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Determination of total As, Cd, Hg, extractable Pb and inorganic As in kaolinitic clay

EURL-HM-21
Proficiency Test Report

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Determination of total As, Cd, Hg, extractable Pb and inorganic As in kaolinitic clay

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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-21) for the determination of total arsenic (As), cadmium (Cd), mercury (Hg), extractable lead (ex-Pb) and inorganic arsenic (iAs) in kaolinitic clay in support to Directive 2002/32/EC on undesirable substances in animal feed.

The present proficiency test (PT) was opened to National Reference Laboratories (NRLs) and official control laboratories (OCLs). Forty six participants from 29 countries registered to the exercise. Four participants did not report results.

The material used as test item was a kaolinitic clay feed additive which, after appropriate processing, was bottled, labelled and dispatched to the participants during the first half of May 2015. Four laboratories with demonstrated measurement capabilities in the field provided results to establish the assigned values. The standard uncertainties associated to the assigned values were calculated according to ISO Guide 35.

Laboratory results were rated using z- and ζ-scores in accordance with ISO 13528. The relative standard deviation for proficiency assessment was set to 20 % of the assigned value for total As, and to 25 % for ex-Pb and total Hg. No scoring was provided for the total Cd and inorganic As.

Most of the laboratories performed satisfactorily (with $|z| \leq 2$) for the determination of Hg (94 %), As (82 %) and ex-Pb (71 %, after rejection of the laboratories reporting total lead mass fraction instead of extractable lead), and reported realistic measurement uncertainties.

Acknowledgements

The authors wish to thank colleagues from the Institute for Reference Materials and Measurements (IRMM) for their valuable contributions they made during the preparation and testing of the PT material.

The laboratories listed below are kindly acknowledged for their participation in this exercise.

Organisation	Country
AGES GmbH	AUSTRIA
CODA-CERVA	BELGIUM
Central Laboratory for Chemical Testing and Control	BULGARIA
Croatian Veterinary Institute	CROATIA
Department of Agriculture	CYPRUS
State Veterinary Institute Olomouc	CZECH REPUBLIC
CISTA	CZECH REPUBLIC
Veterinary and Food Administration	DENMARK
Agricultural Research Centre	ESTONIA
Finnish Food Safety Authority Evira	FINLAND
Laboratoire SCL de Bordeaux	FRANCE
Federal Office for Consumer Protection and Food Safety (BVL)	GERMANY
Regional Center of Plant Protection and Quality Control of Magnissia	GREECE
General Chemical State Laboratory	GREECE
National Food Chain Office Food and Feed Safety Directorate	HUNGARY
National Food Chain Safety Office	HUNGARY
Health Service Executive	IRELAND
Public Analyt's Laboratory Dublin	IRELAND
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
Environmental Health Directorate	MALTA
RIKILT	NETHERLANDS
NIFES	NORWAY
National Veterinary Research Institute in Pulawy	POLAND
Instituto Nacional de Investigação Agrária e Veterinária, I.P	PORTUGAL
Hygiene and Veterinary Public Health Institute	ROMANIA
Sanitary Veterinary and Food Safety Laboratory Bucharest	ROMANIA
Veterinary and food institute in Košice	SLOVAKIA
National Laboratory for Health, Environment and Food - Maribor	SLOVENIA
National Veterinary Institute	SLOVENIA
Jozef Stefan Institute	SLOVENIA
MAGRAMA	SPAIN
National Veterinary Institute	SWEDEN
Fera	UNITED KINGDOM
Glasgow Scientific Services	UNITED KINGDOM
City of Edinburgh Council	UNITED KINGDOM
Staffordshire County Council	UNITED KINGDOM
Kent County Council	UNITED KINGDOM

1. Introduction

The European Union Reference Laboratory for Heavy Metals in Feed and Food (EURL-HM) organised the proficiency test (PT) EURL-HM-21 to assess the performance of National Reference Laboratories (NRLs) and official control laboratories (OCLs) in the determination of total arsenic (As), cadmium (Cd), mercury (Hg), extractable lead (ex-Pb) and inorganic arsenic (iAs) mass fractions in kaolinitic clay. This PT was organised as agreed with the Directorate General Health and Food Safety (DG SANTE) in the annual work program of the EURL-HM.

Kaolinitic clay (KC) is an aluminium silicate mineral, displaying the layered structure of phillosilicates (parallel sheets of silicates). Among various applications, KC is a "technological feed additive" used as a "binder" or "anti-caking agent" originally authorised by Commission Directive 85/429/EEC [1], as listed in the "European Union Register of Feed Additives" [2].

According to Commission Regulation (EU) No 1275/2013 [3] "[…] *Recently, a significant difference has been identified by the European Union Reference Laboratory for heavy metals in feed and food (EURL–HM) between the analytical results obtained by the application of different extraction methods currently used for the determination of lead in kaolinitic clay and feed containing kaolinitic* clay [4]). […] *The maximum levels of heavy metals in feed relate 'to an analytical determination of lead, whereby extraction is performed in nitric acid (5 % w/w) for 30 minutes at boiling temperature'. It is therefore appropriate to provide for the use of that method of extraction for the determination of lead in kaolinitic clay* […]", as prescribed in the European Standard EN 15510:2007 [5]. This Regulation adds that equivalent extraction procedures may be used provided that demonstration of equal efficiency is sound.

Furthermore, Directive 2002/32/EC of the European Parliament and of the Council [6] set maximum levels (MLs) for undesirable substances (such as As, Cd, Hg and Pb) in animal feed. Regarding iAs, this Directive states that the competent authorities may request the additional determination of iAs when total As levels higher than 2 mg kg^{-1} are found; this applies specifically to feedingstuffs for fish.

This report evaluates and summarises the performance of NRLs and OCLs in the determination of total arsenic, cadmium and mercury, extractable lead and inorganic arsenic in kaolinitic clay determined in the frame of the PT exercise. Additionally, it evaluates the ability of laboratories in assessing the compliance of this test item against the maximum levels set in legislation.

2. Scope and aim

As stated in Regulation (EC) 882/2004 [7] one of the core duties of the EURLs is to organise interlaboratory comparisons for the benefit of the NRLs.

The present PT aims to assess the performance of NRLs and OCLs in the determination of total As, Cd, Hg, iAs and extractable Pb mass fractions in kaolinitic clay. In addition, participants were requested to evaluate the conformity of the analysed feed additive according to the maximum levels (MLs) set in legislation.

The assessment of measurement results follows the administrative and logistic procedures of the EC-JRC-IRMM for the organisation of PTs, which is accredited according to ISO/IEC 17043:2010 [8].

The name of this proficiency test round is EURL-HM-21.

3. Set up of the exercise

3.1 Time frame

The organisation of the EURL-HM-21 exercise was agreed upon by the NRL network at the 8th EURL-HM Workshop held in Brussels on September 24, 2013. Invitation letters were sent to the NRLs on February 26, 2015 (Annex 1) and a web announcement (Annex 2) for the exercise was made on the same day on the JRC webpage [9]. The registration deadline was set to April 10, 2015. The reporting deadline was set to July 24, 2015. Dispatch was followed by the PT coordinator using the messenger's parcel tracking system on the internet.

3.2 Confidentiality

According to the IRMM procedure for the organisation of PTs the confidentiality of participants is guaranteed. However, the following confidentiality statement was made to NRLs: "*In case you plan to pay for the participation of official control laboratories belonging to your national network, please inform them that their identity will be disclosed to you*" (Annex 1).

3.3 Distribution

The test item was dispatched to participants on June 8, 2015. Each participant received:

- One glass bottle containing approximately 15 g of test item;
- A "Sample accompanying letter" (Annex 3); and
- A "Confirmation of receipt form" to be sent back to IRMM after receipt of the test item (Annex 4).

3.4 Instructions to participants

Detailed instructions were given to participants in the "Sample accompanying letter" mentioned above. Measurands were defined as "Total As, Cd, Hg, ex-Pb and iAs mass fractions in kaolinitic clay".

Participants were asked to perform two or three independent measurements, to correct their measurements for recovery and to report their calculated mean (x_{lab}), the associated expanded measurement uncertainty (U_{lab}) together with the corresponding coverage factor and the technique used. Unlike other PTs where results are reports related to dry mass, participants were expected to comply with the legal requirements set by the feed legislation and report results referring to 12 % moisture content. When participants reported results referring to dry mass these results were systematically corrected to 12 % moisture content to allow a consistent comparison.

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 5).

Participants were informed that the procedure used for the analysis should resemble as closely as possible the one they use in their routine analysis.

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

4. Test item

4.1 Preparation

The test item used was a commercially available feed additive (kaolinitic clay) kindly provided by AGS Mineraux (France) and Goonvean (United Kingdom). Ca. 7 kg of kaolinitic clay were sent to the IRMM. Once received, the material was stored at + 4 °C until processing. The material was homogenised and portions of 15 g were filled into 125 ml acid-washed amber glass bottles. The bottles were manually filled using acid washed plastic spoons under an air extraction point. The bottles were closed with acid washed inserts and screw caps.

Each vial was identified/labelled with a unique number and with the name of the PT round, following the IRMM procedures.

4.2 Homogeneity and stability

Measurements for the homogeneity and stability studies were performed by Centro de Salud Pública de Alicante (CSPA, Alicante, Spain). Inductively coupled plasma mass spectrometry (ICP-MS), after microwave digestion (0.20 g of feed additive in a mixture of 65 % HNO_3 /37 % HCl) was used to determine the total As and Cd mass fractions. Extractable Pb mass fractions was determined applying the sample extraction procedure described in Annex 6.

An elemental mercury analyser (EMA) was used to quantify the total Hg mass fraction, using approximately 200 mg of feed additive per analysis.

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

Homogeneity was evaluated according to ISO 13528:2005 [10]. The test item proved to be adequately homogeneous for the total As, Hg and ex-Pb. However the test item was found to be not adequately homogeneous for total Cd.

The PT organisers considered that the stability of heavy metals in mineral material (such as kaolinitic clay) is granted and not to be demonstrated. However, 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_{bb}) to the standard measurement uncertainty of the assigned value (u_{ref}) was calculated using SoftCRM [11]. The analytical results reported by the expert laboratory and the statistical evaluation of the homogeneity study are presented in Table 1 and in Annex 7.

5. Assigned values and their uncertainties

5.1 Assigned value, X_{ref}

The assigned values for the five measurands (total As, Cd, Hg, ex-Pb and iAs in kaolinitic clay) were determined by four laboratories, selected on the basis of their demonstrated measurement capabilities (later referred as expert laboratories):

- ALS Scandinavia AB (Luleå, Sweden);
- SCK-CEN - Studiecentrum voor Kernenergie (Mol, Belgium);
- UBA - Environmental Agency Austria (Vienna, Austria);
- CSPA - Centro de Salud Pública de Alicante (Alicante, Spain)

Expert laboratories were asked to use the method of analysis of their choice and no further requirements were imposed regarding methodology. They were requested to analyse three independent replicates per bottle (two bottles were distributed for each expert laboratory), on two different days (one bottle per day).

Expert laboratories were also required to report their results together with the associated expanded measurement uncertainty and with a clear and detailed description on how their measurement uncertainty was evaluated. Expert laboratories were not requested to report values for all measurands.

- ALS Scandinavia used inductively coupled plasma sector field mass spectrometry (ICP-SFMS) after digestion with HNO_3, HCl and HF in sealed Teflon containers in microwave oven, for the analysis of the total As, Cd and Hg. Ion chromatography with post column hydride generation and detection by ICP coupled with mass spectrometry detector (IC-ICP-MS) was used for the determination of iAs. ALS followed the protocol provided by IRMM for the quantification of ex-Pb (Annex 7).
- SCK-CEN applied the k_0-standardized neutron activation analysis (k_0-NAA) for the determination of total As, Cd and Hg. Three test samples of about 400 mg were taken from each bottle and transferred in standard high-density polyethylene vials and weighed. Samples were irradiated for seven hours in the BR1 reactor under a thermal flux of 3 10^{11} n s^{-1} cm^2 together with four IRMM-530 (Al-0.1 % Au alloy) neutron flux monitors, and several reference materials for validation (SMELS II; SMELS III; BCR 176 - fly ash; and BCR 278 - mussel tissue). Two spectra per sample were then collected (after 3 and 14 days) on a k_0-calibrated HPGe detector. No additional sample treatment was applied.
- Umweltbundesamt GmbH (UBA) used graphite furnace atomic absorption spectrometry (GF-AAS) for the analysis of total As and Cd, while cold-vapour atomic absorption spectrometry (CV-AAS) was used to determine the total Hg. Microwave-assisted high-pressure digestion was used with HNO_3, HCl and HF for digestion. Complexation with H_3BO_4 according to ÖNORM EN 13656 was used.
- CSPA used ICP-MS after digestion with an acid mixture of 65 % HNO_3 /37 % HCl, for the determination of the total As and Cd. EMA was used for the total Hg which consists of a single purpose atomic absorption spectrophotometer for Hg determination. For the extractable Pb determination the extraction protocol provided by IRMM was followed, after which, ICP-MS was used as technique.

For this PT, the mean of the retained means reported by the expert laboratories were used to derive the assigned values (X_{ref}) according to ISO Guide 35:2006 [12] (Figure 1).

No reference values were assigned for Cd and iAs, as discussed later.

5.2 Associated uncertainty, u_{ref}

The associated standard measurement uncertainties (u_{ref}) of the assigned values were calculated following the law of propagation of uncertainty, combining the standard measurement uncertainty of the characterization (u_{char}) with the standard uncertainty contribution from homogeneity (u_{bb}) in compliance with ISO Guide 35 [12]:

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

For the total As, Hg and ex-Pb, expert laboratories reported values with overlapping expanded measurement uncertainties (Table 1, Figure 1), hence u_{char} was calculated according to ISO 13528:2005 [10]:

$$u_{char} = \frac{1.25}{p}\sqrt{\sum_1^p u_i^2}$$ Eq. 2

where: p is the number of expert laboratories used to assign the reference value; and u_i is the standard measurement uncertainty reported by the expert laboratories.

Table 1 presents the average measurement values reported by the expert laboratories and their associated expanded measurement uncertainties; the assigned values (X_{ref}, u_{ref} and U_{ref} (k=2)); the standard measurement uncertainty contributions (u_{char} and u_{bb}); and the standard deviation for PT assessment (σ). All values were corrected to 12 % moisture content in order to comply with the feed legislation [6].

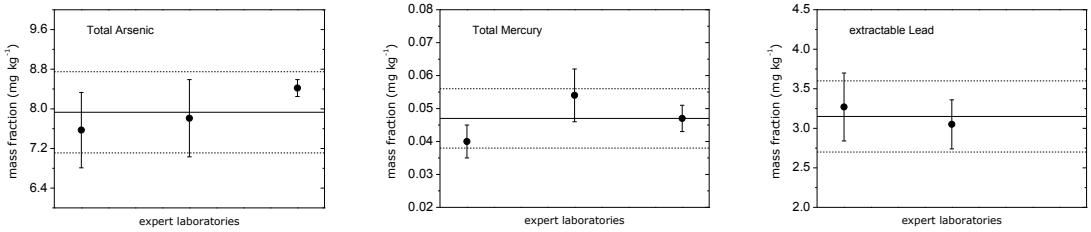

Figure 1: Assigned values for EURL-HM-21. Circles represent the reported values by the retained expert laboratories (± $2u_i$); the solid line represents the assigned value (X_{ref}) while the dashed lines represent the expanded assigned uncertainty interval (X_{ref} ± U_{ref}).

Table 1 – Results reported by expert laboratories and their associated expanded measurement uncertainties; the assigned values (X_{ref}, u_{ref} and U_{ref} (k=2)); the standard measurement uncertainties (u_{char} and u_{bb}); and the standard deviation for PT assessment (σ). All values are expressed in mg kg^{-1}. All values refer to 12% moisture.

