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EURL-HM-24 Proficiency Test Report

Determination of the mass fractions of total As, Cd, Pb and Hg in a herbal supplement

P. Dehouck, F. Cordeiro, A. Cizek-Stroh, H. Emteborg and P. Robouch

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European Union Reference Laboratory
Heavy Metals in Feed and Food

EURL-HM-24 Proficiency test report

Determination of the mass fraction of total As, Cd, Pb and Hg in a herbal supplement

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268-PT Accredited by the
Belgian Accreditation Body (BELAC)

Contents

Executive summary

The European Union Reference Laboratory for Heavy Metals in Feed and Food (EURL-HM) organised a proficiency test (EURL-HM-24) for the determination of the mass fraction of total As, Cd, Pb and Hg in a herbal supplement, to support the Regulation 629/2008 amending Regulation 1881/2006 setting maximum levels for certain contaminants in foodstuffs. This PT was open only to National Reference Laboratories (NRLs).

The blinded reference material SRM® 3262 St. John's Wort (*Hypericum perforatum L.*) was used as test item. The purchased finely ground powder material was rebottled, relabelled and dispatched to participants. The reference values of interest were provided in the SRM certificate by the National Institute of Standards and Technology (NIST).

Thirty six participants from 29 countries registered to the exercise (all EU Member States except Portugal, plus Iceland and Norway). Two participants could not report results, one of them due to technical instrumental problems.

Laboratory results were rated using *z*- (or *z'*- for Pb) and zeta (*ζ*-) scores in accordance with ISO 13528:2015. The following relative standard deviations for proficiency assessment (σ_{pt}) were derived from the modified Horwitz equation: 10 % for Cd; 15% for total As and Hg and 16 % for Pb.

More than 93 % of the participating NRLs reported satisfactory results (according to the z-score or z'-score) for total As, Cd and Pb. Only 52 % reported satisfactorily for Hg, due to the low mass fraction level in the test item.

These results confirmed the ability of most NRLs in monitoring the maximum levels set by the European Regulation (EC) No 629/2008 for food supplements. Furthermore, most of the laboratories provided realistic estimates of their measurement uncertainties.

1 Introduction

The European Union Reference Laboratory for Heavy Metals in Feed and Food (EURL-HM), hosted by the Joint Research Centre in Geel, organised the proficiency test (PT) EURL-HM-24 for the determination of the mass fraction of total As, Cd, Pb and Hg in a herbal supplement. This PT was agreed with the Directorate General for Health and Food Safety (DG SANTE) as part of the EURL-HM annual work programme 2017.

This report summarises the outcome of the PT.

2 Scope

As stated in Regulation (EC) No 882/2004 [1] 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 the mass fraction of total As, Cd, Pb and Hg in a herbal supplement.

In addition, participants were asked to evaluate the conformity of the analysed herbal supplement according to the maximum levels (MLs) set in Regulation 629/2008 amending Regulation 1881/2006 setting maximum levels for certain contaminants in foodstuffs [2].

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/IEC 17043:2010 [3].

This PT is identified as EURL-HM-24.

3 Set up of the exercise

3.1 Time frame

The organisation of the EURL-HM-24 exercise was agreed upon by the NRL network at the 11th EURL-HM Workshop held in Geel on October 5, 2016. The exercise was announced on the JRC webpage on March 2, 2017 (Annex 2) and on March 6, 2017 an invitation letter was sent to all NRLs of the network via e-mail (Annex 3). The registration deadline was set to March 31, 2017. Samples were sent to participants on April 4 and 5, 2017. The 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 May 31, 2017.

3.2 Confidentiality

The procedures used for the organisation of PTs are accredited according to ISO/IEC 17043:2010 [3] and guarantee that the identity of the participants and the information provided by them is treated as confidential. However, lab codes of the National Reference Laboratories appointed in line with Regulation (EC) No 882/2004 will be disclosed to DG SANTE upon request for (long-term) performance assessment.

3.3 Distribution

Each participant received:

- one vial of the test item (containing approx. 3 g) sealed in a sachet;
- 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 and Hg in a herbal supplement.

Participants were asked to perform two or three independent measurements, to report their calculated mean (x_i) with no moisture correction to be applied, the corresponding expanded measurement uncertainty ($U(x_i)$) together with the coverage factor (k), and the analytical technique used for analysis.

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

The reference material SRM® 3262 St. John's Wort (*Hypericum perforatum L.*) was used as the EURL-HM-24 test item. A sufficient number of SRM® 3262 bottles were purchased from the National Institute of Standards and Technology (NIST), US.

The purchased material was rebottled and relabelled at the JRC-Geel. About 3 g of the content of the original aluminium sachets (ca. 16 g) was transferred under a nitrogen flux into acid washed (2 % HNO_3) amber glass 10 mL vials. After transfer the vials were closed with acid washed Teflon-coated inserts and manually crimp-capped with aluminium caps. Each vial was packed in a heat-sealed aluminium sachet.

Two vials containing approximately 1.5 g were used to monitor water uptake. The first vial was closed and weighed twice per week for four weeks. The second vial was left open in the laboratory and weighed four times during 24 hours. The variation in mass observed for both vials was within the variation expected from the uncertainty of weighing. Therefore it was assumed that the water uptake by the test item material was negligible.

5 Assigned values

5.1 Reference values and corresponding uncertainties

The assigned values and expanded uncertainties (x_{pt} and $U(x_{pt})$) of the four measurands (mass fractions of total As, Cd, Hg and Pb in the herbal supplement) were determined by NIST [4]. The SRM certificate provided (i) the certified mass fraction values for total As, Cd and Hg; and (ii) the (informative) reference mass fraction value for Pb. These values reported on a "*dry-mass*" basis were multiplied by 0.9512 (derived from the moisture content determined at NIST) to convert the data to an "*as received*" basis (Table 1).

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

The relative standard deviations for PT assessment (σ_{pt}, in %) presented in Table 1 were calculated using the Horwitz equation modified by Thompson [5].

Table 1: *Assigned values (x_{pt}), corresponding expanded uncertainty ($U(x_{pt})$) and standard deviation for the PT assessment (σ_{pt}).*

Elements	$X_{pt} \pm U(x_{pt})$ * *dry mass*	*Coverage factor, k*	$X_{pt} \pm U(x_{pt})$ * "*as received*"	σ_{pt} *		$u(x_{pt})/\sigma_{pt}$
As	0.152 ± 0.014	2.00	0.145 ± 0.013	0.022	15 %	0.30
Cd	0.3638 ± 0.0094	2.13	0.3460 ± 0.0089	0.0346	10 %	0.12
Pb	0.98 ± 0.14	2.23	0.93 ± 0.13	0.149	16 %	0.38
Hg	0.01479 ± 0.00043	2.36	0.01407 ± 0.00041	0.00211	15 %	0.09

* *values expressed in mg kg^{-1}*

6 Evaluation of results

6.1 Scores and evaluation criteria

The individual laboratory performance was expressed in terms of z- and ζ-scores according to ISO 13528:2015 [6]:

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

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

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.

According to ISO 13528:2015 [6], when $u(x_{pt}) > 0.3\ \sigma_{pt}$ (as for Pb, see Table 1) *the uncertainty of the assigned value can be taken into account by expanding the denominator of the z-score and calculating the z'-score,* as follows:

$$z'_i = \frac{x_i - x_{pt}}{\sqrt{\sigma_{pt}^2 + u(x_{pt})^2}} \qquad \text{Eq. 3}$$

Note: $\sqrt{\sigma_{pt}^2 + u(x_{pt})^2} = \sqrt{0.149^2 + 0.065^2} = 0.16$ mg kg^{-1} (17.2 % of x_{pt}(Pb))

The interpretation of the z-, z'- and ζ- scores is done according ISO 13528:2015 [3]:

|score| ≤ 2	satisfactory performance	(green in Annexes 7-11)
2 < |score| < 3	questionable performance	(yellow in Annexes 7-11)
|score| ≥ 3	unsatisfactory performance	(red in Annexes 7-11)

The z- and z'- scores compare 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 standard measurement uncertainty reported by the laboratory $u(x_i)$. The ζ-score includes all parts of a measurement result, namely the expected value (assigned value), the corresponding measurement uncertainty in the unit of the result as well as the standard uncertainty of the reported values. An unsatisfactory ζ-score can either be caused by an inappropriate estimation of the mass fraction, 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 $\sqrt{3}$, as recommended in the Eurachem guide [7].

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 six NRLs from 29 countries registered to the exercise (all EU Member States except Portugal plus Iceland and Norway). Two participants (L005, L011) could not report results due to technical problems. The participants having reported results are listed in the "Acknowledgment" section.

More than 94% of the laboratories reported results for each measurand.

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

Element	Reported Results	Comments
As	32 (94 %)	No results from L004 and L035 ; 4 "*less than*" values
Cd	34 (100 %)	
Pb	33 (97 %)	No results from L013
Hg	32 (94 %)	No results from L001 and L020 ; 7 "*less than*" values

6.3 Laboratory results and scorings

6.3.1 Performances

Annexes 7 to 10 present the reported results as tables and graphs for each measurand, where NRLs are denoted as "0xx" (from 001 to 036). 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 [8] are also included.

The laboratory performance for the determination of total As, Cd and Hg was assessed using the *z*- and ζ-scores. However, the ISO 13528:2015 recommendation was applied for Pb (for which $u(x_{pt}) > 0.3\ \sigma_{pt}$, see Table 1) and the *z'*-score was used instead of the *z*-score.

Figures 1 and 2 present the laboratory performances for total As, Cd, Pb and Hg, assessed by the *z*- (*z*'- for Pb) and ζ-scores. Most of the participants having reported results performed satisfactorily for total As, Cd and Pb: 93 % and above for the *z*-score and 75 % and above for the ζ-scores.

