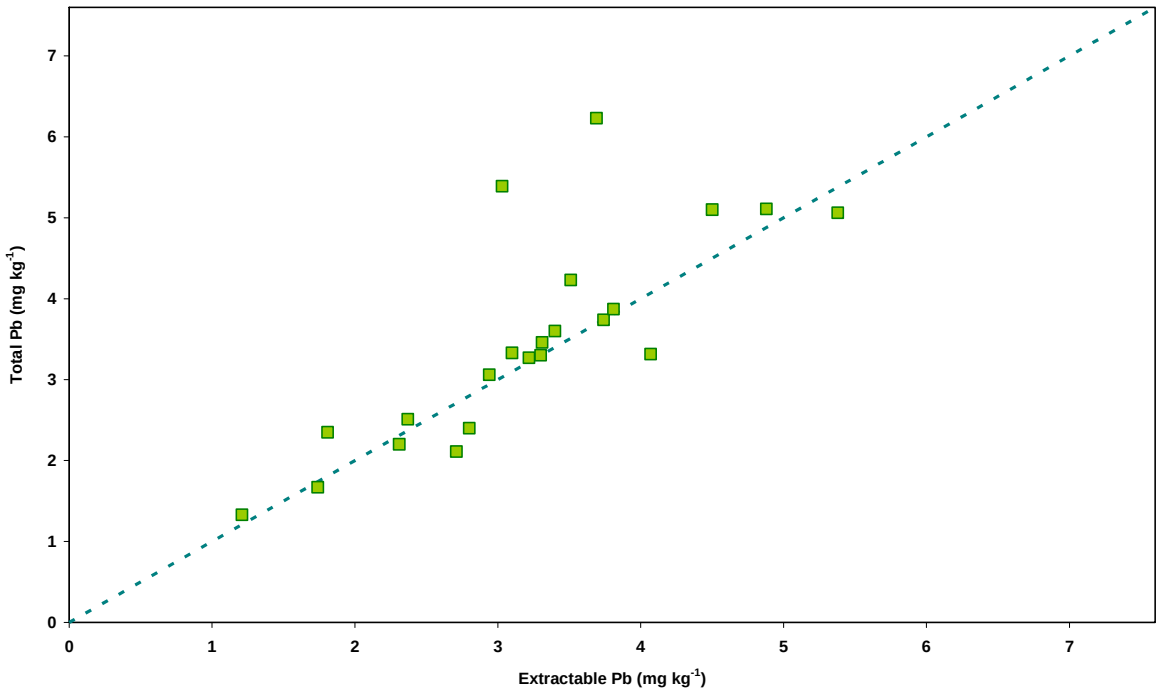


Figure 1: *Youden plot for: a) total and extractable Cd and b) total and extractable Pb.*

8 Evaluation of results

8.1 General observations

Thirty-one laboratories from 26 countries registered for participation in this exercise of which 28 reported results for total Cd and total Pb (1 reported "less than" for total Pb), 25 for total Hg (4 reported "less than") and total Cu, 23 for total As and for extractable Cd and extractable Pb (1 reported "less than" for total As and for extractable Pb). All laboratories responded to the questionnaire included in the on-line reporting form.

8.2 Scores and evaluation criteria

Individual laboratory performance is expressed in terms of z- and ζ-scores in accordance with ISO 13528 [3].

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

$$z = \frac{x_{lab} - X_{ref}}{\hat{\sigma}} \qquad \text{Eq. 3}$$

Where:

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

The assigned reference values (X_{ref}), and their respective uncertainties are summarised in Table 1.

The interpretation of the z- and ζ-score is done as follows:

|score| ≤ 2	satisfactory result (green in the tables of Annexes 6-12)
2 < |score| ≤ 3	questionable result (orange in the tables of Annexes 6-12)
|score| > 3	unsatisfactory result (red in the tables of Annexes 6-12)

The ζ-score states if the laboratory result agrees with the assigned value within the respective uncertainty indicates. The denominator of Eq. 2 is the combined uncertainty of the assigned value and the measurement uncertainty as stated by the laboratory. The ζ-score is therefore the most relevant evaluation parameter, as it includes all parts of a measurement result, namely the expected value (assigned value), its uncertainty and the unit of the result as well as the uncertainty of the reported

values. An unsatisfactory ζ-score can either be caused by an inappropriate estimation of the concentration or of its uncertainty.

The standard uncertainty of the laboratory (u_{lab}) was estimated by dividing the reported expanded uncertainty by the reported coverage factor, *k*. When no uncertainty was reported, it was set to zero (u_{lab} = 0). When k was not specified, the reported expanded uncertainty was considered as the half-width of a rectangular distribution; u_{lab} was then calculated by dividing this half-width by √3, as recommended by Eurachem and CITAC [9].

Uncertainty estimation is not trivial; therefore an additional assessment was provided to each laboratory reporting uncertainty, indicating how reasonable their uncertainty estimate is. The standard uncertainty from the laboratory (u_{lab}) is most likely to fall in a range between a minimum uncertainty (u_{min}), and a maximum allowed (u_{max}). u_{min} is set to the standard uncertainty of the reference value. It is unlikely that a laboratory carrying out the analysis on a routine basis would measure the measurand with a smaller uncertainty than the expert laboratories chosen to establish the assigned value. u_{max} is set to the target standard deviation ($\hat{\sigma}$) accepted for the PT. If u_{lab} is smaller than u_{min}, the laboratory may have underestimated its uncertainty. Such a statement has to be taken with care as each laboratory reported only measurement uncertainty, whereas the uncertainty of the reference value also includes contributions of homogeneity and stability. If those are large, measurement uncertainties smaller than u_{min} are possible and plausible. If $u_{lab} > u_{max}$, the laboratory may have overestimated the uncertainty. An evaluation of this statement can be made when looking at the difference of the reported value and the assigned value: if the difference is small and the uncertainty is large, then overestimation is likely. If, however, the deviation is large but is covered by the uncertainty, then the uncertainty is properly assessed 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 z-score compares the participant's deviation from the reference value with the target standard deviation for proficiency assessment ($\hat{\sigma}$) used as common quality criterion. $\hat{\sigma}$ is defined by the PT organiser as the maximum acceptable standard uncertainty. Values for $\hat{\sigma}$ were calculated applying the modified Horwitz equation for total Cd, As and 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 previous experience of the EU-RL-HM with this network of laboratories. For total Pb, $\hat{\sigma}$ was set 25 % due to some lack of homogeneity observed when small aliquots (around 0.2 g) were taken for analysis. 25 % was also used as target standard deviation for extractable Pb to use the same criteria as for total Pb to score the participants.

8.3 Laboratory results and scorings

The results as reported by the participants for total Cd, Pb, As, Hg and Cu and for extractable Cd and Pb are summarised in Annexes 6 to 12, together with the z- and ζ-scores. These annexes also include figures showing the individual mean values and associated expanded uncertainties. The Kernel distribution plots, obtained using a software tool developed by AMC [10] are presented in Annex 13.

Regarding the z- and ζ-scores, the results for total Cd, Pb, As, Hg and Cu and for extractable Cd and Pb are summarised in Figure 3.

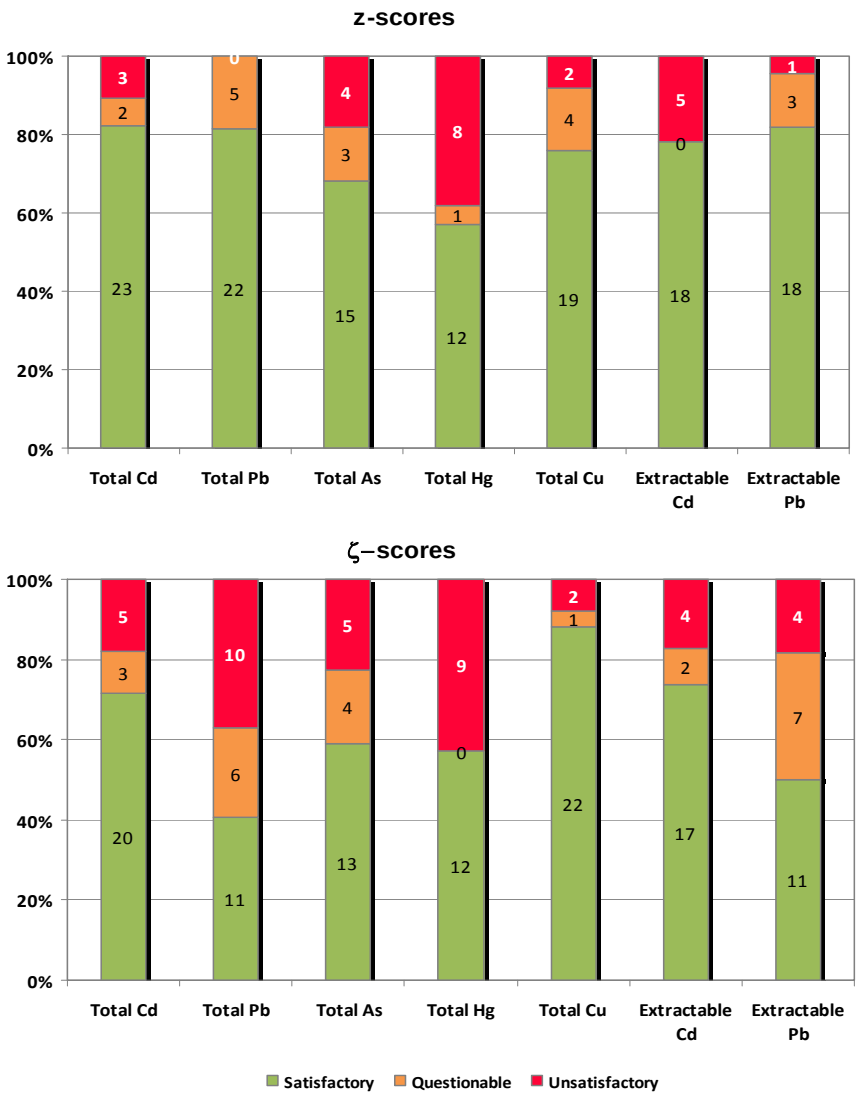


Figure 3: *Number and percentages of laboratories not reporting "less than" with satisfactory, questionable and unsatisfactory scores. (The numbers on the bars correspond to the exact number of laboratories in a certain scoring category).*

Between 70 and 80 % of the participants obtained satisfactory z-scores for all the measurands but for total mercury, for which only 57 % of the laboratories scored satisfactorily and with 43 % of the participants underestimating the concentration of total mercury in the test material. The low percentage of satisfactory results for total Hg was scrutinised because it deviated from the general tendency of the same population in previous exercises (IMEP-102, -103, -104, -109 and -110). In IMEP-106 and IMEP-108, about 60 % of the laboratories obtained satisfactory scores, the poor performance being due to overestimation of the concentration of total mercury. The concentrations of total mercury in IMEP-106 and -108 were 0.013 and 0.016 mg kg^{-1}, respectively. In the mentioned two exercises it was thought that the overestimation was likely due to contamination issues which could be significant at those low concentration levels.

When looking closely at the results, it was observed that all the unsatisfactory results were obtained by laboratories using thermal decomposition-amalgamation (TDA) (solid sampling-amalgamation). None of the participants using solid TDA obtained satisfactory z-scores in IMEP-111. This finding enters in contradiction with the outcome of IMEP-106/28 [11] (heavy metals in food supplements), where participants using solid TDA performed particularly good, with all of them reporting satisfactory results.

An explanation for the outcome of this exercise could be that the mineral matrix used as test material was not totally decomposed during the thermal decomposition introducing in this way a negative bias in the results. This is just a hypothesis and further studies would have to be conducted to elucidate this point. This hypothesis nevertheless has also been indicated in the EPA method 7473 in which it is stated that when mercury can be bound in silicates or other matrices that may not thermally decompose validation of the TDA-based method should be confirmed with total decomposition [12].

Between 40 and 60 % of the laboratories obtained satisfactory ζ-scores for total Pb, As, Hg and extractable Pb, around 70 % for total and extractable Cd and almost 90 % for total Cu. This outcome reflects once again that laboratories should put some effort in making a realistic estimation of the uncertainty associated to their measurements. The only measurand for which the percentage of satisfactory ζ-scores was higher than that of z-scores was total Cu.

