JRC Scientific and Technical Reports

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

IMEP-110: Total arsenic, cadmium, mercury and lead in vegetable food.

M.B. de la Calle, H. Emteborg, J. Charoud-Got, P. Robouch, I. Verbist

EUR 24618 EN - 2010

JRC EUROPEAN COMMISSION

irmm Institute for Reference Materials and Measurements

The mission of the JRC-IRMM is to promote a common and reliable European measurement system in support of EU policies.

European Commission
Joint Research Centre
Institute for Reference Materials and Measurements

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

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

JRC 61841

EUR 24618 EN
ISBN 978-92-79-18674-5
ISSN 1018-5593
doi:10.2787/33321

Luxembourg: Publications Office of the European Union

Printed in Belgium

European Union Reference Laboratory
Heavy Metals in Feed and Food

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

Total cadmium, lead, arsenic and mercury in vegetable food

IMEP

November 2010

María Beatriz de la Calle
Håkan Emteborg
Piotr Robouch
Inge Verbist

Table of contents

1 Summary

The Institute for Reference Materials and Measurements (IRMM) of the Joint Research Centre (JRC) a Directorate General of the European Commission operates the European Union Reference Laboratory for Heavy Metals in Feed and Food (EU-RL-HM). One of its core tasks is to organise interlaboratory comparisons (ILCs) among appointed National Reference Laboratories (NRLs). This report presents the results of the tenth ILC of the EU-RL-HM which focused on the determination of total arsenic, cadmium, mercury and lead in vegetable food.

The test material used in this exercise was the Standard Reference Material SRM 1570a, spinach leaves from the National Institute of Standards and Technology (NIST). The material was rebottled and relabelled to prevent recognition by the participants and was dispatched at the beginning of June 2010. Each participant received one bottle containing approximately 15 g of test material. Thirty-five laboratories from 24 member states registered to the exercise of which 35 reported results for total Cd and total Pb, 32 for total As and 31 for total Hg. The assigned values for total As, Cd and Hg are the certified values taken from the SRM 1570a certificate. For total Pb, the "information value" provided by NIST in the SRM certificate was used as assigned value.

The uncertainties of the assigned values (u_{ref}) for total As, Cd and Hg, were taken directly from the CRM certificate as provided by the producer. No u_{ref} is provided by NIST for the total Pb concentration because the total Pb content is only provided as "information value". Participants were invited to report the uncertainty of their measurements. This was done by the majority of the laboratories taking part in this exercise.

The laboratories' results were rated with z- and ζ-scores (zeta-scores) for total As, Cd, and Hg in accordance to ISO 13528 [1]. No ζ-scores were given for total Pb because u_{ref} was not known for that measurand. The standard deviation for proficiency assessment (also called target standard deviation) was fixed to 15 % for all the measurands by the advisory board of this ILC, on the basis of the outcome of previous ILCs organised by the EU-RL-HM and on the state-of-the-art in this field of analysis.

More than 80 % of the participants performed satisfactorily for total Cd and Hg. Around 70 % of the participants obtained a satisfactory z-score for total arsenic with a relatively high number (8 laboratories) of participants having overestimated the total content of arsenic in the test material. When looking at the ζ-scores, 60 to 65 % of the reported results were satisfactory when the associated uncertainties are taken into account.

2 Introduction

Recently, the European Food Safety Authority (EFSA) made public the Scientific Opinion on Lead [2], on Cadmium [3] and on Arsenic [4] in Food, according to which:

- *"Human exposure to **lead** can occur via food, water, air soil and dust. Food is the major source of exposure to lead". "Overall, cereals, vegetables and tap water were the most important contributors to **lead** exposure in the general European population".*

- *"Foodstuffs are the main source of **cadmium** exposure for the non-smoking general population". "The food groups that contributed to the major part of the dietary **cadmium** exposure, primarily because of the high consumption, were cereals and cereal products, vegetables, nuts and pulses, starch roots or potatoes, and meat and meat products"*

- *"Cereal grains and cereal based products, followed by food for special dietary uses, bottled water, coffee and bear, rice grains and rice based products, fish and vegetables were identified as largely contributing to the **inorganic arsenic** daily exposure in the general European population".*

According to P. Weigert [5], both lead uptake from the soil through the roots and lead deposition on parts of the plant above the ground are important. Lead from emission and stirred up dust is retained by rough, rugged or sticky surfaces and despite intensive cleaning it can only be partly removed. The mean lead content in vegetables such as lettuce and cabbage is 0.2 mg kg^{-1}.

The same source indicates that cadmium in vegetables is preferably absorbed through the roots. The average cadmium values in vegetables range between 0.015 and 0.670 mg kg^{-1} of the fresh material, with the higher concentrations being found in spinach, celery and carrots.

Food plants contain very low concentrations of total arsenic, with mean values of approximately 0.04 mg kg^{-1} [6]. The levels of inorganic arsenic (of relevance from a toxicological point of view) are even lower because normally it coexists with other species in food matrices. However, there is little information available about the concentration of inorganic arsenic in food of plant origin other than rice and algae.

The International Agency for Research on Cancer has classified cadmium as a human carcinogen (Group 1) and lead as probably carcinogenic to humans (Group 2A). Lead has also neurotoxic effects which affect the development of the brain, so that children with high lead levels in blood have a reduced Intelligence Quotient (IQ) score. In adults, high levels of lead in blood can induce an increase in the systolic blood pressure.

To overcome problems associated with a high metal content in food, maximum allowed limits in several food commodities for cadmium, lead and mercury have been laid down in the European legislation [7].

Since cereals and vegetables are, according to the EFSA Scientific Opinions, the main contributors to the dietary intake of cadmium and lead, the Directorate General for Health and Consumers (DG SANCO) of the European Commission requested the EU-RL-HM to evaluate the performance of European laboratories in the determination of heavy metals in vegetables. A proficiency test (PT) for the determination of heavy metals in cereal products had been organised previously (IMEP-101).

With that scope the European Union Reference Laboratory for Heavy Metals in Feed and Food (EU-RL-HM), formerly the Community Reference Laboratory (CRL) organised a PT (IMEP-110) for the network of appointed NRLs to determine total arsenic, cadmium, mercury and lead in vegetable food.

3 Scope

As stated in Regulation (EC) No 882/2004 of the European Parliament and the Council [8], one of the core duties of the EU-RL-HM is to organise interlaboratory comparisons for the benefit of staff from National Reference Laboratories. The scope of this ILC is to test the competence of the appointed NRLs to determine the total concentration of As, Cd, Hg and Pb in vegetable food.

The assessment of the measurement results is undertaken on the basis of requirements laid down in legislation [7,9] and follows the administrative and logistics procedures of IMEP, the International Measurement Evaluation Programme. This programme is accredited according to ISO Guide 43-1. The designation of this PT is IMEP-110.

4 Time frame

This proficiency test was agreed upon by the National Reference Laboratories (NRLs) network at the fourth EU-RL-HM workshop held on 1-2 October 2009. Invitation letters were sent to the participants on the second half of May 2010 (cf Annex 1). The samples were dispatched to the participants on 2nd June 2010. Reporting deadline was 2nd July 2010.

5 Material

5.1 Preparation

The commercially available NIST SRM 1570a (spinach leaves) was used for this PT. NIST dispatched 15 bottles of test materials at room temperature by courier to IRMM.The material was rebottled and relabelled to avoid identification by the participants. Comprehensive information on the preparation of this material can be found in the certification report on the NIST website [10].

5.2 Homogeneity and stability

Information on the homogeneity and stability of the test material was gathered from the certificate of the Standard Reference Material. According to it *"No evidence of statistically significant inhomogeneity was observed. The stability of the material has not been rigorously assessed. However, NIST will monitor this material and will report any substantive changes in certified values to the purchaser"*. Since no information was received indicating the contrary when the material was purchased, it was assumed that the certification values are still valid for the measurands covered in IMEP-110.

5.3 Distribution

The samples were dispatched to the participants by IRMM on the first half of June 2010. Each participant received:

a) one glass bottle containing approximately 15 g of test material,

b) an accompanying letter with instructions for sample handling and reporting (cf. Annex 3) and

c) a form that had to be sent back after receipt of the test material to confirm its arrival (cf. Annex 4).

6 Instructions to participants

Details on this proficiency test were discussed with the NRLs at the fourth workshop organised by the EU-RL-HM, held in Geel on 1-2 October 2009. Concrete instructions were given to all participants in a letter accompanying the test material. The measurands and matrix were defined as "Total As, Cd, Hg and Pb in vegetable food", see Annex 3.

Laboratories were asked to perform two or three independent measurements and to report the mean value, the associated uncertainty, the coverage factor of the associated uncertainty and the technique used to perform the analysis. The measurement results were to be corrected (i) for recovery and (ii) for humidity (following a procedure described in the accompanying letter which has been optimised at IRMM by the Reference Materials Unit). Participants were asked to follow their routine procedures.

The results were to be reported in the same manner (eg. number of significant figures) as those normally reported to the customer.

The results were to be reported in a special on-line form for which each participant received an individual access code. A questionnaire was attached to this on-line form. The questionnaire was intended to provide further information on the measurements and the laboratories. A copy of the questionnaire is presented in Annex 5.

7 Reference values and their uncertainties

The SRM certificate provided certified values and their associated expanded uncertainties for all the measurands included in this study, except for total Pb for which only an "information value" was provided. The certified values for total As, Cd and Hg and the "information value" for total Pb were used as assigned values (X_{ref}) for this PT. The certificate was valid during the time frame of the PT.

The uncertainties given in the certificate (U_{ref}) are expanded uncertainties which correspond to the sum of a 95 % confidence limit and an allowance for systematic error between the methods used (in case the reference value is a weighted mean of results from two or more different analytical methods), or the sum of a 95 % confidence limit and the known systematic error of the method in case only one method of known accuracy was used to determine the reference value. To calculate the standard uncertainty of the reference value (u_{ref}) the relation $U_{ref} = ku_{ref}$ was used. k is the coverage factor which according to the certificate, was determined from the Student's *t*-distribution corresponding to the appropriate associated degrees of freedom and 95 % confidence interval for each analyte. Since the degrees of freedom are not indicated in the certificate, it was assumed k=2 for further calculations.

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

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

Measurand	X_{ref} (mg kg^{-1})	U_{ref} (mg kg^{-1})	u_{ref} (mg kg^{-1})
Total arsenic	0.068	0.012	0.006
Total cadmium	2.89	0.07	0.04
Total mercury	0.030	0.003	0.002
Total lead	0.20	unknown	unknown

X_{ref} = certified value, U_{ref} = expanded standard uncertainty; u_{ref} = standard uncertainty calculated from U_{ref} using a coverage factor k=2.

8 Evaluation of results

8.1 General observations

Thirty-five laboratories from 24 member states registered for participation in this exercise of which 35 reported results for total Cd and total Pb (3 reported "less than" for total Pb), 32 for total As (3 reported "less than") and 31 for total Hg (5 out of the 31 reported "less than"). All laboratories responded to the questionnaire included in the on-line reporting form.

