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Interlaboratory Comparison Report

F. Cordeiro, I. Verbist, P. Robouch, T. Linsinger, M.B. de la Calle

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European Commission
Joint Research Centre
Institute for Reference Materials and Measurements

Contact information
Ms. Beatriz de la Calle
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/

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IMEP-26: Determination of Brominated Flame Retardants in Plastic

Interlaboratory Comparison Report

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Fernando Cordeiro (*a*)
Inge Verbist (*d*)
Piotr Robouch *(c)*
Thomas Linsinger (c)
Beatriz de la Calle (*b, c*)

(a) ILC coordinator, (b) IMEP programme coordinator,
(c) Technical / scientific support, (d) Logistic support

IMEP®

Summary

The Institute for Reference Materials and Measurements (IRMM) of the Joint Research Centre (JRC), a Directorate-General of the European Commission, operates the International Measurement Evaluation Programme® (IMEP). It organises interlaboratory comparisons (ILC's) in support to EU policies. This report presents the results of an ILC which focussed on the determination of total bromine, total sum of polybrominated biphenyls (PBB), total sum of polybrominated diphenylethers (PBDE), several individual brominated diphenylethers (BDE-47, BDE-99, BDE-183 and BDE-209) and decabrominated biphenyl (BB-209) in plastic.

The test material used in this exercise was the Quality Control (QC) material (IRMM-310) from the IRMM, a granulated poly(ethyleneterephthalate) (PET) fortified with commercially available brominated flame retardants (BFRs), namely technical mixtures of polybrominated diphenylethers and polybrominated biphenyls. To avoid easy recognition by participants, the material was relabelled and dispatched middle January 2011. Each participant received one bottle containing approximately 10 g of test material. Twenty-five laboratories from 15 countries registered to the exercise, from which 23 reported results.

For all measurands but BDE-183, the informative values provided by the IRMM-310 material producer were used as assigned values, as they were confirmed by expert laboratories. These values were based on two sources of information, namely the amount of technical mixtures added and the composition of the technical mixtures. While the amount added was known, no precise information on the composition of these mixtures was available. Technical mixtures from the same producers as those used for the preparation of the material but from different batches were available as certified reference materials (CRMs). The composition of these materials was used to calculate theoretical values. These values were confirmed by an earlier interlaboratory comparison exercise [1].
Due to the disagreement between these values for BDE-183, decision was taken not to provide any score for this measurand.

Participants were invited to report the uncertainty of their measurements. This was done by half of the laboratories. Laboratory results were rated with z- and ζ-scores (zeta-scores) in accordance with ISO 13528 [2]. The standard deviation for proficiency assessment was fixed to 25 % of the respective assigned value, by the advisory board of this ILC, on the basis of the estimated variability observed for the IRMM-310 material, on the observed variability (relative between-laboratory standard deviation) on previous ILCs

organized by our institute on an identical material [1, 3] and on the state-of-the-art in this field of analysis.

The outcome of the exercise illustrates the difficulties laboratories have to provide accurate values for the covered measurands; the share of satisfactory z-scores ranged between 61 and 88 %. There was a clear tendency to underestimate most of the measurands. The most influencing variables, leading to the observed variability and lack of trueness, were investigated.

Contents

1 Introduction

Brominated flame retardants are a group of organic compounds containing bromine which are capable of producing an inhibitory effect on the ignition of combustible organic materials such as textiles and plastics. They are extensively used in electronics, clothes and furniture. Despite their ubiquitous use, application has been regulated by the European Union due to the widely spread recognition of their environmental impact. BFRs are not strongly bound to the host polymer (plastic) and thus they are able to "bleed" from it, to become an environmental contaminant. The European Commission Directive 2002/95/EC on the restriction of the use of certain hazardous substances in electrical and electronic equipment (RoHS) [4] bans the use of certain polybrominated flame retardants in electric and electronic devices from 1 July 2006 unless no technical substitutes exist. Moreover, the European Regulation 850/2004 [5] implementing the Stockholm Convention on persistent organic pollutants (POPs) and the Commission Decision 2005/618/EC [6] sets the maximum limits for the total sum of polybrominated biphenyls (PBB) and polybrominated diphenylethers (PBDE) to 0.1 % by weight (w/w). These restrictions have been confirmed by the EU Regulation 756/2010 [7].

Brominated flame retardants are of paramount interest for legislators and thus for the analytical chemical community.

In 2007, a proficiency test (PT) was organized to test the measurement capabilities of laboratories to determine brominated flame retardants in plastic [1]. The outcome of that PT indicated "*a clear need for a learning process among the laboratories involved*". This conclusion was based on the fact that the observed relative between-laboratory standard deviations ranged from 22 to 61 % for the different BFRs congeners. A significant improvement was achieved in the certification exercise of two polymer based test materials where the observed relative between-laboratory variability ranged from 3 to 12 % [3]. This analytical achievement led to the certification of two materials being certified for the determination of several BFRs in 2009 [3].

The present work reports the outcome of a proficiency test exercise (IMEP-26) aimed to estimate the actual analytical performance of laboratories involved in checking the compliance of European legislation regarding the use of polybrominated flame retardants in plastic.

2 IMEP support to EU policy

The International Measurement Evaluation Programme® is owned by the JRC - IRMM. IMEP provides support to the European measurement infrastructure in the following ways:

- IMEP **distributes metrological traceability** from the highest level down to the routine laboratories. These laboratories can benchmark their measurement result against the IMEP reference value. This value is established according to metrological best practice.

- IMEP helps laboratories to assess their estimate of **measurement uncertainty**. The participants are invited to report the uncertainty of their measurement result. IMEP integrates the estimate into the scoring, and provides assistance for the interpretation.

IMEP supports EU policies by organising interlaboratory comparison exercises (ILCs) in the frame of specific EU legislation, or on request of a specific Directorate-General. IMEP-26 provided specific support to the following stakeholders:

- To the European Co-operation for Accreditation (EA) in the frame of a formal collaboration on metrological issues, including the organisation of intercomparisons. National accreditation bodies were invited to nominate a limited number of laboratories for free participation in IMEP-26. Mr. Paul Greenwood from the United Kingdom Accreditation Service (UKAS) liaised between EA and IMEP for this intercomparison. This report does not discern the EA nominees from the other participants. Their results are however summarised in a separate report to EA.

- To the Asia Pacific Laboratory Accreditation Cooperation (APLAC), in the frame of the collaboration with EA. The chair of the APLAC Proficiency Testing Committee, Mr. Daniel Tholen, was invited to register a limited number of laboratories for this collaboration.

- To the Directorate-General Enterprise and Industry (DG ENTR)
- To the Directorate-General Environment (DG ENV)

IMEP-26 supports the activities of the two above mentioned European Commission Directorates on their role of drafting the European legislation on the restriction of hazardous substances in electrical and electronic equipment (RoHS, Directive 2002/95/EC) [4] and its amended version [6] and on the environmental and human health protection regarding some persistent organic pollutants, Regulations (EC) 850/2004 and (EC) 756/2010 [5, 7].

3 Scope

The scope of IMEP-26 is to assess the analytical performance of laboratories involved in the implementation of the European Directive on the restriction of the use of certain hazardous substances in electrical and electronic equipment (RoHS) (Directive 2002/95/EC) and Decision 2005/618/EC [4, 6] and on the legislation after the Stockholm Convention on Persistent Organic Pollutants (POPs) (Regulations (EC) 850/2004 and 756/2010) [5, 7].
The assessment of the measurement results is undertaken on the basis of requirements laid down in the above mentioned EU legislation and follows the administrative and logistics procedures of IMEP. This programme is accredited according to ISO Guide 43-1 [8].

4 Time frame

The ILC was announced to EA and APLAC on 1st October 2010. The exercise was also made public on the IRMM webpage [9].

Initially the registration deadline was set on 15th November 2010. However, the number of registered laboratories at that date was considered unsatisfactory. A second announcement was sent to APLAC and EA at the end of October 2010, and the ILC exercise was announced to laboratories having participated in similar exercises previously (both announcements made on 29th October 2010). The registration period was extended to the 15th December 2010.
Samples were sent out to the laboratories on 13-14th January 2011. The deadline for reporting results was 25th February 2011.

5 Invitation, registration and sample distribution

Invitations for participation were sent to the EA coordinator (Annex 1) to the APLAC responsible (Annex 2) for distribution to nominated and interested laboratories and to EC DG ENV (Annex 3). The web announcement on the IRMM website can be found in Annex 4.

A letter containing instructions on measurands, sample storage conditions, number of measurements, individual access code for the result reporting website and further details on the envisaged time frame was sent to the participants together with the samples (Annex 5).
Figure 1 shows the distribution of participating countries.

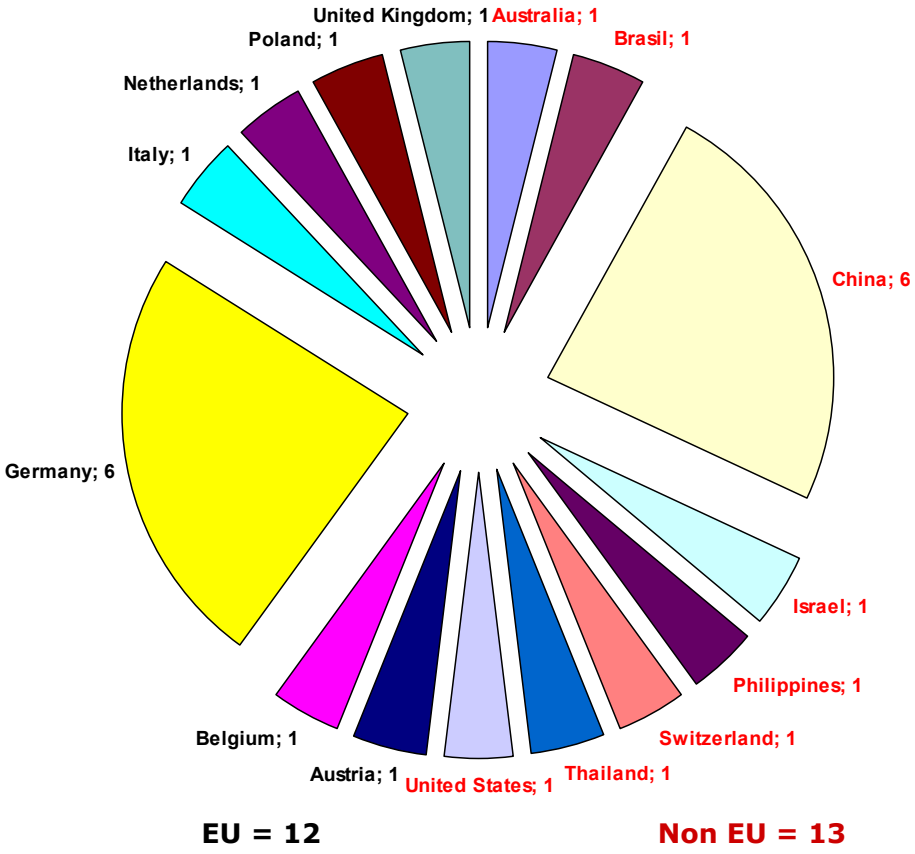


Fig 1- Country distribution in IMEP-26

5.1 Confidentiality

EA was invited to nominate laboratories for participation. The following confidentiality statement was made to EA: "*Confidentiality of the participants and their results towards third parties is guaranteed. However, IMEP will disclose details of the participants that have been nominated by EA to the EA working group for ILCs in Testing. The EA accreditation bodies may wish to inform the nominees of this disclosure.*"

5.2 Sample distribution

The ILC samples were dispatched by IRMM on 13-14 January 2011 to the participants. Each participant received:

- One bottle containing approximately 10 g of test material,
- An accompanying letter with instructions on sample handling and reporting (Annex 5)

- A form that had to be sent after receipt of the test material to confirm its arrival (Annex 6).

The dispatch was followed by the messenger's parcel tracking system on the internet by the ILC coordinator and in all cases the samples were delivered within a week.

5.3 Procedure to apply

Clear instructions were given to participants. The measurands were defined as "*Total bromine, total sum of polybrominated biphenyls (PBBs) and total sum of polybrominated diphenylethers (PBDEs) as well as mass fraction of several specific brominated diphenylethers (BDE-47, BDE-99, BDE-183 and BDE-209) and decabrominated biphenyl (BB-209)*".

Laboratories were asked to use the method that they normally apply for their routine analysis, to perform two or three independent measurements and to report:

- The mean of the results,
- The uncertainty associated to the mean,
- The coverage factor,
- The technique used to perform the measurements.

The results were to be reported in the same manner (e.g. number of significant figures) as those normally reported to customers and using a special on-line form for which each participant received an individual access code. A special questionnaire was attached to this on-line form. The questionnaire was intended to provide further information on the measurements and the laboratories (Annex 7).

6 Test material

6.1 Preparation

The material used for this ILC exercise was a poly(ethyleneterephtalate, PET) with added PBDEs and PBBs at the levels of interest for the compliance with the RoHS Directive [4, 6]. The material was produced for the ILC held in 2007 [1] and was subsequently been made available as quality control material under the name of IRMM-310. Following the release of two certified reference materials for BFRs in polymers (ERM-EC590, ERM-EC591) by IRMM [10], the distribution of the material was stopped in February 2009. The material was re-labelled to avoid identification by participants.

6.2 Homogeneity and stability

The experimental design used for the assessment of the homogeneity of the test sample complies with the requirements set by the ISO 13528 [2] prescribing tests to determine whether the samples are to be considered adequately homogeneous to be used in a proficiency testing (PT) exercise. These tests compare the between bottle standard deviation with the target standard deviation of a PT. The target standard deviation was set to 25 % of the averaged mean obtained from the homogeneity studies for each measurand. The test indicates that the test material was sufficiently homogeneous for the purpose of this PT (Annex 8).

The between bottle relative standard uncertainty (u_{bb}, in %) estimated via one way ANOVA [11] using the SoftCRM software [12] ranged from 0.4 % to 1.1 % for all BFR congeners and 2.1 % for the total bromine content.

Even though the material was considered adequately homogeneous, uncertainties related to possible between-bottle variation (u_{bb}) were included in the combined uncertainty of the assigned value.

Considering the stability of similar test materials, demonstrated in the frame of the long term stability programme of the IRMM reference materials unit, it was assumed no further studies should be carried out on the selected test material.

6.3 Reference values and their uncertainties

To check whether the informative values provided in the information sheet of the quality control material could be used as assigned values (X_{ref}) for this exercise, three expert laboratories, performed analysis on the test material.

The expert laboratories involved in the establishment of the assigned values were:

- Vlaamse Instelling Voor Technologisch Onderzoek (VITO, Belgium)
- TÜV Rheinland Taiwan Ltd (Taiwan)
- Belgian Nuclear Research Centre (SCK/CEN, Mol, Belgium, only for total bromine).

