Results of Proficiency Test Brominated Flame retardants September 2014

Organised by: Institute for Interlaboratory Studies
Spijkenisse, the Netherlands

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1 INTRODUCTION

Worldwide, many consumer products with plastic parts are produced which contain brominated compounds as flame retardants. These brominated compounds are exceptionally effective for fire prevention.
Since the 1990s, scientists have questioned the safety of the Poly Brominated Biphenyls (PBB) and Poly Brominated Diphenyls Ethers (PBDE), because it may bioaccumulate in blood, breast milk and fat tissues. As of June 1, 2006 the State of California began prohibiting the manufacture, distribution, and processing of flame retardant products, containing pentabromodiphenyl ether (penta-BDE) and octabromodiphenyl ether (octa-BDE). The European Union decided to ban the use of both PBB and PBDE in electric and electronic devices. This ban was formalised in the RoHS Directive 2011/65/EU on the restriction of the use of certain hazardous substances in electrical and electronic equipment, and an upper limit of 1000 mg/kg for the sum of PBB and PBDE was set. In February 2009, the Institute for Reference Materials and Measurements (IRMM) released the first certified reference materials (CRMs) to help analytical laboratories better detect these two classes of flame retardants. The certification study of 2007 was followed by an interlaboratory study in 2011. The test material used in this exercise was the earlier produced CRM. To avoid easy recognition by participants, the material was relabelled before use. Twenty-five laboratories from 15 countries participated in the exercise, from which 23 reported results.
A proficiency testing scheme (laboratory-evaluating interlaboratory study) for the determination of PBB and PBDE was started by the Institute for Interlaboratory Studies in 2009.
On request of several participants it was decided to continue the interlaboratory study for the determination of PBB and PBDE. In the interlaboratory study of September 2014, 74 laboratories from 23 different countries participated (See appendix 3). In this report, the results of the 2014 proficiency test are presented and discussed.

2 SET-UP

The Institute for Interlaboratory Studies (iis) in Spijkenisse, the Netherlands, was the organiser of this proficiency test. It was decided to send 2 different plastic samples which are clearly positive on a number of brominated flame retardants and labelled #14152 and #14153 respectively.
Participants were also requested to report some details of the methods used.

2.1 ACCREDITATION

The Institute for Interlaboratory Studies in Spijkenisse, the Netherlands, is accredited in agreement with ISO/IEC 17043:2010 (R007), since January 2000, by the Dutch Accreditation Council (Raad voor Accreditatie). This ensures strict adherence to protocols for sample preparation and statistical evaluation and 100% confidentially of participant's data. Feedback from the participants on the reported data is encouraged and customer's satisfaction is measured on regular basis by sending out questionnaires.

2.2 PROTOCOL

The protocol followed in the organisation was the one as described for proficiency testing in the report 'iis Interlaboratory Studies: Protocol for the Organisation, Statistics and Evaluation' of April 2014 (iis-protocol, version 3.3).

2.3 CONFIDENTIALITY STATEMENT

All data presented in this report must be regarded as confidential and for use by the participating companies only. Disclosure of the information in this report is only allowed by means of the entire report. Use of the contents of this report for third parties is only allowed by written permission of the Institute for Interlaboratory Studies. Disclosure of the identity of one or more of the participating companies will be done only after receipt of a written agreement of the companies involved.

2.4 SAMPLES

Two different samples were selected. The first material (#14152) was a blue coloured Poly Vinyl Chloride (PVC) in granulates, fortified with Deca Bromo Diphenyl Ether (Deca-BDE). The second material (#14153) was a black coloured Poly Vinyl Chloride that was also fortified with Deca-BDE. Sample #14152 and sample #14153 were both divided into 126 subsamples of approx. 5 grams. The homogeneity of subsamples #14152 and #14153 was checked by the determination of Deca-BDE content on 8 stratified randomly selected subsamples.

	Deca-BDE #14152 in mg/kg	Deca-BDE #14153 in mg/kg
Sample 1	1907	5486
Sample 2	1967	5344
Sample 3	2041	5230
Sample 4	1960	5138
Sample 5	1982	5710
Sample 6	1988	5120
Sample 7	1929	5642
Sample 8	1907	5340

Table 1: test results of the homogeneity study on the subsamples #14152 and #14153

From the above test results the repeatabilities were calculated and compared with 0.3 times the corresponding reproducibilities of the target methods, in agreement with the procedure of ISO 13528, Annex B2 in the next table;

	Deca-BDE #14152 in mg/kg	Deca-BDE #14153 in mg/kg
r (observed)	127.25	617.30
reference	IMEP-26	IMEP-26
0.3 x R (reference)	411.6	1129.0

Table 2: evaluation of the observed repeatabilities of the subsamples

Both calculated repeatabilities were in agreement with 0.3 times the assigned target reproducibility. Therefore, homogeneity of the subsamples of #14152 and #14153 was assumed.

To each of the participating laboratories one set of samples, (1* sample #14152 and 1* sample #14153) was sent on August 13, 2014.

2.5 ANALYSIS

The participants were requested to determine on both samples: octa-PBB, nona-PBB, deca-PBB, octa-BDE, nona-BDE and deca-BDE. It was explicitly requested to treat the samples as if they were routine samples and to report the analytical results using the indicated units on the report form and not to round the results, but report as much significant figures as possible. It was also requested not to report 'less than' results, which are above the detection limit, because such results can't be used for meaningful statistical calculations.
To get comparable results a detailed report form, on which the units were prescribed, was sent together with each set of samples. Also, a letter of instructions was added to the package.
The laboratories were requested to complete the report form with some details of the methods used.

3 RESULTS

During four weeks after sample despatch, the results of the individual laboratories were received. The original data are tabulated per sample in the appendix 1 of this report.
The laboratories are represented by the code numbers.

Directly after the deadline, a reminder fax was sent to those laboratories that did not report results at that moment. Shortly after the deadline, the available results were screened for suspect data. A result was called suspect in case the Huber Elimination Rule (a robust outlier test) found it to be an outlier. The laboratories that produced these suspect data were asked to check the results. Additional or corrected results are used for the data analysis and the original results are placed under 'Remarks' in the result tables in appendix 1.

3.1 STATISTICS

Statistical calculations were performed as described in the report 'iis Interlaboratory Studies: Protocol for the Organization, Statistics and Evaluation' of 2014 (iis-protocol, version 3.3).
For the statistical evaluation the *unrounded* (when available) figures were used instead of the rounded results. Results reported as '<…' or '>…" were not used in the statistical evaluation.

First, the normality of the distribution of the various data sets per determination was checked by means of the Lilliefors-test a variant of the Kolmogorov-Smirnov test and by the calculation of skewness and kurtosis. Evaluation of the three normality indicators in combination with the visual evaluation of the graphic Kernel density plot, lead to judgement of the normality being either 'unknown', 'OK', 'suspect' or 'not OK'. After removal of outliers, this check was repeated. Not all data sets proved to have a normal distribution, in which cases the statistical evaluation of the results should be used with due care.

According to ISO 5725 the original results per determination were submitted to Dixon's and/or Grubbs' and/or Rosner's outlier tests. Outliers are marked by D(0.01) for the Dixon's test, by G(0.01) or DG(0.01) for the Grubbs' test and by R(0.01) for the Rosner's test (ref. 18). Stragglers are marked by D(0.05) for the Dixon's test, by G(0.05) or DG(0.05) for the Grubbs' test and by R(0.05) for the Rosner's test. Both outliers and stragglers were not included in the calculations of averages and standard deviations.

For each assigned value the uncertainty was determined in accordance with ISO13528. Subsequently the calculated uncertainty was evaluated against the respective requirement based on the target reproducibility in accordance with ISO13528. When the uncertainty passed the evaluation no remarks are made in the report. However, when the uncertainty failed the evaluation it is mentioned in the report and it will have significant consequences for the evaluation of the test results.