8.2 Scores and evaluation criteria

Individual laboratory performance is expressed in terms of z- and ζ-scores in accordance with ISO 13528 [1].

$$\varsigma = \frac{x_{lab} - X_{ref}}{\sqrt{u_{ref}^2 + u_{lab}^2}} \qquad \text{Eq. 1}$$

$$z = \frac{x_{lab} - X_{ref}}{\hat{\sigma}} \qquad \text{Eq. 2}$$

Where:

x_{lab} is the measurement result reported by a participant

X_{ref} is the certified reference value (assigned value)

u_{ref} is the standard uncertainty of the reference value

u_{lab} is the standard uncertainty reported by a participant

$\hat{\sigma}$ is the standard deviation for proficiency assessment

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

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

|score| ≤ 2 satisfactory result

2 < |score| ≤ 3 questionable result

|score| > 3 unsatisfactory result

The ζ-score states if the laboratory result agrees with the assigned value within the respective uncertainty indicates. The denominator of Eq. 1 is the combined uncertainty of the assigned value and the measurement uncertainty as stated by the laboratory. The ζ-score is therefore the most relevant evaluation parameter, as it includes all parts of a measurement result, namely the expected value

(assigned value), its uncertainty and the unit of the result as well as the uncertainty of the reported values. An unsatisfactory ζ-score can either be caused by an inappropriate estimation of the concentration or of its uncertainty.

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

Uncertainty estimation is not trivial; therefore an additional assessment was provided to each laboratory reporting uncertainty, indicating how reasonable their uncertainty estimate is. The standard uncertainty from the laboratory (u_{lab}) is most likely to fall in a range between a minimum uncertainty (u_{min}), and a maximum allowed (u_{max}). u_{min} is set to the standard uncertainty of the reference value. It is unlikely that a laboratory carrying out the analysis on a routine basis would measure the measurand with a smaller uncertainty than the expert laboratories chosen to establish the assigned value. u_{max} is set to the target standard deviation ($\hat{\sigma}$) accepted for the PT. If u_{lab} is smaller than u_{min}, the laboratory may have underestimated its uncertainty. Such a statement has to be taken with care as each laboratory reported only measurement uncertainty, whereas the uncertainty of the reference value also includes contributions of homogeneity and stability. If those are large, measurement uncertainties smaller than u_{min} are possible and plausible. If $u_{lab} > u_{max}$, the laboratory may have overestimated the uncertainty. An evaluation of this statement can be made when looking at the difference of the reported value and the assigned value: if the difference is small and the uncertainty is large, then overestimation is likely. If, however, the deviation is large but is covered by the uncertainty, then the uncertainty is properly assessed even if large. It should be pointed out that u_{max} is not a normative criterion: it is up to the customer of the respective result to decide which uncertainty is acceptable for a certain measurement.

The z-score compares the participant's deviation from the reference value with the target standard deviation for proficiency assessment ($\hat{\sigma}$) used as common quality criterion. $\hat{\sigma}$, is defined by the PT organiser as the maximum acceptable standard uncertainty. Based on feedback from experts, on the state-of-the-art and on discussions among the members of the advisory board of this PT, values for $\hat{\sigma}$ were set as 15 % of the assigned value for total and inorganic arsenic.

8.3 Laboratory results and scorings

The results as reported by the participants for total Cd, Pb As and Hg are summarised in Annexes 6 to 9, respectively, together with the z- and ζ-scores (no scores were provided for total Pb). These annexes also include figures showing the individual mean values and associated expanded

uncertainties. The Kernel distribution plots, obtained using a software tool developed by AMC [12] are presented in Annex 10.

Regarding the z- and ζ-scores, the results for total Cd, As and Hg are summarised in Table 2. Eighty-six and 81 % of the participants scored satisfactorily for total Cd and Hg, respectively and about 70 % did for total As. All the laboratories that obtained an unsatisfactory z-score have overestimated the concentration of total As in the test material. This could be due to (a) contamination problems affecting the quality of the results especially at the low concentration levels as the one in this test material or (b) the potential $^{40}Ar^{35}Cl^{+}$ interference with ^{75}As mass when performing ICP-MS measurements. However, comparing results reported by the laboratories using ICP-MS with those obtained by hydride generation-atomic absorption spectrometry (HG-AAS) no significant difference was observed. Overestimation of total As was previously observed in other PT (IMEP-108) [13] organised by the EU-RL-HM in which a test material with low concentration of total arsenic was used. When the concentration of total arsenic in the test material was high (several mg kg^{-1}) such a tendency to overestimation was not observed [14,15].

According to the ζ-score between 61 and 66 % of the laboratories provided satisfactory results depending on the measurand.

Table 2: Number and percentages of laboratories reporting results not "less than" with satisfactory, questionable and unsatisfactory scores.

	Total Cd		Total As		Total Hg	
	N°	%	N°	%	N°	%
z						
S	30	85.7	20	69	21	80.8
Q	3	8.6	1	3.5	2	7.7
U	2	5.7	8	27.5	3	11.5
ζ						
S	22	62.9	19	65.5	16	61.5
Q	6	17.1	3	10.4	4	15.4
U	7	20	7	24.1	6	23.1

8.4 Additional information extracted from the questionnaire

Additional information was gathered from the questionnaire that participants were asked to fill in (Annex 5).

8.4.1 Sample treatment related questions

One laboratory did not reply to this question. Nineteen laboratories performed the analysis following an official method. The information provided by the laboratories for their methods of analysis is summarised in Annex 11. No influence of the techniques used was detected for any of the measurands covered in this PT.

Eighteen laboratories corrected their results for recovery. Most laboratories reported recoveries in the range 80 to 110 %, but recoveries < 80 % have also been reported. Laboratories must be aware that such low recoveries indicate that the method is biased and actions should be taken to eliminate the problem. Figure 1 shows the distribution of recoveries reported by the participants.

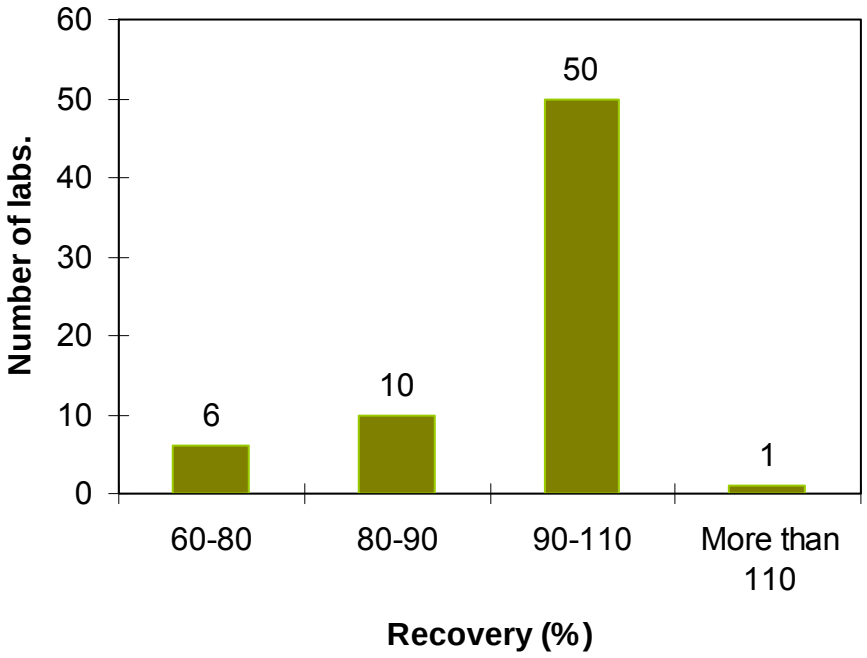


Figure 1: *Distribution of recoveries as reported by the participants*

Seven laboratories calculated the recovery factor adding a known amount of the same analyte to be measured (spiking) and eighteen using a certified reference material (some laboratories have used both approaches). One laboratory added a known amount of analyte to a reagent blank. Thirteen laboratories did not indicate how have they calculated the recovery factors. Different reasons were given by some of the laboratories that did not correct for recovery:

- *"The recovery of the determination for all elements is in the range covered by the uncertainty",*
- *"no significant deviation from 100% of CRMs and spike",*

- *"the recovery factor is near 100 %", "we never apply the recovery factor to the results, we included it in the uncertainty",*
- *"certified reference material as control",*
- *"in routine work we do not use the recovery factor"* and
- *"good results of CRMs measured"*.

All participants but one corrected the results for the water content. The way how the water content of the material was to be determined was described in detail in the accompanying letter (Annex 3) and was optimised at IRMM to obtain the same results as with Karl-Fisher titration.

8.4.2 Uncertainty related questions

Various approaches were used to scrutinise the measurement uncertainty, (Figure 2).

Twenty-five laboratories usually report uncertainty to their customers while 10 never do.

When asked about the level of confidence covered by the reported coverage factor (k), most of the participants reported 95 % and one reported 95,5 %. Three did not understand the question.

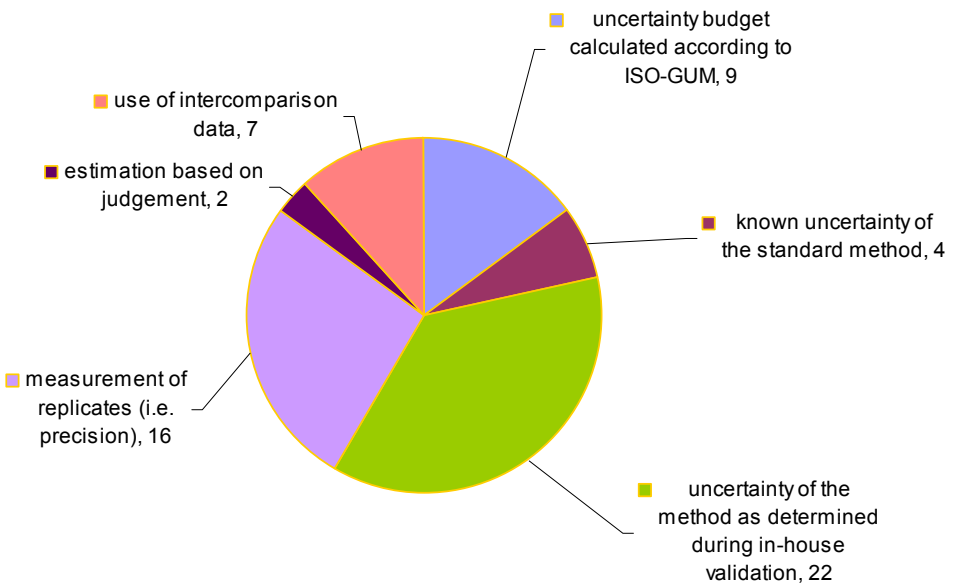


Figure 2: *Different approaches used by the participants in IMEP-110 to estimate the uncertainty of their measurements.*

8.4.3 Quality assurance related questions

Thirty of the 35 participating laboratories regularly take part in PTs, 3 do not and two did not reply to this question.

Participants were asked whether they make use of CRMs in their laboratories and for which purpose (validation and/or calibration). Thirty-three use CRMs, one does not and one did not answer. Twenty-nine use the CRM during the validation procedure and seven use it for calibration purposes.

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

Thirty-one participants carry out this type of analysis on a regular basis, three do not and one did not answer to this question.

The distribution in terms of number of analyses per year is shown in Figure 3.

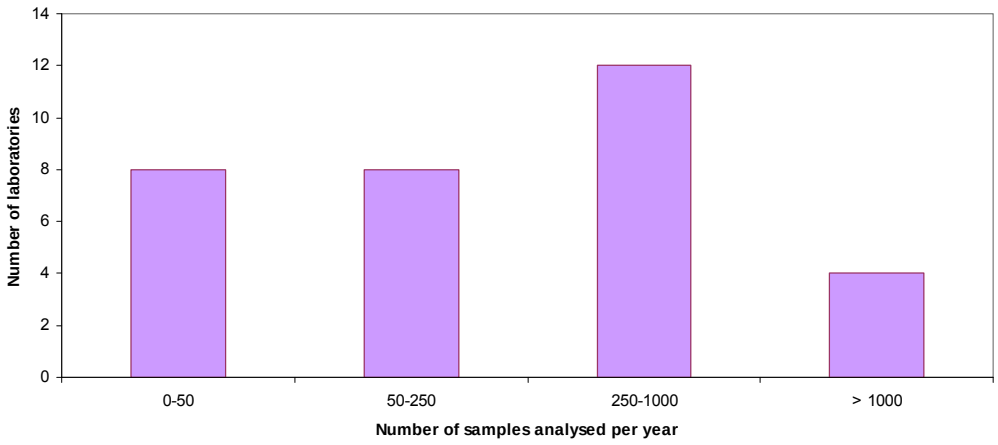


Figure 3: Participants' experience in this type of analysis expressed as number of analyses per year.