The experts were asked to use an analytical method capable of delivering a maximum intermediate precision up to 10 %. Laboratories were also asked to report their results together with the measurement uncertainty and a description of the method they used. The means reported by the expert laboratories and their associated standard uncertainties (u_{exp}) are shown in Table 1. For comparison, the informative values provided by the IRMM-310 information sheet, are also included in Table 1. The uncertainties provided in the

information sheet of the QC material represent the expanded uncertainties (U) with a coverage factor k = 2, corresponding to a level of confidence of about 95 %.

The methods applied by the expert laboratories are summarised in Table 2.

Table 1 - Values for the measurands and their associated expanded uncertainties (U, k = 2) as reported by the expert laboratories (all values in mg kg^{-1}) compared to the IRMM-310 informative values; values for BFRs for IRMM-310 are based on the mass and assumed composition of BFRs added; total Br for IRMM-310, and for SCK/CEN are based on measurements by neutron activation analysis using k_0-internal standardisation.

Measurand	VITO	TÜV Taiwan	SCK/CEN	IRMM-310
	Mean ± U	Mean ± U	Mean ± U	(X ± U)
Total Br	1407 ± 225	1600.1 ± 245	**2245 ± 110**	**2300 ± 120**
Sum of PBDEs	**1507 ± 452**	806.9 ± 7.2		**1800 ± 136**
Sum of PBBs	**825 ± 297**	323.0 ± 7.2		**700 ± 110**
BDE-47	**226 ± 17**	130.3 ± 3.4		**227 ± 25**
BDE-99	**320 ± 45**	168.0 ± 6.2		**307 ± 31**
BDE-183	94 ± 18	40.2 ± 1.4		150 ± 17
BDE-209	**728 ± 160**	339.6 ± 9.2		**689 ± 128**
BB-209	**781 ± 281**	323.0 ± 7.2		**700 ± 110**

Table 2 - Methods used by the expert laboratories

Certifier	Sample treatment and procedure	Detection
VITO	HR-ICP-MS after high pressure asher for total bromine and HR-GC-MS for the other BFRs congeners were used. • For total Br: 0.250 g was weighed, 1 ml of 1 M $AgNO_3$ solution, 4 ml of HNO_3 and 0.5 ml of H_2O_2 were added. The silver ion binds the bromine present forming a precipitate, which is washed several times with 25 ml of Milli-Q water and brought into solution with NH_3. The ^{79}Br isotope is used to measure the total bromine content. The calibration of the HR-ICP-MS system was made using standard solutions of known bromine content (ranging from 0 to 250 µg l^{-1}). • For PBBs and PBDEs: The test sample is cryogenically grinded in a centrifugal grinding. 0.5 g of test material was weighed to a Soxhlet extractor. 60 ml of toluene is added. 25 µl of extracted solution is transferred to an injector vial, 25 µl of PBDEs and 50 µl of PBBs internal standard solutions (isotopically labelled) are added. 1 µl of the extract is injected (splitless mode). Calibration of the GC system is performed by injecting 2 calibration solutions containing the native (purified PBBs and PBDEs) and the internal standards.	MS (SIM mode)

Certifier	Sample treatment and procedure	Detection
TÜV Taiwan	Samples were extracted with organic solvent (toluene) and analyzed by GC-MS. • For total Br, PBBs and PBDEs; Plastic samples were cut to a particle size of 2 mm or less. Weighed 0.5 g of material, 10 ml toluene is added (spiked with 1 mg l^{-1} PCB 209 as internal standard). The vial is shacked by hand and placed in the heating block at 100 °C for 2 H. The hot vial is placed ona shaker at 300 l min^{-1} for 10 min. The heating process is continued for another 2 H. An injection volume of 2.0 µl is used. Several PBBs and PBDEs standard solutions were used as calibrants. The ERM-EC591 was used as matrix matched CRM for method validation. For the total Br BCR-680 was used.	MS (SIM mode)
SCK/CEN	Neutron activation analysis with K_0 internal standardisation	K_0NAA

6.3.1 Total bromine

The IRMM-310 informative value for total Br was based on measurements made by neutron activation analysis with k_0 internal standardisation (k_0NAA). The validity of this method for determining Br in polymers has been demonstrated by the certification of other polymer materials [10]. This value was further confirmed by a third expert laboratory (SCK-CEN) using k_0NAA. Its reported value agreed with the informative value from IRMM-310, which was then used as the assigned value for the total Br for this PT exercise The values reported by VITO and TÜV were significantly lower, due to, most probably, inadequate sample preparation.

VITO used high resolution-inductively coupled plasma – mass spectrometry (HR-ICP-MS for total Br and TÜV Taiwan used gas chromatography coupled with mass spectrometry (GC-MS). VITO recurred to isotopically labelled internal standards for system calibration. Test samples were destroyed in a high pressure asher (for a more comprehensive description, refer to Table 2).

6.3.2 BFRs congeners

VITO used high resolution GC-MS for all the BFRs congeners. Isotopically labelled internal standards were used as calibrants for the total Br and for the PBBs and PBDEs congeners. Test samples were cryogenically grinded and test solutions were extracted using Soxhlet extraction.

TÜV Taiwan cut the sample into small pieces. It was then shaken manually after the addition of organic solvent (toluene) so that the test samples were neither grinded nor underwent Soxhlet extraction (or any other sort of instrumental extraction technique). Moreover, isotopically labelled internal standards were not used as calibrant standard solutions. Results from this expert laboratory were generally (see Table 1) significantly lower than the ones reported by VITO, as well as the IRMM-310 informative values.

6.3.3 Understanding the differences

The importance of an efficient extraction is strongly underlined by the IEC/FDIS 62321 standard method, whereby Soxhlet extraction (or other instrumentally assisted extraction technique) is recommended to be used in the determination of PBBs and PBDEs in polymers by GC-MS [13]. Furthermore, the standard recommends grinding of the sample as a way to increase the extraction efficiency. The PT carried out in 2007 [1] using IRMM-310 as test material and the multivariate data analysis performed on the results reported in the present project identified grinding and Soxhlet extraction as critical parameters to obtain reliable results in the analysis of PBBs and PBDEs.

VITO applied Soxhlet extraction and grinded the test sample, as prescribed by IEC/FDIS 62321. TÜV Taiwan, on the contrary, declared to have followed IEC/FDIS 62321 but did not apply Soxhlet extraction nor grinded the samples. Therefore, results from TÜV Taiwan were not used to establish the assigned values.

Since all the values contained in the IRMM-310 informative sheet, except BDE-183, have been confirmed by at least one expert laboratory using, either a primary method of analysis for total Br (K_0NAA), or isotopically labelled internal standards for PBBs and PBDEs, the decision was taken to use the IRMM-310 values as assigned values for IMEP-26.

Due to the discrepant results between the expert laboratories and the IRMM-310 informative value for BDE-183, no assigned value was established. No scoring was provided to results reported for this BFR congener.

The assigned values for this ILC exercise, combined uncertainties (calculated combining characterization and homogeneity contributions, according to equation 1 and the standard deviation for the proficiency test assessment ($\hat{\sigma}$) are shown in Table 3.

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

Where: u_{ref} is the standard uncertainty for the assigned value

u_{char} is the standard uncertainty as provided in the IRMM-310 information sheet

u_{bb} is the standard uncertainty estimated from homogeneity studies

These combined uncertainties were afterwards expanded using a coverage factor of 2, which gives a level of confidence of, approximately 95 %.

Table 3 - Assigned values and their associated expanded uncertainties for the measurands of this ILC (all values in mg kg^{-1})

Measurand	X_{ref}	U_{ref}	$\hat{\sigma}$ (25%)
Total Br	2300	136	575
Total PBDE	1800	136	450
Total PBB	700	110	175
BDE-47	227	25	56.8
BDE-99	307	31	76.8
BDE-209	689	128	172
BB-209	700	110	175

X_{ref} is the reference value and U_{ref}= k·u_{ref} is the estimated associated expanded uncertainty; with a coverage factor k= 2 corresponding to a level of confidence of about 95 %. The value within brackets refer to the percentage of X_{ref} taken to estimate $\hat{\sigma}$.

7 Evaluation of results

7.1 General observations

From the 25 laboratories that registered 23 submitted results and completed the associated questionnaire. Of the 23 participants, only 8 reported values for total bromine, and 21 laboratories reported results for BFRs. From these results, those reporting "less than" values were not included in the evaluation. This was the case for laboratory L05 for total Br and for the total sum of PBBs.

Relative between-laboratory standard deviations ranged from 48 to 68 %. Those values should be compared with previously obtained values for the ILC exercise carried out in 2007 [1] using the same test material, where they ranged from 22 to 61 % and to the certification exercise where those figures ranged from 3 to 12 % [3]. It is not realistic that the performance of the carefully selected laboratories in the certification campaign can easily be repeated; the performance achieved in the interlaboratory comparison exercise in 2007 should be considered as a realistic target. The figures obtained in IMEP-26 clearly indicate that the performance of laboratories did not improve since 2007, even though all participants declared having a quality system in place.

7.2 Scores and evaluation criteria

Individual laboratory performance is expressed in terms of z- and ζ-scores in accordance with ISO 13528 [2].

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

$$\zeta = \frac{x_{lab} - X_{ref}}{\sqrt{u_{ref}^2 + u_{lab}^2}} \qquad \text{Eq. 3}$$

Where:
- x_{lab} is the measurement result reported by a participant
- X_{ref} is the 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 test assessment

Both scores can be interpreted as:

- Satisfactory result for |score| ≤ 2,
- Questionable result for 2 < |score| ≤ 3,
- Unsatisfactory result for |score| > 3

The z-score compares the participant's deviation from the reference value with the target standard deviation for the 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 25 % of the assigned value for each of the measurands.
Metrologicaly speaking, z-scores are the same as zeta scores assuming a maximum acceptable standard uncertainty of $\hat{\sigma}$.

Should participants feel that these σ values are not fit for their purpose they can recalculate their scorings with a standard deviation matching their requirements.

ζ scores are more valuable than z-scores, as they take both parts, i.e. mean value and its uncertainty into consideration. The ζ-score states if the laboratory result agrees with the assigned value within the respective uncertainties, i.e. if the laboratory is able to assess the reliability of its results correctly. The denominator of its equation 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 the measurement result, the expected value (assigned value), its uncertainty as well as the uncertainty of the reported values. An unsatisfactory ζ-score can either be caused by an inappropriate estimation of the mass fraction or of its uncertainty.
It is a well-established fact that uncertainty estimation is not trivial. Therefore an additional assessment was given as an indication of the plausibility of its uncertainty estimate for each laboratory providing an uncertainty. The standard uncertainty (u_{lab}) is most likely to fall in a range between a minimum uncertainty (u_{min}), and maximum allowed uncertainty (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 accepted for the PT, $\hat{\sigma}$. If u_{lab} is smaller than u_{min}, the laboratory might have underestimated its uncertainty. However, 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 derived from the homogeneity and stability studies. If those are large, measurement uncertainties smaller than u_{min} are possible and plausible. If $u_{lab} > u_{max}$, the laboratory might 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 it 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 standard uncertainty of the laboratory (u_{lab}) was calculated dividing the reported expanded uncertainty by the reported coverage factor (*k*). 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 / CITAC [14]. When no uncertainty was reported, it was set to zero ($u_{lab} = 0$).

7.3 Laboratory results and scorings

The results as reported by the participants are summarised in Annexes 9 to 16. A table of the results and their graphical representation are provided. The tables also contain z-, ζ-scores and the uncertainty estimation. Laboratory codes were given randomly. The plots

display all measurement results and their associated uncertainty. The uncertainties are shown as reported, with various expansion factors (k) and levels of confidence.

Annexes 9 to 16 also includes the distribution of all data as Kernel density plots, which are an alternative to histograms and a useful method to represent the overall structure of a data group, highlighting sub-populations. The software used to calculate Kernel densities was provided by the Statistical Subcommittee of the Analytical Methods Committee (AMC) of the Royal Society of Chemistry [15].

The outcome of the exercise regarding the z- and ζ-scores are summarised in Fig. 2. The percentage of satisfying z-scores ranged between 61 % and 88 %. The share of satisfactory ζ-scores is smaller than for the z-score and ranged between 33 % and 50 %. Shares of unsatisfactory ζ-scores range between 45 % (BDE-209) and 63 % (Total Br). This shows that laboratories are largely unable to correctly assess the reliability of their measurements, which leads to a significant risk of both false-negative and false positive decisions (for this particular exercise, mostly false negative decisions). Furthermore, the share of participants having a satisfying both z- and ζ-score is between 33 % (Sum of PBDEs, Sum of PBBs and BB-209) and 50 %, (BDE-209) the majority of the measurands having this value around 40 %.

Regarding the reported uncertainties Annexes 9-16 shows that the majority of the participants underestimated their measurement uncertainty. The percentage of participants having reported an uncertainty for which the qualitative criteria "b" ($u_{lab} < u_{ref}$) was met, was found to range from 71 to 89 % whereas the qualitative criteria "a" ($u_{ref} < u_{lab} < \hat{\sigma}$) was only found by a percentage of participants which ranged from 11 to 29 %. No participant overestimated the uncertaintyfor all measurands.

Only 60 % of the participants reported an uncertainty associated with their measurement results, despite the fact that estimation of uncertainties is a requirement of ISO 17025, and that 75 % of the laboratories claimed providing uncertainty statements to their customers. For unknown reasons, laboratories did not follow their usual practice of providing uncertainties in this interlaboratory comparison. From the participants who submitted an uncertainty with their results, 2 did not give a value for the coverage factor.
The following information regarding coverage factors can be found in the web page of the National Institute of Standards and Technology (NIST): *"In general, the value of the coverage factor k is chosen on the basis of the desired level of confidence to be associated with the interval defined by* $U = ku_c$*. Typically, k is in the range 2 to 3. When the normal distribution applies and* u_c *is a reliable estimate of the standard deviation of a*

measurement, U = 2 u_c (i.e., k = 2) defines an interval having a level of confidence of approximately 95 %, and U = 3 u_c (i.e., k = 3) defines an interval having a level of confidence greater than 99 %" [16]. Participants who are not familiar with uncertainty estimations are advised to read the EURACHEM / CITAC Guide [14].

