Results of Proficiency Test Brominated Flame retardants September 2010

Organised by: Institute for Interlaboratory Studies
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1 INTRODUCTION

Worldwide, many consumer products with plastic parts are produced that contain brominated compounds as flame retardants. These brominated compounds are exceptionally effective at fire prevention.
Since the 1990s scientists have questioned the safety of the Poly Brominated Biphenyls (PBB) and Poly Brominated Diphenyls Ethers (PBDE), that 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, 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.
As an alternative, participation in a proficiency test may enable the laboratories to check their performance and thus to increase this comparability. Therefore, 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, the Institute for Interlaboratory Studies decided to continue the interlaboratory study for the determination of PBB and PBDE in the 2010/2011 PT program.
In the interlaboratory study of September 2010, 46 laboratories from 18 different countries participated (See appendix 3). In this report, the results of the 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 (approximately 5 gram each), both positive on a number of brominated flame retardants and labelled #1050 and #1051 respectively. Participants were also requested to report some details of the methods used.

2.1 QUALITY SYSTEM

The Institute for Interlaboratory Studies in Spijkenisse, the Netherlands, has implemented a quality system based on ISO guide 43 and ILAC-G13:2007. This ensures 100% confidentially of participant's data. Also, customer's satisfaction is measured on a 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 January 2010 (iis-protocol, version 3.2). This protocol can be downloaded from the iis website http://www.iisnl.com.

2.3 CONFIDENTIALITY STATEMENT

All data present 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, positive for several brominated flame retardants, were selected. The first material (#1050) was a black coloured granulate. The second material (#1051) was also a black coloured granulate. Both materials were divided over plastic bags, approx. 5 grams for each sample.
The homogeneity of the subsamples was checked by determination of PBDE content on 4 stratified random selected subsamples.

	Deca-BDE in #1050	Deca-BDE in #1051
Sample 1	9998 mg/kg	1084 mg/kg
Sample 2	9953 mg/kg	1048mg/kg
Sample 3	10326 mg/kg	1063 mg/kg
Sample 4	10092 mg/kg	1065 mg/kg

Table 1: results of the homogeneity test on the subsamples #1050 and #1051

From the above results of the homogeneity test, the relative between sample standard deviations RSD_r were calculated and compared with 0.3 times the relative proficiency target standard deviations RSD_R in agreement with the procedure of ISO 13528, Annex B2 in the next table:

	Deca-BDE in #1050	Deca-BDE in #1051
RSD_r (observed)	1.7%	1.4%
reference method	Horwitz	Horwitz
0.3 x RSD_R (reference method)	4.0%	5.6%

Table 2: relative repeatability standard deviations of Octa-BDE contents of the subsamples #1050 and #1051

The calculated variation coefficients RSDr are both in good agreement with the estimated targets, calculated using the Horwitz equation. Therefore, homogeneity of all subsamples was assumed.

To each of the participating laboratories one set of samples, (1* sample #1050 and 1* sample #1051) was sent on August 18, 2010.

2.5 ANALYSIS

The participants were requested to determine on both samples: Octa-BB, nona-BB, deca-BB, octa-BDE, nona-BDE and deca-BDE. It was explicitly requested to treat the samples as if it 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 not 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

The statistical calculations were performed as described in the procedures in the report 'iis Interlaboratory Studies, Protocol for the Organisation, Statistics and Evaluation' of January 2010 (iis-protocol, version 3.2).

First, the normality of the distribution of the various data sets per determination was checked by means of the Lilliefors-test. After removal of outliers this check was repeated. All data sets proved to have a normal distribution.

In accordance to ISO 5725 (1986 and 1994) the original results per determination were submitted subsequently to Dixon and Grubbs outlier tests. Outliers are marked by D(0.01) for the Dixon test, by G(0.01) or DG(0.01) for the Grubbs test. Stragglers are marked by D(0.05) for the Dixon test, by G(0.05) or DG(0.05) for the Grubbs test. Both outliers and stragglers were not included in the calculations of averages and standard deviations.

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 under 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; nr.14 and 15).

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.

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:

$\lvert z \rvert < 1$	good
$1 < \lvert z \rvert < 2$	satisfactory
$2 < \lvert z \rvert < 3$	questionable
$3 < \lvert z \rvert$	unsatisfactory

4 EVALUATION

In this interlaboratory study, no problems were encountered with despatch of the samples. Four participants reported results after the final reporting date and three participants did not report any results at all. Not all laboratories were able to report all analytes requested.
Finally, 43 of the 46 participants submitted analysis results. The 43 reporting laboratories reported 219 numerical results. Observed were 28 outlying results, which is 11.3%. In proficiency studies, outlier percentages of 3% - 7.5% are quite normal.
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 reproducibility requirements. Therefore, the target requirements in this study were estimated using the Horwitz equation.

4.1 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 (lit)
Octa-BDE #1050	mg/kg	29	35.0	37.8	27.5
Nona-BDE #1050	mg/kg	37	530.1	548.8	160.0
Deca-BDE #1050	mg/kg	35	9679	2791	1089

Table 3: performance overview for sample #1050

Parameter	unit	n	Average	2.8 * sd	R (lit)
Octa-BDE #1051	mg/kg	11	5.37	5.19	5.61
Nona-BDE #1051	mg/kg	35	78.9	87.9	31.7
Deca-BDE #1051	mg/kg	36	1171.8	456.7	181.2

Table 4: performance overview for sample #1051

Without further statistical calculations, it can be concluded that there is not a good compliance of the group of participating laboratories with the relevant target reproducibility.