8.4 Additional information extracted from the questionnaire

Additional information was gathered from the questionnaire filled in by the participants in (Annex 4).

8.4.1 Sample treatment related questions

Thirteen participants performed the analysis following an official method. The information provided by the laboratories about their methods of analysis is summarised in Annex 14. No influence of the techniques used was detected for any of the measurands covered in this PT except for Hg (Chapter 8.3).

Four participants use the partial extraction method with 5 % HNO_3 at boiling temperature for half an hour in control analysis, all other applied total digestion-based analytical methods.

None of the participants introduced any modification when applying the partial extraction method to determine extractable Cd and Pb.

Eighteen laboratories corrected their results for recovery and three did not. Those that did, applied one or several of the options shown in Figure 4.

Sixteen laboratories reported the recovery used to correct their results. Most laboratories reported recoveries in the range 80-110 % but recoveries lower than 80 % and higher than 110 % have also been reported. Laboratories must be aware that such recoveries indicate that the method is biased and that corrective actions should be taken.

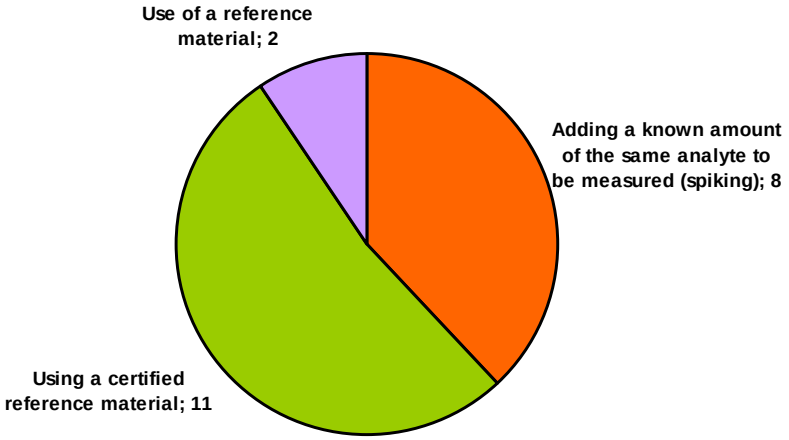


Figure 4: *Distribution of laboratories according to the procedure used to calculate the recovery.*

The CRMs and reference materials used by the participants for the purpose of method validation and/or calibration are given in Table 2.

Attention must be paid to CRM used for validation and/or calibration purposes since it must match the matrix of the test samples as much as possible. For methods of analysis dealing with determination of heavy metals in mineral feed it is advisable to use mineral CRMs or reference materials such as soils or sediments. The CRM BCR-032 used as test material in this exercise would also be a suitable alternative.

Table 2: *List of reference materials used by the participants in IMEP-111 for method validation and/or calibration purposes.*

Lab code	Answer
1	IMEP-105 (Mineral feed)
2	NIST-1547 (Peach leaves), NIST-1570 (Spinach leaves)
7	LGC-7162 (Strawberry leaves), TORT-2 (Lobster hepatopanchreas), INCT-SBF-4 (Soya bean flour)
8	NIST-1568A (Rice flour)
9	BIPEA
11	BCR-151(Skimmed milk), BCR-185R (Bovine liver), ZC7-3012, 1568A (Rice flour), TORT-2 (Lobster hepatopanchreas), DORM-3 (Fish protein)
12	Internal reference material
13	NIST 1573a (Tomato leaves), GBW10016 (Tea), BCR-482 (Lichen), IAEA-336 (Lichen)
14	Reference material remained from evaluated PT
15	BCR-463 (Tuna fish), BCR-708 (Dairy feed)
16	ERM-CE278 (Mussels tissue)
17	NCSDC 73348 (Bush branches and leaves)
18	DC 73348 (Bush branches and leaves)
19	IMEP-105 (Mineral feed), BCR-191 (Brown bread)
21	Past proficiency material
23	NIST, NCS, China National Analysis Centre
24	BCR-186 (Pig kidney), IMEP-103 (Compound feed), IMEP-108 (Vegetable feed), IMEP-109 (Seafood)
25	BCR-279 (Sea lettuce)
26	Milk powder, ERM - CD 281 (Rye grass)
27	BCR-191 (Brown bread)
28	CRM-2976 (Salmon), NIST, PT EU-RL CEFAO Rome; BCR-151 (Skimmed milk)
29	Internal reference material, not a certified reference material
30	BCR-279 (Sea lettuce), NIST-1570a (Spinach leaves), NIST-1573 (Tomato leaves)

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 3 shows the ranges for LOD and LOQ as reported by the participants in IMEP-111 for the different measurands.

Table 3: *Range of LOD and LOQ reported by the participants for the different measurements covered in IMEP-111.*

Measurand	LOD (mg kg^{-1})	LOQ (mg kg^{-1})
Total Cd	0.0000112 - 0.918	0.0000373 - 1.836
Total Pb	0.0000155 - 0.2	0.0000518 - 0.5
Total As	0.0000521 - 0.4	0.0001736 - 0.9
Total Hg	0.00005 - 0.1	0.00016 - 0.02
Total Cu	0.0000119 - 5	0.0000396 - 10

The huge spread of the values (up to five orders of magnitude for some elements) reported as LOD and LOQ could be due to the use of different approaches to calculate the two mentioned performance

characteristics or to actual differences in the methods used. A deeper investigation on this issue will be performed in the PTs that the EU-RL-HM will organise in the future.

All participants but two corrected their results for the water content, determined using the protocol described in the accompanying letter (Annex 2).

8.4.2 Uncertainty related questions

Various approaches were used to scrutinise the measurement uncertainty (Table 4).

Table 4: *Approaches used by the participants in IMEP-111 to estimate the uncertainty of their measurements.*

Approach followed for uncertainty calculation	Number of labs.
Uncertainty of the method as determined in-house validation	21
Measurement of replicates (i.e. precision)	13
Uncertainty budget calculated according to ISO-GUM	6
Known uncertainty of the standard method	3
Use of intercomparison data	3
Estimation based on judgement	2
Other (ISO 5725, combination of other approaches)	3

Seventeen laboratories usually report uncertainty to their customers while 13 never do.

When asked about the level of confidence covered by the reported coverage factor (*k*), most of the participants reported 95 %.

8.4.3 Quality assurance related questions

Most of the laboratories regularly take part in PTs (24 out 28) and use CRMs for validation and/or calibration purposes (25 out of 28). The rest of the laboratories did not answer this question.

8.4.4 Questions related to the experience of the laboratories in this field of analysis.

Twenty-six participants carry out this type of analysis on a regular basis while four do not. The distribution in terms of number of analysis per year is shown in Figure 7.

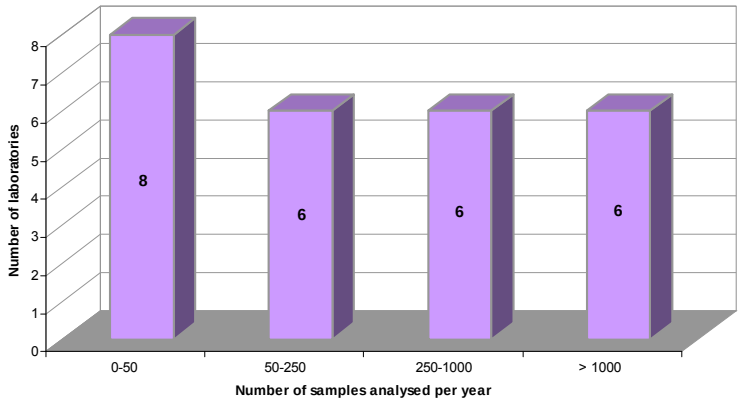


Figure 7: *Participants' experience in this type of analysis expressed as number of analysis per year.*

8.4.5 Quality system related questions

All the participants but one have a quality system in place. In all cases the quality system is based on ISO 17025, in two cases the quality system is also based in ISO 9000. Twenty-two participants are accredited for the methods of analysis used in this exercise. Three laboratories did not answer to this question.

9 Conclusions

It can be concluded from the results submitted to IMEP-111 that the concentrations of total and extractable Pb and total and extractable Cd are identical. This observation applies to the test material used in IMEP-111 and might be different in another material.

IMEP-111 was the first PT organised by the EU-RL-HM in which total Cu was included as measurand. No significant problems were observed.

A major outcome of this PT is the observed clustering of results for total Hg on the basis of the technique used to perform the analysis, where results obtained by thermal decomposition-amalgamation are significantly biased (negatively). Such a bias was not observed in the results obtained with other techniques such as CV-AAS, CV-AFS and ICP-MS.

Once again the need for an extra effort was identified in the evaluation of uncertainties associated to the results, since the number of questionable and unsatisfactory ζ-scores is systematically higher than those of z-scores for all measurands but total Cu. The measurement uncertainty is of paramount importance in cases of litigation and so it is fundamental for control laboratories to be able to report a sound uncertainty.

Most laboratories did not follow the recommendation made in IMEP-105 to use CRMs which mimic the mineral feed matrix, such as soils. Organic matrix CRMs have been mostly used for validation and calibration purposes.

No cluster of laboratories due to the technique used or to any other or the parameters covered in the questionnaire was observed.

10 Acknowledgements

I. Baer and F. Cordeiro are thanked for the fruitful discussions about the organisation of IMEP-111 exercise and the thorough revision of this paper. A.M. Jensen and F. Ulberth are acknowledged for revising the manuscript. J. Charoud-Got is thanked for the relabeling of the bottles.

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

Organisation	Country
AGES-Austrian Agency for Health and Food Safety	AUSTRIA
AGES-Zentrum Analytick und Mikrobiologie	AUSTRIA
Scientific Institute of Public Health	BELGIUM
CODA CERVA	BELGIUM
Central Laboratory of Veterinary Control and Ecology	BULGARIA
CISTA	CZECH REPUBLIC
State Veterinary Institute Olomouc	CZECH REPUBLIC
The Danish Plant Directorate	DENMARK
Agricultural Research Centre	ESTONIA
Evira	FINLAND
Laboratoire SCL de Bordeaux	FRANCE
Federal Office of Consumer Protection and Food Safety	GERMANY
Regional Center Of Plant Protection And Quality Control Of Magnisia	GREECE
General Chemical State Laboratory	GREECE
Central Agricultural Office, Food and Feed Safety Directorate	HUNGARY
Cork Public Analyst's Laboratory (HSE-South)	IRELAND
Istituto Superiore di Sanità	ITALY
Istituto Zooprofilattico Sperimentale del Piemonte Liguria e Valle d'Aosta	ITALY
Institute of Food Safety, Animal Health and Environment	LATVIA
National food and veterinary risk assessment institute	LITHUANIA
Public Health Laboratory	MALTA
Food and Consumer Product Safety Authority	NETHERLANDS
RIKILT	NETHERLANDS
National Veterinary Research Institute	POLAND
Laboratório Nacional de Investigação Veterinária	PORTUGAL
Hygiene Institute of Veterinary Public Health	ROMANIA
State veterinary and food institute - Kosice	SLOVAKIA
National Veterinary Institute	SLOVENIA
Laboratorio Arbitral Agroalimentario	SPAIN
National Vetwerinary Institute (SVA)	SWEDEN

11 References

[1] Directive 2002/32/EC of the European Parliament and of the Council of 7 May 2002 on undesirable substances in animal feed.

[2] Evaluation of measurement data – Guide to the expression of uncertainty in measurements. JCGM 100, (2008).

[3] ISO 13528:2005; Statistical Methods for Use in Proficiency Testing by Interlaboratory Comparisons, ISO, Geneva.

[4] M.B. de la Calle, I. Wysocka, C. Quétel, T. Linsinger, H. Emteborg, F. Cordeiro, A. Semeraro, I. Verbist, D. Vendelbo, P. Taylor, "Report of the fifth interlaboratory comparison organized by the Community Reference Laboratory for Heavy Metals in Feed and Food. Total Cd, Pb and As and extractable Cd and Pb in mineral feed", EUR 23711 EN - 2009.

[5] 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.

[6] M.B. de la Calle, J. van de Kreeke, I. Verbist, S. Bynenes, P. Taylor, "Report of the third interlaboratory comparison organised by the Community Reference Laboratory for Heavy Metals in Feed and Food. Total Cd, Pb and Hg and extractable Cd and Pb in feed", EUR 23236 EN - 2008.