	As	**Hg**	**ex-Pb**	**Cd**	**iAs**
Expert 1	~~5.12 ± 0.50~~[a]	0.040 ± 0.005	3.27 ± 0.43	0.106 ± 0.015	
Expert 2	7.57 ± 0.76	0.054 ± 0.008	3.05 ± 0.31	0.136 ± 0.013	0.91 ± 0.091
Expert 3	7.81 ± 0.78	0.047 ± 0.004		0.041 ± 0.007	
Expert 4	8.42 ± 0.17	< 0.5		< 0.9	
X_{ref}	**7.93**	**0.047**	**3.15**		
u_{char}	0.23	0.002	0.17		
u_{bb}	0.34	0.001	0.15		
u_{ref}	**0.41**	**0.002**	**0.22**		
U_{ref}	0.82	0.004	0.45		
σ	**1.59**	**0.012**	**0.79**	**no scoring**	**no scoring**
σ (%)	20%	25%	25%		
0.3σ	0.48	0.003	0.24		
u_{ref} < 0.3 σ ?	yes	yes	yes		

[a] Rejected result (see Section 6.1)

5.3 Standard deviation for proficiency assessment, σ

The relative standard deviation for proficiency assessment (σ, in %) was set considering the performance of participants in previous PT rounds with similar measurands [9] and taking into account the complexity of the test item investigated. Therefore, σ was set to 20 % of the assigned value for total As, and to 25 % for ex-Pb and Hg (Table 1).

5.4 Scores and evaluation criteria

Individual laboratory performance was expressed in terms of z- and ζ-scores in accordance with ISO 13528:2005 [10]:

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

$$\zeta = \frac{x_{lab} - X_{ref}}{\sqrt{u_{ref}^2 + u_{lab}^2}} \qquad \text{Eq. 4}$$

where: x_{lab} is the measurement result reported by a participant;
u_{lab} is the standard measurement uncertainty reported by a participant;
X_{ref} is the assigned value;
u_{ref} is the standard measurement uncertainty of the assigned value;
σ is the standard deviation for proficiency assessment.

The interpretation of the z- and ζ-scores is done according to ISO 17043:2010 [8]:

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

The z-score compares the participant's deviation from the assigned value with the standard deviation for proficiency assessment (σ) 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_{ref}) and the measurement uncertainty as stated by the laboratory (u_{lab}). 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 the presence of a significant bias (inaccurate measurement) or by a not realistic estimation of its measurement uncertainty (seriously under-estimated), or both.

The standard measurement uncertainty of the laboratory (u_{lab}) 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 ($u_{lab} = 0$).

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

The standard measurement uncertainty from the laboratory (u_{lab}) is most likely to fall in a range between a minimum uncertainty (u_{min}), and a maximum allowed (u_{max}) – case "a": $u_{min} \leq u_{lab} \leq u_{max}$. u_{min} is set to the standard measurement uncertainty of the assigned value ($u_{min} = u_{ref}$). It is unlikely that a laboratory carrying out the analysis on a routine basis would measure 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 ($u_{max} = \sigma$). Consequently, Case "a" becomes: $u_{ref} \leq u_{lab} \leq \sigma$.

If u_{lab} is smaller than u_{min} (case "b": $u_{lab} < u_{ref}$) the laboratory may have underestimated its measurement uncertainty. Such a statement has to be taken with care as each laboratory reported only its measurement uncertainty, whereas the uncertainty associated with the assigned value also includes the contribution for homogeneity of the test item. If that is large, measurement uncertainties smaller than u_{min} are possible and plausible.

If u_{lab} is larger than u_{max} (case "c": $u_{lab} > \sigma$) 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 U_{ref} then overestimation is likely. If the difference is larger but x_{lab} agrees with X_{ref} 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.

More detailed information about measurement uncertainty evaluation can be found in some international standard and other guidance documents [13-17].

6. Evaluation of results

Kaolinitic clay is a layer structured mineral (inorganic) material that can trap/bind ions, metals and mycotoxins. The total extraction of an element (i.e. As, Cd, Hg, Pb) from such matrix would require the use of strong acid mixtures to break the bonds trapping/fixing cations to the clay. Several strong acid mixtures (including HNO_3, HCl and/or H_2SO_4) were used successfully in this exercise. The supplementary addition of HF was proven to be effective by the expert laboratories and participating laboratories.

For the determination of extractable lead the use of 5 % HNO_3 (weaker acid) is prescribed by Commission Regulation (EU) No 1275/2013 [3].

The sample preparation protocol, described in EN 16278 [18] for the determination of inorganic arsenic prescribes the use of HNO_3 and H_2O_2. The effectiveness of this acid mixture is discussed below.

Several challenges are therefore identified for this PT:

- the determination of total arsenic, cadmium and mercury;
- the determination of inorganic arsenic;
- the determination of extractable lead; and
- the compliance assessment of the test item used as feed additive as such, or included in feedingstuffs, according to the relevant EU legislation.

Annexes 8 to 12 present for each measurand the table of results as reported by the participants and systematically corrected to 12 % moisture content to allow a consistent comparison in compliance with European legislation [6]. NRLs and OCLs are denoted as Nxx and Lxx, respectively. The corresponding Kernel density plots are also included, obtained using the software available from the Statistical Subcommittee of the Analytical Methods Committee of the UK Royal Society of Chemistry [19]. All the experimental details collected via the questionnaire are summarised in Annex 13.

From the 46 laboratories having registered to this PT 4 did not report results, of which one NRL. The NRL from Luxemburg did not register to this PT. Some participants reported truncated ("less than") values: 5 for total Cd, 6 for total Hg, and one for iAs. All of them (except one) are realistic, because these values where above the lower limit of the assigned range (X_{ref} - U_{ref}).

Figure 2 presents the z- and ζ-score distribution for NRLs and OCLs.

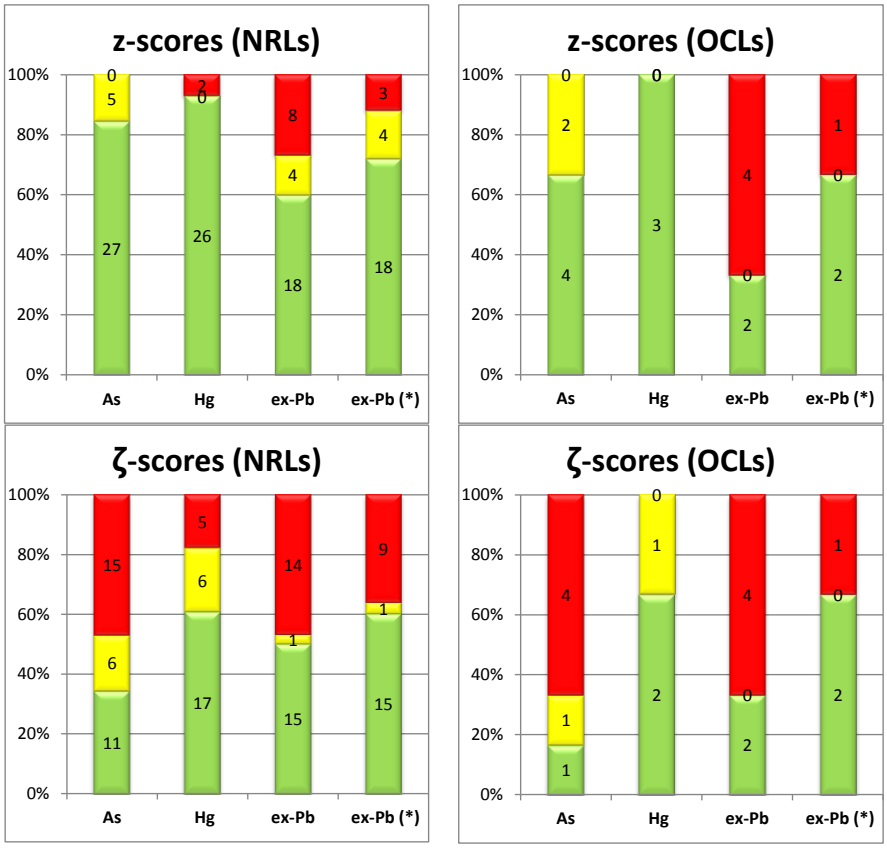

Figure 2: Overview of the z and ζ-scores obtained by NRLs and OCLs for the different measurands. The data shown for ex-Pb (*) are obtained excluding the "outlying" values (see Section 6.5). Satisfactory, questionable and unsatisfactory performances - expressed as z- and ζ-scores - are indicated in green, yellow and red, respectively.

The evaluation of the results reported by the participants is thoroughly discussed hereafter.

6.1 Total arsenic

The homogeneity of the test material was proven to be adequate for total As (Annex 6). One of the expert laboratories applied k_0-NAA, a method of choice for the determination of arsenic in soil type matrices. This result was further confirmed by two other expert laboratories having applied ICP-MS, after closed microwave digestion with a strong acid mixture including HF. However, "Expert 1" did not use HF in the acid mixture for digestion and reported a significantly lower total arsenic value. This may be attributed to an incomplete extraction of total arsenic, and the PT organiser did not include this result in the calculation of the assigned value. The following assigned range was derived: 7.93 ± 0.82 (k=2) mg kg^{-1}; where the standard uncertainty of the assigned value (0.41 mg kg^{-1}) was smaller than 0.3 σ (0.48 mg kg^{-1}, Table 1).

A total of 38 results were reported and the Kernel density plot indicates the presence of two partially overlaying normal distributions (Annex 8). The majority of the laboratories and "Expert 1" belong to the first mode (ca. 5.6 mg kg^{-1}), while laboratory N35 (using k_0-NAA) and laboratories N12, N31 L24 and N27 (having used strong acid mixtures including HF) confirm the second mode at 7.8 mg kg^{-1}, and therefore the assigned value.

Most of the participants used inductively coupled plasma mass spectrometry (ICP-MS), hydride generation atomic absorption spectrometry (HG-AAS) or graphite furnace AAS (GF-AAS). No significant trend could be observed related with the analytical technique.

Due to the challenging extraction of analytes from the clay matrix investigated, the PT organisers set σ to 20 % of the assigned value, a value significantly higher than the one predicted by the Horwitz equation. The resulting acceptable range (X_{ref} ± 2σ) encompasses the whole observed bimodal distribution. Therefore 82 % of the laboratories (31/38) obtained a satisfactory performance, expressed as z-score (|z| ≤ 2, Figure 2). The remaining results were under-estimated (-2.69 < z < -2.03), probably due to the use of milder acid mixtures for digestion (HNO_3 or HNO_3/H_2O_2 at low concentrations, below 10 % v/v).

However, despite the fact that the majority of laboratories reported realistic uncertainties (of the order of 10 to 15 %) a large fraction of the population got an unsatisfactory performance expressed as ζ-score (|ζ|≥ 3, Figure 2). This is attributed to the difference between the two modes of ca. 33 %, which is significantly larger than the standard measurements uncertainty reported. Taking into consideration the difficult matrix analysed, laboratories are advised to revise their sample treatment (digestion, acid mixture) and correct for their bias, instead of reviewing their measurement uncertainty evaluation.

6.2 Inorganic arsenic

While the homogeneous distribution of iAs in the test item was assumed to be similar to the one of total As, only the "Expert 2" laboratory reported a value for iAs (0.91 ± 0.09 mg kg^{-1}) applying ICP-MS after microwave digestion with H_3PO_4 (Table 1). This value is significantly lower than the value reported by "Expert 2" for total As (7.57 ± 0.76 mg kg^{-1}), which seems unrealistic for a mineral/clay matrix, where iAs is expected to be the major arsenic constituent. Hence, no assigned value was attributed by the PT organiser for this measurand and no scoring of results was performed.

Thirteen laboratories reported highly scattered results for iAs, ranging from 0.13 to 6.3 mg kg^{-1} (Annex 9) – well below the value assigned for total As. Figure 2 presents the 12 results reported for As and iAs. Three of the laboratories (N26, N04 and N12) reported satisfactory total arsenic results (|ζ|≤ 1.6), close to the vertical line. Three other laboratories (L44, L45 and N20) used the HCl/HNO_3 (strong) acid mixture for digestion and obtained similar mass fractions for both analytes, (close to the diagonal line). The rest of the participants under-estimated both measurand values. As a conclusion, the classical acid mixture used for the determination of iAs may not be suitable to extract the "total" inorganic arsenic present in kaolinitic clay.

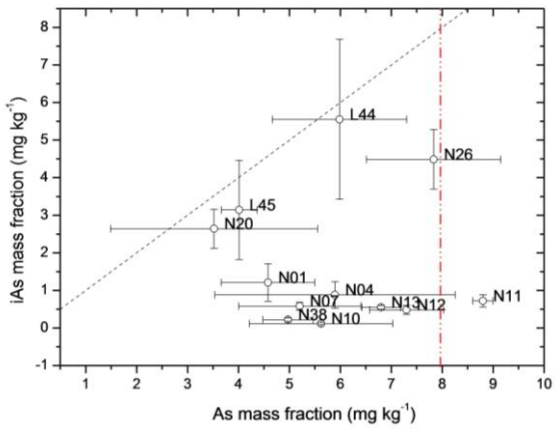

Figure 3: The results of 12 laboratories having reported results for total and inorganic arsenic.

6.3 Total cadmium

The expert laboratories reported highly scattered values for Cd in kaolinitic clay ranging from 0.04 to 0.14 mg kg^{-1} (Table 1) and the homogeneity results could not demonstrate the fitness-for-purpose of the material (u_{bb} > 0.3 σ; Annex 7). Therefore, no assigned value could be established and no scoring of the results was performed.

Nevertheless, a total of 35 results were reported (Annex 10). Most of them were in the same range observed by the expert laboratories. Only three laboratories (N30, L36 and L44) reported significantly higher values (ca. 0.4 mg kg^{-1}). Algorithm A of ISO 13528 was used to compute an informative "consensus value" of 0.065 mg kg^{-1} from all the results reported by the participants. Although the PT organiser does not guarantee the representativeness of this value for the total cadmium content in the kaolinitic clay test item, participants may consider comparing their performance by mean of the D% score, as defined in ISO 13528 [10].

6.4 Total mercury

The homogeneity of the test material was proven to be adequate for total Hg (Annex 7). Due to the challenging matrix investigated and the low mercury content the PT organisers set σ to 25 % of the assigned value. The results provided by the three expert laboratories were in agreement (Table 1).

All the participants using ICP-MS (10 out of 10) and elemental mercury analyser (EMA, 11 out of 11) reported satisfactory results similarly to the 8 participants (out of 10) using CV-AAS. No significant trend could be observed related with the analytical technique. All laboratories used strong acid mixtures with closed microwave digestion systems. The four laboratories (N31, N35, N12 and N27) having added HF confirmed the assigned value (Annex 11).

94 % of the laboratories (29/31) obtained satisfactory performance expressed as z-score ($|z| \leq 2$, Figure 2), while 61 % of the laboratories (19/31) obtained satisfactory performance expressed as ζ-score.

6.5 Extractable lead

The homogeneity of the test material was proven to be adequate for ex-Pb (Annex 7). Two expert laboratories provided results that were in agreement from which the assigned range was derived: 3.15 ± 0.44 (k=2) mg kg^{-1}; where the uncertainty of the assigned value was smaller than 0.3 σ (0.24 mg kg^{-1}, Table 1).

Expert laboratories and all participants were requested to quantify "extractable lead" applying the recommendations set in Commission Regulation (EU) No 1275/2013. Eight participants (out of 36) erroneously applied closed microwave (CMW) digestion with strong acid mixtures (instead of the prescribed 5 % HNO_3) and reported (outlying) values above 40 mg kg^{-1} (Annex 12). Three of them (N17, L42 and L43) acknowledged having analysed "total lead" instead of the requested "extractable lead". Most of the participants followed the standard operating procedure described in EN 15510 (Annex 7) [5], varying the ratio "sample intake / volume of HNO_3 (5 %)". The following instrumental techniques were mainly used: ICP-MS and electro thermal AAS (ET-AAS). No significant trend could be observed related with the analytical technique. None of the participants used the ICP-AES technique recommended in EN 15510 [5].

After removal of the "outlying" data, 71 % (20/28) obtained a satisfactory performance, expressed as z-score ($|z| \leq 2$, Figure 2). Similarly, 61 % (17/28) obtained a satisfactory performance expressed as ζ-score ($|\zeta| \leq 2$, Figure 2). Five laboratories submitted results ranging from 4.4 to 4.9 mg kg^{-1} (48 % above the assigned value) and reported likely under-estimated standard measurement uncertainties (below 10 %).