Finally, the reproducibilities were calculated from the standard deviations by multiplying them with a factor of 2.8.

3.2 GRAPHICS

In order to visualise the data against the reproducibilities from literature, Gauss plots were made, using the sorted data for one determination (see appendix 1). On the Y-axis the reported analysis results are plotted. The corresponding laboratory numbers are on the X-axis.
The straight horizontal line presents the consensus value (a trimmed mean). The four striped lines, parallel to the consensus value line, are the +3s, +2s, -2s and -3s target reproducibility limits of the selected standard. Outliers and other data, which were excluded from the calculations, are represented as a cross. Accepted data are represented as a triangle. Furthermore, Kernel Density Graphs were made. This is a method for producing a smooth density approximation to a set of data that avoids some problems associated with histograms (see appendix 4; nos.14 and 15). Also a normal Gauss curve was projected over the Kernel Density Graph for reference.

3.3 Z-SCORES

To evaluate the performance of the participating laboratories the z-scores were calculated. As it was decided to evaluate the performance of the participants in this proficiency test (PT) against the literature requirements, the z-scores were calculated using a target standard deviation. This results in an evaluation independent of the spread of this interlaboratory study.

The target standard deviation was calculated from the target reproducibility (preferably taken from a standardized test method) by division with 2.8.
The z-scores were calculated in accordance with:

$$z_{(target)} = (\text{result} - \text{average of PT}) / \text{target standard deviation}$$

The $z_{(target)}$ scores are listed in the result tables in appendix 1.

When a laboratory did use a test method with a reproducibility that is significantly different from the reproducibility of the reference test method used in this report, it is strongly advised to recalculate the z-score, while using the reproducibility of the actual test method used. This in order to evaluate the fit-for-useness of the reported test result. See also appendix 4; ref. 16.

Absolute values for z<2 are very common and absolute values for z>3 are very rare. Therefore the usual interpretation of z-scores is as follows:

| z | < 1	good
1 < | z | < 2	satisfactory
2 < | z | < 3	questionable
3 < | z |	unsatisfactory

4 EVALUATION

In this interlaboratory study, no problems were encountered with the dispatch of the samples.
Fourteen participants reported results after the final reporting date and nine participants did not report any results at all. Not all laboratories were able to report all analytes requested.
Finally, 65 of the 76 participants submitted analysis results. The 65 reporting laboratories reported 274 numerical test results. Observed were 18 outlying results, which is 6.2% of all reported numerical test results. In proficiency studies, outlier percentages of 3% - 7.5% are quite normal.

Not all original data sets proved to have a normal Gaussian distribution. These are referred to as “not OK” or “suspect”. The statistical evaluation of these data sets should be used with due care,

For the determination of PBB and PBDE, the IEC62321 method is considered to be the official EC test method. Regretfully, this method does not (yet) mention precision data.

Normally, when no (suitable) reproducibility requirements from a test method are available, target requirements are estimated from the Horwitz equation.
However, from the IMEP-26 results (ref. 17) it was clear that earlier target standard deviations of 3 – 12% were not realistic for non-expert laboratories and that a realistic PT target standard deviation is 25% of the assigned value. This made the reproducibility requirements estimated by using the Horwitz equation to be unrealistically small.
Therefore, the target requirements were taken from the findings of interlaboratory study IMEP-26. In the IMEP-26 report the results of an interlaboratory study are presented on the determination of the sum of polybrominated biphenyls (PBB), the sum of polybrominated diphenylethers (PBDE) and several individual brominated diphenylethers (ref. 17).

4.1 EVALUATION PER COMPONENT AND PER SAMPLE

In this section, the results are discussed per component and per sample.
The participants were requested to report octa-, nona-, and deca-PBB and octa-, nona-, and deca-BDE. None of the participants, except laboratory 632, detected octa-, nona- or deca-PBB in any of the samples (#14152 and #14153) above the limit of detection.
The participants were also requested to report the analytical details of the methods. The analytical details are listed in Appendix 2.

Four of the six test results reported by laboratories 2558 and 3163 appeared to be statistical outliers. Because all test results of one laboratory are correlated, the remaining test results of laboratories 2558 and 3163 (for octa-BDE) were excluded manually prior to the statistical analysis.

Octa-BDE: The majority of the participants (around 40 participants) reported the absence of Octa-BDE or a small concentration that is near or below the LOD. For sample #14152, the reported numerical test results vary from 1.03 mg/kg to 37.5 mg/kg. For sample #14153, the reported numerical test results, except for one extremely high result, vary from 5.20 mg/kg to 51.89 mg/kg. These values may be close to LOD, therefore no further conclusions were drawn.

Nona-BDE: Some analytical problems were observed. For each of the samples #14152 and #14153, four statistical outliers were observed. The calculated reproducibility, after rejection of the four outliers for each of the samples is not in agreement with the target reproducibility. The reported numerical test results vary over a large range for samples #14152 and #14153, respectively 19.9-665 and 26.0–718 mg/kg.

Deca-BDE: Analytical problems were observed for a number of individual laboratories.
For sample #14152, the calculated reproducibility, after rejection of three statistical outliers, is in agreement with the target reproducibility. However, the reported numerical test results, except for one extremely high result, vary over a large range: 95 – 3511 mg/kg. Also for sample #14153 the calculated reproducibility, after rejection of three statistical outliers, is in agreement with the target reproducibility. However, the reported range of the test results is 344.5-10172 mg/kg.

4.2 PERFORMANCE EVALUATION OF THE GROUP OF LABORATORIES

A comparison has been made between the reproducibility as declared by the relevant standard and the reproducibility as found for the group of participating laboratories. The calculated reproducibilities and the target reproducibilities derived from the literature standards are compared in the next tables.

Analytes	unit	n	Average	2.8 * sd	R (target)
Octa-BDE #14152	mg/kg	10	7	9	(5)*
Nona-BDE #14152	mg/kg	52	82	76	57
Deca-BDE #14152	mg/kg	62	1526	1005	1068

Table 3: performance overview for sample #14152

Analytes	unit	n	Average	2.8 * sd	R (target)
Octa-BDE #14153	mg/kg	12	14	21	(10)*
Nona-BDE #14153	mg/kg	53	156	140	109
Deca-BDE #14153	mg/kg	61	3225	2162	2258

Table 4: performance overview for sample #14153

* values between brackets are for concentration near or below the limit of detection.

The observed reproducibilities for nona-BDE are larger than the target reproducibility requirements and therefore it was concluded that the determination of nona-BDE at low concentration levels in the evaluated materials is somewhat problematic.

5 COMPARISON WITH PREVIOUS PROFICIENCY TESTS

The uncertainties in the test results of the determined PBDE in the iis14P06 PT are listed in the next table and are comparable with previous proficiency tests.

	2014	2013	2012	2011	2010	2009	est. IMEP-26
hexa-BDE	n.e.	n.e.	n.e.	28%	n.e.	n.e.	25%
hepta-BDE	n.e.	n.e.	n.e.	15%	n.e.	n.e.	25%
octa-BDE	n.e.	n.e.	41%	25%	35 – 39%	21 – 36%	25%
nona-BDE	32 - 33%	33 – 38%	40 - 51%	15 – 23%	37 - 40%	21 – 39%	25%
deca-BDE	24%	14 – 21%	15 - 16%	20 – 25%	10 – 14%	13 – 37%	25%

table 5: development of uncertainties over the last years

6 DISCUSSION

For the determination of PBB and PBDE, the IEC62321 method is considered to be the official EC test method. In this proficiency test the majority of the participants used a version of IEC62321. Surprisingly not all laboratories that reported to have performed IEC62321 may have followed the guidelines for the sample preparation of this method.
Looking at the reported Analytical Details (see Appendix 2), about 50% of the participants used cryogenic milling to reduce the particle size. Also about 50% of the participants reduced the particle size to <500 µm (as is described in IEC62321). However, when evaluated separately, the effect of cryogenic milling appears to be small in all cases.