For total Hg the satisfactory performance was lower (52 % for the z-score and 56 % for the ζ-score), probably due to the very low mass fraction level of Hg in the material, leading to an overestimated Hg content by a number of laboratories (Annex 10). This overestimation may be attributed to Hg contamination in the laboratory. In addition, all the laboratories reporting truncated values provided realistic "less than" values for Hg (above x_{pt}-$U(x_{pt})$).

Eleven (out of 34) laboratories performed satisfactorily for the determination of all four measurands (total As, Cd, Pb and Hg).

No direct correlations could be found between the analytical methods used by the participants (see Annex 11) and the quality of the reported results.

It can be concluded that most NRLs have proven their competence to measure the mass fractions for total As, Cd and Pb in the investigated herbal supplement. The mass fraction of Hg in this test item was too low to draw the same conclusion for Hg as well.

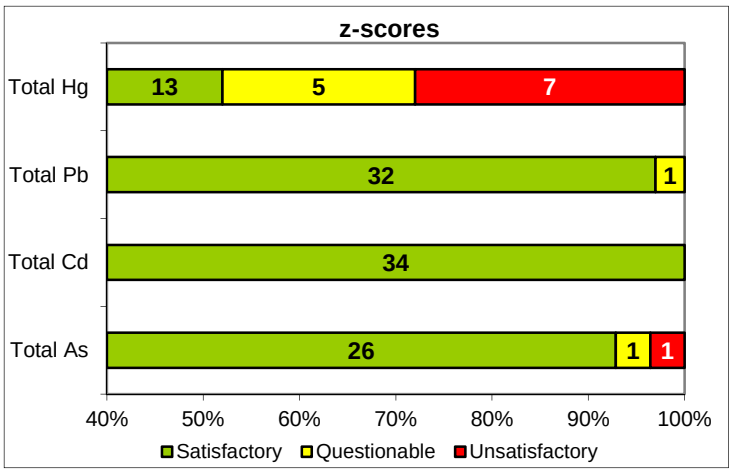

Figure 1:

Overview of laboratory performance per measurand according to z-scores (z'-score in the case of Pb).

Corresponding number of laboratories indicated in the graph.

Satisfactory (green); Questionable (yellow) or Unsatisfactory (red)

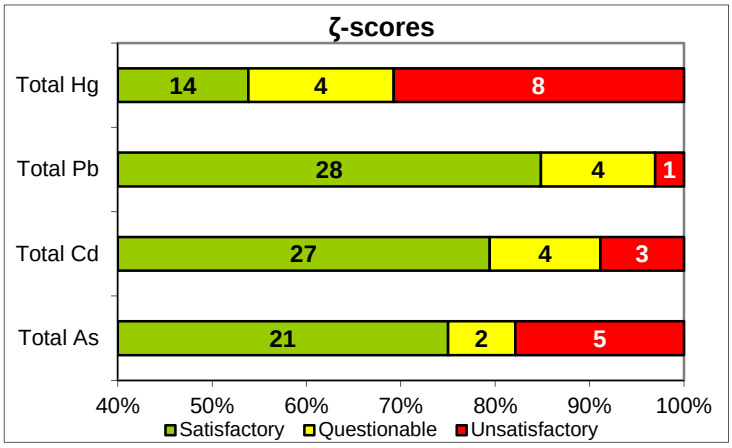

Figure 2:

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

Corresponding number of laboratories indicated in the graph.

Satisfactory (green); Questionable (yellow) or Unsatisfactory (red)

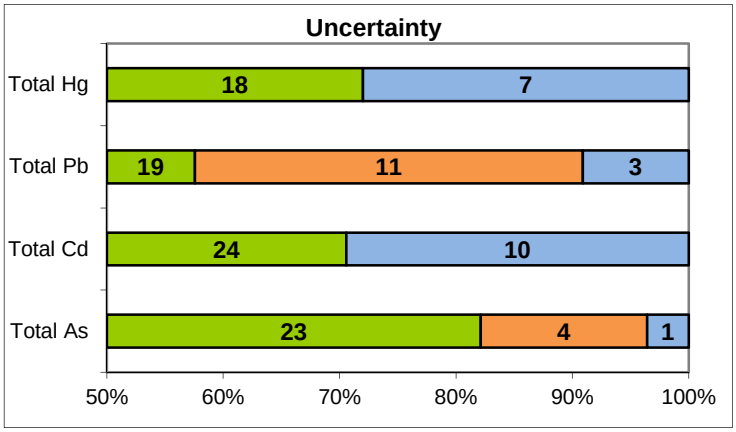

Figure 3:

Overview of uncertainties reported per measurand.

The corresponding number of laboratories indicated in the graph.

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

6.3.2 Uncertainties

Figure 3 presents the uncertainty assessment per measurand. Most of the participants (around 60% and more) reported "realistic" measurement uncertainty estimates ("Case a": $u(x_{pt}) \leq u(x_i) \leq \sigma_{pt}$).

In the case of Pb, eleven laboratories reported standard measurement uncertainties (k = 1) smaller than the uncertainty of the assigned value, and were systematically attributed a "Case b" (Figure 4). This apparent "under-estimation" may be due to the higher standard uncertainty set by NIST for the "informative" reference value of Pb (0.93 ± 0.065 mg kg^{-1}, k = 1). This is further confirmed by the fact that six of the above mentioned laboratories (007, 009, 014, 018, 027 and 029) reported relative uncertainties of 4 to 7 % and obtained satisfactory z- and ζ– scores. Similarly, laboratories 017, 021 and 023 reported relative uncertainties of 2 % associated to accurate results.

On the other hand, four laboratories (010, 012, 030 and 036) seem to overestimate their measurement uncertainties for several measurands. They should consider reviewing their measurement uncertainty budget.

The evaluation of measurement uncertainties (as case "a", "b" and "c") provides useful additional information when combined with the z and ζ assessments.

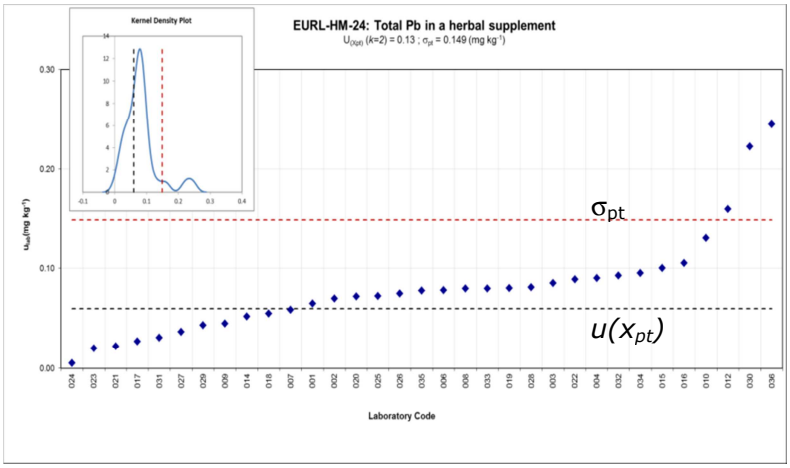

Figure 4:

Standard uncertainties $u(x_i)$ reported by the participants.

The black and red dashed lines correspond to $u(x_{pt})$ and σ_{pt}, respectively - defining the Case "a", "b" and "c" ranges

6.3.3 Compliance

The mass fractions of all the investigated elements (As, Cd, Pb and Hg) in the test item were below the Maximum Limits (MLs) set in Regulation 629/2008 (Table 3). The low Hg level mentioned earlier is seven times lower than the MRL. All NRLs stated correctly that the investigated test item was compliant according to Regulation 629/2008.

Table 3: *Maximum residues levels (MLs) set in Regulation 629/2008, compared to the assigned range ($x_{pt} \pm U(x_{pt})$, with k values as listed in Table 1). All values expressed in mg kg^{-1}.*

Elements	Assigned values	MLs
As	0.145 ± 0.013	--
Cd	0.3460 ± 0.0089	1.0
Pb	0.93 ± 0.13	3.0
Hg	0.01407 ± 0.00041	0.10

6.3.4 Additional information from the questionnaire

The questionnaire was answered by 33 (out of 34) participants giving valuable information on the laboratories, their way of working and their analytical methods.

From the standard analytical methods used, EN 15763:2009 was used most (11 laboratories) [9], as can be seen in Table 4.

Table 4: *Standard methods used by the participants*

Standard method	Title	N° of labs
EN 15763	Foodstuffs. Determination of trace elements. Determination of arsenic, cadmium, mercury and lead in foodstuffs by inductively coupled plasma mass spectrometry (ICPMS) after pressure digestion	11
EN 13805	Foodstuffs. Determination of trace elements. Pressure digestion	2
EN 13806	Foodstuffs. Determination of trace elements. Determination of mercury by cold-vapour atomic absorption spectrometry (CVAAS) after pressure digestion	2
EN 14083	Foodstuffs. Determination of trace elements. Determination of lead, cadmium, chromium and molybdenum by graphite furnace atomic absorption spectrometry (GFAAS) after pressure digestion	2
EN 14084	Foodstuffs. Determination of trace elements. Determination of lead, cadmium, zinc, copper and iron by atomic absorption spectrometry (AAS) after microwave digestion	2
EN 14546	Foodstuffs. Determination of trace elements. Determination of total arsenic by hydride generation atomic absorption spectrometry (HGAAS) after dry ashing	2
EN 14627	Foodstuffs. Determination of trace elements. Determination of total arsenic and selenium by hydride generation atomic absorption spectrometry (HGAAS) after pressure digestion	1
EN 16206	Animal feeding stuffs. Determination of arsenic by hydride generation atomic absorption spectrometry (HGAAS) after microwave pressure digestion (digestion with 65 % nitric acid and 30 % hydrogen peroxide)	1
EN 15550	Animal feeding stuffs. Determination of cadmium and lead by graphite furnace atomic absorption spectrometry (GF-AAS) after pressure digestion	1
NMKL 186	Trace elements - As, Cd, Hg, Pb and other elements. Determination by ICP-MS after pressure digestion	1

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

Approach	N° of labs
According to ISO-GUM	10
Known uncertainty of a standard method	1
Obtained from in-house validation study	23
Measurement of replicates (precision)	8
Estimation based on judgment	2
Obtained from interlaboratory comparison data	8
Obtained from control chart	1
According to NORDTEST guidelines	1

Several approaches were used to estimate measurement uncertainties (Table 5). Most of the laboratories derive their uncertainty estimates from their single laboratory validation study. The majority of the NRLs (29 out of 33) routinely report uncertainties for this type of analysis to their customers.