8.4.5 Quality system related questions

Thirty-four laboratories have a quality system in place and one does not. Thirty have a quality system based on ISO 17025, 3 on ISO 17025 and ISO 9000 and 1 on ISO 17025 and ISO Guide 43.

Figure 4 shows the amount of laboratories that are accredited for the different elements covered in IMEP-110.

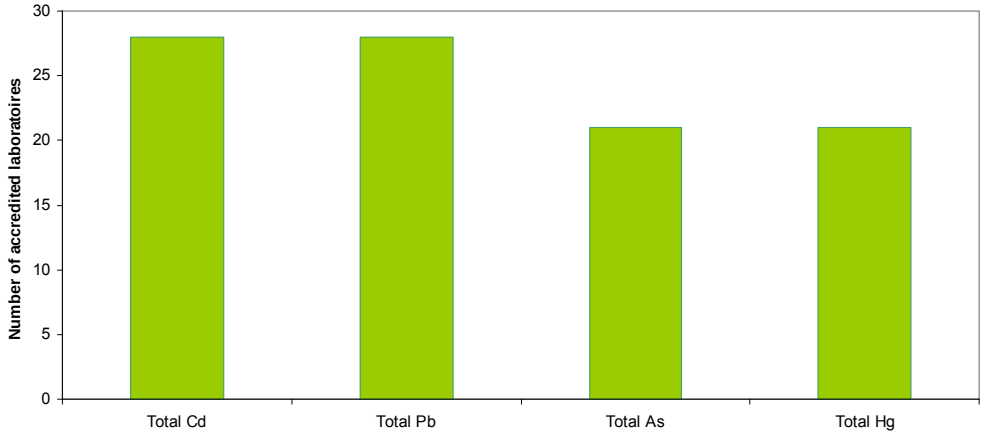


Figure 4: Number of accredited laboratories for the different measurands covered in IMEP-110.

9 Conclusions

From IMEP-110 it can be concluded that most of the National Reference Laboratories do not have problems in carrying out analyses of total Cd and Hg in a matrix of vegetable food, as reflected by the percentage of satisfactory z scores. Although no scorings were provided for total Pb results due to the lack of a traceable assigned value, the population is normally distributed and the consensus value (robust statistics), 0.185 ± 0.044 mg kg^{-1}, is in quite good agreement with the indicative value reported by the producer of the CRM used as test material, 0.20 mg kg^{-1}.

Some participants overestimated the concentration of total As in the test material, probably due to a contamination problem. This was previously observed in the proficiency tests organised by the EU-RL-HM in which the total concentration of arsenic was low (IMEP-107, -108) but not when the arsenic concentration was high (IMEP-104, -105, -109).

Around 40 % of the participants have difficulties in making a proper uncertainty estimation, as reflected by the ζ-scores.

10 Acknowledgements

P. Connely from the Reference Materials Unit is acknowledged for his support in optimising the drying method. I. Baer and F. Cordeiro are thanked for the fruitful discussions about the organisation of the

IMEP-110 exercise and the thorough revision of this paper. A. M. Jensen and F. Ulberth are acknowledged for revising the manuscript.

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

Organisation	Country
AGES - Austrian Agency for Health and Food Safety	Austria
AGES	Austria
Scientific Institute of Public Health	Belgium
European Commission, JRC, IRMM	Belgium
CODA CERVA	Belgium
State General Laboratory	Cyprus
CISTA	Czech Republic
State Veterinary Institute Olomouc	Czech Republic
DTU Food	Denmark
Central Veterinary and Food Laboratory	Estonia
Agricultural Research Centre	Estonia
Finnish Customs Laboratory	Finland
Evira	Finland
AFSSA	France
Laboratoire SCL de Bordeaux	France
Federal Office of Consumer Protection and Food Safety	Germany
General Chemical State Laboratory	Greece
Regional Center Of Plant Protection And Quality Control Of Magnisia	Greece
Central Agricultural Office, Food and Feed Safety Directorate	Hungary
Central Agricultural Office	Hungary
Health Service Executive	Ireland
Istituto Superiore Di Sanita'	Italy
Istituto Zooprofilattico Sperimentale del Piemonte Liguria e Valle d'Aosta	Italy
Institute of Food Safety, Animal Health and Environment „BIOR”	Latvia
National food and veterinary risk assessment institute	Lithuania
Public Health Laboratory Malta	Malta
Food and Consumer Product Safety Authority	Netherlands
RIKILT	Netherlands
National Institute of Public Health-National Institute of Hygiene	Poland
Sanitary Veterinary and Food Safety Directorate	Romania
State veterinary and food institute - Kosice	Slovakia
National Veterinary Institute	Slovenia
Laboratorio Arbitral Agroalimentario	Spain
National Food Administration	Sweden
The Food and Environment Research Agency	United Kingdom

11 References

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

[2] Scientific Opinion on Lead in Food, EFSA Panel on Contaminants in the Food Chain (CONTAM), EFSA Journal, (2010), 8(4), 1570.

[3] Cadmium in Food, Scientific Opinion of the Panel on Contaminants in the Food Chain, EFSA Journal, (2009), 980, 1-139).

[4] Scientific Opinion on Arsenic in Food, EFSA Panel on Contaminants in the Food Chain (CONTAM), EFSA Journal, (2009), 7(10), 1351.

[5] P. Weigert "Metal Loads of Food of Vegetable Origin including Mushrooms" in: Metals and their Compounds in the Environment. Occurrence, Analysis and Biological Relevance. Ed: E. Merian, VCH, Wheimheim, (1991).

[6] A. Léonard, “Arsenic”, in: Metals and their Compounds in the Environment. Occurrence, Analysis and Biological Relevance. Ed: E. Merial, VCH, (1991).

[7] Commission Regulation (EC) No 1881/2006 of 19 December 2006 setting maximum levels for certain contaminants in foodstuffs.

[8] Regulation (EC) No 882/2004 of the European Parliament and of the Council of 29 April 2004 on official controls performed to ensure the verification of compliance with feed and food law, animal health and animal welfare rules.

[9] Commission Regulation (EC) No 333/2007 of 28 March 2007 laying down the methods of sampling and analysis for the official control of the levels of lead, cadmium, mercury, inorganic tin, 3-MCPD and benzo(a)pyrene in foodstuffs.

[10] https://www-s.nist.gov/srmors/view_detail.cfm?srm=1570A

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

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

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

[14] Report of the fourth interlaboratory comparison organised by the Community Reference Laboratory for Heavy Metals in Feed and Food. Total Cd, Pb, As, Hg and methylmercury in seafood. M.B. de la Calle, D. Vendelbo, A. Bernreuther, H. Emteborg, I. Verbist, P. Taylor, EUR 23505 EN, (2008).

[15] Report of the fifth interlaboratory comparison organised by the Community Reference Laboratory for heavy Metals in Feed and Food. M.B. de la Calle, I. Wysocka, C. Quétel, T. Linsinger, H. Emteborg, F. Cordeiro, A. Semeraro, I. Verbist, D. Vendelbo, P. Taylor, EUR 23711 EN, (2009).

Annexes

Annex 1: Invitation letter

EUROPEAN COMMISSION
JOINT RESEARCH CENTRE

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

CRL
Heavy Metals in Feed and Food

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

Dear Madam / Sir,

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

On behalf of the EU-RL Heavy Metals in Feed and Food, I would like to invite you to participate in the Proficiency Test [IMEP-110] for the **"Determination of total As, Cd, Hg and Pb in vegetable food"**.

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

Please register electronically for this inter-laboratory comparison using the following link: https://irmm.jrc.ec.europa.eu/ilc/ilcRegistration.do?selComparison=480
Your participation is free of charge.

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

The **deadline for registration is 31 May 2010**. Samples will be sent to participants during the first half of June. The deadline for submission of results is 2 July 2010.

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

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

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

Yours sincerely

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

Cc: Franz Ulberth

2

Annex 2: Certificate of the SRM used in IMEP-110

National Institute of Standards & Technology

Certificate of Analysis

Standard Reference Material® 1570a

Trace Elements in Spinach Leaves

This Standard Reference Material (SRM) is intended primarily for use in evaluating the reliability of analytical methods for the determination of major, minor, and trace elements; proximates; calories; and total dietary fiber in botanical materials, agricultural food products, and materials of similar matrix. A unit of SRM 1570a consists of 60 g of finely powdered dried spinach leaves.

Certified Concentration Values: The certified concentration values of the constituent elements are given in Table 1. These concentrations are based on the agreement of results from at least two independent analytical methods or from a method of known accuracy. Analytical methods are provided in Appendix A.

Reference Concentration Values: Reference concentration values of constituent elements are provided in Table 2; analytical methods are provided in Appendix A. Reference concentration values for selected proximates and total dietary fiber are provided in Table 3; analytical methods are provided in Appendix B. Reference values are noncertified values that are the best estimates of the true values; however, the values do not meet NIST criteria for certification and are provided with associated uncertainties that may reflect only measurement precision, may not include all sources of uncertainty, or may reflect a lack of sufficient statistical agreement among multiple analytical methods.

Information Concentration Values: Information concentration values for additional constituent elements are provided in Table 4. Information values for carbohydrate, caloric content, fat, and individual fatty acids are provided in Table 5. These are noncertified values with no reported uncertainties as there is insufficient information to assess uncertainties. The information values are given to provide additional characterization of the material. Use of this SRM to quantitatively monitor method performance for analytes other than those with certified or reference concentration values in Tables 1 through 3 is not warranted.

Expiration of Certification: The certification of **SRM 1570a** is valid, within the measurement uncertainty specified, until **31 August 2013**, provided the SRM is handled in accordance with the instructions given in this certificate (see "Instructions for Use"). The certification is nullified if the SRM is damaged, contaminated, or otherwise modified.

Maintenance of SRM Certification: NIST will monitor this SRM over the period of its certification. If substantive technical changes occur that affect the certified values before the expiration of this certificate, NIST will notify the purchaser. Registration (see attached sheet) will facilitate notification.

Support aspects involved in the issuance of this SRM were coordinated through the NIST Measurement Services Division.

Stephen A. Wise, Chief
Analytical Chemistry Division

Gaithersburg, MD 20899
Certificate Issue Date: 08 October 2008
See Certificate Revision History on Page 6

Robert L. Watters, Jr., Chief
Measurement Services Division

Coordination of analytical measurements for the characterization of this SRM was performed by D.A. Becker and K.E. Sharpless of the NIST Analytical Chemistry Division.