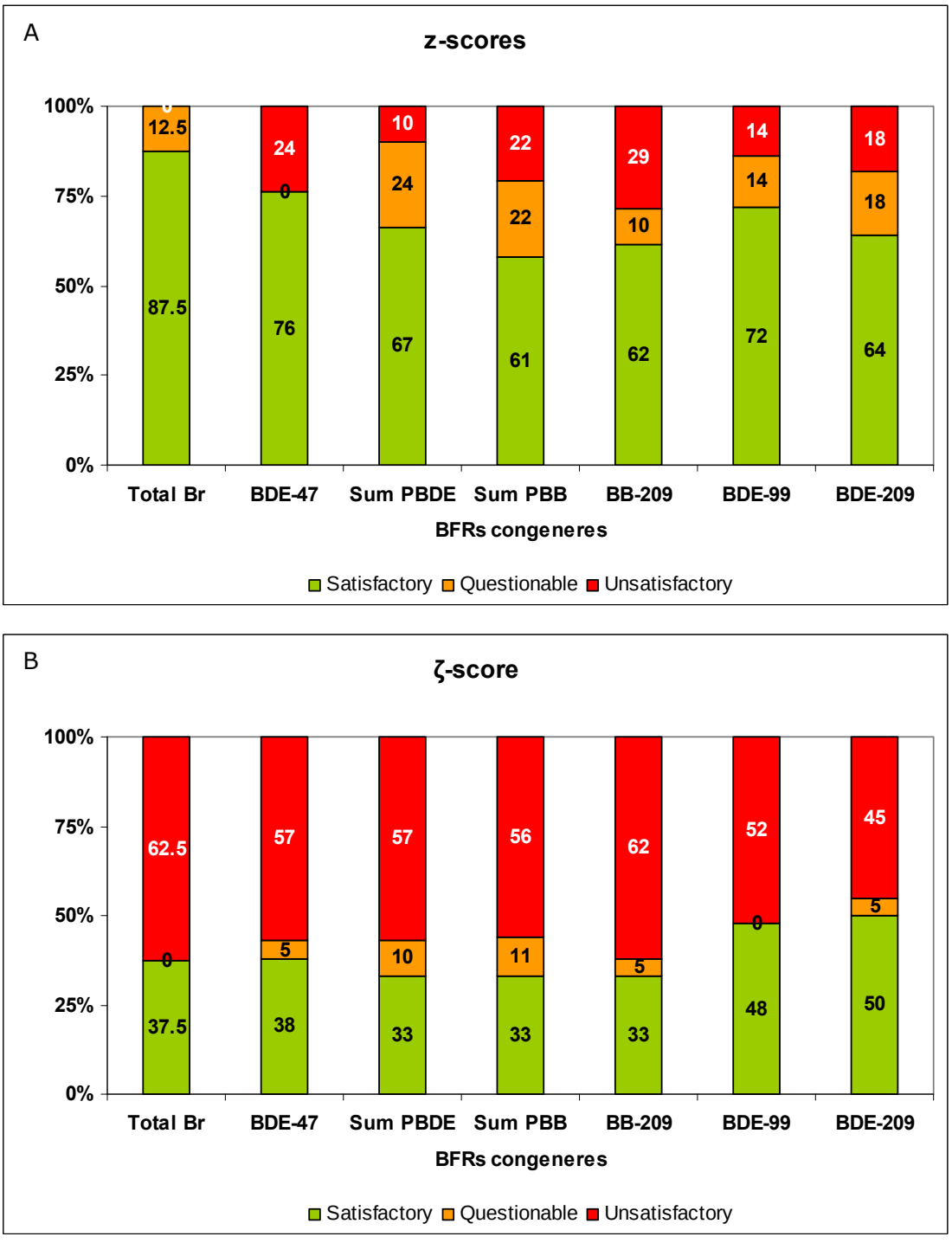


Fig 2 - Overview of scores: A) z-score, B) ζ-score

7.3.1 Bimodal distribution of the results

A bi-modal distribution was observed for almost all BFRs congeners when looking at the Kernel density plots (Annexes 9 to 16, exception for BDE-47 and for the total sum of PBBs, where only a large distribution can be observed). It appears that, for most of the BFRs congeners two populations can be identified, one of them showing an average which agrees with the IRMM-310 informative value while the other has an average value which is roughly half of it.

As an attempt to identify the reasons for such discrepancies between the reported values, the answers to the questionnaire (Annex 7) were scrutinized.

Instead of the traditional approach whereby each question needs an independent statistical scrutiny for its influence on the performance level of each participant (procedure extensively followed in [1, 3]) a holistic approach was selected, making use of multivariate statistical models. Projection to latent structures-regression models, PLS-R, (using The Unscrambler 9.8 CAMO Software AS, OSLO, Norway) for each BFR congener (except for total Br where the reduced number of reported values made it irrelevant), were performed, aiming at identifying and quantifying the multivariate relationship between the answers to the questionnaire (transformed into categorical variables, or X-variables) and the laboratory performance expressed as the z-score (as Y-variable).

All PLS-R models were cross-validated recurring to 5 randomly selected segments among all the observations. The models succeeded to "capture" most of the structured information among the data (the percentage of the total explained covariance between the X- and the Y-data ranged from 79 to 92 %). Each model had an estimated model error lower than the experimental variability (expressed as the standard deviation for each corresponding Y-data (z-score)).

Table 4 presents the summary of the model performance characteristics and the list of the most influencing X-variables. Figure 3 illustrates one PLS-R model (taking z-score for BDE-209 as example). The score plot (Fig. 3A) provides the sample patterns allowing the identification of any clustering among the calculated z-scores, while the loading plot (Fig. 3B) illustrates the interrelationship among all the X-variables and their relationship with the corresponding z-score. It enables the identification of the X-variables which have the biggest influence in the PLS-R model (also highlighted in Table 4) ultimately providing reasons for the observed bimodality of the distributions.

Table 4 shows that the same questions consistently appear as influencing parameters for all the BFRs congeners. The most positively influencing parameters (the majority of the laboratories having answering yes to these questions got a higher z-score, i.e. their reported values were satisfactorily located around the assigned value) are:

i) Grinding the test samples (Q 15),
ii) The extraction technique used (either Soxhlet (Q 12a) or ultrasonic (Q 12c)),
iii) The use of GC-MS (as opposed to GC-HRMS, GC-ECD or HPLC-UV-FLD),
iv) Carrying out this type of analysis regularly (Q 23),
v) Taking part in interlaboratory comparisons for this type of analysis (Q 20),

Other z-score positively related influencing answers, for some particular BFRs congeners were the use of a cross check between the measured BFR mass fraction and the total Br mass fraction for QC purposes (BDE-47), the use of special UV protection (to prevent any sample degradation) which was identified for total PBBs, BB-209 and BDE-99, and the use of BDE-206/BDE-209 ratio as quality control to check for degradation of BDE-209 (Q 19), which, obviously applies to BDE-209.
Furthermore, the majority of the participants using isotopically labelled internal standards, got a satisfactory z-score.

Similarly, the most consistently negatively influencing parameters (the majority of participants having answered yes to these questions got a lower z-score, i.e., their reported values are clustering around the lower distribution) are:

i) The use of static extraction (Q 12d) and,
ii) The use of long (30-50 m) GC columns (Q 07).

Additionally, it was found that the 15 participants that did not follow IEC / FDIS 62321:2008 [13], reported lower values for BB-209 than those that did. It must be recalled that TÜV Taiwan claimed to have followed the above mentioned standard method when in reality it deviated significantly from it (e.g. no Soxhlet extraction, nor any grinding for the test sample were used).

It should be noted, however, that due to the high interlaboratory variability observed during the writing of the above mentioned international standard, the method for BFRs was defined as an informative annex only. Additionally, the standard provides a list of commercially available calibration BFRs congeners which can be considered suitable for these analyses. However, the calibration standards, considered suitable for the analysis, are listed in the Standard without any considerations for their minimum required purity. Moreover, the use of matrix matched certified reference materials should also be considered to improve the state of the art in this field (ERM-EC590 and ERM-EC591).

It is worthwhile to recall that the effect of several experimental parameters were also investigated on the first interlaboratory comparison exercise [1], such as the use of common standard solutions, the application of a standard method or other method related parameters, e.g., grinding test samples to less than, bigger or equal to 0.5 mm, were all not identified as capable to introduce any significant differences among the participants. On the other hand, for the certification exercise [3], several effects were identified as significant, thus some recommendations were provided to the participants. Giving an example, the use of short (10-15 m) analytical columns for PBDEs and, in particular, for BDE-209 was recommended. This experimental parameter aimed to reduce the residence time of the high BRFs congeners, hence reducing its potential degradation during analysis. These findings were confirmed by the results submitted to IMEP-26.

Final comments made by participants are listed in table 5.

Table 5 – Final comments as reported by the participants

Lab ID	Do you have any comments? Please let us know: …
L01	This sample contained significantly higher PBDE levels than our routine samples
L05	Answer to question no. 3 (non-clickable option): GC-quadrupole-MS
L06	Question 3) b) quadrupole MS. Question 5) We use split/splitless Injector in splitless mode
L08	What's meaning about
L09	Our laboratory has not instrumentation to make full range of tests required by Interlaboratory Comparison
L10	1) Our quantification technique is GC-quadrupole-MS. 2) We don't understand the meaning of 23.1. What's meaning about "food category"? Is it QC sample? Our QC sample is tested every 10 sample.
L13	ECD was used since GC-MS system had permanent errors
L17	Apologies for late data submission. Our HPLC is still under repair - ideally would like to analyse Deca species by HPLC to minimise thermal decomposition.
L22	Nil

Table 4 PLS-R model performance characteristics and list of most influencing questions from the questionnaire

Measurand	Explained variance [a] (%)	Model error (RMSEC)[b]	Observed variability [c]	Most influencing answers from the questionnaire (X-variables)	
				Negatively correlated with the z-score (The majority of the participants having responded Yes to these questions have generally lower (<) z-scores) (Left mode in Fig. 3)	**Positively correlated with the z-score** (The majority of the participants having responded Yes to these questions have generally higher (>) z-scores) (Right mode in Fig. 3)
Total PBDEs	**89**	**0.57**	**1.87**	**Q 07: Longer columns used** **Q 18: The correctness of the calibration curves was checked with independent standards from another supplier** **Q 22: Apply a recovery factor to correct their** measurements	Q 15: Samples grinded Q 19: BDE-206/BDE-209 ratio used as quality control to check for degradation of BDE-209 Q 20: Take part in ILCs for this type of analysis on a regular basis Q 23: Carry out this type of analysis regularly
Total PBBs	**84**	**0.73**	**1.97**	**Q 07: Longer columns used** **Q 18: The correctness of the calibration curves was checked with independent standards from another supplier** **Q 22: Apply a recovery factor to correct their measurements**	Q 15: Samples grinded Q 16: Apply special UV protection
BDE-47	**92**	**0.36**	**1.31**	**Q 12d: Static extraction used** **Q 18: The correctness of the calibration curves was checked with independent standards from another supplier** **Q 22: Apply a recovery factor to correct their measurements**	Q 15: Samples grinded Q 17: Perform a cross-check between the BFR mass fraction and the total Br for QC purposes Q 23: Carry out this type of analysis regularly
BDE-99	**88**	**0.45**	**1.41**	**Q 07: Longer columns used** **Q 12d: Static extraction used** **Q 22: Apply a recovery factor to correct their measurements**	Q 12c: Ultrasonic used as extraction technique Q 15: Samples grinded Q 16: Apply special UV protection
BDE-209	**85**	**0.68**	**1.82**	**Q 07: Longer columns used** **Q 18: The correctness of the calibration curves was checked with independent standards from another supplier** **Q 22: Apply a recovery factor to correct their measurements**	Q 12a: Soxhlet used as extraction technique Q 15: Samples grinded Q 20: Take part in ILCs for this type of analysis on a regular basis Q 23: Carry out this type of analysis regularly
BB-209	**79**	**0.74**	**1.73**	**Q 07: Longer columns used** **Q 14: A standard method was followed** **Q 18: The correctness of the calibration curves was checked with independent standards from another supplier** **Q 22: Apply a recovery factor to correct their measurements**	Q 04: Higher injection temperature used Q 15: Samples grinded Q 16: Apply special UV protection

[a] *Using the first 3 PLS components*

[b] *RMSEC refer to root mean square error (a measurement of the average difference between predicted and measured response (z-scores) values, using the first 3 PLS components)*

[c] *Expressed as 1 standard deviation for all the calculated z-scores for each measurand*

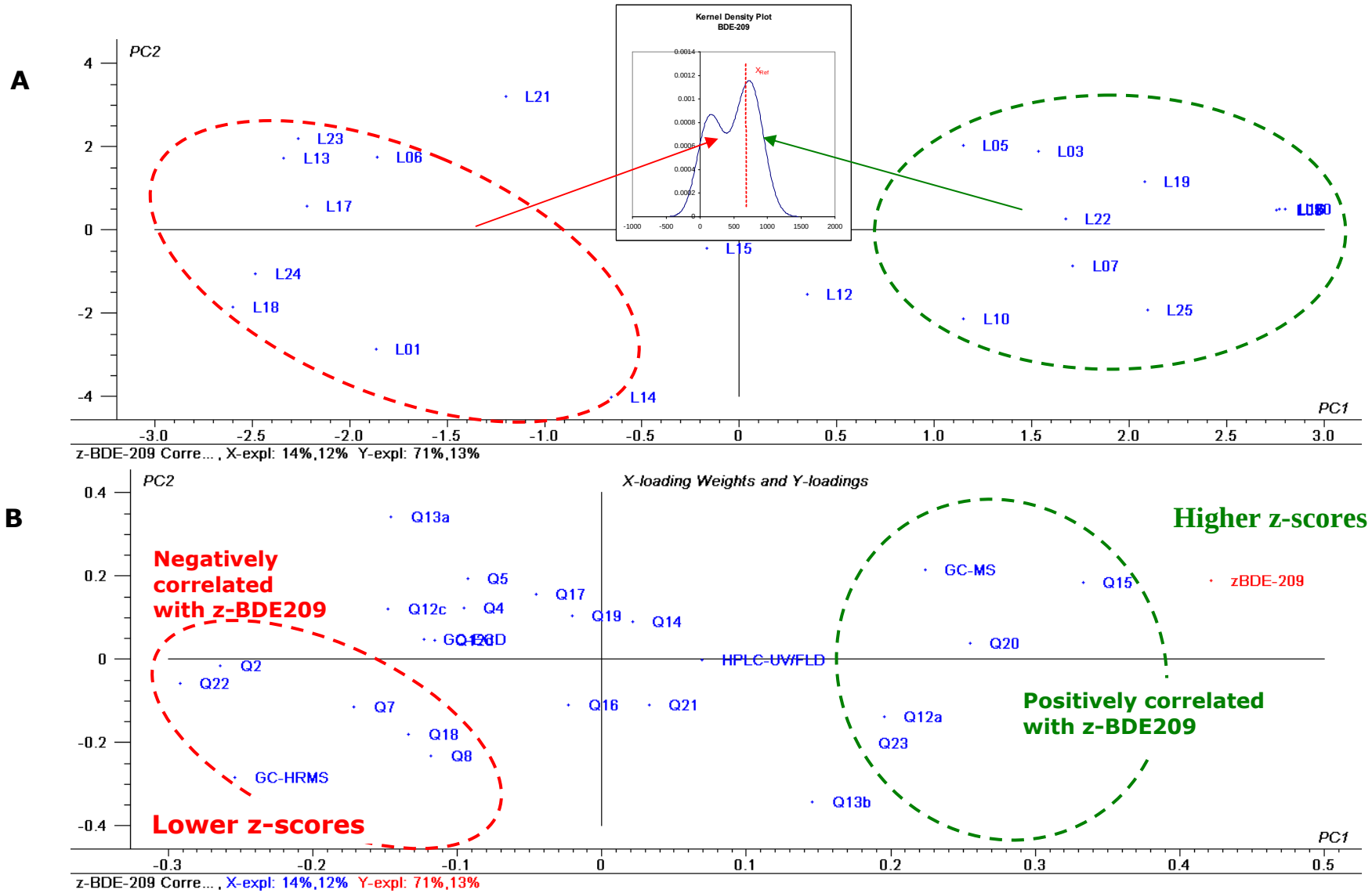


Fig 3 – Score (A) and loading (B) plot for the PLS-R model relating all answers to the z-BDE-209 value. Only the two first PLS components are shown. The model identifies the data bimodality and explains which X-variables are mostly responsible for it.