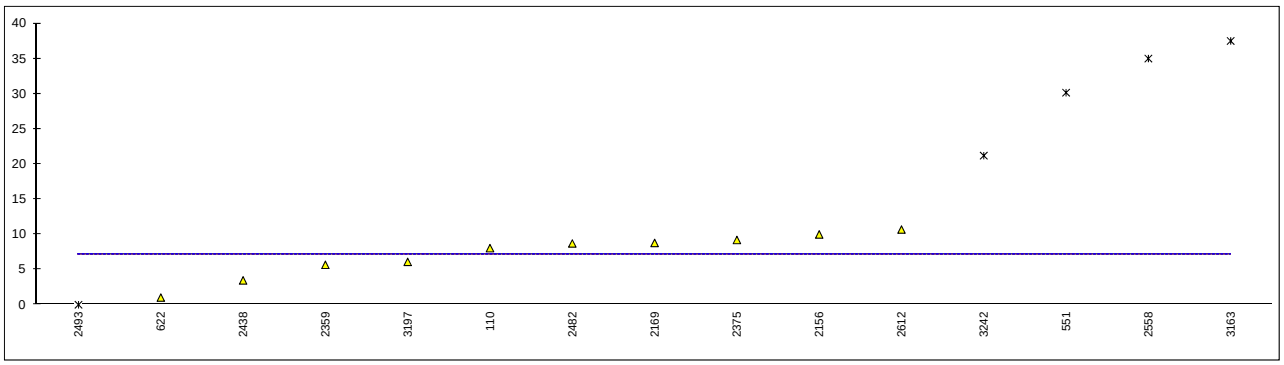
In answer to the question “What extraction solvent was used?”, most participants reported to have used Toluene, except three laboratories. From these three laboratories one laboratory reported to have used Dichloromethane, another laboratory a mixture of Toluene, THF and hexane and one laboratory used thermal desorption.
Other parts of the determination that may need attention are the possible congener degradation. IEC62321 mentions in Annex A.8 the necessary QC to check the congener degradation. Therefore the participants were requested to check the recovery. From the laboratories that answered this question with “YES”, the majority reported a recovery between 80% and 100%.
The test results of the laboratory using thermal desorption showed that the nona-BDE determination gave significantly higher values than the consensus values and significantly lower values for the deca-BDE. Unfortunately this laboratory did not check the recovery. The test results for this laboratory were outliers in both the nona-BDE and deca-BDE. This may suggest that the thermal desorption procedure may have caused congener degradation and changed the sample in a way that it affects the actual flame retardant concentrations.

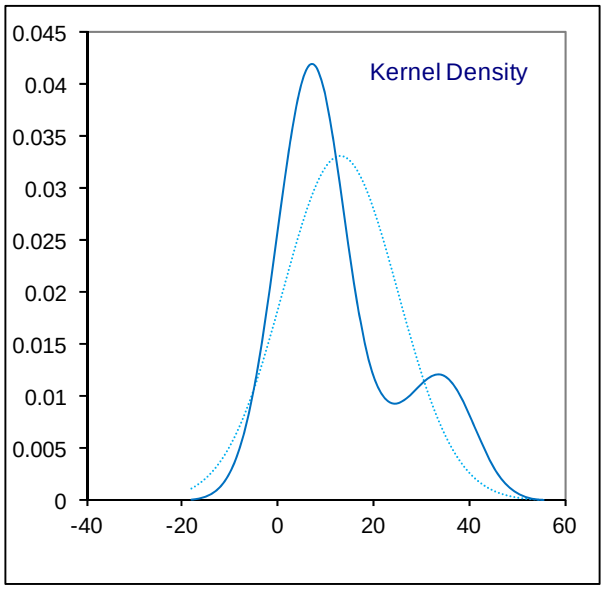
APPENDIX 1

Determination of Octabromo diphenyl ether on sample #14152; results in mg/kg

lab	method	value	mark	z(targ)	remarks
110	INH-3352	8.0525		-----	
339	IEC62321Mod.	<25		-----	
551	IEC62321	30.15	C,G(0.05)	-----	First reported: 34.05
601	IEC62321	n.d.		-----	
605	IEC62321	n.d.		-----	
607	IEC62321	n.d.		-----	
622	IEC62321	1.03		-----	
632		-----		-----	
826	IEC62321	n.d.		-----	
840	IEC62321	n.d.		-----	
1213	IEC62321	n.d.		-----	
2115	IEC62321	n.d.		-----	
2129		-----		-----	
2135		-----		-----	
2137	IEC62321	<1		-----	
2139	IEC62321	n.d.		-----	
2156	IEC62321	10		-----	
2165	IEC62321	<5		-----	
2169	IEC62321	8.79		-----	
2172	IEC62321	<5		-----	
2199	EPA3540	<10		-----	
2201	IEC62321	<5		-----	
2202		-----		-----	
2212	in house	<100		-----	
2216	in house	<100		-----	
2237		-----		-----	
2247	IEC62321	<5		-----	
2251		-----		-----	
2256	IEC62321	n.d.		-----	
2290	IEC62321	<5		-----	
2309	IEC62321	<50		-----	
2316	IEC62321	<50		-----	
2349	IEC62321	n.d.		-----	
2350		-----		-----	
2353	IEC62321	<5		-----	
2359	IEC62321	5.68		-----	
2365	GB/T26125	n.d.		-----	
2366	IEC62321	<5		-----	
2369	IEC62321	<5		-----	
2370	IEC62321	n.d.		-----	
2372	IEC62321	n.d.		-----	
2375	EPA3550C	9.21		-----	
2386	IEC62321	<50		-----	
2390		-----		-----	
2403	IEC62321	n.d.		-----	
2413		-----		-----	
2415	IEC62321	n.d.	C	-----	First reported: 73.19
2425		-----		-----	
2438	EN62321	3.47		-----	
2477		-----		-----	
2482	IEC62321	8.72		-----	
2488		-----		-----	
2492		-----		-----	
2493	in house	0	ex	-----	Result excluded, zero is not a real value
2500	IEC62321	n.d.		-----	
2558	EN62321	35	ex,C	-----	Result excluded, see §4.1, first reported: 120
2612	IEC62321	10.7		-----	
2620	in house	<1		-----	
3100	IEC62321	n.d.		-----	
3106		-----		-----	
3146	in house	<10		-----	
3153	IEC62321	<20		-----	
3163	in house	37.5	ex	-----	Result excluded, see §4.1
3172		-----		-----	
3182		-----		-----	
3185	IEC62321	n.d.		-----	
3190	IEC62321	<5		-----	
3191	IEC62321	<10		-----	
3197	IEC62321	6.1		-----	
3214	IEC62321	n.d.		-----	
3218	IEC62321	<5		-----	
3225	IEC62321	n.d.		-----	
3228	IEC62321	n.d.		-----	
3242	IEC62321	21.20	G(0.05)	-----	

normality	OK	
n	10	and 43 participants reported not detected or a 'less than' value
outliers	2 (+3ex)	
mean (n)	7.18	
st.dev. (n)	3.077	
R(calc.)	8.61	
R(IMEP-26)	(5.02)	

