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EURL-HM-23 Proficiency Test Report

Determination of total As, Cd, Pb, Hg and inorganic As in palm kernel expeller

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European Union Reference Laboratory
Heavy Metals in Feed and Food

EURL-HM-23 Proficiency test report

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Executive summary

The European Union Reference Laboratory for Heavy Metals in Feed and Food (EURL-HM) organised a proficiency test (EURL-HM-23) for the determination of total As, Cd, Pb, Hg, and inorganic As (iAs) mass fractions in palm kernel expeller to support Directive 2002/32/EC on undesirable substances in animal feed. This PT was open only to National Reference Laboratories (NRLs).

The EURL-HM-23 test item was a palm kernel expeller spiked with As, Cd, Hg and Pb. The homogeneity and stability of the test item were evaluated and the assigned values were derived from the results reported by the selected expert laboratories.

Thirty four National Reference Laboratories from thirty countries (all EU member states plus Iceland and Norway) registered to the exercise and reported results.

Laboratory results were rated using *z*- and zeta (ζ-) scores in accordance with ISO 13528:2015. The following relative standard deviations for proficiency assessment (σ_{pt}) were set according to the modified Horwitz equation: 15% for total As and iAs; 16% for Cd; 17% for Pb and 22% for Hg.

More than 87% of the participating NRLs reported satisfactory results (according to the z-score) for total As, Cd, Pb and Hg, and more than 76% for iAs, thus confirming their ability in monitoring maximum levels set by the EU Directive 2002/32/EC.

Most of the laboratories provided realistic estimates of their measurement uncertainties.

1 Introduction

Palm kernel expeller (PKE) is a by-product from the crushing and expelling of oil from the kernel (seed) of palm tree fruits. Because of its medium-grade protein, high fibre, good level of residual oil and high palmitic acid, it is widely used in compound feeds for adult ruminant livestock such as dairy cow, beef cow and sheep [1],[2],[3].

The European Directive 2002/32/EC on undesirable substances in animal feed [4] set a maximum level for arsenic in PKE of 4 mg kg^{-1} relative to a feed with a moisture content of 12 %. In 2011 several notifications were introduced in the the Rapid Alert System for Food and Feed (RASFF) related to high arsenic content in PKE to be imported into a Member State (https://webgate.ec.europa.eu/rasff-window/).

The European Union Reference Laboratory for Heavy Metals in Feed and Food (EURL-HM), hosted by the Joint Research Centre in Geel (JRC-Geel), organised the proficiency test (PT) EURL-HM-23 for the determination of total arsenic (As), cadmium (Cd), lead (Pb), mercury (Hg) and inorganic Arsenic (iAs) mass fractions in PKE. This PT was agreed with the Directorate General for Health and Food Safety (DG SANTE) in the annual work programme 2016 of the EURL-HM.

This report summarises the outcome of this PT.

2 Scope

As stated in Regulation (EC) No 882/2004 [5] one of the core duties of EURLs is to organise interlaboratory comparisons for the benefit of NRLs.

The present PT aims to assess the performance of NRLs in the determination of total As, Cd, Pb, Hg and iAs mass fractions in a PKE dry powder.

In addition, participants were asked to evaluate the conformity of the analysed material according to the maximum levels (MLs) set in legislation.

The reported results were assessed following the administrative and logistic procedures of the JRC Unit in charge of the EURL-HM, which is accredited for the organisation of PTs according to ISO 17043:2010 [6].

This PT is identified as EURL-HM-23.

3 Set up of the exercise

3.1 Time frame

The organisation of the EUR-HM-23 exercise was agreed upon by the NRL network at the 10th EURL-HM Workshop held in Brussels on September 28-29, 2015. The exercise was announced on the JRC webpage on March 18, 2016 (Annex 2) and an invitation letter was sent (via e-mail) to all NRLs of the network on April 4, 2016 (Annex 3). The registration deadline was set to April 29, 2016. Samples were sent to participants on May 12, 2016. Dispatch was monitored by the PT coordinator using the messenger's parcel tracking system on the internet. The deadline for reporting of results was set to June 30, 2016.

3.2 Confidentiality

The procedures used for the organisation of PTs, are accredited according to ISO 17043:2010 [6] and guarantee that the identity of the participants and the information provided by them is treated as confidential.

3.3 Distribution

Each participant received:

- One bottle of the test item (approx. 20 g of material);
- The "Test item accompanying letter" (Annex 4); and
- A "Confirmation of receipt form" to be sent back to JRC-Geel after receipt of the test item (Annex 5).

3.4 Instructions to participants

Detailed instructions were given to participants in the "Test item accompanying letter" mentioned above. Measurands were defined as "the mass fractions of total As, Cd, Pb, Hg and iAs in palm kernel expeller dry powder".

Participants were asked to perform two or three independent measurements, to report their calculated mean (x_i) and the associated expanded measurement uncertainty (U(x_i)) together with the coverage factor (k) and analytical technique used for the analysis.

Results were to be reported relative to a feed with a moisture content of 12 % as required by Directive 2002/32/EC.

Upon specific request from DG SANTE, no instructions were provided by the EURL-HM to laboratories on how to perform the moisture corrections necessary for reporting, since official control laboratories are supposed to know the proper procedure.

Participants received an individual code to access the on-line reporting interface, to report their measurement results and to complete the related questionnaire. A dedicated questionnaire was used to gather additional information related to measurements and laboratories (Annex 6).

Participants were informed that the procedure used for the analysis should resemble as closely as possible their routine procedures for this type of matrix/analytes and mass fraction levels.

The laboratory codes were given randomly and communicated to the participants by e-mail.

4 Test item

4.1 Preparation

The Belgian NRL (CODA-CERVA) kindly provided the starting material - 10 kg of PKE in granulated form - that was used for the preparation of the test items. The delivered material was directly stored at 4 °C until processing.

The material was first cryogenically milled using a Palla VM-KT vibrating mill from Humboldt-Wedag (Köln, Germany). After milling, the material was sieved over a 250 µm stainless steel sieve. About 8.5 kg of the fine fraction was collected and stored at 4 °C.

About 4.9 kg was mixed in a Dynamix CM-200 (WAB, Basel, Switzerland) for one hour. The material was then spiked with As, Cd, Pb and Hg: 4840.6 g of powder were placed in a 60 L plastic drum to which 10 L of MilliQ water were added to make a homogeneous suspension. Then 1 L of spike solution was added to the suspension and was stirred for 30 min. The spiked material was freeze dried in a Martin Christ model Epsilon 2-100D freeze dryer (Osterode, Germany). The freeze dried palm kernel expeller powder was mixed in a Dynamix CM-200 for one hour.

Portions of 20 g were manually filled into 100 ml amber glass acid-washed bottles using acid washed plastic spoons under an extraction point. The bottles were closed with acid washed inserts and screw caps.

Each vial was identified with a unique number and the name of the PT exercise.

4.2 Homogeneity and stability

Measurements for the homogeneity and stability studies were performed by ALS Scandinavia AB (Luleå, Sweden).

Inductively coupled plasma mass spectrometry (ICP-MS) was used after microwave digestion (0.3-0.5 g of sample in a mixture of HNO_3/H_2O_2) to determine the mass fractions of total As, Cd, Pb and Hg.

The statistical treatment of data was performed by the EURL-HM.

Homogeneity was evaluated according to ISO 13528:2015 [7]. The test item proved to be adequately homogeneous for the investigated analytes.

The stability study confirmed that the material was stable and the uncertainty contribution due to stability was set to zero ($u_{st} = 0$) for all analytes.

The contribution from homogeneity (u_{hom}) to the standard uncertainty of the assigned value ($u(x_{pt})$) was calculated using SoftCRM [8]. The analytical results reported by the expert laboratory and the statistical evaluation of the homogeneity and stability studies are presented in Annex 7 and Table 1.

5 Assigned values and corresponding uncertainties

5.1 Assigned values

The assigned values (x_{pt}) of the five measurands (mass fractions of total As, Cd, Pb, Hg and iAs in palm kernel expeller *relative to a moisture content of 12 %*), were derived from the results reported by expert laboratories, all selected on the basis of their demonstrated measurement capabilities.

The following expert laboratories analysed one or more measurands:

- ALS Scandinavia AB (Luleå, Sweden);
- CSPA - Centro de Salud Pública de Alicante (Alicante, Spain);
- SCK-CEN - Studiecentrum voor Kernenergie (Mol, Belgium);
- UBA - Umweltbundesamt GmbH (Wien, Austria);
- Institute for Chemistry, University of Graz (Graz, Austria)
- JRC-Geel, Directorate F - Health, Consumers and Reference Materials (Geel, Belgium)
- Faculty of Chemistry, University of Barcelona (Barcelona, Spain)

Expert laboratories were asked to use the method of analysis of their choice and no further requirements were imposed regarding methodology. They were also requested to report their results together with the associated expanded measurement uncertainty and with a clear and detailed description on how their measurement uncertainty was calculated. Results were to be reported *relative to a feed with a moisture content of 12 %* as required by Directive 2002/32/EC.

- ALS Scandinavia used inductively coupled plasma mass spectrometry (ICP-MS) after closed microwave digestion of the sample (approx. 0.3-0.5 g in closed Teflon containers) using HNO_3 and H_2O_2. Analyses were made according to the modified ISO 17294-1, 2 and modified US EPA Method 200.8 for the measurement of total As, Cd, Pb and Hg.

- CSPA used ICP-MS after microwave digestion of the sample (approx. 0.25 g in quartz digestion vessels) using HNO_3 and H_2O_2 for measuring total As, Cd and Pb. The measurement of Hg was performed by Direct Mercury Analyser (DMA).

- SCK-CEN applied instrumental neutron activation analysis (k_0-NAA) for the determination of total As, Cd and Hg mass fractions. Three samples of (approx. 350 mg) were transferred in standard high-density polyethylene vials and weighed. Samples were irradiated for seven hours in channel Y4 of the BR1 reactor under a thermal flux of 3 10^{11} n s^{-1} cm^2 together with several IRMM-530 (Al-0.1 % Au alloy) neutron flux monitors and two reference materials (SMELLS II and NIST 1633b 'Coal fly ash') used for validation. Three spectra of each sample were collected on a k_0-calibrated HPGe detector under repeatability conditions: 1 day, 2 days and 13-15 days after irradiation for the determination of As, Ca and finally Hg, respectively. Only an indicative value was reported for Hg.

- UBA used ICP-MS according to ISO 17294-2 for the determination of As, Cd and **Pb**. The measurement of Hg was done by Cold Vapour Atomic Absorption Spectrometry (CV-AAS) according to ISO 12846, while iAs was determined using HPLC-ICP-MS according to ISO 17294-2.

- The University of Graz determined total As in about 250 mg of the sample after microwave-assisted digestion with HNO_3 by ICP-MS using (i) helium as the collision cell gas to remove polyatomic interferences and (ii) ^{74}Ge and ^{115}In as internal standards. For iAs, samples of about 500 mg were heated with a solution of CF_3COOH/H_2O_2 (95 ^{o}C for 60 min) and analysed by HPLC-ICP-MS.

- JRC-Geel analysed total As by ICP-MS; Cd and Pb by ID-ICP-MS; and Hg by CV-AAS, applying the following experimental protocols:

  Samples (0.25 to 0.5 g) were digested in a Milestone Ultraclave micro-wave digestion apparatus with (i) 5 mL concentrated nitric acid (for As) or with (ii) 5 mL concentrated nitric acid and 0.5 mL of concentrated hydrofluoric acid (for Cd, Hg and Pb).

  Digests for As, Cd and Pb measurement were diluted in 2 % nitric acid solution, and for Pb measurement, about 1 µg/L Tl (IRMM-649 isotopic certified reference material) was added.

  As, Cd and Pb were measured on an Agilent 7500ce inductively coupled plasma mass spectrometer, using a He-filled collision cell for As measurement. Arsenic was measured by external calibration with 5 standards.

  For isotope dilution measurements, samples were blended with IRMM-622 (^{111}Cd enriched) and Inorganic Ventures (^{206}Pb enriched) isotopic certified reference materials prior to sample digestion. For Cd isotope dilution measurements, the $^{113}Cd/^{111}Cd$ ratio was measured using digests of an unspiked sample and tabulated natural isotopic abundances as reference. For Pb measurement, the Pb molar mass was measured in an unspiked sample using the Tl internal standard (IRMM-649) as reference, and the isotope dilution measurement used the $^{206}Pb/^{208}Pb$ ratio, again using the Tl internal standard as reference.

Digests for Hg measurement were mixed with 1 ml of a 6 % potassium permanganate solution and a 20 % hydroxylamine solution is added until the solution is colourless. The digests were made up to about 35 mL before measurement. Hg was measured on an Analytik-Jena Zeenit 600 atomic absorption spectrometer fitted with a "Hydrea" cold-vapour generation system and Ir-coated graphite furnace for sample concentration. Sub-samples of 10 mL of digests were measured batch-wise alongside 4 standards for external calibration.

- The University of Barcelona analysed iAs weighing about 0.2 g of test material in PTFE vessels and carrying out a microwave digestion with a HNO_3/H_2O_2 solution followed by an HPLC-ICP-MS analysis.

5.2 Associated uncertainties

The associated standard uncertainties of the assigned values ($u(x_{pt})$) were calculated following the law of uncertainty propagation, combining the standard measurement uncertainty of the characterization (u_{char}) with the standard uncertainty contributions from homogeneity (u_{hom}) and stability (u_{st}), in compliance with ISO Guide 35 [9].

$$\boldsymbol{u(x_{pt}) = \sqrt{u_{char}^2 + u_{hom}^2 + u_{stab}^2}}$$

The uncertainty u_{char} is estimated according to the recommendations of ISO Guide 35 [9]:

$$\boldsymbol{u_{char} = \frac{s}{\sqrt{p}}}$$

where "s" refers to the standard deviation of the mean values obtained by the expert laboratories and "p" refers to the number of expert laboratories.