The recovery factor was mostly determined by using a (certified) reference material (21 laboratories) or by spiking with a known amount of the same analyte (8 laboratories). Four laboratories did not report any recovery factor.

All laboratories reported to be accredited according to ISO/IEC 17025 but only 21 (out of 33) were accredited for the four measured elements in food supplements.

No correlation between performance and experience (evaluated as number of analyses per year) on the specific analysis could be identified for any of the measurands.

7 Conclusion

The EURL-HM-24 PT was organised in 2017 to assess the analytical capabilities of the NRLs from the EU using the blinded reference material SRM® 3262 St. John's Wort (*Hypericum perforatum L.*) as test item.

The overall performance of the participants in the determination of total As, Cd and Pb in the herbal supplement was satisfactory. However, only 52 % of the laboratories reported satisfactory results for Hg, due to the low Hg mass fraction level in the samples.

This confirms the analytical capabilities of most of the NRLs to enforce the European Regulation (EC) No 629/2008 amending Regulation 1881/2006 setting maximum levels for certain contaminants in foodstuffs.

The reasonable measurement uncertainty estimates reported by the NRLs demonstrate the effectiveness of the various PTs and training courses organised by the EURL-HM in the past 10 years.

Acknowledgements

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

The 34 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 Institute of Public Health	Croatia
State General Laboratory	Cyprus
Central Institute for Supervising and Testing in Agriculture (UKZUZ)	Czech Republic
State Veterinary Institute Olomouc	Czech Republic
Danish Veterinary and Food Administration	Denmark
National Food Institute (DTU Food)	Denmark
Agricultural Research Centre	Estonia
Finnish Customs Laboratory	Finland
Laboratoire SCL de Bordeaux	France
Federal Office of Consumer Protection and Food Safety	Germany
General Chemical State Laboratory	Greece
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	Iceland
Health Service Executive	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 Laboratory	Malta
RIKILT	Netherlands
NIFES	Norway
ALcontrol Stjørdal	Norway
National Institute of Public Health - National Institute of Hygiene (NIPH-NIH)	Poland
Sanitary Veterinary and Food safety Directorate Bucharest	Romania
Veterinary and Food Institute in Košice	Slovakia
NLZOH	Slovenia
Laboratorio Arbitral Agroalimentario (MAPAMA)	Spain
National Food Agency	Sweden
Fera	United Kingdom

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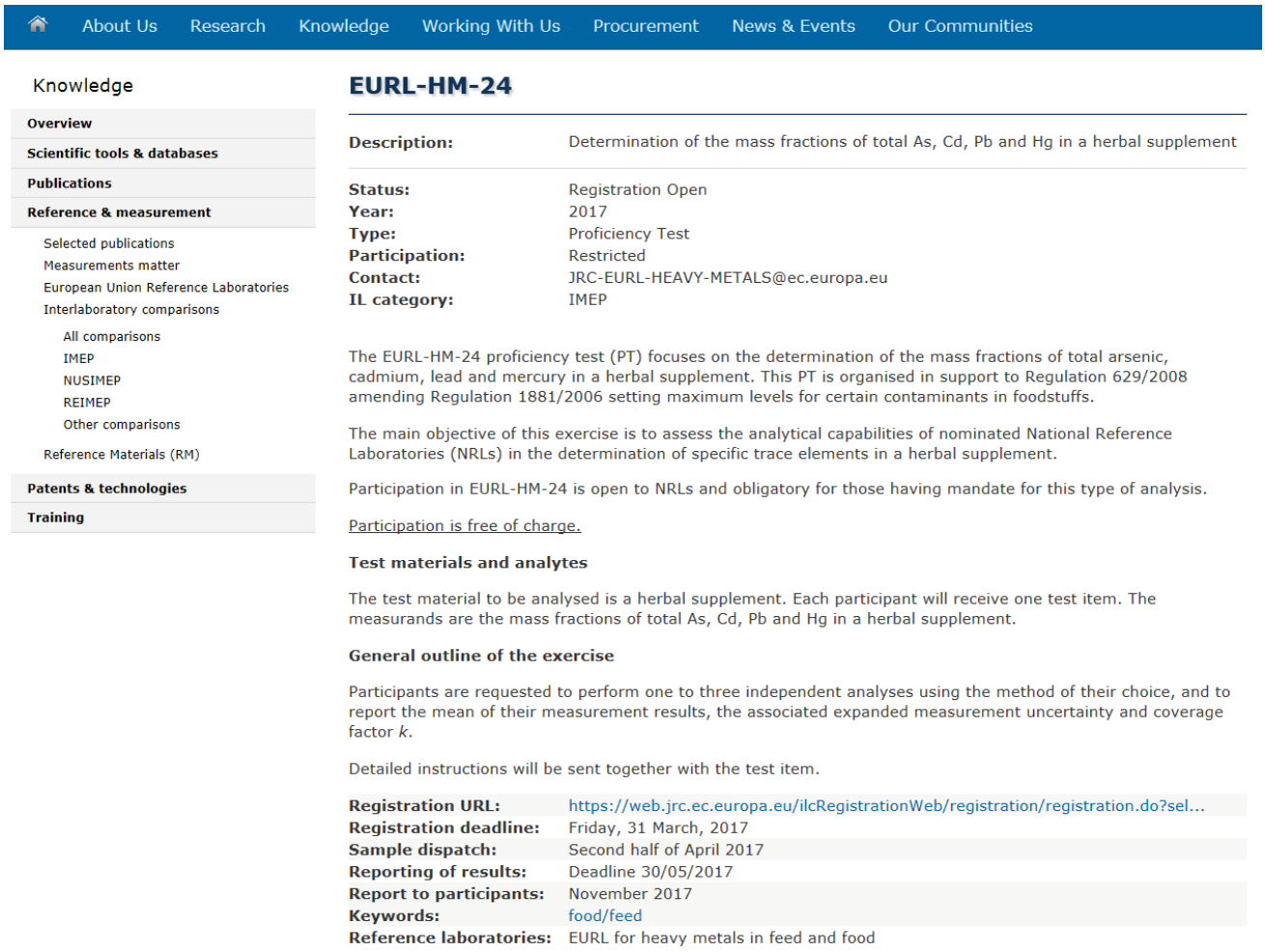
Annex 1: List of abbreviations

AAS	Atomic Absorption Spectrometry
CEN	European Committee for Standardization
CV-AAS	Cold Vapour Atomic Absorption Spectroscopy
CV-AFS	Cold Vapour Atomic Fluorescence Spectroscopy
DMA	Direct Mercury Analyser (also called Elemental Mercury Analyzer, EMA)
EU	European Union
EURL-HM	European Union Reference Laboratory for Heavy Metals in Feed and Food
GFAAS	Graphite Furnace Atomic Absorption Spectroscopy
ICP-MS	Inductively Coupled Plasma – Mass Spectrometry
ISO	International Organization for Standardization
JRC	Joint Research Centre
NIST	National Institute of Standards and Technology, US
NRL	National Reference Laboratory
PT	Proficiency Test
SRM	Standard Reference Material

Annex 2: JRC Web Announcement



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    - NUSIMEP
    - REIMEP
    - Other comparisons
  - Reference Materials (RM)
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- **Training**

EURL-HM-24

Description: Determination of the mass fractions of total As, Cd, Pb and Hg in a herbal supplement

Status: Registration Open
Year: 2017
Type: Proficiency Test
Participation: Restricted
Contact: JRC-EURL-HEAVY-METALS@ec.europa.eu
IL category: IMEP

The EURL-HM-24 proficiency test (PT) focuses on the determination of the mass fractions of total arsenic, cadmium, lead and mercury in a herbal supplement. This PT is organised in support to Regulation 629/2008 amending Regulation 1881/2006 setting maximum levels for certain contaminants in foodstuffs.

The main objective of this exercise is to assess the analytical capabilities of nominated National Reference Laboratories (NRLs) in the determination of specific trace elements in a herbal supplement.

Participation in EURL-HM-24 is open 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 a herbal supplement. Each participant will receive one test item. The measurands are the mass fractions of total As, Cd, Pb and Hg in a herbal supplement.

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, 31 March, 2017
Sample dispatch: Second half of April 2017
Reporting of results: Deadline 30/05/2017
Report to participants: November 2017
Keywords: food/feed
Reference laboratories: EURL for heavy metals in feed and food

Annex 3: Invitation letter to NRLs

EUROPEAN COMMISSION
Joint Research Centre
Directorate F – Health, Consumers & Reference Materials
European Union Reference Laboratory for Heavy Metals

Ref. Ares(2017)1163913 - 06/03/2017

Geel, 6 March 2017

(sent by e-mail)

Subject: Invitation to participate in EURL-HM-24

Dear National Reference Laboratory representative,

The EURL-HM would like to invite you to participate in the proficiency test EURL-HM-24 for the **"Determination of the mass fractions of total As, Cd, Pb and Hg in a herbal supplement"**. This PT is organised in support to Regulation 629/2008 amending Regulation 1881/2006 setting maximum levels for certain contaminants in foodstuffs.