[7] M.B. de la Calle, A. Krata, C. Quétel, T. Linsinger, E. Perez Przyk, I. Verbist. Report of the eighth interlaboratory comparison organized by the Community Reference Laboratory for Heavy Metals in Feed and Food. Total Cd, Pb, As, Hg and Sn and extractable Cd and Pb in feed or plant origin", EUR 24278 EN - 2010.

[8] http://www.irmm.jrc.be/html/reference_materials_catalogue/catalogue/attachements/BCR-032_report.pdf

[9] Eurachem/CITAC guide; Quantifying Uncertainty in Analytical Measurements, 2000 (www.eurachem.ul.pt).

[10] The software to calculate Kernel densities is provided by the Statistical Subcommittee of the Analytical Methods Committee (AMC) of the Royal Society of Chemistry and described in the AMC Technical Brief "Representing data distibutions with Kernel density estimates" (2006), see www.rsc.org/amc

[11] I. Baer, H. Emteborg, B. de la Calle, " 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, (2011), 1498-1504.

[12] EPA Method 7473 "Mercury in solids and solutions by thermal decomposition amalgamation, and atomic absorption spectrophotometry", (1998).

Annexes

Annex 1: Invitation letter

EUROPEAN COMMISSION
JOINT RESEARCH CENTRE

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

European Union Reference Laboratory
Heavy Metals in Feed and Food

Geel, 4 October 2010
JRC.DDG.D6/BCa/ive/ARES(2010)655297

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

Dear Madam / Sir,

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

On behalf of the EU-RL Heavy Metals in Feed and Food, I would like to invite you to participate in the Proficiency Test [IMEP-111] for the **"Determination of total Cd, Pb, As, Hg and Cu and 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"**.

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

Please register electronically for this inter-laboratory comparison using the following link: https://irmm.jrc.ec.europa.eu/ilc/ilcRegistration.do?selComparison=580

Your participation is free of charge.

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

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

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

The **deadline for registration is 15 October 2010**. Samples will be sent to participants during the second half of October. The deadline for submission of results is 30 November 2010.

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

Yours sincerely

Dr. M.B. de la Calle
Operating Manager EU-RL-HM

Cc: Franz Ulberth

Annex 2: Accompanying letter

EUROPEAN COMMISSION
JOINT RESEARCH CENTRE

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

European Union Reference Laboratory
Heavy Metals in Feed and Food

Geel, 26 October 2010
JRC.DDG.D6/BCD/ive/ARES(2010)/736481

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

Participation to IMEP-111, a proficiency test exercise for the determination of total Cd, Pb, As, Hg and Cu and 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

Dear «TITLE» «SURNAME»,

Thank you for participating in the IMEP-111 intercomparison for the determination of total Cd, Pb, As, Hg and Cu and 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. This exercise takes place in the frame of the CRL Heavy Metals in Feed and Food.

This parcel contains:
a) One glass bottle containing approximately 100 g of the test material
b) A "Confirmation of Receipt" form
c) This accompanying letter

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

The measurands are: **total** Cd, Pb, As, Hg and Cu and **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.

As agreed upon during the workshop held in September, 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

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

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

(IMEP-111)

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): 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** Cd, Pb, As, Hg and Cu the procedure that you use should resemble as closely as possible the one that you use in routine sample analysis.

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

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 °C for 2 hours in triplicate

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

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

The deadline for submission of results is 30/11/2010.

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

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

With kind regards

Dr. M.B. de la Calle
IMEP-111 Co-ordinator

Enclosures: 1) one glass bottle containing the test material; 2) confirmation of receipt form; 3) Accompanying letter.

Cc: F. Ulberth

3

Annex 3: Acknowledgement of receipt form

EUROPEAN COMMISSION
JOINT RESEARCH CENTRE

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

European Union Reference Laboratory
Heavy Metals in Feed and Food

Annex to JRC.DDG.D6/BCD/ive/ARES(2010)/736481

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

EU-RL-HM-11 / IMEP-111

total Cd, Pb, As, Hg and Cu and 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 Beatriz de la Calle

IMEP-110 Coordinator
EC-JRC-IRMM
Retieseweg 111
B-2440 GEEL, Belgium

Fax : +32-14-571865
e-mail : JRC-IRMM-CRL-HEAVY-METALS@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) 571 299. Fax: (32-14) 571 865.

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

IMEP

Annex 4: Questionnaire

Submission Form

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

Please complete below table.

Questions/Response table	Total Cd	Total Pb	Total As	Total Hg	Total Cu
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 (k) factors stated above? (in %)**

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

- ☐ 1. uncertainty budget calculated according to iso-gum
- ☐ 2. known uncertainty of the standard method
- ☐ 3. uncertainty of the method as determined in-house validation
- ☐ 4. measurement of replicates (i.e. precision)
- ☐ 5. expert guestimate
- ☐ 6. use of intercomparison data
- ☐ 7. other

3.1. If other, please specify

4. **Do you usually provide an uncertainty statement to your 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:

7.2. If no, please describe (in max. 150 characters for each reply) 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 the anlytes, matrix and methods) on a regular basis?**

- ○ no
- ○ yes

8.1. If Yes, please estimate the number of samples (As, Cd, Pb, Hg, Cu 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:

- ☐ a) ISO 17025
- ☐ b) ISO 9000 series
- ☐ c) Other

9.1.1. If other, please specify

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 an interlaboratory comparison for this type of analysis on a regular basis?**

- ○ no
- ○ yes

12.1. If yes, which one(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 5: Certificate of the CRM used in IMEP-111

EUROPEAN COMMISSION
JOINT RESEARCH CENTRE
Institute for Reference Materials and Measurements

CERTIFIED REFERENCE MATERIAL
BCR® – 032

CERTIFICATE OF ANALYSIS

NATURAL MOROCCAN PHOSPHATE ROCK
(Phosphorite)

	Mass fraction based on dry mass		Number of accepted individual measurements
	Certified value [1] [g/kg]	Uncertainty [2] [g/kg]	
Ca expressed as CaO	518	4	70
Total P expressed as P_2O_5	329.8	1.7	85
Carbonate Carbon expressed as CO_2	51.0	0.8	60
F	40.4	0.6	80
Si expressed as SiO_2	20.9	1.2	60
Total S expressed as SO_3	18.4	0.8	75
Al expressed as Al_2O_3	5.5	0.6	80
Mg expressed as MgO	4.0	0.1	65
Fe expressed as Fe_2O_3	2.3	0.1	65

[1] The certified value is the unweighted mean of individual measurements obtained by different laboratories. The certified value is traceable to SI.
[2] The uncertainty is estimated standard deviation of reproducibility which. It accounts for the precision and bias of the participating laboratories as well as for any inhomogeneity of the material.

This certificate is valid for one year after purchase.

Sales date:

The minimum amount of sample to be used is 1 g.

NOTE

This material has been certified by BCR (Community Bureau of Reference, the former reference materials programme of the European Commission). The certificate has been revised under the responsibility of IRMM.

Brussels, November 1979
Latest revision: March 2010

Signed:

Prof. Dr. Hendrik Emons
European Commission
Joint Research Centre
Institute for Reference Materials and Measurements
Retieseweg 111
B-2440 Geel, Belgium

JRC EUROPEAN COMMISSION

Page 1 of 4

Indicative Values

	Mass fraction based on dry mass		Number of accepted sets of data p
	Certified value [1] [mg/kg]	Uncertainty [2] [mg/kg]	
As	9.5	0.5	7
B	22.6	2.2	6
Cd	20.8	0.7	12
Cr	257	16	12
Co	0.59	0.06	9
Cu	33.7	1.4	14
Hg	0.055	0.011	6
Mn	18.8	1.3	13
Ni	34.6	1.9	11
Ti	171	10	10
V	153	7	12
Zn	253	6	9

1) This value is the unweighted mean of p accepted sets of results. The certified value is traceable to SI.
2) The 95% confidence interval is a measure of the uncertainty and is applicable when the reference material is used for calibration purposes.

When the reference material is used to assess the performance of a method, the user should refer to the recommendations laid down in the last chapter (instructions for use) of the certification report. In particular he should use the values of the within-laboratory set standard deviation (S_W), and of the between-laboratory set standard deviation (S_B) given there.

Additional Material Information

	Mass fraction based on dry mass	
	Estimated value	
Na expressed as Na_2O	8.6	g/kg
K expressed as K_2O	0.9	g/kg
Organic C expressed as C	1.6	g/kg
Ag	2	mg/kg
Mo	2-4	mg/kg
Pb	5.4	mg/kg
Sb	3	mg/kg
Se	10	mg/kg
Th	2	mg/kg
U	125	mg/kg

DESCRIPTION OF THE SAMPLE

The sample consists of approximately 100 g of thoroughly mixed finely ground material (particle size < 100 µm) taken from a batch of a natural Moroccan phosphate rock usually employed for the production of phosphate fertilizers. The sample is homogenous at least to a 1 g level. The sample is available in brown glass bottles closed with a double plastic stopper.

ANALYTICAL METHOD USED FOR CERTIFICATION

CaO	:	Volumetric method with $KMnO_4$, titration with EDTA
P_2O_5	:	Quinoline phosphomolybdate gravimetry, spectrophotometric method, X-ray fluorescence
CO_2	:	Gravimetry of CO_2 evolved by acid attack, titration of CO_2 in non-aqueous medium, conductimetric measurement of CO_2
F	:	Spectrophotometric and volumetric methods after distillation of F, ion selective electrode
SiO_2	:	Gravimetric methods, spectrophotometric method after alkaline fusion, X- ray fluorescence, inductively coupled plasma
SO_3	:	Gravimetry after acid dissolution, reduction to S^{2-} and titration with mercuric solution
Al_2O_3	:	Atomic absorption spectrometry, gravimetric method with 8-hydroxyquinoline, spectrophotometric method, X-ray fluorescence, neutron activation analysis
MgO	:	Atomic absorption spectrometry, inductively coupled plasma
Fe_2O_3	:	Atomic absorption spectrometry, spectrophotometric methods, X-ray fluorescence, inductively coupled plasma.

- Hydride atomic absorption spectrometry
- Neutron Activation analysis
- Spectrophotometry
- Voltammetry
- Photoneutron activation analysis
- Photon activation analysis
- Charged particle activation analysis
- Inductively coupled plasma emission spectrometry
- Neutron capture activation analysis
- Atomic absorption spectrometry
- Isotope dilution mass spectrometry
- Potentiometric stripping analysis
- Graphite furnace atomic absorption spectrometry
- Solid sample atomic absorption spectrometry
- Micro wave plasma emission spectrometry
- Cold vapour atomic absorption spectrometry
- Cold vapour atomic fluorescence spectrometry

PARTICIPANTS

- ANIC, Milano (IT)
- APC, Toulouse (FR)
- ARBED SA, Esch-sur-Alzette (LU)
- Bundesanstalt für Materialprüfung, Berlin (DE)
- Centre National de la Recherche Scientifique (CNRS), Centre de Recherches Petrografiques et Geochimiques, Vandœuvre-le-Nancy (FR)
- Centro Italiano Studi Esperienze (CISE), Milano (IT)
- Centro Nazionale Ricerche; Centro di Radiochimica e Analisi per Attivazione, Pavia (IT)
- CNR, Centro Radiochimica, Pavia (IT)
- ECN - Netherlands Energy Research Foundation; Research Centre, Petten (NL)
- European Commission, Joint Research Centre, Chemistry Division and CETIS, Ispra (IT)
- Fabbrica Perfosfati, Cerea (IT)
- Général des Engrais SA, Rouen (FR)
- Gesellschaft für Strahlen- und Umweltforschung, Neuherberg (DE)
- Joint Research Centre - Commission of the European Communities (EEC), Ispra (IT)
- Laboratoria van het SCK/CEN, Mol (BE)
- Laboratory of the Governemental Chemist, London (GB)
- Landwirtschaftskammer Rheinland, Landwirtschaftliche Untersuchungs- und Forschungsantstalt Bonn, Bonn (DE)
- Landwirtschaftskammer Schleswig-Holstein, Landwirtschaftliche Untersuchungs- und Forschungsantstalt Kiel, Kiel (DE)
- Nitriging Eireann Teoranta, Arklow (IE)
- Produits Chimiques Ugine Kuhlmann, Levallois (FR)
- Rijkslandbouwproefstation, Maastricht (NL)
- Rijksuniversiteit Gent; Instituut voor Nucleaire Wetenschappen, Gent (BE)
- Services Techniques de l'Agriculture, Ettelbruck (LU)

- Station Agronomique de l'Aisne, Laon (FR)
- Technical and Analytical Services, Stockton-on-Tees (GB)
- Ugine-Kuhlmann, Levallois-Perret (FR)
- UKF-SBB, Geleen (NL)
- Università di Bologna, Istituto Chimica Agraria, Bologna (IT)
- Universtiät Hohenheim, Landesanstalt für Landwirtschaftliche Chemie, Stuttgart (DE)
- Windmill Holland BV, Vlaardingen (NL)

SAFETY INFORMATION

The usual laboratory safety precautions apply.