8 Conclusion

From the results submitted to IMEP-26 we must conclude that the analytical capabilities in routine laboratories for all brominated flame retardants congeners in general still requires further improvement. This leads to the following conclusions:

The results of a significant fraction of laboratories are not sufficiently accurate to allow a reliable assessment whether a material is in compliance with legislation. This leads to insecurity of producers, but also of distributors of electric and electronic equipment. E.g., 7 out 21 (33 %) reported values for the total sum of PBDEs significantly lower (even considering their expanded uncertainties) than the limit set by the legislation (1 g Kg^{-1}) where in reality, the material had a mass fraction of 1.8 g kg^{-1}.
The use of matrix matched certified reference materials should also be considered to improve the state of the art in this field (ERM-EC590 and ERM-EC591).

The use of multivariate data analysis provides the identification of the most influencing answers to the questionnaire leading to the extraction of quite significant information which can be given to the participants having in mind the improvement of the observed variability and the overall trueness of the exercise. Among them (a) grinding the samples, (b) use an instrumental extraction technique (i.e., Soxhlet or ultrasonic) and (c) use of short GC columns are of critical importance.

9 Acknowledgements

J. Charoud-Got (Reference Materials Unit of IRMM) is acknowledged for relabeling the test material. Franz Ulberth is thanked for revising the manuscript.

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

ORGANISATION	COUNTRY
National Measurements Institute	Australia
Umweltbundesamt Austria	Austria
SGS Belgium NV	Belgium
SGS do Brasil Ltd	Brasil
Intertek Testing Services Wuxi Ltd	China
Intertek Testing Services Guangzhou Ltd	China
Intertek Testing Services Shenzhen Ltd	China
SGS Hong Kong Ltd	China
CMA Industrial Development Foundation Ltd	China
Electronics Testing Center, Taiwan	China
PICA Prüfinstitut Chemische Analytik GmbH	Germany
Intertek Consumer Goods GmbH	Germany
Fraunhofer Institut für Verlahrenstechnik und Verpackung IVV	Germany
Ostthüringische Materialprüfgesellschaft für Textil und Kunststoffe GmbH	Germany
Pruefinstitute Hansecontrol	Germany
Eurofins GfA GmbH	Germany
IISG Istituto Italiano Sicurezza dei Giocattoli	Italy
Israel Chemicals – Industrial Products	Israel
Institute for Environmental Studies (IVM)	Netherlands
KOMAG Institute of Mining Technology	Poland
SGS Philippines, Inc.	Philippines
Swiss Quality Testing Services SQTS	Switzerland
Intertek Testing Services (Thailand) Ltd	Thailand
St. Louis Testing Laboratories	United States
Intertek Consumer Goods, UK Ltd	United Kingdom

Abbreviations

AMC	Analytical Methods Committee of the Royal Society of Chemistry
APLAC	Asia Pacific Laboratory Accreditation Cooperation
CITAC	Co-operation for International Traceability in Analytical Chemistry
CRM	Certified Reference Material
EA	European Co-operation for Accreditation
EN	European Standard
EU	European Union
EURACHEM	Eurachem, a network of organisations in Europe, having the objective of establishing a system for the international traceability of chemical measurements and the promotion of good quality practices
HG-AAS	Hydride generation-atomic absorption spectrometry
ILC	Interlaboratory Comparison
IMEP	International Measurement Evaluation Programme
IRMM	Institute for Reference Materials and Measurements
ISO	International Organization for Standardization
JRC	Joint Research Centre
PT	Proficiency Test

References

[1] "*Results of an interlaboratory comparison on the determination of polybrominated flame retardants in poly(ethyleneterephthalate)*", T. P. Linsinger, S. Voorspoels and A. Liebich, Anal. Bioanal. Chem., 390, 399-409, 2008

[2] ISO 13528, "*Statistical Methods for Use in Proficiency Testing by Interlaboratory Comparisons*" (2005), issued by ISO-Geneva (CH), International Organization for Standardization

[3] "*Development of the first certified reference materials for several brominated flame retardants in polymers*", T. P. Linsinger, A. Birgersson-Liebich, A. Lamberty, F. Pellizzato, T. Venelinov and S. Voorspoels, Anal. Chem. 81, (10) 3792-3800, 2009

[4] European Directive 2002/95/EC on the restriction of the use of hazardous substances in electrical and electronic equipment (RoHS)

[5] Commission Regulation (EC) 850/2004 on persistent organic pollutants (POPs)

[6] Commission Decision 2005/618/EC amending Directive 2002/95/EC for the purpose of establishing the maximum concentration values for certain hazardous substances in electrical and electronic equipment

[7] Commission Regulation (EC) 756/2010 amending Regulation 850/2004

[8] ISO/IEC Guide 43-1:1997 "*Proficiency testing by interlaboratory comparisons - Part 1: Development and operation of proficiency testing schemes*"

[9] IMEP Web page: http://irmm.jrc.ec.europa.eu/interlaboratory_comparisons/imep/Imep-26/Pages/IMEP-26.aspx

[10] http://www.erm-crm.org/ERM_products/search/reports/EC590-591.pdf

[11] "*Uncertainty calculations in the certification of reference materials. 2. Homogeneity study*" Van der Veen A.M.H., Linsinger T.P.J., Pauwels J. (2001), Accreditation and Quality Assurance, 6: 26-30.

[12] www.softCRM.com

[13] IEC 62321 Ed.1: "*Electrotechnical products – Determination of levels of six regulated substances (lead, mercury, cadmium, hexavalent chromium, polybrominated biphenyls, polybrominated diphenyl ethers)*", IEC/FDIS 2008.

[14] EURACHEM/CITAC (2000) "*Quantifying Uncertainty in Analytical Measurement*", http://www.eurachem.org.

[15] "*Representing data distributions with Kernel density estimates*" (2006), Issued by the Statistical Subcommittee of the Analytical Methods Committee (AMC) of the Royal Society of Chemistry (RSC), AMC Technical Brief N° 4

[16] http://physics.nist.gov/cuu/Uncertainty/coverage.html.

Annexes

Annex 1 : Invitation to EA to nominate laboratories

EUROPEAN COMMISSION
JOINT RESEARCH CENTRE

Institute for Reference Materials and Measurements

Geel, 1 October 2010
JRC.DG.D6/FCR/ive/ARES(2010)656935

Mr Paul Greenwood
United Kingdom Accreditation Service
21-47 High Street
Feltham
Middlesex
TW13 4UN
UNITED KINGDOM

Dear Paul,

Intercomparison for brominated flame retardants in plastic

The Institute for Reference Materials and Measurements (IRMM) organises IMEP-26, an interlaboratory comparison for the **"Determination of brominated flame retardants in plastic"**. This exercise aims to assess the analytical performance of laboratories involved in the compliance with the European Directive on the "Restriction of the use of certain hazardous substances in electrical and electronic equipment" (RoHS) (Directive 2002/95/EC) and on the legislation after the Stockholm Convention on Persistent Organic Pollutants (POPs) (Regulation (EC) No 850/2004). The concerned measurands are: total bromine, total sum of polybrominated biphenyls (PBB), total sum of polybrominated diphenylethers (PBDE), brominated diphenylethers (BDE-47, BDE-99, BDE-183 and BDE-209) and decabrominated biphenyl (BB-209).
In the frame of the EA-IRMM collaboration agreement, IRMM kindly invites EA to nominate laboratories for free participation. These laboratories must be involved in assuring the compliance to RoHS on the determination of hazardous substances in electrical and electronic equipment and on the determination of persistent organic pollutants (POP) as established in the Commission Regulation. They should also hold (or be in the process of obtaining) an accreditation for this type of measurement.
I suggest that you forward this invitation to the national EA accreditation bodies for their consideration. You may appoint 2-3 nominees per country.

Confidentiality of the participants and their results towards third parties is guaranteed. However, IMEP will disclose details of the participants that have been nominated by EA to the EA working group for ILCs in Testing. Please inform the nominees of this disclosure.
Registration of participants is open until the **15th November 2010**. Distribution of the samples is foreseen for the second half of November 2010. The deadline for the reporting of results is then scheduled for the 28th January 2011. In order to register, laboratories must:

1. **Enter** their details online:

https://irmm.jrc.ec.europa.eu/ilc/ilcRegistration.do?selComparison=560
When accessing this page you might be confronted with a Certificate Error page, please press the continue button to proceed with the registration.

2. **Print** the completed form when the system asks to do so and clearly indicate on the printed form that they have been appointed by the European Cooperation for Accreditation to take part in this exercise. **Otherwise the laboratory will be invoiced 235 € for participation**, normally applied for non-nominated laboratories.

3. **Send** the printout to both the IMEP-26 and the EA-IMEP-26 coordinators:

IMEP-26 coordinator
Dr. Fernando Cordeiro
Fax +32 14 571865
E-mail jrc-irmm-imep@ec.europa.eu

EA-IMEP-26 coordinator
Mr. Paul Greenwood
Fax +44 208 917 8500
E-mail pg@UKAS.com

Please contact me if you have any questions or comments. We are looking forward to our cooperation!

With kind regards

Dr. Fernando Cordeiro
IMEP-26 Coordinator

Annex 2 : Invitation to APLAC to nominate laboratories

EUROPEAN COMMISSION
JOINT RESEARCH CENTRE

Institute for Reference Materials and Measurements

Geel, 1 October 2010
JRC.DDG.D6/FCR/ive/ARES(2010)/656967

Mr Daniel Tholen
Chairman, APLAC PT Committee

Dear Daniel,

Intercomparison for brominated flame retardants in plastic

The Institute for Reference Materials and Measurements (IRMM) organises IMEP-26, an interlaboratory comparison for the **"Determination of brominated flame retardants in plastic"**. This exercise aims to assess the analytical performance of laboratories involved in the compliance with the European Directive on the "Restriction of the use of certain hazardous substances in electrical and electronic equipment" (RoHS) (Directive 2002/95/EC) and on the legislation after the Stockholm Convention on Persistent Organic Pollutants (POPs) (Regulation (EC) No 850/2004). The concerned measurands are: total bromine, total sum of polybrominated biphenyls (PBB), total sum of polybrominated diphenylethers (PBDE), brominated diphenylethers (BDE-47, BDE-99, BDE-183 and BDE-209) and decabrominated biphenyl (BB-209).
IRMM kindly invites APLAC to nominate 10 laboratories for free participation. However, they should hold (or be in the process of obtaining) an accreditation for this type of measurement. I suggest that you forward this invitation to a selection of specialised laboratories in this area.
In addition to the 10 laboratories above mentioned, other laboratories may take part in IMEP-26 paying a registration fee of 235 €.
Confidentiality of the participants and their results towards third parties is guaranteed.
Registration of APLAC participants is open until the **15th November 2010**. Distribution of the samples is foreseen for second half of November 2010. Deadline for submission of results is the 28th January 2011.
In order to register, laboratories must:

4. **Enter** their details online:

https://irmm.jrc.ec.europa.eu/ilc/ilcRegistration.do?selComparison=560

5. **Print** the completed form when the system asks to do so and clearly indicate on the printed form that they have been appointed by APLAC to take part in this exercise **otherwise your laboratory will be invoiced 235 € for participation** normally applied for non-appointed laboratories.

6. **Send** the printout to both the IMEP-26 and the APLAC coordinators:

IMEP-26 coordinator	**APLAC coordinator**
Dr. Fernando Cordeiro	Mr Daniel Tholen
Fax +32 14 571 865	Fax +1 231 941 9713
E-mail: jrc-irmm-imep@ec.europa.eu	E.Mail: aplac.pt@gmail.com

Please contact me if you have any questions or comments. We are looking forward to our cooperation!
With kind regards

Dr. Fernando Cordeiro
IMEP-26 Coordinator

Annex 3 : Announcement letter to EC DG ENV

EUROPEAN COMMISSION
JOINT RESEARCH CENTRE

Institute for Reference Materials and Measurements

Geel, 4 October 2010
JRC.DDG.D6/FCO/ive/ARES(2010)/659709

Mr Peter Korytar
EC, DG ENV

Dear Peter,

Intercomparison for brominated flame retardants in plastic

The Institute for Reference Materials and Measurements (IRMM) organises IMEP-26, proficiency test for the **"Determination of brominated flame retardants in plastic"**. This exercise aims to assess the analytical performance of laboratories involved in the compliance with the European Directive on the "Restriction of the use of certain hazardous substances in electrical and electronic equipment" (RoHS) (Directive 2002/95/EC) and on the legislation after the Stockholm Convention on Persistent Organic Pollutants (POPs) (Regulation (EC) No 850/2004). The concerned measurands are: total bromine, total sum of polybrominated biphenyls (PBB), total sum of polybrominated diphenylethers (PBDE), brominated diphenylethers (BDE-47, BDE-99, BDE-183 and BDE-209) and decabrominated biphenyl (BB-209).
IRMM kindly invites you to inform stakeholders that might be interested in this activity.
The registration fee that interested laboratories should pay to take part in IMEP-26 is 235 €.
Confidentiality of the participants and their results towards third parties is guaranteed.
The registration deadline is **15th November 2010**. Distribution of the samples is foreseen for second half of November 2010. Deadline for submission of results is the 28th January 2011.

In order to register, laboratories must:

7. **Enter** their details online:

https://irmm.jrc.ec.europa.eu/ilc/ilcRegistration.do?selComparison=560

8. **Print** the completed form when the system asks to do so.