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=1721

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 **March 31, 2017**.

Samples will be sent to participants during the **first half of April 2017**.

The deadline for submission of results is **May 31, 2017**.

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

Yours sincerely

/signed electronically in Ares/

Dr. Pieter Dehouck
EURL-HM-24 Coordinator

/signed electronically in Ares/

Dr. Piotr Robouch
Operating Manager EURL-HM

Cc: Hendrik Emons (Head of Unit, Food & Feed Compliance, F.5)

EUROPEAN COMMISSION
JOINT RESEARCH CENTRE
Directorate F – Health, Consumers and Reference Materials
European Union Reference Laboratory for Heavy Metals

Geel, 07 April 2017
Ares(2017)1763469

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

Subject: Participation in EURL-HM-24 - Determination of the mass fractions of total As, Cd, Pb and Hg in a herbal supplement

Dear «Title» «Surname»,

Thank you for participating in the EURL-HM-24 proficiency test (PT) for the **"Determination of the mass fractions of total As, Cd, Pb and Hg in a herbal supplement".** This PT is organised in support to Regulation 629/2008 amending Regulation 1881/2006 setting maximum levels for certain contaminants in foodstuffs.

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. 3 g) sealed in a sachet; 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 room temperature.

The measurands are total As, Cd, Pb and Hg in an herbal supplement.

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

Perform two or three independent measurements and report:

Joint Research Centre
Retiesweg 111, B-2440 Geel - Belgium
Tel.: +32 14 57 12 11 • Direct line: +32 14 57 17 67
e-mail: irc-eurl-heavy-metals@ec.europa.eu
URL: https://ec.europa.eu/jrc/en/eurl/heavy-metals

- the **mean** of your two or three measurements results (in mg kg^{-1}) with no moisture correction to be applied
- the associated expanded **uncertainty** (in mg kg^{-1})
- the **coverage factor** and
- the analytical technique used.

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 **31/05/2017**.

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 Dehouck

EURL-HM-24 Coordinator

Cc: H. Emons (Head of Unit, Food & Feed Compliance, F.5),
P. Robouch (Operating Manager EURL-HM)

Joint Research Centre
Retiesweg 111, B-2440 Geel - Belgium
Tel.: +32 14 57 12 11 • Direct line: +32 14 57 17 67
e-mail: irc-eurl-heavy-metals@ec.europa.eu
URL: https://ec.europa.eu/jrc/en/eurl/heavy-metals

Annex 5: Confirmation of receipt form

EUROPEAN COMMISSION
JOINT RESEARCH CENTRE
Directorate F – Health, Consumers and Reference Materials
European Union Reference Laboratory for Heavy Metals

Geel, 07 April 2017
Ares(2017)1763469

Attn.: «Title» «Firstname» «Surname»
«Organisation»
«Department»
«Address»
«Zip» «Town»
«Country»

Subject: "Confirmation receipt" form
EURL-HM-24 – Heavy metals in a herbal supplement

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-24 Coordinator
e-mail : jrc-eurl-heavy-metals@ec.europa.eu

Joint Research Centre
Retieseweg 111, B-2440 Geel - Belgium
Tel.: +32 14 57 12 11 • Direct line: +32 14 57 17 67
e-mail: jrc-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. **Which recovery factors and LODs did you determine?**

Recovery factors and LODs

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

4. **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

4.1. If "Other" please specify.

4.2. If you used a (certified) reference material, specify which one.

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

6. **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

6.1. If "Other", please specify.

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

- ○ a) Yes
- ○ b) No

8. **Considering your results, is the investigated test item compliant according to Regulation 629/2008?**

- ○ a) Yes
- ○ b) No

8.1. If not compliant, specify why?

9. **Which quality system does your laboratory have?**

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

9.1. If "Other", please specify.

10. **Are you accredited for the determination of these analytes in food supplements?**

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

11. **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	☐	☐	☐	☐	☐	

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

Annex 7: Results for total As

Assigned range: x_{pt} = 0.145; $U(x_{pt})$ (k = *2.00*) = 0.013; σ_{pt} = 0.022 (all values in mg kg^{-1})

Lab Code	X_{lab}	U_{lab}	k[a]	technique	u_{lab}	z-score[b]	zeta-score[b]	u_{lab}[c]
001	<0.2			AAS				
002	0.152	0.03	2	ICP-MS	0.015	0.34	0.45	a
003	0.14	0.03	2	ICP-MS	0.015	-0.21	-0.28	a
006	0.162	0.024	2	ICP-MS	0.012	0.80	1.27	a
007	0.138	0.034	2	ICP-MS	0.017	-0.30	-0.36	a
008	<0.10			ICP-MS				
009	0.18	0.01	2	ICP-MS	0.005	1.63	4.25	b
010	0.079	0.032	2	ICP-MS	0.016	-3.02	-3.78	a
012	0.12	0.038	2	ICP-MS	0.019	-1.13	-1.22	a
013	0.123	0.025	2	AAS	0.0125	-1.00	-1.52	a
014	<0.50			AAS				
015	0.14	0.03	2	ICP-MS	0.015	-0.21	-0.28	a
016	0.18	0.015	2	ICP-MS	0.0075	1.63	3.53	a
017	0.17	0.029	2	ICP-MS	0.0145	1.17	1.59	a
018	0.13	0.021	2	ICP-MS	0.0105	-0.67	-1.17	a
019	0.164	0.03116	2	ICP-MS	0.01558	0.90	1.15	a
020	0.128	0.026	2	AAS	0.013	-0.76	-1.14	a
021	0.151	0.008	2	ICP-MS	0.004	0.30	0.83	b
022	0.123	0.028	2	ICP-MS	0.014	-1.00	-1.39	a
023	0.16	0.01	2	ICP-MS	0.005	0.71	1.85	b
024	0.17	0.03	2	ICP-MS	0.015	1.17	1.55	a
025	0.142	0.03	2	ICP-MS	0.015	-0.12	-0.16	a
026	<0.25			ICP-MS				
027	0.175	0.02	2	HydrEA	0.01	1.40	2.53	a
028	0.139	0.032	2	ICP-MS	0.016	-0.26	-0.32	a
029	0.161	0.019	2	ICP-MS	0.0095	0.76	1.42	a
030	0.15	0.06	2	ICP-MS	0.03	0.25	0.18	c
031	0.17	0.022	2	ICP-MS	0.011	1.17	1.98	a
032	0.15	0.038	2	ICP-MS	0.019	0.25	0.27	a
033	0.11	0.01	2	AAS	0.005	-1.59	-4.15	b
034	0.185	0.022	2	ICP-MS	0.011	1.86	3.14	a
036	0.09	0.04	2	AAS	0.02	-2.52	-2.59	a

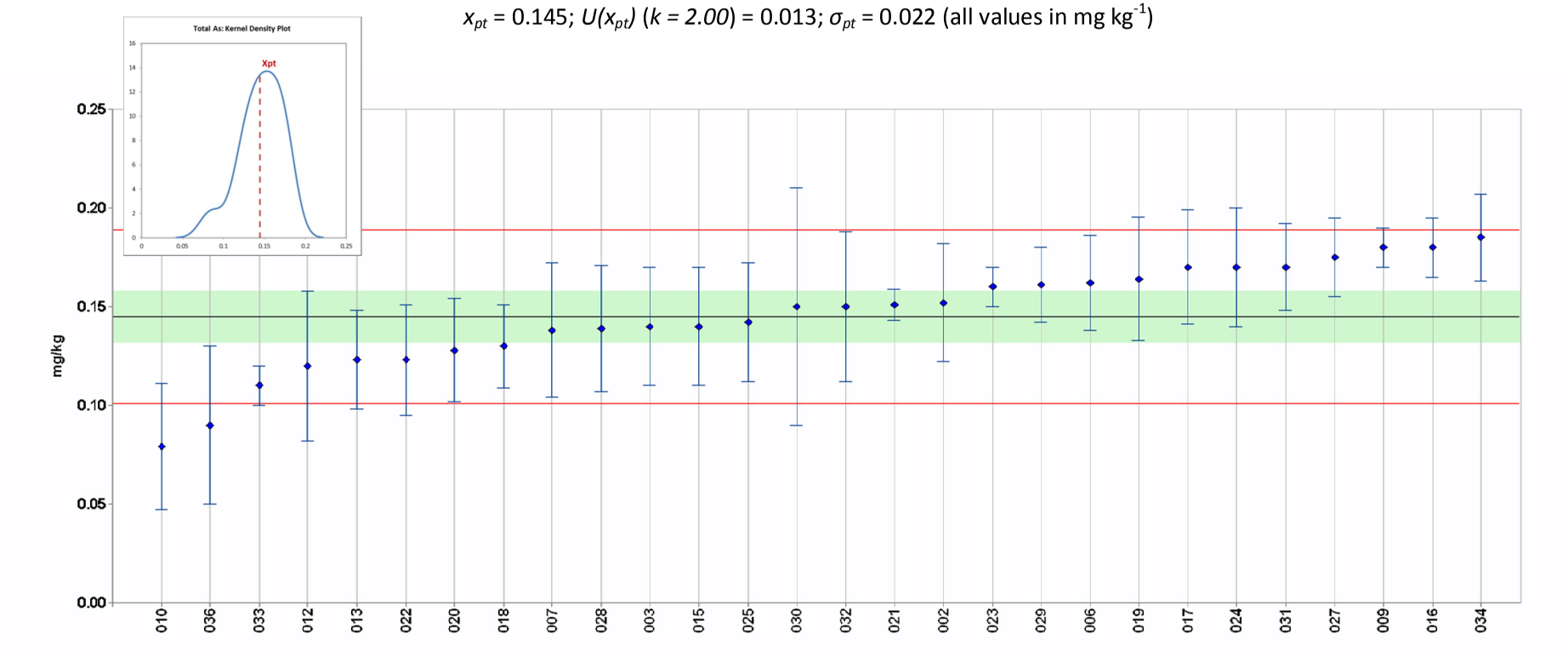
[a] √3 is set by the ILC coordinator when no coverage factor k is reported. The reported uncertainty was assumed to have a rectangular distribution with k = √3,