INSTRUCTIONS FOR USE

Once the bottle has been opened, the material is susceptible to contamination (e.g. by laboratory dust or vapour) or losses. Precautions with regards to storage container and temperature should be taken.
The portion for analysis shall be taken as it is. The moisture content should be determined by drying a portion of the sample at 105 °C during 2 hours.

STORAGE

The material can be stored at room temperature.
However, the European Commission cannot be held responsible for changes that happen during storage of the material at the customer's premises, especially of opened samples.

LEGAL NOTICE

Neither IRMM, its subsidiaries, its contractors nor any person acting on their behalf.
(a) make any warranty or representation, express or implied that the use of any information, material, apparatus, method or process disclosed in this document does not infringe any privately owned intellectual property rights;
or
(b) assume any liability with respect to, or for damages resulting from, the use of any information, material, apparatus, method or process disclosed in this document save for loss or damage arising solely and directly from the negligence of IRMM or any of its subsidiaries.

NOTE

A technical report on the production of BCR-032 is available on the internet (http://www.irmm.jrc.be).
A paper copy can be obtained from IRMM on request.

European Commission – Joint Research Centre
Institute for Reference Materials and Measurements (IRMM)
Retieseweg 111, 2440 Geel (Belgium)
Telephone: +32-(0)14-571.722 - Telefax: +32-(0)14-590.406

Annex 6: Total Cd in mineral feed

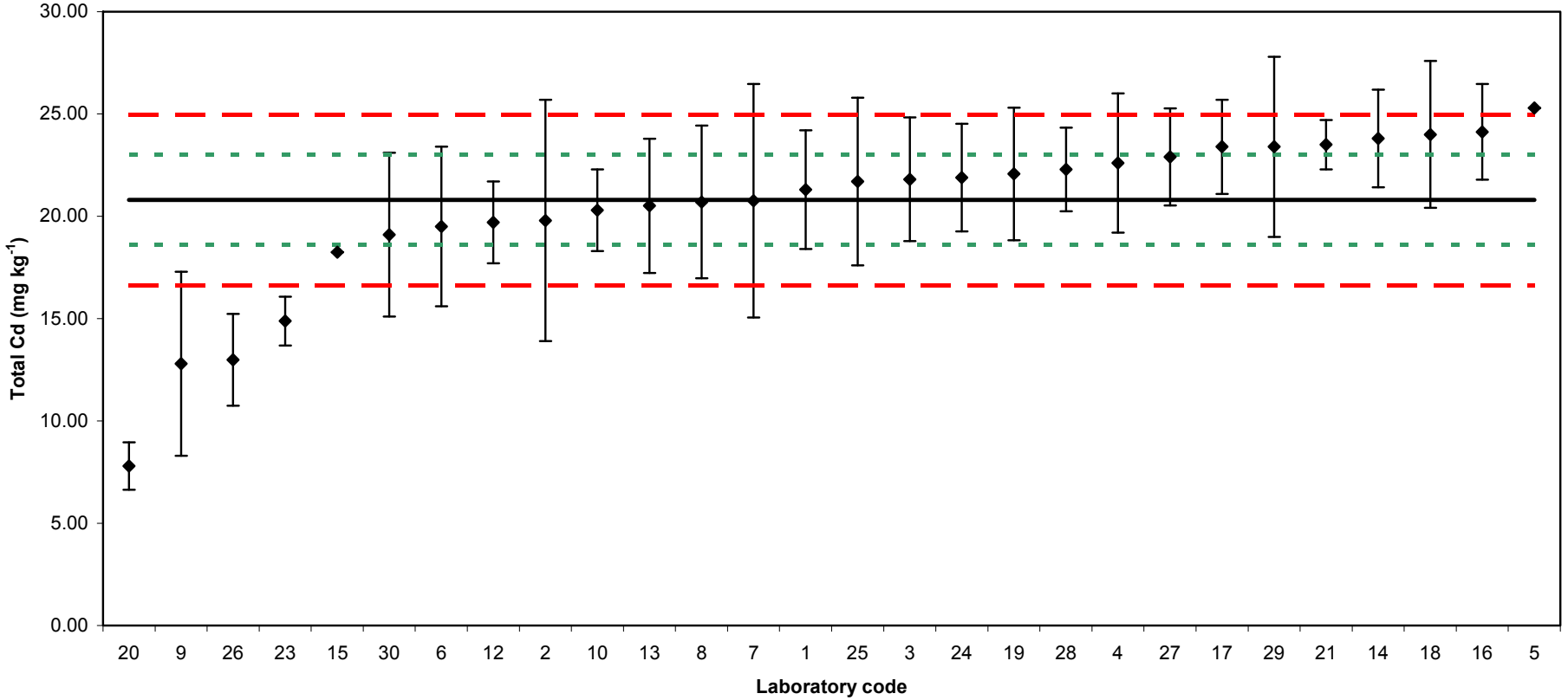
X_{ref} = 20,8 ± 2,2 mg kg^{-1} (*k*=2)

Lab ID	X_{lab} (mg kg^{-1})	U_{lab} (mg kg^{-1})	k	u_{lab} (mg kg^{-1})	Technique	z	ζ	$Qual_u$
1	21,30	2,90	2	1,45	ETAAS	0,2	0,3	**a**
2	19,8	5,9	2	3,0	ICP-MS	-0,5	-0,3	**c**
3	21,81	3,02	2	1,51	ETAAS	0,5	0,5	**a**
4	22,6	3,4	2	1,7	ICP-MS	0,9	0,9	**a**
5	25,290	0,001	2	0,001	ETAAS	2,2	4,1	**b**
6	19,5	3,9	2	2,0	ICP-MS	-0,6	-0,6	**a**
7	20,76	5,71	2	2,86	ICP-MS	0,0	0,0	**c**
8	20,70	3,73	2	1,87	ICP-OES	0,0	0,0	**a**
9	12,8	4,5	2	2,3	ICP-OES	-3,8	-3,2	**c**
10	20,3	2,0	2	1,0	ICP-MS	-0,2	-0,3	**b**
12	19,7	2,0	2	1,0	ICP-MS	-0,5	-0,7	**b**
13	20,51	3,28	2	1,64	ZETAAS	-0,1	-0,1	**a**
14	23,8	2,38	2	1,19	FAAS	1,4	1,9	**a**
15	18,243	0	√3	0	FAAS	-1,2	-2,3	**b**
16	24,13	2,34	2	1,17	ZETAAS	1,6	2,1	**a**
17	23,4	2,3	2	1,2	ICP-OES	1,3	1,6	**a**
18	24,0	3,59	2	1,80	FAAS	1,5	1,5	**a**
19	22,07	3,24	2	1,62	ETAAS	0,6	0,6	**a**
20	7,80	1,16	2	0,58	ICP-MS	-6,3	-10,5	**b**
21	23,5	1,2	2	0,6	ETAAS	1,3	2,2	**b**
23	14,88	1,1904	√3	0,6873	ICP-MS	-2,8	-4,6	**b**
24	21,89	2,63	2	1,32	AAS	0,5	0,6	**a**
25	21,7	4,1	2	2,1	ETAAS	0,4	0,4	**a**
26	12,99	2,24	2	1,12	ETAAS	-3,8	-5,0	**a**
27	22,9	2,37	2	1,19	ICP-MS	1,0	1,3	**a**
28	22,29	2,04	2	1,02	ETAAS	0,7	1,0	**b**
29	23,4	4,4	2	2,2	ICP-OES	1,3	1,1	**c**
30	19,1	4	2	2	ETAAS	-0,8	-0,7	**a**

$Qual_u$: qualitative information about u_{lab}**: a**: $u_{ref}<u_{lab}<\hat{\sigma}$; **b**: $u_{lab}<u_{ref}$; **c**: $\hat{\sigma}<u_{lab}$. For further information on these codes, please read chapter 8.2.

IMEP-111: Results for total Cd

Certified range: 20,8 ± 2,2 mg kg^{-1} (*k* =2)



This graph displays all measurements results and their associated uncertainties.
The uncertainties are shown as reported, with various expansion factors and levels of confidence.
The black line represents Xref, the green dotted lines delimit the reference interval **(X_{ref} ± 2u_{ref}: 20,8 ± 2,2 mg kg^{-1})**, the red dashed lines delimit the target interval **(X_{ref} ± 2σ: 20,8 ± 4,2 mg kg^{-1})**

Annex 7: Total Pb in mineral feed

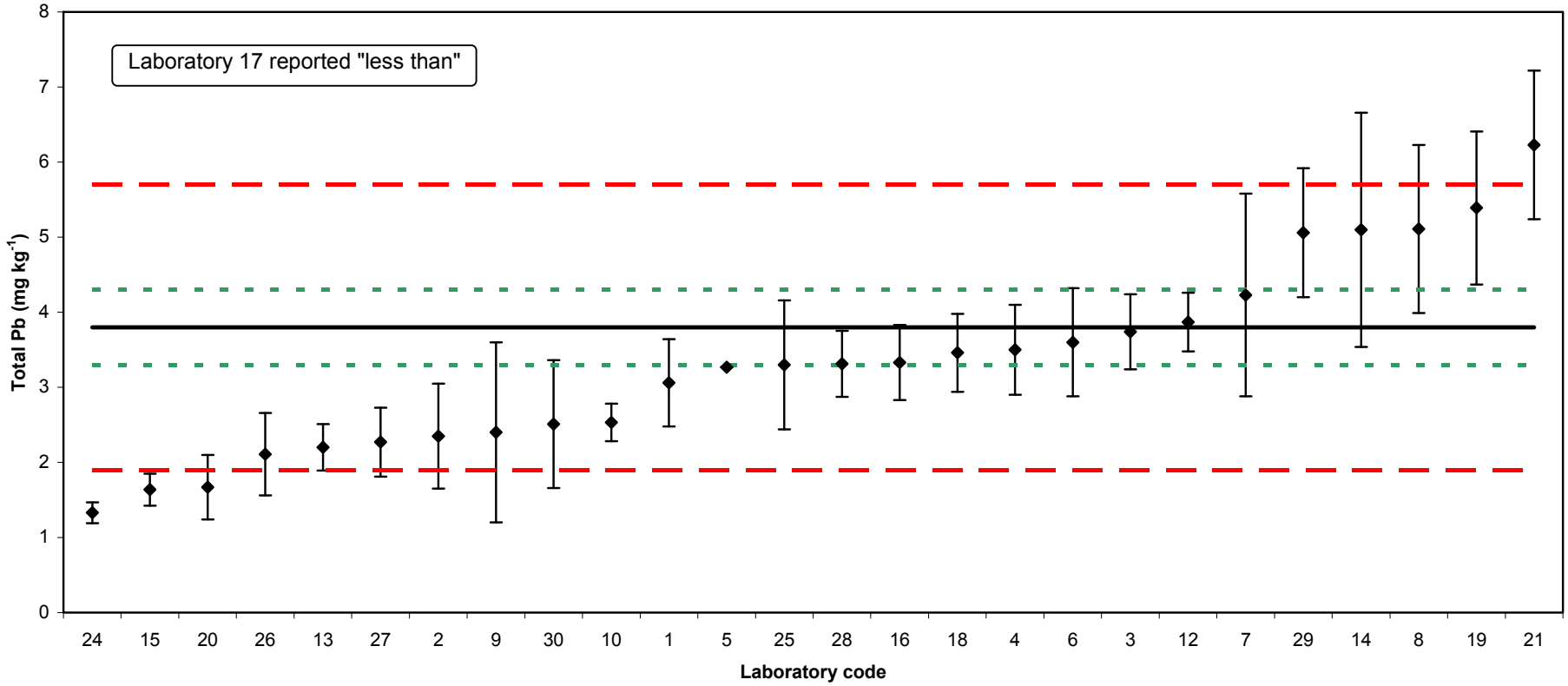
X_{ref} = 3,8 ± 0,5 mg kg^{-1} (*k*=2)