9. **Send** the printout to the IMEP-26 coordinator:

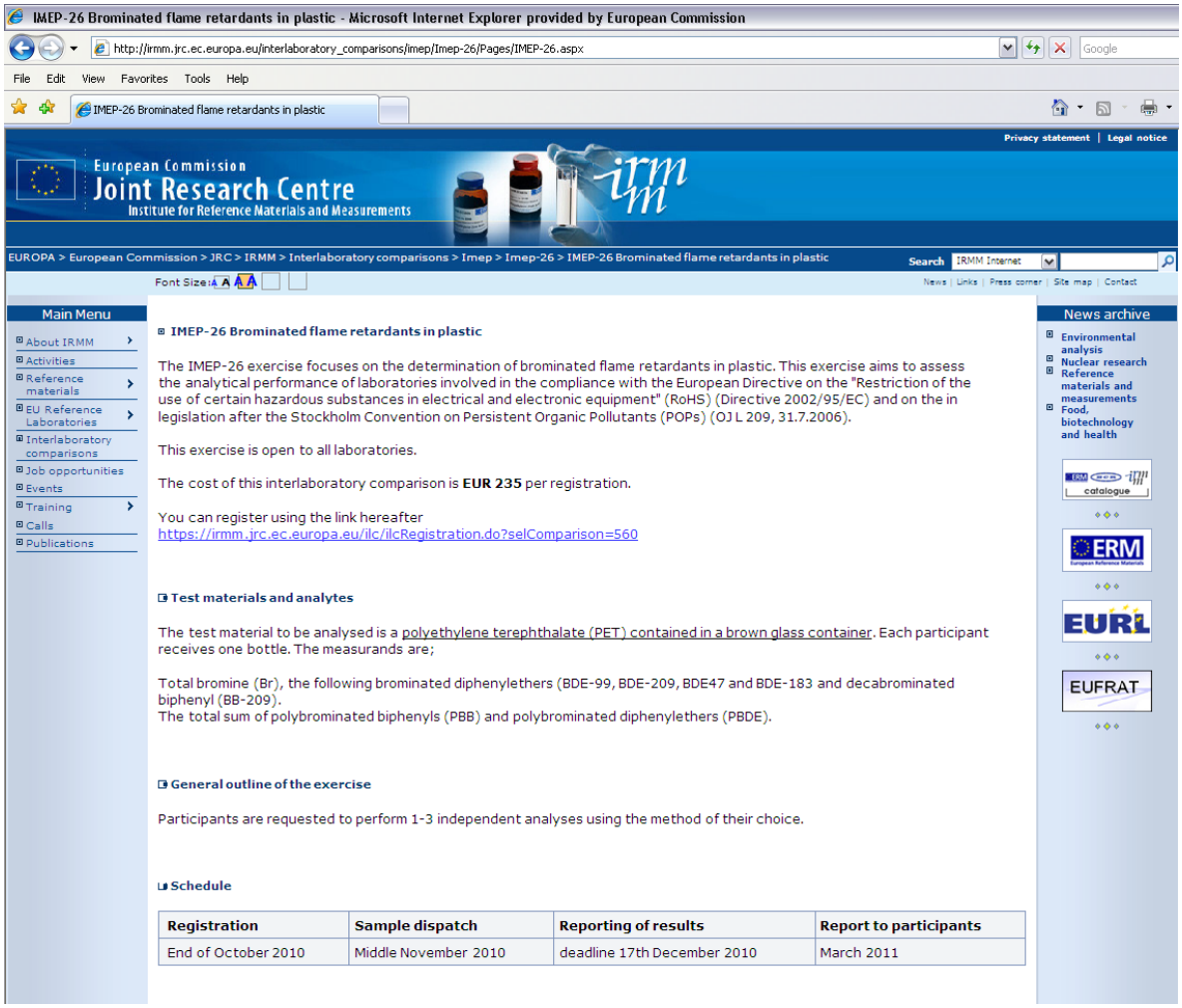
IMEP-26 coordinator
Mr Fernando Cordeiro
Fax +32 14 571 865
E-mail: jrc-irmm-imep@ec.europa.eu

Please contact me if you have any questions or comments. We are looking forward to our cooperation!

With kind regards

Dr. Fernando Cordeiro
IMEP-26 Coordinator

Annex 4 : IRMM IMEP WEB announcement



Annex 5

: Letter accompanying the test samples

EUROPEAN COMMISSION
JOINT RESEARCH CENTRE

Institute for reference materials and measurements
Food Safety and Quality

Geel, 13 January 2011
JRC.DDG.D6/FCO/ive/ARES(2011)/34912

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

Participation to IMEP-26, a proficiency test exercise for the determination of brominated flame retardants in plastic

Dear «TITLE» «SURNAME»,

Thank you for participating in the IMEP-26 intercomparison for the determination of **brominated flame retardants** in plastic

This parcel contains:
a) One bottle containing ~ 10 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, please send the "Confirmation of receipt" form back (fax: +32-14-571865, e-mail: jrc-irmm-imep@ec.europa.eu). You should store the sample in a dark and cold place (at 4 ºC) until analysis.

The measurands are:

- Total bromine,
- The following brominated diphenylethers (BDE-47, BDE-99, BDE-183 and BDE-209),
- The following decabrominated biphenyl (BB-209),
- The total sum of polybrominated biphenyls (PBB),
- The total sum of polybrominated diphenylethers (PBDE).

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.

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.
After entering all results, please also complete the relating questionnaire.
Do not forget to save, submit and confirm 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 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 25/02/2011.

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-IMEP@ec.europa.eu

With kind regards

Dr. Fernando Cordeiro
IMEP-26 Co-ordinator

Enclosures:
1) One bottle containing ~ 10 g of the test material,
2) Confirmation of receipt form.

Annex 6 : Sample receipt confirmation form

EUROPEAN COMMISSION
JOINT RESEARCH CENTRE

Institute for reference materials and measurements
Food Safety and Quality

Annex to JRC.DDG.D6/FCO/ive/ARES(2011)/

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

IMEP-26
Brominated flame retardants in plastic

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. Fernando Cordeiro Raposo
IMEP-26 Co-ordinator
EC-JRC-IRMM
Retieseweg 111
B-2440 GEEL, Belgium
Fax : +32-14-571865
e-mail : jrc-irmm-imep@ec.europa.eu

Annex 7 : Questionnaire

Submission Form

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

- ○ No
- ○ Yes

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

- ○ No
- ○ Yes

3. **Which quantification technique have you used?**

- ○ a) HPLC-UV, b) GC-quadrupole-MS, c) GC-SF-MS, d) other

4. **Which injection temperature have you used?**

5. **Which injection technique have you used?**

- ○ a) Cool-on-column
- ○ b) GC-quadrupole-MS
- ○ c) GC-SF-MS
- ○ d) Other

6. **Which GC column have you used?**

7. **Which column length have you used?**

8. **Have you used one or two GC analytical columns?**

9. **Which ionization technique have you used?**

10. **Which internal standard(s) have you used? (13C-labeled?)**

11. **Which clean-up technique have you used?**

12. **Which extraction technique have you used?**

- ○ a) Soxhlet
- ○ b) Pressurized liquid extraction
- ○ c) Ultrasonic
- ○ d) Static extraction
- ○ e) Microwave-assisted
- ○ f) None

13. **Which calibration technique have you used?**

- ○ a) External
- ○ b) Internal standard
- ○ c) Standard addition

14. **Have you followed a standard method?**

- ○ No
- ○ Yes

15. **Did you grind your sample? To which diameter? (if applicable)?**

15.1. Which grinder was used?

16. **Did you apply special UV protection?**

- ○ No
- ○ Yes

16.1. If yes, which?

17. **Did you perform a cross-check between the measured BFR mass fraction and the total Br mass fraction for quality control purposes?**

- ○ No
- ○ Yes

18. **Did you check the correctness of the calibration curves with independent standards from another supplier?**

- ○ No
- ○ Yes

19. **Do you use the BDE-206/BDE-209 ratio as quality control to check for degradation of BDE-209?**

- ☐ No
- ☐ Yes

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

- ○ No
- ○ Yes

21. **Is your laboratory certified, accredited or authorised for this type of analysis?**

- ○ No
- ○ Yes

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

- ○ No
- ○ Yes

23. **Does your laboratory carry out this type of analysis regularly (as regards the analytes, matrix and methods)**

- ○ No
- ○ Yes

23.1. If YES, how many samples does your laboratory analyse each year for this food category? *

- ○ a) < 10
- ○ b) 10-50
- ○ c) 50-100
- ○ d) > 100

24. **Which sample volume have you injected (µL)?**

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

Annex 8 : Homogeneity studies (all results expressed in mg kg^{-1})

	BDE-47		BDE-99		BDE-183		BDE-209		BB-209 [a)]		Sum PBDEs		Total Br	
Measurement results (mg kg^{-1})														
Bottle N°	**R_1**	**R_2**	**R_1**	**R_2**	**R_1**	**R_2**	**R_1**	**R_2**	**R_1**	**R_2**	**R_1**	**R_2**	**R_1**	**R_2**
1	128.54	136.22	167.33	167.72	38.01	40.09	329.54	335.15	316.97	319.15	792.04	813.52	1560.9	1645.9
2	133.86	128.26	168.86	168.18	38.68	39.12	329.87	334.78	316.16	322.41	801.11	799.9	1537.5	1499.1
3	134.26	131.28	168.75	169.45	39.79	39.49	338.32	338.78	324.24	323.27	813.58	811.53	1496.3	1530.3
4	132.88	131.46	171.2	168.29	40.59	39.58	339.95	335.74	319.47	318.9	816.18	804.93	1470.5	1372.4
5	133.05	132.79	163.77	162.67	38.51	39.09	339.29	339.78	320.07	318.95	805.57	805.45	1423.8	1536.3
6	134.05	130.78	165.54	164.61	38.3	39.06	341.4	340.2	328.5	323.96	806.89	802.08	1525.8	1401.5
7	131.04	129.48	165.36	162.34	39.5	39.1	341.44	341.06	323.38	324.07	806.6	801.73	1518.9	1427.3
8	130.08	132.24	166.06	164.77	39.17	39.76	343.26	344.15	325	328.78	808.6	809.08	1572.3	1645.3
9	127.55	130.52	163.42	165.41	38.73	39.52	349.36	341.62	330.38	324.06	802.8	804.79	1576.1	1454.2
10	134.86	127.98	166.84	162.96	38.77	38.62	346.13	342.17	330.47	326.12	815.26	797.19	1538.6	1660.2
Mean	**131.56**		**166.18**		**39.17**		**339.60**		**323.22**		**805.94**		**1519.66**	
σ (25 %)	**32.9**		**41.5**		**9.8**		**84.9**		**80.8**		**201.5**		**379.9**	
u_{BB} (%)	**1.10**		**0.40**		**0.70**		**0.40**		**0.40**		**0.40**		**2.10**	
Homogeneity test according to the ISO 13528 (in mg kg^{-1})														
0.3 σ	**9.87**		**12.46**		**2.94**		**25.47**		**24.24**		**60.45**		**113.97**	
S_x	**1.23**		**2.34**		**0.45**		**4.55**		**3.90**		**3.70**		**64.89**	
S_w	**2.96**		**1.44**		**0.62**		**2.75**		**2.65**		**6.97**		**67.44**	
S_S	**0.00**		**2.11**		**0.12**		**4.11**		**3.42**		**0.00**		**44.01**	
$S_S \leq 0.3\sigma$?	**Yes**		**Yes**		**Yes**		**Yes**		**Yes**		**Yes**		**Yes**	
Test result	**Passed**		**Passed**		**Passed**		**Passed**		**Passed**		**Passed**		**Passed**	

Notes: R_1, R_2 refers to replicate 1 and 2 respectively. For all the other abbreviations see the respective references

The standard deviation for the proficiency assessment σ in use in this table was calculated as a fraction of the mean obtained from the homogeneity studies and not as a fraction of the assigned value

u_{BB} = between bottle standard deviation (inhomogeneity contribution)

S_x = std of sample averages

S_w = within-sample std

S_S = between-sample std

$S_{All} = 0.3\ \sigma$ allowable std (criterion)

Bottle ID are arbitrarily numbered as from 1 to 10 and not correponding to the real bottle ID as analysed.

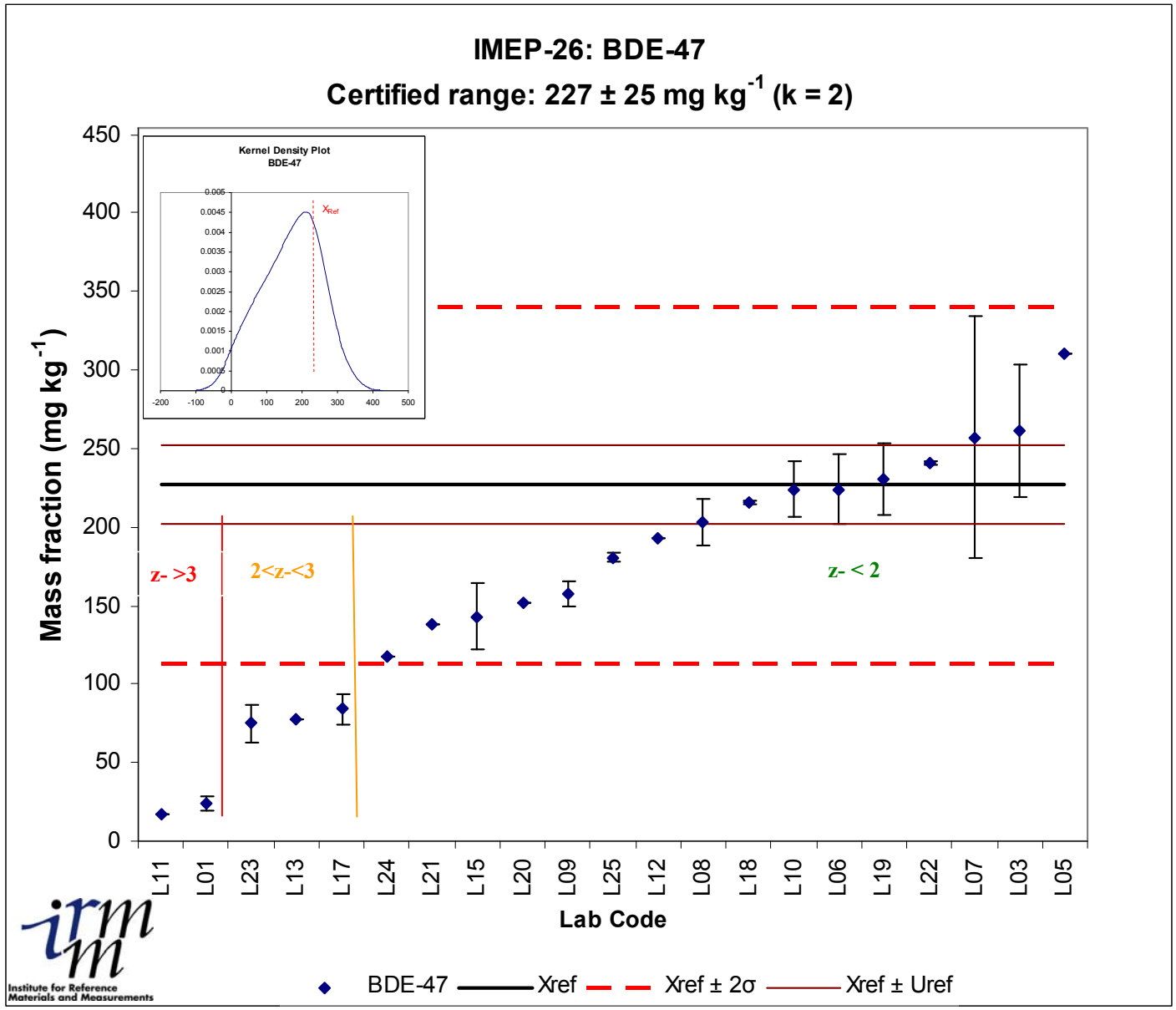
[a)] Equals the sum of all PBBs

Annex 9 : Results for BDE-47 (mg kg^{-1})

X_{Ref} = 227 ± 25 mg kg^{-1} (k = 2)

Lab ID	BDE-47	U	k	u	z-score	ζ-score	$Qual_u$
L11	16.7	0	√3	0.0	-3.71	-16.82	b
L01	24	5	2	2.5	-3.58	-15.92	b
L23	75	12	2	6.0	-2.68	-10.96	b
L13	77	0	√3	0.0	-2.64	-12.00	b
L17	84	10	2	0.0	-2.52	-11.44	b
L24	117.88	0	√3	0.0	-1.92	-8.73	b
L21	138	0	√3	0.0	-1.57	-7.12	b
L15	142.8	21.3	1	21.3	-1.48	-3.41	a
L20	152	0	√3	0.0	-1.32	-6.00	b
L09	157.51	7.83	2	3.9	-1.22	-5.31	b
L25	180.7	2.52	4	0.6	-0.82	-3.70	b
L12	192.76	0.04	1	0.0	-0.60	-2.74	b
L08	203	15	2	7.5	-0.42	-1.65	b
L18	216	1	√3	0.6	-0.19	-0.88	b
L10	224	17.9	2	9.0	-0.05	-0.20	b
L06	224	22	√3	12.7	-0.05	-0.17	a
L19	230	22.7	2	11.4	0.05	0.18	b
L22	240.62	0.79	2	0.4	0.24	1.09	b
L07	257	77.1	3	25.7	0.53	1.05	a
L03	261	42	2	21.0	0.60	1.39	a
L05	310	0	√3	0.0	1.46	6.64	b

$Qual_u$: 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 7.2.