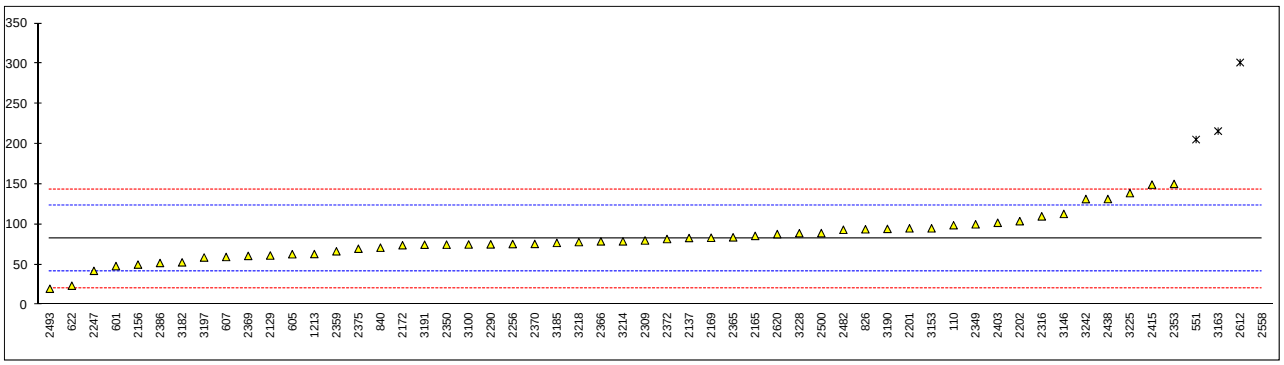


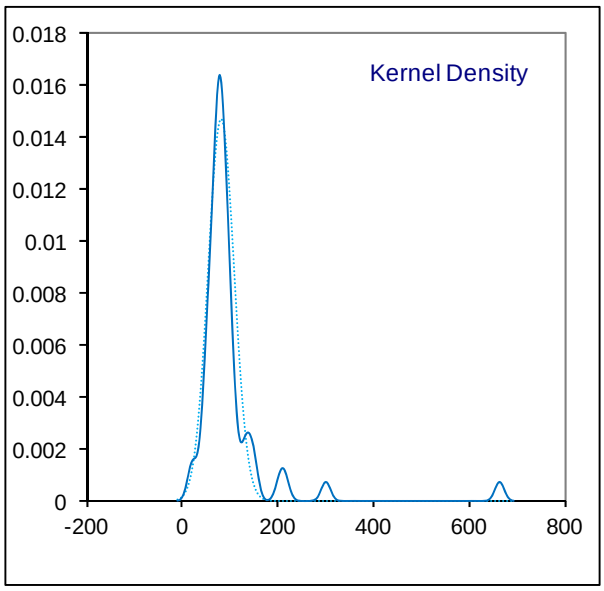


Determination Nonabromo diphenyl ether on sample #14152; results in mg/kg

lab	method	value	mark	z(targ)	remarks
110	INH-3352	98.942		0.82	
339	IEC62321Mod.	<25		< -2.78	
551	IEC62321	205.51	C,R(0.01)	6.02	First reported: 231.98
601	IEC62321	48.1		-1.65	
605	IEC62321	62.88		-0.93	
607	IEC62321	59.45		-1.10	
622	IEC62321	23.70		-2.84	
632		-----		-----	
826	IEC62321	93.9		0.58	
840	IEC62321	71		-0.54	
1213	IEC62321	63.1		-0.92	
2115	IEC62321	n.d.		-----	False negative?
2129	EN62321	61.3		-1.01	
2135		-----		-----	
2137	IEC62321	83.03	C	0.05	First reported: <1
2139	IEC62321	n.d.		-----	False negative?
2156	IEC62321	50		-1.56	
2165	IEC62321	85.7		0.18	
2169	IEC62321	83.4		0.07	
2172	IEC62321	74.09		-0.39	
2199	EPA3540	<10	C	< -3.51	First reported: 670
2201	IEC62321	95.1		0.64	
2202	in house	104	C	1.07	First reported: 250
2212		-----		-----	
2216		-----		-----	
2237		-----		-----	
2247	IEC62321	42.21		-1.94	
2251		-----		-----	
2256	IEC62321	75.52		-0.32	
2290	IEC62321	75.1243		-0.34	
2309	IEC62321	80		-0.10	
2316	IEC62321	110	C	1.36	First reported: 350
2349	IEC62321	100.1		0.88	
2350	IEC62321	74.8		-0.35	
2353	IEC62321	150.3		3.33	
2359	IEC62321	66.5		-0.76	
2365	GB/T26125	83.9		0.09	
2366	IEC62321	78.84		-0.16	
2369	IEC62321	60.8		-1.04	
2370	IEC62321	75.7		-0.31	
2372	IEC62321	81.8		-0.01	
2375	EPA3550C	69.73		-0.60	
2386	IEC62321	52		-1.46	
2390		-----		-----	
2403	IEC62321	102		0.97	
2413		-----		-----	
2415	IEC62321	149.47	C	3.29	First reported: 320.97
2425		-----		-----	
2438	EN62321	131.51		2.41	
2477		-----		-----	
2482	IEC62321	93.29		0.55	
2488		-----		-----	
2492		-----		-----	
2493	in house	19.92		-3.03	
2500	IEC62321	89.1		0.35	
2558	EN62321	665	C,R(0.01)	28.43	First reported: 1222
2612	IEC62321	301.3	C,R(0.01)	10.69	First reported: 232
2620	in house	87.9		0.29	
3100	IEC62321	75.02		-0.34	
3106		-----		-----	
3146	in house	113		1.51	
3153	IEC62321	95.1		0.64	
3163	in house	216	R(0.01)	6.53	
3172		-----		-----	
3182	IEC62321	52.76		-1.43	
3185	IEC62321	77		-0.25	
3190	IEC62321	94.4		0.60	
3191	IEC62321	74.7		-0.36	
3197	IEC62321	58.8		-1.13	
3214	IEC62321	78.9		-0.15	
3218	IEC62321	78		-0.20	
3225	IEC62321	138.90		2.77	
3228	IEC62321	89		0.34	
3242	IEC62321	131.50		2.41	

normality	OK
n	52
outliers	4
mean (n)	82.02
st.dev. (n)	27.244
R(calc.)	76.28
R(IMEP-26)	57.42