Lab ID	X_{lab} (mg kg^{-1})	U_{lab} (mg kg^{-1})	k	u_{lab} (mg kg^{-1})	Technique	z	ζ	$Qual_u$
1	3,06	0,58	2	0,29	ETAAS	-0,8	-1,9	**b**
2	2,35	0,70	2	0,35	ICP-MS	-1,5	-3,4	**a**
3	3,74	0,50	2	0,25	ICP-MS	-0,1	-0,2	**b**
4	3,5	0,6	2	0,3	ICP-MS	-0,3	-0,8	**a**
5	3,269	0,001	2	0,001	ET AAS	-0,6	-2,1	**b**
6	3,6	0,72	2	0,4	ICP-MS	-0,2	-0,5	**a**
7	4,23	1,35	2	0,68	ICP-MS	0,5	0,6	**a**
8	5,11	1,12	2	0,56	ICP-OES	1,4	2,1	**a**
9	2,4	1,2	2	0,6	ICP-OES	-1,5	-2,2	**a**
10	2,53	0,25	2	0,13	ICP-MS	-1,3	-4,5	**b**
12	3,87	0,39	2	0,20	ICP-MS	0,1	0,2	**b**
13	2,20	0,31	2	0,16	ZETAAS	-1,7	-5,4	**b**
14	5,1	1,56	2	0,8	ETAAS	1,4	1,6	**a**
15	1,636	0,213	2	0,107	FAAS	-2,3	-8,0	**b**
16	3,33	0,50	2	0,25	ZETAAS	-0,5	-1,3	**b**
17	<0,7				ICP-OES			
18	3,46	0,52	2	0,26	ETAAS	-0,4	-0,9	**b**
19	5,39	1,02	2	0,51	ETAAS	1,7	2,8	**a**
20	1,67	0,43	2	0,22	ICP-MS	-2,2	-6,5	**b**
21	6,23	0,99	2	0,50	ETAAS	2,6	4,4	**a**
23	1,01	0,1212	√3	0,07	ICP-MS	-2,9	-10,7	**b**
24	1,33	0,14	2	0,07	AAS	-2,6	-9,5	**b**
25	3,3	0,86	2	0,4	ETAAS	-0,5	-1,0	**a**
26	2,11	0,55	2	0,28	ETAAS	-1,8	-4,5	**b**
27	2,27	0,46	2	0,23	ICP-MS	-1,6	-4,5	**b**
28	3,315	0,44	2	0,220	ETAAS	-0,5	-1,5	**b**
29	5,06	0,86	2	0,43	ICP-OES	1,3	2,5	**a**
30	2,51	0,853	2	0,43	ETAAS	-1,4	-2,6	**a**

$Qual_u$: qualitative information about u_{lab}**: a**: $u_{ref}<u_{lab}<\hat{\sigma}$; **b**: $u_{lab}<u_{ref}$; **c**: $\hat{\sigma}<u_{lab}$. For further information on these codes, please read chapter 8.2.

IMEP-111: Results for total Pb

Certified range: 3,8 ± 0,5 mg kg^{-1} (*k* =2)



This graph displays all measurements results and their associated uncertainties.
The uncertainties are shown as reported, with various expansion factors and levels of confidence.
The black line represents Xref, the green dotted lines delimit the reference interval **(X_{ref} ± 2u_{ref}: 3,8 ± 0,5 mg kg^{-1})**, the red dashed lines delimit the target interval **(X_{ref} ± 2σ: 3,8 ± 2,0 mg kg^{-1})**

Annex 8: Total As in mineral feed

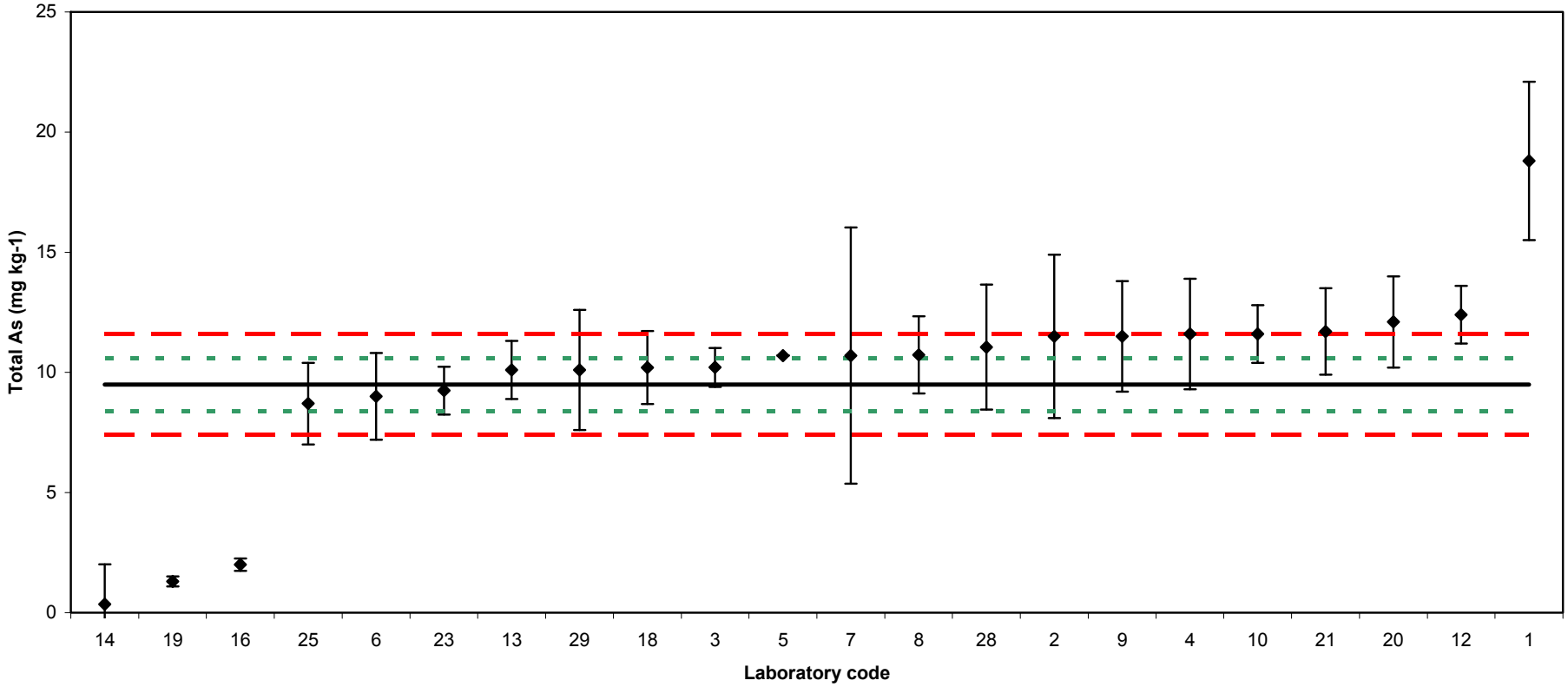
X_{ref} = 9,5 ± 1,1 mg kg^{-1} (*k*=2)

Lab ID	X_{lab} (mg kg^{-1})	U_{lab} (mg kg^{-1})	k	u_{lab} (mg kg^{-1})	Technique	z	ζ	$Qual_u$
1	18,8	3,3	2	1,7	HG-AAS	8,9	5,3	**c**
2	11,5	3,4	2	1,7	ICP-MS	1,9	1,1	**c**
3	10,21	0,81	2	0,41	ICP-MS	0,7	1,0	**b**
4	11,6	2,3	2	1,2	ICP-MS	2,0	1,6	**c**
5	10,699	0,007	2	0,004	HG-AAS	1,1	2,2	**b**
6	9,0	1,8	2	0,9	ICP-MS	-0,5	-0,5	**a**
7	10,70	5,33	2	2,67	ICP-MS	1,1	0,4	**c**
8	10,73	1,61	2	0,81	HG-AAS	1,2	1,3	**a**
9	11,5	2,3	2	1,2	ICP-OES	1,9	1,6	**c**
10	11,6	1,2	2	0,6	HG-AAS	2,0	2,6	**a**
12	12,4	1,2	2	0,6	ICP-MS	2,8	3,6	**a**
13	10,10	1,21	2,04	0,59	ZETAAS	0,6	0,7	**b**
14	0,35	1,66	2	0,83	HG-AAS	-8,8	-9,2	**a**
16	2,00	0,26	2	0,13	ZETAAS	-7,2	-13,3	**b**
18	10,2	1,52	2	0,76	HG-AAS	0,7	0,7	**a**
19	1,30	0,21	2	0,11	ETAAS	-7,8	-14,6	**b**
20	12,1	1,9	2	1,0	ICP-MS	2,5	2,4	**a**
21	11,7	1,8	2	0,9	HG-AAS	2,1	2,1	**a**
23	9,24	0,994	√3	0,574	ICP-MS	-0,2	-0,3	**b**
25	8,7	1,7	2	0,9	ETAAS	-0,8	-0,8	**a**
26					no detected			
28	11,05	2,6	2	1,3	HG-AAS	1,5	1,1	**c**
29	10,1	2,5	2	1,3	HG-AAS	0,6	0,4	**c**

$Qual_u$: qualitative information about u_{lab}**: a**: $u_{ref}<u_{lab}<\hat{\sigma}$; **b**: $u_{lab}<u_{ref}$; **c**: $\hat{\sigma}<u_{lab}$. For further information on these codes, please read chapter 8.2.

IMEP-111: Results for total As

Certified range: 9,5 ± 1,1 mg kg^{-1} (*k* =2)



This graph displays all measurements results and their associated uncertainties.
The uncertainties are shown as reported, with various expansion factors and levels of confidence.
The black line represents Xref, the green dotted lines delimit the reference interval **(X_{ref} ± 2u_{ref}: 9,5 ± 1,1 mg kg^{-1})**, the red dashed lines delimit the target interval **(X_{ref} ± 2σ: 9,5 ± 2,0 mg kg^{-1})**