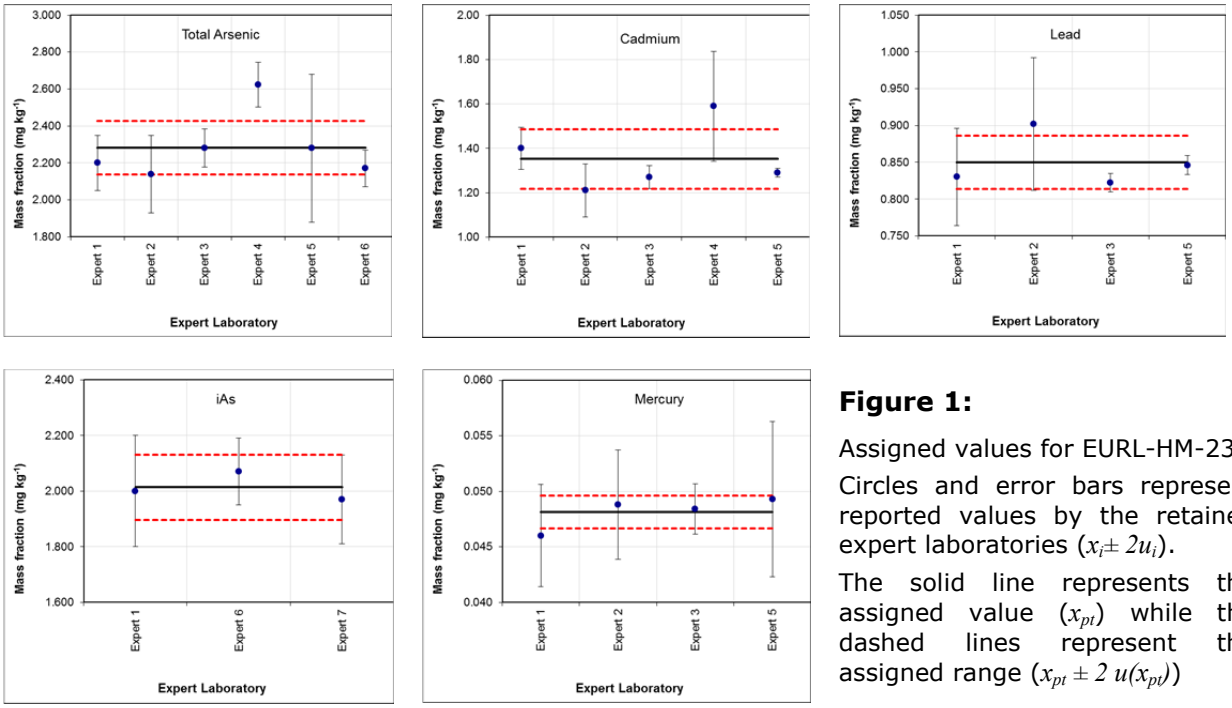

Figure 1:

Assigned values for EURL-HM-23.

Circles and error bars represent reported values by the retained expert laboratories ($x_i \pm 2u_i$).

The solid line represents the assigned value (x_{pt}) while the dashed lines represent the assigned range ($x_{pt} \pm 2\ u(x_{pt})$)

5.3 Standard deviation of the proficiency test assessment, σ_{pt}

All the relative standard deviations for PT assessment (σ_{pt}, in mg kg^{-1} and %) presented in Table 1 were calculated using the Horwitz equation modified by Thompson [10].

Table 1: Results and associated expanded measurement uncertainties (as) reported by expert laboratories; the assigned values (x_{pt}, $u(x_{pt})$ and $U(x_{pt})(k=2)$); the standard uncertainties (u_{char}, u_{st} and u_{hom});and the standard deviation for PT assessment σ_{pt}. Values are expressed in mg kg^{-1} relative to PKE with a moisture content of 12 %.

	tot-As	Cd	Pb	Hg	iAs
Expert 1	2.2 ± 0.15	1.4 ± 0.095	0.83 ± 0.066	0.046 ± 0.0046	2.0 ± 0.2
Expert 2	2.14 ± 0.21	1.21 ± 0.12	0.902 ± 0.09	0.0488 ± 0.0049	
Expert 3	2.28 ± 0.103	1.27 ± 0.0521	0.822 ± 0.0127	0.0484 ± 0.00227	
Expert 4	2.624 ± 0.121	1.589 ± 0.247			
Expert 5	2.28 ± 0.4	1.29 ± 0.019	0.8461 ± 0.013	0.0493 ± 0.007	
Expert 6	2.17 ± 0.1				2.07 ± 0.12
Expert 7					1.97 ± 0.16
x_{pt}	**2.28**	**1.35**	**0.850**	**0.0481**	**2.01**
u_{char}	0.072	0.067	0.018	0.00073	0.030
u_{hom}	0.037	0.015	0.008	0.00080	0.032
u_{st}	0	0	0	0	0
$u(x_{pt})$	0.081	0.068	0.020	0.00109	0.044
$U(x_{pt})$*	**0.16**	**0.14**	**0.039**	**0.0022**	**0.09**
σ_{pt}	0.34	0.22	0.145	0.0106	0.30
σ_{pt} (%)	15%	16%	17%	22%	15%
$u(x_{pt})/\sigma_{pt}$	0.24	0.32	0.14	0.10	0.14

6 Evaluation of results

6.1 Scores and evaluation criteria

Individual laboratory performance was expressed in terms of z- and ζ-scores according to ISO 13528:2015 [7]:

$$z_i = \frac{x_i - x_{pt}}{\sigma_{pt}} \qquad \text{Eq. 1}$$

$$\zeta_i = \frac{x_i - x_{pt}}{\sqrt{u^2(x_i) + u^2(x_{pt})}} \qquad \text{Eq. 2}$$

where: x_i is the measurement result reported by a participant;

$u(x_i)$ is the standard measurement uncertainty reported by a participant;

x_{pt} is the assigned value;

$u(x_{pt})$ is the standard measurement uncertainty of the assigned value;

σ_{pt} is the standard deviation for proficiency test assessment.

The interpretation of the z- and ζ- scores is done according ISO 13528:2015 [7]:

|score| ≤ 2	satisfactory performance	(green in Annexes 8-13,15)
2 < |score| < 3	questionable performance	(yellow in Annexes 8-13,15)
|score| ≥ 3	unsatisfactory performance	(red in Annexes 8-13,15)

The z-score compares the participant's deviation from the assigned value with the standard deviation for proficiency test assessment (σ_{pt}) used as common quality criterion.

The ζ-score states whether the laboratory's result agrees with the assigned value within the respective uncertainty. The denominator is the combined uncertainty of the assigned value $u(x_{pt})$ and the measurement uncertainty as stated by the laboratory $u(x_i)$. The ζ-score includes all parts of a measurement result, namely the expected value (assigned value), its measurement uncertainty in 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 measurement uncertainty, or both.

The standard measurement uncertainty of the laboratory $u(x_i)$ was obtained by dividing the reported expanded measurement uncertainty by the reported coverage factor, k. When no uncertainty was reported, it was set to zero ($u(x_i) = 0$). When k was not specified, the reported expanded measurement uncertainty was considered as the half-width of a rectangular distribution; $u(x_i)$ was then calculated by dividing this half-width by √3, as recommended by Eurachem and CITAC [11].

Uncertainty estimation is not trivial, therefore an additional assessment was provided to each laboratory reporting measurement uncertainty, indicating how reasonable their measurement uncertainty estimation was.

The standard measurement uncertainty from the laboratory $u(x_i)$ is most likely to fall in a range between a minimum and a maximum allowed uncertainty (Case "a": $u_{min} \leq u_{lab} \leq u_{max}$). u_{min} is set to the standard uncertainties of the assigned values $u(x_{pt})$. It is unlikely that a laboratory carrying out the analysis on a routine basis would determine the measurand with a smaller measurement uncertainty than the expert laboratories chosen to establish the assigned value. u_{max} is set to the standard deviation accepted for the PT assessment (σ_{pt}). Consequently, Case "a" becomes: $u(x_{pt}) \leq u(x_i) \leq \sigma_{pt}$.

If $u(x_i)$ is smaller than $u(x_{pt})$ (Case "b") the laboratory may have underestimated its measurement uncertainty. Such a statement has to be taken with care as each laboratory reported only measurement uncertainty, whereas the uncertainty associated with the assigned value also includes contributions for homogeneity and stability of the test item. If those are large, measurement uncertainties smaller than u_{ref} are possible and plausible.

If $u(x_i)$ is larger than σ_{pt} (Case "c") the laboratory may have overestimated its measurement uncertainty. An evaluation of this statement can be made when looking at the difference between the reported value and the assigned value: if the difference is smaller than the expanded uncertainty $U(x_{pt})$ then overestimation is likely. If the difference is larger but x_i agrees with x_{pt} within their respective expanded measurement uncertainties, then the measurement uncertainty is properly assessed resulting in a

satisfactory performance expressed as a ζ-score, though the corresponding performance, expressed as a z-score, may be questionable or unsatisfactory.

It should be pointed out that "u_{max}" is a normative criterion when set by legislation.

6.2 General observations

Thirty four NRLs from thirty countries registered to the exercise, covering all EU member states plus Iceland and Norway. All registered NRLs reported results. The participants having reported results are listed in the "Acknowledgment" section.

Thirty two (out of 34) laboratories reported results for As, Cd, Pb while thirty one laboratories for Hg. Only 21 results were reported for iAs (Table 2).

Table 2: Overview of the number of reported results per measurand (out of 34).

	Reported Results	Comments
As	32 (94%)	No results from laboratories 020 and 034
Cd	32 (94%)	No results from laboratories 020 and 034
Pb	32 (94%)	Of which one "less than X" value; No results from laboratories 020 and 034
Hg	31 (91%)	Of which one "less than X" value; No results from laboratories 022, 034 and 036
iAs	21 (62%)	No results from 13 laboratories

6.3 Laboratory results and scorings

6.3.1 Performances

Annexes 8 to 12 present the reported results as tables and graphs for each measurand, where NRLs are denoted as "0XX". The corresponding Kernel density plots, obtained using the software available from the Statistical Subcommittee of the Analytical Methods Committee of the UK Royal Society of Chemistry [12] are also included.

The laboratory performance for the "determination of total As, Cd, Pb Hg and iAs in PKE relative to 12 % moisture content" were assessed using the z- and ζ-scores, since the ISO 13528 recommendation ($u(x_{pt}) \leq 0.3\ \sigma_{pt}$) was fulfilled for all measurands.

<u>Total (As, Cd, Pb, Hg) and iAs</u>

Figures 1 and 2 present the laboratory performances for total As, Cd, Pb and Hg, assessed by the z- and ζ-scores. Most of the participants having reported results performed satisfactorily for these measurands: above 87% for the z-score and 77% for the ζ-scores. Twenty three laboratories (out of 34) performed satisfactorily for the determination of the four measurands (total As, Cd, Pb and Hg). Similarly, most of the participants reporting for iAs performed satisfactorily for this measurand, with 76% of the z-scores and ζ-scores ≤ 2.

For As and Cd no direct correlations could be found between the analytical methods used by the laboratories and the quality of the reported results (see Annex 14).

Two unsatisfactory performances and a truncated value ("less than") were obtained for Pb applying AAS. This may be attributed to the relatively low level of Pb in the test item (0.85 mg kg^{-1}) compared to the higher MRL for Pb in animal feed (10 mg kg^{-1}). Annex 15

shows that for Pb LODs for AAS methods are generally higher than those for ICP-MS methods. Nevertheless, laboratory 003 may consider re-evaluating the high limit of quantification reported ("less than 1.8").

Similarly, two laboratories using CV-AAS reported the highest Hg results leading to z-scores above 3. Two other results for Hg obtained by AAS were flagged as unsatisfactory and questionable.

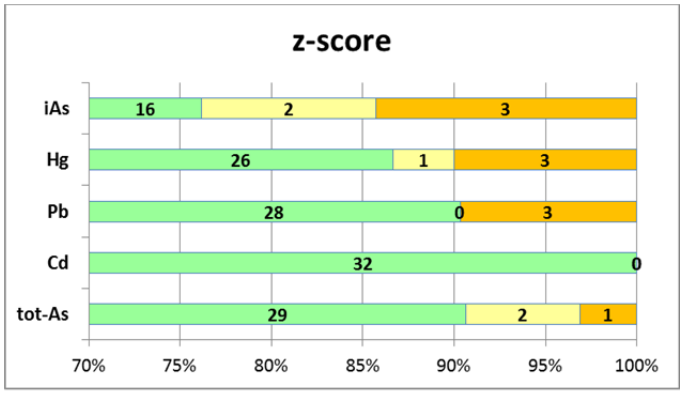

Figure 2:

Overview of laboratory performance per measurand according to z-scores.

Corresponding number of laboratories indicated in the graph.