Figure 2 also presents the z- and ζ-score of the complete set of results reported for extractable lead (including the "outlying" values mentioned above) for which the number of unsatisfactory results (|z| and |ζ| > 3) is significantly increased.

6.6 Compliance

Kaolinitic clay is commonly classified as "technological feed additive" and used as "binder" or "anti-caking agent" [1, 2].

Similarly to other bentonite/montmorillonite clays, this feed additive (FA) is intended to be included in feedingstuffs (FS) at concentration levels ranging from 1 to 25 g kg^{-1} [20].

The assigned values for total As, Hg and ex-Pb are compared *as such* (X_{ref} in FA) or converted into an "hypothetical" content in feed (25 g of kaolinitic clay per kilogram feed, corresponding to a dilution factor of 40) to the maximum levels for undesirable substances (i.e. As, Cd, Hg and Pb) set by Directive 2002/32/EC [6] (Table 2). Since all levels are below the MLs, the test item is considered by the PT organiser as compliant.

Table 2 - Assigned values (X_{ref}) and maximum limits (ML) in Feed Additive (FA) or Feedingstuffs (FS). All values are expressed in mg kg^{-1}.

Analyte	X_{ref} in FA	X_{ref} in FS[a]	ML [6]	in which matrix?
As	7.93	0.20	2 12	in feed material in mineral feedingstuffs
Cd	--	--	2	in binder or anticaking FA
Hg	0.047	0.001	0.1	in feed material
ex-Pb	3.15	--	30	in binder or anticaking FA

[a] Applying a dilution factor of 40 to take into account the condition of use of this feed additive in feedingstuffs.

Annex 14 summarises the compliance statements provided by the participants. 69 % of the 39 laboratories stated correctly that the material is compliant (cf. green cells in Annex 14). 13 % of them concluded that the material was not compliant, based on their outlying results reported while analysing lead - instead of extractable lead (yellow cells in Annex 14). Finally, six laboratories interpreted erroneously Directive 2002/32/EC [6] comparing their results for As in kaolinitic clay (feed additive) to the ML for As in feed material and concluded incorrectly that the material was not compliant.

6.7 Additional observations

Most of the participants (85 %) are NRLs, accredited according to ISO/IEC 17025 for the analysis of As, Cd, Hg and Pb in feed. However, they do not monitor regularly inorganic arsenic in mineral matrices; hence, this type of analysis is usually not included in their accreditation scope.

Participants claiming to analyse more than 250 samples/year reported satisfactory results for As and/or Hg.

Several CEN standard methods (i.e. EN 15510 [5]; EN 15550 [21], EN 15621 [22] and EN 16206 [23]) are available for the elemental analysis in feed, applying GF-AAS or ICP-AES. However, none of these standards are designed for the accurate quantification of total As, Hg and Pb in clay matrices. Laboratories used the sample preparation protocol described in the standard but did not use the instrumental approach prescribed. The only standard available for the determination of iAs in feedingstuffs (EN 16278 [18]) may not be adequate for the analysis of clay matrices (i.e. kaolinitic clay), since it uses "diluted hydrochloric acid and hydrogen peroxide solution coupled with microwave assisted heating". None of the participants succeeded to extract properly the "total" inorganic arsenic present in the clay.

Participants evaluated their measurement uncertainty using one or several of the following approaches: - applying the "Guide to the expression of uncertainty in measurement, GUM" [13] (9 laboratories); - from their in-house method validation studies (27 laboratories); - from inter-laboratory comparison results (8 laboratories) and/or - from precision data (8 laboratories). Two thirds of all laboratories seem to report realistic uncertainties (case "a", Annex 8-12). However, this did not ensure systematically satisfactory z-scores. This may be attributed to the significant biases observed, such as (i) the insufficient extraction of the "total" As from the clay matrix (as indicated by the 1st mode at 5.6 mg kg^{-1}); or (ii) the over-estimated extractable Pb levels due to the use of an extraction procedure stronger than the one prescribed [3,5].

7. Conclusion

Considering the overall satisfactory performance of the participating laboratories in EURL-HM-21, the analytical capability of the participating laboratories for the determination of total As, Hg and extractable Pb in kaolinitic clay was successfully demonstrated at the investigated concentration levels.

As a whole, the NRLs presented good uncertainty evaluations. This may be due to (i) the several PTs organised so far by the EURL-HM and (ii) the various trainings on relevant topics related to the analyses of heavy metals in feed and food provided by the EURL-HM during the annual workshops.

No scoring was provided for total Cd and inorganic As. The first showed inadequate homogeneity, while the latter appeared to be difficult to extract from the clay matrix when mild acid mixtures (5 % HNO_3/H_2O_2) for digestion are used.

For the accurate determination of extractable lead mass fractions in kaolinitic clays (and other phyllosilicates) laboratories must follow the experimental protocol prescribed by Commission Regulation (EU) No. 1275/2013. The use of higher concentration of acid mixtures for sample digestion may lead to significantly over-estimated results.

In order to assess the compliance of this particular clay, laboratories must properly interpret the EU legislation and select the relevant legal maximum levels in feed additives (e.g. Cd, ex-Pb) and in various feedingstuffs (e.g. As, Hg).

Taking into consideration the difficult matrix analysed, laboratories are advised to revise their sample treatment (digestion procedure and acid mixtures) rather than reviewing their measurement uncertainty evaluation.

8. References

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9. Abbreviations

AAS	Atomic Absorption Spectroscopy
CITAC	Cooperation on International Traceability in Analytical Chemistry
CRM	Certified Reference Material
CV-AAS	Cold Vapour Atomic Absorption Spectrometry
CV-AFS	Cold Vapour Atomic Fluorescence Spectrometry
CMW	Closed microwave
DA	Dry Ashing
EMA	Elemental Mercury Analyser (or direct mercury analyser, DMA, Annex 11)
ET-AAS	Electro Thermal Atomic Absorption Spectrometry (also called Graphite Furnace Atomic Absorption Spectroscopy, GF-AAS)
EURL-HM	European Union Reference Laboratory for Heavy Metals in Feed and Food
EU	European Union
GUM	Guide to the expression of Uncertainty in Measurement
HG-AAS	Hydride Generation Atomic Absorption Spectroscopy
HPLC-ICP-MS	High Performance Liquid Chromatography coupled with ICP-MS
IC-ICP-MS	Ion chromatography coupled with ICP-MS
ICP-AES	Inductively Coupled Plasma Atomic Emission Spectrometry
ICP-MS	Inductively Coupled Plasma Mass Spectrometry
ICP-OES	Inductively Coupled Plasma Optical Emission Spectrometry
ICP-ID-MS	Inductively Coupled Plasma Isotope Dilution Mass Spectrometry
ICP-SF-MS	Inductively Coupled Plasma Sector Field Mass Spectrometry
ILC	Interlaboratory Comparison
IMEP	International Measurement Evaluation Programme
IRMM	Institute for Reference Materials and Measurements
ISO	International Organisation for Standardisation
JRC	Joint Research Centre
LC-ICP-MS	Liquid Chromatography coupled with ICP-MS
k_0-NAA	k_0-standardised Neutron Activation Analysis
NRL	National Reference Laboratory
ML	Maximum level
OCL	Official Control Laboratory
PT	Proficiency Testing
Q-ICP-MS	Quadrupole Inductively Coupled Plasma Mass Spectroscopy
Z-ET-AAS	Zeeman- Electro Thermal Atomic Absorption Spectrometry

Annex 1: 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

Geel, 26 February 2015
JRC.D.5/PRO/FCR/acs/ARES

Sent by e-mail

Subject: Proficiency testing for the determination of total As, Cd, Hg, iAs and extractable Pb in kaolinitic clay (EURL-HM-21)

Dear National Reference Laboratory representative,

We would like to invite you on behalf of the EURL-HM in Feed and Food to participate in the Proficiency Test EURL-HM-21 for the **"Determination of total As, Cd, Hg, iAs and extractable Pb in kaolinitic clay"**.

You are kindly reminded that according to Regulation (EC) No 882/2004 it is your duty as NRL to participate in proficiency tests 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=1381

Once you submitted your registration copy the confirmation page that will appear and send it to JRC-IRMM-EURL-HEAVY-METALS@ec.europa.eu. This e-mail will be the confirmation of your participation.

If you know a laboratory interested in participating in the EURL-HM-21 exercise, please forward this link: https://ec.europa.eu/jrc/en/interlaboratory-comparison/eurl-hm-21?search&form-return

In case you plan to pay for the participation of official food control laboratories belonging to your national network, please inform them that their identity will be disclosed to you.

The **deadline for registration is 10 April 2015**. Samples will be sent to participants during the first half of May 2015. The deadline for submission of results is **12 June 2015**.

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

Yours sincerely

Dr. Fernando Cordeiro
EURL-HM-21 Coordinator

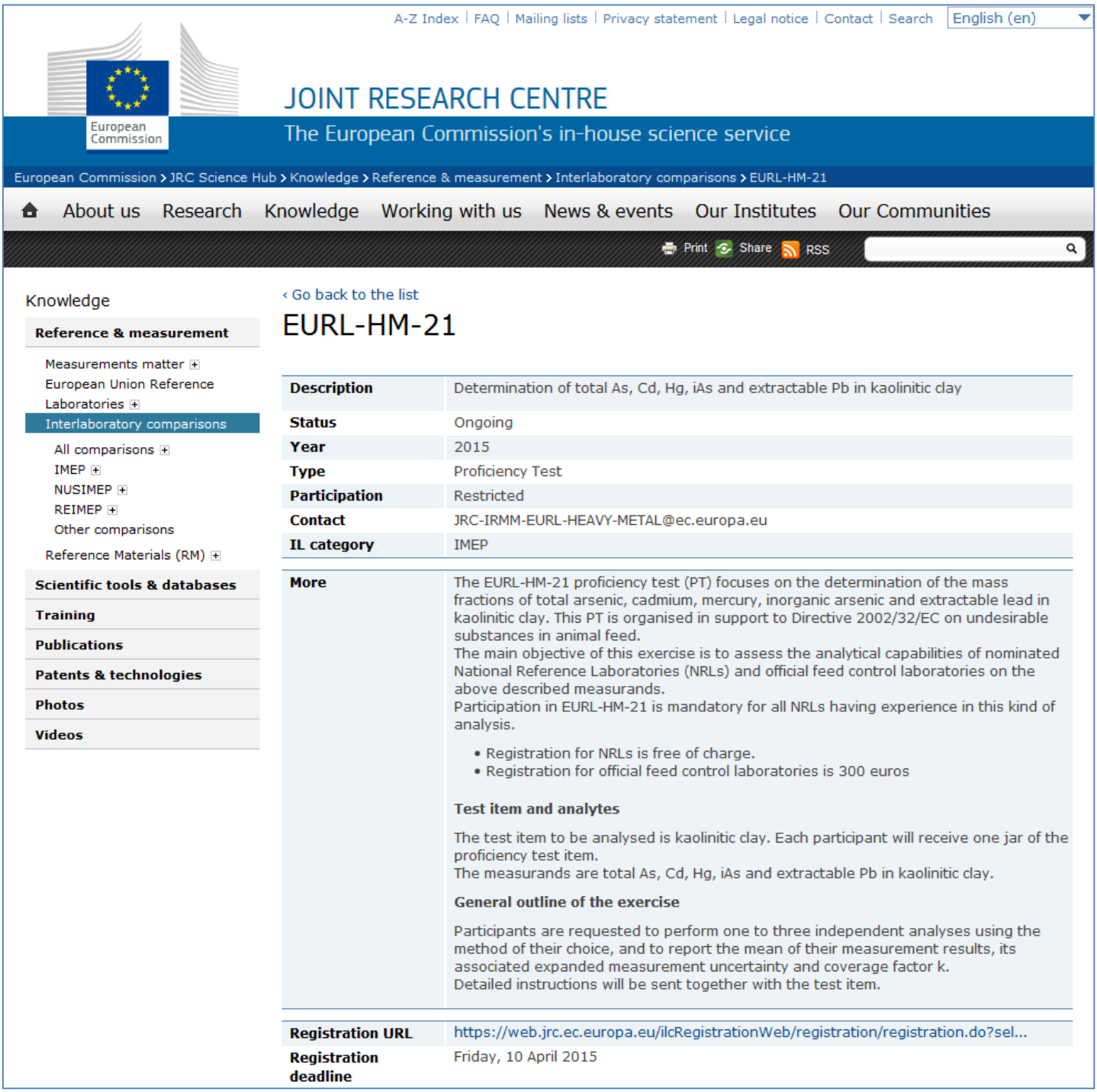
Dr. Piotr Robouch
Operating Manager EURL-HM

Cc: Franz Ulberth (Head of Unit SFB)

Retieseweg 111, B-2440 Geel - Belgium. Telephone: +32-(0)14-571 211.
Telephone: direct line +32-(0)14-571 687, Fax: +32-(0)14-571 865.
E-mail: JRC-IRMM-EURL-HEAVY-METALS@ec.europa.eu
Web site: https://ec.europa.eu/jrc/en/eurl/heavy-metals

Annex 2: JRC web announcement

https://ec.europa.eu/jrc/en/interlaboratory-comparison/eurl-hm-21?search&form-return



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  - European Union Reference Laboratories
  - Interlaboratory comparisons
    - All comparisons
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EURL-HM-21

Description	Determination of total As, Cd, Hg, iAs and extractable Pb in kaolinitic clay
Status	Ongoing
Year	2015
Type	Proficiency Test
Participation	Restricted
Contact	JRC-IRMM-EURL-HEAVY-METAL@ec.europa.eu
IL category	IMEP

More

The EURL-HM-21 proficiency test (PT) focuses on the determination of the mass fractions of total arsenic, cadmium, mercury, inorganic arsenic and extractable lead in kaolinitic clay. This PT is organised in support to Directive 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) and official feed control laboratories on the above described measurands.
Participation in EURL-HM-21 is mandatory for all NRLs having experience in this kind of analysis.

- Registration for NRLs is free of charge.
- Registration for official feed control laboratories is 300 euros

Test item and analytes

The test item to be analysed is kaolinitic clay. Each participant will receive one jar of the proficiency test item.
The measurands are total As, Cd, Hg, iAs and extractable Pb in kaolinitic clay.

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, its 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, 10 April 2015

Annex 3: Sample accompanying letter

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

Geel, 22 April 2015
JRC.D5/FCR/acs/Ares(2015)1702206

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

Participation in a proficiency testing round to determine the total mass fraction of arsenic (As), cadmium (Cd), mercury (Hg), inorganic arsenic (iAs) and extractable lead (Ex-Pb) in kaolinitic clay – EURL-HM-21.

Dear «Title» «Surname»,

Thank you for participating in the proficiency testing round for the determination of total As, Cd, Hg, iAs and extractable Pb in kaolinitic clay. This proficiency testing round (PT) is organised in support to Directive 2002/32/EC on undesirable substances in animal feed.

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

This parcel contains:
a) One bottle containing approximately 15 g of the proficiency test item
b) A "Confirmation of Receipt" form
c) This accompanying letter.

Please check whether the bottle containing the test item remained undamaged during transport. Then, send the "Confirmation of receipt" form back (fax: +32-14-571865, e-mail: JRC-IRMM-EURL-HEAVY-METALS@ec.europa.eu). You should store the sample in a dark place at 4°C until analysis.

The measurands are total As, Cd, Hg, iAs and extractable Pb in kaolinitic clay.

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

Reporting of results

Please perform two or three independent measurements, correct the measurements results for recovery and report on the reporting website:

- the **mean** of your two or three measurement results (mg kg^{-1}) and its associated expanded **uncertainty** (mg kg^{-1}),
- the **coverage factor** and
- the **technique** used.

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

The reporting website is https://irmm.jrc.ec.europa.eu/ilc/ilcReporting.do

To access the webpage you need a personal password key, which is: **«Part_key».** The system will guide you through the reporting procedure. After entering your results, please complete also the relating questionnaire.

Do not forget to submit and confirm always when required.

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

The **deadline** for submission of results is **12/06/2015**.

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

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

With kind regards,

Fernando Cordeiro (Ph.D.)
EURL-HM-21 Coordinator

Cc: F. Ulberth (Head of Unit)

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Telephone: direct line +32-(0)14-571 687, Fax: +32-(0)14-571 865.