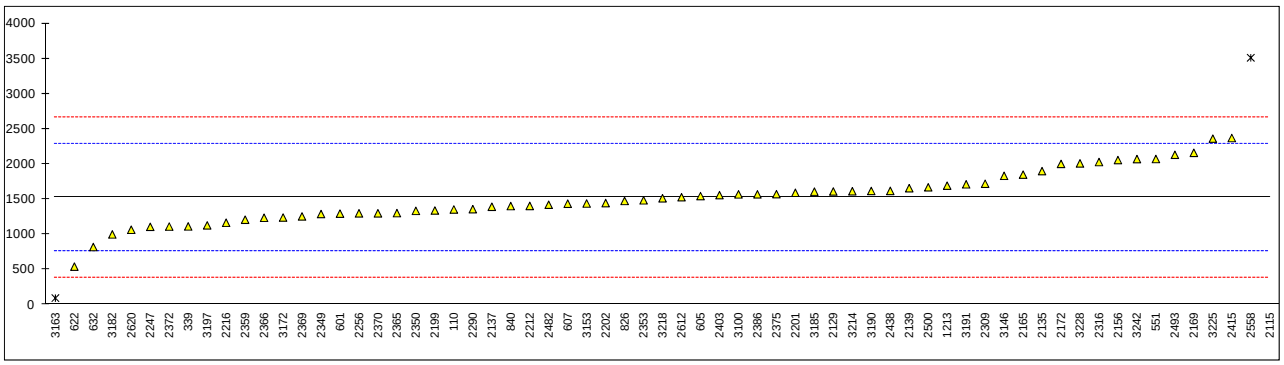


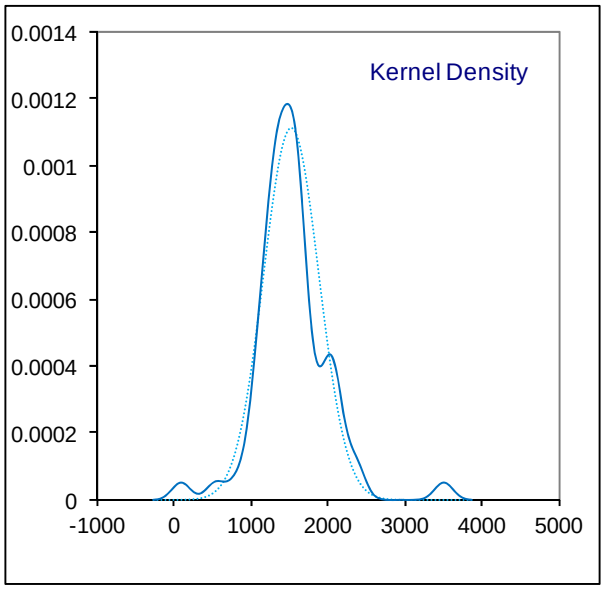


Determination of Decabromo diphenyl ether on sample #14152; results in mg/kg

lab	method	value	mark	z(targ)	remarks
110	INH-3352	1354.85		-0.45	
339	IEC62321Mod.	1114		-1.08	
551	IEC62321	2071.76	C	1.43	First reported: 2250.77
601	IEC62321	1295.4		-0.60	
605	IEC62321	1544.86		0.05	
607	IEC62321	1436.78		-0.23	
622	IEC62321	542.63		-2.58	
632	in house	820.75	C	-1.85	First reported: 401.38
826	IEC62321	1476.1		-0.13	
840	IEC62321	1403		-0.32	
1213	IEC62321	1693.1		0.44	
2115	IEC62321	114263.74	R(0.01)	295.52	
2129	EN62321	1610.7		0.22	
2135	in house	1900		0.98	
2137	IEC62321	1393.16		-0.35	
2139	IEC62321	1657.37		0.34	
2156	IEC62321	2057		1.39	
2165	IEC62321	1849.6		0.85	
2169	IEC62321	2160		1.66	
2172	IEC62321	2002		1.25	
2199	EPA3540	1340	C	-0.49	First reported: 2990
2201	IEC62321	1591.7		0.17	
2202	in house	1446		-0.21	
2212	in house	1405		-0.32	
2216	in house	1166.6		-0.94	
2237		-----		-----	
2247	IEC62321	1107.92		-1.10	
2251		-----		-----	
2256	IEC62321	1300		-0.59	
2290	IEC62321	1359.2325		-0.44	
2309	IEC62321	1720.5		0.51	
2316	IEC62321	2029		1.32	
2349	IEC62321	1290.0		-0.62	
2350	IEC62321	1335		-0.50	
2353	IEC62321	1485.3		-0.11	
2359	IEC62321	1209		-0.83	
2365	GB/T26125	1302.8		-0.58	
2366	IEC62321	1237.5		-0.76	
2369	IEC62321	1256.5		-0.71	
2370	IEC62321	1300		-0.59	
2372	IEC62321	1112		-1.09	
2375	EPA3550C	1572.6		0.12	
2386	IEC62321	1570		0.12	
2390		-----		-----	
2403	IEC62321	1559		0.09	
2413		-----		-----	
2415	IEC62321	2370.50	C	2.21	First reported: 1478.08
2425		-----		-----	
2438	EN62321	1618.82		0.24	
2477		-----		-----	
2482	IEC62321	1422	C	-0.27	First reported: 4161
2488		-----		-----	
2492		-----		-----	
2493	in house	2132	C	1.59	First reported: 4594.2
2500	IEC62321	1670.2		0.38	
2558	EN62321	3511	C,R(0.01)	5.20	First reported: 8091
2612	IEC62321	1529		0.01	
2620	in house	1066.2		-1.21	
3100	IEC62321	1569.46		0.11	
3106		-----		-----	
3146	in house	1833		0.80	
3153	IEC62321	1440		-0.23	
3163	in house	95	R(0.05)	-3.75	
3172		1240.4		-0.75	
3182	IEC62321	1000.30		-1.38	
3185	IEC62321	1608		0.22	
3190	IEC62321	1618.0		0.24	
3191	IEC62321	1712.5	C	0.49	First reported: 6628.7
3197	IEC62321	1128.7		-1.04	
3214	IEC62321	1614.0		0.23	
3218	IEC62321	1514		-0.03	
3225	IEC62321	2361.62		2.19	
3228	IEC62321	2010		1.27	
3242	IEC62321	2071.46		1.43	

normality	OK
n	62
outliers	3
mean (n)	1525.95
st.dev. (n)	359.099
R(calc.)	1005.48
R(IMEP-26)	1068.16