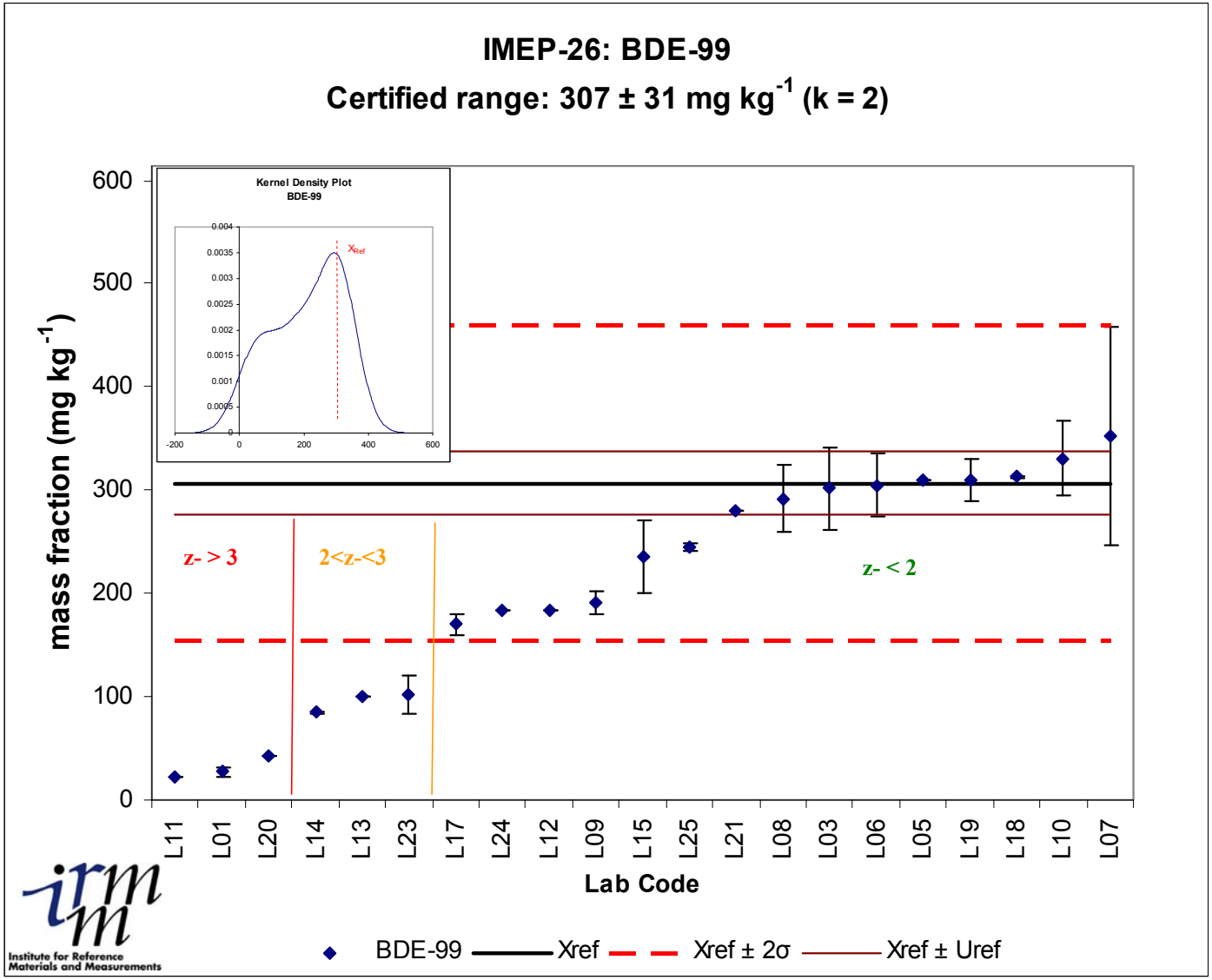

IMEP-26: BDE-47
Certified range: 227 ± 25 mg kg-1 (k = 2)
Kernel Density Plot
BDE-47
Mass fraction (mg kg-1)
z- >3
2<z-<3
z- < 2
Lab Code
L11 L01 L23 L13 L17 L24 L21 L15 L20 L09 L25 L12 L08 L18 L10 L06 L19 L22 L07 L03 L05
Institute for Reference Materials and Measurements
BDE-47
Xref
Xref ± 2σ
Xref ± Uref

Annex 10 : Results for BDE-99 (mg kg^{-1})

X_{Ref} = 307 ± 31 mg kg^{-1} (k = 2)

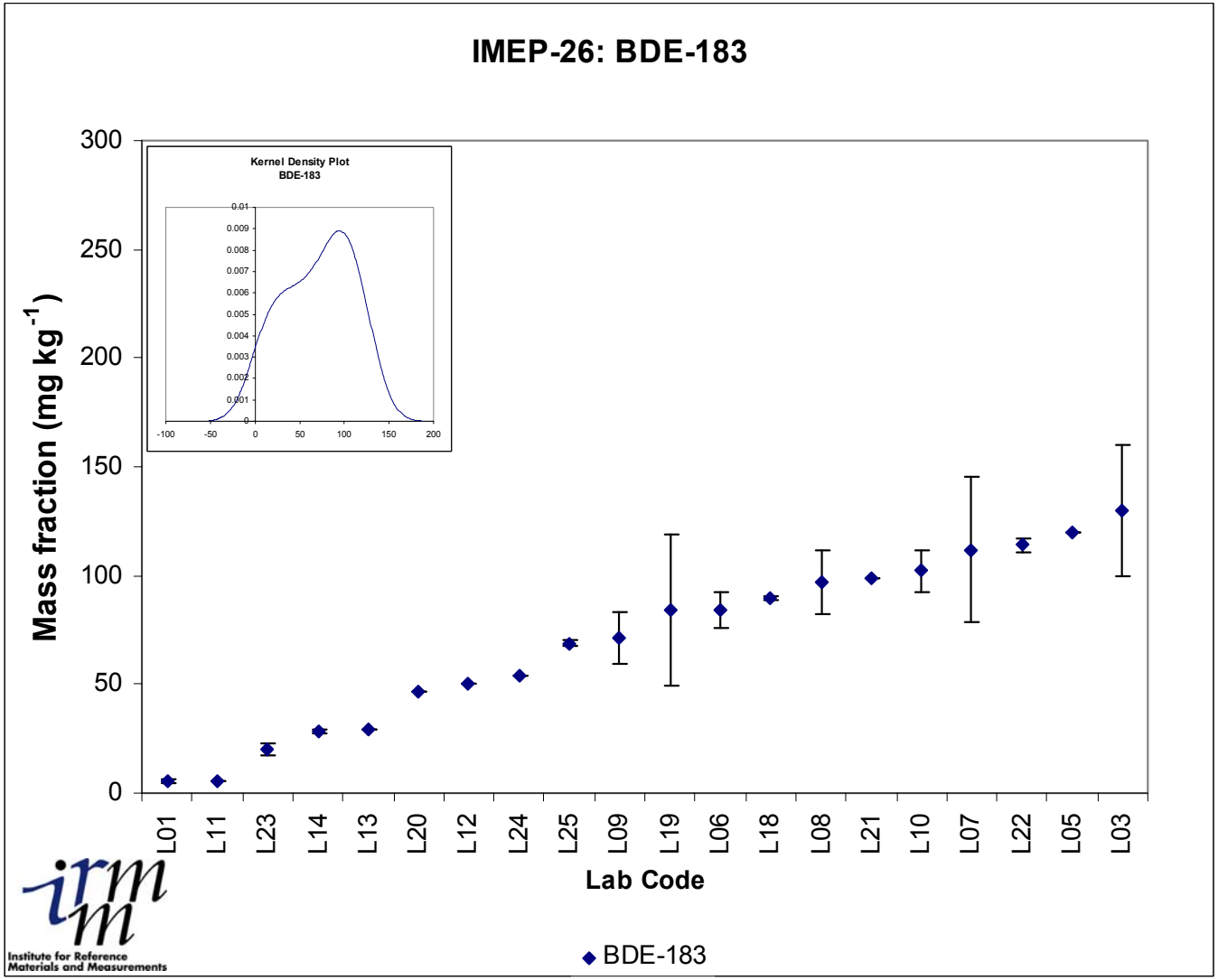
Lab ID	BDE-99	U	k	u	z-score	ζ-score	$Qual_u$
L11	21.6	0	√3	0.0	-3.72	-18.41	b
L01	27	5	2	2.5	-3.65	-17.83	b
L20	43	0	√3	0.0	-3.44	-17.03	b
L14	85.2	1	1	1.0	-2.89	-14.28	b
L13	100	0	√3	0.0	-2.70	-13.35	b
L23	102	18	2	9.0	-2.67	-11.44	b
L17	170	10	2	5.0	-1.79	-8.41	b
L24	183.16	0	√3	0.0	-1.61	-7.99	b
L12	183.36	0.04	1	0.0	-1.61	-7.98	b
L09	191.03	11.72	2	5.9	-1.51	-7.00	b
L15	236	35.4	1	35.4	-0.93	-1.84	a
L25	244.8	3.05	4	0.8	-0.81	-4.01	b
L21	281	0	√3	0.0	-0.34	-1.68	b
L08	292	33	2	16.5	-0.20	-0.66	a
L03	302	40	2	20.0	-0.07	-0.20	a
L06	305	30	√3	17.3	-0.03	-0.09	a
L05	310	0	√3	0.0	0.04	0.19	b
L19	310	20.5	2	10.3	0.04	0.16	b
L18	313	1	√3	0.6	0.08	0.39	b
L10	331	36.4	2	18.2	0.31	1.00	a
L07	352	105.6	3	35.2	0.59	1.17	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 7.2.


IMEP-26: BDE-99
Certified range: 307 ± 31 mg kg-1 (k = 2)
mass fraction (mg kg-1)
600
500
400
300
200
100
0
Kernel Density Plot
BDE-99
0.004
0.0035
0.003
0.0025
0.002
0.0015
0.001
0.0005
0
XRef
-200
0
200
400
600
z- > 3
2<z-<3
z- < 2
L11
L01
L20
L14
L13
L23
L17
L24
L12
L09
L15
L25
L21
L08
L03
L06
L05
L19
L18
L10
L07
Lab Code
Institute for Reference Materials and Measurements
BDE-99
Xref
Xref ± 2σ
Xref ± Uref

Annex 11 : Results for BDE-183 (mg kg^{-1})

Lab ID	BDE-183	U	k	u
L01	5.5	1	2	0.5
L11	5.9	0	√3	0.0
L23	20	3	2	1.5
L14	28	1	1	1.0
L13	29	0	√3	0.0
L20	47	0	√3	0.0
L12	49.97	0.04	1	0.0
L24	53.56	0	√3	0.0
L25	68.9	1.51	4	0.4
L09	71.32	11.77	2	5.9
L19	84	34.9	2	17.5
L06	84	8	√3	4.6
L18	90	1	√3	0.6
L08	97	15	2	7.5
L21	99	0	√3	0.0
L10	102	9.2	2	4.6
L07	112	33.6	3	11.2
L22	113.93	3.08	2	1.5
L05	120	0	√3	0.0
L03	130	30	2	15.0

