Report of the first interlaboratory comparison organised by the Community Reference Laboratory Heavy Metals in Feed and Food

Total Cd, Hg and Pb in a food matrix of plant origin

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Table of Contents

1 Summary

The Institute for Reference Materials and Measurements (IRMM) of the European Commission's Directorate-General Joint Research Centre holds the Community Reference Laboratory for Heavy Metals in Feed and Food (CRL-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 first ILC of the new CRL-HM which focused on the determination of total Cd, Pb and Hg content (related to dry mass) in food of plant origin.

The test material used in this exercise was the Certified Reference Material (CRM) BCR-191, lyophilised brown bread. The material was rebottled to prevent recognition by the participants and dispatched in October 2006. Each participant received one sample containing 40 g of test material. There were 28 participants from 19 countries, of which 24 (i.e. 86 %) submitted results.

The assigned values for Cd and Pb were the certified values taken from the BCR-191 certificate. This certificate however provides no certified value for Hg; only an indicative value is given in the certification report. Since only eight participants reported values for Hg, with the rest of the participants giving only "smaller than" values or no values at all, no scoring is provided for this measurand.

The uncertainty of the assigned values was calculated by combining the uncertainty of characterisation and a contribution for between-bottle homogeneity (which was calculated from the certification report). Participants were invited to report the uncertainty on their measurements. This was done by most of the participants.

Laboratory results were rated with z and zeta scores in accordance with ISO 13528[1]. Standard deviations for proficiency assessment (also called target standard deviations) for Cd and Pb were calculated using the modified Horwitz equation[2].

2 Introduction

Due to their ubiquitous occurrence, heavy metals are present in all foodstuffs. The metal load of food and feed depends on the conditions under which feed and food are produced and processed. While some metals have nutritional importance and are essential, others such as Pb, Cd, and Hg are toxic and their presence can lead to health problems.

Apart from genetic factors the nature of the soil has the most important influence on the content of elements in plant food and feed. Besides the existing heavy metals content of the soil, the elemental content of the soil can be anthropogenically influenced, for instance by the use of sewage sludge contaminated with heavy metals or sediments dredged from polluted rivers. Factors such as climate or the ripeness of crops can lead to seasonal dependency of the elemental concentration on plants.

In humans, about one third of the total Cd burden originates from animal products and two-thirds from plant products. In plants Cd is predominantly absorbed through the roots and only slightly through the surface of leaves. The average Cd content of the cereals greatly varies; average values of 0.016 mg·kg^{-1} fresh material are found in rye, while wheat contains an average of 0.056 mg·kg^{-1} and rice of 0.075 mg·kg^{-1}.

The Pb content of plant foods is very variable and is a consequence of exogenous influences. Both the lead uptake from the soil through the roots and Pb deposition on parts of the plant above the ground are important, being the latter the predominant source of Pb. The average composition of Pb in bread is of 0.035 mg·kg^{-1} fresh material with maximum values of up to 0.42 mg·kg^{-1}.

A lot of attention is paid to the presence of Hg in plant food and feed, as it is one of the most toxic elements for humans and animals. Hg occurs in most plants in minute traces. In the particular case of cereals mean values of 0.006-0.030 mg·kg^{-1} are found.

To overcome problems associated with a high metal content in food and feed maximum allowed limits in several commodities have been laid down in the European legislation, a.o. Commission Directive 2001/22/EC[3], Commission Directive 2002/32/EC[4] and Commission Regulation (EC) 466/2001[5].

Laboratory proficiency testing is an essential element of laboratory quality assurance. The analysis of an external quality control test material allows individual laboratories to compare their analytical results with those from other laboratories while providing them objective standards to perform against. The Community Reference Laboratory Heavy Metals in Feed and Food (CRL-HM) has organised a PT for the network of appointed NRLs to determine **total** Cd, Pb and Hg content (related to dry mass) in food of plant origin.

3 Scope

It is one of the core duties of the CRL-HM to organise interlaboratory comparisons, as is stated in Regulation (EC) No 882/2004 of the European Parliament and of the Council[6]. The scope of this comparison is to test the competence of the appointed NRLs to analyse **total** Cd, Pb and Hg content (related to dry mass) in food of plant origin.

The assessment of the measurement results is undertaken on the basis of requirements laid down in legislation[3,5], and follows the administrative and logistic procedures of IMEP[7], the International Measurement Evaluation Programme of the Institute for Reference Materials and Measurements (IRMM) of the European Commission's Directorate-General Joint Research Centre. The number of this interlaboratory comparison is IMEP-101.

4 Time frame

The interlaboratory comparison was first announced to the NRL network at the first CRL-HM workshop on 25/26 September 2006. Invitation letters were sent to the laboratories on 3 October 2006 (cf. Annex 1). The samples were dispatched to participants on 26 October 2006. Reporting deadline was 20 November 2006, and this was extended until 30 November 2006 for four laboratories who encountered difficulties (a.o. because of delayed sample delivery).

5 Test material

5.1 Preparation

The commercially available CRM BCR-191 (trace elements in lyophilised brown bread) was used for this ILC. The material was re-bottled and re-labelled to avoid identification by the participants as an existing CRM. No further manipulation of the material took place. Comprehensive information on the preparation of the CRM can be found in the certification report on the IRMM website.[8]

5.2 Homogeneity

The samples had been tested for homogeneity by the CRM supplier, see the certification report[8]. Homogeneity was considered sufficient for this intercomparison.

5.3 Distribution

The samples were dispatched to the participants by IRMM on 26 October 2006. Each participant received: a) a bottle containing the test material, b) an accompanying letter with instructions on sample handling and reporting (cf. Annex 2) and c) a form that had to be sent back after receipt of the sample to confirm its arrival (cf. Annex 3).

6 Instructions to participants

Details of this intercomparison were presented to the NRLs at the first workshop, held in Geel on 25 and 26 September 2006. Concrete instructions were given to all participants in a letter that accompanied the samples. The measurands and matrix were clearly defined as "total Cd, Pb and Hg in a food matrix of plant origin".

Laboratories were asked to perform two or three independent measurements and report them, together with the mean of the results and its associated uncertainty. The measurement results were to be corrected for moisture and recovery. Participants were asked to follow their routine procedures. The results were to be reported in the same manner (e.g., number of significant figures) as those normally reported to the customer.

The results were to be reported in a special online form for which each participant received an individual access code. A special questionnaire was attached to this online form. The questionnaire is intended to provide further information on the measurements and the laboratories. A copy of the questionnaire is presented in Annex 4.

7 Reference values and their uncertainties

The CRM certificate provided certified values for Cd and Pb which were used as the reference values (X_{ref}) for this intercomparison. The CRM certification report only provided an indicative value of 0.002 $mg \cdot kg^{-1}$ for Hg. No further calculation was performed with this value.

The certificate was valid during the time frame of the intercomparison.

Information on the 95% confidence interval (95%CI) of the mean values was provided on the CRM certificate for Cd and Pb. An uncertainty contribution for between-bottle homogeneity had not been included in the provided uncertainties.
This contribution was calculated according to the procedure of Linsinger *et al.*[9] as described hereafter:

The standard uncertainty of characterisation (u_{char}) for Cd and Pb is derived from 95%CI:

$$u_{char} = 95\%CI \; / \; t_{95\%}(\nu) \qquad \text{Eq. 1}$$

where $t_{95\%}(\nu)$ is the Student's *t* factor with ν degrees of freedom that defines an interval encompassing 95% of the distribution of results. For this intercomparison, $t_{95\%}(\nu) = 2.20$ ($\nu = 11$, based on the 12 accepted set of results for both Cd and Pb, as stated on the material certificate).

The maximum heterogeneity that could be hidden by method repeatability (u^*_{bb}) is determined:

$$u^*_{bb} = (s_{homo} / \sqrt{n}) * (2/\nu_{shomo})^{1/4} \qquad \text{Eq. 2}$$

where

s_{homo} is the within-bottle standard deviation obtained by the homogeneity study, $s_{homo} = 0.125X_{ref}$ for both Cd and Pb, as stated in the certification report

n is the number of replicate measurements per bottle (n=1)

ν_{shomo} is the degrees of freedom for the determination of this standard deviation ($\nu_{shomo} = 19$ for both Cd and Pb, as 20 bottles were analysed).

The uncertainty of the assigned values (u_{ref}) was calculated by combining the uncertainty of characterisation (u_{char}) and the contribution for between-bottle homogeneity (u^*_{bb}), as follows:

$$u_{ref} = \sqrt{(u_{char}^2 + u^*_{bb}{}^2)} \qquad \text{Eq. 3}$$

According to the CRM provider, no special contribution for stability was necessary. The values of X_{ref}, u_{char}, u^*_{bb}, u_{ref} and the expanded uncertainty (U_{ref}) are summarised in Table 1.

Table 1: Reference values and their uncertainties for the parameters of this intercomparison.

	X_{ref} [mg·kg^{-1}]	u_{char} [mg·kg^{-1}]	u^*_{bb} [mg·kg^{-1}]	u_{ref} [mg·kg^{-1}]	U_{ref} [mg·kg^{-1}]
Cd	0.0284	0.00064	0.0020	0.0021	0.0042
Hg	no value	no value	no value	no value	no value
Pb	0.187	0.0064	0.013	0.015	0.030

X_{ref} is the certified reference value and u_{ref} the corresponding standard uncertainty; U_{ref} is the estimated expanded uncertainty, with a coverage factor k=2, corresponding to a level of confidence of about 95 %, as defined in the Guide to the Expression of Uncertainty in Measurement (GUM), ISO, 1995. u_{char} is the uncertainty of characterisation, as stated on the material certificate, and u^*_{bb} the maximum heterogeneity that could be hidden by method repeatability.

8 Evaluation of results

8.1 General observations

Twenty-eight laboratories from nineteen countries had registered for participation. They all received a sample. Twenty-four laboratories reported results. All participants reported one or more measurement values for Cd and Pb. Only eight participants reported values for Hg, whereas other participants reported either a "smaller than" value, or no value at all. As requested, most of the laboratories reported the measurement uncertainty. All participants responded to the special questionnaire that was attached to the online reporting form.

8.2 Scores and evaluation criteria

Individual laboratory performance is expressed in terms of z and zeta scores in accordance with ISO 13528[1] and the International Harmonised Protocol[10]

$$z = \frac{x_{lab} - X_{ref}}{\hat{\sigma}} \qquad \text{Eq. 4}$$

$$zeta = \frac{x_{lab} - X_{ref}}{\sqrt{u_{ref}^2 + u_{lab}^2}} \qquad \text{Eq. 5}$$

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 z score compares the participant's deviation from the reference value with $\hat{\sigma}$ derived from the improved Horwitz equation.[2] $\hat{\sigma}$ is equal to 0.0062 mg·kg^{-1} for Cd (i.e. 0.22X_{ref}) and to 0.037 mg·kg^{-1} for Pb (i.e. 0.20X_{ref}). x_{lab} is the mean of the individual measurement results, either as reported by the participant, or as calculated by the ILC organiser in case no mean was reported. The z score can be interpreted as:

$\lvert z\rvert \le 2$	satisfactory result
$2 < \lvert z\rvert \le 3$	questionable result
$\lvert z\rvert > 3$	unsatisfactory result

According to the International Harmonised Protocol[10] the zeta score provides an indication of whether the estimate of uncertainty is consistent with the laboratory's deviation from the reference value. The interpretation of the zeta score is similar to the interpretation of the z score.