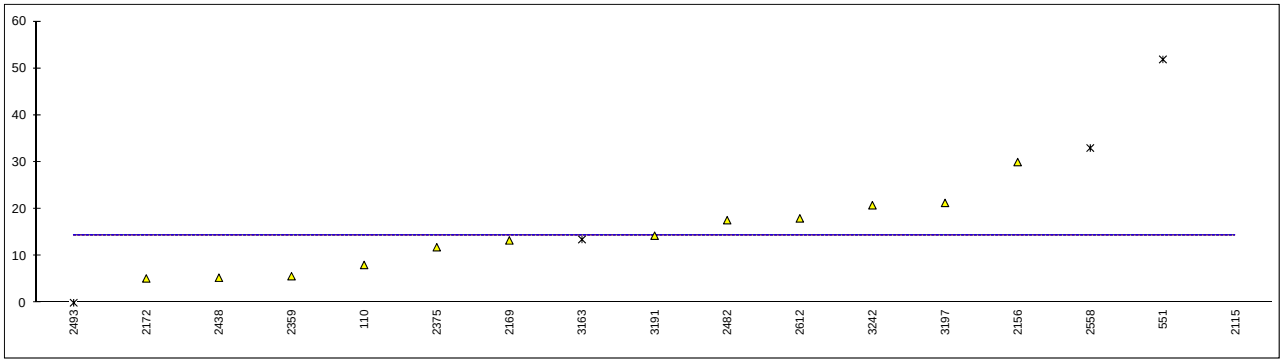


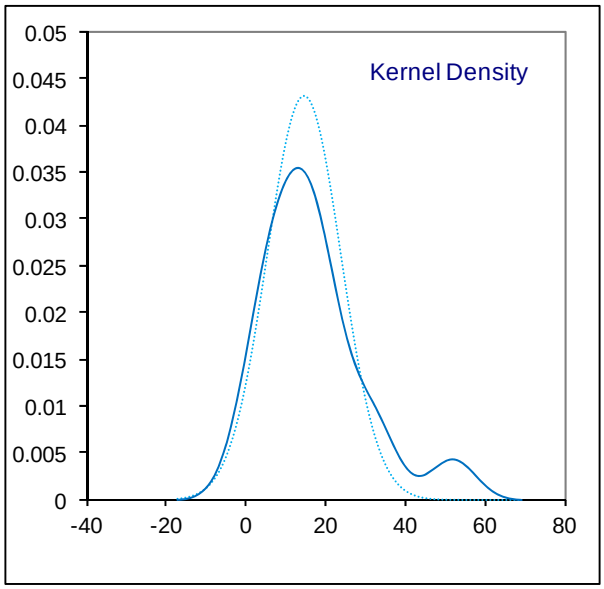


Determination of Octabromo diphenyl ether on sample #14153; results in mg/kg

lab	method	value	mark	z(targ)	remarks
110	INH-3352	8.0689		-----	
339	IEC62321Mod.	<25		-----	
551	IEC62321	51.89	C,G(0.01)	-----	First reported: 53.35
601	IEC62321	n.d.		-----	
605	IEC62321	n.d.		-----	
607	IEC62321	n.d.		-----	
622	IEC62321	n.d.		-----	
632		-----		-----	
826	IEC62321	n.d.		-----	
840	IEC62321	n.d.		-----	
1213	IEC62321	n.d.		-----	
2115	IEC62321	22060.79	G(0.01)	-----	False positive?
2129		-----		-----	
2135		-----		-----	
2137	IEC62321	<1		-----	
2139	IEC62321	n.d.		-----	
2156	IEC62321	30		-----	
2165	IEC62321	<5		-----	
2169	IEC62321	13.3		-----	
2172	IEC62321	5.197		-----	
2199	EPA3540	<10		-----	
2201	IEC62321	<5		-----	
2202		-----		-----	
2212	in house	<100		-----	
2216	in house	<100		-----	
2237		-----		-----	
2247	IEC62321	<5		-----	
2251		-----		-----	
2256	IEC62321	n.d.		-----	
2290	IEC62321	<5		-----	
2309	IEC62321	<50		-----	
2316	IEC62321	<50	C	-----	First reported: 209
2349	IEC62321	n.d.		-----	
2350		-----		-----	
2353	IEC62321	<5		-----	
2359	IEC62321	5.67		-----	
2365	GB/T26125	n.d.		-----	
2366	IEC62321	<5		-----	
2369	IEC62321	<5		-----	
2370	IEC62321	n.d.		-----	
2372	IEC62321	n.d.		-----	
2375	EPA3550C	11.85		-----	
2386	IEC62321	<50		-----	
2390		-----		-----	
2403	IEC62321	n.d.		-----	
2413		-----		-----	
2415	IEC62321	n.d.	C	-----	First reported: 74.86
2425		-----		-----	
2438	EN62321	5.35		-----	
2477		-----		-----	
2482	IEC62321	17.62		-----	
2488		-----		-----	
2492		-----		-----	
2493	in house	0	ex	-----	Result excluded, zero is not a real value
2500	IEC62321	n.d.		-----	
2558	EN62321	33	ex,C	-----	Result excluded, §4.1, first reported: 148
2612	IEC62321	18.0		-----	
2620	in house	<1		-----	
3100	IEC62321	n.d.		-----	
3106		-----		-----	
3146	in house	<10		-----	
3153	IEC62321	<20		-----	
3163	in house	13.5	ex	-----	Result excluded, §4.1
3172		-----		-----	
3182		-----		-----	
3185	IEC62321	n.d.		-----	
3190	IEC62321	<5		-----	
3191	IEC62321	14.3		-----	
3197	IEC62321	21.3		-----	
3214	IEC62321	n.d.		-----	
3218	IEC62321	<5		-----	
3225	IEC62321	n.d.		-----	
3228	IEC62321	n.d.		-----	
3242	IEC62321	20.80		-----	

normality	OK	
n	12	and 41 participants reported not detected or a 'less than value'
outliers	2 (+3ex)	
mean (n)	14.29	
st.dev. (n)	7.662	
R(calc.)	21.45	
R(IMEP-26)	(10.00)	

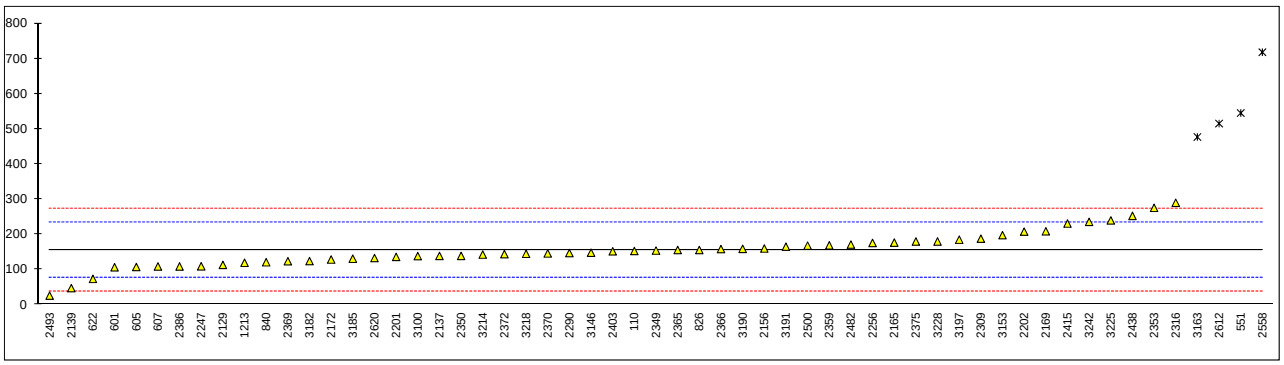


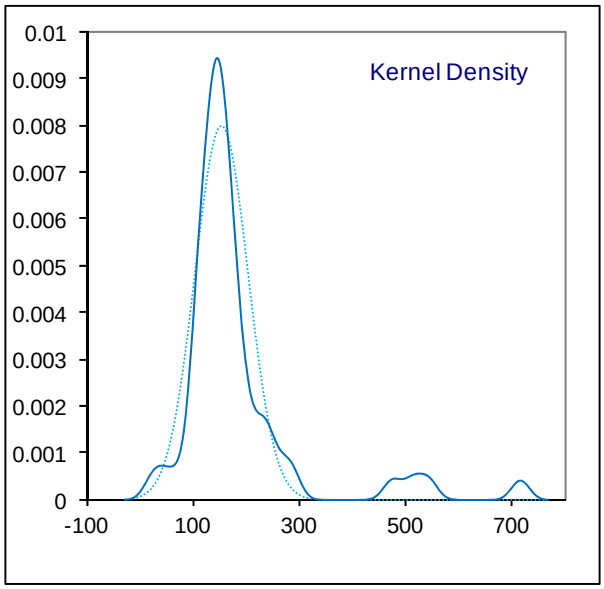


Determination of Nonabromo diphenyl ether on sample #14153; results in mg/kg

lab	method	value	mark	z(targ)	remarks
110	INH-3352	152.8896		-0.07	
339	IEC62321Mod.	<25		< -3.36	
551	IEC62321	545.13	C,R(0.01)	10.00	First reported: 575.21
601	IEC62321	106.7		-1.26	
605	IEC62321	107.48		-1.24	
607	IEC62321	108.93		-1.20	
622	IEC62321	73.60		-2.11	
632		-----		-----	
826	IEC62321	155.8		0.00	
840	IEC62321	121		-0.89	
1213	IEC62321	119.6		-0.93	
2115	IEC62321	n.d.		-----	False negative?
2129	EN62321	113.3		-1.09	
2135		-----		-----	
2137	IEC62321	138.83	C	-0.43	First reported: <1
2139	IEC62321	47.32		-2.78	
2156	IEC62321	160		0.11	
2165	IEC62321	176.8		0.54	
2169	IEC62321	209		1.37	
2172	IEC62321	128.7		-0.70	
2199	EPA3540	<10	C	< -3.75	First reported: 1580
2201	IEC62321	136.2		-0.50	
2202	in house	208	C	1.34	First reported: 342
2212		-----		-----	
2216		-----		-----	
2237		-----		-----	
2247	IEC62321	109.39		-1.19	
2251		-----		-----	
2256	IEC62321	175.8		0.51	
2290	IEC62321	147.1104		-0.22	
2309	IEC62321	188.0		0.83	
2316	IEC62321	290	C	3.45	First reported: 840
2349	IEC62321	154.1		-0.04	
2350	IEC62321	139		-0.43	
2353	IEC62321	275.7		3.08	
2359	IEC62321	169		0.34	
2365	GB/T26125	155.8		0.00	
2366	IEC62321	158.4		0.07	
2369	IEC62321	123.8		-0.82	
2370	IEC62321	146		-0.25	
2372	IEC62321	144		-0.30	
2375	EPA3550C	179.93		0.62	
2386	IEC62321	109		-1.20	
2390		-----		-----	
2403	IEC62321	152		-0.10	
2413		-----		-----	
2415	IEC62321	231.04	C	1.93	First reported: 698.79
2425		-----		-----	
2438	EN62321	252.79		2.49	
2477		-----		-----	
2482	IEC62321	171.24		0.40	
2488		-----		-----	
2492		-----		-----	
2493	in house	26.00	C	-3.33	First reported: 11.29
2500	IEC62321	168.1		0.32	
2558	EN62321	718	C,R(0.01)	14.44	First reported: 1449
2612	IEC62321	515.2	C,R(0.01)	9.23	First reported: 406
2620	in house	132.9		-0.59	
3100	IEC62321	138.34		-0.45	
3106		-----		-----	
3146	in house	148		-0.20	
3153	IEC62321	198		1.08	
3163	in house	477	R(0.01)	8.25	
3172		-----		-----	
3182	IEC62321	124.30		-0.81	
3185	IEC62321	131		-0.64	
3190	IEC62321	159.0		0.08	
3191	IEC62321	165.3		0.24	
3197	IEC62321	185.1		0.75	
3214	IEC62321	142.8		-0.33	
3218	IEC62321	145		-0.28	
3225	IEC62321	239.90	C	2.16	First reported: 300.11
3228	IEC62321	180		0.62	
3242	IEC62321	235.80		2.06	

normality	suspect
n	53
outliers	4
mean (n)	155.77
st.dev. (n)	49.937
R(calc.)	139.82
R(IMEP-26)	109.04