[b] performance: satisfactory, questionable, unsatisfactory,

[c] a : $u_{min}\,(u(x_{pt})) \leq u_{lab} \leq u_{max}(\sigma_{pt})$; b : $u_{lab} < u_{min}$; and c : $u_{lab} > u_{max}$

EURL-HM-24: Total As in a herbal supplement

x_{pt} = 0.145; $U(x_{pt})$ (k = 2.00) = 0.013; σ_{pt} = 0.022 (all values in mg kg^{-1})



Measurement results and associated uncertainties (reported uncertainties shown)

Reference value x_{pt}: solid black line; Reference interval $x_{pt} \pm U_{(Xpt)}$: green interval; Target interval ($X_{pt} \pm 2\sigma_{pt}$): red lines

Annex 8: Results for total Cd

Assigned range: x_{pt} = 0.3460; $U(x_{pt})$ (k = 2.13) = 0.0089; σ_{pt} = 0.0346 (all values in mg kg^{-1})

Lab Code	X_{lab}	U_{lab}	k[a]	technique	u_{lab}	z-score[b]	zeta-score[b]	u_{lab}[c]
001	0.33	0.045	2	AAS	0.0225	-0.46	-0.70	a
002	0.293	0.06	2	ICP-MS	0.03	-1.53	-1.75	a
003	0.38	0.08	2	ICP-MS	0.04	0.98	0.84	c
004	0.39	0.04	2	ICP-MS	0.02	1.27	2.15	a
006	0.315	0.032	2	ICP-MS	0.016	-0.90	-1.88	a
007	0.338	0.051	2	AAS	0.0255	-0.23	-0.31	a
008	0.33	0.06	2	ICP-MS	0.03	-0.46	-0.53	a
009	0.35	0.02	2	ICP-MS	0.01	0.11	0.36	a
010	0.34	0.1	2	ICP-MS	0.05	-0.17	-0.12	c
012	0.31	0.12	2	ICP-MS	0.06	-1.04	-0.60	c
013	0.387	0.077	2	AAS	0.0385	1.18	1.06	c
014	0.386	0.031	√3	AAS	0.017898	1.15	2.17	a
015	0.35	0.09	2	ICP-MS	0.045	0.11	0.09	c
016	0.37	0.06	2	ICP-MS	0.03	0.69	0.79	a
017	0.36	0.064	2	ICP-MS	0.032	0.40	0.43	a
018	0.34	0.055	2	ICP-MS	0.0275	-0.17	-0.22	a
019	0.346	0.06574	2	ICP-MS	0.03287	0.00	0.00	a
020	0.292	0.024	2	AAS	0.012	-1.56	-4.25	a
021	0.388	0.019	2	ICP-MS	0.0095	1.21	4.04	a
022	0.34	0.078	2	ICP-MS	0.039	-0.17	-0.15	c
023	0.37	0.04	2	ICP-MS	0.02	0.69	1.17	a
024	0.28	0.06	2	ICP-MS	0.03	-1.91	-2.18	a
025	0.365	0.055	2	ICP-MS	0.0275	0.55	0.68	a
026	0.3475	0.07	2	ICP-MS	0.035	0.04	0.04	c
027	0.338	0.015	2	GFAAS	0.0075	-0.23	-0.94	a
028	0.355	0.053	2	ICP-MS	0.0265	0.26	0.33	a
029	0.313	0.031	2	ICP-MS	0.0155	-0.95	-2.06	a
030	0.34	0.136	2	ICP-MS	0.068	-0.17	-0.09	c
031	0.308	0.022	2	ICP-MS	0.011	-1.10	-3.23	a
032	0.33	0.083	2	ICP-MS	0.0415	-0.46	-0.38	c
033	0.31	0.05	2	AAS	0.025	-1.04	-1.42	a
034	0.34	0.046	2	ICP-MS	0.023	-0.17	-0.26	a
035	0.33	0.0592	2	AAS	0.0296	-0.46	-0.54	a
036	0.3	0.11	2	AAS	0.055	-1.33	-0.83	c

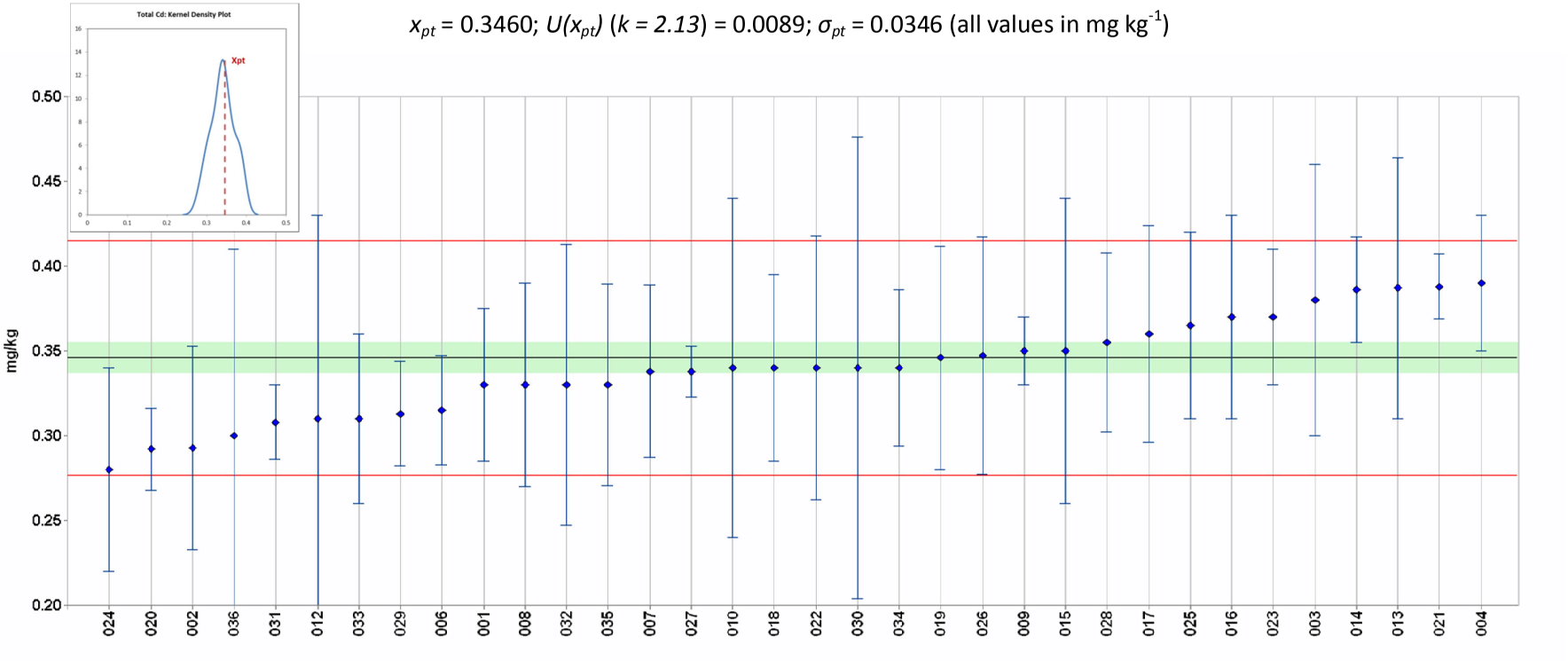
[a] √3 is set by the ILC coordinator when no coverage factor k is reported. The reported uncertainty was assumed to have a rectangular distribution with k = √3,

[b] performance: satisfactory, questionable, unsatisfactory,

[c] a : $u_{min}(u(x_{pt})) \leq u_{lab} \leq u_{max}(\sigma_{pt})$; b : $u_{lab} < u_{min}$; and c : $u_{lab} > u_{max}$

EURL-HM-24: Total Cd in a herbal supplement

x_{pt} = 0.3460; $U(x_{pt})$ (k = 2.13) = 0.0089; σ_{pt} = 0.0346 (all values in mg kg^{-1})



Measurement results and associated uncertainties (reported uncertainties shown)

Reference value x_{pt}: solid black line; Reference interval $x_{pt} \pm U_{(Xpt)}$: green interval; Target interval ($X_{pt} \pm 2\sigma_{pt}$): red lines

Annex 9: Results for total Pb

Assigned range: x_{pt} = 0.93; $U(x_{pt})$ (k = 2.23) = 0.13; σ_{pt} = 0.149 (all values in mg kg^{-1})