Satisfactory (green); Questionable (yellow); Unsatisfactory (orange)

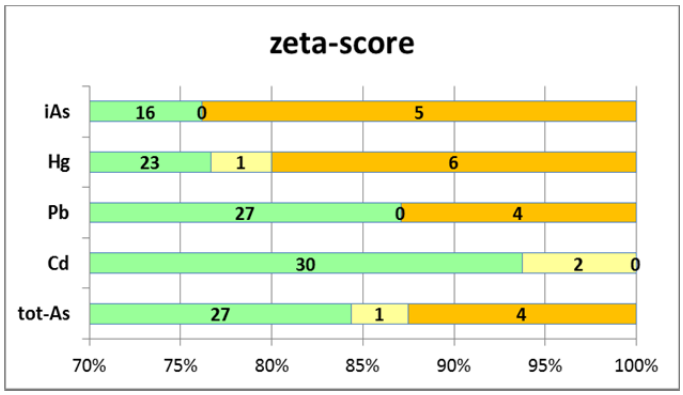

Figure 3:

Overview of laboratory performance per measurand according to ζ-scores.

Corresponding number of laboratories indicated in the graph.

Satisfactory (green); Questionable (yellow); Unsatisfactory (orange)

Truncated values

Two "less than X" values were reported, one for Pb and one for Cd. The limit values "X" reported by the laboratories usually correspond to the limits of quantification (LOQ) or limits of detection (LOD) of the applied methods. Those reporting "less than X" values were not included in the data evaluation. However, reported "less than X" values were compared with the corresponding $x_{pt} - U(x_{pt})$. If the reported limit value "X" is lower than the corresponding $x_{pt} - U(x_{pt})$, this statement is considered incorrect, since the laboratory should have detected the respective analyte. The two "less than X" values in this exercise were correct statements.

6.3.2 Uncertainties

Figure 3 presents the uncertainty assessment per measurand. Most of the participants (above 70%) reported realistic measurement uncertainty estimates for Cd, Hg, Pb and iAs (case "a": $u(x_{pt}) \leq u(x_i) \leq \sigma_{pt}$).

A lower number of realistic "case a" (59%) is obtained for total As. Of the 19% of underestimated "case b", three laboratories reported combined uncertainties ranging from 0.058 to 0.07 - to be compared to $u(x_{pt})$ = 0.08 mg kg^{-1}. Similarly, of the 22% of "case c", four laboratories reported combined uncertainties ranging from 0.35 to 0.37 - to be compared to σ_{pt} = 0.34 mg kg^{-1}.

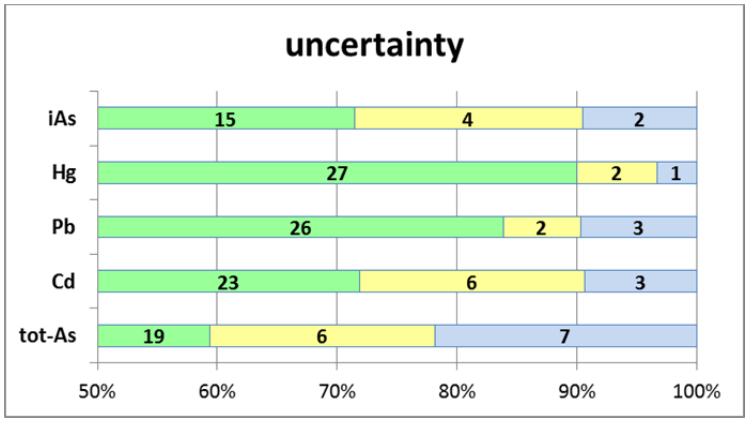

Figure 4:

Review of uncertainties reported per measurand.

Corresponding number of laboratories indicated in the graph.

Case "a" (green): $u(x_{pt}) \leq u(x_i) \leq \sigma_{pt}$
Case "b" (yellow) $u(x_i) < u(x_{pt})$;
Case "c" (blue)= $u(x_i) > \sigma_{pt}$

6.3.3 Compliance assessment

When comparing the maximum levels (MLs) - set in the European Directive 2002/32/EC for undesirable substances in animal feed - to the assigned ranges in the palm kernel expeller (Table 3), one concludes that the test item is non-compliant for cadmium (only) for which $x_{pt} - U(x_{pt})$ > ML.

Table 3: Maximum limits (MLs), assigned values and their associated expanded uncertainties. All values expressed in mg kg^{-1}, relative to PKE with a moisture content of 12 %.

Elements	$x_{pt} \pm U(x_{pt})$	MLs
As	2.28 ± 0.16	4
Cd	1.35 ± 0.14	1
Pb	0.85 ± 0.039	10
Hg	0.048 ± 0.0022	0.1

Participants were requested to assess the compliance of the test item according to Directive 2002/32/EC, and provide proper justification to support their statement. In order to assess the consistency of the laboratory compliance statement, one must consider the following three components:

1) the laboratory compliance statement (Compliant or Non-Compliant)
2) the laboratory measurement results:
   - reported (or not) for the relevant analyte (Cd);
   - to be compared to the relevant ML: $x_i - U_i$ > ML?
3) the laboratory justification (correct, incorrect or partially incorrect).

The answers received (Annex 14) are summarised in Table 4. Sixteen (out of 34) laboratories assessed correctly the test item to be non-compliant (47 % true non-compliant, TNC). Other four laboratories stated the material to be non-compliant while presenting partially incorrect justifications (12 % false non-compliant, FNC). Six laboratories assumed the material to be compliant (17 % true compliant, TC) due to either their low measurement results for Cd (cf. laboratories 003 and 036) or their large measurement uncertainty reported (cf. laboratories 004, 019, 005 and 013). Finally, four laboratories gave an inconsistent assessment (12 % false compliant, FC), while four other laboratories (12 %) did not provide any statement.

Table 4: Laboratory statements on the compliance assessment, laboratory measurement results for Cd compared to the ML, laboratory justifications (correct, incorrect or partially incorrect) and a categorisation of the laboratory compliance assessment into FC (false compliant), TC (true compliant), TNC (true non-compliant) and FNC (false non-compliant).

Laboratory Statement	Laboratory Measurement	Laboratory Justification	Category	Nr. of labs	Comment
Compliant	$x_i - U_i$ > ML	Correct	FC	1	025: x_i > ML
		None		2	
	No Cd result	None	FC	1	
	$x_i - U_i \leq$ ML	None	TC	6	
Non-Compliant	$x_i - U_i$ > ML	Correct	TNC	16	
		Part. incorrect	FNC	3	007: wrong ML(As); 012:wrong ML(Cd); 033: As & Hg
	$x_i - U_i \leq$ ML	Part. incorrect		1	008: x_i > ML
No Assessment				4	

6.3.4 Additional information from the questionnaire

The questionnaire was answered by all 34 participants. Different approaches were used to evaluate measurement uncertainties (Table 4). The majority of the NRLs carry out an in-house validation in order to estimate the measurement uncertainty (19 out of 34). Twenty-five out of 34 usually report uncertainty to their customers.

Laboratories were asked to report the LODs of the methods used for the determination of the five measurands. Annex 14 presents LODs, the general experimental conditions and the techniques used for the determination of total As, Cd, Pb and Hg. Large discrepancies in reported LODs are observed even among laboratories using the same technique.

Table 5: Approaches used to estimate measurement uncertainties. Multiple selections were possible.

Approach followed for uncertainty calculation	**Number of labs.**
According to ISO-GUM	7
According to ISO 21748	0
Derived from a single-laboratory validation study	19
Determined as standard deviation of replicate measurements	8
Estimation based on judgment	1
Derived from inter-comparison data	8
According to the NORDTEST guidelines	2
Applying the Horwitz equation	1

The reported recovery factors ranged from 80 to 113 % and two main approaches were used for the determination of recoveries: spiking and use of reference materials.

All of the NRLs stated that they have an ISO/IEC 17025 accreditation and 26 NRLs confirmed they are accredited for one or more of the investigated measurands in feed.

For some participants, the unsatisfactory performance could be linked to a lack of experience (evaluated as number of analyses per year) for this type of analysis.

7 Conclusion

The EURL-HM-23 PT was organised in 2016 to assess the analytical capabilities of the NRLs for the EU using a palm kernel expeller spiked with As, Cd, Pb and Hg as test item.

The overall performance of the participants in the determination of total As, Cd, Hg, Pb and iAs was satisfactory. This confirms the analytical capabilities of the NRLs to enforce the European Directive 2002/32/EC setting levels for undesirable substances in feed. However, 13 out 34 did not report results for iAs.

As for compliance assessment, only 47 % of the participants stated correctly (providing proper justification) that the test item was non-compliant according to the maximum level set by Directive 2002/32/EC for cadmium in palm kernel expeller. Other laboratories having reported satisfactory results should therefore improve their assessment procedure selecting relevant MLs and phrasing accurately their justification, or providing realistic (not over-estimated) measurement uncertainties.

Overall, NRLs reported good measurement uncertainty estimates, thus demonstrating the effectiveness of the various PTs and training courses organised by the EURL-HM in the past 10 years.

Acknowledgements

The EURL-HM wishes to thank the Belgian NRL (CODA-CERVA) for providing the palm kernel expeller granulates later processed and used as test item for this proficiency test.

The authors wish to thank colleagues from the JRC-Geel site for their valuable contributions during the preparation of the proficiency test item.

The thirty four laboratories listed hereafter are kindly acknowledged for their participation in the PT.

Organisation	***Country***
AGES GmbH	Austria
CODA-CERVA	Belgium
Central Laboratory for Chemical Testing and Control (CLCTC)	Bulgaria
Croatian Veterinary Institute	Croatia
Department of Agriculture	Cyprus
State Veterinary Institute Olomouc	Czech Republic
Central Institute for Supervising and Testing in Agriculture (UKZUZ)	Czech Republic
Danish Veterinary and Food Administration	Denmark
Technical University Denmark (DTU) Food	Denmark
Agricultural Research Centre	Estonia
Finnish Food Safety Authority Evira	Finland
Laboratoire SCL de Bordeaux - NRL	France
Federal Office for Consumer Protection and Food Safety (BVL)	Germany
Regional Center Of Plant Protection And Quality Control Of Magnissia	Greece
National Food Chain Office Food and Feed Safety	Hungary
National Food Chain Safety Office	Hungary
Matis ohf	Iceland
The State Laboratory	Ireland
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
Laboratoire National de Santé	Luxembourg
Public Health Laboratoy	Malta
RIKILT	Netherlands
National Institute of Nutrition and Seafood Research (NIFES)	Norway
National Veterinary Research Institute	Poland
Instituto Português do Mar e da Atmosfera (IPMA)	Portugal
Hygiene and Veterinary Public Health Institute	Romania
State veterinary and food institute Dolný Kubín, Veterinary and food institute Košice	Slovakia
National Veterinary Institute	Slovenia
National Laboratory of Health, Environment and Food (NLZOH)	Slovenia
Laboratorio Arbitral Agroalimentario (MAGRAMA)	Spain
National Food Agency	Sweden
Fera Science Ltd	United Kingdom

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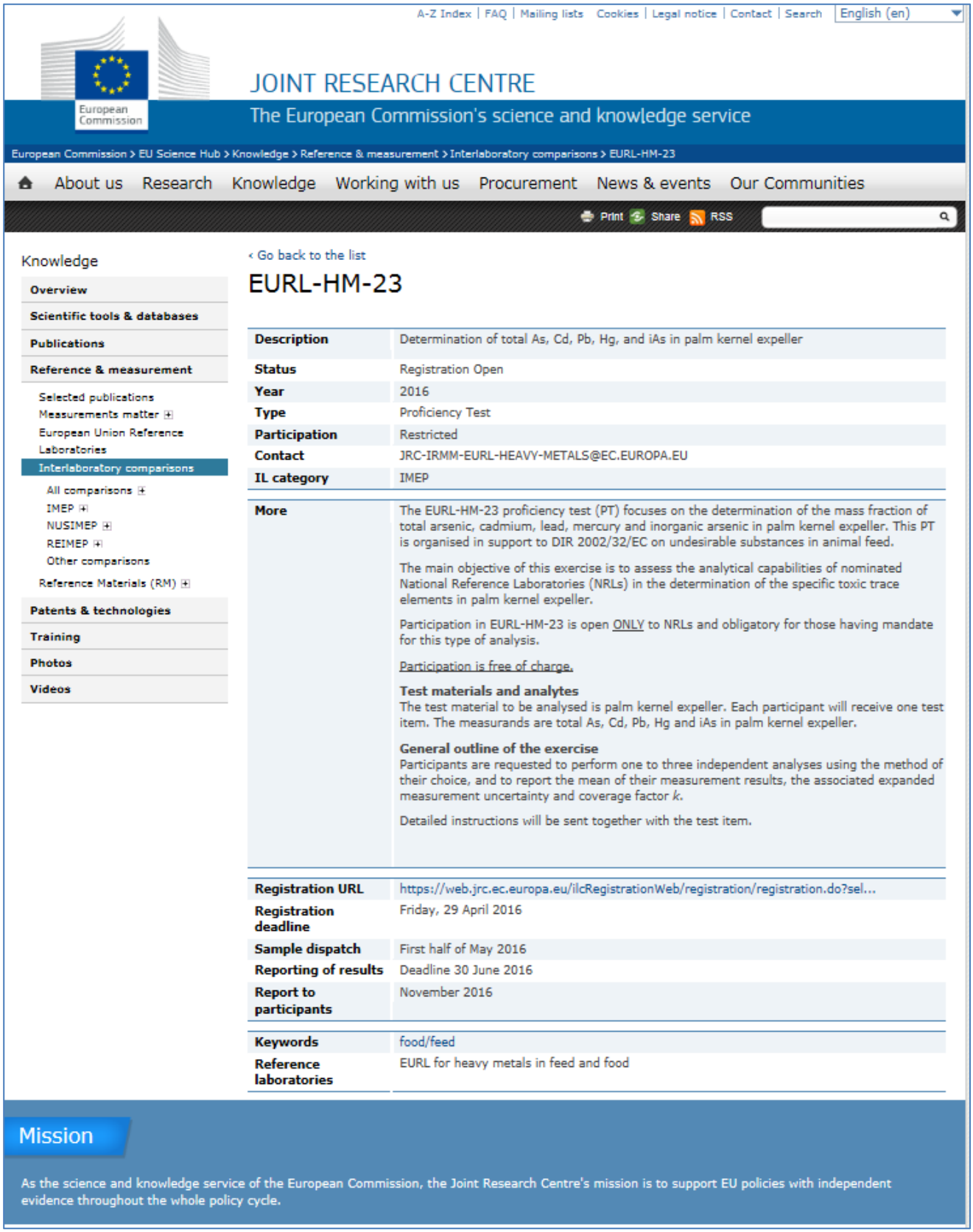
Annexes