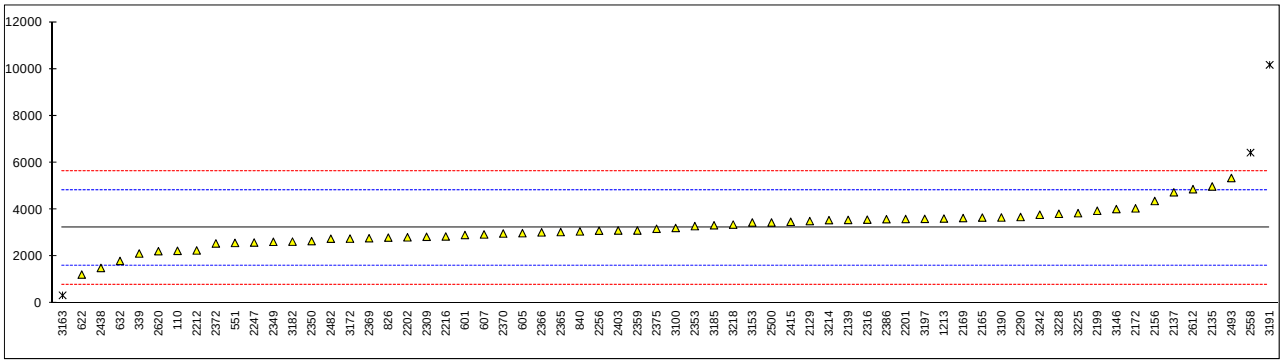


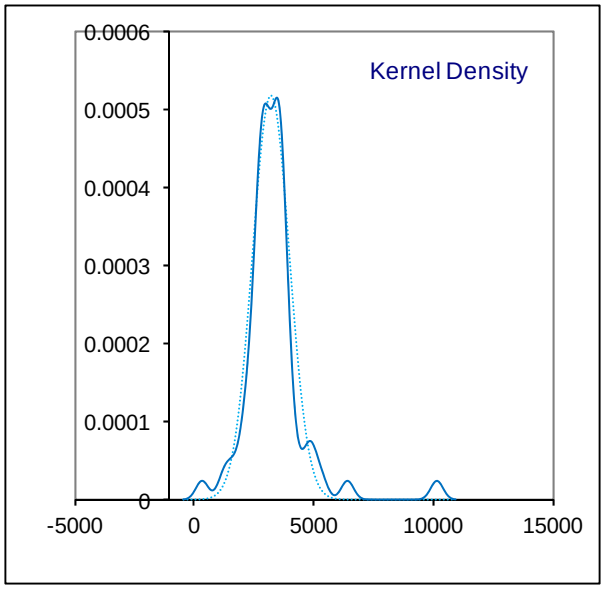


Determination of Decabromo diphenyl ether on sample #14153; results in mg/kg

lab	method	value	mark	z(targ)	remarks
110	INH-3352	2242.14		-1.22	
339	IEC62321Mod.	2129		-1.36	
551	IEC62321	2578.66	C	-0.80	First reported: 2471.35
601	IEC62321	2916.5		-0.38	
605	IEC62321	2993.72		-0.29	
607	IEC62321	2941.18		-0.35	
622	IEC62321	1228.38		-2.48	
632	in house	1810.92		-1.75	
826	IEC62321	2805.8		-0.52	
840	IEC62321	3070		-0.19	
1213	IEC62321	3618.6		0.49	
2115	IEC62321	n.d.		-----	False negative?
2129	EN62321	3510.3		0.35	
2135	in house	4986		2.18	
2137	IEC62321	4737.36		1.88	
2139	IEC62321	3559.36		0.41	
2156	IEC62321	4367		1.42	
2165	IEC62321	3659.8		0.54	
2169	IEC62321	3640		0.51	
2172	IEC62321	4053		1.03	
2199	EPA3540	3950	C	0.90	First reported: 13010
2201	IEC62321	3599.0		0.46	
2202	in house	2818		-0.51	
2212	in house	2258		-1.20	
2216	in house	2853.3		-0.46	
2237		-----		-----	
2247	IEC62321	2596.01		-0.78	
2251		-----		-----	
2256	IEC62321	3100		-0.16	
2290	IEC62321	3685.0493		0.57	
2309	IEC62321	2839.8		-0.48	
2316	IEC62321	3570	C	0.43	First reported: 4050
2349	IEC62321	2625.1		-0.74	
2350	IEC62321	2656		-0.71	
2353	IEC62321	3294.3		0.09	
2359	IEC62321	3109		-0.14	
2365	GB/T26125	3041.7		-0.23	
2366	IEC62321	3027.9		-0.24	
2369	IEC62321	2778.0		-0.55	
2370	IEC62321	2980		-0.30	
2372	IEC62321	2556		-0.83	
2375	EPA3550C	3180.6		-0.06	
2386	IEC62321	3590		0.45	
2390		-----		-----	
2403	IEC62321	3108		-0.15	
2413		-----		-----	
2415	IEC62321	3480.26	C	0.32	First reported: 6416
2425		-----		-----	
2438	EN62321	1510.48		-2.13	
2477		-----		-----	
2482	IEC62321	2758	C	-0.58	First reported: 10573
2488		-----		-----	
2492		-----		-----	
2493	in house	5347.27		2.63	
2500	IEC62321	3450.1		0.28	
2558	EN62321	6427	C,R(0.05)	3.97	First reported: 16890
2612	IEC62321	4870		2.04	
2620	in house	2226.5		-1.24	
3100	IEC62321	3216.20		-0.01	
3106		-----		-----	
3146	in house	4021		0.99	
3153	IEC62321	3450		0.28	
3163	in house	344.5	R(0.05)	-3.57	
3172		2761.9		-0.57	
3182	IEC62321	2634.02		-0.73	
3185	IEC62321	3332		0.13	
3190	IEC62321	3663.8		0.54	
3191	IEC62321	10172.0	C,R(0.01)	8.61	First reported: 18981.3
3197	IEC62321	3605.1		0.47	
3214	IEC62321	3550.0		0.40	
3218	IEC62321	3361		0.17	
3225	IEC62321	3847.29		0.77	
3228	IEC62321	3820		0.74	
3242	IEC62321	3779.97		0.69	

normality	OK
n	61
outliers	3
mean (n)	3225.38
st.dev. (n)	772.046
R(calc.)	2161.73
R(IMEP-26)	2257.77