The standard uncertainty of the laboratory (the term u_{lab} in the zeta score equation) was calculated as follows. First, the reported uncertainty was determined. It is equal to the reported uncertainty of the mean, as far as stated by the participant. If no mean was provided it was calculated as the average of the uncertainties of the individual measurements. If no uncertainties were reported it was set to zero for the purpose of calculating the zeta score. Second, the standard uncertainty u_{lab} was calculated by dividing the reported uncertainty by the coverage factor *k*. If no coverage factor was specified, the reported uncertainty was considered as the half-width of a rectangular distribution, and the standard uncertainty was calculated by dividing this half-width by √3. This approach is in accordance with recommendations issued by Eurachem and CITAC[11].

Measurement results reported as "smaller than" (<-values) were not used in any calculations and no evaluation of these results were made. No scores were given.

8.3 Laboratory results and scores

The results, as reported by the participants, are summarised in Table 2a-c for Cd, Pb and Hg, respectively, together with the z- and the zeta scores. Laboratory codes were given randomly.

Three sets of figures are provided for Cd, Pb and Hg (Fig 1-3). Each set includes (a) the Kernel Density plot, (b) individual mean value and associated expanded uncertainty, (c) the z- and zeta scores. No scores were calculated for mercury. In Figures 1b and 2b the solid line represents the assigned value, the dotted lines delimit the reference interval ($X_{ref} \pm 2u_{ref}$) and the dashed lines delimit the target interval ($X_{ref} \pm 2\hat{\sigma}$). The Kernel plots were made using a software tool developed by AMC.[12]

Considering the z scores, all participants performed well against the target standard deviation as calculated from the modified Horwitz equation[2] for Cd: twenty-two laboratories obtained z scores $\lvert z\rvert \le 3$ and two reported "less-than" values.

The situation is slightly different for Pb analysis: eighteen laboratories (75%) reported satisfactory, two (8%) questionable, three (13%) unsatisfactory results and one (4%) reported a "less-than" value. This could be due to the intrinsic difficulty of the determination of lead in complex matrices.

Considering the zeta scores for Cd eighteen laboratories (75%) reported satisfactory, two (8%) questionable, two (8%) unsatisfactory results and two (8%) reported a "less-than" value. For Pb analysis, thirteen laboratories (54%) reported satisfactory, two (8%) questionable, eight (33%) unsatisfactory results and one (4%) reported "less-than" value.

As explained in the International Harmonised Protocol[10], an unsatisfactory zeta score might be due to an underestimation of the uncertainty, or to a gross error causing a large deviation from the reference value. Thus, a laboratory having a satisfactory z score and an unsatisfactory zeta score is likely to have an underestimated uncertainty. This occurred several times, which stresses the need for training in uncertainty budget calculation.

A reporting error was detected for laboratory 9 who reported to have performed Pb measurements by GF-AAS and by CV-AAS, as the latter technique cannot be used for Pb analysis.

For mercury (Figures 3a,b), four laboratories reported results confirming the "indicative value" of 0.002 $mg \cdot kg^{-1}$ provided in the certification report[8]. Three other values seem to be in quite a good agreement with the result obtained by RNAA (Neutron Activation Analysis with radiochemical separation), 0.011 $mg \cdot kg^{-1}$ that was rejected by the certification panel[8]. Laboratory 11 reported an extreme value. As stated earlier, no assigned value nor scorings were calculated for mercury.

Additional information was gathered from the questionnaire completed by the participants. A summary of the methods of analysis that were used is compiled in Annex 6. Eleven participants used standardised methods. Ten laboratories out of the twenty-four corrected their results for recovery (73-108 %).

When asked about the basis of their uncertainty estimate, eleven laboratories reported to have used method validation data, nine reported precision, five gave the value associated with the standardized method that they used and one laboratory calculated uncertainty using the ISO-GUM. Combinations of two or more of those options were used by several laboratories. Nineteen participants reported a coverage factor for their uncertainty, three declared not to have used any and two provided a seemingly wrong answer to this question. Fifteen participants reported systematically uncertainty values to their customers.

Twenty-one laboratories corrected their results for humidity (3-8.6 %), one replied that correction for humidity had not been requested, and two did not correct their results for humidity because they considered the water content negligible.

Twenty-three laboratories were accredited according to ISO/IEC 17025 and one laboratory according to a National Accreditation System.

With the exception of one laboratory all the others participate regularly in various proficiency tests as shown in Annex 7.

All laboratories use CRMs for the validation of their methods and/or for calibration purposes.

Annex 8 shows the distribution of laboratories according to the number of samples of this type that they analyse per year. Only laboratory 15 reported to analyse feedstuff and not food commodities. This may explain the high limits of detection reported (Table 2a-c) for this type of matrix.

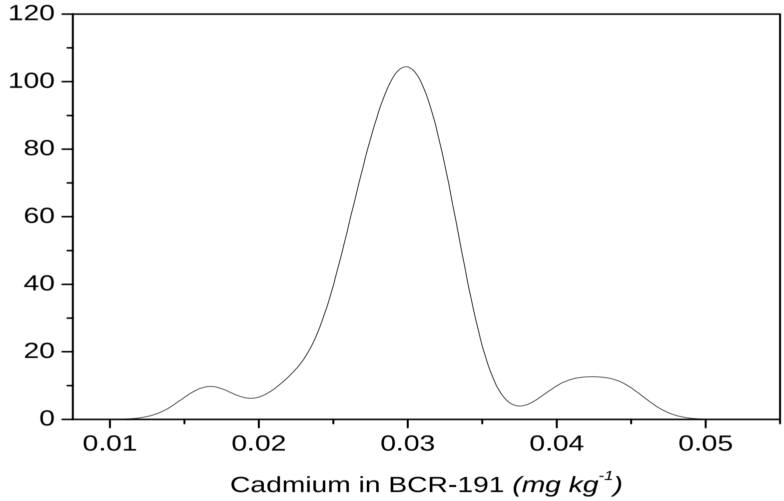


Figure 1a
Cadmium in BCR-191
Kernel Density,
All results

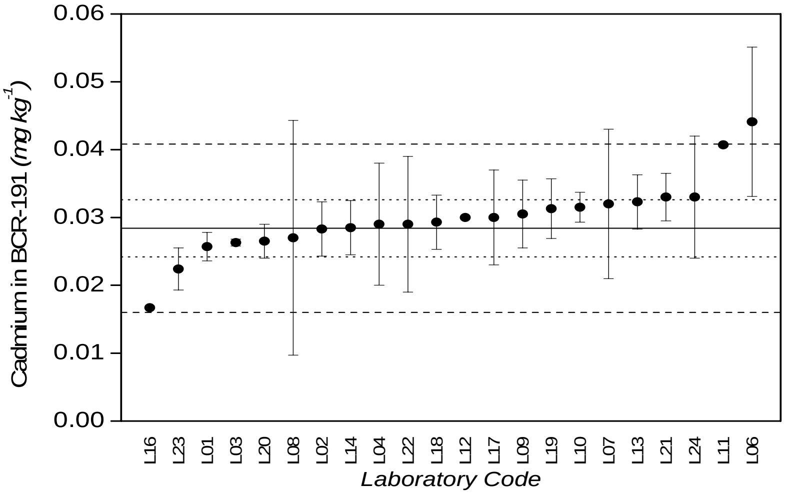


Figure 1b
Reported results and corresponding expanded uncertainties.

X_{ref} = 0.0284
u_{ref} = 0.0021
$\hat{\sigma}$ = 0.0062 (22%)
in mg·kg^{-1}

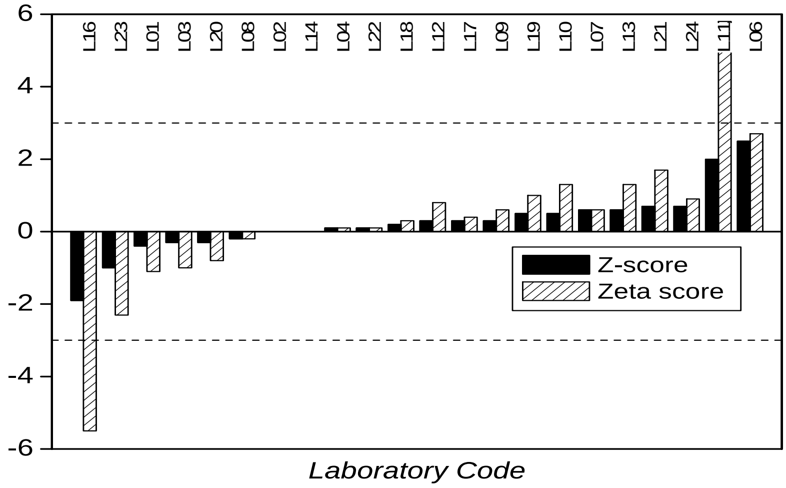


Figure 1c
Performance evaluation
$z = (X_{lab}-X_{ref})/\ \hat{\sigma}$
$zeta = (X_{lab}-X_{ref})/\ \sqrt{(u_{lab}^2+u_{ref}^2)}$

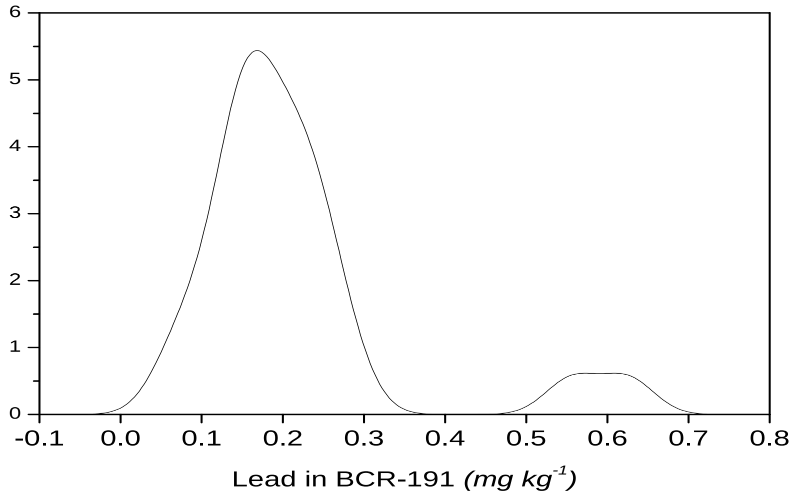


Figure 2a
Lead in BCR-191
Kernel Density,
All results

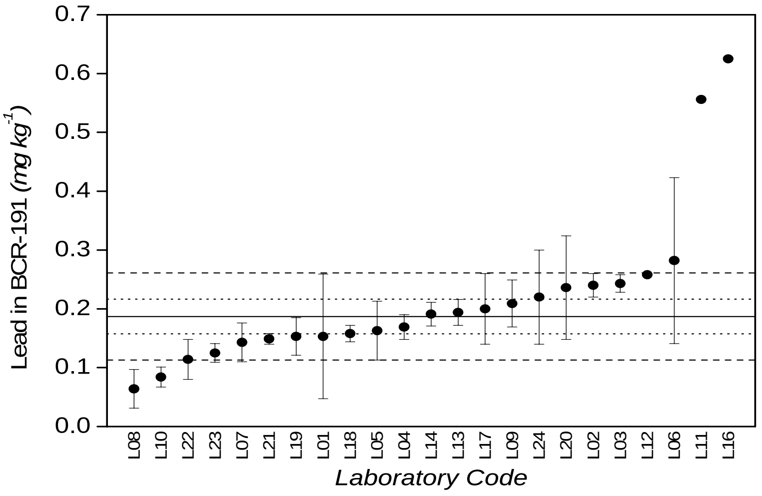


Figure 2b
Reported results and corresponding expanded uncertainties.