Analytical measurements at NIST were performed by E.S. Beary, D.A. Becker, C.M. Beck II, M.S. Epstein, J.D. Fassett, K.M. Garrity, R.R. Greenberg, R.M. Lindstrom, E.A. Mackey, P. Morales, K.E. Murphy, P.J. Paulsen, B.J. Porter, T.A. Rush, R. Saraswati, J.M. Smeller, G.C. Turk, R.D. Vocke, R.L. Watters, Jr., and L.J. Wood. Additional elemental analyses were performed by D.L. Anderson (Center for Food Safety and Applied Nutrition, U.S. Food and Drug Administration, Washington, DC), A.R. Byrne (Nuclear Chemistry Department, Jozef Stefan Institute, Ljubljana, Slovenia), and J. Kucera (Nuclear Physics Institute, Academy of Sciences of the Czech Republic, Rez, Czech Republic). Several elements were also measured in an International Atomic Energy Agency (IAEA) interlaboratory comparison exercise. Proximates, calories, fatty acids, and total dietary fiber were determined by Covance Laboratories (Madison, WI), Lancaster Laboratories (Lancaster, PA), Medallion Laboratories (Minneapolis, MN), and Southern Testing and Research Laboratories (Wilson, NC).

Statistical analysis of the experimental data was performed by W. Guthrie, S.B. Schiller, and L.M. Gill of the NIST Statistical Engineering Division.

NOTICE AND WARNINGS TO USERS

Stability: This material was radiation sterilized at an estimated minimum dose of 27.8 kGy for microbiological control; however, its stability has not been rigorously assessed. Spinach leaves have a tendency to rapidly bleach and to turn a tan or light brown color in the presence of visible light. Based on 15 years experience with the original SRM 1570, there is no evidence documenting any change in elemental concentrations as a result of that color change. However, NIST will monitor this material and will report any substantive changes in certified values to the purchaser.

Storage: The material should be kept tightly closed in its original bottle and stored in the dark at a temperature between 10 °C and 30 °C. It should not be exposed to intense sources of radiation. Ideally, the bottle should be kept in a desiccator under the conditions indicated above.

Instructions for Use: The contents of a bottle should be thoroughly mixed by rotating and/or rolling before each use. Allow the contents to settle for 1 minute prior to opening to minimize the loss of fine dust particles. A minimum sample mass of 150 mg of the material, dried as described in the section (see "Instructions for Drying"), should be used to relate analytical determinations to the certified values on this certificate. In some cases, especially for volatile elements such as mercury, it is preferable to analyze samples from the bottle without drying, determine the moisture content on a separate sample from the same bottle taken at the same time, and convert the analytical results to a dry-mass basis.

Digestion procedures should be designed to avoid loss of volatile elements, such as arsenic and mercury. Digestion of the SRM in nitric and perchloric acids was found to be incomplete, with a small residue of siliceous material remaining. This residue must be considered an integral part of this SRM and should be dissolved with a small amount of hydrofluoric acid to obtain total dissolution. All certified values are based on the total dissolution.

Instructions for Drying: Samples of this SRM must be dried by one of the following two procedures in order for certified values to be valid:

1. Drying in a desiccator at room temperature (approximately 22 °C) for 120 h over fresh anhydrous magnesium perchlorate. The sample depth should not exceed 1 cm.

2. Freeze-drying for 24 h at a pressure of 13.3 Pa or lower and a shelf temperature of –5 °C or lower after having frozen the sample (not to exceed 1 cm in depth) at –40 °C or lower for at least 1 h. At the end of the 24 h period, samples should be placed immediately in a desiccator with fresh anhydrous magnesium perchlorate. Samples should be weighed after allowing a minimum of 4 h to establish temperature equilibrium.

Note: Vacuum drying at room temperature and oven drying at elevated temperatures have resulted in excessive mass losses and therefore are **NOT** recommended.

Source and Preparation of Material: The material (approximately 2270 kg) for this SRM was obtained from commercial supplier Oregon Freeze-Drying Corp., Albany, OR. It consists of U.S. Grade A chopped frozen spinach. The material was thawed, placed in a ribbon mixer, thoroughly mixed, and blended. After mixing, the spinach was freeze-dried. The freeze-dried material was then ground in a stainless steel grinder and shipped to NIST. At NIST, the freeze-dried material was sieved through a polypropylene sieve having openings of 0.25 mm (equivalent to a U.S. Series 60 standard sieve). The sieved material was then jet milled and air classified to a particle size of approximately 75 µm (200 mesh). After mixing in a large blender, the spinach was irradiated with cobalt-60 radiation to a minimum absorbed dose of approximately 27.8 kGy for microbiological control and bottled.

Homogeneity Assessment: Samples from randomly selected bottles of SRM 1570a were tested for homogeneity by instrumental neutron activation analysis (INAA). No evidence of statistically significant inhomogeneity was observed.

Table 1. Certified Concentration Values of Constituent Elements [a,b]

Element	Mass Fraction (%)
Calcium	1.527 ± 0.041
Phosphorus	0.518 ± 0.011
Potassium	2.903 ± 0.052
Sodium	1.818 ± 0.043

Element	Mass Fraction (mg/kg)	Element	Mass Fraction (mg/kg)
Aluminum	310 ± 11	Mercury	0.030 ± 0.003
Arsenic	0.068 ± 0.012	Nickel	2.14 ± 0.10
Boron	37.6 ± 1.0	Selenium	0.117 ± 0.009
Cadmium	2.89 ± 0.07	Strontium	55.6 ± 0.8
Cobalt	0.39 ± 0.05	Thorium	0.048 ± 0.003
Copper	12.2 ± 0.6	Vanadium	0.57 ± 0.03
Manganese	75.9 ± 1.9	Zinc	82 ± 3

(a) The certified concentrations are equally weighted means of results from two or more different analytical methods or the mean of results from a single method of known high accuracy. In the case of two or more methods, each uncertainty is the sum of a 95 % confidence limit and an allowance for systematic error between the methods used. In the case of a method of known accuracy, each uncertainty is the sum of a 95 % confidence limit and the known systematic error of the method.

(b) These certified values are reported on a dry-mass basis. For certified values to be valid, the material must be dried according to the instructions provided above.

Table 2. Reference Concentration Values of Constituent Elements [a,b,c]

Element	Mass Fraction (%)
Nitrogen (Total)[d]	6.06 ± 0.20
Nitrogen (Organic)[d]	6.20 ± 0.25
Nitrogen (Protein)[d]	5.68 ± 0.13

Element	Mass Fraction (mg/kg)	Element	Mass Fraction (mg/kg)
Europium	0.0055 ± 0.0010	Rubidium	12.7 ± 1.6
Scandium	0.0055 ± 0.0006	Uranium	0.155 ± 0.023

(a) NIST has replaced the previously used term "non-certified" with "reference value" or "information value," as appropriate.

(b) Each reference concentration value, expressed as a mass fraction on a dry-mass basis, is an equally weighted mean of results provided by NIST and/or collaborating laboratories. The uncertainty in the reference concentration values is calculated as $U = ku_c$. The quantity u_c is the combined standard uncertainty calculated according to the ISO and NIST Guides [1], which accounts for the combined effect of the within-laboratory variance for all participating laboratories at one standard deviation and bias between methods. The coverage factor, k, is determined from the Student's t-distribution corresponding to the appropriate associated degrees of freedom and 95 % confidence for each analyte.

(c) These reference values are reported on a dry-mass basis. In order for these reference values to be valid, the material must be dried according to the instructions provided above.

(d) Data from three methods for the determination of nitrogen have been treated separately. Total nitrogen was determined by prompt gamma activation analysis; "organic" nitrogen was determined by the Dumas method; and "protein" nitrogen was determined by the Kjeldahl method.

Table 3. Reference Concentration Values of Selected Proximates and Total Dietary Fiber [a]

Analyte	Mass Fraction, as received (%)	Mass Fraction, dry-mass basis (%) [b]
Moisture[c]	3.45 ± 0.25	0 (by definition)
Solids[c]	96.55 ± 0.25	100 (by definition)
Ash	14.66 ± 0.38	15.18 ± 0.38
Protein[d]	35.8 ± 3.0	37.0 ± 3.1
Total dietary fiber	30.5 ± 4.3	31.6 ± 4.4

(a) Each reference concentration value, expressed as a mass fraction on an as-received or dry-mass basis, is an equally weighted mean of results from the laboratories shown in Appendix C. (NIST and one of these laboratories provided results used in value assignment of mass fractions of moisture and solids; see footnote c.) The uncertainty in the reference values is expressed as an expanded uncertainty, U, at the 95 % level of confidence, and is calculated according to the method described in the ISO and NIST Guides [1]. The expanded uncertainty is calculated as $U = ku_c$, where u_c is intended to represent, at the level of one standard deviation, the combined effect of between-laboratory and within-laboratory components of uncertainty. The coverage factor, k, is determined from the Student's t-distribution corresponding to the appropriate associated degrees of freedom and 95 % confidence for each analyte. Analytical methodology information is provided in Appendix B.

(b) Results have been converted to a dry-mass basis using the reference value for solids. Uncertainty in the solids determination has been included in the uncertainties provided for the mass fractions on a dry-mass basis.

(c) Moisture has been determined by NIST (using freeze-drying and desiccation) and one of the collaborating laboratories (using desiccation) as specified in this certificate. Drying in a forced-air or vacuum oven by three laboratories resulted in a moisture value of 6.3 % ± 1.5 %.

(d) The protein concentration was calculated from the nitrogen values reported by the laboratories (two laboratories using the Dumas method, two laboratories using Kjeldahl) using a conversion factor of 6.25. The value for protein is the mean of the individual protein calculations reported by the laboratories shown in Appendix C. If the mean nitrogen values above are used for calculation, the mean protein concentrations are 35.8 % and 37.1 % on an as-received and dry-mass basis, respectively.

Table 4. Information Concentration Values of Constituent Elements [a]

Element	Mass Fraction (%)
Magnesium	0.89
Sulfur	0.46
Element	**Mass Fraction (mg/kg)**
Lead	0.20

[a] NIST has replaced the previously used term "non-certified" with "reference value" or "information value," as appropriate.

Table 5. Information Concentration Values of Carbohydrate, Fat, Caloric Content, and Selected Fatty Acids (as Triglycerides)[a]

Analyte	Mass Fraction, as received (%)	Mass Fraction, dry-mass basis (%)
Carbohydrate[b]	45	46
Fat	2	2
Calories[b,c]	340 kcal/100g	350 kcal/100g
Pentadecanoic Acid (C15:0)	0.010	0.011
Hexadecanoic Acid (C16:0) (Palmitic Acid)	0.61	0.64
Heptadecanoic Acid (C17:0) (Margaric Acid)	0.006	0.006
Octadecanoic Acid (C18:0) (Stearic Acid)	0.031	0.032
(Z)-9-Octadecenoic Acid (C18:1) (Oleic Acid)	0.25	0.26
(Z,Z)-9,12-Octadecadienoic Acid (C18:2) (Linoleic Acid)	0.27	0.28
(Z,Z,Z)-9,12,15-Octadecatrienoic Acid (C18:3) (Linolenic Acid)	0.63	0.65
Linolenic Acid (C18:3)	0.048	0.050
Docosanoic Acid (C22:0) (Behenic Acid)	0.028	0.029
Tetracosanoic Acid (C24:0) (Lignoceric Acid)	0.044	0.046

[a] These information values, reported on an as-received and dry-mass basis, are the equally weighted means of results reported by the collaborating laboratories shown in Appendix C. These values are based on results from determinations by two to four of the laboratories and are included to provide additional characterization of the material; no uncertainties are provided. Analytical methodology information is provided in Appendix B.

[b] These information values are calculated from the results reported by one laboratory.

[c] If the mean proximate values in Tables 2 and 4 are used for calculation, with caloric equivalents of 9, 4, and 4 for fat, protein, and carbohydrate, respectively, the mean caloric content is 340 kcal/100 g and 350 kcal/100g on an as-received and dry-mass basis, respectively.