Lab Code	X_{lab}	U_{lab}	k[a]	technique	u_{lab}	z'-score[b]	zeta-score[b]	u_{lab}[c]
001	0.72	0.13	2	AAS	0.065	-1.32	-2.40	a
002	0.688	0.14	2	ICP-MS	0.07	-1.52	-2.65	a
003	0.82	0.17	2	ICP-MS	0.085	-0.70	-1.08	a
004	0.94	0.18	2	ICP-MS	0.09	0.05	0.07	a
006	1.04	0.156	2	ICP-MS	0.078	0.67	1.10	a
007	0.779	0.117	2	AAS	0.0585	-0.95	-1.83	b
008	0.81	0.16	2	ICP-MS	0.08	-0.76	-1.22	a
009	0.95	0.09	2	ICP-MS	0.045	0.11	0.24	b
010	0.85	0.26	2	ICP-MS	0.13	-0.51	-0.57	a
012	0.8	0.32	2	ICP-MS	0.16	-0.82	-0.77	c
014	1.05	0.09	1.732051	AAS	0.051962	0.73	1.49	b
015	0.71	0.2	2	ICP-MS	0.1	-1.38	-1.91	a
016	0.8	0.21	2	ICP-MS	0.105	-0.82	-1.09	a
017	0.9	0.054	2	ICP-MS	0.027	-0.20	-0.49	b
018	0.82	0.11	2	ICP-MS	0.055	-0.70	-1.38	b
019	0.801	0.1602	2	ICP-MS	0.0801	-0.81	-1.31	a
020	0.831	0.144	2	AAS	0.072	-0.63	-1.08	a
021	0.88	0.044	2	ICP-MS	0.022	-0.32	-0.82	b
022	0.775	0.178	2	ICP-MS	0.089	-0.98	-1.47	a
023	0.81	0.04	2	ICP-MS	0.02	-0.76	-1.94	b
024	0.62	0.01	2	ICP-MS	0.005	-1.94	-5.21	b
025	0.907	0.145	2	ICP-MS	0.0725	-0.16	-0.27	a
026	0.7294	0.15	2	ICP-MS	0.075	-1.26	-2.11	a
027	0.856	0.073	2	GFAAS	0.0365	-0.47	-1.09	b
028	0.852	0.162	2	ICP-MS	0.081	-0.50	-0.80	a
029	0.869	0.087	2	ICP-MS	0.0435	-0.39	-0.85	b
030	0.89	0.445	2	ICP-MS	0.2225	-0.26	-0.18	c
031	0.735	0.062	2	ICP-MS	0.031	-1.22	-2.93	b
032	0.74	0.185	2	ICP-MS	0.0925	-1.19	-1.75	a
033	0.78	0.16	2	AAS	0.08	-0.95	-1.52	a
034	0.94	0.19	2	ICP-MS	0.095	0.05	0.07	a
035	0.86	0.1552	2	AAS	0.0776	-0.45	-0.74	a
036	0.9	0.49	2	AAS	0.245	-0.20	-0.13	c

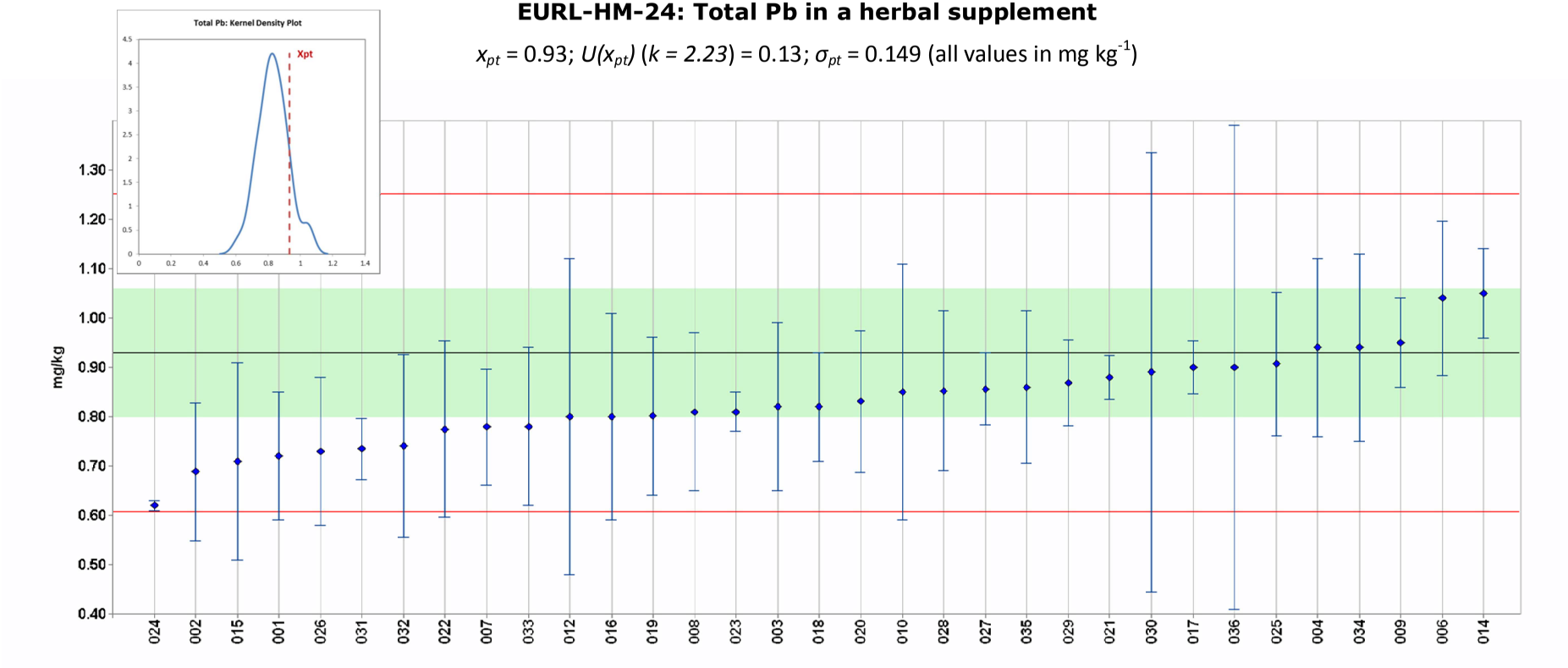
[a] √3 is set by the ILC coordinator when no coverage factor k is reported. The reported uncertainty was assumed to have a rectangular distribution with k = √3,

[b] performance: satisfactory, questionable, unsatisfactory,

[c] a : u_{min} ($u(x_{pt})$) ≤ u_{lab} ≤ $u_{max}(\sigma_{pt})$; b : $u_{lab} < u_{min}$; and c : $u_{lab} > u_{max}$

EURL-HM-24: Total Pb in a herbal supplement

x_{pt} = 0.93; $U(x_{pt})$ (k = 2.23) = 0.13; σ_{pt} = 0.149 (all values in mg kg^{-1})



Measurement results and associated uncertainties (reported uncertainties shown)

Reference value x_{pt}: solid black line; Reference interval $x_{pt} \pm U_{(Xpt)}$: green interval; Target interval ($X_{pt} \pm 2\sigma'_{pt}$): red lines

Annex 10: Results for total Hg

Assigned range: x_{pt} = 0.01407; $U(x_{pt})$ (k = *2.36*) = 0.00041; σ_{pt} = 0.00211 (all values in mg kg^{-1})

Lab Code	X_{lab}	U_{lab}	k[a]	technique	u_{lab}	z-score[b]	zeta-score[b]	u_{lab}[c]
002	0.024	0.005	2	ICP-MS	0.0025	4.71	3.96	c
003	0.016	0.004	2	DMA	0.002	0.92	0.96	a
004	0.019	0.003	2	DMA	0.0015	2.34	3.27	a
006	0.015	0.003	2	DMA	0.0015	0.44	0.62	a
007	0.0158	0.0032	2	AAS	0.0016	0.82	1.08	a
008	0.018	0.003	2	AAS	0.0015	1.86	2.60	a
009	0.016	0.002	2	ICP-MS	0.001	0.92	1.90	a
010	0.022	0.008	2	DMA	0.004	3.76	1.98	c
012	<0.05			ICP-MS				
013	<0.050			AAS				
014	<0.05			AAS				
015	<0.095			ICP-MS				
016	<0.018			ICP-MS				
017	0.0235	0.0061	2	ICP-MS	0.00305	4.47	3.09	c
018	0.013	0.002	2	ICP-MS	0.001	-0.51	-1.05	a
019	0.0254	0.002286	2	AAS	0.001143	5.37	9.80	a
021	0.023	0.002	2	ICP-MS	0.001	4.23	8.80	a
022	0.016	0.003	2	DMA	0.0015	0.92	1.28	a
023	0.02	0.004	2	ICP-MS	0.002	2.81	2.95	a
024	0.072	0.02	2	DMA	0.01	27.45	5.79	c
025	0.0155	0.0021	2	CV-AFS	0.00105	0.68	1.35	a
026	0.0166	0.0035	2	CV-AFS	0.00175	1.20	1.44	a
027	0.0145	0.001	2	DMA	0.0005	0.20	0.82	a
028	0.0169	0.0044	2	ICP-MS	0.0022	1.34	1.28	c
029	0.0137	0.0014	2	DMA	0.0007	-0.17	-0.51	a
030	0.02	0.028	2	ICP-MS	0.014	2.81	0.42	c
031	0.02	0.004	2	ICP-MS	0.002	2.81	2.95	a
032	0.019	0.005	2	ICP-MS	0.0025	2.34	1.97	c
033	0.01	0.001	2	DMA	0.0005	-1.93	-7.69	a
034	0.034	0.004	2	ICP-MS	0.002	9.45	9.93	a
035	<0.04			CV-AAS				
036	<0.10			AAS				