X_{ref} = 0.187
u_{ref} = 0.015
$\hat{\sigma}$ = 0.037 (20%)
in mg·kg^{-1}

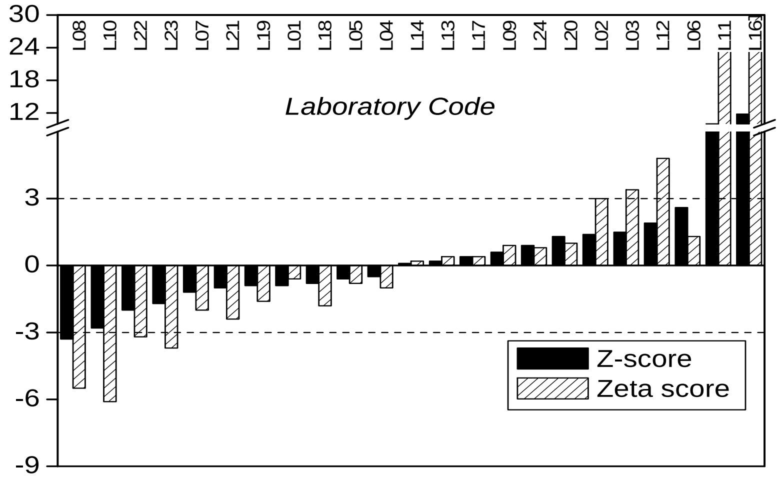


Figure 2c
Performance evaluation
z = (X_{lab}-X_{ref})/ $\hat{\sigma}$
zeta = (X_{lab}-X_{ref})/ $\sqrt{(u_{lab}^2+u_{ref}^2)}$

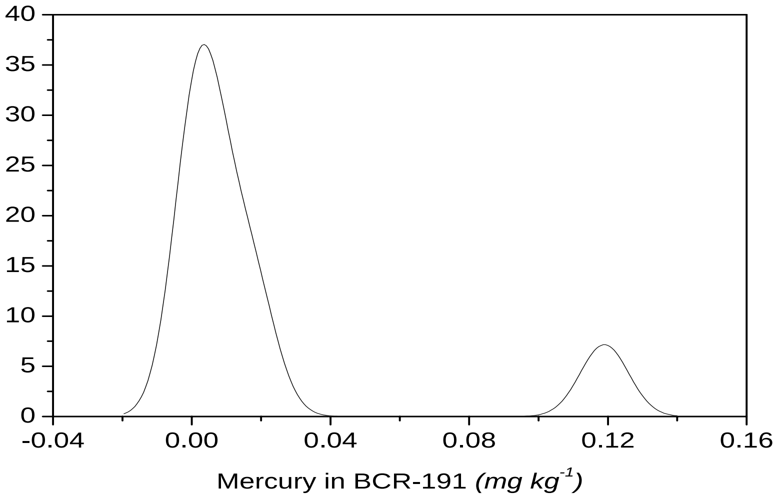


Figure 3a
Mercury in BCR-191
Kernel Density,
All results

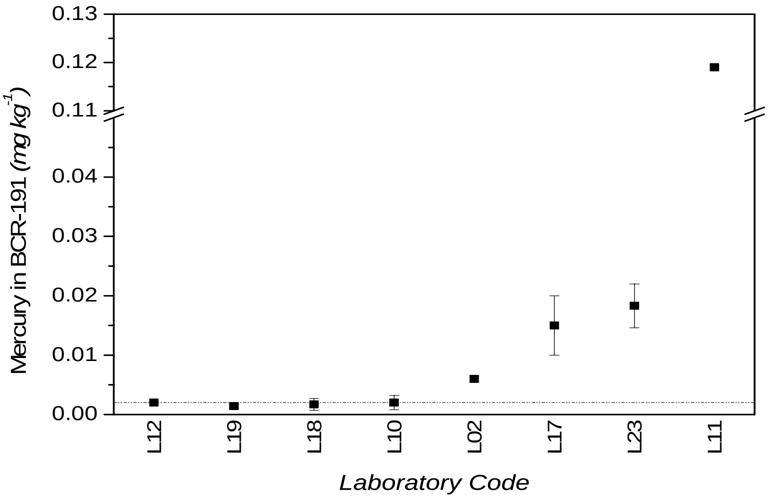


Figure 3b
Reported results and corresponding expanded uncertainties.

Indicative value ≈ 0.002 *mg·kg*$^{-1}$

Table 2a: Cadmium, quantitative information reported by participants plus the laboratory scorings provided by the organiser

	Lab-Code	Units	x1	x2	x3	Instrumental Method	reported mean	reported uncertainty	coverage factor	z	zeta
Cd	1	mg/kg	0.0253	0.0258	0.026	GF-AAS	0.0257	0.0018	nr	-0.4	-1.1
	2	mg/kg	0.027	0.029	0.029	GF-AAS	0.028	0.004	2	0.0	0.0
	3	µg/kg	26.9	26.2	25.9	ICP-MS	26.3	0.5	2	-0.3	-1.0
	4	mg/kg	0.028	0.03		FAAS	0.029	0.009	2	0.1	0.1
	5	mg/kg	< 0.05	< 0.05		ICP-MS					
	6	µg/kg	44.3	45.3	42.8	ICP-MS	44.1	11.025	2	2.5	2.7
	7	mg/kg	0.033	0.031		GF-AAS	0.032	0.011	2	0.6	0.6
	8	mg/kg	0.031	0.02	0.03	nr	0.027	0.015	nr	-0.2	-0.2
	9	mg/kg	0.03	0.031		GF-AAS	nr	0.005	2	0.3	0.6
	10	µg/kg	31.39	32.4	30.6	GF-AAS	31.5	2.2	2	0.5	1.3
	11	µg/g	0.039	0.041	0.042	FAAS	0.041	nr	2	2.0	5.8
	12	mg/kg	0.03			GF-AAS	nr	nr	nr	0.3	0.8
	13	mg/kg	0.032	0.033	0.032	ICP-MS	nr	0.004	2	0.6	1.3
	14	µg/kg	28	29		ICP-MS	nr	4	2	0.0	0.0
	15	mg/kg	< 0.023	< 0.025	< 0.025	ICP-OES					
	16	mg/kg	0.01	0.02	0.02	GF-AAS	0.02	nr	nr	-1.9	-5.5
	17	mg/kg	0.029	0.028	0.033	GF-AAS	0.03	0.007	2	0.3	0.4
	18	mg/kg	0.031	0.03	0.027	ICP-MS	0.029	0.004	2	0.2	0.3
	19	µg/kg	35	29	30	GF-AAS	nr	4.4	2	0.5	1.0
	20	ng/g	26	27		ICP-MS	26	2.7	2.2	-0.3	-0.8
	21	mg/kg	0.033	0.033	0.033	ICP-MS	nr a)	0.003	nr	0.7	1.7
	22	µg/kg	29	37	21	GF-AAS	nr	10	2	0.1	0.1
	23	µg/kg	22.7	22		ICP-OES	22.4	3.0	2	-1.0	-2.3
	24	mg/kg	0.031	0.035		GF-AAS	0.033	0.009	2	0.7	0.9

nr: not reported

a) Participant reported a fourth measurement value (x4) instead of the mean. It was discarded.

Table 2b: Lead, quantitative information reported by participants plus the laboratory scorings provided by the organiser

	Lab-Code	Units	x1	x2	x3	Instrumental Method	reported mean	reported uncertainty	coverage factor	z	zeta
Pb	1	mg/kg	0.144	0.192	0.124	GF-AAS	0.154	0.092	nr	-0.9	-0.6
	2	mg/kg	0.23	0.26	0.23	GF-AAS	0.24	0.02	2	1.4	3.0
	3	µg/kg	256	227	246	ICP-MS	243	15	2	1.5	3.4
	4	mg/kg	0.163	0.175		FAAS	0.169	0.021	2	-0.5	-1.0
	5	mg/kg	0.16	0.166		ICP-MS	0.16	0.05	2	-0.6	-0.8
	6	µg/kg	305.9	265.4	275.2	GF-AAS	282.2	141.1	2	2.6	1.3
	7	mg/kg	0.172	0.113		GF-AAS	0.143	0.033	2	-1.2	-2.0
	8	mg/kg	0.053	0.067	0.073	nr	0.0642	0.029	nr	-3.3	-5.5
	9	mg/kg	0.204	0.213		GF-AAS	nr	0.04	2	0.6	0.9
	10	µg/kg	75.64	87.5	88.2	GF-AAS	83.8	16.9	2	-2.8	-6.1
	11	µg/g	0.537	0.576	0.556	Flame AAS	0.556	nr	2	10.0	25.0
	12	mg/kg	0.258			GF-AAS	nr	nr	nr	1.9	4.8
	13	mg/kg	0.197	0.191	0.193	ICP-MS	nr	0.022	2	0.2	0.4
	14	µg/kg	197	184		ICP-MS	nr	20	2	0.1	0.2
	15	mg/kg	< 0.23	< 0.25	< 0.25	ICP-OES	< 0.25				
	16	mg/kg	0.61	0.64		GF-AAS	0.63	nr	nr	11.8	29.7
	17	mg/kg	0.19	0.2	0.21	GF-AAS	0.2	0.06	2	0.4	0.4
	18	mg/kg	0.163	0.16	0.15	ICP-MS	0.158	0.014	2	-0.8	-1.8
	19	µg/kg	161	154	143	GF-AAS	nr	32	2	-0.9	-1.6
	20	ng/g	220	251		ICP-MS	236	97	2.2	1.3	1.0
	21	mg/kg	0.155	0.15	0.143	ICP-MS	nr [a)]	0.008	nr	-1.0	-2.4
	22	µg/kg	112	103	128	GF-AAS	nr	34	2	-2.0	-3.2
	23	mg/kg	0.131	0.118		ICP-OES	0.124	0.015	2	-1.7	-3.8
	24	mg/kg	0.25	0.19		GF-AAS	0.22	0.08	2	0.9	0.8

nr: not reported

[a)] Participant reported a fourth measurement value (x4) instead of the mean. It was discarded.