Annex 9: Total Hg in mineral feed

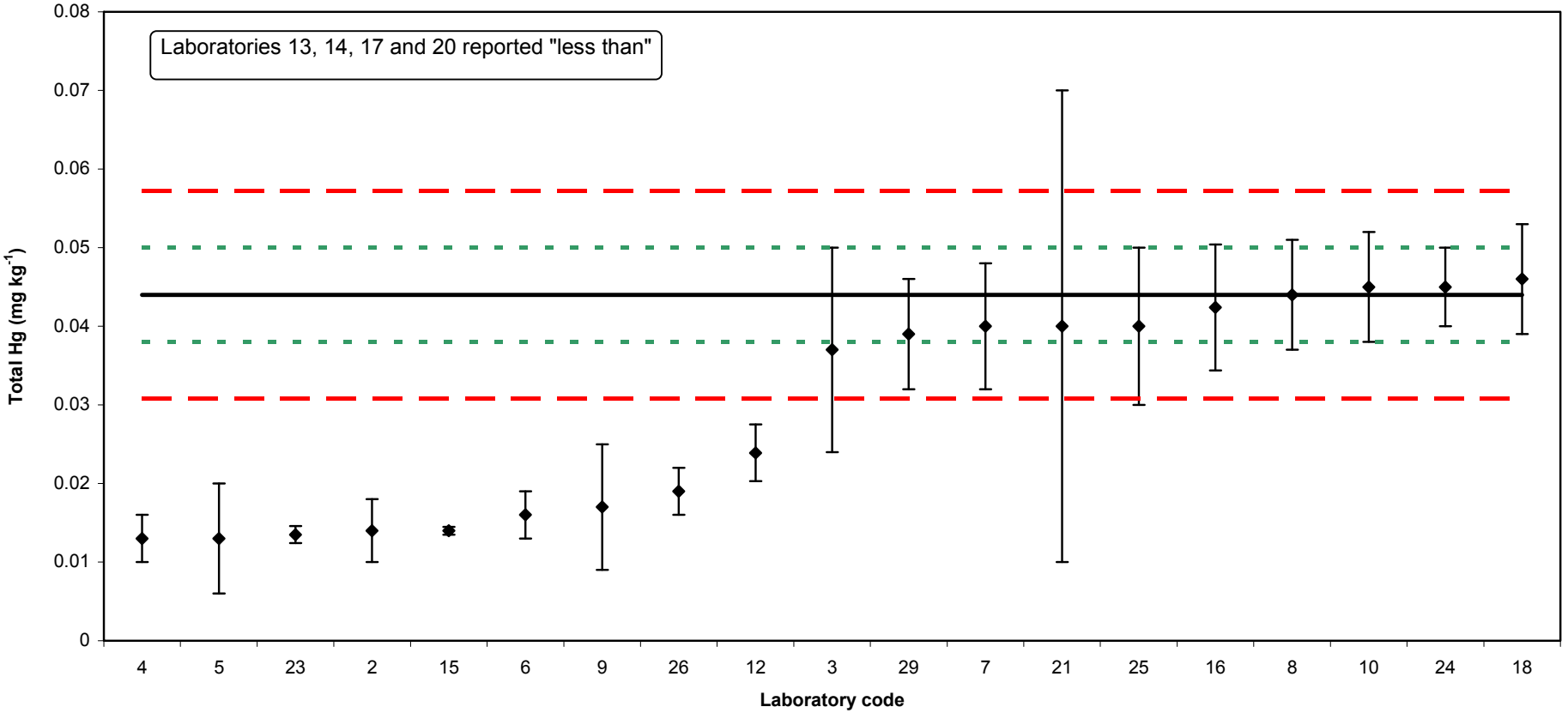
X_{ref} = 0,044 ± 0,006 mg kg^{-1} (*k*=2)

Lab ID	X_{lab} (mg kg^{-1})	U_{lab} (mg kg^{-1})	k	u_{lab} (mg kg^{-1})	Technique	z	ζ	$Qual_u$
1	0,053	0,007	2	0,004	CV-AAS	1,4	2.0	**a**
2	0,014	0,004	2	0,002	AMA	-4,5	-8.3	**b**
3	0,037	0,013	2	0,007	CV-AAS	-1,1	-1.0	**a**
4	0,013	0,003	2	0,002	AMA	-4,7	-9.2	**b**
5	0,013	0,007	2	0,004	AMA-254	-4,7	-6.7	**a**
6	0,016	0,003	2	0,002	AMA	-4,2	-8.3	**b**
7	0,04	0,008	2	0,004	ICP-MS	-0,6	-0.8	**a**
8	0,044	0,007	2	0,004	CV-AAS	0,0	0.0	**a**
9	0,017	0,008	2	0,004	AMA	-4,1	-5.4	**a**
10	0,045	0,007	2	0,004	ICP-MS	0,2	0.2	**a**
12	0,0239	0,0036	2	0,0018	AMA 254	-3,0	-5.7	**b**
13	<0,034				TDA-AAS			
14	<0,1				HG-AAS			
15	0,014	0,0005	2	0,0003	AMA 254	-4,5	-10.0	**b**
16	0,0424	0,008	2	0,004	CV-AAS	-0,2	-0.3	**a**
17	<0,015				CV-ICP-OES			
18	0,046	0,007	2	0,004	CV-AAS	0,3	0.4	**a**
20	<0,1				ICP-MS			
21	0,04	0,03	2	0,02	HG-AAS	-0,6	-0.3	**c**
23	0,0135	0,00108	√3	0,00062	AMA	-4,6	-10.0	**b**
24	0,045	0,005	2	0,003	HG-AAS	0,2	0.3	**a**
25	0,040	0,010	2	0,005	CV, AFS	-0,6	-0.7	**a**
26	0,019	0,003	2	0,002	AMA 254	-3,8	-7.5	**b**
28	0,049	0,0072	2	0,0036	CV-AAS	0,8	1.1	**a**
29	0,039	0,007	2	0,004	CV-AAS	-0,8	-1.1	**a**

$Qual_u$: qualitative information about u_{lab}**: a**: $u_{ref} < u_{lab} < \hat{\sigma}$; **b**: $u_{lab} < u_{ref}$; **c**: $\hat{\sigma} < u_{lab}$. For further information on these codes, please read chapter 8.2.

IMEP-111: Results for total Hg

Certified range: 0,044 ± 0,006 mg kg^{-1} (*k* =2)



This graph displays all measurements results and their associated uncertainties.
The uncertainties are shown as reported, with various expansion factors and levels of confidence.
The black line represents Xref, the green dotted lines delimit the reference interval **(X_{ref} ± 2u_{ref}: 0,044 ± 0,006 mg kg^{-1})**, the red dashed lines delimit the target interval **(X_{ref} ± 2σ: 0,044 ± 0,014 mg kg^{-1})**

Annex 10: Total Cu in mineral feed

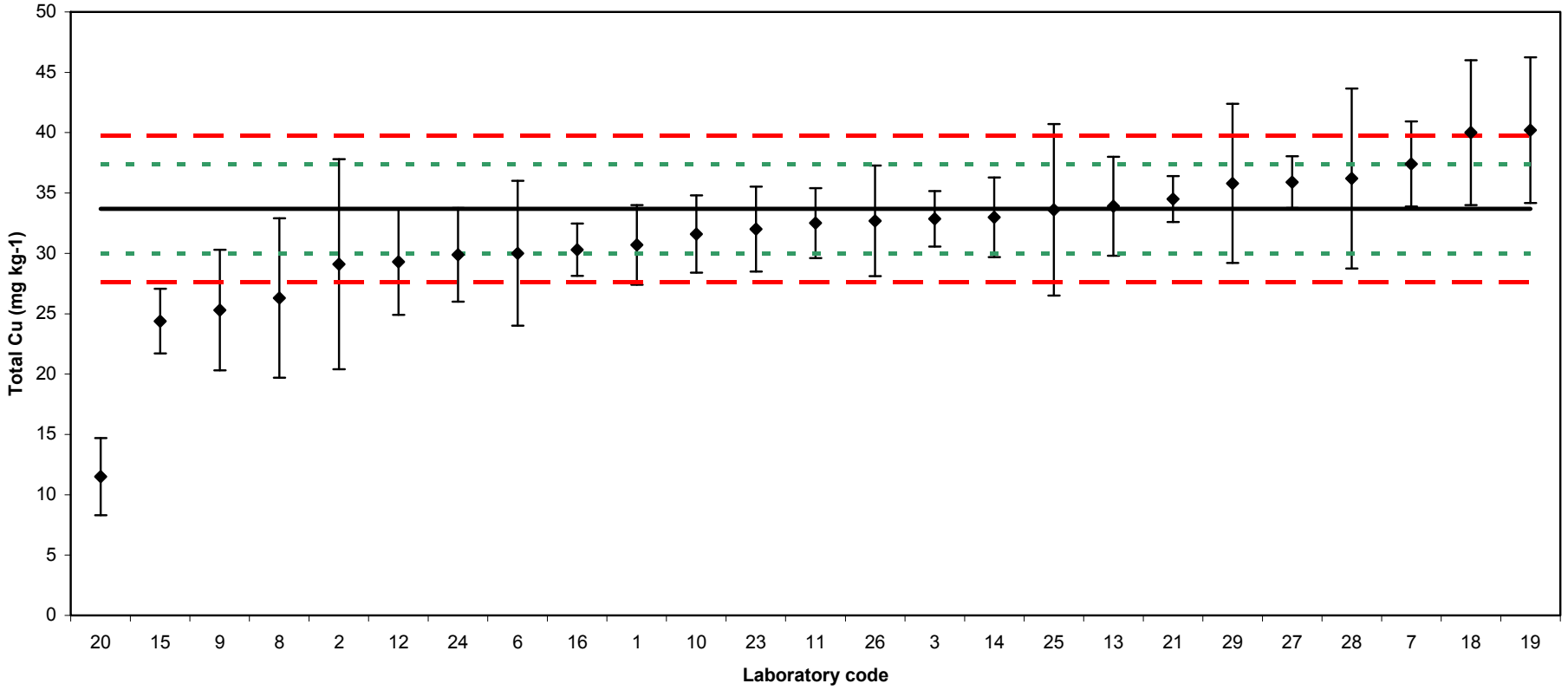
X_{ref} = 33,7 ± 3,7 mg kg^{-1} (*k*=2)

Lab ID	X_{lab} (mg kg^{-1})	U_{lab} (mg kg^{-1})	k	u_{lab} (mg kg^{-1})	Technique	z	ζ	$Qual_u$
1	30,7	3,3	2	1,7	FAAS	-1,0	-1,2	**a**
2	29,1	8,7	2	4,4	ICP-MS	-1,5	-1,0	**c**
3	32,86	2,30	2	1,15	ICP-MS	-0,3	-0,4	**a**
6	30	6	2	3	ICP-MS	-1,2	-1,0	**a**
7	37,4	3,52	2	1,76	FAAS	1,2	1,4	**a**
8	26,3	6,6	2	3,3	ICP-OES	-2,4	-2,0	**c**
9	25,3	5	2	3	ICP-OES	-2,8	-2,7	**a**
10	31,6	3,2	2	1,6	ICP-MS	-0,7	-0,9	**a**
11	32,5	2,9	2	1,5	FAAS	-0,4	-0,5	**a**
12	29,3	4,4	2	2,2	FAAS	-1,5	-1,5	**a**
13	33,9	4,1	2,02	2,0	FAAS	0,1	0,1	**a**
14	33,0	3,3	2	1,7	FAAS	-0,2	-0,3	**a**
15	24,38	2,68	2	1,34	FAAS	-3,1	-4,1	**a**
16	30,3	2,17	2	1,09	FAAS	-1,1	-1,6	**a**
18	40,0	6,0	2	3,0	FAAS	2,1	1,8	**a**
19	40,21	6,03	2	3,02	ETAAS	2,1	1,8	**c**
20	11,5	3,2	2	1,6	ICP-MS	-7,3	-9,1	**a**
21	34,5	1,9	2	1,0	ETAAS	0,3	0,4	**a**
23	32,0	3,52	√3	2,03	ICP-MS	-0,6	-0,6	**a**
24	29,88	3,88	2	1,94	AAS	-1,3	-1,4	**a**
25	33,6	7,1	2	3,6	FAAS	0,0	0,0	**c**
26	32,69	4,58	2	2,29	FAAS	-0,3	-0,3	**a**
27	35,9	2,15	2	1,08	ICP-MS	0,7	1,0	**a**
28	36,21	7,46	2	3,73	FAAS	0,8	0,6	**c**
29	35,8	6,6	2	3,3	FAAS	0,7	0,6	**c**

$Qual_u$: qualitative information about u_{lab}**: a**: u_{ref}<u_{lab}< $\hat{\sigma}$; **b**: u_{lab}<u_{ref}; **c**: $\hat{\sigma}$ <u_{lab}. For further information on these codes, please read chapter 8.2.