E-mail: JRC-IRMM-EURL-HEAVY-METALS@ec.europa.eu
Web site: http://irmm.jrc.ec.europa.eu

Retieseweg 111, B-2440 Geel - Belgium. Telephone: +32-(0)14-571 211.
Telephone: direct line +32-(0)14-571 687, Fax: +32-(0)14-571 865.

E-mail: JRC-IRMM-EURL-HEAVY-METALS@ec.europa.eu
Web site: http://irmm.jrc.ec.europa.eu

Annex 4: 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

JRC.D5/IF/acs/ARES(2015)1702206

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

EURL-HM-21

Total mass fraction of arsenic (As), cadmium (Cd), mercury (Hg), inorganic arsenic (iAs) and extractable lead (Ex-Pb) in kaolinitic clay

Confirmation of receipt of the samples

Please return this form at your earliest convenience.
This confirms that the sample package arrived.
In case the package is damaged,
please state this on the form and contact us immediately.

ANY REMARKS .....
.....

Date of package arrival .....

Signature .....

Please return this form to:

Fernando Cordeiro (Ph.D.)

EURL-HM-21 Coordinator
EC-JRC-IRMM
Retieseweg 111
B-2440 GEEL, Belgium

Fax : +32-14-571865
JRC-IRMM-EURL-HEAVY-METALS@ec.europa.eu

Annex 5: Questionnaire

*1. You are:

- a National ReferenceLaboratory (NRL)
- an Official Control Laboratory (OCL)
- other

*2. Does the koalinitic clay you analysed comply with the maximum levels (MLs) set in the Directive 2002/32/EC?

- yes
- no

*2.1 specify why

3. Which type of sample digestion did you use?

	1. closed microwave	2. Pressure Bomb	3. Open microwave	4. Dry ashing	5. H2SO4	6. Other
tot As						
tot Cd						
tot Hg						
ex-Pb						
iAs						

4. Which digestion mixture did you use?

	1. H2O2	2. HCl	3. HClO4	4. HNO3	5. H2SO4	6. HF
tot As						
tot Cd						
tot Hg						
ex-Pb						
iAs						

*5. Have you followed a standard method of analysis

- yes
- no

5.1. If yes - which one(s)

5.2. Experiementql details (for extractable lead)

	Answers
sample intake (in g)	
volume of 5% HNO3 added (ml)	
Extraction time (min)	
Extraction temperature (oC)	
External calibration (Yes/No)	
Standard Addition (Yes/No)	

* 6. Did you correct for recovery?

- ○ yes
- ○ no

* 7. Provide the estimated analytical recovery; specify how the recovery was determined; provide the LOD of your method

	tot As	tot Cd	tot Hg	ex-Pb	iAs
Recovery (%)					
spiking with a known amount of the same analyte					
using a CRM					
other					
LOD (mg/kg)					

* 8. additional relevant remarks concerning the method of analysis

9. did you use a CRM for instrumental calibration?

	tot As	tot Cd	tot Hg	ex-Pb	iAs
CRM used	○	○	○	○	○

* 10. Did you correct for moisture content?

- ○ yes
- ○ no

* what was the moisture content in your sample?

11. Does your laboratory carry out **this type of analysis** on a regular basis? (How many samples per year)

	Never	1-50	51-250	251-1000	1000+
tot As	○	○	○	○	○
tot Cd	○	○	○	○	○
tot Hg	○	○	○	○	○
ex-Pb	○	○	○	○	○
iAs	○	○	○	○	○

* 12. How did you estimate your uncertainty budget?
(you may select several options)

- ☐ ISO GUM
- ☐ ISO 21758 - uncertainty of standard methods
- ☐ from in-house validation study
- ☐ measurement replicates (precision)
- ☐ estimation based on judgement
- ☐ from inter-laboratory comparison data

* 13. Do you provide uncertainty statements to your customers?

- ○ yes
- ○ no

* 14. Does your laboratory participate to PTs of this type?

- ○ yes
- ○ no

* 15. Which quality system does your laboratory have

- ○ ISO 9000
- ○ ISO 17025
- ○ other

if "other" - which one?

16. For which "analyte in clay" are you accredited?

	tot As	tot Cd	tot Hg	ex-Pb	iAs
accreditation	○	○	○	○	○

Do you have any additional comments?

Annex 6: Sample preparation

for the determination of extractable lead in kaolinitic clay

The extractable lead should be analysed following the protocol:

a) Weigh about 2 g of the test sample to the nearest 1 mg into a 250 mL beaker;

b) Add 85 mL of a 5 % (w/w) HNO_3 solution(#);

c) Cover the beaker with a watch-glass and boil for 30 min on a hot plate (make sure that the plate warms up homogeneously all over the surface);

d) Allow to cool. Decant the liquid into a 100 mL volumetric flask, rinsing the beaker and the watch-glass several times with 5 % (w/w) HNO_3;

e) Dilute to the mark with 5 % (w/w) HNO_3;

f) After homogenising, filter through a dry folded filter paper into a dry container. Use the first portion of the filtrate to rinse the glassware and discard that part. If the determination is not carried out immediately, the container with filtrate shall be covered;

g) Carry out a blank test at the same time as the extraction, with only the reagents and follow the same procedure as for the samples.

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

Note: Method derived from EN 15510:2007 [5] and recommended in the JRC report [4].

Annex 7: Homogeneity studies

Normalised values to the mean for each set (X): x_i/X (all values in mg kg^{-1})

	As		Cd		Hg		ex-Pb	
Sample Nr.	**R_1**	**R_2**	**R_1**	**R_2**	**R_1**	**R_2**	**R_1**	**R_2**
2	1.01	1.00	1.067	0.950	0.933	1.044	1.082	1.082
133	1.07	1.04	1.183	1.083	0.978	0.978	1.096	1.099
25	0.97	0.95	0.867	0.867	1.111	0.933	0.984	1.041
144	1.01	1.04	1.092	1.075	1.089	1.022	1.008	0.953
161	0.96	0.97	0.875	0.875	1.022	1.000	1.038	0.973
91	0.96	0.95	0.950	1.017	1.089	1.044	1.011	0.970
113	1.08	1.06	0.992	0.983	1.000	1.067	0.997	0.964
39	0.95	0.95	0.925	0.925	0.933	0.867	0.975	0.970
63	1.03	1.03	1.233	1.175	1.089	1.000	0.874	0.984
77	0.97	0.98	0.967	0.958	0.978	1.022	0.951	0.934
Mean	1.00		1.000		1.000		1.000	
σ	1.35		0.010		0.012		0.61	
0.3*σ	**0.41**		**0.003**		**0.003**		**0.183**	
S_x	0.272		0.013		0.002		0.198	
S_w	0.079		0.005		0.003		0.131	
S_S (u_{bb})	**0.27**		**0.013**		**0.001**		**0.174**	
$S_S \leq 0.3*\sigma$?	**Yes**		**No**		**Yes**		**Yes**	

where:
- σ is the standard deviation for the PT assessment (as a % of X_{ref}),
- 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.

Annex 8: Results for total arsenic (As)

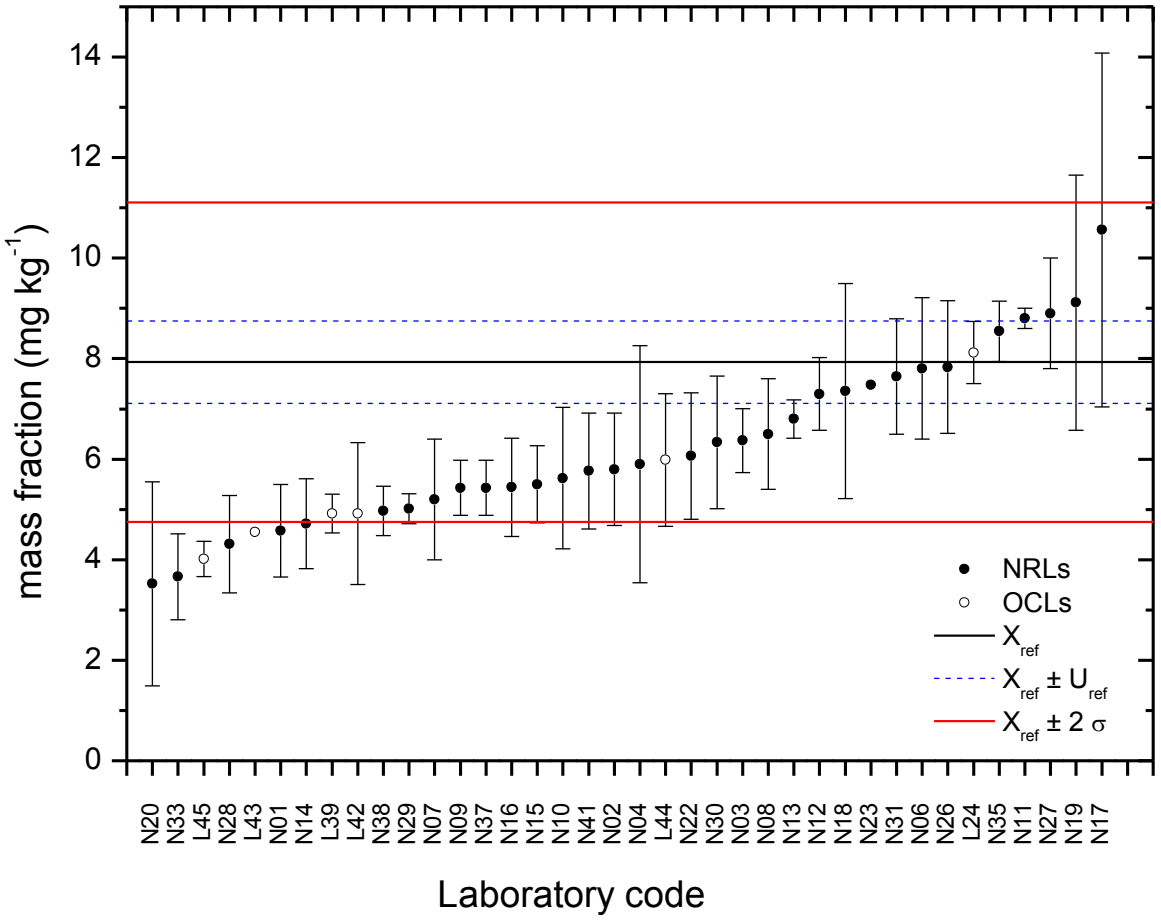
Assigned values: X_{ref} = 7.93; U_{ref} = 0.82; σ = 1.59
(all values in mg kg^{-1}, referring to 12% moisture content)

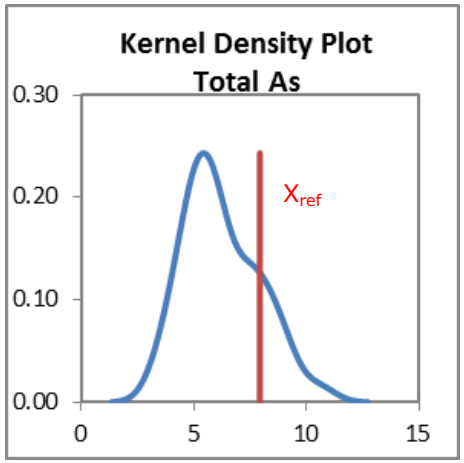
Lab code		X_{lab}	U_{lab}	$X_{lab12\%}$	$U_{lab12\%}$	k	$u_{lab12\%}$	Technique	z-score[a]	ζ-score[a]	MU[b]
N01	**12%**	4.58	0.92	4.58	0.92	2	0.46	ICP-MS Q	**-2.11**	**-5.43**	**a**
N02	**NC**	6.59	1.27	5.80	1.12	2	0.56	AAS	**-1.34**	**-3.08**	**a**
N03	**DM**	7.24	0.72	6.37	0.63	2	0.32	ICP	**-0.98**	**-3.01**	**b**
N04	**DM**	6.7	2.68	5.90	2.36	2	1.18	ICP-MS	**-1.28**	**-1.63**	**a**
N06	**DM**	8.87	1.6	7.81	1.41	2	0.70	ICP	**-0.08**	**-0.16**	**a**
N07	**12%**	5.2	1.2	5.2	1.2	2	0.6	ICP-MS	**-1.72**	**-3.76**	**a**
N08	**12%**	6.5	1.1	6.5	1.1	2	0.55	ICP-MS	**-0.90**	**-2.09**	**a**
N09	**DM**	6.17	0.62	5.43	0.55	2	0.27	ICP-MS	**-1.58**	**-5.07**	**b**
N10	**DM**	6.39	1.6	5.62	1.41	2	0.70	ICP-MS	**-1.46**	**-2.83**	**a**
N11	**12%**	8.8	0.2	8.8	0.2	2	0.1	ICP	**0.55**	**2.05**	**b**
N12	**12%**	7.298	0.726	7.298	0.726	2	0.363	HG-AAS	**-0.40**	**-1.16**	**b**
N13	**12%**	6.8	0.38	6.8	0.38	2	0.19	ICP-MS	**-0.71**	**-2.50**	**b**
N14	**DM**	5.3584	1.0181	4.7154	0.8959	2	0.4480	ICP-IDMS	**-2.03**	**-5.29**	**a**
N15	**12%**	5.5	0.77	5.5	0.77	2	0.39	GF-AAS	**-1.53**	**-4.32**	**b**
N16	**12%**	5.44	0.98	5.44	0.98	2	0.49	ICP-MS	**-1.57**	**-3.90**	**a**
N17	**DM**	12	4	10.56	3.52	2	1.76	ICP-OES	**1.66**	**1.45**	**c**
N18	**DM**	8.36	2.431	7.36	2.14	2	1.07	ICP	**-0.36**	**-0.50**	**a**
N19	**12%**	9.115	2.538	9.115	2.538	2	1.27	HG-AAS	**0.75**	**0.89**	**a**
N20	**DM**	4	2.31	3.52	2.03	2	1.02	HG-AAS	**-2.78**	**-4.02**	**a**
N22	**DM**	6.89	1.43	6.06	1.26	2	0.63	ICP-MS	**-1.18**	**-2.49**	**a**
N23	**NC**	8.5		7.48				HG-AAS	**-0.29**	**-1.10**	**b**
N26	**DM**	8.9	1.5	7.83	1.32	2	0.66	ICP-MS	**-0.06**	**-0.13**	**a**
N27	**12%**	8.9	1.1	8.9	1.1	2	0.55	Z-ET-AAS	**0.61**	**1.41**	**a**
N28	**DM**	4.9	1.1	4.31	0.97	2	0.48	SFICP-MS	**-2.28**	**-5.70**	**a**
N29	**NC**	5.7	0.34	5.02	0.30	2	0.15	ICP	**-1.84**	**-6.67**	**b**
N30	**DM**	7.2	1.5	6.34	1.32	2	0.66	ICP-MS	**-1.01**	**-2.05**	**a**
N31	**DM**	8.69	1.304	7.65	1.15	2	0.57	GF-AAS	**-0.18**	**-0.40**	**a**
N33	**DM**	4.16	0.97	3.66	0.85	2	0.43	SFICP-MS	**-2.69**	**-7.21**	**a**
N35	**DM**	9.71	0.68	8.54	0.60	2	0.30	k_0-INAA	**0.39**	**1.20**	**b**
N37	**DM**	6.17	0.62	5.43	0.55	2	0.27	ICP-MS	**-1.58**	**-5.07**	**b**
N38	**DM**	5.65	0.56	4.97	0.49	3.18	0.15	ICP	**-1.87**	**-6.74**	**b**
N41	**NC**	6.554	1.311	5.77	1.15	2	0.58	HG-AAS	**-1.36**	**-3.06**	**a**
L24	**NC**	9.23	0.7	8.12	0.62	2	0.308	ET-AAS	**0.12**	**0.37**	**b**
L39	**DM**	5.59	0.44	4.92	0.39	4.3	0.01	HG-AAS	**-1.90**	**-7.33**	**b**
L42	**12%**	4.92	1.41	4.92	1.41	2	0.71	ICP-MS	**-1.90**	**-3.69**	**a**
L43	**DM**	5.17		4.55				ICP-MS	**-2.13**	**-8.23**	**b**
L44	**DM**	6.8	1.5	5.98	1.32	2	0.66	ICP	**-1.23**	**-2.51**	**a**
L45	**DM**	4.56	0.4	4.01	0.35	2	0.176	HG-AAS	**-2.47**	**-8.76**	**b**

[a] performance: satisfactory, questionable, unsatisfactory,
[b] a: $u_{ref} \leq u_{lab} \leq \sigma$; b: $u_{lab} < u_{ref}$; and c: $u_{lab} > \sigma$
DM: dry mass; NC: not corrected for moisture content; 12 %: moisture content of 12 %.