Table 2c: Mercury, quantitative information reported by participants [a)]

	Lab-Code	Units	x1	x2	x3	Instrumental Method	reported mean	reported uncertainty	coverage factor
Hg	1	mg/kg	< 0.003	< 0.003	< 0.003	CV-AAS			
	2	mg/kg	0.0058	0.0062	0.0059	CV-AAS	0.006	0.0005	2
	3	µg/kg	< 10	< 10	< 10	AMA			
	4	mg/kg	< 0.1						
	5	mg/kg	< 0.02	< 0.02		ICP-MS			
	6	µg/kg	< 50	< 50	< 50	CV-AAS			
	7	mg/kg	< 0.019	< 0.018		CV-AAS			
	10	µg/kg	2.18	2.4	1.48	Flow-Injection AAS	2	1.2	2
	11	µg/g	0.116	0.122		CV-AAS	0.119	nr	2
	12	mg/kg	0.002			AMA 254	nr	nr	nr
	13	mg/kg	< 0.04	< 0.04	< 0.04	ICP-MS			
	15	ng/g	< 5	< 5	< 5	CV-ICP-AES			
	16	mg/kg	< 0.07	< 0.07	< 0.07	CV-AAS			
	17	mg/kg	0.012	0.017	0.016	Fluorescence AAS	0.015	0.005	2
	18	mg/kg	0.002	0.001	0.002	ICP-MS	0.002	0.001	2
	19	µg/kg	1.2	1.6	1.3	CV-AAS	1.4	0.27	2
	20	ng/g	< 3	< 3		ICP-MS			
	21	mg/kg	< 0.02	< 0.02	< 0.02	ICP-MS			
	22	µg/kg	< 10	< 10	< 10	Advanced Hg Analysis by Amalgamation AAS			
	23	µg/kg	20	16.6		Flow injection Mercury system	18.3	3.7	2
	24	mg/kg	< 0.05	< 0.05					

nr: not reported

[a)] Laboratories 8, 9 and 14 did not report measurement values and are not included in the table.

9 Acknowledgements

Authors would like to thank T. Linsinger for his assistance relating to the BCR CRM used. The NRLs participating in this exercise - listed below - are kindly acknowledged.

Organisation	Country
Austrian Agency for Health and Food Safety - AGES (AGES)	Austria
AGES Wieningerstrasse	Austria
Institute of Public Health	Belgium
State General Laboratory	Cyprus
The State Veterinary Institute (SVI) in Olomouc	Czech Republic
The Danish Institute for Food and Veterinary Research (DFVF)	Denmark
The Danish Plant Directorate	Denmark
Veterinary and Food Laboratory	Estonia
Finnish Food Safety Authority	Finland
Finnish Customs Laboratory	Finland
Agence Française de Sécurité Sanitaire des Aliments (AFSSA), Laboratoire d'Études et de Recherches sur la Qualité des Aliments et des Procédés Agro-Alimentaires (LERQAP)	France
Laboratoire de la Direction Générale de la Concurrence, de la Consommation et de la Répression des fraudes (DGCCRF)	France
General Chemical State Lab	Greece
National Institute for Agricultural Quality Control	Hungary
National Institute for Food Safety and Nutrition	Hungary
Health Service Executive	Ireland
Istituto Zooprofilattico Sperimentale (IZS) del Piemonte	Italy
National Veterinary Laboratory	Lithuania
National Institute of Hygiene	Poland
Veterinary Faculty	Slovenia
Laboratorio Arbitral Agroalimentario	Spain
National Food Administration	Sweden
National Veterinary Institute	Sweden
Central Science Laboratory	United Kingdom

Countries not appearing on the above list did not register to this interlaboratory comparison, either because they were not nominated at the time of the comparison, or because of technical problems.

10 References

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

[2] M. Thompson, *Analyst*, (2000), **125**, 385-386.

[3] Commission Directive 2001/22/EC of 8 March 2001 laying down the sampling methods and the methods of analysis for the official control of the levels of lead, cadmium, mercury and 3-MCPD in foodstuffs

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

[5] Commission Regulation (EC) No 466/2001 of 8 March 2001 setting maximum levels for certain contaminants in foodstuffs

[6] 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

[7] IMEP report "Trace Elements, PCBs, PAHs in Sewage Sludge. Report to Participants", see http://www.irmm.jrc.be/html/interlaboratory_comparisons/imep/index.htm

[8] BCR report "The certification of the contents (mass fractions) of Cd, Pb, Se, Cu, Zn, Fe and Mn in wholemeal flour and lyophilised brown bread reference materials", see http://www.irmm.jrc.be/html/reference_materials_catalogue/catalogue/attachements/BCR-191_report.pdf

[9] T. Linsinger *et al*., *Accreditation and Quality Assurance in Analytical Chemistry* (2001), **6**, 20-25

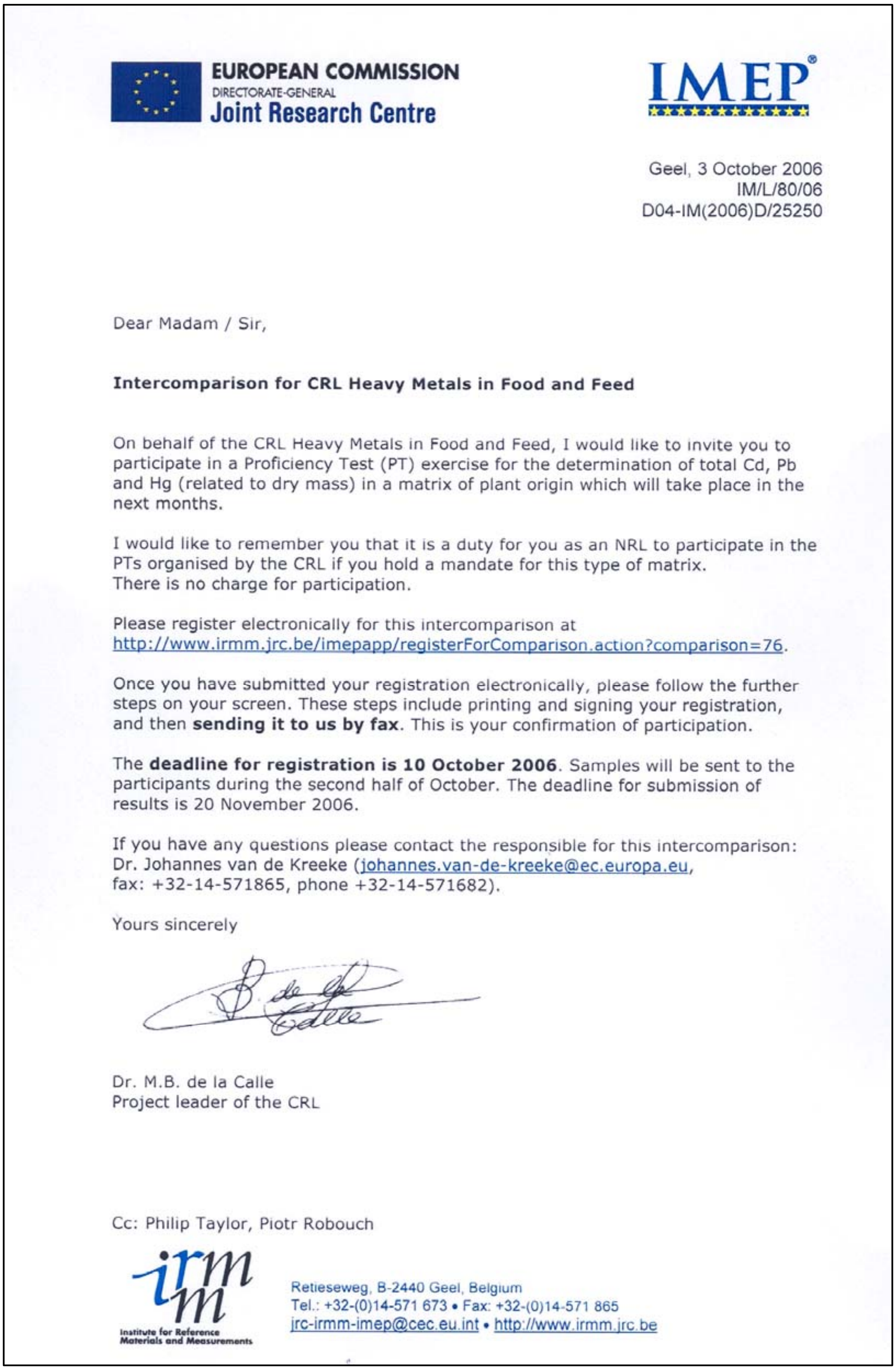
[10] The International Harmonised Protocol for the Proficiency Testing of Analytical Chemistry Laboratories by M. Thompson *et al.*, *Pure and Applied Chemistry* (2006), **78**, 145–196

[11] Eurachem/CITAC guide "Quantifying Uncertainty in Analytical Measurement" (2000), see 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

Annexes

Annex 1: Invitation letter to laboratories



EUROPEAN COMMISSION
DIRECTORATE-GENERAL
Joint Research Centre

IMEP

Geel, 3 October 2006
IM/L/80/06
D04-IM(2006)D/25250

Dear Madam / Sir,

Intercomparison for CRL Heavy Metals in Food and Feed

On behalf of the CRL Heavy Metals in Food and Feed, I would like to invite you to participate in a Proficiency Test (PT) exercise for the determination of total Cd, Pb and Hg (related to dry mass) in a matrix of plant origin which will take place in the next months.

I would like to remember you that it is a duty for you as an NRL to participate in the PTs organised by the CRL if you hold a mandate for this type of matrix.
There is no charge for participation.

Please register electronically for this intercomparison at http://www.irmm.jrc.be/imepapp/registerForComparison.action?comparison=76.

Once you have submitted your registration electronically, please follow the further steps on your screen. These steps include printing and signing your registration, and then **sending it to us by fax**. This is your confirmation of participation.

The **deadline for registration is 10 October 2006**. Samples will be sent to the participants during the second half of October. The deadline for submission of results is 20 November 2006.

If you have any questions please contact the responsible for this intercomparison: Dr. Johannes van de Kreeke (johannes.van-de-kreeke@ec.europa.eu, fax: +32-14-571865, phone +32-14-571682).