Annex 1: List of abbreviations

CV-AAS	Cold Vapour Atomic Absorption Spectrometry
DG SANTE	Directorate General for Health and Food Safety
DMA	Direct Mercury Analyser (also called Elemental Mercury Analyzer, EMA)
ET-AAS	Electro Thermal – Atomic Absorption Spectrometry (also called Graphite Furnace Atomic Absorption Spectroscopy, GF-AAS)
GUM	Guide for the Expression of Uncertainty in Measurement
HG-AAS	Hydride Generation – Atomic Absorption Spectrometry
HPLC	High Performance Liquid Chromatography
ICP-(Q)MS	Inductively Coupled Plasma –(Quadrupole) Mass Spectrometry
ID-GC-ICP-MS	Isotope Dilution – Gas Chromatography – ICP-MS
JRC	Joint Research Centre
LOD	Limit of detection
NRL	National Reference Laboratory
PKE	Palm Kernel Expeller
PT	Proficiency Test
Z-ET-AAS	Zeeman ET-AAS

Annex 2: JRC web announcement



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European Commission > EU Science Hub > Knowledge > Reference & measurement > Interlaboratory comparisons > EURL-HM-23

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    - REIMEP
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EURL-HM-23

Description	Determination of total As, Cd, Pb, Hg, and iAs in palm kernel expeller
Status	Registration Open
Year	2016
Type	Proficiency Test
Participation	Restricted
Contact	JRC-IRMM-EURL-HEAVY-METALS@EC.EUROPA.EU
IL category	IMEP
More	The EURL-HM-23 proficiency test (PT) focuses on the determination of the mass fraction of total arsenic, cadmium, lead, mercury and inorganic arsenic in palm kernel expeller. This PT is organised in support to DIR 2002/32/EC on undesirable substances in animal feed. The main objective of this exercise is to assess the analytical capabilities of nominated National Reference Laboratories (NRLs) in the determination of the specific toxic trace elements in palm kernel expeller. Participation in EURL-HM-23 is open ONLY to NRLs and obligatory for those having mandate for this type of analysis. Participation is free of charge. **Test materials and analytes** The test material to be analysed is palm kernel expeller. Each participant will receive one test item. The measurands are total As, Cd, Pb, Hg and iAs in palm kernel expeller. **General outline of the exercise** Participants are requested to perform one to three independent analyses using the method of their choice, and to report the mean of their measurement results, the associated expanded measurement uncertainty and coverage factor *k*. Detailed instructions will be sent together with the test item.
Registration URL	https://web.jrc.ec.europa.eu/ilcRegistrationWeb/registration/registration.do?sel...
Registration deadline	Friday, 29 April 2016
Sample dispatch	First half of May 2016
Reporting of results	Deadline 30 June 2016
Report to participants	November 2016
Keywords	food/feed
Reference laboratories	EURL for heavy metals in feed and food

Mission

As the science and knowledge service of the European Commission, the Joint Research Centre's mission is to support EU policies with independent evidence throughout the whole policy cycle.

Annex 3: Invitation letter to NRLs

EUROPEAN COMMISSION
DIRECTORATE-GENERAL
JOINT RESEARCH CENTRE
Directorate D - Institute for Reference Materials and Measurements
European Union Reference Laboratory for Heavy Metals

Ref. Ares(2016)1582310 - 04/04/2016

Geel, 4 April 2016

(sent by e-mail)

Subject: **Invitation to participate in EURL-HM-23**

Dear National Reference Laboratory representative,

The EURL-HM would like to invite you to participate in the proficiency test EURL-HM-23 for the "**Determination of total As, Cd, Pb, Hg and iAs in palm kernel expeller**".

According to Regulation (EC) No 882/2004 it is your duty as NRL to participate in PTs organised by the EURL-HM if you hold a mandate for this type of matrix.

Your participation is free of charge.

Please register using the following link:
https://web.jrc.ec.europa.eu/ilcRegistrationWeb/registration/registration.do?selComparison=1641

Once you submitted your registration online, check carefully the generated registration form. In case of identified mistakes please contact the ILC coordinator as soon as possible before the registration deadline.

The deadline for registration is **April 29, 2016**.

Samples will be sent to participants during the first half of May 2016.

The deadline for submission of results is **June 30, 2016**.

Do not hesitate to contact us, in case of questions/doubts,

Yours sincerely

/signed electronically in Ares/

Dr. Pieter Dehouck
EURL-HM-23 Coordinator

/signed electronically in Ares/

Dr. Piotr Robouch
Operating Manager EURL-HM

Cc: Franz Ulberth (Head of Unit SFB)

Retieseweg 111, B-2440 Geel - Belgium.
Tel.: +32 14 57 12 11 • Direct line: +32 14 57 17 67 • Fax: +32 14 57 18 65
email: JRC-IRMM-EURL-HEAVY-METALS@ec.europa.eu • URL: https://ec.europa.eu/jrc/en/eurl/heavy-metals

EUROPEAN COMMISSION
DIRECTORATE-GENERAL
JOINT RESEARCH CENTRE
Directorate D - Institute for Reference Materials and Measurements
European Union Reference Laboratory for Heavy Metals

Geel, 11 May 2016
Ares(2016) 2196382

«Title» «Firstname» «Surname»
«Organisation»
«Department»
«Address»
«Address2»
«Zip» «Town»
«Country»

Subject: Participation in EURL-HM-23

Dear «Title» «Surname»,

Thank you for participating in the EURL-HM-23 proficiency test (PT) for the "**Determination of total As, Cd, Pb, Hg and iAs in palm kernel expeller**". This PT is organised in support to DIR 2002/32/EC on undesirable substances in animal feed.

Please keep this letter. You will need it to report your results.

The parcel you received contains, in addition to this letter:

- one vial of the test item (approx. 20 g); and
- the "Confirmation of receipt" form.

Upon arrival of this parcel, please check whether the test item is undamaged after transport, and send us by fax or email the "Confirmation of receipt" form.

Store the samples until analysis in a dark place at maximum temperature of + 4°C (fridge).

The measurands are total As, Cd, Pb, Hg and iAs in palm kernel expeller.

The procedure used for the analyses should resemble as closely as possible the one you use in routine analyses.

Determine the moisture content and correct the measurement results for moisture content as prescribed in DIR 2002/32/EC on undesirable substances in animal feed.

Perform two or three independent measurements and report:

- the result for the moisture content determination (in % w/w)
- the **mean** of your two or three measurements results (in mg kg^{-1})
- the associated expanded **uncertainty** (in mg kg^{-1})
- the **coverage factor** and
- the analytical technique used.

Retiesweg, 111, B-2440 Geel - Belgium.
Tel.: +32 14 57 12 11 • Direct line: +32 14 57 17 67 • Fax: +32 14 57 18 65
e-mail: JRC-IRMM-EURL-HEAVY-METALS@ec.europa.eu • URL: https://ec.europa.eu/jrc/en/eurl/heavy-metals

The results should be reported in the same form (e.g. number of significant figures) as you normally report to customers.

The reporting website is https://web.jrc.ec.europa.eu/ilcReportingWeb

To access the webpage you need the following personal password key: **«Part_key»**.

The system will guide you through the reporting procedure. Then complete the corresponding questionnaire. **Do not forget to submit and confirm when required.**

Directly after submitting your results and the questionnaire information online, you will be requested to print the completed report form.

Please check carefully this report. In the case mistakes are detected contact the ILC coordinator as soon as possible before the reporting deadline.

The deadline for submission of results is **30/06/2016**.

Remember 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.

Do not hesitate to contact me for further information.

With kind regards,

/signed electronically in Ares/

Dr. Pieter Dahouck

EURL-HM-23 Coordinator

Cc: F. Ulberth (Head of Unit, Standards for Food Bioscience), P. Robouch (Operating Manager EURL-HM)

Retiesweg, 111, B-2440 Geel - Belgium.
Tel.: +32 14 57 12 11 • Direct line: +32 14 57 17 67 • Fax: +32 14 57 18 65
e-mail: JRC-IRMM-EURL-HEAVY-METALS@ec.europa.eu • URL: https://ec.europa.eu/jrc/en/eurl/heavy-metals

Annex 5: Confirmation of receipt form

EUROPEAN COMMISSION
DIRECTORATE-GENERAL
JOINT RESEARCH CENTRE
Directorate D - Institute for Reference Materials and Measurements
European Union Reference Laboratory for Heavy Metals

Geel, 11 May 2016
Ares(2016) 2196382

«Title» «Firstname» «Surname»
«Organisation»
«Department»
«Address»
«Address2»
«Zip» «Town»
«Country»

Subject: **"Confirmation receipt" form**
EURL-HM-23 - Heavy Metals in Palm Kernel Expeller

Please return this form at your earliest convenience, to confirm that the package arrived well. If samples are damaged, mention it under "Remarks" and contact us as soon as possible.

Date of package arrival _____

Remarks _____

_____

Signature _____

Thank you for returning this form by email to:

Dr. Pieter Dehouck
EURL-HM-23 Coordinator
e-mail : JRC-IRMM-EURL-HEAVY-METALS@ec.europa.eu

Retieseweg 111, B-2440 Geel - Belgium.
Tel.: +32 14 57 12 11 • Direct line: +32 14 57 17 67
e-mail: JRC-IRMM-EURL-HEAVY-METALS@ec.europa.eu • URL: https://ec.europa.eu/jrc/en/eurl/heavy-metals

Annex 6: Questionnaire

1. **Did you use a standard method for analysis?**

- ○ a) Yes
- ○ b) No

1.1. If "Yes", specify which one.

2. **Which digestion type, acid mixture, temperature and time did you use? [For the digestion type use: 1 for Dry ashing, 2 for Open wet, 3 for Open microwave, 4 for Closed microwave, 5 for Pressure bomb, if "other" specify the method]**

Which digestion type, acid mixture, temperature and time did you use?

Questions/Response table	As	Cd	Pb	Hg
Digestion type				
Acid mixture				
Temperature				
Time				

3. **Describe briefly the analytical method used for the determination of iAs.**

4. **Which recovery factors and LODs did you determine?**

Recovery factors and LODs

Questions/Response table	As	iAs	Cd	Pb	Hg
Recovery %					
LODs (mg/kg)					

5. **How did you determine the recovery factor?**

- ☐ a) Adding a known amount of the same analyte to be measured (spiking)
- ☐ b) Using a certified reference material
- ☐ c) Other

5.1. If "Other" please specify.

6. **Describe the method applied for the water content determination.**

7. **Did you use a certified reference material for this analysis?**

- ○ a) Yes
- ○ b) No

7.1. If "Yes", specify which one.

8. **Additional remarks/comments regarding the method of analysis (specify the analyte concerned).**

9. How did you estimate your measurement uncertainty? (multiple answers are possible)

- ☐ a) Uncertainty budget (ISO GUM)
- ☐ b) Known uncertainty of the standard method
- ☐ c) Uncertainty of the method (in-house validation)
- ☐ d) Measurement of replicates (precision)
- ☐ e) Estimation based on judgement
- ☐ f) From interlaboratory comparison data
- ☐ g) Other

9.1. If "Other", please specify.

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

- ○ a) Yes
- ○ b) No

11. Considering your results, is the investigated test item compliant according to DIR 2002/32/EC on undesirable substances in animal feed?