IMEP-111: Results for total Cu

Certified range: 33,7 ± 3,7 mg kg^{-1} (k =2)



This graph displays all measurements results and their associated uncertainties.
The uncertainties are shown as reported, with various expansion factors and levels of confidence.
The black line represents Xref, the green dotted lines delimit the reference interval **(X_{ref} ± 2u_{ref}: 33,7 ± 3,7 mg kg^{-1})**, the red dashed lines delimit the target interval **(X_{ref} ± 2σ: 33,7 ± 6,0 mg kg^{-1})**

Annex 11: Extractable Cd in mineral feed

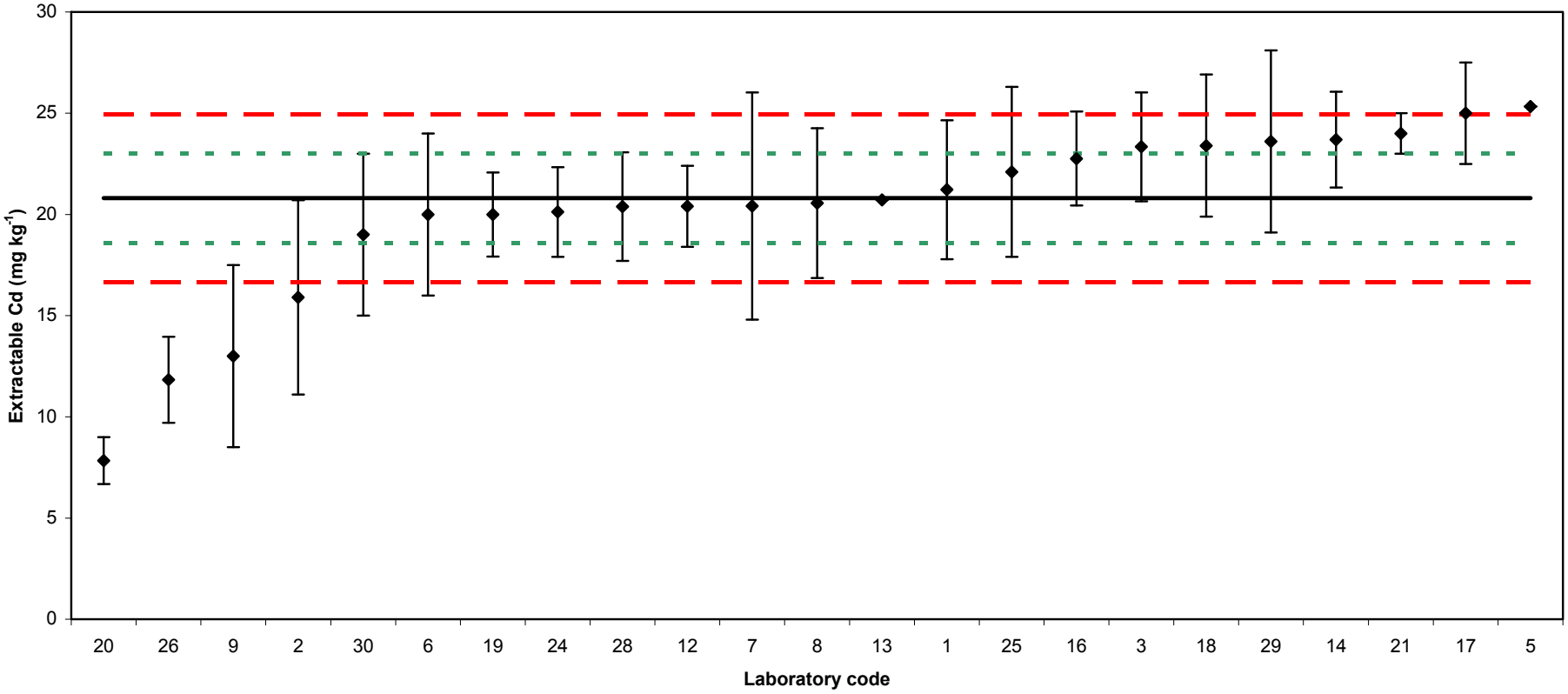
X_{ref} = 20,8 ± 2,2 mg kg^{-1} (*k*=2)

Lab ID	X_{lab} (mg kg^{-1})	U_{lab} (mg kg^{-1})	k	u_{lab} (mg kg^{-1})	Technique	z	ζ	$Qual_u$
1	21,22	3,43	2	1,72	ETAAS	0,2	0,2	**a**
2	15,9	4,8	2	2,4	ICP-MS	-2,4	-1,9	**c**
3	23,34	2,69	2	1,35	ETAAS	1,2	1,5	**a**
5	25,331	0,001	2	0,001	ETAAS	2,2	4,1	**b**
6	20	4	2	2	ICP-MS	-0,4	-0,4	**a**
7	20,41	5,61	2	2,81	ICP-MS	-0,2	-0,1	**c**
8	20,56	3,70	2	1,85	ICP-OES	-0,1	-0,1	**a**
9	13,0	4,5	2	2,3	ICP-OES	-3,8	-3,1	**c**
12	20,4	2,0	2	1,0	ICP-MS	-0,2	-0,3	**b**
13	20,72	0	√3	0	ZETAAS	0,0	-0,1	**b**
14	23,7	2,37	2	1,19	FAAS	1,4	1,8	**a**
16	22,76	2,32	2	1,16	ZETAAS	0,9	1,2	**a**
17	25,0	2,5	2	1,3	ICP-OES	2,0	2,5	**a**
18	23,4	3,51	2	1,76	FAAS	1,3	1,3	**a**
19	20,00	2,08	2	1,04	ETAAS	-0,4	-0,5	**b**
20	7,84	1,16	2	0,58	ICP-MS	-6,2	-10,4	**b**
21	24,0	1,0	2	0,5	ETAAS	1,5	2,6	**b**
24	20,12	2,22	2	1,11	AAS	-0,3	-0,4	**a**
25	22,1	4,2	2	2,1	ETAAS	0,6	0,5	**a**
26	11,83	2,13	2	1,07	ETAAS	-4,3	-5,9	**b**
28	20,39	2,68	2	1,34	FAAS	-0,2	-0,2	**a**
29	23,6	4,5	2	2,3	ICP-OES	1,3	1,1	**c**
30	19	4	1,732	2	ETAAS	-0,9	-0,7	**a**

$Qual_u$: qualitative information about u_{lab}**: a**: $u_{ref}<u_{lab}<\hat{\sigma}$; **b**: $u_{lab}<u_{ref}$; **c**: $\hat{\sigma}<u_{lab}$. For further information on these codes, please read chapter 8.2.

IMEP-111: Results for Extractable Cd

Certified range: 20,8 ± 2,2 mg kg^{-1} (*k* =2)



This graph displays all measurements results and their associated uncertainties.
The uncertainties are shown as reported, with various expansion factors and levels of confidence.
The black line represents Xref, the green dotted lines delimit the reference interval **(X_{ref} ± 2u_{ref}: 20,8 ± 2,2 mg kg^{-1})**, the red dashed lines delimit the target interval **(X_{ref} ± 2σ: 20,8 ± 4,2 mg kg^{-1})**

Annex 12: Extractable Pb in mineral feed

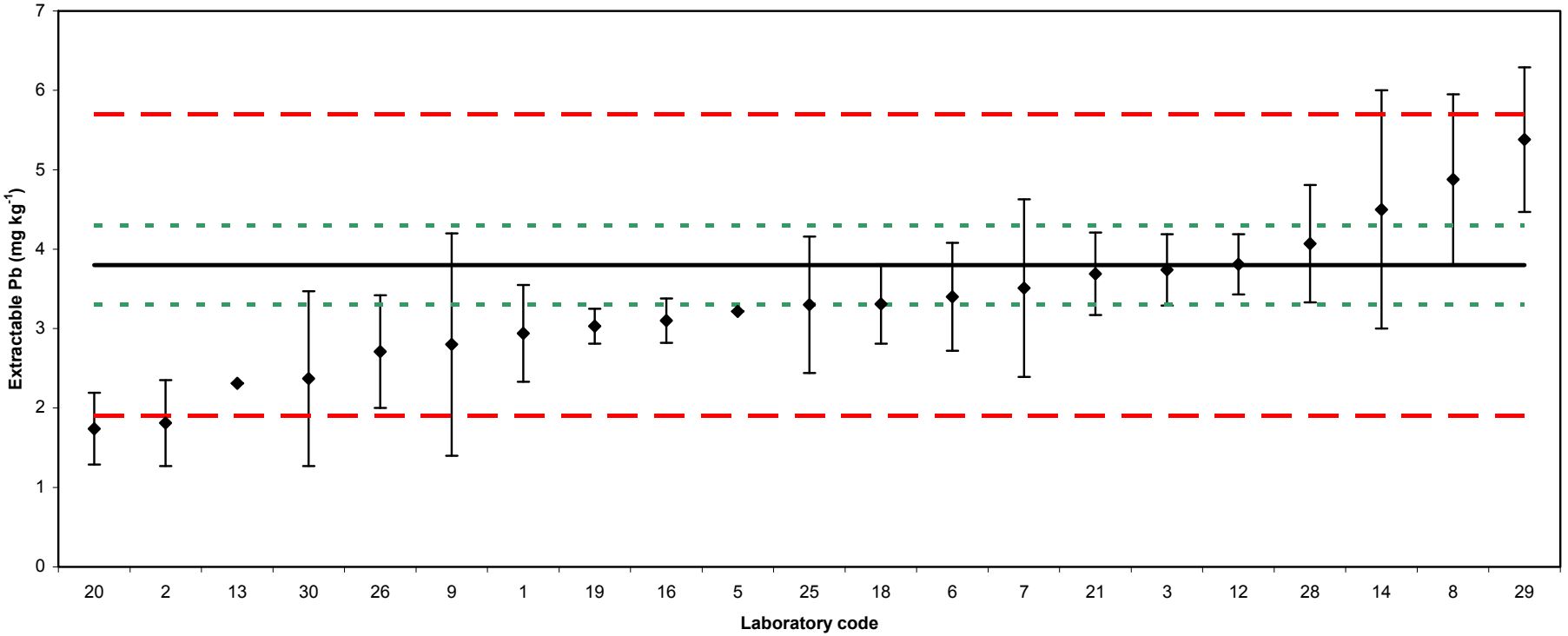
X_{ref} = 3,8 ± 0,5 mg kg^{-1} (*k*=2)

Lab ID	X_{lab} (mg kg^{-1})	U_{lab} (mg kg^{-1})	k	u_{lab} (mg kg^{-1})	Technique	z	ζ	$Qual_u$
1	2,94	0,61	2	0,31	ETAAS	-1,1	-2,2	**a**
2	1,81	0,54	2	0,27	ICP-MS	-2,6	-5,4	**b**
3	3,74	0,45	2	0,23	ICP-MS	-0,1	-0,2	**b**
5	3,218	0,001	2	0,001	ETAAS	-0,8	-2,3	**b**
6	3,4	0,68	2	0,34	ICP-MS	-0,5	-0,9	**a**
7	3,51	1,12	2	0,56	ICP-MS	-0,4	-0,5	**a**
8	4,88	1,07	2	0,54	ICP-OES	1,4	1,8	**a**
9	2,8	1,4	2	0,7	ICP-OES	-1,3	-1,3	**a**
12	3,81	0,38	2	0,19	ICP-MS	0,0	0,0	**b**
13	2,31	0	√3	0	ZETAAS	-2,0	-6,0	**b**
14	4,5	1,5	2	0,8	ETAAS	0,9	0,9	**a**
16	3,10	0,28	2	0,14	ZETAAS	-0,9	-2,4	**b**
17	<0,70				ICP-OES			
18	3,31	0,50	2	0,25	ETAAS	-0,6	-1,4	**b**
19	3,03	0,22	2	0,11	ETAAS	-1,0	-2,8	**b**
20	1,74	0,45	2	0,23	ICP-MS	-2,7	-6,1	**b**
21	3,69	0,52	2	0,26	ETAAS	-0,1	-0,3	**b**
24	1,21	0,13	2	0,07	AAS	-3,4	-10,0	**b**
25	3,3	0,86	2	0,43	ETAAS	-0,7	-1,0	**a**
26	2,71	0,71	2	0,36	ETAAS	-1,4	-2,5	**a**
28	4,070	0,74	2	0,37	FAAS	0,4	0,6	**a**
29	5,38	0,91	2	0,46	ICP-OES	2,1	3,0	**a**
30	2,37	1,1	1,732	0,6	ETAAS	-1,9	-2,1	**a**

$Qual_u$: qualitative information about u_{lab}**: a**: $u_{ref}<u_{lab}<\hat{\sigma}$; **b**: $u_{lab}<u_{ref}$; **c**: $\hat{\sigma}<u_{lab}$. For further information on these codes, please read chapter 8.2.