Yours sincerely

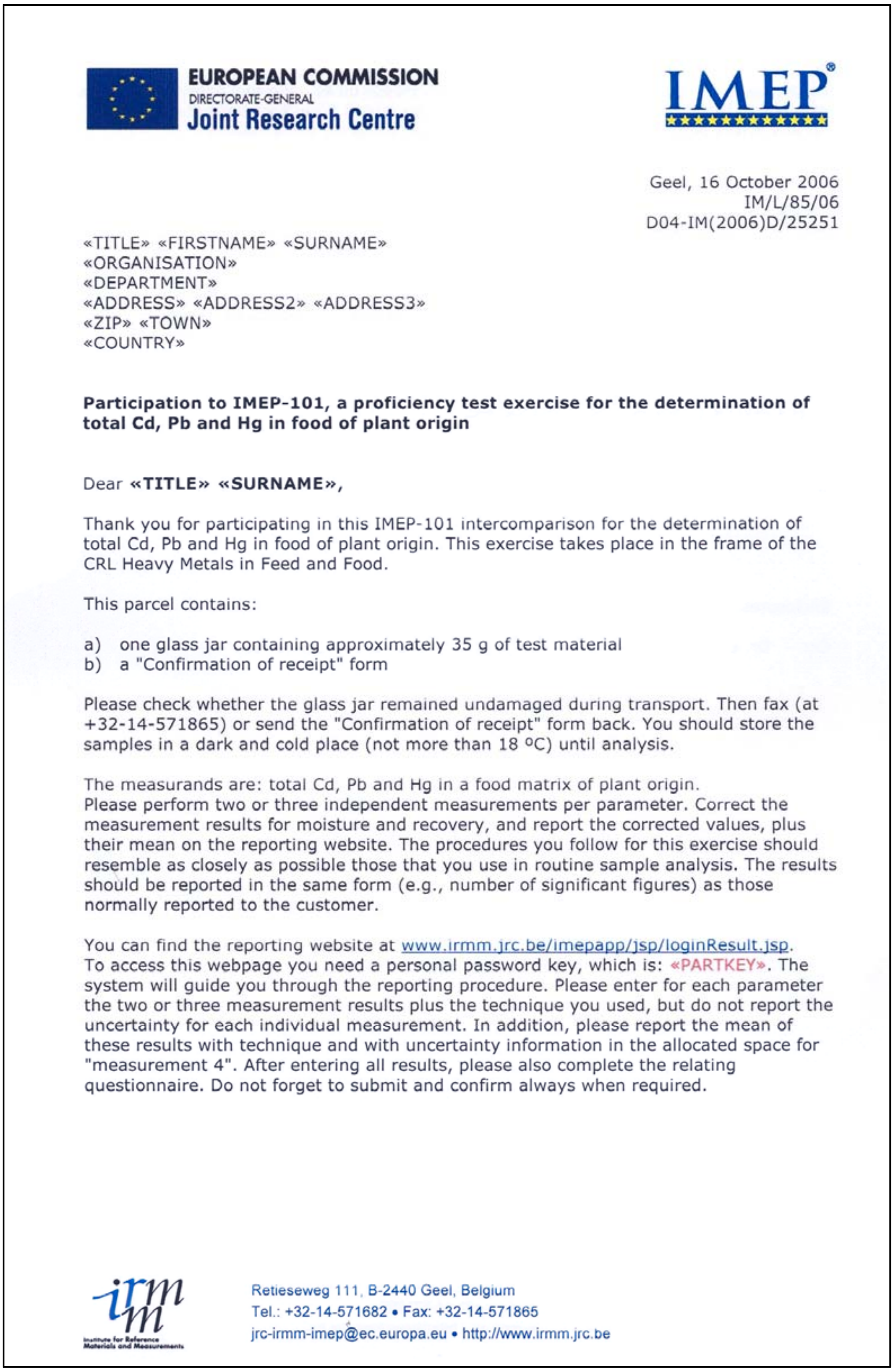
Dr. M.B. de la Calle
Project leader of the CRL

Cc: Philip Taylor, Piotr Robouch

irmm
Institute for Reference Materials and Measurements

Retieseweg, B-2440 Geel, Belgium
Tel.: +32-(0)14-571 673 • Fax: +32-(0)14-571 865
jrc-irmm-imep@cec.eu.int • http://www.irmm.jrc.be

Annex 2: Letter accompanying the sample



EUROPEAN COMMISSION
DIRECTORATE-GENERAL
Joint Research Centre

IMEP®

Geel, 16 October 2006
IM/L/85/06
D04-IM(2006)D/25251

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

Participation to IMEP-101, a proficiency test exercise for the determination of total Cd, Pb and Hg in food of plant origin

Dear **«TITLE» «SURNAME»,**

Thank you for participating in this IMEP-101 intercomparison for the determination of total Cd, Pb and Hg in food of plant origin. This exercise takes place in the frame of the CRL Heavy Metals in Feed and Food.

This parcel contains:

a) one glass jar containing approximately 35 g of test material
b) a "Confirmation of receipt" form

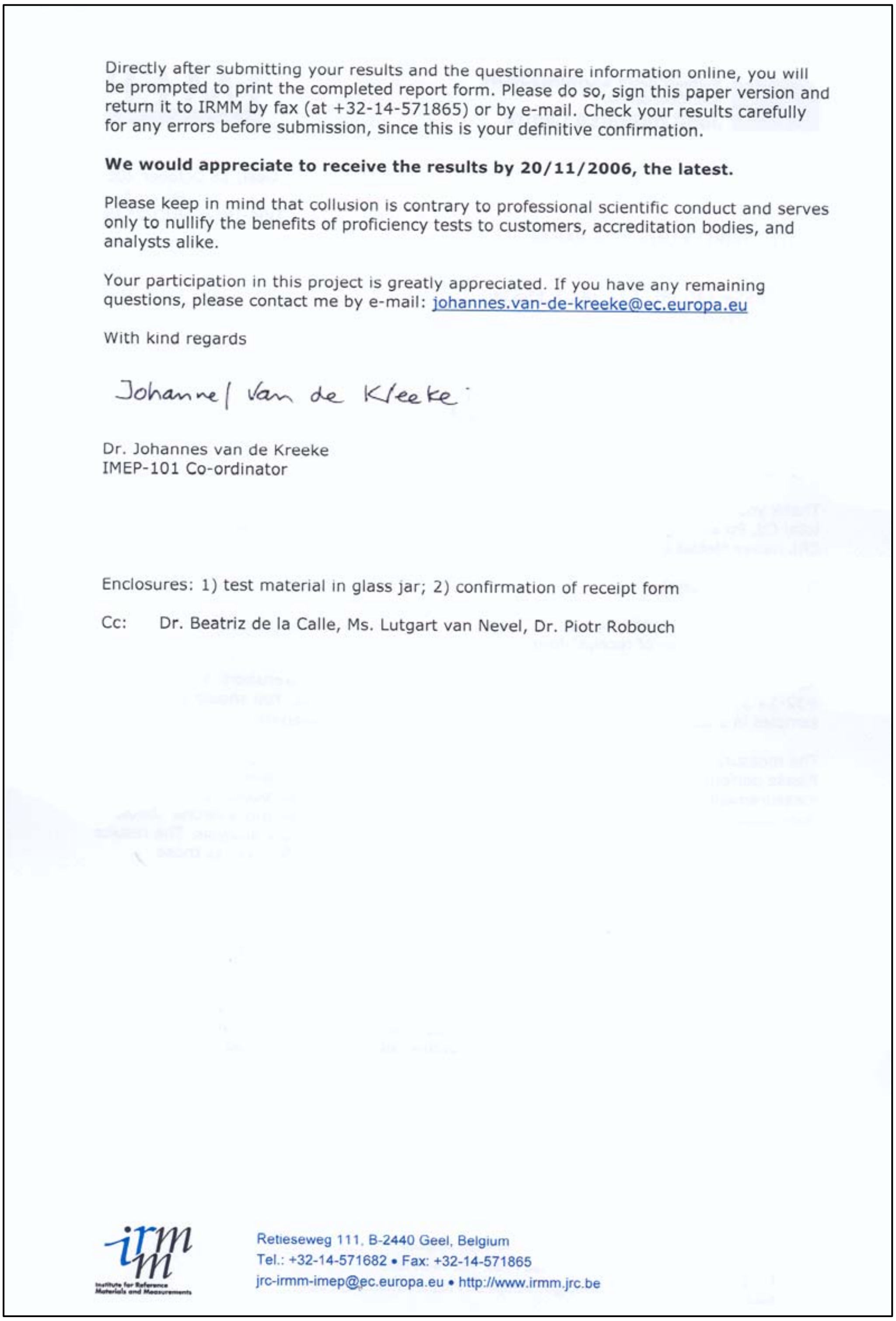
Please check whether the glass jar remained undamaged during transport. Then fax (at +32-14-571865) or send the "Confirmation of receipt" form back. You should store the samples in a dark and cold place (not more than 18 °C) until analysis.

The measurands are: total Cd, Pb and Hg in a food matrix of plant origin.
Please perform two or three independent measurements per parameter. Correct the measurement results for moisture and recovery, and report the corrected values, plus their mean on the reporting website. The procedures you follow for this exercise should resemble as closely as possible those that you use in routine sample analysis. The results should be reported in the same form (e.g., number of significant figures) as those normally reported to the customer.

You can find the reporting website at www.irmm.jrc.be/imepapp/jsp/loginResult.jsp.
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 parameter the two or three measurement results plus the technique you used, but do not report the uncertainty for each individual measurement. In addition, please report the mean of these results with technique and with uncertainty information in the allocated space for "measurement 4". After entering all results, please also complete the relating questionnaire. Do not forget to submit and confirm always when required.

irmm
Institute for Reference Materials and Measurements

Retieseweg 111, B-2440 Geel, Belgium
Tel.: +32-14-571682 • Fax: +32-14-571865
jrc-irmm-imep@ec.europa.eu • http://www.irmm.jrc.be



Directly after submitting your results and the questionnaire information online, you will be prompted to print the completed report form. Please do so, sign this paper version and return it to IRMM by fax (at +32-14-571865) or by e-mail. Check your results carefully for any errors before submission, since this is your definitive confirmation.

We would appreciate to receive the results by 20/11/2006, the latest.

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: johannes.van-de-kreeke@ec.europa.eu

With kind regards

Johannes van de Kreeke

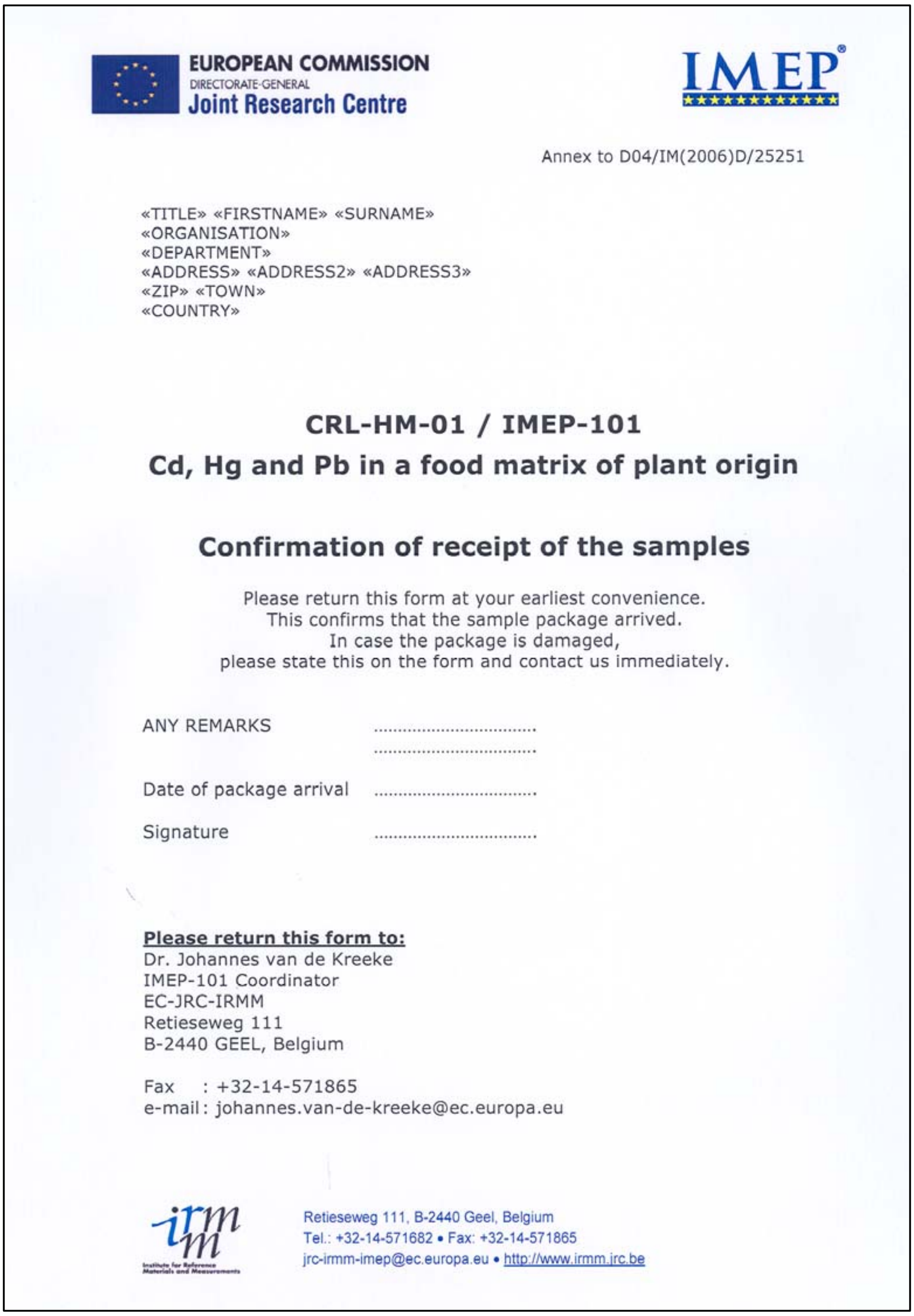
Dr. Johannes van de Kreeke
IMEP-101 Co-ordinator