- ○ a) Yes
- ○ b) No

11.1. If not compliant, specify why?

12. Which quality system does your laboratory have?

- ☐ a) ISO 17025
- ☐ b) ISO 9001
- ☐ c) Other
- ☐ d) None

12.1. If "Other", please specify.

13. Are you accredited for the determination of these analytes in feed?

Questions/ Response table	**1. As**	**2. Cd**	**3. Pb**	**4. Hg**	**5. iAs**	*Info*
Accredited for:	☐	☐	☐	☐	☐	

14. How many analyses of this type does your laboratory perform on a regular basis? (samples per year)

Questions/ Response table	**01-50**	**051-250**	**251-1000**	**> 1000**	**Never**	*Info*
As	☐	☐	☐	☐	☐	
Cd	☐	☐	☐	☐	☐	
Pb	☐	☐	☐	☐	☐	
Hg	☐	☐	☐	☐	☐	
iAs	☐	☐	☐	☐	☐	

15. Do you have any comments? Please let us know.

Annex 7: Homogeneity and stability results

7.1 Homogeneity study (all values in mg kg^{-1})

	As		Cd		Pb		Hg	
Bottle ID	*R1*	*R2*	*R1*	*R2*	*R1*	*R2*	*R1*	*R2*
125	2.58	2.40	1.46	1.38	0.90	0.91	0.0544	0.0532
23	2.59	2.58	1.48	1.38	0.94	0.90	0.0570	0.0557
83	2.56	2.47	1.41	1.39	0.88	0.91	0.0547	0.0525
149	2.58	2.40	1.40	1.36	0.90	0.88	0.0575	0.0522
5	2.43	2.47	1.42	1.39	0.92	0.90	0.0552	0.0551
67	2.44	2.56	1.40	1.41	0.90	0.90	0.0547	0.0532
162	2.59	2.44	1.37	1.36	0.89	0.91	0.0531	0.0538
59	2.40	2.53	1.37	1.37	0.89	0.89	0.0507	0.0523
119	2.51	2.46	1.39	1.40	0.89	0.88	0.0530	0.0519
182	2.51	2.45	1.41	1.40	0.93	0.88	0.0542	0.0549
Mean	2.50		1.40		0.90		0.0540	
s_p	0.34		0.22		0.14		0.0106	
0.3* s_p	0.10		0.06		0.04		0.0032	
Critical value	0.03		0.01		0.00		0.0000	
s_x	0.04		0.02		0.01		0.0014	
s_w	0.08		0.03		0.02		0.0015	
s_s	0.00		0.00		0.00		0.0009	
$s_s \leq 0.3 * \sigma_{pt}$	passed		passed		passed		passed	

Where: σ_{pt} is the standard deviation for the PT assessment,
s_x is the standard deviation of the sample averages,
s_w is the within-sample standard deviation,
s_s is the between-sample standard deviation,

7.2 Stability study (at 60°C, all values in mg kg^{-1})

Time	0 w	3 w	5 w	8 w	Slope significance (a)	Assessment
As	2.18	2.11	2.25	2.17		
	2.20	2.27	2.14	2.12	No	Stable
Cd	1.21	1.19	1.19	1.24		
	1.24	1.21	1.19	1.16	No	Stable
Pb	0.879	0.823	0.832	0.855		
	0.830	0.798	0.782	0.792	No	Stable
Hg	0.0452	0.0480	0.0464	0.0489		
	0.0487	0.0499	0.0476	0.0458	No	Stable

(a) Slope of the linear regression significantly different from "0" at a 95 % level

Annex 8: Results for total As

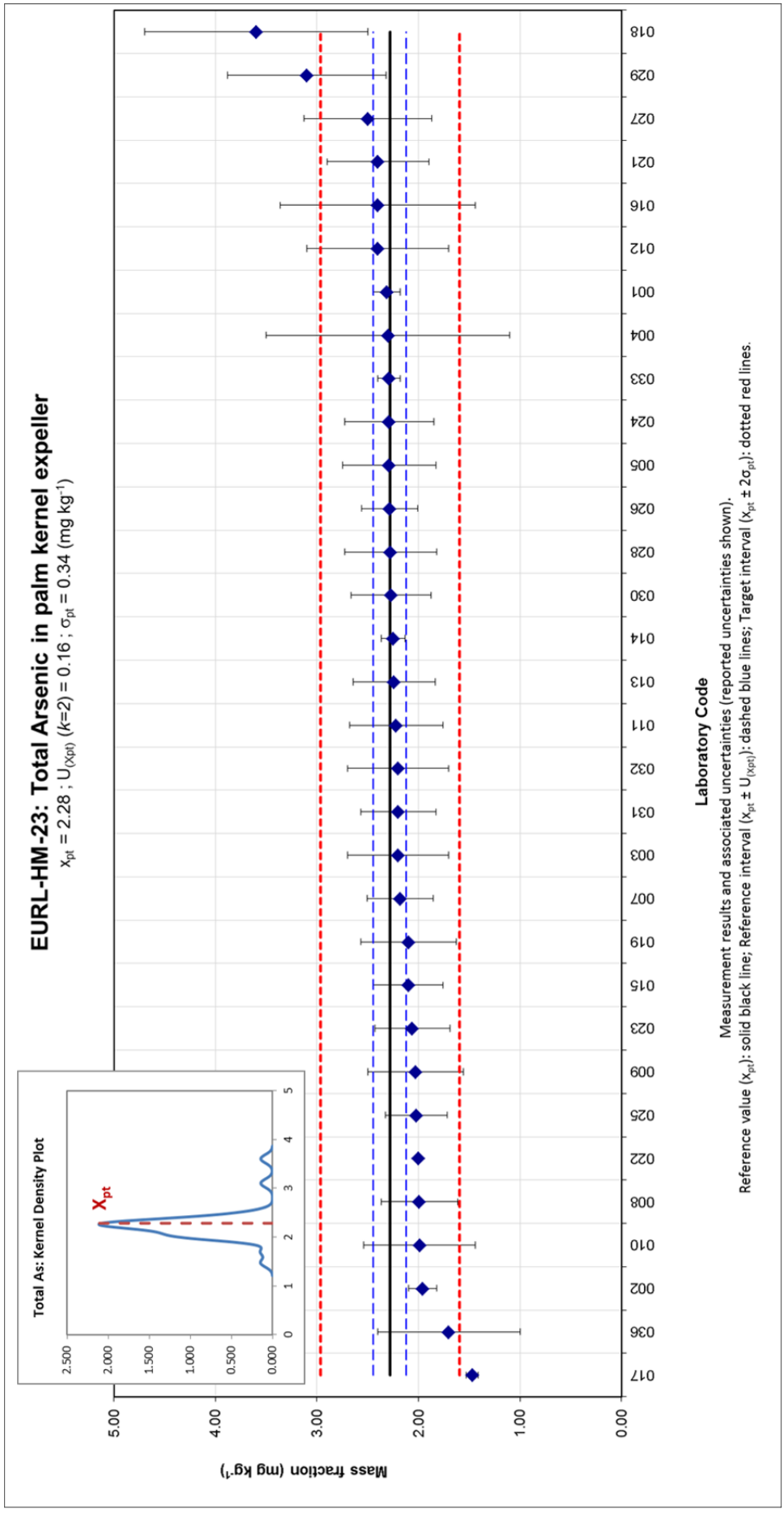
Assigned values: x_{pt} = 2.28; $U(x_{pt})$ = 0.16 (k=2) and σ_{pt} = 0.34; all values in mg kg^{-1}, relative to a feed with a moisture content of 12 %

Lab Code	X_i	$U(x_i)$	k[a]	technique	$u(x_i)$	z-score[b]	ζ-score	uncert.[c]
001	2.31	0.13	2	ICP-MS	0.065	0.08	0.27	b
002	1.96	0.14	2	ICP-MS	0.07	-0.94	-3.01	b
003	2.2	0.5	2	AAS	0.25	-0.24	-0.31	a
004	2.3	1.2	2	AAS	0.6	0.05	0.03	c
005	2.29	0.46	2	ICP-MS	0.23	0.02	0.03	a
007	2.180	0.327	2	ICP-MS	0.1635	-0.30	-0.56	a
008	1.991	0.37829	2	ICP-MS	0.189145	-0.85	-1.42	a
009	2.03	0.47	2	ICP-MS	0.235	-0.74	-1.02	a
010	1.99	0.55	2	HG-AAS	0.275	-0.85	-1.02	a
011	2.22	0.46	2	ICP-MS	0.23	-0.18	-0.26	a
012	2.4	0.7	2	ICP-OES	0.35	0.34	0.33	c
013	2.241	0.403	2	AAS	0.2015	-0.12	-0.19	a
014	2.251	0.116	2	ICP-MS	0.058	-0.09	-0.31	b
015	2.10	0.34	2	ICP-MS	0.17	-0.53	-0.97	a
016	2.4	0.96	2	ICP-MS	0.48	0.34	0.24	c
017	1.47	0.06	2	AAS	0.03	-2.37	-9.41	b
018	3.6	1.1	3	ICP-MS	0.366667	3.85	3.51	c
019	2.1	0.47	2	AAS	0.235	-0.53	-0.73	a
020								
021	2.4	0.5	2	ICP-MS	0.25	0.34	0.45	a
022	2.0		√3	AAS	0	-0.82	-3.49	b
023	2.06	0.37	2	ICP-MS	0.185	-0.65	-1.10	a
024	2.29	0.44	2	AAS	0.22	0.02	0.03	a
025	2.021	0.303	2	AAS	0.1515	-0.76	-1.52	a
026	2.285	0.274	2	ICP-MS	0.137	0.01	0.02	a
027	2.50	0.63	√3	ICP-MS	0.363731	0.64	0.58	c
028	2.274	0.455	2	ICP-MS	0.2275	-0.02	-0.03	a
029	3.10	0.78	2	ICP-MS	0.39	2.39	2.05	c
030	2.271	0.393	2	ICP-MS	0.1965	-0.03	-0.05	a
031	2.2	0.37	2	ICP-MS	0.185	-0.24	-0.41	a
032	2.20	0.50	2	ICP-MS	0.25	-0.24	-0.31	a
033	2.29	0.11	2	ICP-MS	0.055	0.02	0.08	b
034								
036	1.7	0.7	2	ICP-MS	0.35	-1.70	-1.62	c

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

[b] score evaluation colours: satisfactory, questionable, unsatisfactory,

[c] Case "a": $u(x_{pt}) \leq u(x_i) \leq \sigma_{pt}$; Case "b": $u(x_i) < u(x_{pt})$; and Case "c": $u(x_i) > \sigma_{pt}$


EURL-HM-23: Total Arsenic in palm kernel expeller
x_{pt} = 2.28 ; $U_{(Xpt)}$ (k=2) = 0.16 ; σ_{pt} = 0.34 (mg kg^{-1})
Mass fraction (mg kg^{-1})
5.00
4.00
3.00
2.00
1.00
0.00
Laboratory Code
017
036
002
010
008
022
025
009
023
015
019
007
003
031
032
011
013
014
030
028
026
005
024
033
004
001
012
016
021
027
029
018
Total As: Kernel Density Plot
X_{pt}
2.500
2.000
1.500
1.000
0.500
0.000
0
1
2
3
4
5
Measurement results and associated uncertainties (reported uncertainties shown).
Reference value (x_{pt}): solid black line; Reference interval ($x_{pt} \pm U_{(Xpt)}$): dashed blue lines; Target interval ($x_{pt} \pm 2\sigma_{pt}$): dotted red lines.

Annex 9: Results for Cd

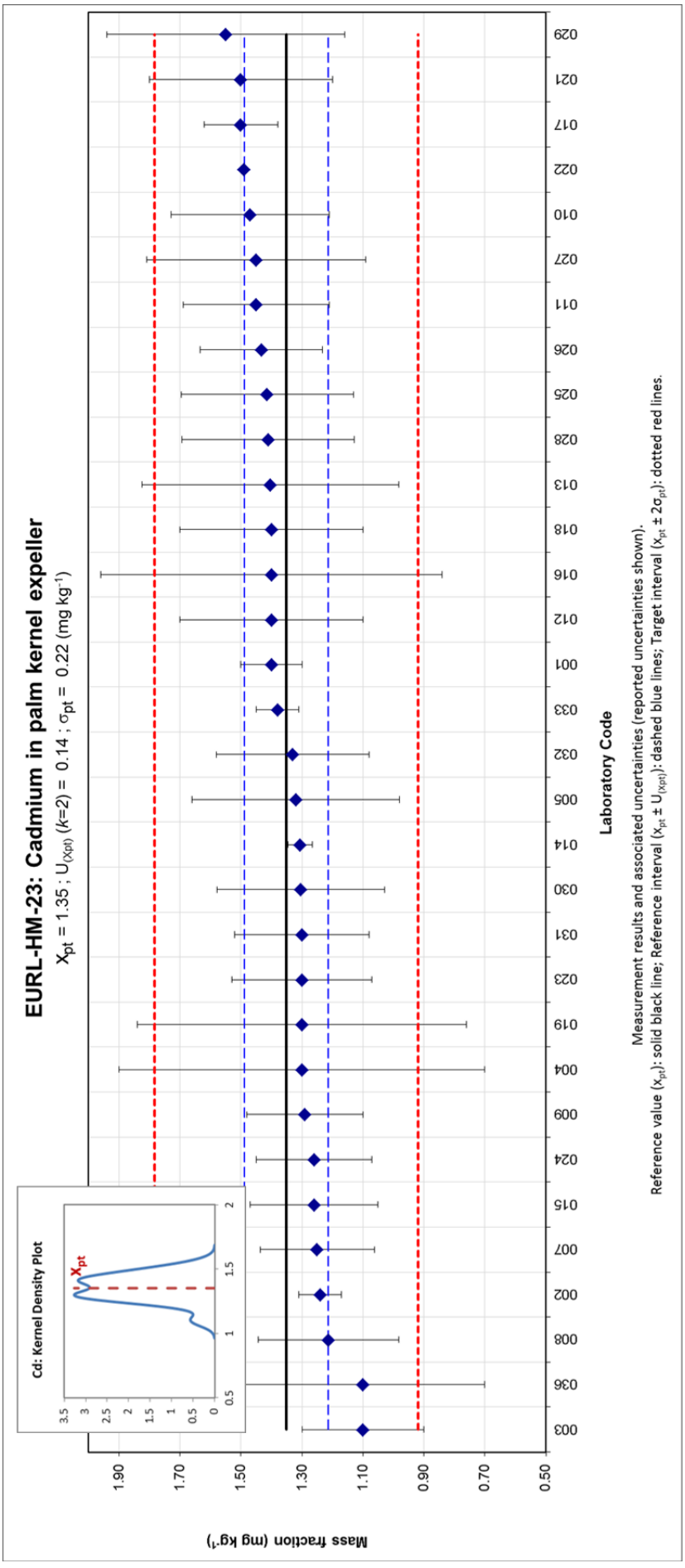
Assigned values: x_{pt} = 1.35; $U(x_{pt})$ = 0.14 (k=2); and σ_{pt} = 0.22; all values in mg kg^{-1}, relative to a feed with a moisture content of 12 %