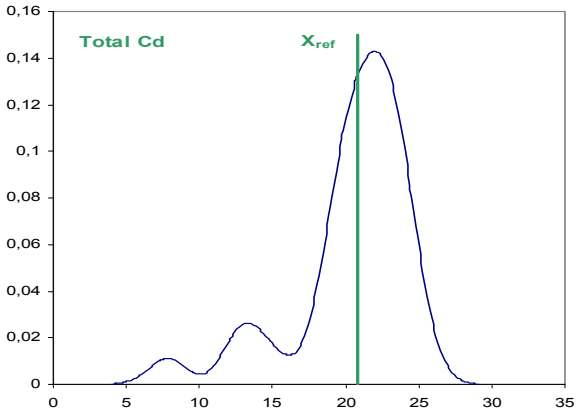
IMEP-111: Results for extractable Pb

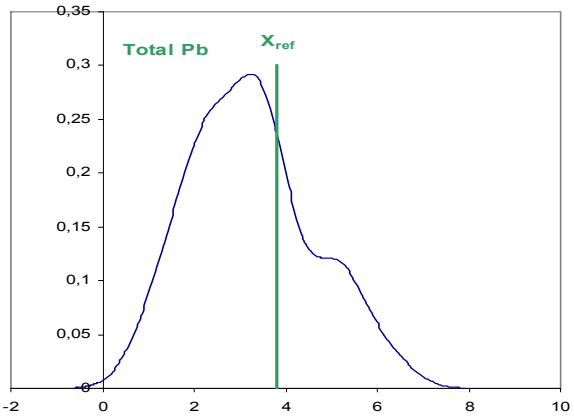
Certified range: 3,8 ± 0,5 mg kg^{-1} (*k* =2)

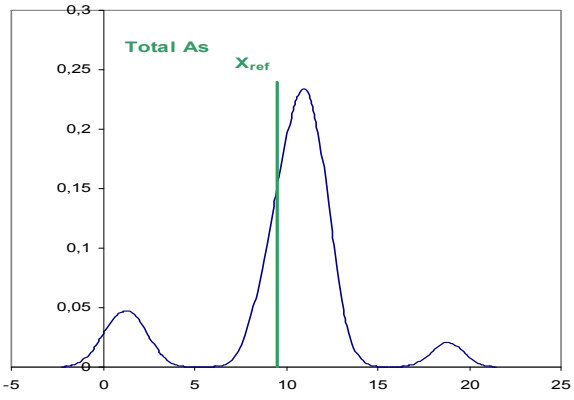


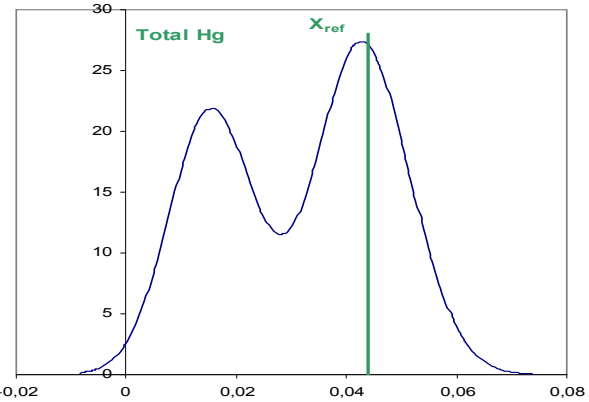
This graph displays all measurements results and their associated uncertainties.
The uncertainties are shown as reported, with various expansion factors and levels of confidence.
The black line represents Xref, the green dotted lines delimit the reference interval **(X_{ref} ± 2u_{ref}: 3,8 ± 0,5 mg kg^{-1})**, the red dashed lines delimit the target interval **(X_{ref} ± 2σ: 3,8 ± 2,0 mg kg^{-1})**

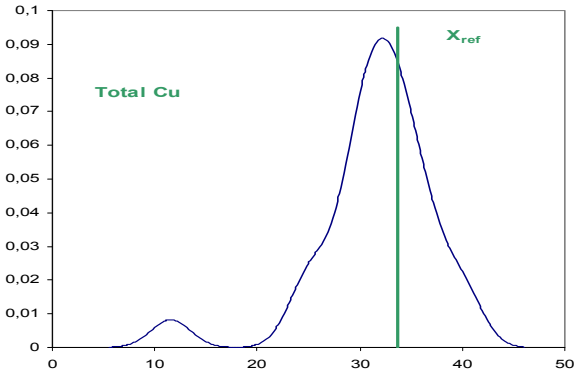
Annex 13: Kernel distributions

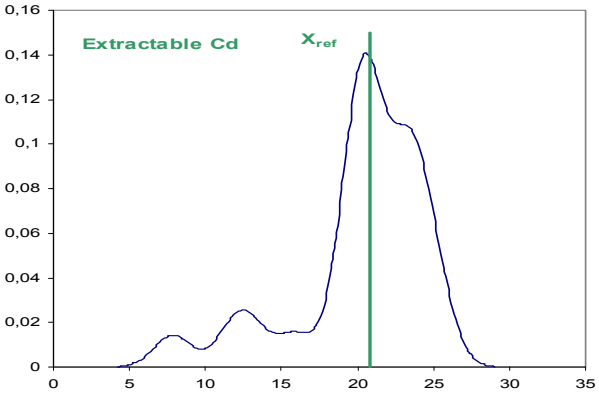


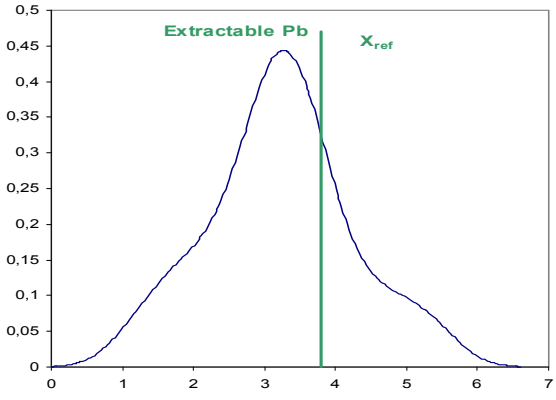












Annex 14: Experimental details for total Cd, Pb, As, Hg and Cu determinations

LCode	SOP?	If yes which	Sample pre-treatment	Digestion step	Extraction/separation step	Instrument calibration
1	yes	AOAC 999.11 Pb, Cd, Cu; AOAC 971.21 - Hg; In-house -As				
2	no		Mixing	Nitric acid, 180°C microwave		External linear
3	yes	EN15550				
4	no		No	HNO_3 + H_2O_2	No	External calibration
5	yes					
6	no			Microwave with ac. Nitric		
7	no		No pre treatment required, weighing of sample with analytical balance	Microwave digestion with H_2O_2, HNO_3 and Water	Dilution of digested solution to 100ml.	ICP-MS Calibrated with Pb, Cd, As, Hg standard solutions. AAS calibrated with Cu standard solutions.
8	yes	EN 15550, CEN/TS 15621, EN 13806				
9	no		Internal method with AAE	-1,0%	Filtration with Teflon filter 1µm	Yes before analysis
10	no		None	high pressure microwave with conc. HNO_3 and H_2O_2		External calibration, internal standard indium
11	yes	AOAC				
12	no					ICP-MS with collision/reaction cell
13	yes	Cu: Reg. 152/2009: As: ISTISAN 34/96		Microwave high pressure digestion with H_2O_2 30%, HNO_3 conc. and HF conc.		ADD. METHOD: STD solutions: CD 2ppb; Pb 50 ppb; As 20 ppb; Linear calib: Cu 1,3,4,5 ppm. Non linear calib: Hg from 25 ppb to 5 ppm
14			Homogenisation	Microwave digestion	No	5 points calibration
15	yes	EN 14082				
16	yes	For Pb, Cd LST EN 15550:2008, For Hg SOP 161:2010, For Cu LST EN ISO 6869:2003		For As Micro wave		1-10 ppb
17	no		Bomb digestion with nitric acid (Cd and Pb). Hg digestion with perchloric acid and nitric acid	Bomb digestion for 3 hours at 160 degrees (Pb and Cd). Hg digestion in open vessels overnight with final temp 180 degrees.	After digestion dilution to 10 ml with ultra-pure water (Pb and Cd). Hg dilution with 0.5 M HCl to 25 ml sample solution	Pb and Cd 5 standard solutions 0, 0.05, 0.10, 0,25 and 0,50 mg/l. For Hg 0, 1.0, 4.0, 8.0, 12.0 and 16.0 µg/ml
18	no	VO (EG) Nr. 152/2009 for Cu		Open digestion with conc. HNO_3 for Pb; open digestion with conc. HNO_3/$HClO_4$ for As, Cd and Hg;		External Calibration for all Methods

LCode	SOP?	If yes which	Sample pre-treatment	Digestion step	Extraction/separation step	Instrument calibration
19	no			Nitric acid, 220 C, 30min		External calibration
20	no		Addition of nitric acid and hydrogen peroxide, let it stand for 1 hour	Microwave	Dilution	External standard
21	no		None	Open tube using nitric acid and ashing for As	None	NA
23	yes	Official Methods of Analysis AOAC				
24	no					
25	yes	In house validated method RSV 1057				
26	no		Dry in oven	Ashing in muffle furnace, dissolved in HCL, Hg - AMA 254		Calibration curve for Pb (10-60 ug/l); Cd (1-10 ug/l); Hg (0.05-5ug/l); Cu (0.2-3.0 ug/l
27	no		Sample homogenisation by shaking	Microwave digestion with 3 ml nitric acid and 1 ml hydrogen peroxide		Aqueous solutions, internal standard Rh
28	yes	SR EN 13806; SR EN 14082; SR EN 14083; SR EN 14546				
29	yes	Cu: EC 152/2009, Pb/Cd DS/EN 15510:2007 (mod.), Hg DS/EN 13806:2002 (mod.)	As: CEN Draft method; 2g of sample is pre-dried at 100 C with a magnesium solution.	As: Ashing at 595 C over night	Extraction of As ash with 6M hydrochloric acid	HG-AAS with external calibration
30	yes	AOAC 999.11				
31	no	SOP FFF/B1-2005				

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Abstract
The Institute for Reference Materials and Measurements (IRMM) of the Joint Research Centre, a Directorate General of the European Commission, operates the European Union Reference Laboratory for Heavy Metals in Feed and Food (EU-RL-HM). One of its core tasks is to organize interlaboratory comparisons (ILCs) among appointed National Reference Laboratories. This report presents the results of the eleventh proficiency test (PT) of the EU-RL-HM which focused on the determination of total Cd, Pb, As, Hg and Cu and 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. The material was relabelled to prevent identification by the participants and was dispatched the second half of October 2010. Each participant received one bottle containing approximately 100 g of test material. Thirty-one laboratories from 26 countries registered to the exercise of which 28 reported results for total Cd and total Pb, 25 for total Hg and total Cu, 23 for total As and for extractable Cd and extractable Pb. The assigned values (X_{ref}) for total Cd, As and Cu are the indicative values taken from the BCR-032 certificate. The assigned values (X_{ref}) for total Pb, total Hg and for extractable Cd and Pb were provided by IRMM using isotope dilution-inductively coupled plasma-mass spectrometry (ID-ICP-MS).

For total Cd, As, Hg and Cu and for extractable Cd, the uncertainty of the assigned values (u_{ref}) was calculated by combining the uncertainty of the characterization (u_{char}) and a contribution for between-bottle homogeneity (u_{bb}) (which was calculated from the certification report). For total and extractable 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} included a contribution for the homogeneity. For total Cd, As and Cu, u_{char} were taken from the CRM certificate as indicated by the producer. For extractable Cd the same u_{char} as for total Cd was used. For total Pb and Hg and for extractable Pb, u_{char} was calculated according to the ISO Guide for the Expression of Uncertainty in Measurement (GUM). Participants were invited to report the uncertainties of their measurements. This was done by the majority of the laboratories taking part in this exercise.

Laboratory results were rated using z- and ζ-scores (zeta-scores) in accordance with ISO 13528. The standard deviation for proficiency assessment ($\hat{\sigma}$), also called target standard deviation, were calculated applying the modified Horwitz equation for total Cd, As and Cu and for extractable Cd. However, for total Hg, $\hat{\sigma}$ was set to 15 % on the basis of previous experience of the EU-RL-HM with this network of laboratories. For total Pb, $\hat{\sigma}$ was set at 25 % due to micro-inhomogeneity observed when small aliquots were taken for analysis. For extractable Pb we used the same criteria as for total Pb to score the participants ($\hat{\sigma}$ = 25 %).

Between 70 and 80 % of the laboratories reported satisfactory results for all measurands but Hg. For the latter, only 57 % of the laboratories submitted satisfactory results. All the questionable and unsatisfactory results for Hg were obtained using direct thermal decomposition-based methods.

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