EURL-HM-21: Total As in kaolinitic clay

X_{ref} = 7.93; U_{ref} (k=2) = 0.82; σ = 1.59 (all values in mg kg^{-1}, referring to 12% moisture content)





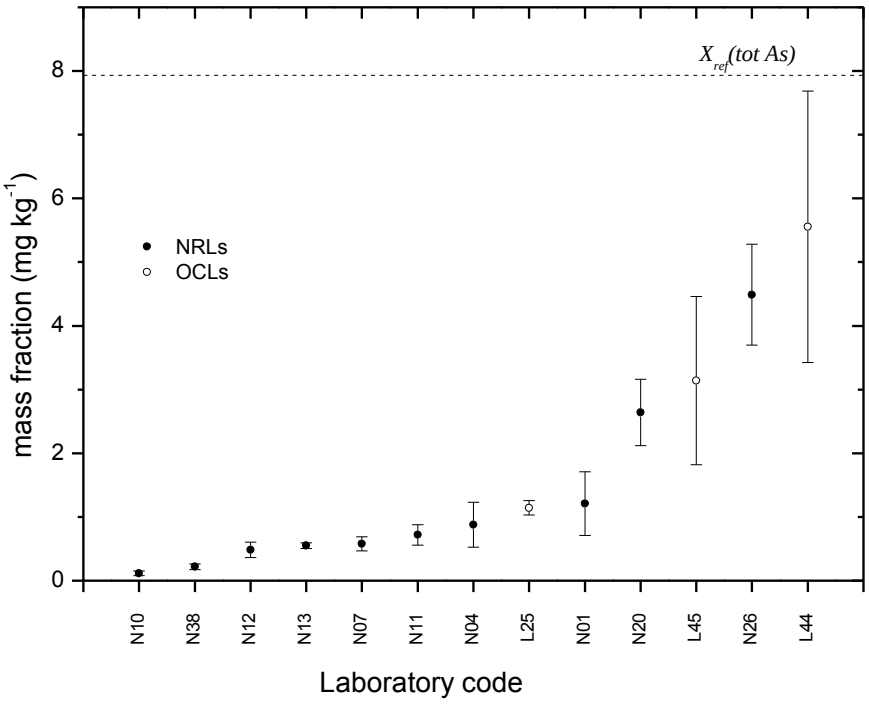
Measurement results and associated expanded measurement uncertainties (referring to 12% moisture content)

Annex 9: Results for inorganic arsenic (iAs)

Lab code		X_{lab}	U_{lab}	$X_{lab12\%}$	$U_{lab12\%}$	k	$u_{lab12\%}$	Technique
N01	**12%**	1.21	0.5	1.21	0.5	2	0.25	HPLC-ICP-MS
N04	**DM**	1	0.4	0.88	0.35	2	0.18	HPLC-ICP-MS
N06	**DM**	< 0.2						ICP
N07	**12%**	0.58	0.11	0.58	0.11	2	0.06	HPLC-ICP-MS
N10	**DM**	0.132	0.04	0.116	0.035	2	0.018	LC-ICP-MS
N11	**12%**	0.72	0.16	0.72	0.16	2	0.08	HPLC-ICP-MS
N12	**12%**	0.483	0.12	0.483	0.12	2	0.06	LC-ICP-MS
N13	**12%**	0.55	0.044	0.55	0.044	2	0.022	HPLC-ICP-MS
N20	**DM**	3	0.59	2.64	0.52	2	0.26	HG-AAS
N26	**DM**	5.1	0.9	4.49	0.79	2	0.40	ICP-MS
N38	**DM**	0.25	0.05	0.22	0.04	3.18	0.01	HG-AAS
L25	**DM**	1.3	0.13	1.14	0.11	2	0.06	LC-ICP-MS
L44	**DM**	6.31	2.42	5.55	2.13	2	1.06	ICP
L45	**DM**	3.57	1.5	3.14	1.32	2	0.66	HG-AAS

DM: dry mass; NC: not corrected for moisture content; 12 %: moisture content of 12 %.

EURL-HM-21: iAs in kaolinitic clay



Measurement results and associated expanded measurement uncertainties
(referring to 12% moisture content)

Annex 10: Results for total cadmium (Cd)

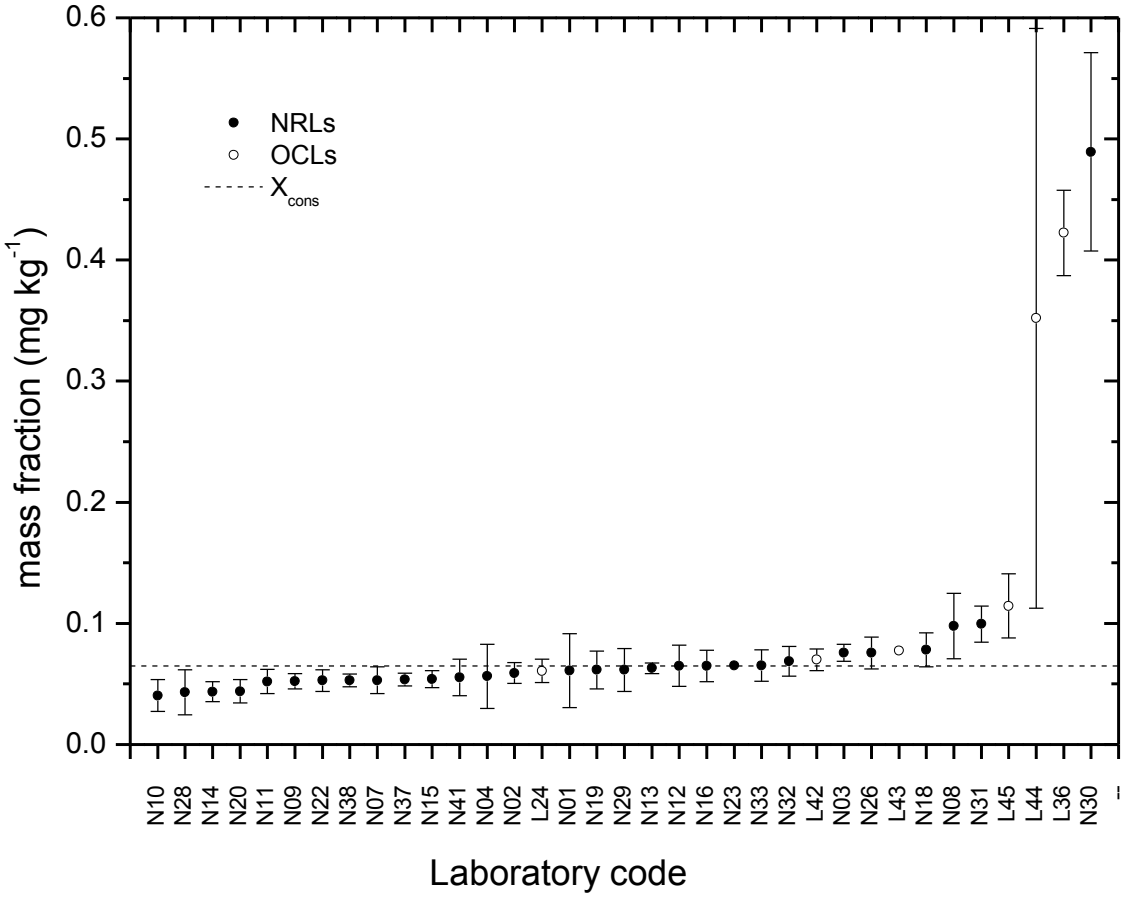
Consensus from participants:
X_{cons} = 0.065 mg kg^{-1}, referring to 12% moisture content

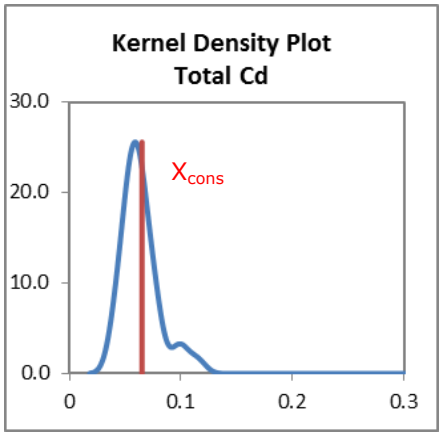
Lab code		X_{lab}	U_{lab}	$X_{lab12\%}$	$U_{lab12\%}$	k	$u_{lab12\%}$	Technique
N01	**12%**	0.0611	0.0305	0.0611	0.0305	2	0.0153	ICP-MS
N02	**NC**	0.067	0.0098	0.059	0.009	2	0.004	AAS
N03	**DM**	0.086	0.008	0.076	0.007	2	0.004	ICP
N04	**DM**	0.064	0.03	0.056	0.026	2	0.013	ICP-MS
N05	**DM**	< 0.5						AAS
N06	**DM**	< 0.2						ICP
N07	**12%**	0.053	0.011	0.053	0.011	2	0.006	ICP-MS
N08	**12%**	0.098	0.027	0.098	0.027	2	0.014	ICP-MS
N09	**DM**	0.0593	0.0071	0.0522	0.0062	2	0.0031	ICP-MS
N10	**DM**	0.046	0.015	0.040	0.013	2	0.007	ICP-MS
N11	**12%**	0.052	0.01	0.052	0.01	2	0.005	ICP
N12	**12%**	0.065	0.017	0.065	0.017	2	0.009	ET-AAS
N13	**12%**	0.063	0.0044	0.063	0.0044	2	0.0022	ICP-MS
N14	**DM**	0.0495	0.0094	0.0436	0.0083	2	0.0041	ICP-IDMS
N15	**12%**	0.054	0.007	0.054	0.007	2	0.004	GF-AAS
N16	**12%**	0.065	0.013	0.065	0.013	2	0.007	ICP-MS
N17	**DM**	< 0.1						ICP-OES
N18	**DM**	0.089	0.016	0.078	0.014	2	0.007	AAS
N19	**12%**	0.0616	0.0157	0.0616	0.0157	2	0.008	GF-AAS
N20	**DM**	0.05	0.011	0.044	0.010	2	0.005	ET-AAS
N22	**DM**	0.06	0.01	0.053	0.009	2	0.004	ICP-MS
N23	**NC**	0.074		0.065				GF-AAS
N26	**DM**	0.086	0.015	0.076	0.013	2	0.007	ICP-MS
N27	**12%**	< 0.25						Z-ET-AAS
N28	**DM**	0.049	0.021	0.043	0.018	2	0.009	ET-AAS
N29	**NC**	0.07	0.02	0.062	0.018	2	0.009	ICP
N30	**DM**	0.556	0.093	0.489	0.082	2	0.041	ICP-MS
N31	**DM**	0.113	0.017	0.099	0.015	2	0.007	GF-AAS
N32	**DM**	0.078	0.014	0.069	0.012	2	0.006	AAS
N33	**DM**	0.0742	0.0147	0.065	0.013	2	0.006	SFICP-MS
N37	**DM**	0.061	0.006	0.054	0.005	2	0.003	ICP-MS
N38	**DM**	0.06	0.006	0.053	0.005	3.18	0.002	ICP
N41	**NC**	0.063	0.017	0.055	0.015	2	0.007	GF-AAS
L24	**NC**	0.069	0.011	0.061	0.010	2	0.005	ET-AAS
L36	**DM**	0.48	0.04	0.422	0.035	2	0.018	AAS
L39	**DM**	< 0.100						AAS
L43	**DM**	0.088		0.077				ICP-MS
L42	**12%**	0.07	0.009	0.07	0.009	2	0.005	ICP
L44	**DM**	0.4	0.272	0.352	0.239	2	0.120	ICP
L45	**DM**	0.13	0.03	0.114	0.026	2	0.013	AAS

DM: dry mass; NC: not corrected for moisture content; 12 %: moisture content of 12 %.

EURL-HM-21: Total Cd in kaolinitic clay

X_{cons} = 0.065 mg kg^{-1}, referring to 12% moisture content





Measurement results and associated expanded measurement uncertainties (referring to 12% moisture content)

Annex 11: Results for total mercury (Hg)

Assigned values: X_{ref} = 0.047; U_{ref} (k=2) = 0.004; σ = 0.012

(all values in mg kg^{-1}, referring to 12% moisture content)

Lab code		X_{lab}	U_{lab}	$X_{lab12\%}$	$U_{lab12\%}$	k	$u_{lab12\%}$	Technique	z-score[a]	ζ-score[a]	MU[b]
N01	**12%**	0.0454	0.0227	0.0454	0.0227	2	0.011	ICP-MS	**-0.11**	**-0.11**	**a**
N02	**NC**	0.21	0.048	0.18	0.042	2	0.021	CV-AAS	**11.85**	**6.50**	**c**
N03	**DM**	< 0.05						ICP			
N04	**DM**	0.03	0.012	0.026	0.011	2	0.005	ICP-MS	**-1.74**	**-3.48**	**a**
N05	**DM**	0.0487	0.0019	0.0429	0.002	2	0.001	DMA	**-0.32**	**-1.46**	**b**
N06	**DM**	< 0.05						DMA			
N07	**12%**	0.044	0.007	0.044	0.007	2	0.004	DMA	**-0.23**	**-0.62**	**a**
N08	**12%**	0.045	0.009	0.045	0.009	2	0.005	DMA	**-0.14**	**-0.32**	**a**
N09	**DM**	0.0469	0.0047	0.0413	0.004	2	0.002	DMA	**-0.46**	**-1.67**	**b**
N10	**DM**	0.061	0.018	0.054	0.016	2	0.008	DMA	**0.60**	**0.85**	**a**
N11	**DM**	0.053	0.01	0.047	0.009	2	0.004	ICP	**0.00**	**0.00**	**a**
N12	**12%**	0.047	0.008	0.047	0.008	2	0.004	CV-AFS	**0.03**	**0.08**	**a**
N13	**12%**	0.054	0.0057	0.054	0.0057	2	0.003	ICP-MS	**0.63**	**1.96**	**a**
N14	**DM**	0.0413	0.0022	0.0363	0.002	2	0.001	DMA	**-0.88**	**-3.90**	**b**
N15	**12%**	0.051	0.009	0.051	0.009	2	0.005	CV-AAS	**0.37**	**0.85**	**a**
N16	**12%**	0.058	0.009	0.058	0.009	2	0.005	ICP-MS	**0.97**	**2.22**	**a**
N17	**DM**	0.042	0.003	0.037	0.003	2	0.001	DMA	**-0.83**	**-3.47**	**b**
N18	**DM**	0.071	0.013	0.062	0.011	2	0.006	DMA	**1.36**	**2.54**	**a**
N19	**12%**	0.057	0.0065	0.057	0.0065	2	0.003	CV-AAS	**0.89**	**2.54**	**a**
N20	**DM**	0.1	0.03	0.09	0.026	2	0.013	CV-AAS	**3.55**	**3.08**	**c**
N22	**DM**	< 0.05						ICP-MS			
N26	**DM**	0.069	0.011	0.061	0.010	2	0.005	ICP-MS	**1.21**	**2.59**	**a**
N27	**12%**	0.047	0.008	0.047	0.008	2	0.004	DMA	**0.03**	**0.08**	**a**
N28	**DM**	0.078	0.034	0.069	0.030	2	0.015	CV-AAS	**1.89**	**1.45**	**c**
N29	**NC**	< 0.08						ICP			
N30	**DM**	0.038	0.012	0.0334	0.011	2	0.005	ICP-MS	**-1.13**	**-2.27**	**a**
N31	**DM**	0.048	0.011	0.0422	0.010	2	0.005	DMA	**-0.38**	**-0.81**	**a**
N32	**DM**	< 0.1						CV-AAS			
N33	**DM**	0.0501	0.0157	0.0441	0.014	2	0.007	SFICP-MS	**-0.22**	**-0.35**	**a**
N35	**DM**	0.051	0.003	0.045	0.003	2	0.001	CV-AAS	**-0.15**	**-0.63**	**b**
N37	**DM**	0.052	0.008	0.046	0.007	2	0.004	DMA	**-0.08**	**-0.21**	**a**
N38	**DM**	0.045	0.015	0.040	0.013	3.18	0.004	ICP	**-0.60**	**-1.46**	**a**
N41	**NC**	0.073	0.023	0.064	0.020	2	0.010	CV-AAS	**1.51**	**1.69**	**a**
L39	**DM**	0.039	0.012	0.034	0.011	2	0.005	CV-AAS	**-1.06**	**-2.12**	**a**
L43	**DM**	0.057		0.050				ICP-MS	**0.30**	**1.43**	**b**
L44	**DM**	**< 0.025**						LECO AMA			
L45	**DM**	0.07	0.05	0.06	0.04	2	0.02	CV-AAS	**1.28**	**0.68**	**c**