REFERENCE

[1] ISO; *Guide to the Expression of Uncertainty in Measurement*; ISBN 92-67-10188-9, 1st ed., International Organization for Standardization: Geneva, Switzerland (1993); see also Taylor, B.N.; Kuyatt, C.E.; *Guidelines for Evaluating and Expressing the Uncertainty of NIST Measurement Results*, NIST Technical Note 1297, U.S. Government Printing Office: Washington, DC (1994); available at http://physics.nist.gov/Pubs/.

Certificate Revision History: 08 October 2008 (Update of expiration date and editorial changes); 31 August 2001 (This technical revision reports the addition of reference and information values for proximates, calories, total dietary fiber, and fatty acids and a change from non-certified to reference and information values for several inorganic constituents); 15 July 1996 (Editorial change); 20 October 1994 (Original certificate date).

Users of this SRM should ensure that the certificate in their possession is current. This can be accomplished by contacting the SRM Program at: telephone (301) 975-2200; fax (301) 926-4751; e-mail srminfo@nist.gov; or via the Internet at http://www.nist.gov/srm.

APPENDIX A

Methods Used in Elemental Determinations

Element	Method Code[a]	Element	Method Code[(a)]
Aluminum	ICP INAA	Nitrogen	DUMAS KJEL PGAA
Arsenic	FI-HGAAS RNAA	Phosphorus	COLOR ICP
Boron	IDICPMS PGAA	Potassium	IDTIMS INAA
Cadmium	IDICPMS PGAA RNAA	Rubidium	IAEA INAA
Calcium	IDTIMS INAA	Scandium	IAEA INAA
Cobalt	INAA RNAA	Selenium	FI-HGAAS INAA RNAA
Copper	ICP RNAA	Sodium	PGAA INAA
Europium	IAEA INAA	Strontium	IDTIMS INAA
Lead	IAEA IDICPMS	Sulfur	PGAA IAEA
Magnesium	IDICPMS INAA	Thorium	INAA RNAA
Manganese	INAA LEAFS	Uranium	RNAA
Mercury	CVAAS RNAA	Vanadium	IDTIMS INAA
Nickel	IDICPMS RNAA	Zinc	ICP INAA

[a] Acronyms for analytical methods:

CVAAS = Cold-Vapor Atomic Absorption Spectrometry
FI-HGAAS = Flow Injection Hydride Generation Atomic Absorption Spectrometry
IAEA = International Atomic Energy Agency Interlaboratory Comparison Exercise
ICP = Inductively Coupled Plasma Optical Emission Spectrometry
IDICPMS = Isotope Dilution, Inductively Coupled Plasma Mass Spectrometry
IDTIMS = Isotope Dilution, Thermal Ionization Mass Spectrometry
INAA = Instrumental Neutron Activation Analysis
KJEL = Kjeldahl Nitrogen Determination
LEAFS = Laser-Excited Atomic Fluorescence Spectrometry
PGAA = Prompt Gamma Activation Analysis
RNAA = Radiochemical Neutron Activation Analysis

APPENDIX B

Methods Used in the Determination of Proximates, Caloric Content, Fatty Acids, and Total Dietary Fiber

Ash – mass loss after ignition in a muffle furnace
Calories – calculated; [(9 × fat) + (4 × protein) + (4 × carbohydrate)]
Carbohydrate – calculated; [solids – (protein + fat + ash)]
Fat – sum of individual fatty acids
Fatty acids – hydrolysis followed by gas chromatography
Moisture – mass loss after drying at room temperature in a desiccator (1 laboratory + NIST); freeze-drying (NIST)
Nitrogen – Dumas (1 laboratory); modified Dumas (1 laboratory); Kjeldahl (2 laboratories + NIST)
Protein – calculated from nitrogen reported by 4 laboratories using a factor of 6.25
Solids – calculated; (sample mass – moisture)
Total dietary fiber – enzymatic digestion followed by gravimetry

APPENDIX C

Collaborating Laboratories for Proximate, Fatty Acid, Total Dietary Fiber, and Caloric Determinations

Covance Laboratories, Madison, WI, USA
Lancaster Laboratories, Lancaster, PA, USA
Medallion Laboratories, Minneapolis, MN, USA
Southern Testing and Research Laboratories, Wilson, NC, USA

Annex 3: Accompanying letter

EUROPEAN COMMISSION
JOINT RESEARCH CENTRE

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

CRL Heavy Metals in Feed and Food

Geel, 2 June 2010
JRC.DDG.D6/BCa/ive/ARES(2010)/295839

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

Participation in IMEP-110, a proficiency test exercise for the determination of total As, Cd, Hg and Pb in vegetable food.

Dear «TITLE» «SURNAME»,

Thank you for participating in the IMEP-110 intercomparison for the determination of **total** As, Cd, Hg and Pb in vegetable food. This exercise takes place in the frame of the EU-RL Heavy Metals in Feed and Food.

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

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

The measurands are: **total** As, Cd, Hg and Pb in vegetable food. The procedure used for the analyses should resemble as closely as possible the one that you use in routine sample analysis.

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

«PARTKEY»

Retieseweg 111, B-2440 Geel - Belgium. Telephone: (32-14) 571 211. http://irmm.jrc.ec.europa.eu
Telephone: direct line (32-14) 571 252. Fax: (32-14) 571 865.

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

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

1. *Weigh accurately 0.5 g of test material in a glass container of 5-7 cm diameter, Preferably with a lid because when the prescribed drying time has passed, the glass container must cool down about 30 minutes in a desiccator before weighing.*
2. *Place it in an oven for 120 ± 5 min at 80 ± 2 °C.*
3. *Place the glass container covered with a lid in a desiccator and wait 30 min before weighing the test material again.*

Note 1: perform the measurements of the water content in triplicate.
Note 2: ***do not use for the heavy metal determinations the aliquots of test material that you have used for the water content determination!***

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

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

The deadline for submission of results is 02/07/2010.

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

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

With kind regards

Dr. M.B. de la Calle
IMEP-110 Co-ordinator

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

Cc: F. Ulberth

Annex 4: Acknowledgement of receipt form

EUROPEAN COMMISSION
JOINT RESEARCH CENTRE

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

CRL Heavy Metals in Feed and Food

Annex to JRC.DDG.D6/BCa/ive/ARES(2010)/295839

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

CRL-HM-10 / IMEP-110

total As, Cd, Hg and Pb in vegetable food

Confirmation of receipt of the samples

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

ANY REMARKS ……
……

Date of package arrival ……

Signature ……

Please return this form to:
Dr Beatriz de la Calle

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

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

Retieseweg 111, B-2440 Geel - Belgium. Telephone: (32-14) 571 211. http://irmm.jrc.ec.europa.eu
Telephone: direct line (32-14) 571 252. Fax: (32-14) 571 865.

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

IMEP

Annex 5: Questionnaire

Comparison for IMEP-110

This questionnaire is offline

Please fill in the questionnaire

Submission Form

1. **Did you apply a recovery factor to correct your measurement results?**

- ○ no
- ○ yes

1.1. If Yes, what are the recovery factors (R, in %) you used:

1.1.1. for Cd (in %)

1.1.2. for Pb (in %)

1.1.3. for As (in %)

1.1.4. for Hg (in %)

1.2. If Yes, did you determine R by:

- ☐ 1. adding a known amount of the same analyte to the sample
- ☐ 2. using a certified reference material
- ☐ 3. other

1.2.1. If other, please specify

1.3. If No, what was the reason not to do this?

2. **What is the level of confidence reflected by the coverage (k) factors stated above? (in %)**

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

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

3.1. If other, please specify

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

- ○ no
- ○ yes

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

- ○ no
- ○ yes

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

- ○ no
- ○ yes

6.1. If yes, which:

6.2. If no, please describe (in max 150 characters for each reply) your:

6.2.1. sample pre-treatment

6.2.2. digestion step

6.2.3. extraction / separation step

6.2.4. instrument calibration step

7. **Does your laboratory carry out this type of analysis (as regards the measurands, matrix and methods**

- ○ no
- ○ yes

7.1. If Yes, please estimate the number of samples (Cd, Hg, Pb, As measurements together):

- ○ a) 0-50 samples per year
- ○ b) 50-250 samples per year
- ○ c) 250- 1000 samples per year
- ○ d) more than 1000 samples per year

8. **Does your laboratory have a quality system in place?**

- ○ no
- ○ yes

8.1. If yes, which:

- ☐ iso 9000 series
- ☐ iso/iec 17025
- ☐ other

8.1.1. If other, please specify

9. **Is your laboratory accredited for this type of analysis?**

Questions/Response table	**No**	**Yes**	*Info*
Total Hg	○	○	
Total As	○	○	
Total Pb	○	○	
Total Cd	○	○	

10. **If you are accredited, by which Accreditation Body?**

11. **Does your laboratory take part in an interlaboratory comparison for this type of analysis on a regu**

- ○ no
- ○ yes

11.1. If yes, which one(s):

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

- ○ no
- ○ yes

12.1. If yes, is the material used for the validation of procedures?

- ○ no
- ○ yes

12.2. If yes, is the material used for calibration of instrument?

- ○ no
- ○ yes

12.3. If yes, which one(s):

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

Annex 6: Total Cd in vegetable food

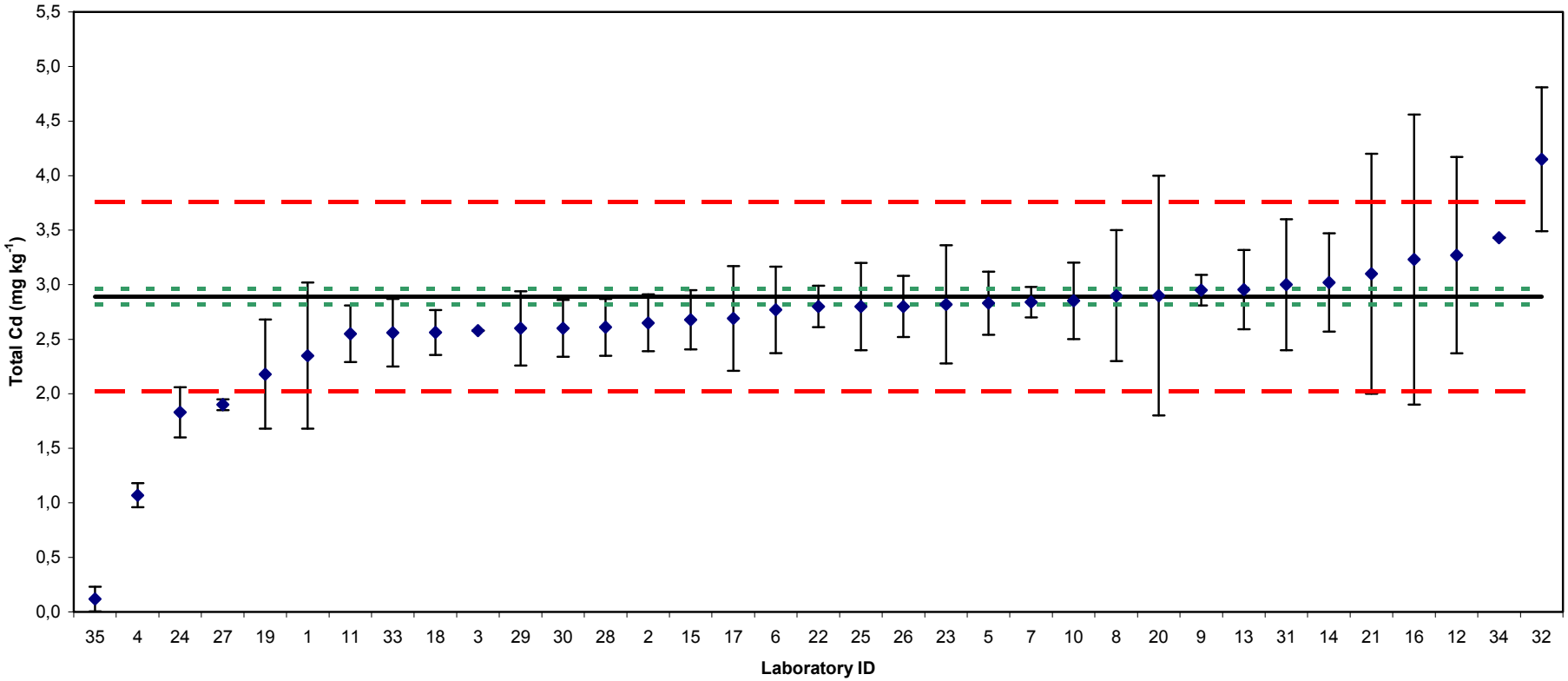
X_{ref} = 2,89 ± 0,07 mg kg^{-1} (k=2)