Lab Code	X_i	$U(x_i)$	k[a]	technique	$u(x_i)$	z-score[b]	ζ-score	uncert.[c]
001	1.4	0.1	2	ICP-MS	0.05	0.22	0.57	b
002	1.24	0.07	2	ICP-MS	0.035	-0.52	-1.46	b
003	1.1	0.2	2	AAS	0.1	-1.16	-2.08	a
004	1.3	0.6	2	AAS	0.3	-0.24	-0.17	c
005	1.32	0.34	2	ICP-MS	0.17	-0.15	-0.17	a
007	1.250	0.187	2	ICP-MS	0.0935	-0.47	-0.88	a
008	1.213	0.23047	2	ICP-MS	0.115235	-0.64	-1.04	a
009	1.29	0.19	2	ICP-MS	0.095	-0.29	-0.53	a
010	1.47	0.26	2	AAS	0.13	0.55	0.80	a
011	1.45	0.24	2	ICP-MS	0.12	0.45	0.71	a
012	1.4	0.3	2	ICP-OES	0.15	0.22	0.29	a
013	1.403	0.421	2	AAS	0.2105	0.24	0.23	a
014	1.305	0.040	2	ICP-MS	0.02	-0.22	-0.66	b
015	1.26	0.21	2	ICP-MS	0.105	-0.42	-0.73	a
016	1.4	0.56	2	ICP-MS	0.28	0.22	0.17	c
017	1.50	0.12	2	AAS	0.06	0.69	1.63	b
018	1.4	0.3	3	ICP-MS	0.1	0.22	0.40	a
019	1.3	0.54	2	AAS	0.27	-0.24	-0.19	c
020								
021	1.5	0.3	2	ICP-MS	0.15	0.69	0.90	a
022	1.49		√3	AAS	0	0.64	2.02	b
023	1.30	0.23	2	ICP-MS	0.115	-0.24	-0.39	a
024	1.26	0.19	2	AAS	0.095	-0.42	-0.78	a
025	1.414	0.283	2	AAS	0.1415	0.29	0.40	a
026	1.433	0.201	2	ICP-MS	0.1005	0.38	0.67	a
027	1.45	0.36	√3	ICP-MS	0.207846	0.45	0.45	a
028	1.411	0.282	2	ICP-MS	0.141	0.27	0.38	a
029	1.55	0.39	2	ICP-MS	0.195	0.92	0.96	a
030	1.303	0.275	2	ICP-MS	0.1375	-0.23	-0.32	a
031	1.3	0.22	2	ICP-MS	0.11	-0.24	-0.40	a
032	1.33	0.25	2	ICP-MS	0.125	-0.10	-0.15	a
033	1.38	0.07	2	ICP-MS	0.035	0.13	0.37	b
034								
036	1.1	0.4	2	ICP-MS	0.2	-1.16	-1.19	a

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

[b] score evaluation colours: satisfactory, questionable, unsatisfactory,

[c] Case "a": $u(x_{pt}) \leq u(x_i) \leq \sigma_{pt}$; Case "b": $u(x_i) < u(x_{pt})$; and Case "c": $u(x_i) > \sigma_{pt}$


EURL-HM-23: Cadmium in palm kernel expeller
X_{pt} = 1.35 ; $U_{(Xpt)}$ (k=2) = 0.14 ; σ_{pt} = 0.22 (mg kg^{-1})
Mass fraction (mg kg^{-1})
Laboratory Code
Cd: Kernel Density Plot
X_{pt}
Measurement results and associated uncertainties (reported uncertainties shown).
Reference value (x_{pt}): solid black line; Reference interval ($x_{pt} \pm U_{(xpt)}$): dashed blue lines; Target interval ($x_{pt} \pm 2\sigma_{pt}$): dotted red lines.

Annex 10: Results for Pb

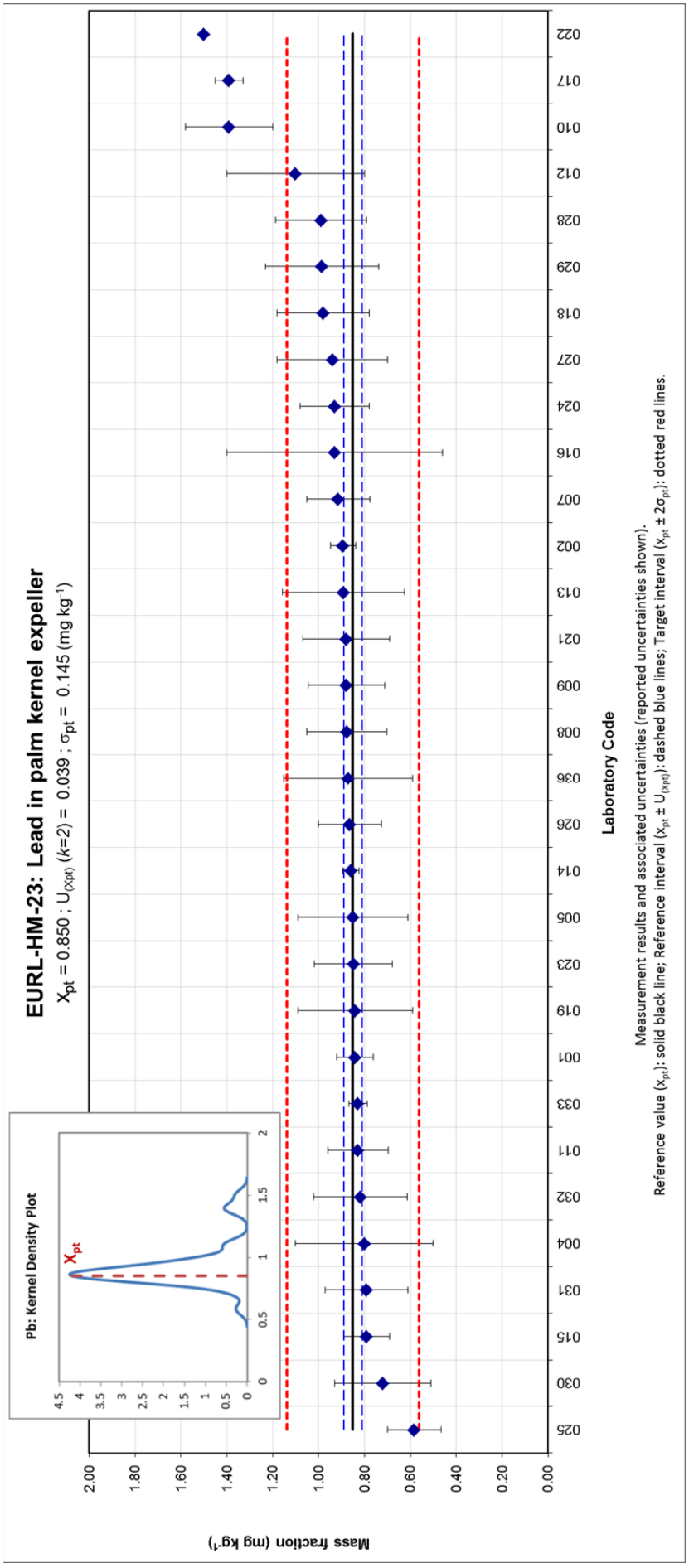
Assigned values: : x_{pt} = 0.850; $U(x_{pt})$ = 0.039 (k=2); and σ_{pt} = 0.145 ; all values in mg kg^{-1}, relative to a feed with a moisture content of 12 %

Lab Code	X_i	$U(x_i)$	k[a]	technique	$u(x_i)$	z-score[b]	ζ-score	uncert.[c]
001	0.84	0.08	2	ICP-MS	0.04	-0.07	-0.22	a
002	0.893	0.054	2	ICP-MS	0.027	0.30	1.29	a
003	< 1.8			AAS				
004	0.8	0.3	2	AAS	0.15	-0.35	-0.33	c
005	0.85	0.24	2	ICP-MS	0.12	0.00	0.00	a
007	0.914	0.137	2	ICP-MS	0.0685	0.44	0.90	a
008	0.876	0.1752	2	ICP-MS	0.0876	0.18	0.29	a
009	0.879	0.167	2	ICP-MS	0.0835	0.20	0.34	a
010	1.39	0.19	2	AAS	0.095	3.74	5.57	a
011	0.828	0.132	2	ICP-MS	0.066	-0.15	-0.32	a
012	1.1	0.3	2	ICP-OES	0.15	1.73	1.65	c
013	0.891	0.267	2	AAS	0.1335	0.28	0.30	a
014	0.858	0.036	2	ICP-MS	0.018	0.06	0.30	b
015	0.79	0.10	2	ICP-MS	0.05	-0.42	-1.12	a
016	0.93	0.47	2	ICP-MS	0.235	0.55	0.34	c
017	1.39	0.06	2		0.03	3.74	15.07	a
018	0.98	0.2	3	ICP-MS	0.066667	0.90	1.87	a
019	0.84	0.25	2	AAS	0.125	-0.07	-0.08	a
020								
021	0.88	0.19	2	ICP-MS	0.095	0.21	0.31	a
022	1.5		√3	AAS	0	4.50	33.16	b
023	0.848	0.170	2	ICP-MS	0.085	-0.01	-0.02	a
024	0.93	0.15	2	AAS	0.075	0.55	1.03	a
025	0.583	0.117	2	AAS	0.0585	-1.85	-4.33	a
026	0.864	0.137	2	ICP-MS	0.0685	0.10	0.20	a
027	0.94	0.24	√3	ICP-MS	0.138564	0.62	0.64	a
028	0.988	0.198	2	ICP-MS	0.099	0.96	1.37	a
029	0.985	0.246	2	ICP-MS	0.123	0.93	1.08	a
030	0.720	0.209	2	ICP-MS	0.1045	-0.90	-1.22	a
031	0.79	0.18	2	ICP-MS	0.09	-0.42	-0.65	a
032	0.818	0.204	2	ICP-MS	0.102	-0.22	-0.31	a
033	0.828	0.041	2	ICP-MS	0.0205	-0.15	-0.78	a
034								
036	0.87	0.28	2	ICP-MS	0.14	0.14	0.14	a

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

[b] score evaluation colours: satisfactory, questionable, unsatisfactory,

[c] Case "a": $u(x_{pt}) \leq u(x_i) \leq \sigma_{pt}$; Case "b": $u(x_i) < u(x_{pt})$; and Case "c": $u(x_i) > \sigma_{pt}$


EURL-HM-23: Lead in palm kernel expeller
X_{pt} = 0.850 ; $U_{(Xpt)}$ (k=2) = 0.039 ; σ_{pt} = 0.145 (mg kg^{-1})
Pb: Kernel Density Plot
X_{pt}
Mass fraction (mg kg^{-1})
Laboratory Code
025 030 015 031 004 032 011 033 001 019 023 005 014 026 036 008 009 021 013 002 007 016 024 027 018 029 028 012 010 017 022
Measurement results and associated uncertainties (reported uncertainties shown).
Reference value (x_{pt}): solid black line; Reference interval ($x_{pt} \pm U_{(Xpt)}$): dashed blue lines; Target interval ($x_{pt} \pm 2\sigma_{pt}$): dotted red lines.

Annex 11: Results for Hg

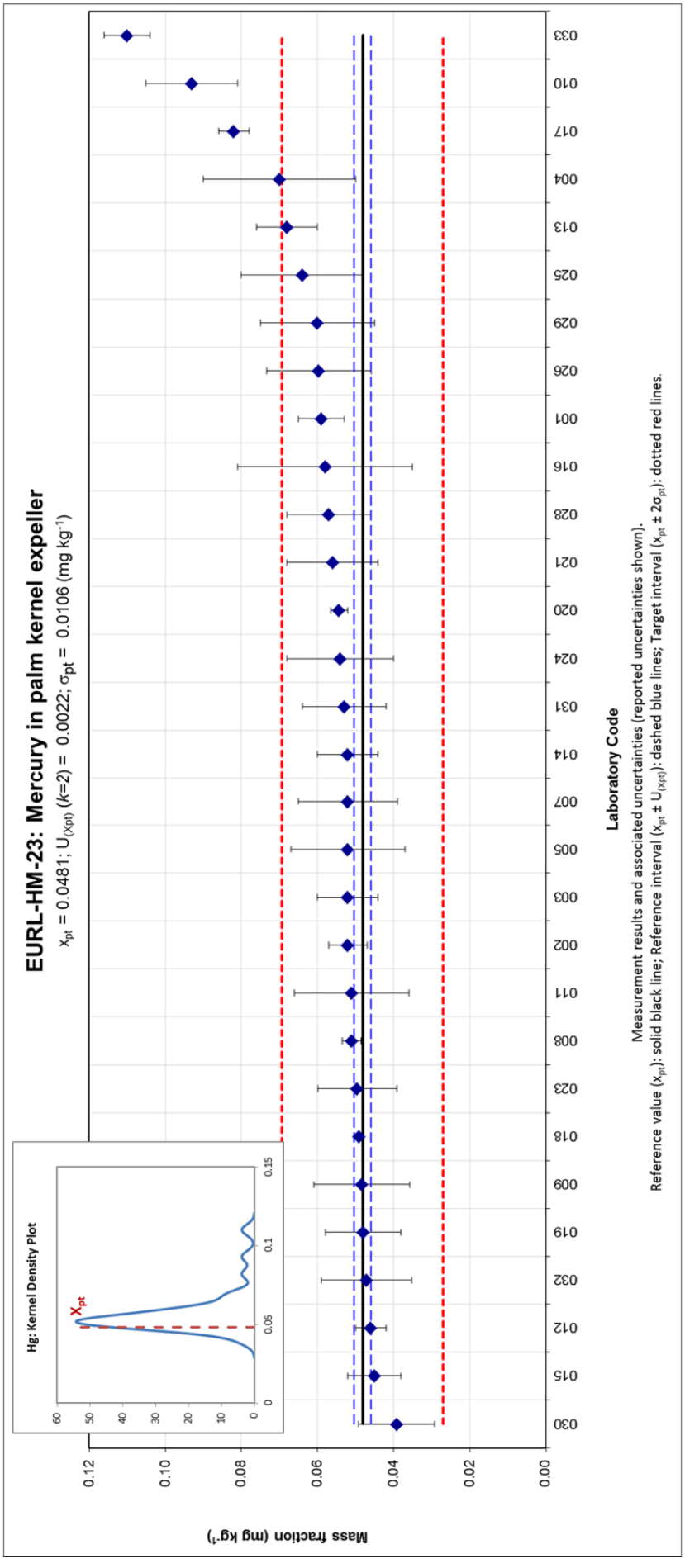
Assigned values: x_{pt} = 0.0481; $U(x_{pt})$ = 0.0022 (k=2); and σ_{pt} = 0.0106 ; all values in mg kg^{-1}, relative to a feed with a moisture content of 12 %