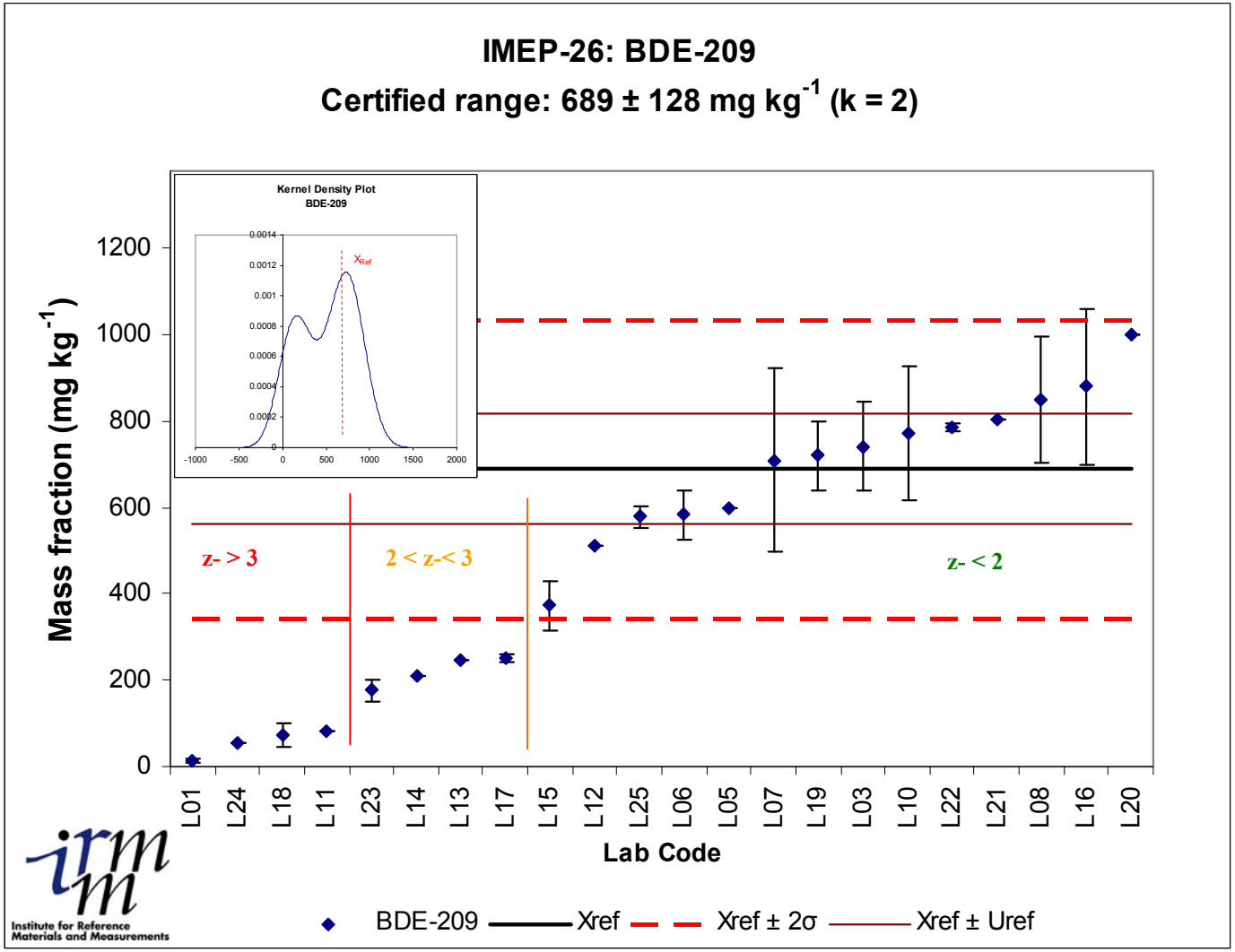

IMEP-26: BDE-183
Kernel Density Plot
BDE-183
Mass fraction (mg kg-1)
300
250
200
150
100
50
0
L01
L11
L23
L14
L13
L20
L12
L24
L25
L09
L19
L06
L18
L08
L21
L10
L07
L22
L05
L03
Lab Code
BDE-183
Institute for Reference Materials and Measurements

Annex 12 : Results for BDE-209 (mg kg^{-1})

X_{Ref} = 689 ± 128 mg kg^{-1} (k = 2)

Lab ID	BDE-209	U	k	u	z-score	ζ-score	$Qual_u$
L01	15	5	2	2.5	-3.91	-10.52	b
L24	53.8	0	√3	0.0	-3.69	-9.93	b
L18	73	26	√3	15.0	-3.58	-9.37	b
L11	80.9	0	√3	0.0	-3.53	-9.50	b
L23	177	25	2	12.5	-2.97	-7.85	b
L14	209	1	1	1.0	-2.79	-7.50	b
L13	248	0	√3	0.0	-2.56	-6.89	b
L17	250	10	2	5.0	-2.55	-6.84	b
L15	373	56	1	56.0	-1.83	-3.72	b
L12	512.02	0.04	1	0.04	-1.03	-2.77	b
L25	577.9	25.1	4	6.3	-0.64	-1.73	b
L06	582	58	√3	33.5	-0.62	-1.48	b
L05	600	0	√3	0.0	-0.52	-1.39	b
L07	709	212.7	3	70.9	0.12	0.21	a
L19	720	80	2	40.0	0.18	0.41	b
L03	740	102	2	51.0	0.30	0.62	b
L10	770	154	2	77.0	0.47	0.81	a
L22	784.9	9.44	2	4.7	0.56	1.49	b
L21	805	0	√3	0.0	0.67	1.81	b
L08	848	145	2	72.5	0.92	1.64	a
L16	880	180	2	90.0	1.11	1.73	a
L20	1000	0	√3	0.0	1.81	4.86	b

$Qual_u$: 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 7.2.

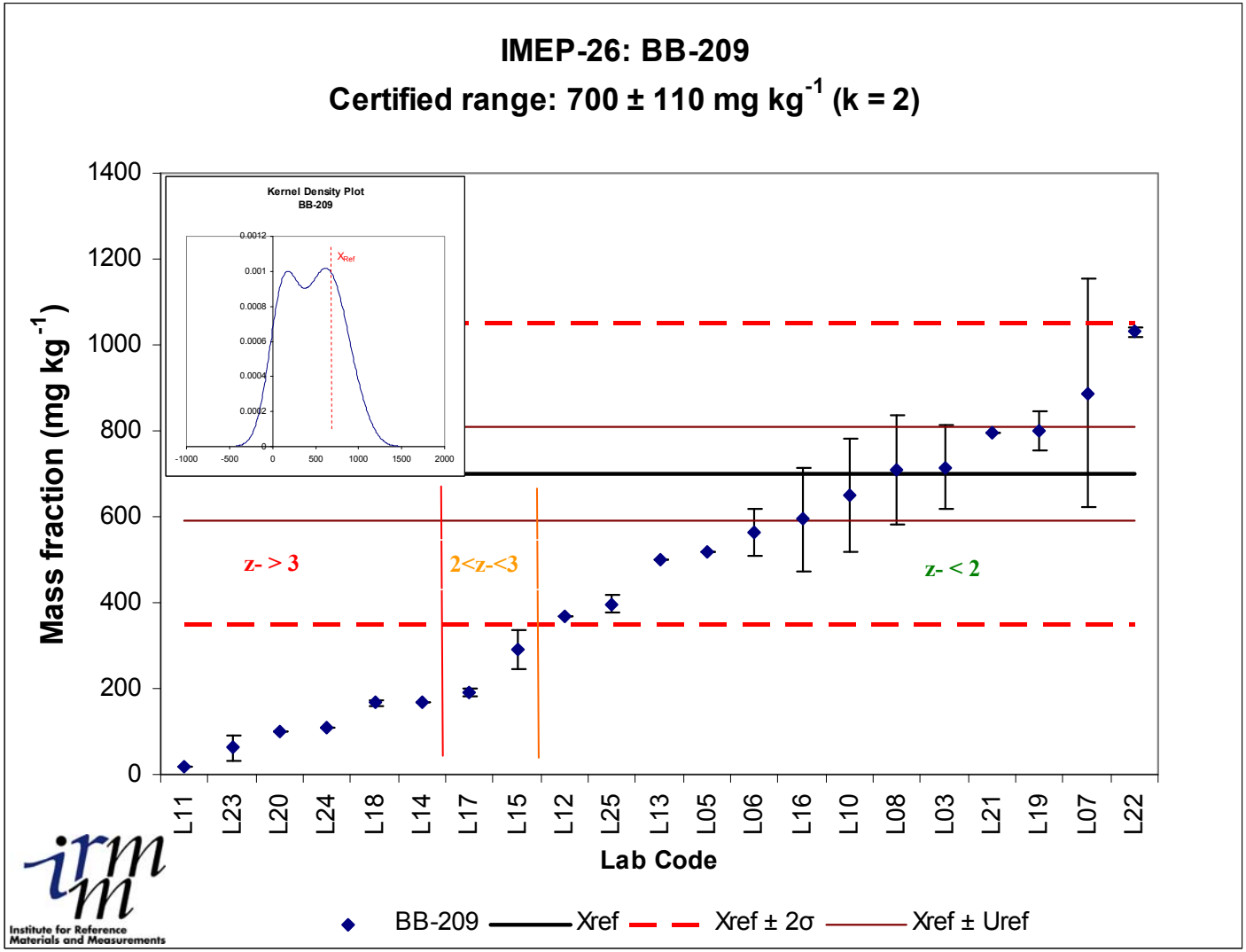

IMEP-26: BDE-209
Certified range: 689 ± 128 mg kg-1 (k = 2)
Kernel Density Plot
BDE-209
XRef
Mass fraction (mg kg-1)
z- > 3
2 < z-< 3
z- < 2
Lab Code
L01 L24 L18 L11 L23 L14 L13 L17 L15 L12 L25 L06 L05 L07 L19 L03 L10 L22 L21 L08 L16 L20
BDE-209
Xref
Xref ± 2σ
Xref ± Uref
Institute for Reference Materials and Measurements

Annex 13 : Results for BB-209 (mg kg^{-1})

X_{Ref} = 700 ± 110 mg kg^{-1} (k = 2)

Lab ID	BB-209	U	k	u	z-score	ζ-score	$Qual_u$
L11	16.5	0	√3	0.0	-3.91	-12.43	b
L23	62	29	2	14.5	-3.65	-11.22	b
L20	100	0	√3	0.0	-3.43	-10.91	b
L24	108.9	0	√3	0.0	-3.38	-10.75	b
L18	166	6	√3	3.5	-3.05	-9.69	b
L14	167	1	1	1.0	-3.05	-9.69	b
L17	190	10	2	5.0	-2.91	-9.23	b
L15	290	44.1	1	44.1	-2.34	-5.82	b
L12	366.92	0.04	1	0.0	-1.90	-6.06	b
L25	396.8	20.75	4	5.2	-1.73	-5.49	b
L13	501	0	√3	0.0	-1.14	-3.62	b
L05	520	0	√3	0.0	-1.03	-3.27	b
L06	563	56	√3	32.3	-0.78	-2.15	b
L16	594	120	2	60.0	-0.61	-1.30	a
L10	650	130	2	65.0	-0.29	-0.59	a
L08	708	128	2	64.0	0.05	0.09	a
L03	714	98	2	49.0	0.08	0.19	b
L21	795	0	√3	0.0	0.54	1.73	b
L19	800	47.2	2	23.6	0.57	1.67	b
L07	888	266.4	3	88.8	1.07	1.80	a
L22	1030.35	11.78	2	5.9	1.89	5.97	b

$Qual_u$: 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 7.2.

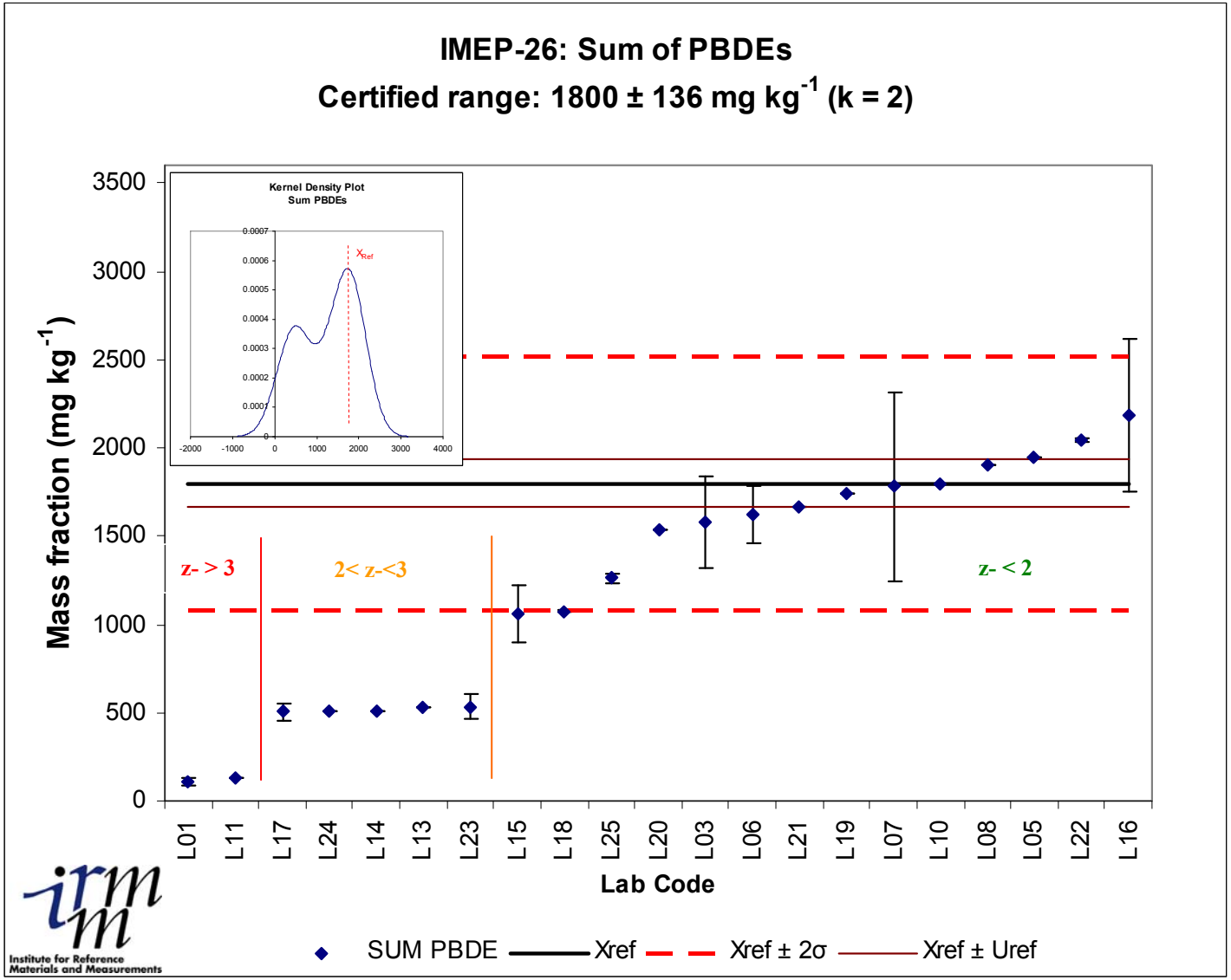

IMEP-26: BB-209
Certified range: 700 ± 110 mg kg-1 (k = 2)
Mass fraction (mg kg-1)
1400
1200
1000
800
600
400
200
0
Kernel Density Plot
BB-209
XRef
0.0012
0.001
0.0008
0.0006
0.0004
0.0002
0
-1000
-500
0
500
1000
1500
2000
z- > 3
2<z-<3
z- < 2
L11
L23
L20
L24
L18
L14
L17
L15
L12
L25
L13
L05
L06
L16
L10
L08
L03
L21
L19
L07
L22
Lab Code
BB-209
Xref
Xref ± 2σ
Xref ± Uref
Institute for Reference Materials and Measurements

Annex 14 : Results for the total sum of PBDEs (mg kg^{-1})

X_{Ref} = 1800 ± 136 mg kg^{-1} (k = 2)

Lab ID	SUM PBDEs	U	k	u	z-score	ζ-score	$Qual_u$
L01	107	25	2	12.5	-3.76	-24.66	b
L11	125.1	0	√3	0.0	-3.72	-24.81	b
L17	504	50	2	25.0	-2.88	-18.00	b
L24	509.94	0	√3	0.0	-2.87	-19.11	b
L14	512	1	1	1.0	-2.86	-19.08	b
L13	525	0	√3	0.0	-2.83	-18.89	b
L23	535	68	2	34.0	-2.81	-16.74	b
L15	1060	159	1	159.0	-1.64	-4.28	a
L18	1073	5	√3	2.9	-1.62	-10.76	b
L25	1259.5	30.8	4	7.7	-1.20	-7.96	b
L20	1530	0	√3	0.0	-0.60	-4.00	b
L03	1578	260	2	130.0	-0.49	-1.52	a
L06	1623	162	√3	93.5	-0.39	-1.53	a
L21	1661	0	√3	0.0	-0.31	-2.06	b
L19	1740	0	√3	0.0	-0.13	-0.89	b
L07	1781	534.3	3	178.1	-0.04	-0.10	a
L10	1799	0	2	0.0	0.00	-0.01	b
L08	1906	0	√3	0.0	0.24	1.57	b
L05	1950	0	√3	0.0	0.33	2.22	b
L22	2046.98	9.38	2	4.7	0.55	3.65	b
L16	2182	430	2	215.0	0.85	1.70	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 7.2.