Enclosures: 1) test material in glass jar; 2) confirmation of receipt form

Cc: Dr. Beatriz de la Calle, Ms. Lutgart van Nevel, Dr. Piotr Robouch

Institute for Reference Materials and Measurements
Retieseweg 111, B-2440 Geel, Belgium
Tel.: +32-14-571682 • Fax: +32-14-571865
jrc-irmm-imep@ec.europa.eu • http://www.irmm.jrc.be

Annex 3: Sample receipt confirmation form



EUROPEAN COMMISSION
DIRECTORATE-GENERAL
Joint Research Centre

IMEP

Annex to D04/IM(2006)D/25251

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

CRL-HM-01 / IMEP-101

Cd, Hg and Pb in a food matrix of plant origin

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.

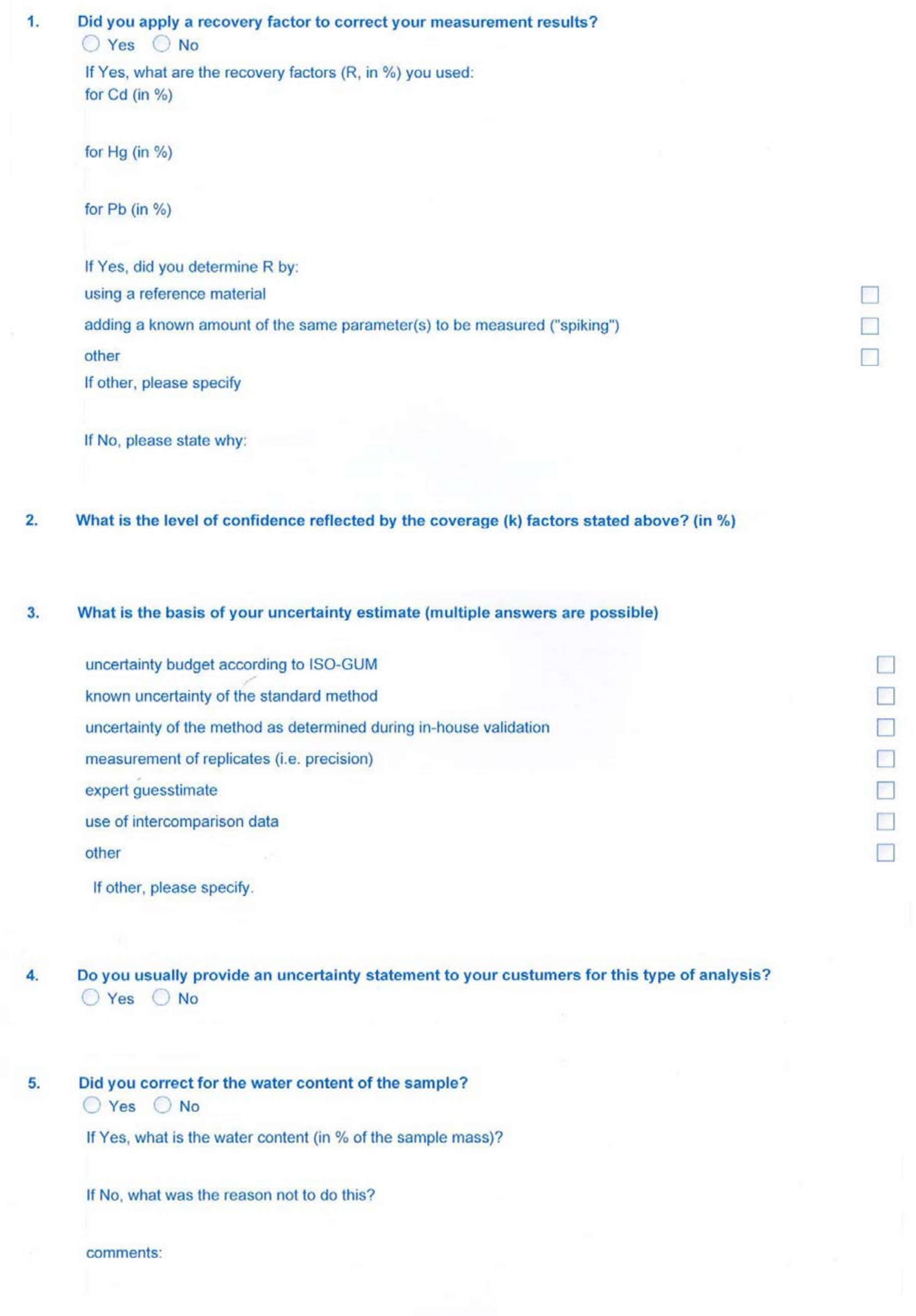
ANY REMARKS	....
Date of package arrival	....
Signature	....

Please return this form to:
Dr. Johannes van de Kreeke
IMEP-101 Coordinator
EC-JRC-IRMM
Retieseweg 111
B-2440 GEEL, Belgium

Fax : +32-14-571865
e-mail : johannes.van-de-kreeke@ec.europa.eu

Retieseweg 111, B-2440 Geel, Belgium
Tel.: +32-14-571682 • Fax: +32-14-571865
jrc-irmm-imep@ec.europa.eu • http://www.irmm.jrc.be

Annex 4: Questionnaire



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

○ Yes ○ No

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

for Cd (in %)

for Hg (in %)

for Pb (in %)

If Yes, did you determine R by:

using a reference material ☐

adding a known amount of the same parameter(s) to be measured ("spiking") ☐

other ☐

If other, please specify

If No, please state why:

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)

uncertainty budget according to ISO-GUM ☐

known uncertainty of the standard method ☐

uncertainty of the method as determined during in-house validation ☐

measurement of replicates (i.e. precision) ☐

expert guesstimate ☐

use of intercomparison data ☐

other ☐

If other, please specify.

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

○ Yes ○ No

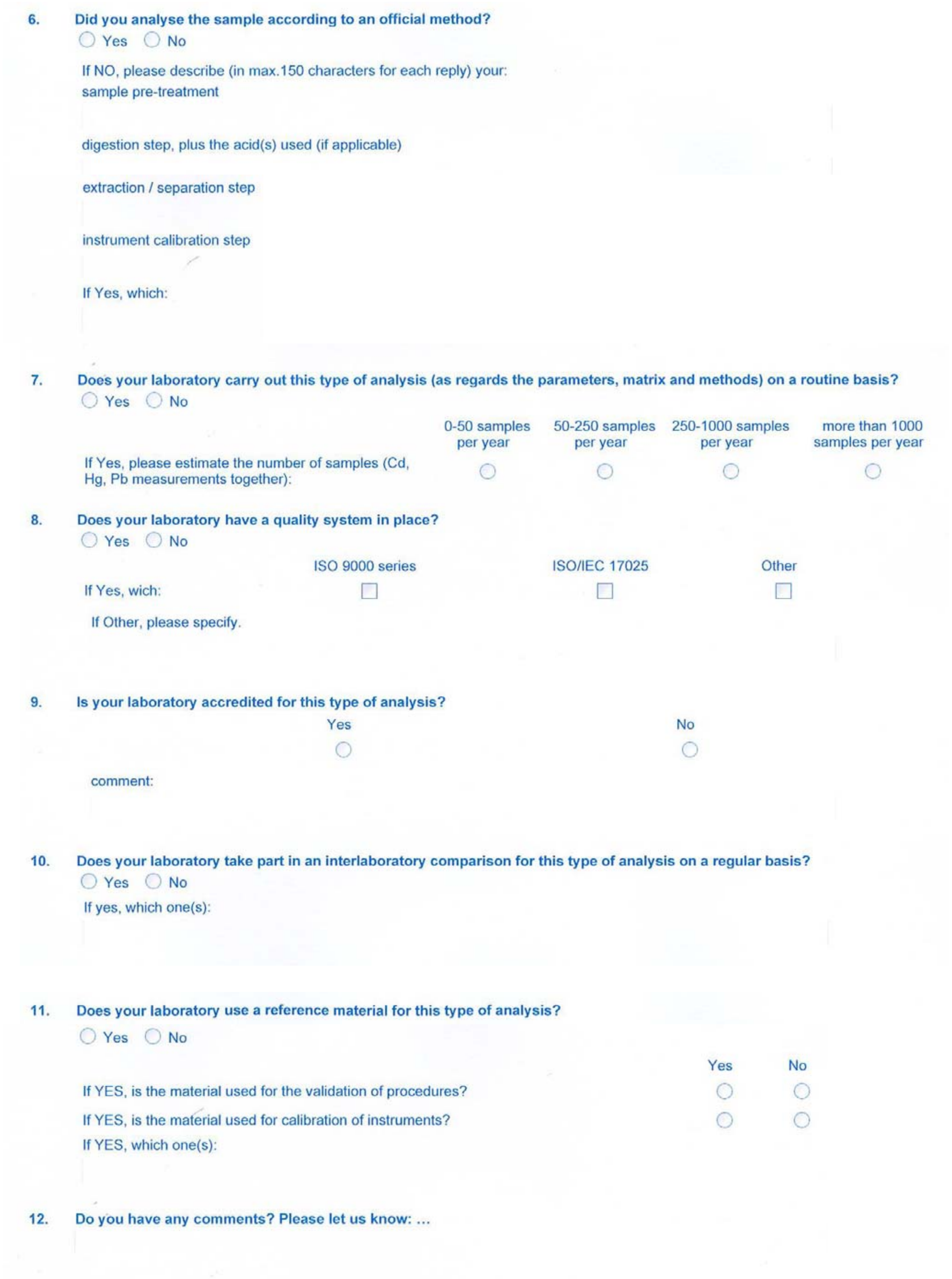
5. Did you correct for the water content of the sample?