Lab Code	X_i	$U(x_i)$	k[a]	technique	$u(x_i)$	z-score[b]	ζ-score	uncert.[c]
001	0.059	0.006	2	ICP-MS	0.003	1.03	3.41	a
002	0.052	0.005	2	DMA	0.0025	0.37	1.43	a
003	0.052	0.008	2	AAS	0.004	0.37	0.94	a
004	0.07	0.02	2	AAS	0.01	2.07	2.18	a
005	0.052	0.015	2	ICP-MS	0.0075	0.37	0.51	a
007	0.052	0.013	2	AMA-254	0.0065	0.37	0.59	a
008	0.051	0.00255	2	AMA-254	0.001275	0.27	1.72	a
009	0.0483	0.0126	2	ICP-MS	0.0063	0.02	0.03	a
010	0.093	0.012	2	CV-AAS	0.006	4.24	7.36	a
011	0.051	0.015	2	ICP-MS	0.0075	0.27	0.38	a
012	0.046	0.004	2	AMA-254	0.002	-0.20	-0.92	a
013	0.068	0.008	2	AAS	0.004	1.88	4.80	a
014	0.052	0.008	2	ICP-MS	0.004	0.37	0.94	a
015	0.045	0.007	2	ICP-MS	0.0035	-0.29	-0.84	a
016	0.058	0.023	2	ICP-MS	0.0115	0.93	0.86	c
017	0.082	0.004	2	AAS	0.002	3.20	14.85	a
018	0.0490	0.0010	3	DMA	0.000333	0.08	0.78	b
019	0.048	0.01	2	AAS	0.005	-0.01	-0.02	a
020	0.0543	0.00217	2	AMA-254	0.001085	0.58	4.01	b
021	0.056	0.012	2	DMA	0.006	0.75	1.30	a
022								
023	0.0495	0.0104	2	AAS	0.0052	0.13	0.26	a
024	0.054	0.014	2	HG-CVAAS	0.007	0.56	0.83	a
025	0.064	0.016	2	AAS	0.008	1.50	1.97	a
026	0.0596	0.0137	2	ICP-MS	0.00685	1.08	1.66	a
027	< 0.08			ICP-MS				
028	0.057	0.011	2	ICP-MS	0.0055	0.84	1.59	a
029	0.06	0.015	2	ICP-MS	0.0075	1.12	1.57	a
030	0.0392	0.010	2	DMA	0.005	-0.84	-1.74	a
031	0.053	0.011	2	DMA	0.0055	0.46	0.87	a
032	0.0471	0.0118	2	ICP-MS	0.0059	-0.09	-0.17	a
033	0.110	0.006	2	CV-AAS	0.003	5.84	19.37	a
034								
036								

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

[b] score evaluation colours: satisfactory, questionable, unsatisfactory,

[c] Case "a": $u(x_{pt}) \leq u(x_i) \leq \sigma_{pt}$; Case "b": $u(x_i) < u(x_{pt})$; and Case "c": $u(x_i) > \sigma_{pt}$


EURL-HM-23: Mercury in palm kernel expeller
x_{pt} = 0.0481; $U_{(xpt)}$ (k=2) = 0.0022; σ_{pt} = 0.0106 (mg kg^{-1})
Hg: Kernel Density Plot
X_{pt}
Mass fraction (mg kg^{-1})
0.12
0.10
0.08
0.06
0.04
0.02
0.00
030
015
012
032
019
009
018
023
008
011
002
003
005
007
014
031
024
020
021
028
016
001
026
029
025
013
004
017
010
033
Laboratory Code
Measurement results and associated uncertainties (reported uncertainties shown).
Reference value (x_{pt}): solid black line; Reference interval ($x_{pt} \pm U_{(xpt)}$): dashed blue lines; Target interval ($x_{pt} \pm 2\sigma_{pt}$): dotted red lines.

Annex 12: Results for iAs

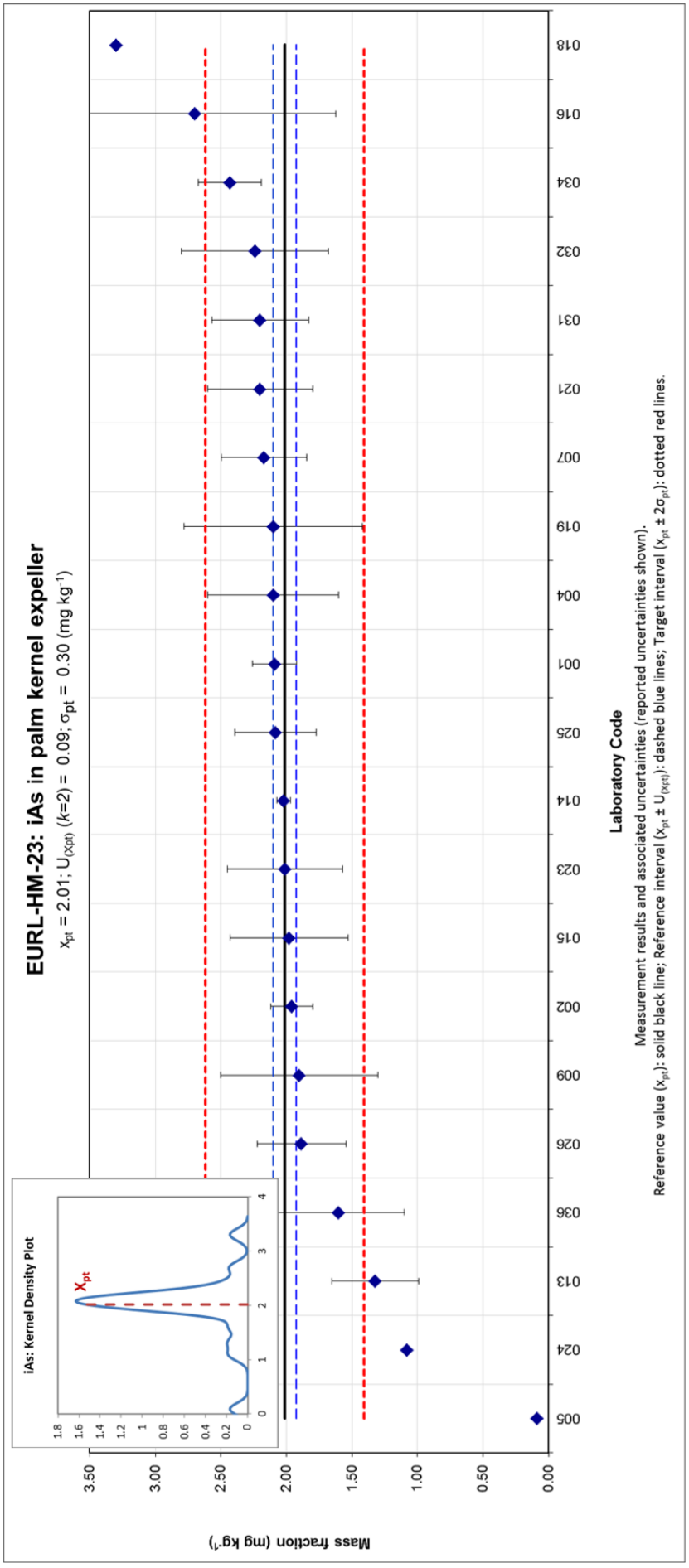
Assigned values: x_{pt} = 2.01; $U(x_{pt})$ = 0.09 (k=2); and σ_{pt} = 0.30 ; all values in mg kg^{-1}, relative to a feedingstuffs with a moisture content of 12 %

Lab Code	X_i	$U(x_i)$	k[a]	technique	$u(x_i)$	z-score[b]	ζ-score	uncert.[c]
001	2.09	0.17	2	HPLC-ICPMS	0.085	0.25	0.80	a
002	1.96	0.16	2	HPLC-ICP-MS	0.08	-0.18	-0.58	a
003								
004	2.1	0.5	2	AAS	0.25	0.29	0.34	a
005	0.086	0.015	2	HPLC-ICP-MS	0.0075	-6.38	-43.40	b
007	2.169	0.325	2	HPLC-ICP-MS	0.1625	0.52	0.92	a
008								
009	1.9	0.6	2	AAS	0.3	-0.38	-0.37	a
010								
011								
012								
013	1.321	0.33	2	HPLC-ICP-MS	0.165	-2.29	-4.06	a
014	2.021	0.05	2	HG-AAS	0.025	0.03	0.15	b
015	1.98	0.45	2	ICP-MS	0.225	-0.11	-0.15	a
016	2.7	1.08	2	HPLC-ICP-MS	0.54	2.27	1.27	c
017								
018	3.3		√3	ICP-MS	0	4.26	29.40	b
019	2.1	0.68	2	HPLC-ICP-MS	0.34	0.29	0.25	c
020								
021	2.2	0.4	2	HPLC-ICP-MS	0.2	0.62	0.91	a
022								
023	2.01	0.44	2	ICP-MS	0.22	-0.01	-0.01	a
024	1.08		√3	AAS	0	-3.09	-21.33	b
025	2.083	0.312	2	AAS	0.156	0.23	0.43	a
026	1.885	0.339	2	ICP-MS	0.1695	-0.42	-0.73	a
027								
028								
029								
030								
031	2.2	0.37	2	HPLC-ICP-MS	0.185	0.62	0.98	a
032	2.24	0.56	2	ICP-MS	0.28	0.75	0.80	a
033								
034	2.43	0.24	2	HPLC-ICP-MS	0.12	1.38	3.26	a
036	1.6	0.5	2	LC-ICP-MS	0.25	-1.37	-1.63	a

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

[b] score evaluation colours: satisfactory, questionable, unsatisfactory,

[c] Case "a": $u(x_{pt}) \leq u(x_i) \leq \sigma_{pt}$; Case "b": $u(x_i) < u(x_{pt})$; and Case "c": $u(x_i) > \sigma_{pt}$


EURL-HM-23: iAs in palm kernel expeller
x_{pt} = 2.01; $U_{(Xpt)}$ (k=2) = 0.09; σ_{pt} = 0.30 (mg kg^{-1})
iAs: Kernel Density Plot
X_{pt}
Mass fraction (mg kg^{-1})
Laboratory Code
Measurement results and associated uncertainties (reported uncertainties shown).
Reference value (x_{pt}): solid black line; Reference interval ($x_{pt} \pm U_{(Xpt)}$): dashed blue lines; Target interval ($x_{pt} \pm 2\sigma_{pt}$): dotted red lines.

Annex 13: Overview of performance versus technique

Lab	total As	Cd	Pb	Hg	iAs
001	ICP-MS	ICP-MS	ICP-MS	ICP-MS	HPLC-ICP-MS
002	ICP-MS	ICP-MS	ICP-MS	DMA	HPLC-ICP-MS
003	AAS	AAS	--	AAS	--
004	AAS	AAS	AAS	AAS	AAS
005	ICP-MS	ICP-MS	ICP-MS	ICP-MS	HPLC-ICP-MS
007	ICP-MS	ICP-MS	ICP-MS	AMA 254	HPLC-ICP-MS
008	ICP-MS	ICP-MS	ICP-MS	AMA 254	--
009	ICP-MS	ICP-MS	ICP-MS	ICP-MS	AAS
010	HG-AAS	AAS	AAS	CV-AAS	--
011	ICP-MS	ICP-MS	ICP-MS	ICP-MS	--
012	ICP-OES	ICP-OES	ICP-OES	AMA254	--
013	AAS	AAS	AAS	AAS	HPLC-ICP-MS
014	ICP-MS	ICP-MS	ICP-MS	ICP-MS	HG–AAS
015	ICP-MS	ICP-MS	ICP-MS	ICP-MS	ICP-MS
016	ICP-MS	ICP-MS	ICP-MS	ICP-MS	HPLC-ICP-MS
017	AAS	AAS		AAS	--
018	ICP-MS	ICP-MS	ICP-MS	DMA	ICP-MS
019	AAS	AAS	AAS	AAS	HPLC-ICPMS
020	--	--	--	AMA-254	--
021	ICP-MS	ICP-MS	ICP-MS	DMA	HPLC-ICP-MS
022	AAS	AAS	AAS	--	--
023	ICP-MS	ICP-MS	ICP-MS	AAS	ICP-MS
024	AAS	AAS	AAS	HG-CVAAS	AAS
025	AAS	AAS	AAS	AAS	AAS
026	ICP-MS	ICP-MS	ICP-MS	ICP-MS	ICP-MS
027	ICP-MS	ICP-MS	ICP-MS	--	--
028	ICP-MS	ICP-MS	ICP-MS	ICP-MS	--
029	ICP-MS	ICP-MS	ICP-MS	ICP-MS	--
030	ICP-MS	ICP-MS	ICP-MS	DMA	--
031	ICP-MS	ICP-MS	ICP-MS	DMA	HPLC-ICP-MS
032	ICP-MS	ICP-MS	ICP-MS	ICP-MS	ICP-MS
033	ICP-MS	ICP-MS	ICP-MS	CV-AAS	--
034	--	--	--	--	HPLC-ICP-MS
036	ICP-MS	ICP-MS	ICP-MS	--	LC-ICP-MS

Z-Score evaluation colours: satisfactory, questionable, unsatisfactory.