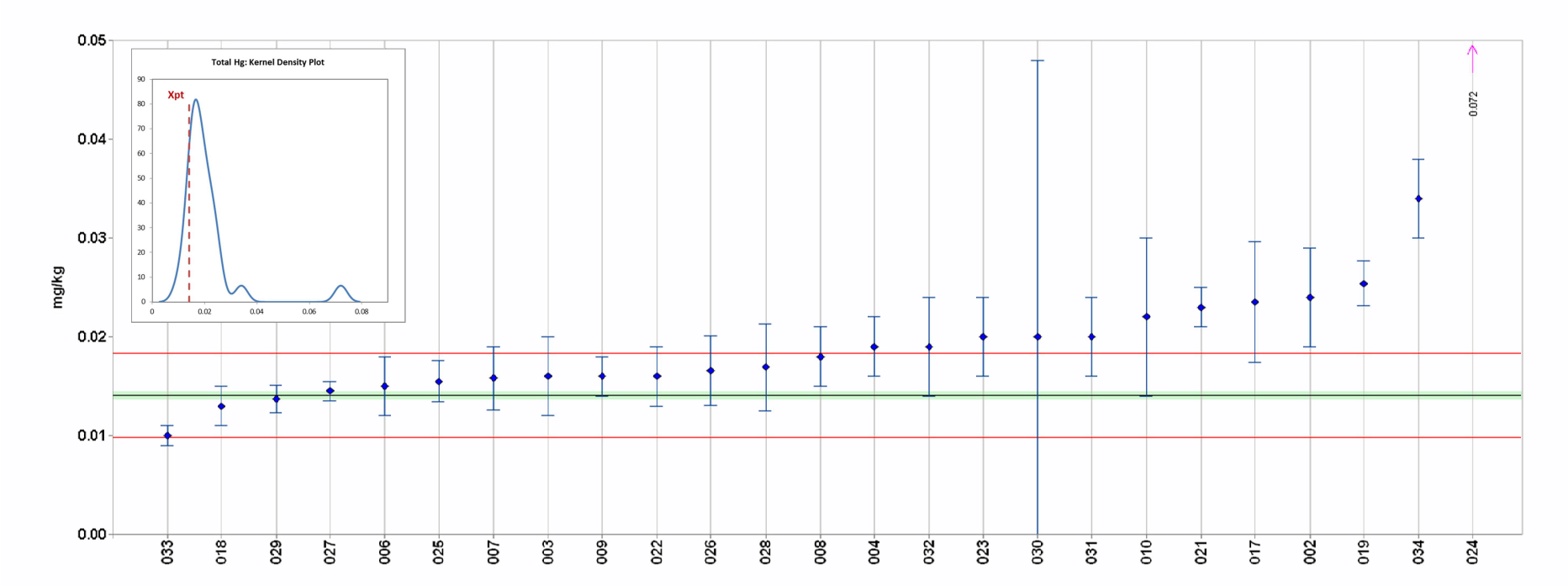
[a] √3 is set by the ILC coordinator when no coverage factor k is reported. The reported uncertainty was assumed to have a rectangular distribution with k = √3,

[b] performance: satisfactory, questionable, unsatisfactory,

[c] a : $u_{min}\,(u(x_{pt})) \leq u_{lab} \leq u_{max}(\sigma_{pt})$; b : $u_{lab} < u_{min}$; *and* c : $u_{lab} > u_{max}$

EURL-HM-24: Total Hg in a herbal supplement

x_{pt} = 0.01407; $U(x_{pt})$ (k = 2.36) = 0.00041; σ_{pt} = 0.00211 (all values in mg kg^{-1})



Measurement results and associated uncertainties (reported uncertainties shown)

Reference value x_{pt}: solid black line; Reference interval $x_{pt} \pm U_{(Xpt)}$: green interval; Target interval ($X_{pt} \pm 2\sigma_{pt}$): red lines

Annex 11: Experimental details and performance

(expressed as z-score)

LCode		Standard method?	Digestion type	Acid Mixture	Time (min)	Temp. (°C)	Recovery (%)	LOD (mg kg^{-1})	Recovery factor	Accredited	Analysis/ year	Technique
001	As	No	PB	$HNO_3+H_2O_2$	20+ 20hold	180	80-110	0.067	Using a (certified) reference material		051-250	AAS
	Cd		PB	$HNO_3+H_2O_2$	20+ 20hold	180	80-110	0.0033			051-250	AAS
	Pb		PB	$HNO_3+H_2O_2$	20+ 20hold	180	80-110	0.17			051-250	AAS
	Hg										051-250	
002	As	Yes	CMW	HNO_3	10	200		0,002	Using a (certified) reference material			ICP-MS
	Cd		CMW	HNO_3	10	200		0,03				ICP-MS
	Pb		CMW	HNO_3	10	200		0,04				ICP-MS
	Hg		**CMW**	**HNO_3**	**10**	**200**		**0.02**				**ICP-MS**
003	As	No	CMW	HNO_3	30	180	90-110	0.0009	Using a (certified) reference material	Y	051-250	ICP-MS
	Cd		CMW	HNO_3	30	180	100-102	0.0012		Y	051-250	ICP-MS
	Pb		CMW	HNO_3	30	180	95-102	0.007		Y	051-250	ICP-MS
	Hg		DMA				100	0.00009		Y	051-250	DMA
004	As	No							Using a (certified) reference material			
	Cd		CMW	$HNO_3+H_2O_2$	28	200	99.3	0.003		Y	01-50	ICP-MS
	Pb		CMW	$HNO_3+H_2O_2$	28	200	106.7	0.004		Y	01-50	ICP-MS
	Hg						100.0	0.002		Y	01-50	DMA
006	As	EN 15763:2009, EN 13805:2014	OMW	HNO_3	20	190	98-102	0,006	Using a (certified) reference material		051-250	ICP-MS
	Cd		OMW	HNO_3	20	190	98-102	0,006			051-250	ICP-MS
	Pb		OMW	HNO_3	20	190	98-102	0,090			051-250	ICP-MS
	Hg		DA (DMA)	no acids	270s		98-102	0,0003			051-250	DMA
007	As	EN 14084, EN 13806, EN 15763	CMW	HNO_3+HCl	60	230	100	0,03	Using a (certified) reference material	Y	051-250	ICP-MS
	Cd		CMW	HNO_3+HCl	60	230	100	0,005		Y	01-50	AAS
	Pb		CMW	HNO_3+HCl	60	230	100	0,003		Y	01-50	AAS
	Hg		CMW	HNO_3+HCl	60	230	100	0,06		Y	01-50	AAS
008	**As**	SIST EN 15763, EPA 7473	**CMW**	**$HNO_3+H_2O_2$**	**20**	**200**	**96**	**0.05**	Using a (certified) reference material		**051-250**	**ICP-MS**
	Cd		CMW	$HNO_3+H_2O_2$	20	200	93	0.005			051-250	ICP-MS
	Pb		CMW	$HNO_3+H_2O_2$	20	200	99	0.01			051-250	ICP-MS
	Hg		DA		150 s	850	101	0.002			051-250	AAS

LCode		Standard method?	Digestion type	Acid Mixture	Time (min)	Temp. (°C)	Recovery (%)	LOD (mg kg^{-1})	Recovery factor	Accredited	Analysis/ year	Technique
009	As	EN 15763	CMW	conc HNO_3	20	200	100	0.009	Adding a known amount of the same analyte to be measured (spiking)	Y	251-1000	ICP-MS
	Cd		CMW	conc HNO_3	20	200	101	0.003		Y	> 1000	ICP-MS
	Pb		CMW	conc HNO_3	20	200	99	0.006		Y	> 1000	ICP-MS
	Hg		CMW	conc HNO_3	20	200	106	0.002		Y	> 1000	ICP-MS
010	**As**	based on NF EN 15763	**CMW**	**HNO_3**	**40**	**200**	**100**	**0.007**	Other	**Y**	**251-1000**	**ICP-MS**
	Cd		CMW	HNO_3	40	200	100	0.002		Y	251-1000	ICP-MS
	Pb		CMW	HNO_3	40	200	100	0.006		Y	251-1000	ICP-MS
	Hg		**other - AMA**	**other - AMA**	**other**		**100**	**0.015**		**Y**	**051-250**	**DMA**
012	As	EN 15763:2009 (modified)	CMW	HNO_3+H_2O_2	15	180	96	0.007	Using a (certified) reference material	Y	01-50	ICP-MS
	Cd		CMW	HNO_3+H_2O_2	15	180	92	0.003		Y	051-250	ICP-MS
	Pb		CMW	HNO_3+H_2O_2	15	180	91	0.007		Y	051-250	ICP-MS
	Hg		CMW	HNO_3+H_2O_2	15	180	104	0.02		Y	01-50	ICP-MS
013	As	MSZ EN 16206:2012; MSZ EN 15550:2008	CMW	HNO_3+H_2O_2	15	200	98	0,050	Adding a known amount of the same analyte to be measured (spiking)		01-50	AAS
	Cd		CMW	HNO_3+H_2O_2	15	200	106	0,050			01-50	AAS
	Pb		CMW	HNO_3+H_2O_2	15	200					01-50	
	Hg		CMW	HNO_3+H_2O_2	15	200		0,050			01-50	AAS
014	As	EN 14084, EN 13806, EN 14627	CMW	HNO_3+H_2O_2	10	185		0.036	Using a (certified) reference material. Other	Y	01-50	AAS
	Cd		CMW	HNO_3+H_2O_2	10	185		0.002		Y	051-250	AAS
	Pb		CMW	HNO_3+H_2O_2	10	185	81	0.011		Y	051-250	AAS
	Hg		CMW	HNO_3+H_2O_2	10	185	-	0.024		Y	01-50	AAS
015	As	EN 15763:2009	CMW	HNO_3+HCl	25	220	89	0,011	Using a (certified) reference material. Other	Y	01-50	ICP-MS
	Cd		CMW	HNO_3+HCl	25	220	95	0,0018		Y	251-1000	ICP-MS
	Pb		CMW	HNO_3+HCl	25	220	100	0,0047		Y	251-1000	ICP-MS
	Hg		CMW	HNO_3+HCl	25	220	94	0,031		Y	01-50	ICP-MS
016	As	No	CMW	HNO_3+H_2O_2 3:1	15	max 200	97.3	0.027	Using a (certified) reference material	Y	051-250	ICP-MS
	Cd		CMW	HNO_3+H_2O_2 3:1	15	max 200	92.5	0.01		Y	051-250	ICP-MS
	Pb		CMW	HNO_3+H_2O_2 3:1	15	max 200	87.2	0.007		Y	051-250	ICP-MS
	Hg		CMW	HNO_3+H_2O_2 3:1	15	max 200	91.6	0.005		Y	051-250	ICP-MS
017	As	AOAC Vol. 96, No 5, 2013.06	CMW	HNO_3+H_2O_2	65	200	101.5	0.0055	Adding a known amount of the same analyte to be measured (spiking)		01-50	ICP-MS
	Cd		CMW	HNO_3+H_2O_2	65	200	102.1	0.0025			01-50	ICP-MS
	Pb		CMW	HNO_3+H_2O_2	65	200	101.4	0.014			01-50	ICP-MS
	Hg		**CMW**	**HNO_3+H_2O_2**	**65**	**200**	**105.4**	**0.0012**			**01-50**	**ICP-MS**