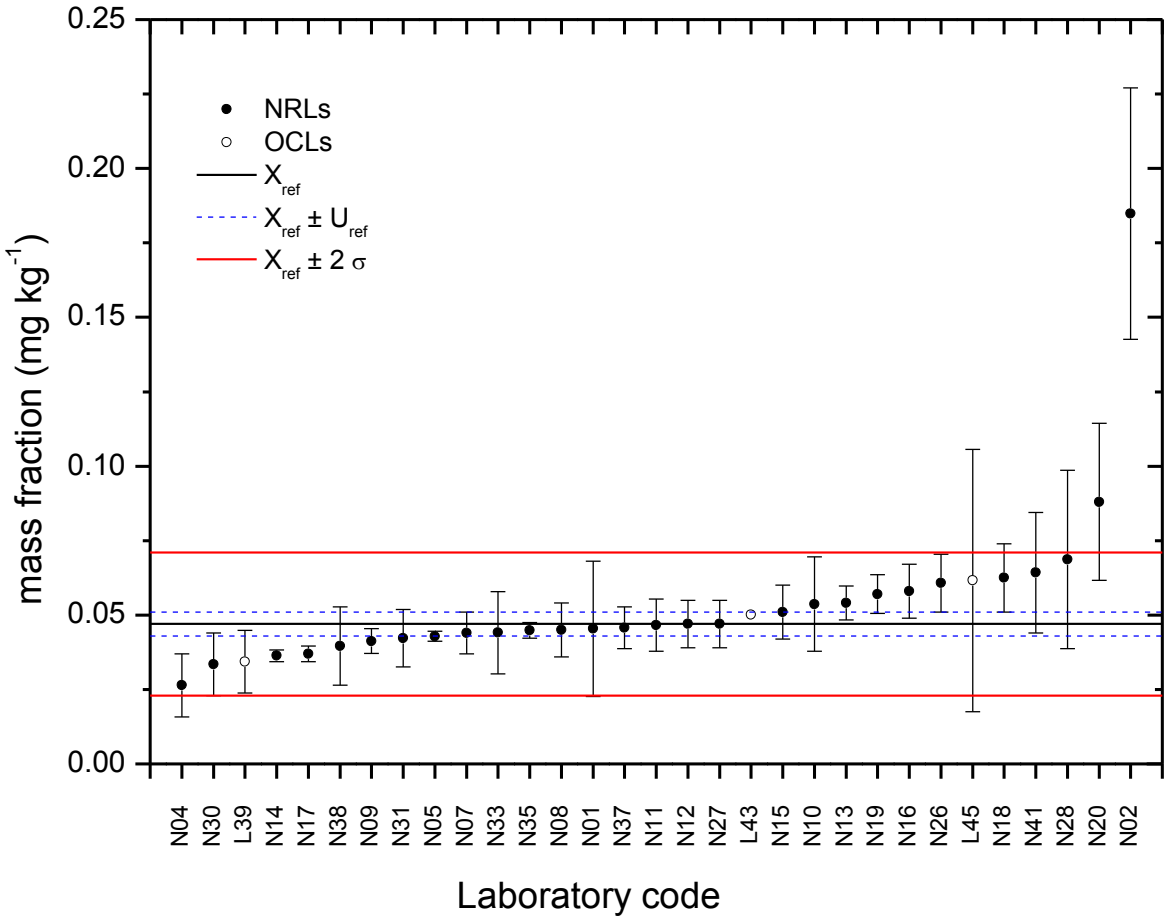
[a] performance: satisfactory, questionable, unsatisfactory,

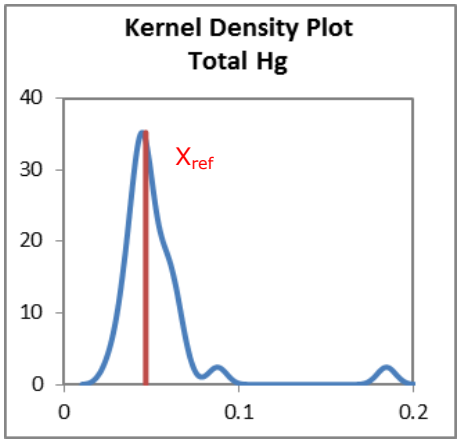
[b] a: $u_{ref} \leq u_{lab} \leq \sigma$; b: $u_{lab} < u_{ref}$; and c: $u_{lab} > \sigma$

DM: dry mass; NC: not corrected for moisture content; 12 %: moisture content of 12 %.

EURL-HM-21: Total Hg in kaolinitic clay

X_{ref} = 0.047; U_{ref} (k=2) = 0.004; σ = 0.012 (all values in mg kg^{-1}, referring to 12% moisture content)





Measurement results and associated expanded measurement uncertainties (referring to 12% moisture content)

Annex 12: Results for extractable lead (ex-Pb)

Assigned values: X_{ref} = 3.15; U_{ref} (k=2) = 0.45; σ = 0.79

(all values in mg kg^{-1}, referring to 12% moisture content)

Lab code		X_{lab}	U_{lab}	$X_{lab12\%}$	$U_{lab12\%}$	k	$u_{lab12\%}$	Technique	z-score[a]	ζ-score[a]	MU[b]
N01	**12%**	2.73	1.37	2.73	1.37	2	0.69	ICP-MS	**-0.54**	**-0.59**	**a**
N02	**NC**	4.35	0.59	3.83	0.52	2	0.260	AAS	**0.85**	**1.96**	**a**
N03	**DM**	75.1	7.5	66.09	6.6	2	3.3	ICP	**79.79**	**19.03**	**c**
N04	**DM**	69	34.5	60.7	30.4	2	15.18	ICP-MS	**72.99**	**3.79**	**c**
N05	**DM**	4.085	0.817	3.595	0.719	2	0.359	AAS	**0.56**	**1.04**	**a**
N06	**DM**	5.3	1.7	4.664	1.496	2	0.748	ICP	**1.91**	**1.93**	**a**
N07	**12%**	5.3	1.3	5.3	1.3	2	0.65	ICP-MS	**2.72**	**3.12**	**a**
N08	**12%**	4.6	0.78	4.6	0.78	2	0.39	ICP-MS	**1.83**	**3.21**	**a**
N09	**DM**	5.02	0.55	4.42	0.48	2	0.24	ICP-MS	**1.60**	**3.83**	**a**
N10	**DM**	4.31	1.07	3.79	0.94	2	0.47	ICP-MS	**0.81**	**1.22**	**a**
N11	**12%**	7.2	1.6	7.2	1.6	2	0.8	ET-AAS	**5.13**	**4.87**	**c**
N12	**12%**	4.5	0.67	4.5	0.67	2	0.34	ICP-MS Q	**1.71**	**3.34**	**a**
N13	**12%**	3.7	0.35	3.7	0.35	2	0.18	ICP-MS	**0.69**	**1.92**	**b**
N15	**12%**	4.8	0.5	4.8	0.5	2	0.25	GF-AAS	**2.09**	**4.90**	**a**
N17	**DM**	**79**	20	**69.5**	17.6	2	8.8	ICP-OES	**84.15**	**7.54**	**c**
N18	**DM**	4.106	1.198	3.613	1.054	2	0.527	AAS	**0.58**	**0.80**	**a**
N19	**12%**	4.079	0.9635	4.079	0.9635	2	0.482	GF-AAS	**1.17**	**1.74**	**a**
N20	**DM**	4	0.89	3.5	0.78	2	0.4	ET-AAS	**0.46**	**0.81**	**a**
N22	**DM**	10.09	3.25	8.88	2.86	2	1.43	ICP-MS	**7.26**	**3.95**	**c**
N23	**NC**	80.3		70.7				ICP	**85.60**	**300.85**	**b**
N26	**DM**	3.8	0.5	3.34	0.4	2	0.22	ICP-MS	**0.24**	**0.60**	**b**
N27	**12%**	4.9	0.6	4.9	0.6	2	0.3	Z-ET-AAS	**2.21**	**4.66**	**a**
N28	**DM**	5.39	1.51	4.74	1.33	2	0.66	ET-AAS	**2.01**	**2.27**	**a**
N29	**NC**	60.5	15.3	53.2	13.5	2	6.73	ICP	**63.50**	**7.44**	**c**
N30	**DM**	3.63	0.62	3.19	0.55	2	0.27	ICP-MS	**0.05**	**0.11**	**a**
N31	**DM**	3.389	0.508	2.982	0.447	2	0.224	GF-AAS	**-0.22**	**-0.54**	**b**
N32	**DM**	3.96	0.713	3.48	0.63	2	0.31	AAS	**0.42**	**0.86**	**a**
N37	**DM**	3.57	0.36	3.14	0.32	2	0.1584	ICP-MS	**-0.02**	**-0.05**	**b**
N38	**DM**	3.98	0.7	3.50	0.62	3.2	0.19	ICP	**0.44**	**1.17**	**b**
N41	**NC**	6.683	1.337	5.88	1.18	2	0.59	GF-AAS	**3.46**	**4.33**	**a**
L36	**DM**	3.4	0.39	2.99	0.34	2	0.195	AAS	**-0.21**	**-0.55**	**b**
L39	**DM**	3.98	0.74	3.50	0.65	3.18	0.23	AAS	**0.44**	**1.08**	**a**
L42	**12%**	**46.5**	11.7	**46.5**	11.7	2	5.85	ICP-MS	**54.96**	**7.40**	**c**
L43	**DM**	**74.3**		**65.4**				ICP-MS	**78.90**	**277**	**b**
L44	**DM**	13.1	4.4	11.5	3.9	2	2.2	ICP	**10.62**	**3.79**	**b**
L45	**DM**	73.8	15.6	64.9	13.7	2	7.8	AAS	**78.34**	**7.92**	**c**

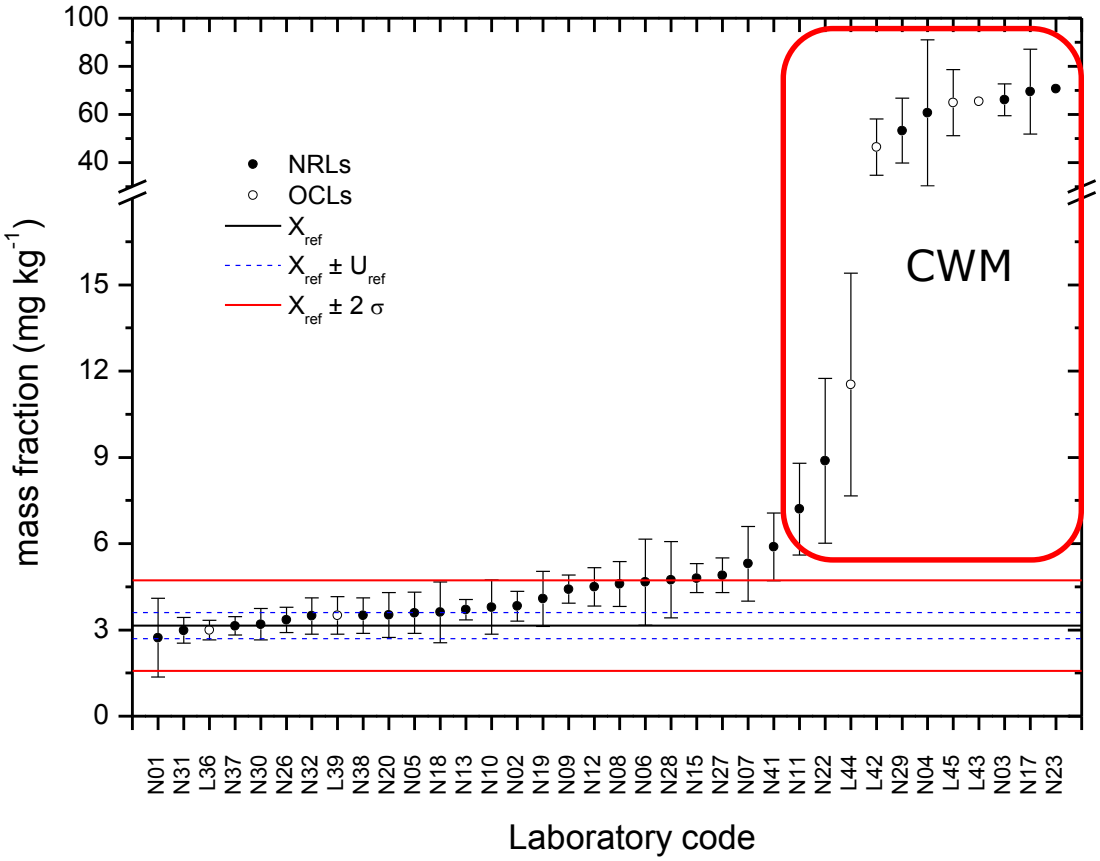
[a] performance: satisfactory, questionable, unsatisfactory,

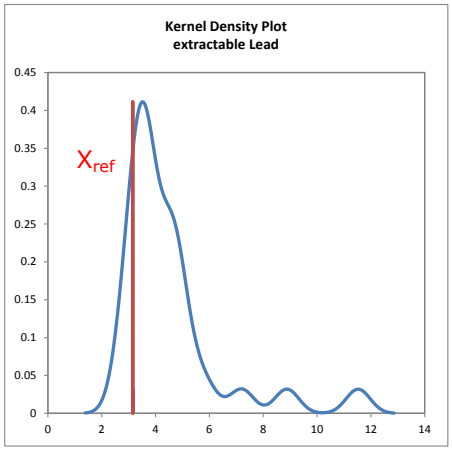
[b] a: $u_{ref} \leq u_{lab} \leq \sigma$; b: $u_{lab} < u_{ref}$; and c: $u_{lab} > \sigma$

DM: dry mass; NC: not corrected for moisture content; 12 %: moisture content of 12 %.