Annex 14: Conformity as expressed by the participants.

Lab	Comply	If not compliant, specify why.[a]	$x_i - U_i$ [b]	Eval.[c]
001	Yes		> ML	FC
002	No	Result of Cd exceeds the maximum level (ML) as laid down in DIR 2002/32/EC for "Feed materials of vegetable origin". Results of As, iAs, Pb and Hg do not exceed the MLs.	> ML	TNC
003	Yes		< ML	TC
004	Yes		< ML	TC
005	Yes		< ML	TC
007	No	because of exceeding ML for Cd (feed materials of vegetable origin 1 ppm) and exceeding ML for inorg. As (2ppm/88 % dry mass)	> ML	FNC
008	No	Cd is more than 1 mg/kg	< ML	FNC
009	No	Cd is above MRL (1,0 mg/kg)	> ML	TNC
010	No	For Cd the maximum level is 1 mg/Kg in feed materials of vegetable origin	> ML	TNC
011	No	The content of cadmium (minus measurement uncertainty) is higher than maximum permitted content.	> ML	TNC
012	No	Cd exceeds allowed maximum content (0.5 mg/kg 12 % moisture)	> ML	FNC
013	Yes		< ML	TC
014	No	Cd content is higher than 1 mg/kg	> ML	TNC
015	No	Cd: Reg.value 1mg/kg. Our result 1.05mg/kg (after UM subtracted)	> ML	TNC
016	?		< ML	
017	No	Not compliant for Cd	> ML	TNC
018	?		> ML	
019	Yes		< ML	TC
020	Yes	*(Note authors: No Cd results)*	nd	FC
021	No	Cd concentration: 1.456 mg/kg - 0.288 mg/kg = 1.168 mg/kg > 1 mg/kg (the maximum level for Cd in feed materials of vegetable origin)	> ML	TNC
022	No	Out of limits for Cd	> ML	TNC
023	No	Cd content value exceeds the maximum allowed	> ML	TNC
024	No	Cd content is over the maximum level (1mg/Kg)	> ML	TNC
025	Yes	The Cd content is over 1 mg/kg	> ML	FC
026	No	ML for Cadmium for plant ingredient is 1mg/kg, which is violated even after substracting the measurement uncertainty	> ML	TNC
027	No	Non compliant for Cd	> ML	TNC
028	?		> ML	
029	Yes		> ML	FC
030	No	Because concentration of Cd is above limit of 1 mg/kg (calculating Measurement Uncertainty)	> ML	TNC
031	No	The concentration of cadmium in the sample (after subtracting the uncertainty) is above 1 mg/Kg, which, according to regulation 574/2011 is the maximum limit for Feed materials of vegetable origin.	> ML	TNC
032	No	Cd-level above ML (1 mg/kg)	> ML	TNC
033	No	As, Cd, Hg are more then limit	> ML	FNC
034	?	No MLs for iAs in palm kernel expeller *(Note Authors: no Cd results)*	nd	
036	Yes		< ML	TC

[a] Wrong justifications are marked in yellow.

[b] Maximum Level for Cd in palm kernel expeller set by DIR 2002/32/EC: ML = 1 mg kg^{-1}

[c] TNC: True Non-Compliant, TC: True Compliant, FNC: False Non-Compliant, FC: False Compliant.

Annex 15: Experimental details (as reported by the participants)

Lab Code	Measurand	Digestion type	Acid mixture	Temperature (°C)	Time (min)	Recovery %	LODs (mg/kg)
001	As	CMW	HNO3	166	54	104	0,005
001	Cd	CMW	HNO3	166	54	104	0,002
001	Pb	CMW	HNO3	166	54	97	0,003
001	Hg	CMW	HNO3	166	54	95	0,001
002	As	CMW	HNO3/H2O2	150C/180	20/10	108	0.0009
002	Cd	CMW	HNO3/H2O2	150C/180	20/10	90	0.0003
002	Pb	CMW	HNO3/H2O2	150C/180	20/10	111	0.004
002	Hg	no dig.	-	-	-	101	0.0002
003	As	CMW	HNO3/H202/HF	200	28	91.76	0.18
003	Cd	CMW	HNO3/H202/HF	200	28	98.21	0.075
003	Pb	CMW	HNO3/H202/HF	200	28	88.75	0.50
003	Hg	--	--	--	--	94.12	0.010
004	As	Dry Ash	HNO3	445	24 h	96	0.063
004	Cd	OWD	HNO3/H2O2	170	1 h	88	0.01
004	Pb	OWD	HNO3/H2O2	170	1 h	100	0.05
004	Hg	CMW	HNO3/H2O2	170	20	112	0.025
005	As	CMW	HNO3/HCl	220	25	100	0,01
005	Cd	CMW	HNO3/HCl	220	25	100	0,003
005	Pb	CMW	HNO3/HCl	220	25	100	0,004
005	Hg	CMW	HNO3/HCl	220	25	100	0,019
007	As	OMW	HNO3	200	10	98-102	0,006
007	Cd	OMW	HNO3	200	10	98-102	0,006
007	Pb	OMW	HNO3	200	10	98-102	0,09
007	Hg	no dig.	no acids	dry combustion in oxygen	270s temp. programe	98-102	0,0006
008	As	CMW	HNO3/H2O2	max.190	51	102	0.00231
008	Cd	CMW	HNO3/H2O2	max.190	51	89	0.00160
008	Pb	CMW	HNO3/H2O2	max.190	51	102	0.00135
008	Hg	Dry Ash	--	--	--	102	0.000146
009	As	CMW	HNO3/H2O2	200	60	88	0,1
009	Cd	CMW	HNO3/H2O2	200	60	95	0,01
009	Pb	CMW	HNO3/H2O2	200	60	95	0,01
009	Hg	CMW	HNO3/H2O2	200	60		0,01
010	As	Dry Ash	HNO3/HCl	450	12 h	102	0.100
010	Cd	Dry Ash	HNO3/HCl	450	24 h	94.2	0.07
010	Pb	Dry Ash	HNO3/HCl	450	24 h	100	0.5
010	Hg	CMW	HNO3	180	50	98	0.003
011	As	CMW	HNO3/H2O2	200	20	100	0.008
011	Cd	CMW	HNO3/H2O2	200	20	89	0.002
011	Pb	CMW	HNO3/H2O2	200	20	100	0.005
011	Hg	CMW	HNO3/H2O2	200	20	84	0.008
012	As	CMW	HNO3/H2O2	100-200	22	93	0,5
012	Cd	CMW	HNO3/H2O2	100-200	22	92	0,1
012	Pb	CMW	HNO3/H2O2	100-200	22	83	0,5
012	Hg	none	none	200-650	3		
013	As	Dry Ash	--	550	24 h	89	0.002
013	Cd	Dry Ash	--	450	24 h	93	0.001
013	Pb	Dry Ash		450	24h	94	0.002
013	Hg	Pressure bomb		-	3		0.001

Lab Code	Measurand	Digestion type	Acid mixture	Temperature (°C)	Time (min)	Recovery %	LODs (mg/kg)
014	As	CMW	HNO3/H2O2	180	30	104	0,010
014	Cd	CMW	HNO3/H2O2	180	30 min	102	0,002
014	Pb	CMW	HNO3/H2O2	180	30 min	100	0,005
014	Hg	CMW	HNO3/H2O2	180	30 min	101	0,010
015	As	CMW	HNO3/HCl	240	15	100	0.003
015	Cd	CMW	HNO3/HCl	240	15	102	0.08
015	Pb	CMW	HNO3/HCl	240	15	110	0.02
015	Hg	CMW	HNO3, HCl	240	15	113	0.002
016	As	CMW	HNO3				0,01
016	Cd	CMW	HNO3				0,005
016	Pb	CMW	HNO3				0,03
016	Hg	CMW	HNO3				0,005
017	As	CMW	HNO3/H2O2	185	15	97.3	0.06
017	Cd	CMW	HNO3/H2O2	185	15	96.6	0.01
017	Pb	CMW	HNO3/H2O2	185	15	99.6	0.07
017	Hg	CMW	HNO3/H2O2	185	15	100.8	0.01
018	As	MW	HNO3/H2O2	180	10		1
018	Cd	MW	HNO3/H2O2	180	10		0.5
018	Pb	MW	HNO3/H2O2	180	10		0.1
018	Hg	--	--	--	--		0.005
019	As	CMW	HNO3	210	30		0.03
019	Cd	CMW	HNO3	210	30		0.004
019	Pb	CMW	HNO3	210	30		0.02
019	Hg	CMW	HNO3	210	30		0.01
020	As						
020	Cd						
020	Pb						
020	Hg					95.8	0.00042
021	As	CMW	HNO3	180	30	110	0.0006
021	Cd	CMW	HNO3	180	30	103.5	0.0017
021	Pb	CMW	HNO3	180	30	99.7	0.0048
021	Hg					105	0.0002
022	As	CMW	HNO3/H2O2	200	40	80	0.08
022	Cd	CMW	HNO3/H2O2	200	40	85	0.1
022	Pb	CMW	HNO3/H2O2	200	40	90	0.05
022	Hg		HNO3/H2O2	200	40		
023	As	CMW	HNO/H2O2	200	20	101	0.020
023	Cd	CMW	HNO/H2O2	200	20	102	0.005
023	Pb	CMW	HNO/H2O2	200	20	96	0.020
023	Hg	Dry Ash	-	850	150 s	103	0.005
024	As	Pressure bomb	HNO3/H2O2	180	Ramp/hold 20/20	80-110	0.067
024	Cd	Pressure bomb	HNO3/H2O2	180	Ramp/hold 20/20	80-110	0.0033
024	Pb	Pressure bomb	HNO3/H2O2	180	Ramp/hold 20/20	80-110	0.010
024	Hg	Pressure bomb	HNO3/H2O2	180	Ramp/hold 20/20	80-110	0.016
025	As	CMW	HNO3/H2O2	200	20	98	0.04
025	Cd	CMW	HNO3/H2O2	200	20	110	0.04
025	Pb	CMW	HNO3/H2O2	200	20	90	0.04
025	Hg	CMW	HNO3/H2O2	200	20	92	0.04

Lab Code	Measurand	Digestion type	Acid mixture	Temperature (°C)	Time (min)	Recovery %	LODs (mg/kg)
026	As	CMW	HNO3	220	20	102	0.013
026	Cd	CMW	HNO3	220	20	100	0.0014
026	Pb	CMW	HNO3	220	20	102	0.006
026	Hg	CMW	HNO3	220	20	105	0.003
027	As	MW	HNO3	200	30	111	0.05
027	Cd	MW	HNO3	200	30	111	0.02
027	Pb	MW	HNO3	200	30	107	0.27
027	Hg	MW	HNO3	200	30	103	0.08
028	As	CMW	HNO3/H2O2	200	8		0,002
028	Cd	CMW	HNO3/H2O2	200	8		0,02
028	Pb	CMW	HNO3/H2O2	200	8		0,02
028	Hg	CMW	HNO3/H2O2	200	8		0,03
029	As	CMW	HNO3/H2O2	230	50		0.01
029	Cd	CMW	HNO3/H2O2	230	50		0.01
029	Pb	CMW	HNO3/H2O2	230	50		0.02
029	Hg	CMW	HNO3/H2O2	230	50		0.01
030	As	CMW	HNO3/H2O2	210	30	98,81	10
030	Cd	CMW	HNO3/H2O2	210	30	98,81	10
030	Pb	CMW	HNO3/H2O2	210	30	99,45	10
030	Hg	-	-	-	-	96	1
031	As	CMW	HNO3/H2O2	200	40	97	0.020
031	Cd	CMW	HNO3/H2O2	200	40	94	0.004
031	Pb	CMW	HNO3/H2O2	200	40	95	0.006
031	Hg					102	0.010
032	As	CMW	HNO3	230	20	100	0,025
032	Cd	CMW	HNO3	230	20	100	0,006
032	Pb	CMW	HNO3	230	20	100	0,02
032	Hg	CMW	HNO3	230	20	100	0,013
033	As	CMW	HNO3/H2O2	180°C	30.	100	0.005
033	Cd	CMW	HNO3/H2O2	180°C	30.	100	0.005
033	Pb	CMW	HNO3/H2O2	180°C	30.	100	0.010
033	Hg	OWD	HNO3/H2SO4	200°C	15 min.	100	0.005
034	As						
034	Cd						
034	Pb						
034	Hg						
036	As	CMW	HNO3	200	20	100	0.2
036	Cd	CMW	HNO3	200	20	100	0.05
036	Pb	CMW	HNO3	200	20	100	0.05
036	Hg					100	0.015

CMW: closed microwave digestion; OWD: open wave digestion

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