Lab ID	x_{lab} (mg kg^{-1})	U_{lab} (mg kg^{-1})	k	u_{lab} (mg kg^{-1})	Technique	z	ζ	$Qual_u$
1	2,35	0,67	2	0,34	ICP-MS	-1,2	-1,6	a
2	2,65	0,26	2	0,13	ICP-MS	-0,6	-1,8	a
3	2,58	0	√3	0	ETAAS	-0,7	-8,9	b
4	1,07	0,11	2	0,06	ICP-MS	-4,2	-27,9	a
5	2,83	0,29	2	0,15	ICP-MS	-0,1	-0,4	a
6	2,77	0,396	2	0,198	ICP-MS	-0,3	-0,6	a
7	2,84	0,14	2	0,07	ICP-MS	-0,1	-0,6	a
8	2,9	0,60	2	0,30	ICP-MS	0,0	0,0	a
9	2,95	0,14	2	0,07	ETAAS	0,1	0,8	a
10	2,852	0,351	2	0,176	ETAAS	-0,1	-0,2	a
11	2,55	0,26	2	0,13	ETAAS	-0,8	-2,5	a
12	3,2711	0,900	2	0,450	ICP-MS	0,9	0,8	c
13	2,955	0,364	2	0,182	ETAAS	0,1	0,4	a
14	3,02	0,45	2	0,23	ICP-MS	0,3	0,6	a
15	2,679	0,271	3,182	0,085	FAAS	-0,5	-2,3	a
16	3,23	1,33	2	0,67	ICP-MS	0,8	0,5	c
17	2,69	0,48	2	0,24	ETAAS	-0,5	-0,8	a
18	2,562	0,206	√3	0,119	ICP-MS	-0,8	-2,6	a
19	2,180	0,501	2	0,251	CV-AAS	-1,6	-2,8	a
20	2,9	1,1	2	0,6	ICP-MS	0,0	0,0	c
21	3,1	1,1	2	0,6	ETAAS	0,5	0,4	c
22	2,8	0,19	2	0,10	ICP-MS	-0,2	-0,9	a
23	2,82	0,542	2	0,271	ICP-MS	-0,2	-0,3	a
24	1,83	0,23	2	0,12	ICP-AES	-2,4	-8,8	a
25	2,80	0,40	2	0,20	ETAAS	-0,2	-0,4	a
26	2,80	0,28	2	0,14	ICP-MS	-0,2	-0,6	a
27	1,90	0,05	2	0,03	ICP-MS	-2,3	-23,0	b
28	2,61	0,261	2	0,131	ETAAS	-0,6	-2,1	a
29	2,60	0,34	2	0,17	ETAAS	-0,7	-1,7	a
30	2,60	0,26	2	0,13	ETAAS	-0,7	-2,2	a
31	3,00	0,6	2	0,3	ICP-MS	0,3	0,4	a
32	4,15	0,66	2	0,33	ZETAAS	2,9	3,8	a
33	2,56	0,31	0,968	0,32	ETAAS	-0,8	-1,0	a
34	3,43	0,0007	2	0,0004	ETAAS	1,2	15,4	b
35	0,118	0,112	2	0,056	ETAAS	-6,4	-42,0	a

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

IMEP-110: results for total Cd

Certified range: 2,89 ± 0.07 mg kg^{-1} (k=2)



This graph displays all measurements results and their associated uncertainties.
The uncertainties are shown as reported, with various expansion factors and levels of confidence.
The black line represents Xref, the green dotted lines delimit the reference interval **(X_{ref} ± 2u_{ref}: 2,89 ± 0.07 mg kg^{-1})**, the red dashed lines delimit the target interval **(X_{ref} ± 2σ: 2,89 ± 0,87 mg kg^{-1})**

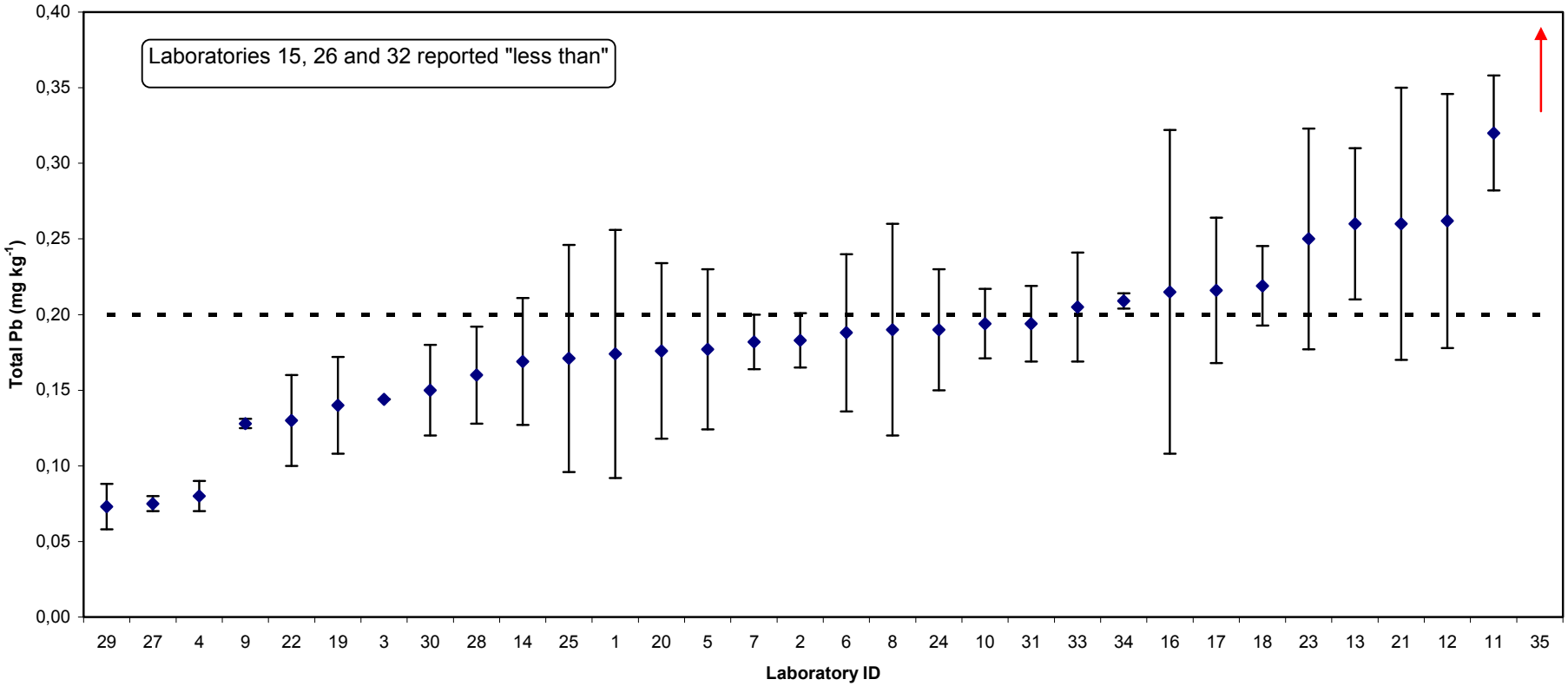
Annex 7: Total Pb in vegetable food

Indicative value in the SRM certificate = 0,20 mg kg^{-1}

Lab ID	x_{lab} (mg kg^{-1})	U_{lab} (mg kg^{-1})	k	Technique
1	0,174	0,082	2	ICP-MS
2	0,183	0,018	2	ICP-MS
3	0,144	0	√3	ETAAS
4	0,08	0,01	2	ICP-MS
5	0,177	0,053	2	ICP-MS
6	0,188	0,052	2	ICP-MS
7	0,182	0,018	2	ICP-MS
8	0,19	0,07	2	ICP-MS
9	0,128	0,003	2	ETAAS
10	0,194	0,023	2	ETAAS
11	0,320	0,038	2	ICP-MS
12	0,2619	0,084	2	ICP-MS
13	0,26	0,05	2	ETAAS
14	0,169	0,042	2	ICP-MS
15	<0,20			FAAS
16	0,215	0,107	2	ICP-MS
17	0,216	0,048	2	ETAAS
18	0,219	0,0263	√3	ICP-MS
19	0,140	0,032	2	CV-AAS
20	0,176	0,058	2	ICP-MS
21	0,260	0,09	2	ETAAS
22	0,13	0,03	2	ICP-MS
23	0,250	0,073	2	ICP-MS
24	0,19	0,04	2	ICP-AES
25	0,171	0,075	2	ETAAS
26	<0,3			ICP-MS
27	0,075	0,005	2	ICP-MS
28	0,16	0,032	2	ETAAS
29	0,073	0,015	2	ETAAS
30	0,15	0,03	2	ETAAS
31	0,194	0,025	2	ICP-MS
32	<1,80			ZETAAS
33	0,205	0,036	0,963	ETAAS
34	0,209	0,005	2	ETAAS
35	1,594	0,224	2	ETAAS

IMEP-110: results for total Pb

Informative value: 0.20 mg kg^{-1}



This graph displays all measurements results and their associated uncertainties.
The uncertainties are shown as reported, with various expansion factors and levels of confidence.
The dotted black line represents the informative concentration provided by the CRM producer in the certificate of this material