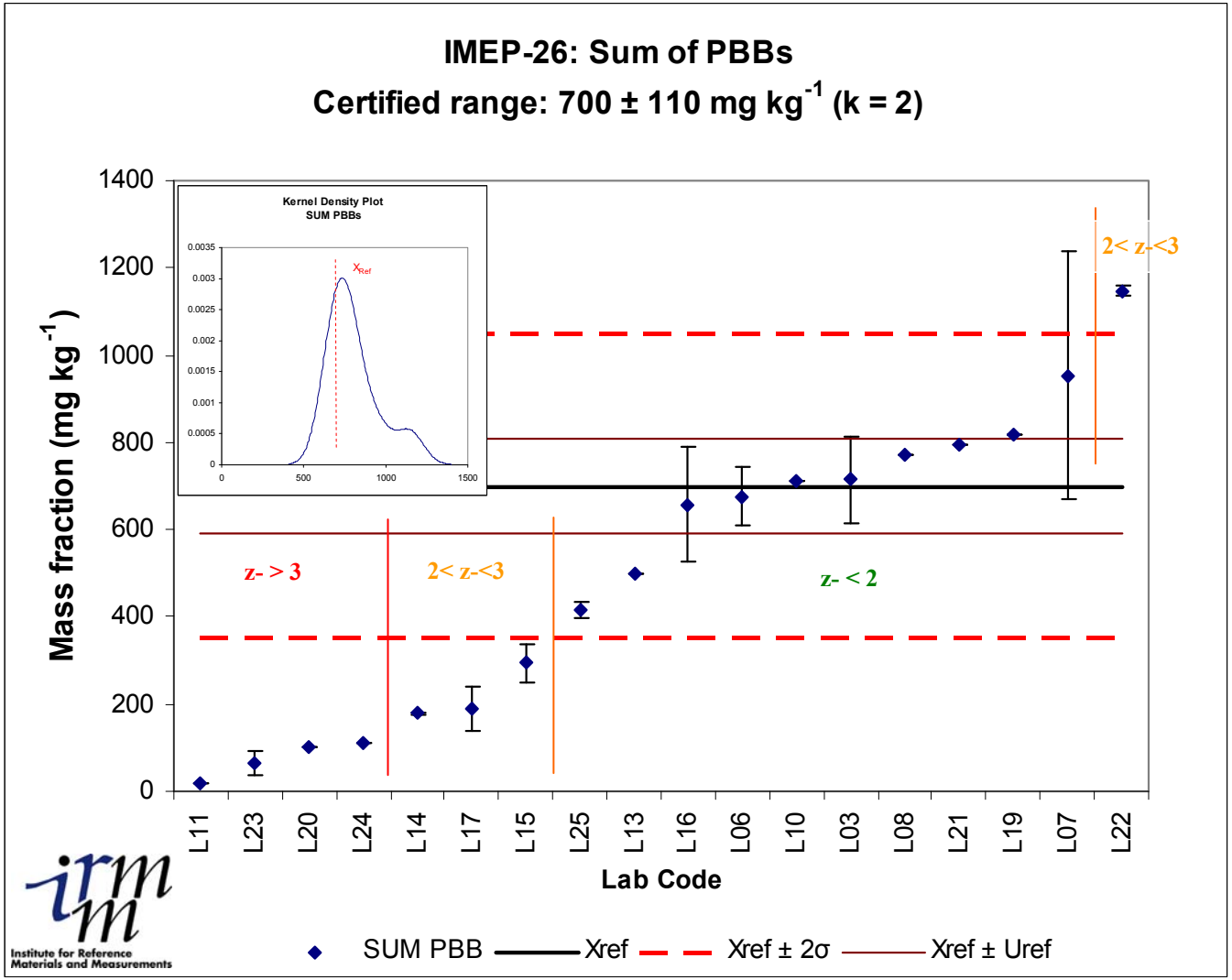

IMEP-26: Sum of PBDEs
Certified range: 1800 ± 136 mg kg-1 (k = 2)
Mass fraction (mg kg-1)
3500
3000
2500
2000
1500
1000
500
0
Kernel Density Plot
Sum PBDEs
0.0007
0.0006
0.0005
0.0004
0.0003
0.0002
0.0001
0
-2000
-1000
0
1000
2000
3000
4000
XRef
z- > 3
2< z-<3
z- < 2
L01
L11
L17
L24
L14
L13
L23
L15
L18
L25
L20
L03
L06
L21
L19
L07
L10
L08
L05
L22
L16
Lab Code
Institute for Reference Materials and Measurements
SUM PBDE
Xref
Xref ± 2σ
Xref ± Uref

Annex 15 : Results for the total sum of PBBs (mg kg^{-1})

X_{Ref} = 700 ± 110 mg kg^{-1} (k = 2)

Lab ID	SUM PBBs	U	k	u	z-score	ζ-score	$Qual_u$
L11	16.5	0	√3	0.0	-3.91	-12.43	b
L23	64	27	2	13.5	-3.63	-11.23	b
L20	100	0	√3	0.0	-3.43	-10.91	b
L24	108.9	0	√3	0.0	-3.38	-10.75	b
L14	178	1	1	1.0	-2.98	-9.49	b
L17	190	50	2	25.0	-2.91	-8.44	b
L15	294	44.1	1	44.1	-2.32	-5.76	b
L25	416	20.25	4	5.1	-1.62	-5.14	b
L13	501	0	√3	0.0	-1.14	-3.62	b
L16	658	130	2	65.0	-0.24	-0.49	a
L06	676	68	√3	39.3	-0.14	-0.36	b
L10	712	0	2	0.0	0.07	0.22	b
L03	714	100	2	50.0	0.08	0.19	b
L08	772	0	√3	0.0	0.41	1.31	b
L21	795	0	√3	0.0	0.54	1.73	b
L19	820	0	√3	0.0	0.69	2.18	b
L07	954	286.2	3	95.4	1.45	2.31	a
L22	1146.66	12.15	2	6.1	2.55	8.07	b

$Qual_u$: 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 7.2.


IMEP-26: Sum of PBBs
Certified range: 700 ± 110 mg kg-1 (k = 2)
Mass fraction (mg kg-1)
1400
1200
1000
800
600
400
200
0
Kernel Density Plot
SUM PBBs
0.0035
0.003
0.0025
0.002
0.0015
0.001
0.0005
0
0
500
1000
1500
XRef
2< z-<3
z- > 3
2< z-<3
z- < 2
L11
L23
L20
L24
L14
L17
L15
L25
L13
L16
L06
L10
L03
L08
L21
L19
L07
L22
Lab Code
Institute for Reference Materials and Measurements
SUM PBB
Xref
Xref ± 2σ
Xref ± Uref

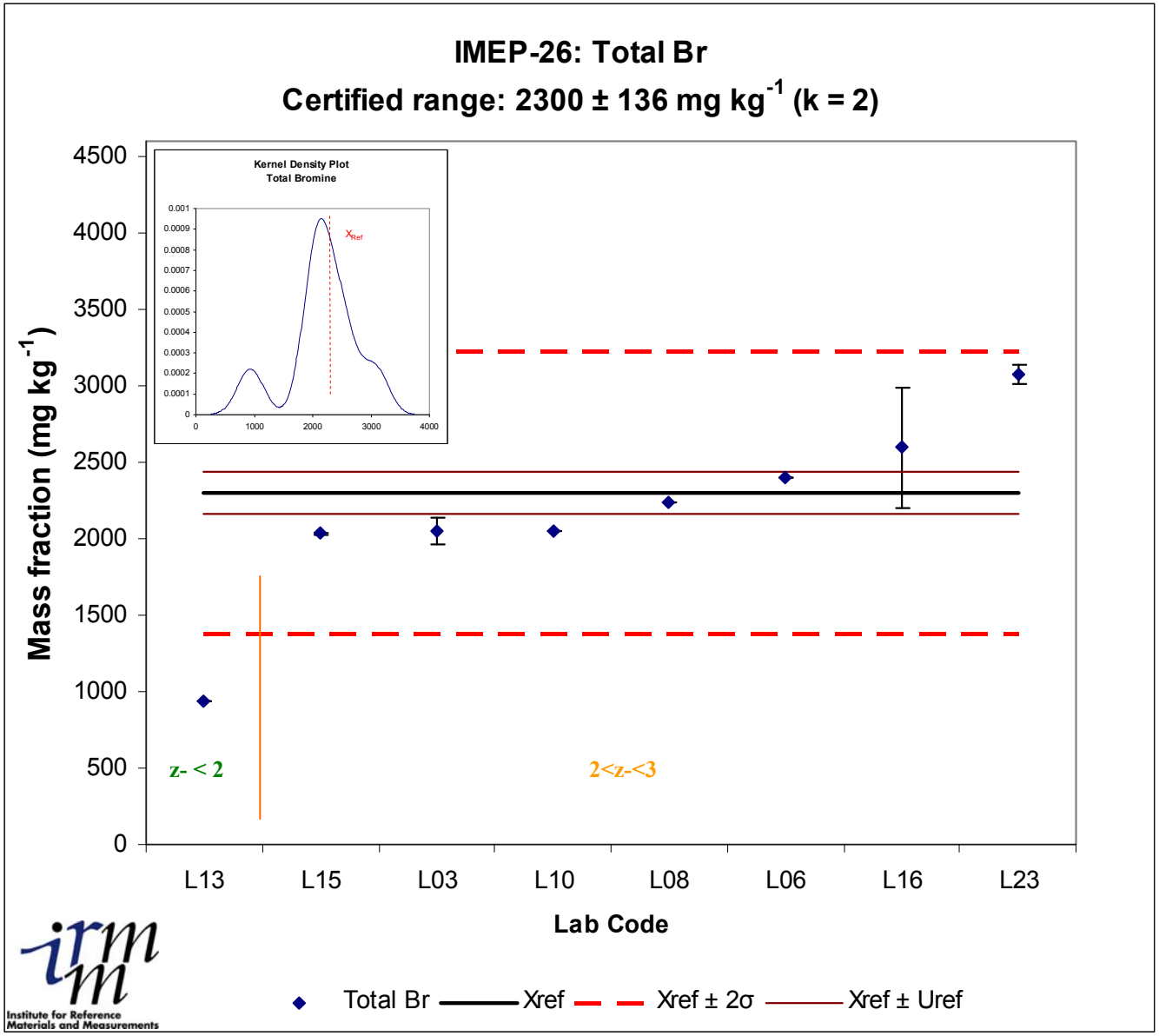
Annex 16 : Results for Total bromine (mg kg^{-1})

X_{Ref} = 2300 ± 136 mg kg^{-1} (k = 2)

Lab ID	Total Br	U	k	u	z-score	ζ-score	$Qual_u$
L13	933	0	√3	0.0	-2.38	-20.12	b
L15	2034	9	1	9.0	-0.46	-3.88	b
L03	2048	90	2	45.0	-0.44	-3.09	b
L10	2050	0	2	0.0	-0.43	-3.68	b
L08	2239	0	√3	0.0	-0.11	-0.90	b
L06	2400	0	√3	0.0	0.17	1.47	b
L16	2594	390	2	195.0	0.51	1.42	a
L23	3075	63	3	21.0	1.35	10.90	b

$Qual_u$: 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 7.2.


IMEP-26: Total Br
Certified range: 2300 ± 136 mg kg-1 (k = 2)
Kernel Density Plot
Total Bromine
Mass fraction (mg kg-1)
4500
4000
3500
3000
2500
2000
1500
1000
500
0
z- < 2
2<z-<3
L13
L15
L03
L10
L08
L06
L16
L23
Lab Code
Total Br
Xref
Xref ± 2σ
Xref ± Uref
Institute for Reference Materials and Measurements

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Abstract
This report presents the results of an interlaboratory comparison (ILC) which focussed on the determination of total bromine, total sum of polybrominated biphenyls (PBB), total sum of polybrominated diphenylethers (PBDE), brominated diphenylethers (BDE-47, BDE-99, BDE-183 and BDE-209) and decabrominated biphenyl (BB-209) in plastic.

The test material used in this exercise was the Quality Control material (IRMM-310) from the Institute for Reference Materials and Measurements (IRMM) a poly(ethyleneterephthalate, PET) granulated that has been fortified with commercially available technical mixtures of polybrominated diphenylethers and polybrominated biphenyls. The material was relabelled to avoid its recognition. Twenty-five laboratories from 15 countries registered to the exercise, from which 23 reported results.

The assigned values and their associated uncertainties for all measurands were taken as the informative values provided by the IRMM-310 material information sheet. As these values were measured in 2007, decision was made to contact expert laboratories in the field to re-evaluate the material. All the values were comparable with the informative values (except for BDE-183 where no scoring was provided).
At the time of producing this material it was considered as a candidate certified reference material, hence no studies have been carried out to assess the adequacy of the material concerning homogeneity and stability except for the total bromine content. For this reason it was judged appropriate to conduct studies to asses the adequacy of the selected test material regarding its homogeneity for all the selected measurands.

Participants were invited to report the uncertainty of their measurements. This was done by, roughly, one half of the laboratories taking part in this exercise. Laboratory results were rated with z- and ζ-scores (zeta-scores) in accordance with ISO 13528. The standard deviation for proficiency assessment was fixed to 25 % by the advisory board of this ILC, on the basis of the estimated variability observed for the IRMM-310 material, on the observed variability (relative between-laboratory standard deviation) on previous ILCs organized by our institute on identical test samples and based on the state-of-the-art in this field of analysis.

The outcome of the exercise was illustrating quite well the difficulties laboratories do have to provide consistent values for the investigated measurands; the share of satisfactory z-scores ranged between 61 and 88 %. There was a clear tendency to underestimate most of the measurands. The most influencing variables, leading to the observed variability and lack of trueness, were investigated.

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.

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