APPENDIX 2: Analytical details for sample #14152

Lab	cryogenic milled	max. particle size	particle size checked	extraction solvent used	recovery checked	internal standard used
110	Yes		No	Toluene	Yes, 110% for Deca BDE	Deca chloro biphenyl, Accustandard
339	No	<2 mm	with a rubber	Toluene	No	PCB 209, Fluka
551	No	<1 mm		Toluene		
601	No	<1 mm		Toluene	Yes, 100.9%	PCB 209, Dr. Ehrenstorfer GmbH
605	No	<500 µm	through a sieve of 0.5 mm	Toluene	Yes, 106%	PCB 209, Dr. Ehrenstorfer GmbH
607	No	<500 µm	through a sieve of 0.5 mm	Toluene	Yes, 92%	PCB 209, Dr. Ehrenstorfer GmbH
622	Yes	<1 mm		Toluene	No	
632	No			Toluene		
826	Yes	<500 µm	No	Toluene	Yes, 78%	CB209, Supelco
840	No	<1 mm	No	Toluene	Yes, 104 and 92%	CB209, Chemservice
1213	Yes	<500 µm		Toluene	No	PCB-209
2115	Yes			Toluene	Yes	No
2129	Yes	<500 µm	No	Dichloro-methane	No	PCB-209, Riedel de Haen 35587
2135	No	<500 µm		Chloroform	No	
2137	Yes	<500 µm		Toluene	No	
2139	Yes			Toluene	No	
2156	Yes	<1 mm		Toluene	No	
2165	No	<1 mm	through a sieve of 1 mm	Toluene	No	PCB209
2169	Yes	<250 µm	Visual Check	Toluene	Yes	Phenanthrene-d10, Wako Pure Chemical Industries Ltd
2172	Yes	<500 µm	through a sieve of 0.5 mm	Toluene	Yes, 95%	Anthrene-D10 Dr. E
2199		<1 mm		Toluene	No	
2201	Yes	<500 µm	through a sieve of 0.5 mm	Toluene	No	No
2202	No			Toluene, THF/Hexane	Yes, 96.8%	4,4-Dibromo octafluoro biphenyl (Accustandard)
2212	No	<1 mm	through a sieve of 1 mm	Toluene	No	Decachlorobiphenyl
2216	Yes			Toluene		
2237						
2247	Yes	<75 µm	Visual Experience	Toluene	Yes, 89%	No
2251						
2256	Yes	<500 µm	through a sieve of 0.5 mm	Toluene	Yes, 85%	Decachlorodiphenyl
2290	No	<1 mm		Toluene	Yes, 81%	PCB 209, Accustandard
2309	Yes	<250 µm	through a sieve of 250 µm	Toluene	Yes, 98%	Deca chloro biphenyl, Accustandard
2316	Yes	<500 µm	through a sieve of 0.5 mm	Toluene	Yes, 90 to 110%	CB209:Deca chloro biphenyl, Accustandard
2349	No	<500 µm	through a sieve of 0.5 mm	Toluene	No	IEC 62321
2350	No	<1 mm		Toluene	Yes, 109%	Decachlorodiphenyl, Supelco
2353	Yes	<250 µm	through a sieve of 500 µm	Toluene	No	PCB 209 (Dr. E)
2359	No	1*1*1 mm		Toluene	Yes	Mirex, Dr E, Casno 2385-85-5, QCB, Dr. E, Casno. 608-93-5
2365	No	<500 µm	through a sieve of 0.5 mm	Toluene	Yes, 110%	PCB 209, Accustandard

Lab	cryogenic milled	max. particle size	particle size checked	extraction solvent used	recovery checked	internal standard used
2366	No	<500 µm	through a sieve of 0.5 mm	Toluene	No	No
2369	No	<1 mm	through a sieve of 1 mm	Toluene	Yes, 99.2%	CB209, Chemservice
2370	Yes	<500 µm	through a sieve of 0.5 mm	Toluene	Yes, 97.8%	2,2',3,3',4,4',5,5',6,6'_Decachlorobiphenyl brand: Accustandard
2372	Yes	<500 µm	through a sieve of 0.5 mm	Toluene	No	Decachlorobiphenyl
2375	No	2.9*2.9 mm	with vernier	Toluene	Yes, 85%	Decachlorobiphenyl, Dr. Ehrenstorfer
2386	Yes	<1 mm		Toluene	No	$^{13}C_{12}$ BDE-209 and $^{13}C_{12}$ BDE-206 Cambridge Isotope Laboratories
2390						
2403	No	<500 µm	through a sieve of 0.5 mm	Toluene	Yes, 97%	DecaCB
2413						
2415	Yes	<1 mm	through a sieve of 1 mm	Toluene	No	No
2425						
2438	No	<2 mm	not measured	Toluene	Yes, 60% / 64%	2,2',3,3',4,4',5,5',6,6'_Decachlorobiphenyl (Accustandard)
2477						
2482	No			Toluene	Yes, 94.6%	PCB 209
2488						
2492						
2493	No	<3 mm		Toluene	No	C13 PBBE 209
2500	Yes	<1 mm	through a sieve of 1 mm	Toluene	Yes, 85%	Anthracene-d10
2558	No			Toluene	No	PCB 209
2612	No	as received	as received	Toluene	No	PCB 209 (1000 microgram/ml), Neochema
2620	Yes			Toluene	Yes, 131% / 179%	^{13}C labelled BDE-209 (Wellington)
3100	No	<500 µm	through a sieve of 0.5 mm	Toluene	No	
3106						
3146	No	No	No	---	Yes, 90%	PCB 209
3153	Yes	<500 µm	through a sieve of 0.5 mm	Toluene	No	Tribromodiphenyl ether, Wellington
3163				Thermische desorptie		
3172	Yes	<500 µm		Toluene	Yes, 90%	MBDE $^{13}C_{12}$ -209
3182	Yes	<500 µm	through a sieve of 0.5 mm	Toluene	No	External
3185	No	<500 µm	through a sieve of 0.5 mm	Toluene	Yes, 92%	2,2',3,3',4,4',5,5',6,6'_Decachlorobi-phenyl Accustandard
3190	Yes	<125 µm	through a sieve of 125 µm	Toluene	No	None
3191	Yes	<500 µm	through a sieve of 0.5 mm	Toluene	No	PCB 209, Dr. Ehrenstorfer GmbH
3197	Yes	<500 µm	through a sieve of 0.5 mm	Toluene	No	PCB 209, Dr. Ehrenstorfer GmbH
3214	Yes	<500 µm	through a sieve of 0.5 mm	Toluene	Yes, 92%	Decachlorobiphenyl, Chem Service
3218	Yes	<200 µm	through a sieve of 200 µm	Toluene	No	
3225	No	<1 mm		---	Yes	According to IEC62321
3228	No	<1 mm	through a sieve of 1 mm	Toluene	No	4,4-Dibromo octafluoro biphenyl
3242	No	<1 mm		Toluene	Yes, 80%	

APPENDIX 3

Number of participating laboratories per country

1 lab in BANGLADESH
3 labs in BRAZIL
1 lab in FRANCE
9 labs in GERMANY
6 labs in HONG KONG
1 lab in HUNGARY
4 labs in INDIA
1 lab in INDONESIA
2 labs in ITALY
1 lab in JAPAN
5 labs in KOREA
4 labs in MALAYSIA
1 lab in MEXICO
17 labs in P.R. of CHINA
1 lab in PAKISTAN
1 lab in PHILIPPINES
1 lab in SINGAPORE
3 labs in TAIWAN R.O.C.
1 lab in THAILAND
1 lab in THE NETHERLANDS
3 labs in TURKEY
3 labs in U.S.A.
4 labs in VIETNAM

APPENDIX 4

Abbreviations:

C = final result after checking of first reported suspect result
D(0.01) = outlier in Dixon's outlier test
D(0.05) = straggler in Dixon's outlier test
G(0.01) = outlier in Grubbs' outlier test
G(0.05) = straggler in Grubbs' outlier test
DG(0.01) = outlier in Double Grubbs' outlier test
DG(0.05) = straggler in Double Grubbs' outlier test
R(0.01) = outlier in Rosner outlier test
R(0.05) = straggler in Rosner outlier test
n.a. = not applicable
n.d. = not detected
IMEP = International Measurement Evaluation Programme

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