Annex 8: Total As in vegetable food

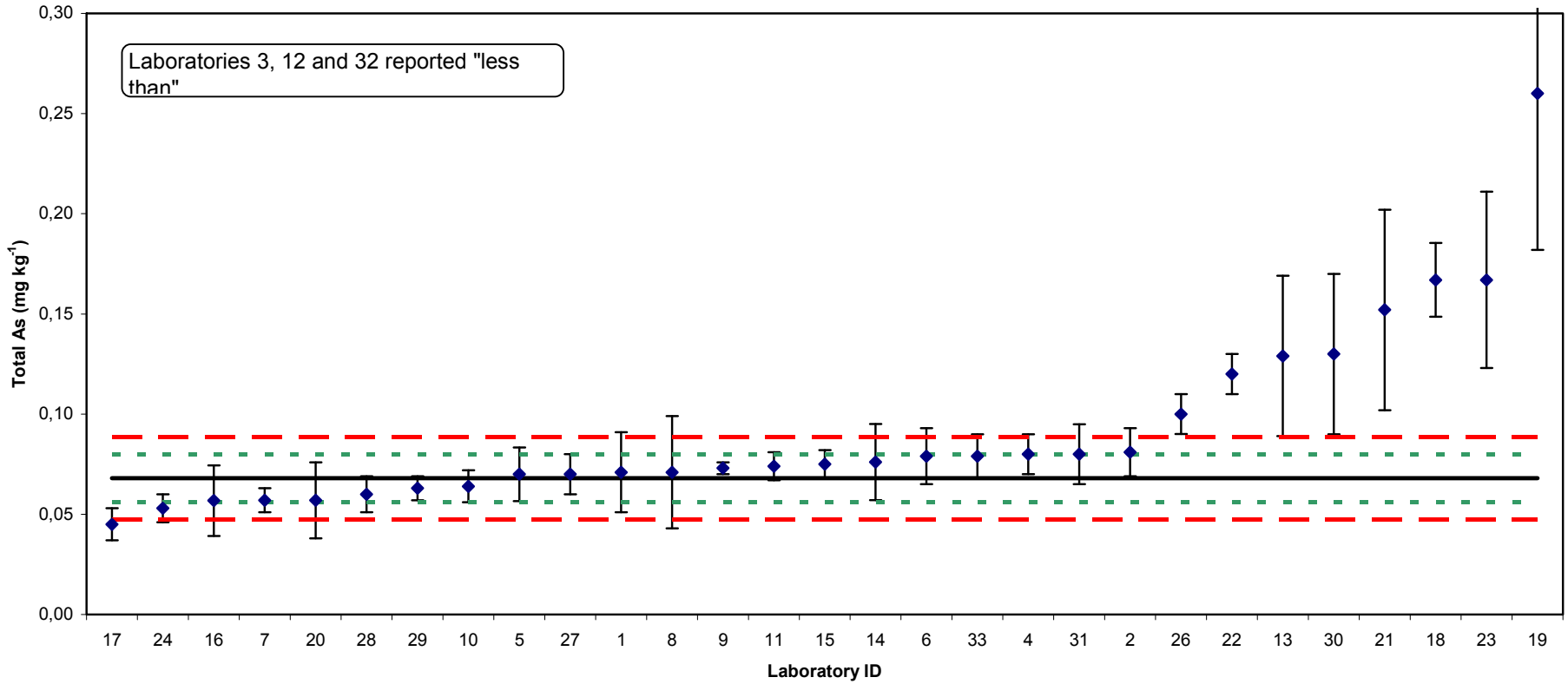
X_{ref} = 0,068 ± 0,012 mg kg^{-1} (k=2)

Lab ID	x_{lab} (mg kg^{-1})	U_{lab} (mg kg^{-1})	k	u_{lab}	Technique	z	ζ	$Qual_u$
1	0,071	0,020	2	0,010	ICP-MS	0,3	0,3	a
2	0,081	0,012	2	0,006	ICP-MS	1,3	1,5	a
3	<0,1				ETAAS			
4	0,08	0,01	2	0,01	ICP-MS	1,2	1,5	a
5	0,070	0,0134	2	0,0067	ICP-MS	0,2	0,2	a
6	0,079	0,014	2	0,007	ICP-MS	1,1	1,2	a
7	0,057	0,006	2	0,003	HG-AAS	-1,1	-1,6	b
8	0,071	0,028	2	0,014	ICP-MS	0,3	0,2	c
9	0,073	0,003	2	0,002	ETAAS	0,5	0,8	b
10	0,064	0,008	2	0,004	ICP-MS	-0,4	-0,6	b
11	0,074	0,007	2	0,004	HG-AAS	0,6	0,9	b
12	<0,20				ICP-MS			
13	0,129	0,040	2	0,020	HG-AAS	6,0	2,9	c
14	0,0761	0,0190	2	0,0095	ICP-MS	0,8	0,7	a
15	0,075	0,007	4,303	0,002	HG-AAS	0,7	1,1	b
16	0,0568	0,0176	2	0,0088	ICP-MS	-1,1	-1,1	a
17	0,045	0,008	2	0,004	HG-AAS	-2,3	-3,2	b
18	0,167	0,0184	√3	0,0106	ICP-MS	9,7	8,1	c
19	0,260	0,078	2	0,039	CV-AAS	18,8	4,9	c
20	0,057	0,019	2	0,010	ICP-MS	-1,1	-1,0	a
21	0,152	0,05	2	0,03	ETAAS	8,2	3,3	c
22	0,12	0,01	2	0,01	ICP-MS	5,1	6,7	a
23	0,167	0,044	2	0,022	ICP-MS	9,7	4,3	c
24	0,053	0,007	2	0,004	ICP-AES	-1,5	-2,2	b
26	0,10	0,01	2	0,01	ICP-MS	3,1	4,1	a
27	0,070	0,010	2	0,005	ICP-MS	0,2	0,3	b
28	0,06	0,009	2	0,005	HG-AAS	-0,8	-1,1	b
29	0,063	0,006	2	0,003	CV-AAS	-0,5	-0,7	b
30	0,13	0,04	2	0,02	ETAAS	6,1	3,0	c
31	0,08	0,015	2	0,008	High resolution-ICP-MS	1,2	1,2	a
32	<0,85				ZETAAS			
33	0,079	0,011	0,946	0,012	HG-AAS	1,1	0,8	c

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

IMEP-110: results for total As

Certified range: 0,068 ± 0.012 mg kg^{-1} (k=2)



This graph displays all measurements results and their associated uncertainties.
The uncertainties are shown as reported, with various expansion factors and levels of confidence.
The black line represents Xref, the green dotted lines delimit the reference interval **(X_{ref} ± 2u_{ref}: 0,068 ± 0.012 mg kg^{-1})**, the red dashed lines delimit the target interval **(X_{ref} ± 2σ: 0,068 ± 0,020 mg kg^{-1})**

Annex 9: Total Hg in vegetable food

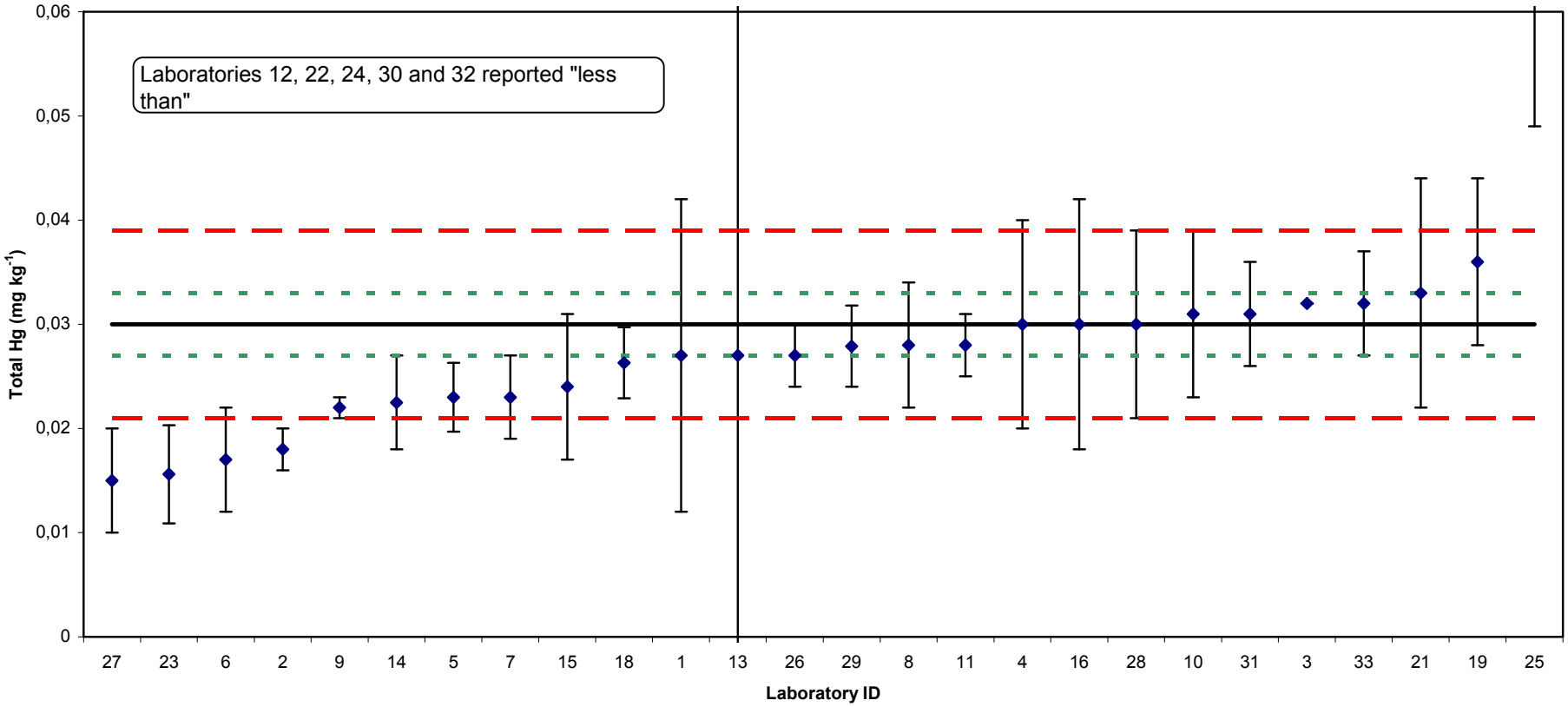
X_{ref} = 0,030 ± 0,003 mg kg^{-1} (k=2)

Lab ID	x_{lab} (mg kg^{-1})	U_{lab} (mg kg^{-1})	k	u_{lab}	Technique	z	ζ	$Qual_u$
1	0,027	0,015	2	0,008	AMA	-0,7	-0,4	c
2	0,018	0,002	2	0,001	ICP-MS	-2,7	-6,7	b
3	0,032	0	√3	0	CV-AFS	0,4	1,3	b
4	0,03	0,01	2	0,01	ICP-MS	0,0	0,0	c
5	0,023	0,0033	2	0,0017	CV-AAS	-1,6	-3,1	b
6	0,017	0,005	2	0,003	aas/ama254 mercury analyzer	-2,9	-4,5	a
7	0,023	0,004	2	0,002	ICP-MS	-1,6	-2,8	a
8	0,028	0,006	2	0,003	CV-AAS	-0,4	-0,6	a
9	0,022	0,001	2	0,001	CV-AAS	-1,8	-5,1	b
10	0,031	0,008	2	0,004	AMA	0,2	0,2	a
11	0,028	0,003	2	0,002	CV-AAS	-0,4	-0,9	a
12	<0,05				ICP-MS			
13	0,027	0,434	2	0,217	HG-AAS	-0,7	0,0	c
14	0,0225	0,0045	2	0,0023	CV-AAS	-1,7	-2,8	a
15	0,024	0,007	3,182	0,002	CV-AAS	-1,3	-2,3	a
16	0,0300	0,0120	2	0,0060	ICP-MS	0,0	0,0	c
18	0,0263	0,00341	√3	0,00197	AMA	-0,8	-1,5	b
19	0,036	0,008	2	0,004	CV-AFS	1,3	1,4	a
21	0,033	0,011	2	0,006	ETAAS	0,7	0,5	c
22	<0,1				HG-AAS			
23	0,0156	0,0047	2	0,0024	ICP-MS	-3,2	-5,2	a
24	<0,1				ICP-AES			
25	0,085	0,036	2	0,018	CV-AAS	12,2	3,0	c
26	0,027	0,003	2	0,002	AMA-254	-0,7	-1,4	a
27	0,015	0,005	2	0,003	ICP-MS	-3,3	-5,1	a
28	0,03	0,009	2	0,0045	CV-AAS	0,0	0,0	a
29	0,0279	0,0039	2	0,0020	CV-AAS	-0,5	-0,9	a
30	<0,060				HG-AAS			
31	0,031	0,005	2	0,003	ICP-MS	0,2	0,3	a
32	<0,034				TDA-AAS			
33	0,032	0,005	√3	0,003	CV-AAS	0,4	0,6	a