○ Yes ○ No

If Yes, what is the water content (in % of the sample mass)?

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

comments:



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

○ Yes ○ No

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

sample pre-treatment

digestion step, plus the acid(s) used (if applicable)

extraction / separation step

instrument calibration step

If Yes, which:

7. **Does your laboratory carry out this type of analysis (as regards the parameters, matrix and methods) on a routine basis?**

○ Yes ○ No

	0-50 samples per year	50-250 samples per year	250-1000 samples per year	more than 1000 samples per year
If Yes, please estimate the number of samples (Cd, Hg, Pb measurements together):	○	○	○	○

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

○ Yes ○ No

	ISO 9000 series	ISO/IEC 17025	Other
If Yes, wich:	☐	☐	☐

If Other, please specify.

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

Yes	No
○	○

comment:

10. **Does your laboratory take part in an interlaboratory comparison for this type of analysis on a regular basis?**

○ Yes ○ No

If yes, which one(s):

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

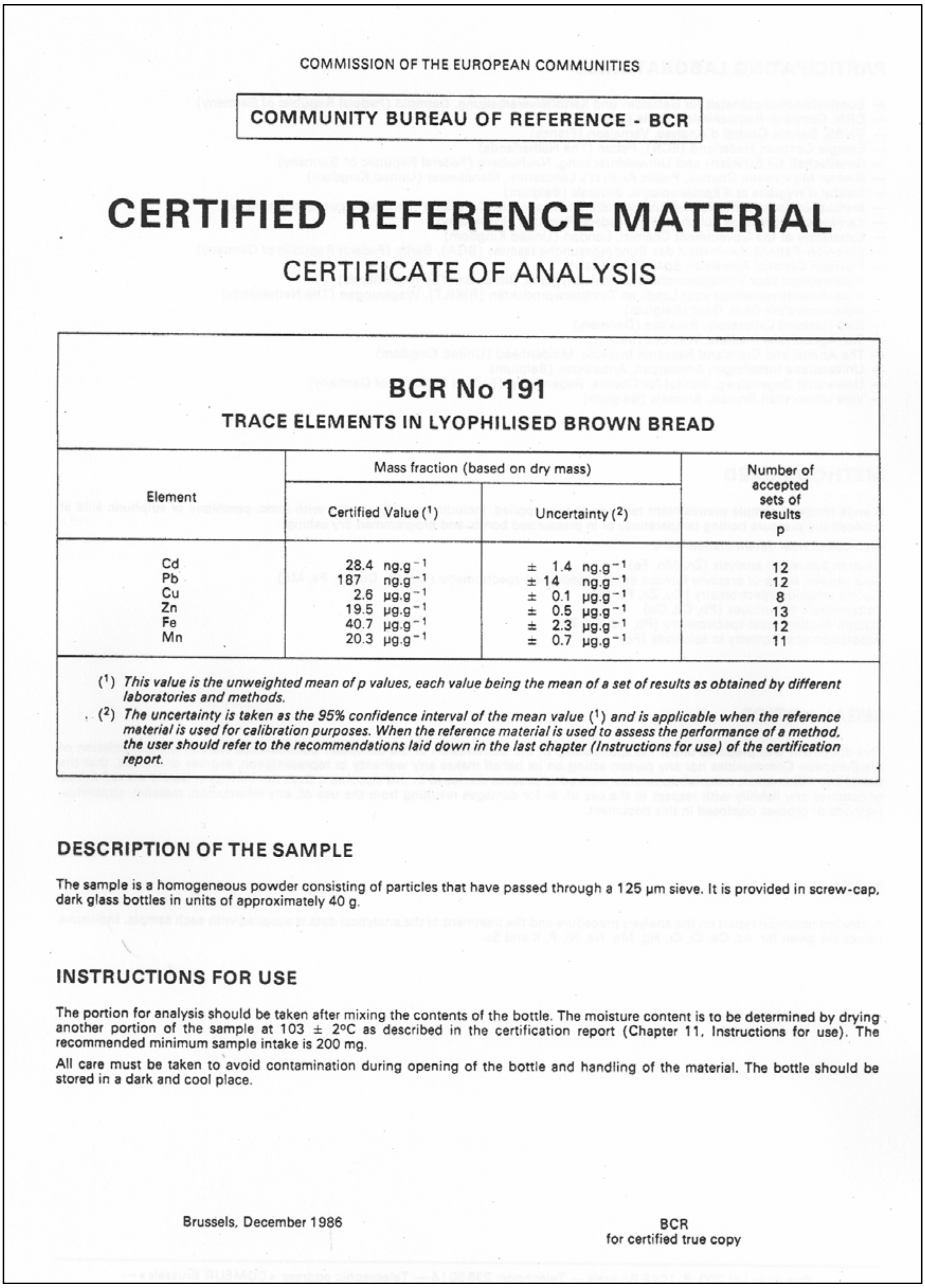
○ Yes ○ No

	Yes	No
If YES, is the material used for the validation of procedures?	○	○
If YES, is the material used for calibration of instruments?	○	○

If YES, which one(s):

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

Annex 5: Material Certificate of BCR-191



COMMISSION OF THE EUROPEAN COMMUNITIES

COMMUNITY BUREAU OF REFERENCE - BCR

CERTIFIED REFERENCE MATERIAL

CERTIFICATE OF ANALYSIS

BCR No 191

TRACE ELEMENTS IN LYOPHILISED BROWN BREAD

Element	Mass fraction (based on dry mass)		Number of accepted sets of results p
	Certified Value (1)	Uncertainty (2)	
Cd	28.4 ng.g^{-1}	± 1.4 ng.g^{-1}	12
Pb	187 ng.g^{-1}	± 14 ng.g^{-1}	12
Cu	2.6 µg.g^{-1}	± 0.1 µg.g^{-1}	8
Zn	19.5 µg.g^{-1}	± 0.5 µg.g^{-1}	13
Fe	40.7 µg.g^{-1}	± 2.3 µg.g^{-1}	12
Mn	20.3 µg.g^{-1}	± 0.7 µg.g^{-1}	11

(1) *This value is the unweighted mean of p values, each value being the mean of a set of results as obtained by different laboratories and methods.*

(2) *The uncertainty is taken as the 95% confidence interval of the mean value (1) and is applicable when the reference material is used for calibration purposes. When the reference material is used to assess the performance of a method, the user should refer to the recommendations laid down in the last chapter (Instructions for use) of the certification report.*

DESCRIPTION OF THE SAMPLE

The sample is a homogeneous powder consisting of particles that have passed through a 125 µm sieve. It is provided in screw-cap, dark glass bottles in units of approximately 40 g.

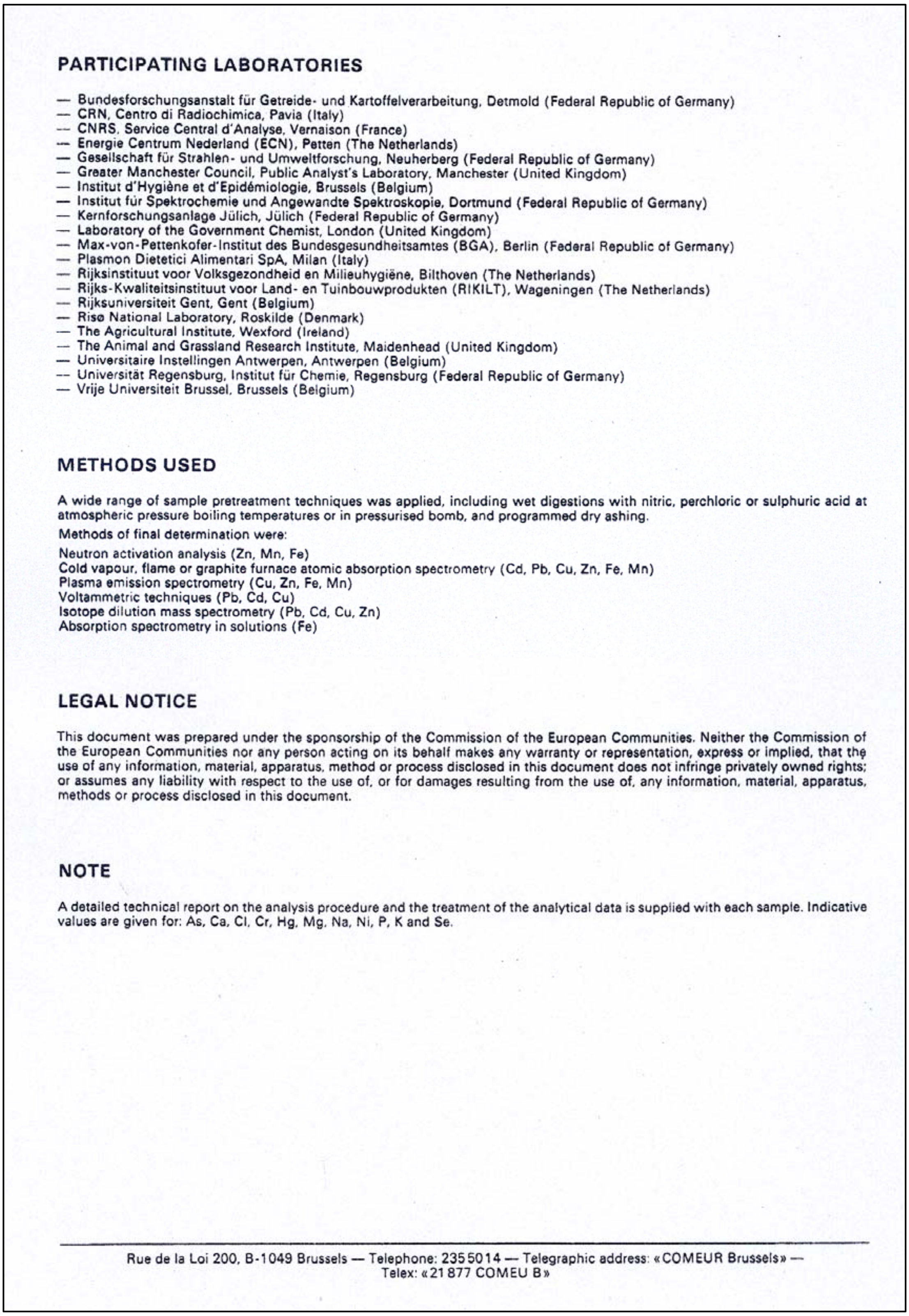
INSTRUCTIONS FOR USE

The portion for analysis should be taken after mixing the contents of the bottle. The moisture content is to be determined by drying another portion of the sample at 103 ± 2°C as described in the certification report (Chapter 11, Instructions for use). The recommended minimum sample intake is 200 mg.

All care must be taken to avoid contamination during opening of the bottle and handling of the material. The bottle should be stored in a dark and cool place.