EURL-HM-21: ex-Pb in kaolinitic clay

X_{ref} = 3.15; U_{ref} (k=2) = 0.45; σ = 0.79 (all values in mg kg^{-1}, referring to 12% moisture content)





Measurement results and associated expanded measurement uncertainties (referring to 12% moisture content)

Annex 13: Experimental details and scoring (z-scores)

Lab ID		Sample digestion	Digestion mixture	Std. method?	Correct recovery?	Recovery (R, in %)			LOD (mg/Kg)	Additional remarks regarding the method of analysis?	Experimental details for Ex-Pb				
						R	Spiking	CRM			Weighed mass (g)	Volume HNO_3 (mL)	Extraction time (min.)	External Cal.?	Standard additions?
N01	As	CMW	HNO_3	No	No	100			0.025	For the determination of As (m/z 75) with ICPMS there is an interference on Sm or Nd (m/z 150++), so we measured As in MS/MS mode with O2 (m/z 91)					
	Cd	CMW	HNO_3	No	No	100			0.006						
	Hg	CMW	HNO_3	No	No	100			0.013						
	iAs	Other	HNO_3	No	No	100			0.02						
	Ex-Pb	Other		No	No	100			0.04		1	8 ml	30	Yes	No
N02	As	CMW	H_2O_2+HNO_3	No	No	80-110	No	Yes	0.067						
	Cd	CMW	H_2O_2+HNO_3	No	No	80-110	No	Yes	0.0033						
	Hg	CMW	H_2O_2+HNO_3	No	No	80-110	No	Yes	0.050						
	Ex-Pb	Other		No	No		No	No			2	85 ml	30	Yes	No
N03	As	CMW	H_2O_2+HCl+HNO_3	No	No	80-110		Yes	0.005						
	Cd	CMW	H_2O_2+HCl+HNO_3	No	No			Yes	0.005						
	Hg	CMW	H_2O_2+HCl+HNO_3	No	No			Yes	0.05						
	Ex-Pb	CMW		No	No			Yes	0.010		0.5	10	30	Yes	
N04	As	CMW	HNO_3	Yes											
	Cd	CMW	HNO_3	Yes											
	Hg	CMW	HNO_3	Yes											
	iAs	CMW	HCl	Yes											
	Ex-Pb	CMW		Yes											
N05	Cd	DA	HNO_3	No	No				0.163						
	Hg			No	No				0.0005						
	Ex-Pb			No	No						2	85 mL	30	No	No
N06	As	CMW	H_2O_2+HNO_3	Yes	No	95	No	Yes	2						
	Cd	CMW	H_2O_2+HNO_3	Yes	No	92	No	Yes	0.1						
	Hg	Other		Yes	No	96	No	Yes	0.050						
	iAs	CMW	HCl	Yes	No	93	No	Yes	0.050						
	Ex-Pb	Other		Yes	No		No	No	1.0		0.25-0.50	50 ml	30	Yes	No
N07	As	CMW	HNO_3	No	No	100	No	Yes	0.0012						
	Cd	CMW	HNO_3	No	No	100	No	Yes	0.0003						
	Hg			No	No	100	No	Yes	0.000051						
	iAs	CMW	H_2O_2+HNO_3	No	No	100	No	Yes	0.0024						
	Ex-Pb	Other		No	No		No		0.0018		1	8	30	Yes	No
N08	As	CMW	H_2O_2+HNO_3	No	No	95	Yes	No		We also analyzed extractable As, together with extractable Pb, applying the method prescribed in the legislation for extractable Pb. The result for extractable As was 1.2 mg/Kg.					
	Cd	CMW	H_2O_2+HNO_3	No	No	105	Yes	No							
	Hg	Other		No	No	97	Yes	No							
	Ex-Pb	Other		No	No	97	Yes	No			0.5	50 mL	30	Yes	No
N09	As	CMW	H_2O_2+HNO_3	Yes	No	100	No	Yes	0.001						
	Cd	CMW	H_2O_2+HNO_3	Yes	No	104	No	Yes	0.0003						
	Hg	Other		Yes	No	99	No	Yes	0.0001						
	Ex-Pb	Other		Yes	No	102	No	Yes	0.018		0.2	50	30	Yes	No

Lab ID		CRM for Ins. cal.?	Moisture correction?	Moisture (% m/m)	Samples / year	Measurement Uncertainty		Quality system	ILC?	Accredited?	Do you have any comments? Let us know!
						Estimation	Reported				
N01	As		Yes	0,86	250-1000	From interlaboratory comparison data	Yes	Yes	Yes	Yes	According to the report of the workshop 2014 the results are reported relative to a feedingstuff with a moisture content of 12 %
	Cd		Yes		> 1000		Yes	Yes	Yes	Yes	
	Hg		Yes		> 1000		Yes	Yes	Yes	Yes	
	iAs		Yes		50-250		Yes	Yes	Yes		
	Ex-Pb		Yes		0-50		Yes	Yes	Yes	Yes	
N02	As		No		50-250	From in-house validation	Yes	Yes	Yes	Yes	
	Cd		No		50-250		Yes	Yes	Yes	Yes	
	Hg		No		Never		Yes	Yes	Yes		
	Ex-Pb		No		Never		Yes	Yes	Yes		
N03	As		No		0-50	Uncertainty budget (ISO GUM)	Yes	Yes	Yes		Measurements results can affect: unusual matrix, we doesn't have the same reference material and No specific sample preparation method for kaolinitic clay. For ext. Pb determination we used the same method as for As and Cd (microwave digestion)
	Cd		No		0-50		Yes	Yes	Yes		
	Hg		No		0-50		Yes	Yes	Yes		
	Ex-Pb		No		0-50		Yes	Yes	Yes		
N04	As		No		> 1000	From in-house validation	No	Yes		Yes	We used the routine analyse for Pb
	Cd		No		> 1000		No	Yes		Yes	
	Hg		No		> 1000		No	Yes		Yes	
	iAs		No		250-1000		No	Yes			
	Ex-Pb		No		> 1000		No	Yes		Yes	
N05	Cd	Yes	Yes	0.407	50-250	From in-house validation	No	Yes	Yes	Yes	
	Hg	Yes	Yes		50-250		No	Yes	Yes	Yes	
	Ex-Pb	Yes	Yes				No	Yes	Yes		
N06	As		No		0-50		Yes	Yes	No		
	Cd		No		0-50		Yes	Yes	No		
	Hg		No		0-50		Yes	Yes	No		
	iAs		No		0-50		Yes	Yes	No		
	Ex-Pb		No		0-50		Yes	Yes	No		
N07	As	Yes	Yes	1.2 %; afterwards result corrected to 12 % moisture content	0-50	From in-house validation, Estimation based on judgment	No	Yes	Yes		
	Cd	Yes	Yes		0-50		No	Yes	Yes		
	Hg	Yes	Yes		0-50		No	Yes	Yes		
	iAs	Yes	Yes		0-50		No	Yes	Yes		
	Ex-Pb	Yes	Yes		Never		No	Yes	Yes		
N08	As	Yes	Yes	0.69 % (The results are refer to a 12 % of water content)	50-250	From in-house validation	Yes	Yes	Yes	Yes	We have analyzed inorganic As in the sample by HPLC-ICP-MS, applying the same extraction method we use for food matrixes (microwave -50 min in HNO_3 0.3% + 3%H_2O_2). However, the result was very low compare to total As, so we think that the extraction conditions are too soft to recover the As in this kind of matrix.
	Cd	Yes	Yes		50-250		Yes	Yes	Yes	Yes	
	Hg	Yes	Yes		50-250		Yes	Yes	Yes	Yes	
	Ex-Pb	Yes	Yes		Never		Yes	Yes	Yes		
N09	As	Yes	Yes	0.77	50-250	Uncertainty budget (ISO GUM), From in-house validation	Yes	Yes	Yes	Yes	Our reported results in table are recalculated as concentration of HM in 100%of dry mass. Our NRL used to express results for feed refer to a moisture content of 12% in accordance with Directive 2002/32/EC.
	Cd	Yes	Yes		50-250		Yes	Yes	Yes	Yes	
	Hg	Yes	Yes		50-250		Yes	Yes	Yes	Yes	
	Ex-Pb	Yes	Yes		0-50		Yes	Yes	Yes	Yes	

Lab ID		Sample digestion	Digestion mixture	Std. method?	Correct recovery?	Recovery (R, in %)			LOD (mg/Kg)	Additional remarks regarding the method of analysis?	Experimental details for Ex-Pb				
						R	Spiking	CRM			Weighed mass (g)	Volume HNO_3 (mL)	Extraction time (min.)	External Cal.?	Standard additions?
N10	As	CMW	HNO_3	No	No	100		Yes	0.05						
	Cd	CMW	HNO_3	No	No	100		Yes	0.01						
	Hg	Other		No	No	100		Yes	0.01						
	iAs	Other		No	No	100		Yes	0.100						
	Ex-Pb	Other		No	No	100		Yes	0.01		1	20	30	No	No
N11	As	CMW	HNO_3	No	No										
	Cd	CMW	HNO_3	No	No										
	Hg	CMW	HNO_3	No	No					Results reported as 12 % moisture					
	iAs	Other		No	No										
	Ex-Pb	Other		No	No						2	86	30	Yes	No
N12	As	CMW	HNO_3+HF	No	Yes	94	Yes	Yes	0.075						
	Cd	CMW	HNO_3+HF	No	Yes	106	Yes	Yes	0.0024						
	Hg	CMW	HNO_3+HF	No	Yes	120	Yes	Yes	0.010						
	iAs	CMW	H_2O_2+HNO_3	No	Yes	30	Yes		0.010						
	Ex-Pb	CMW		No	Yes	98	Yes	Yes	0.002		0.5	21 mL	30	Yes	Yes
N13	As	CMW	HNO_3	No	Yes	100	Yes	Yes	0,0025						
	Cd	CMW	HNO_3	No	Yes	105	Yes	Yes	0,0007						
	Hg	CMW	HNO_3	No	Yes	94	Yes	Yes	0,0005						
	iAs	Other	H_2O_2+HNO_3	No	Yes	100	Yes	Yes	0,030						
	Ex-Pb	Other		No	Yes	99	Yes	Yes			2	100 ml	30	Yes	No
N14	As	CMW	H_2O_2+HNO_3	Yes	No										
	Cd	CMW	H_2O_2+HNO_3	Yes	No										
	Hg	CMW	H_2O_2+HNO_3	Yes	No										
N15	As	CMW	H_2O_2+HNO_3	No	No	92.8	Yes		0.050						
	Cd	CMW	H_2O_2+HNO_3	No	No	101.2	Yes		0.050						
	Hg	CMW	H_2O_2+HNO_3	No	No	95.5	Yes		0.02						
	Ex-Pb	Other		No	No	102.6	Yes		0.50		0.20	100	30	Yes	No
N16	As	CMW	H_2O_2+HNO_3	No	No										
	Cd	CMW	H_2O_2+HNO_3	No	No										
	Hg	CMW	H_2O_2+HNO_3	No	No										
N17	As	CMW	H_2O_2+HNO_3	No	Yes	99,7	Yes	Yes	0,5						
	Cd	CMW	H_2O_2+HNO_3	No	Yes	97,0	Yes	Yes	0,1	The sample for As, Cd and Pb analysis was digested under pressure: 0,55 g / 5 ml 67 % HNO_3 /in 50 ml					
	Hg			No	Yes			Yes	0,01						
	Ex-Pb	CMW		No	Yes	82,9	Yes	Yes	0,5		0,55	5ml		Yes	No
N18	As	CMW	HCl+HNO_3	No	No	121	No	Yes	0.001						
	Cd	CMW	HCl+HNO_3	No	No	114	No	Yes	0.001						
	Hg	CMW	HCl+HNO_3	No	No	114	No	Yes	0.001						
	Ex-Pb	Other		No	No	92	No	Yes	0.002		0.500	10 ml	30	Yes	No
N19	As	DA	HCl+HNO_3	Yes	No	96.84	No	Yes	0.1						
	Cd	CMW	H_2O_2+HNO_3	Yes	No	96.97	No	Yes	0.003	For all analitical method used, at the bottom of all crucibles and digestion vessels, there was a white sediment.					
	Hg	CMW	H_2O_2+HNO_3	Yes	No	88.64	No	Yes	0.003						
	Ex-Pb	Other		Yes	No	81.32	No	Yes	0.050		2	85	30	Yes	No

Lab ID		CRM for Ins. cal.?	Moisture correction?	Moisture (% m/m)	Samples / year	Measurement Uncertainty		Quality system	ILC?	Accredited?	Do you have any comments? Let us know!
						Estimation	Reported				
N10	As	Yes	Yes	it was written "Concentration in dry mass" on the result input page (moisture content : 0.5 %)	50-250	From interlaboratory comparison data	Yes	Yes	Yes		
	Cd	Yes	Yes		50-250		Yes	Yes	Yes		
	Hg	Yes	Yes		50-250		Yes	Yes	Yes		
	iAs	Yes	Yes		0-50		Yes	Yes	Yes		
	Ex-Pb	Yes	Yes		0-50		Yes	Yes	Yes		
N11	As		Yes	0.5	50-250	From in-house validation	Yes	Yes	No	Yes	
	Cd		Yes		50-250		Yes	Yes	No	Yes	
	Hg		Yes		50-250		Yes	Yes	No	Yes	
	iAs		Yes		0-50		Yes	Yes	No		
	Ex-Pb		Yes				Yes	Yes	No		
N12	As		Yes	0.44	0-50	From in-house validation	Yes	Yes	Yes	Yes	
	Cd		Yes		0-50		Yes	Yes	Yes	Yes	
	Hg		Yes		0-50		Yes	Yes	Yes	Yes	
	iAs		Yes		0-50		Yes	Yes	Yes		
	Ex-Pb		Yes		0-50		Yes	Yes	Yes		
N13	As		Yes	0,81	250-1000	From in-house validation	Yes	Yes	Yes	Yes	
	Cd		Yes		250-1000		Yes	Yes	Yes	Yes	
	Hg		Yes		250-1000		Yes	Yes	Yes	Yes	
	iAs		Yes		0-50		Yes	Yes	Yes	Yes	
	Ex-Pb		Yes		Never		Yes	Yes	Yes		
N14	As	Yes	Yes	0.38	250-1000	From in-house validation	Yes	Yes		Yes	
	Cd	Yes	Yes		250-1000		Yes	Yes		Yes	
	Hg	Yes	Yes		250-1000		Yes	Yes		Yes	
N15	As	Yes	Yes	0.6	0-50	From in-house validation	Yes	Yes	No	Yes	All results are in mg/ kg (ppm) relative to a feedingstuff with a moisture content of 12 %
	Cd	Yes	Yes		0-50		Yes	Yes	No	Yes	
	Hg	Yes	Yes		0-50		Yes	Yes	No	Yes	
	Ex-Pb	Yes	Yes		0-50		Yes	Yes	No		
N16	As	Yes	No		0-50	From in-house validation, From interlaboratory comparison data	Yes	Yes	No		
	Cd	Yes	No		0-50		Yes	Yes	No		
	Hg	Yes	No		0-50		Yes	Yes	No		
N17	As		Yes	0,3	50-250	From in-house validation, From interlaboratory comparison data	Yes	Yes	Yes	Yes	
	Cd		Yes		50-250		Yes	Yes	Yes	Yes	
	Hg		Yes		50-250		Yes	Yes	Yes	Yes	
	Ex-Pb		Yes				Yes	Yes	Yes		
N18	As	Yes	Yes	0.86	0-50	Uncertainty budget (ISO GUM), From in-house validation	Yes	Yes	Yes	Yes	
	Cd	Yes	Yes		0-50		Yes	Yes	Yes	Yes	
	Hg	Yes	Yes		0-50		Yes	Yes	Yes	Yes	
	Ex-Pb	Yes	Yes		Never		Yes	Yes	Yes		
N19	As		No		250-1000	Uncertainty budget (ISO GUM), From in-house validation	No	Yes	Yes	Yes	For Cd determination, we also used the extractable Cd method and results was comparable with those obtained by digestion method.
	Cd		No		250-1000		No	Yes	Yes	Yes	
	Hg		No		250-1000		No	Yes	Yes	Yes	
	Ex-Pb		No				No	Yes	Yes		