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

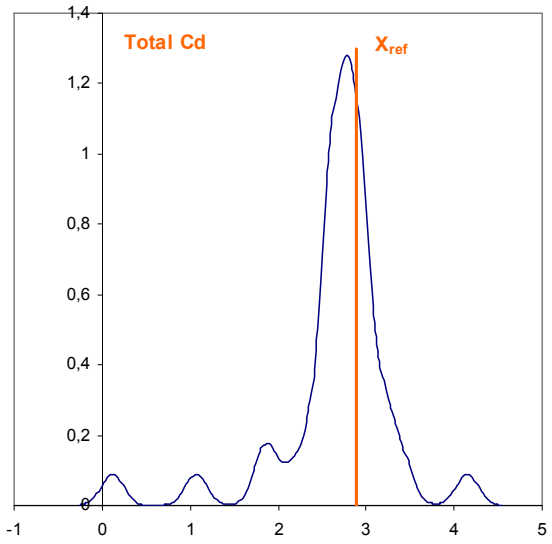
IMEP-110: results for total Hg

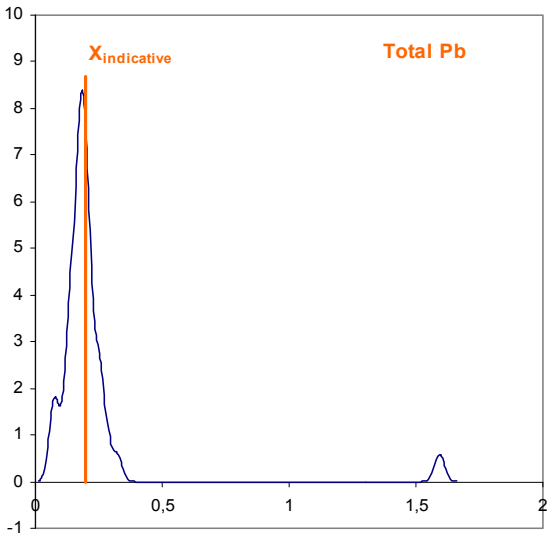
Certified range: 0,030 ± 0,003 mg kg^{-1} (k=2)

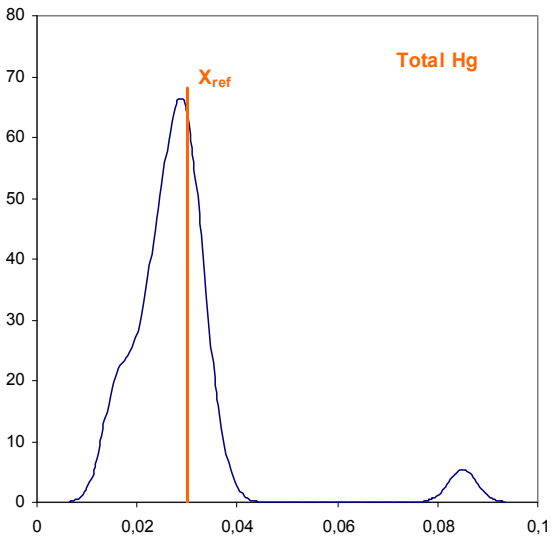


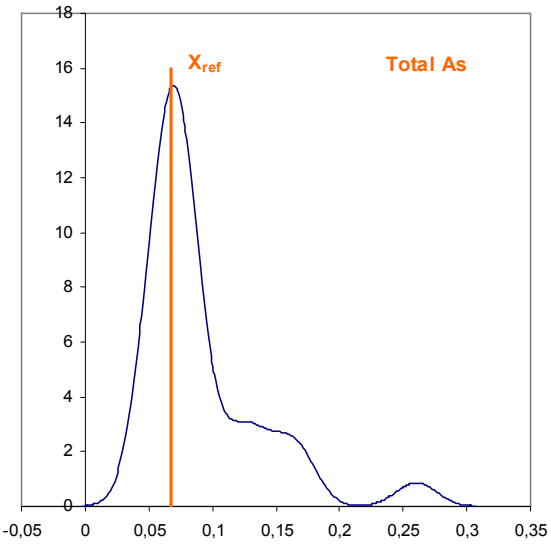
This graph displays all measurements results and their associated uncertainties.
The uncertainties are shown as reported, with various expansion factors and levels of confidence.
The black line represents Xref, the green dotted lines delimit the reference interval **(X_{ref} ± 2u_{ref}: 0,030 ± 0.003 mg kg^{-1})**, the red dashed lines delimit the target interval **(X_{ref} ± 2σ: 0,030 ± 0,009 mg kg^{-1})**

Annex 10: Kernel distributions









Annex 11: Experimental details for total Cd, Pb, As and Hg determinations

LCode	SOP?	If yes, which:	Sample pre-treatment	Digestion step	Extraction / separation step	Answer
1	No		Shaking	Microwave assisted, HNO_3 50% at 180°C for 45 min		External, 0 to 10 ppb.
2	No					
3	Yes	Institute SOP A1057				
4	No		Mixing	µ-wave assisted acid digestion with conc HNO_3		Addition calibration
5	No					
6	No		Microwave digestion with nitric acid and hydrogen peroxide for As, Cd, Pb. For mercury no pre-treatment			
7	No		None	High pressure microwave digestion with HNO_3 and H_2O_2		External calibration, internal standard Indium
8	No			Microwave with Ac. Nitric		ICP-MS
9	Yes	LST EN 14084:2003, ASU L 00.00-19/3, ASU L 00.00-19/4,				
10	No		No pre-treatment	HNO_3 and H_2O_2	No	External calibration
11	Yes	AOAC				
12	No		Microwave Digestion	Acid digestion : Nitric acid, Hydrogen Peroxide and water	N/A	ICP-MS calibration using calibration standards
13	No		None	Ashing for lead and open tube digestion for Cd, As and Hg.		
14	Yes	EN 13805 for digestion, EN 15763 for As, Cd, Pb and EN 13806 for Hg				

LCode	SOP?	If yes, which:	Sample pre-treatment	Digestion step	Extraction / separation step	Answer
15	Yes	Cd, Pb: EN 14082:2003; As: EN14546; Hg-no		For Hg: HNO_3+H_2SO_4		0.050 µg
16	Yes	NMKL Trace Elements-As, Cd, Hg, Pb and other elements. No. 186, 2007.				
17	Yes	As - EN 14546:2004; Pb, Cd - LMBG 35:1993				
18	Yes	Official Methods of Analysis AOAC				
19	Yes	EN 14332:2004; EN 13804:2002; EN 13805:2002; EN ISO 15586:2004				
20	Yes	SS-EN 15763:2009				
22	Yes	UNI EN 13804 2002, UNI EN 13805:2002, UNI EN 13806:2003				
23	No		Homogenise	Microwave digestion	n.a.	Calibration using certified standard solutions
24	No		Addition of acid and hydrogen peroxide, let it stand for one hour	Microwave	Dilution	External calibration
25	Yes	AOAC 974.14 Final Action, AOAC 999.10 Final Action				
26	No					ICP-MS
27	Yes	EN ISO 13805 and EN 15763				
28	Yes	As EN 14332:2004; Pb, Cd EN 14084:2003; Hg National Feed Codex				
29	Yes	EN 14083:2004; EN 14546:2005				

LCode	SOP?	If yes, which:	Sample pre-treatment	Digestion step	Extraction / separation step	Answer
30	Yes	AOAC Official Method 999.10, AOAC Methods of Analysis, 2000, chapter 9, p.16-19.				
31	No		None	Aliquots (0.5 g) of test sample were digested in nitric acid using a high pressure, closed vessel microwave digestion system.	Digest solutions were made up to volume (10 ml) with deionised water and then diluted 5-fold with internal standard solution (Rh and Ga).	Calibration standards were prepared by serial dilution and run with the test solutions.
32	No			Pb,Cd,As: microwave high pressure digestion with H_20_2 (30%) and HNO_3 conc and HF conc.		ADD. METHOD: STD SOLUTION: Cd 2 PPB; Pb 50 PPB; As 20 PPB. Hg non linearity calibration from 25 ppb to 5 ppm
33	Yes	Hg-AOAC 971.21; Cd, Pb - AOAC 999.11;in-house-As	reduce As(v) to As(III) with KJ	Dry	No	
34	Yes	SR EN 13805, SR EN 14084				
35	Yes	AOAC 999.10				

European Commission

EUR 24618 EN – Joint Research Centre – Institute for Reference Materials and Measurements
Title: Report of the tenth interlaboratory comparison organised by the European Union Reference Laboratory for Heavy Metals in Feed and Food. Total arsenic, cadmium, mercury and lead.
Author(s): M.B. de la Calle, H. Emteborg, J. Charoud-Got, P. Robouch, I. Verbist.
Luxembourg: Publications Office of the European Union
2010 – 45 pp. – 21 x 29.7 cm
EUR – Scientific and Technical Research series – ISSN 1018-5593
ISBN 978-92-79-18674-5
doi:10.2787/33321

Abstract

The Institute for Reference Materials and Measurements (IRMM) of the Joint Research Centre (JRC) a Directorate General of the European Commission operates the European Union Reference Laboratory for Heavy Metals in Feed and Food (EU-RL-HM). One of its core tasks is to organise interlaboratory comparisons (ILCs) among appointed National Reference Laboratories (NRLs). This report presents the results of the tenth ILC of the EU-RL-HM which focused on the determination of total arsenic, cadmium, mercury and lead in vegetable food.

The test material used in this exercise was the Standard Reference Material SRM 1570a, spinach leaves of the National Institute of Standards and Technology (NIST). The material was rebottled and relabelled to prevent recognition by the participants and was dispatched at the beginning of June. Each participant received one bottle containing approximately 15 g of test material. Thirty-five laboratories from 24 countries registered to the exercise of which 35 reported results for total Cd and total Pb, 32 for total As and 31 for total Hg. The assigned values for total As, Cd and Hg are the certified values taken from the SRM 1570a certificate. For total Pb, the "information value" provided by NIST in the SRM certificate was used as assigned value.

The uncertainties of the assigned values (u_{ref}) for total As, Cd and Hg, were taken directly from the CRM certificate as provided by the producer. No u_{ref} is provided by NIST for the total Pb concentration because the total Pb content is only provided as "information value". Participants were invited to report the uncertainty of their measurements. This was done by the majority of the laboratories taking part in this exercise.

Laboratories' results were rated with z- and ζ-scores (zeta-scores) for total As, Cd, and Hg in accordance to ISO 13528. No ζ-scores were given for total Pb because u_{ref} was not known for that measurand. The standard deviation for proficiency assessment (also called target standard deviation) was fixed to 15 % for all the measurands by the advisory board of this ILC, on the basis of the outcome of previous ILCs organised by the EU-RL-HM and on the state-of-the-art in this field of analysis.

More than 80 % of the participants performed satisfactory for total Cd and Hg. Around 70 % of the participants obtained a satisfactory z-score for total arsenic with a relatively high number (8 laboratories) of participants having overestimated the total content of arsenic in the test material. When looking at the ζ-scores, 60 to 65 % of the reported results were satisfactory when the associated uncertainties are taken into account.

The mission of the JRC is to provide customer-driven scientific and technical support for the conception, development, implementation and monitoring of EU policies. As a service of the European Commission, the JRC functions as a reference centre of science and technology for the Union. Close to the policy-making process, it serves the common interest of the Member States, while being independent of special interests, whether private or national.

LA-NA-24618-EN-C