LCode		Standard method?	Digestion type	Acid Mixture	Time (min)	Temp. (°C)	Recovery (%)	LOD (mg kg^{-1})	Recovery factor	Accredited	Analysis/ year	Technique
018	As	No	CMW	HNO_3+HCl	35.5	240	101	0.001	Adding a known amount of the same analyte to be measured (spiking)	Y	> 1000	ICP-MS
	Cd		CMW	HNO_3+HCl	35.5	240	102	0.0004		Y	> 1000	ICP-MS
	Pb		CMW	HNO_3+HCl	35.5	240	102	0.001		Y	> 1000	ICP-MS
	Hg		CMW	HNO_3+HCl	35.5	240	100	0.003		Y	251-1000	ICP-MS
019	As	STN EN 15763	CMW	HNO_3+H_2O_2	45	190	70-130	0.00231	Using a (certified) reference material	Y	251-1000	ICP-MS
	Cd		CMW	HNO_3+H_2O_2	45	190	70-130	0.0016		Y	251-1000	ICP-MS
	Pb		CMW	HNO_3+H_2O_2	45	190	70-130	0.00135		Y	251-1000	ICP-MS
	Hg		**DMA**				**95**	**0.000136**		**Y**	**251-1000**	**AAS**
020	As	No	CMW	HNO_3	35	200		0.03	Other		01-50	AAS
	Cd		CMW	HNO_3	35	200		0.003		Y	01-50	AAS
	Pb		CMW	HNO_3	35	200		0.008		Y	01-50	AAS
	Hg											
021	As	No	CMW	HNO_3+H_2O_2	30	200	100	0.005	Using a (certified) reference material	Y	01-50	ICP-MS
	Cd		CMW	HNO_3+H_2O_2	30	200	100	0.005		Y	01-50	ICP-MS
	Pb		CMW	HNO_3+H_2O_2	30	200	100	0.01		Y	01-50	ICP-MS
	Hg		**CMW**	**HNO_3**	**30**	**180**	**100**	**0.005**		**Y**	**01-50**	**ICP-MS**
022	As	No	CMW	HNO_3+H_2O_2	30	200	99	0.007	Adding a known amount of the same analyte to be measured (spiking)	Y	01-50	ICP-MS
	Cd		CMW	HNO_3+H_2O_2	30	200	90	0.0013		Y	01-50	ICP-MS
	Pb		CMW	HNO_3+H_2O_2	30	200	90	0.002		Y	01-50	ICP-MS
	Hg						101	0.003		Y	01-50	DMA
023	As	No	CMW	HNO_3+H_2O_2	30	170	90.7	0.03	Using a (certified) reference material	Y	01-50	ICP-MS
	Cd		CMW	HNO_3+H_2O_2	30	170	87.3	0.01		Y	01-50	ICP-MS
	Pb		CMW	HNO_3+H_2O_2	30	170	95.5	0.02		Y	01-50	ICP-MS
	Hg		CMW	HNO_3+H_2O_2	30	170	95.7	0.02		Y	01-50	ICP-MS
024	As	SOP A 21	CMW	HNO_3+H_2O_2	15	180		0.01			251-1000	ICP-MS
	Cd		CMW	HNO_3+H_2O_2	15	180		0.02		Y	251-1000	ICP-MS
	Pb		CMW	HNO_3+H_2O_2	15	180		0.01		Y	251-1000	ICP-MS
	Hg		**DA**	**none**	**2**	**600**		**0.01**			**251-1000**	**DMA**
025	As	No	CMW	HNO_3+HF	10	220	95	0.005	Adding a known amount of the same analyte to be measured (spiking). Using a (certified) reference material	Y	051-250	ICP-MS
	Cd		CMW	HNO_3+HF	10	220	105	0.001		Y	051-250	ICP-MS
	Pb		CMW	HNO_3+HF	10	220	105	0.002		Y	051-250	ICP-MS
	Hg		CMW	HNO_3+HF	10	220	101	0.002		Y	051-250	CV-AFS

LCode		Standard method?	Digestion type	Acid Mixture	Time (min)	Temp. (°C)	Recovery (%)	LOD (mg kg^{-1})	Recovery factor	Accredited	Analysis/ year	Technique
027	As		DA	HNO_3+HCl	12 h	425	98	0.01	Using a (certified) reference material		01-50	HydrEA
	Cd		CMW	HNO_3	30	200	100	0.006		Y	051-250	GF-AAS
	Pb		CMW	HNO_3	30 h	200	96	0.02		Y	051-250	GF-AAS
	Hg		without prep.				100	0.005		Y	051-250	DMA
028	As	LST EN 15763:2010	CMW	HNO_3+H_2O_2	60	210	94-109	0.03	Using a (certified) reference material	Y	01-50	ICP-MS
	Cd		CMW	HNO_3+H_2O_2	60	210	99-114	0.007		Y	051-250	ICP-MS
	Pb		CMW	HNO_3+H_2O_2	60	210	96-110	0.007		Y	051-250	ICP-MS
	Hg		CMW	HNO_3+H_2O_2	60	210	88-108	0.003		Y	051-250	ICP-MS
029	As	No	CMW	HNO_3+H_2O_2	20/10 min	150/180	96	0.0009	Using a (certified) reference material	Y	051-250	ICP-MS
	Cd		CMW	HNO_3+H_2O_2	20/10 min	150/180	94	0.0003		Y	051-250	ICP-MS
	Pb		CMW	HNO_3+H_2O_2	20/10 min	150/180	107	0.004		Y	051-250	ICP-MS
	Hg		without dig.				94	0.0002		Y	051-250	DMA
030	As	NMKL nr.186 2007	OW	HNO_3+H_2O_2	40	260		0.003		Y	> 1000	ICP-MS
	Cd		OW	HNO_3+H_2O_2	40	260		0.002		Y	> 1000	ICP-MS
	Pb		OW	HNO_3+H_2O_2	40	260		0.002		Y	> 1000	ICP-MS
	Hg		OW	HNO_3+H_2O_2	40	260		0.02		Y	> 1000	ICP-MS
031	As	Yes	CMW	HNO_3+H_2O_2	30	180	98	0.01	Adding a known amount of the same analyte to be measured (spiking)	Y	01-50	ICP-MS
	Cd		CMW	HNO_3+H_2O_2	30	180	93	0.002		Y	051-250	ICP-MS
	Pb		CMW	HNO_3+H_2O_2	30	180	94	0.006		Y	051-250	ICP-MS
	Hg		CMW	HNO_3+H_2O_2	30	180	87	0.006		Y	051-250	ICP-MS
032	As	EN 15763	CMW	HNO_3+H_2O_2	50	max 220		0.01		Y	01-50	ICP-MS
	Cd		CMW	HNO_3+H_2O_2	50	max 220		0.01		Y	01-50	ICP-MS
	Pb		CMW	HNO_3+H_2O_2	50	max 220		0.02		Y	01-50	ICP-MS
	Hg		CMW	HNO_3+H_2O_2	50	max 220		0.01		Y	01-50	ICP-MS
033	As	PN-EN 14083:2004; PN-EN 14546:2005	DA	HNO_3			81.2	0.025	Using a (certified) reference material	Y	01-50	AAS
	Cd		CMW	HNO_3+H_2O_2			99.0	0.002		Y	051-250	AAS
	Pb		CMW	HNO_3+H_2O_2			92.0	0.012		Y	051-250	AAS
	Hg		DMA	-			93.0	0.0002		Y	01-50	DMA
034	As	based on EN15763	CMW	HNO_3	40	200	108	0.001	Using a (certified) reference material	Y	051-250	ICP-MS
	Cd		CMW	HNO_3	40	200	99	0.001		Y	051-250	ICP-MS
	Pb		CMW	HNO_3	40	200	102	0.02		Y	051-250	ICP-MS
	Hg		**CMW**	**HNO_3**	**40**	**200**	**121**	**0.0015**		**Y**	**051-250**	**ICP-MS**

LCode		Standard method?	Digestion type	Acid Mixture	Time (min)	Temp. (°C)	Recovery (%)	LOD (mg kg^{-1})	Recovery factor	Accredited	Analysis/ year	Technique
035	As	EN13805/2003, EN 14083/2003, EN 13806/2003							Using a (certified) reference material			
	Cd		CMW	$HNO_3+H_2O_2$	20	180	97	0.001			Never	AAS
	Pb		CMW	$HNO_3+H_2O_2$	20	180	98	0.005			Never	AAS
	Hg		CMW	$HNO_3+H_2O_2$	20	180	97	0.04			Never	CV-AFS
036	As	Total As: EN 14546:2005	DA	HNO_3+HCl	34 hrs	440	80.2	0.016	Adding a known amount of the same analyte to be measured (spiking)		01-50	AAS
	Cd		OW	HNO_3	60	170	93.9	0.013			051-250	AAS
	Pb		OW	HNO_3	60	170	106.1	0.13			051-250	AAS
	Hg		OW	HNO_3	60	170		0.1			051-250	AAS

Where "PB": pressure bomb, "CMW": closed microwave, "DA": dry ashing, "OW": open wet, "OMW": open microwave.

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