Lab ID		Sample digestion	Digestion mixture	Std. method?	Correct recovery?	Recovery (R, in %)			LOD (mg/Kg)	Additional remarks regarding the method of analysis?	Experimental details for Ex-Pb				
						R	Spiking	CRM			Weighed mass (g)	Volume HNO_3 (mL)	Extraction time (min.)	External Cal.?	Standard additions?
N20	As	DA	$HCl+HNO_3$	Yes	Yes	108	Yes	No	0.125						
	Cd	CMW	HNO_3	Yes	Yes	115	Yes	No	0.003						
	Hg	CMW	HNO_3	Yes	Yes	99	Yes	No	0.025						
	iAs	DA	$HCl+HNO_3$	Yes	Yes	54	Yes	No	0.125						
	Ex-Pb	Other		Yes	Yes	139	Yes	No	0.25		0.2	85mL	30	Yes	No
N22	As	CMW	$H_2O_2+HNO_3$	No	Yes	109.8		Yes	0.05						
	Cd	CMW	$H_2O_2+HNO_3$	No	Yes	115.4		Yes	0.003	Did Not recovery correct for Extractable Pb (No CRM available)					
	Hg	CMW	$H_2O_2+HNO_3$	No	Yes	118.4		Yes	0.01						
	Ex-Pb	Other		No	Yes				0.03		0.50	10	30	No	No
N23	As	CMW	$H_2O_2+HNO_3$		No	91	No	Yes							
	Cd	CMW	$H_2O_2+HNO_3$		No	91	No	Yes							
	Ex-Pb	CMW			No						0.5	8 mL		No	No
L24	As	CMW	$HCl+HNO_3+HF$	No											
	Cd	CMW	$HCl+HNO_3+HF$	No											
L25	iAs	Other		No	Yes	121	Yes		0.01						
N26	As	CMW	$HCl+HNO_3$	No	Yes	98	Yes	Yes	0.01						
	Cd	CMW	$HCl+HNO_3$	No	Yes	98	Yes	Yes	0.001						
	Hg	CMW	$HCl+HNO_3$	No	Yes	97	Yes	Yes	0.02						
	iAs	Other	HCl	No	Yes	73	Yes	Yes	0.05						
	Ex-Pb	Other		No	Yes	102	Yes	No	0.01		2	85	30	Yes	No
N27	As	CMW	$H_2O_2+HNO_3+HF$	Yes	Yes	104.5	No	Yes	0.18						
	Cd	CMW	$H_2O_2+HNO_3+HF$	Yes	Yes	108.5	No	Yes	0.075						
	Hg			Yes	Yes	99.8	No	Yes	0.010						
	Ex-Pb	Other		Yes	Yes	101.1	No	Yes			2	85	30	Yes	No
N28	As	CMW	$H_2O_2+HNO_3$	Yes	No			No	0,2						
	Cd	CMW	$H_2O_2+HNO_3$	Yes	No			No							
	Hg	CMW	$H_2O_2+HNO_3$	Yes	No			No	0.02						
	Ex-Pb	Other		Yes	No			No	0.012		2		30	Yes	
N29	As	CMW	$H_2O_2+HNO_3$	No	Yes	98	Yes								
	Cd	CMW	$H_2O_2+HNO_3$	No	Yes	101	Yes								
	Hg	CMW	$H_2O_2+HNO_3$	No	Yes	98	Yes								
	Ex-Pb	CMW		No	Yes	101	Yes				0.5	3	20	Yes	No
N30	As	CMW	$H_2O_2+HNO_3$	No	Yes	100	No	Yes	0.008						
	Cd	CMW	$H_2O_2+HNO_3$	No	Yes	89	No	Yes	0.002						
	Hg	CMW	$H_2O_2+HNO_3$	No	Yes	84	No	Yes	0.007						
	Ex-Pb	Other		No	Yes	100	No	Yes	0.005		2	85 mL	30	Yes	No
N31	As	CMW	HNO_3+HF	No	No		No	No	0,01						
	Cd	CMW	HNO_3+HF	No	No		No	No	0,01						
	Hg	Other		No	No		No	No	0,001						
	Ex-Pb	Other		No	No		No	No	0,01		0.5	30	30	Yes	No

Lab ID		CRM for Ins. cal.?	Moisture correction?	Moisture (% m/m)	Samples / year	Measurement Uncertainty		Quality system	ILC?	Accredited?	Do you have any comments? Let us know!
						Estimation	Reported				
N20	As		Yes	0.6	0-50	From replicates (precision), From interlaboratory comparison data	No	Yes	Yes		
	Cd		Yes		250-1000		No	Yes	Yes		
	Hg		Yes		0-50		No	Yes	Yes		
	iAs		Yes		0-50		No	Yes	Yes		
	Ex-Pb		Yes		0-50		No	Yes	Yes		
N22	As		Yes	91	> 1000	Uncertainty budget (ISO GUM), From in-house validation, From replicates (precision), From interlaboratory comparison data	No	Yes	Yes		This laboratory does Not analyses Feed samples and does Not have accreditation for heavy metals in Feed. It is accredited for Heavy Metals in all Food matrices
	Cd		Yes		> 1000		No	Yes	Yes		
	Hg		Yes		> 1000		No	Yes	Yes		
	Ex-Pb		Yes		0-50		No	Yes	Yes		
N23	As	No	No	0.77	0-50			Yes			
	Cd	No	No		0-50			Yes			
	Ex-Pb	No	No		Never			Yes			
L24	As		No			From replicates (precision), Estimation based on judgment		Yes			
	Cd		No					Yes			
L25	iAs	Yes	Yes	0.4	Never	From in-house validation	No	Yes	No		Sample quantity was very small.
N26	As		Yes	0.9	> 1000	From interlaboratory comparison data	No	Yes	No	Yes	
	Cd		Yes		> 1000		No	Yes	No	Yes	
	Hg		Yes		> 1000		No	Yes	No	Yes	
	iAs		Yes		50-250		No	Yes	No	Yes	
	Ex-Pb		Yes		Never		No	Yes	No		
N27	As		Yes	1.51	250-1000	Uncertainty budget (ISO GUM), From in-house validation, From replicates (precision)	Yes	Yes	Yes	Yes	Result of 12% of moisture. Results of Pb in ZETAAAS after microwave digestion in very different
	Cd		Yes		250-1000		Yes	Yes	Yes	Yes	
	Hg		Yes		250-1000		Yes	Yes	Yes	Yes	
	Ex-Pb		Yes				Yes	Yes	Yes		
N28	As		Yes	0.51	50-250	From in-house validation	Yes	Yes	No		To low amount of sample for PT
	Cd		Yes		50-250		Yes	Yes	No	Yes	
	Hg		Yes		50-250		Yes	Yes	No	Yes	
	Ex-Pb		Yes		Never		Yes	Yes	No	Yes	
N29	As		No		250-1000	From in-house validation	Yes	Yes	Yes	Yes	
	Cd		No		250-1000		Yes	Yes	Yes	Yes	
	Hg		No		50-250		Yes	Yes	Yes	Yes	
	Ex-Pb		No		250-1000		Yes	Yes	Yes	Yes	
N30	As		Yes	0.80	0-50	From in-house validation	No	Yes	No		
	Cd		Yes		0-50		No	Yes	No		
	Hg		Yes		0-50		No	Yes	No		
	Ex-Pb		Yes		0-50		No	Yes	No		
N31	As	Yes	No		Never	From interlaboratory comparison data	No	Yes	No		
	Cd	Yes	No		Never		No	Yes	No		
	Hg	Yes	No		Never		No	Yes	No		
	Ex-Pb		No		Never		No	Yes	No		

Lab ID		Sample digestion	Digestion mixture	Std. method?	Correct recovery?	Recovery (R, in %)			LOD (mg/Kg)	Additional remarks regarding the method of analysis?	Experimental details for Ex-Pb				
						R	Spiking	CRM			Weighed mass (g)	Volume HNO_3 (mL)	Extraction time (min.)	External Cal.?	Standard additions?
N32	Cd	Other		No	Yes	93	Yes	No	0.002	The test material is Not a routine sample, the method is Not accredited and it was first time analyzed in our lab.					
	Hg	CMW	HF	No	Yes	97	Yes	No	0.05						
	Ex-Pb			No	Yes	80	Yes	No	0.007		1	25	30	Yes	Yes
N33	As	CMW	H_2O_2+HNO_3+HF	Yes	No			Yes	0,005						
	Cd	CMW	H_2O_2+HNO_3+HF	Yes	No			Yes	0,001						
	Hg	CMW	H_2O_2+HNO_3+HF	Yes	No			Yes	0,01						
N35	As	Other		No	No				0.31	k0-INAA is Non-destructive technique.					
	Hg	Other	HCl+HNO_3+HF	No	No				0.001						
L36	Cd	Other	HNO_3	No	Yes	94.6	Yes	Yes	0.30						
	Ex-Pb	Other		No	Yes	104.9	Yes		1.35		2	85 mL	30		
N37	As	Other	HCl+HNO_3	No	No			Yes	0.006						
	Cd	Other	HCl+HNO_3	No	No			Yes	0.006						
	Hg	DA		No	No			Yes	0.0003						
	Ex-Pb	Other		No	No			Yes	0.09		2	85	30	Yes	No
N38	As	CMW	H_2O_2+HNO_3	Yes	No	113	Yes	No	0.1						
	Cd	CMW	H_2O_2+HNO_3	Yes	No	100	Yes	No	0.02						
	Hg	CMW	H_2O_2+HNO_3	Yes	No		Yes	No	0.025						
	iAs	Other	HCl	Yes	No	110	Yes	No	0.1						
	Ex-Pb	Other		Yes	No		No	No	0.02		0,5	25 ml	30	Yes	No
L39	As	DA		Yes	No	78	Yes	No	0.003						
	Cd	DA		Yes	No				0.100						
	Hg	Other	HNO_3+H_2SO_4	Yes	No				0.010						
	Ex-Pb	Other		Yes	No				0.50		0,5	25 ml	30	Yes	No
N41	As	CMW	H_2O_2+HNO_3	Yes	No	96		Yes	0,05						
	Cd	CMW	H_2O_2+HNO_3	Yes	No	108		Yes	0,05						
	Hg	CMW	H_2O_2+HNO_3	Yes	No	94	Yes	No	0,05						
	Ex-Pb	CMW		Yes	No	98	Yes	No	0,05		2,00	85ml	30	Yes	Yes
L42	As	CMW	H_2O_2+HNO_3	No	No	90.2		Yes	0.03						
	Cd	CMW	H_2O_2+HNO_3	No	No	95.6		Yes	0.06						
	Ex-Pb	CMW		No	No	118		Yes	0.02		0.5	200	30	Yes	No
L43	As	CMW	HNO_3	No	Yes	116		Yes	0.1						
	Cd	CMW	HNO_3	No	Yes	103		Yes	0.02						
	Hg	CMW	HNO_3	No	Yes	116		Yes	0.02						
	Ex-Pb	CMW		No	Yes	98		Yes	0.1		0.5				
L45	As	DA	HCl	No	Yes	97	Yes	No	0.025						
	Cd	DA	HCl	No	Yes	93	Yes	No	0.03						
	Hg	H_2SO_4	HCl+HNO_3+H_2SO_4	No	Yes	80	Yes	No	0.02						
	iAs	DA	HCl	No	Yes	79	Yes	No	0.06						
	Ex-Pb	DA		No	Yes	84	Yes	No	0.08		3	N/A		Yes	No

Lab ID		CRM for Ins. cal.?	Moisture correction?	Moisture (% m/m)	Samples / year	Measurement Uncertainty		Quality system	ILC?	Accredited?	Do you have any comments? Let us know!
						Estimation	Reported				
N32	Cd		Yes	0.66	250-1000	From in-house validation	Yes	Yes	Yes		The test material is Not a routine sample, the method is Not accredited and it was first time analyzed in our lab.
	Hg		Yes		Never		Yes	Yes	Yes		
	Ex-Pb		Yes		Never		Yes	Yes	Yes		
N33	As		Yes	99.2	50-250	Uncertainty budget (ISO GUM)	Yes	Yes	Yes	Yes	We have send the material to a subcontracter for analysis of total As, Cd, Hg. The aim was to check the subcontracter
	Cd	Yes	Yes		50-250		Yes	Yes	Yes	Yes	
	Hg	Yes	Yes		50-250		Yes	Yes	Yes	Yes	
N35	As	Yes	Yes	1.18	250-1000	Uncertainty budget (ISO GUM)	Yes	Yes	Yes	Yes	
	Hg	Yes	Yes		50-250		Yes	Yes	Yes		
L36	Cd		Yes	0.90	0-50	From in-house validation	No	Yes	No		
	Ex-Pb		Yes		0-50		No	Yes	No		
N37	As		Yes	0.80	50-250	Uncertainty budget (ISO GUM), From in-house validation, From replicates (precision)	Yes	Yes	Yes	Yes	I would like to ask you politely to send larger amount of the proficiency test item for the next time. The amount of 15 g is really small to perform all requested measurements. Can you also mention the information concerning determination of water content in the accompanying letter? Methods for water content can vary through laboratories.
	Cd		Yes		50-250		Yes	Yes	Yes	Yes	
	Hg		Yes		50-250		Yes	Yes	Yes	Yes	
	Ex-Pb		Yes		0-50		Yes	Yes	Yes		
N38	As	Yes	No		0-50	From replicates (precision)	Yes	Yes	No		
	Cd	Yes	No		0-50		Yes	Yes	No		
	Hg		No		0-50		Yes	Yes	No		
	iAs		No		0-50		Yes	Yes	No		
	Ex-Pb		No		0-50		Yes	Yes	No		
L39	As		Yes	0.65	0-50	From replicates (precision)	Yes	Yes	No		
	Cd		Yes		0-50		Yes	Yes	No		
	Hg		Yes		0-50		Yes	Yes	No		
	Ex-Pb		Yes		0-50		Yes	Yes	No		
N41	As		No		250-1000	Estimation based on judgment	Yes	Yes	Yes	Yes	
	Cd		No		250-1000		Yes	Yes	Yes	Yes	
	Hg		No		50-250		Yes	Yes	Yes	Yes	
	Ex-Pb		No		0-50		Yes	Yes	Yes		
L42	As		No		0-50	From in-house validation	No	Yes	Yes	Yes	
	Cd		No		0-50		No	Yes	Yes	Yes	
	Ex-Pb		No		0-50		No	Yes	Yes		
L43	As		Yes	< 0.1	250-1000	From in-house validation From replicates (precision)	No	Yes	Yes		
	Cd		Yes		250-1000		No	Yes	Yes		
	Hg		Yes		250-1000		No	Yes	Yes		
	Ex-Pb		Yes		250-1000		No	Yes	Yes		
L45	As		Yes	1.1	50-250	From in-house validation	Yes	Yes	Yes	Yes	Sample size given for the PT was too small
	Cd		Yes		50-250		Yes	Yes	Yes	Yes	
	Hg		Yes		50-250		Yes	Yes	Yes	Yes	
	iAs		Yes		50-250		Yes	Yes	Yes	Yes	
	Ex-Pb		Yes		50-250		Yes	Yes	Yes	Yes	

Annex 14: Compliance assessment

ML	2 or 12 mg kg^{-1}	2 mg kg^{-1}	30 mg kg^{-1}	0.1 mg kg^{-1}	[6] and Table 2	
Lab	**As**	**Cd**	**ex-Pb**	**Hg**	**Compliance**	**due to**
N01	4.58	0.0611	2.73	0.0454	C	
N02	5.80	0.059	3.83	0.18	C	
N03	6.37	0.076	66.1	< 0.05	NC	Pb
N04	5.9	0.056	60.7	0.026	NC	Pb; As
N05		< 0.5	3.595	0.0429	C	
N06	7.81	< 0.2	4.664	< 0.05	C	
N07	5.2	0.053	5.3	0.044	NC	As
N08	6.5	0.098	4.6	0.045	C	
N09	5.43	0.0522	4.42	0.0413	C	
N10	5.62	0.040	3.79	0.054	C	
N11	8.8	0.052	7.2	0.047	NC	As
N12	7.298	0.065	4.5	0.047	C	
N13	6.8	0.063	3.7	0.054	C	
N14	4.715	0.0436		0.0363	NC	As
N15	5.5	0.054	4.8	0.051	NC	As
N16	5.44	0.065		0.058	C	
N17	10.6	< 0.1	69.5	0.042	C	Pb
N18	7.36	0.078	3.613	0.062	C	
N19	9.115	0.0616	4.079	0.057	C	
N20	3.52	0.04	3.5	0.09	C	
N22	6.06	0.053	8.88	< 0.05	C	
N23	7.48	0.065	70.7		NC	Pb
N26	7.83	0.076	3.34	0.061	C	
N27	8.9	< 0.25	4.9	0.047	C	
N28	4.3	0.043	4.74	0.069	NC	
N29	5.0	0.062	53.2	< 0.08	C	
N30	6.3	0.489	3.19	0.033	C	
N31	7.65	0.099	2.982	0.042	C	
N32		0.069	3.48	< 0.1	C	
N33	3.66	0.0650		0.0441	NC	As
N35	8.54			0.045	C	
N37	5.43	0.054	3.14	0.046	C	
N38	4.97	0.053	3.50	0.040	C	
N41	5.770	0.055	5.88	0.064	C	
L24	8.12	0.061				
L36		0.42	2.99		C	
L39	4.92	< 0.100	3.50	0.034	C	
L42	4.92	0.07	46.5		NC	Pb
L43	4.55	0.077	65.4	0.050	NC	Pb; As
L44	5.98	0.35	11.50	< 0.025		
L45	4.01	0.11	64.9	0.06	NC	Pb

C = Compliant; NC = not-compliant; as assessed by participant

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