Brussels, December 1986

BCR
for certified true copy



PARTICIPATING LABORATORIES

- Bundesforschungsanstalt für Getreide- und Kartoffelverarbeitung, Detmold (Federal Republic of Germany)
- CRN, Centro di Radiochimica, Pavia (Italy)
- CNRS, Service Central d'Analyse, Vernaison (France)
- Energie Centrum Nederland (ECN), Petten (The Netherlands)
- Gesellschaft für Strahlen- und Umweltforschung, Neuherberg (Federal Republic of Germany)
- Greater Manchester Council, Public Analyst's Laboratory, Manchester (United Kingdom)
- Institut d'Hygiène et d'Epidémiologie, Brussels (Belgium)
- Institut für Spektrochemie und Angewandte Spektroskopie, Dortmund (Federal Republic of Germany)
- Kernforschungsanlage Jülich, Jülich (Federal Republic of Germany)
- Laboratory of the Government Chemist, London (United Kingdom)
- Max-von-Pettenkofer-Institut des Bundesgesundheitsamtes (BGA), Berlin (Federal Republic of Germany)
- Plasmon Dietetici Alimentari SpA, Milan (Italy)
- Rijksinstituut voor Volksgezondheid en Milieuhygiëne, Bilthoven (The Netherlands)
- Rijks-Kwaliteitsinstituut voor Land- en Tuinbouwprodukten (RIKILT), Wageningen (The Netherlands)
- Rijksuniversiteit Gent, Gent (Belgium)
- Risø National Laboratory, Roskilde (Denmark)
- The Agricultural Institute, Wexford (Ireland)
- The Animal and Grassland Research Institute, Maidenhead (United Kingdom)
- Universitaire Instellingen Antwerpen, Antwerpen (Belgium)
- Universität Regensburg, Institut für Chemie, Regensburg (Federal Republic of Germany)
- Vrije Universiteit Brussel, Brussels (Belgium)

METHODS USED

A wide range of sample pretreatment techniques was applied, including wet digestions with nitric, perchloric or sulphuric acid at atmospheric pressure boiling temperatures or in pressurised bomb, and programmed dry ashing.

Methods of final determination were:

Neutron activation analysis (Zn, Mn, Fe)
Cold vapour, flame or graphite furnace atomic absorption spectrometry (Cd, Pb, Cu, Zn, Fe, Mn)
Plasma emission spectrometry (Cu, Zn, Fe, Mn)
Voltammetric techniques (Pb, Cd, Cu)
Isotope dilution mass spectrometry (Pb, Cd, Cu, Zn)
Absorption spectrometry in solutions (Fe)

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NOTE

A detailed technical report on the analysis procedure and the treatment of the analytical data is supplied with each sample. Indicative values are given for: As, Ca, Cl, Cr, Hg, Mg, Na, Ni, P, K and Se.

Rue de la Loi 200, B-1049 Brussels — Telephone: 2355014 — Telegraphic address: «COMEUR Brussels» —
Telex: «21 877 COMEU B»

Annex 6: Experimental details

LabCode	SOP?	which SOP	sample pre-treatment	digestion step + acids used	extraction / separation step	instrument calibration
1	Yes	EN 13805 and EN 14083 for Pb and Cd resp. EN 13806 for Hg				
2	Yes	EN 14083				
3	No		After shaking and mixing for the homogeneity, one weighs of about 0.25 g of sample	Wet digestion; HNO3 + H2O2 in PFA tubes at 180 °C	none	Externe Standard Calibration
4	No		Dry ashing	dissolving the ash in diluted hydrochloric acid	Complexes of Pb and Cd with DDDC are extracted into MIBK	matrix mached calibration curve
5	No		0.5g of sample used	added 2ml of water, 4ml conc. nitric acid, 2ml hydrogen peroxide. Microwave digestion in closed vessels.	Added internal standard and made up to final volume of 200ml	Blank and 5 standards used (0.1-5ppb for Cd, Pb, 0.02-1ppb for Hg). 10ppb internal standard
6	Yes	National Feed Codex				
7	Yes	Slightly modified versions of NMKL method no 161 and no 170				
8	Yes	AOAC 999.10 (First Action)				
9	Yes	ASU L00.00-19/3				

LabCode	SOP?	which SOP	sample pre-treatment	digestion step + acids used	extraction / separation step	instrument calibration
10	Yes	A.O.A.C. Official Method 999.10, 2000, Pb,Cd,Zn,Cu,Fe in foods. AAS after microwave digestion				
11	No		dry ashing	with nitric acid	-	before all of the measurements is applied
12	No		0.5g in 5 ml 10% HNO3	High Pressure Microwave digestion in HNO3	High Pressure Microwave digestion in HNO3	Cd: wavelength 228.8nm, slit 0.7 low and lamp current 4 mA, Pb: wavelength 283.3nm, slit 0.7 low and 10mA
13	No		none (homogeneisation if necessary)	closed microwave system, nitric acid	none	linear calibration (2 - 5 - 10 - 20 and 50 µg/L)
14	No		Microwave	ac. nitric	no	yes
15	No		Drying and milling if necessary	Bombdigestion with conc nitric acid för 3 h at 160 degrees	none	Calibration with certified standard solutions
16	No		none	digestion with H2O2 (30%) , HF and HNO3 conc. by microwave high pressure(for Pb ,Cd); digestion with solfonitric mixture (H2SO4+HNO3 1:1) (for Hg)	none	add method ; std. solution 2ppb (for Cd), 50ppb (for Pb). Linear Method with std solution 10ppb 20 ppb 30ppb 40 ppb (for Hg)

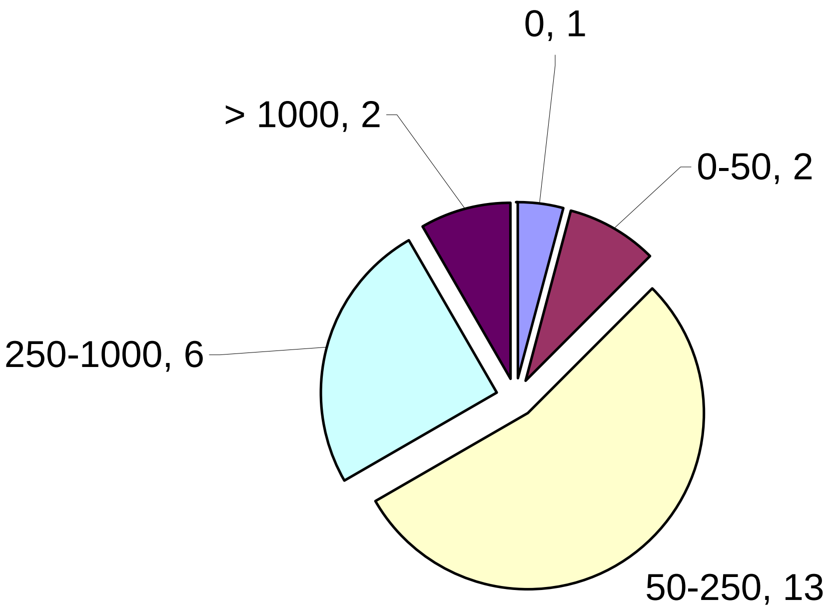
LabCode	SOP?	which SOP	sample pre-treatment	digestion step + acids used	extraction / separation step	instrument calibration
17	Yes	EVS-EN 13804:2002; EVS-EN 13805:2002; AOAC 999.11				
18	No		None	0.5g sample digested in 5ml nitric acid in quartz high pressure sealed vessels + microwave heating	None	External calibration using acid matched standards
19	Yes	AOAC				
20	No		Vigorous mixing of sample in its container	0.4 g subsampled and ashed in 4 mL of nitric acid using µ-wave assisted high pressure ashing (<70 bar)	none	mass calibration and abundance sensitivity routinely adjusted according to manufacturers manual
21	No		high pressure microwave digestion	nitric acid and perhydrol	no	0.5 1.0 2.0 5.0 10.0 20.0 µg/L
22	No		1g of sample	5 ml nitric acid suprapur ; 3 hours at 90 °C	adjust to 20 ml + filtration	Cd (0 to 10 µg/l) ; Pb (0 to 100µg/l) ; Hg direct calibration
23	Yes	78/633/EØF				
24	Yes	EN 14084				

Annex 7: Summary of laboratories participation in proficiency test exercises

LabCode	To which ILC do you participate?
1	Yes (not specified which one)
2	FAPAS, Trace Elements-National Food Administration, Sweden
3	FAPAS and CRL-ISS
4	FAPAS, CRL-ISS
5	FAPAS
6	UKZUZ, ISO standardization
7	NFA Trace elements in Food, FAPAS, CRL-ISS
8	CRL-ISS, NFA, FAPAS
9	IMEP, FAPAS, KIWA
10	Fapas
11	FAPAS interlaboratory comparisons
12	IAG, NJF
13	FAPAS, CRL, IAEA
14	FAPAS
15	International Plant Analytical Exchange Program IPE, Wageningen (WEPAL) NL
16	FAPAS; National Institute for Agricultural Quality Control; CEN TC 327
17	FAPAS, APLAC, IMEP
18	FAPAS, LEAP, CRL-ISS
19	FAPAS,IMEP,CRL-ISS,APLAC,NFA
20	FAPAS proficiency testing and EUs CRL in Rome
21	None
22	BIPEA elements traces
23	ALVA ring test and collaboratory studies in the Nordic Countries.
24	FAPAS, CHEK

Annex 8: Number of Samples analysed per year

(number of samples, number of laboratories)



European Commission

EUR 22663 EN – DG Joint Research Centre, Institute for Reference Materials and Measurements –
Report of the first interlaboratory comparison organised by the Community Reference Laboratory in Feed and Food: total Cd, Hg and Pb in a food matrix of plant origin
Authors:J. van de Kreeke, B. de la Calle, P. Robouch and P.D.P. Taylor
Luxembourg: Office for Official Publications of the European Communities
2006 – 34 pp. – 21 x 29.7 cm
EUR - Scientific and Technical Research series; ISSN 1018-5593

Abstract

The Institute for Reference Materials and Measurements (IRMM) of the European Commission's Directorate-General Joint Research Centre holds the Community Reference Laboratory for Heavy Metals in Feed and Food (CRL-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 first ILC of the new CRL-HM which focused on the determination of total Cd, Pb and Hg content (related to dry mass) in food of plant origin.

The test material used in this exercise was the Certified Reference Material (CRM) BCR-191, lyophilised brown bread. The material was rebottled to prevent recognition by the participants and dispatched in October 2006. Each participant received one sample containing 40 g of test material. There were 28 participants from 19 countries, 24 (i.e. 86 %) of which submitted results.

The assigned values for Cd and Pb were the certified values taken from the BCR 191 certificate. This certificate however provides no certified value for Hg; only an indicative value is given in the certification report. Since only eight participants reported values for Hg, with the rest of the participants giving only "smaller than" values or no values at all, no scoring is provided for this measurand.

The uncertainty of the assigned values was calculated by combining the uncertainty of characterisation and a contribution for between-bottle homogeneity (which was calculated from the certification report). Participants were invited to report the uncertainty on their measurements. This was done by most of the participants.

Laboratory results were rated with z and zeta scores in accordance with ISO 13528 . Standard deviations for proficiency assessment (also called target standard deviations) for Cd and Pb were calculated using the modified Horwitz equation.

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