The analytes that were problematic are discussed in paragraph 4.2.

4.2 EVALUATION PER COMPONENT

In this section the results are discussed per analyte.

Several participants reported a significant number of test results, that were not at all in agreement with the consensus value for the respective component. Therefore, it was decided that all results reported by these participants (2199, 2312, 3163, 3213 and 3225) were excluded from the statistical evaluations.

PBB: In the samples #1050 and #1051 no PBB's were detected by the participating laboratories. Therefore, no conclusions can be drawn about the determination of these components.

Octa-BDE: Analytical problems were observed for a number of individual laboratories at the low concentration levels 5-35 mg/kg in the evaluated materials.
For sample #1050 the calculated reproducibility after rejection of the statistical outliers, is not in full agreement with the target requirement estimated from the Horwitz equation. Two participants reported a false negative result. Also, two test results were excluded from the statistical evaluation.
The Octa-BDE concentration in sample #1051 was very low and no significant conclusions were drawn. Several laboratories may have reported false positive test results.

Nona-BDE: Analytical problems were observed for a number of individual laboratories.
For sample #1050, the calculated reproducibility after rejection of the statistical outliers is not at all in agreement with the target requirement estimated from the Horwitz equation. The reported test results vary over a large range (48 – 4797 mg/kg). One result was excluded from the statistical evaluation.
Also for sample #1051, the calculated reproducibility after rejection of the statistical outliers is not at all in agreement with the target requirement estimated from the Horwitz equation. Again the reported test results vary over a large range (10 – 631 mg/kg). Two participants may have reported a false negative test result. Also, one test result was excluded from the statistical evaluation.

Deca-BDE: Analytical problems were observed for a number of individual laboratories.
For sample #1050, the calculated reproducibility after rejection of the statistical outliers is not at all in agreement with the target requirement estimated from the Horwitz equation. The reported test results vary over a large range (0 – 15828 mg/kg). Two results were excluded from the statistical evaluation.
Also, for sample #1051, the calculated reproducibility after rejection of the statistical outlier is not at all in agreement with the target requirement estimated from the Horwitz equation. The reported test results vary over a large range (0– 3100 mg/kg). One test result was excluded from the statistical evaluation.

4.3 EVALUATION OF THE METHODS USED

The reported details of the methods that were used by the participants are listed in appendix 2.

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 and almost all laboratories used GC/MS for separation, detection and quantification (none used HPLC). Surprisingly not all laboratories that reported to have performed IEC62321 may have followed the guidelines for the sample preparation of this method. Several laboratories that reported to have performed IEC62321 did answer the question “To what particle size was the sample reduced prior to analysis?” with “as received”, “1mm” or “2mm”, while the correct procedure should be dissolution or when the samples cannot be dissolved, cooling and milling.
A number of participants used ultrasonification instead of Soxhlet extraction to release the components from the plastic matrix. These results were not significantly different from the other results, although several very low results are reported by these participants.

4.4 COMPARISON WITH PREVIOUS PROFICIENCY TESTS

The number of participants was the same to last year’s proficiency test. The percentage of outliers increased from 6.2% last year to 11.3% of the numerical results in 2010.

The evolution of the relative reproducibilities for PBDE as observed in this proficiency scheme and the comparison with the findings in the previous round is visualized in the next table.

Range	Octa-BDE	None-BDE	Deca-BDE
2009	60 – 102%	60 – 110%	36 – 103%
2010	97 – 108%	104 - 112%	29 – 39%

Table 5: comparison of the relative PBDE reproducibilities in the previous round and in the present round

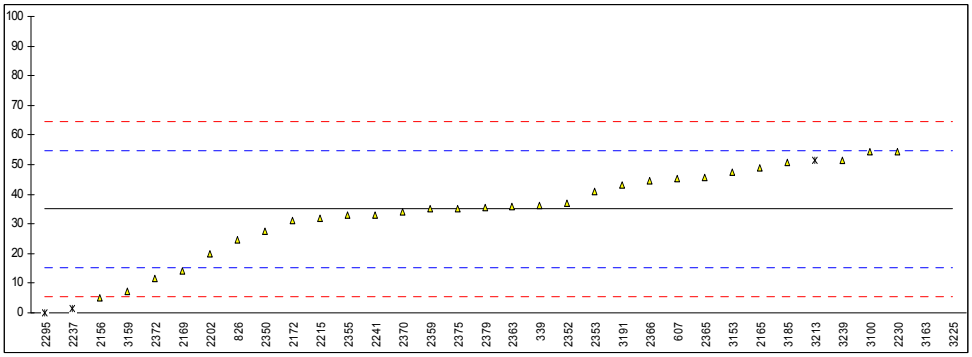
5 CONCLUSIONS

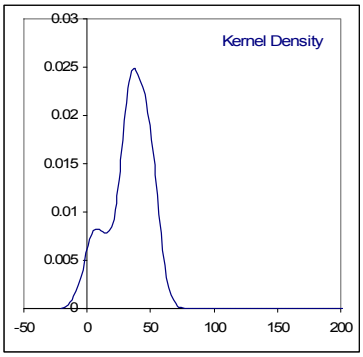
Most of the observed reproducibilities are larger than the target reproducibility requirements and therefore it had to be concluded that the determination of the PBDE in the evaluated materials obviously is rather problematic.
Each laboratory has to evaluate its performance in this study and make decisions about necessary corrective actions. Therefore, participation on a regular basis in this scheme could be helpful to improve the performance and the quality of the analytical results.

APPENDIX 1

Determination of Octabromo diphenyl ether on sample #1050; results in mg/kg

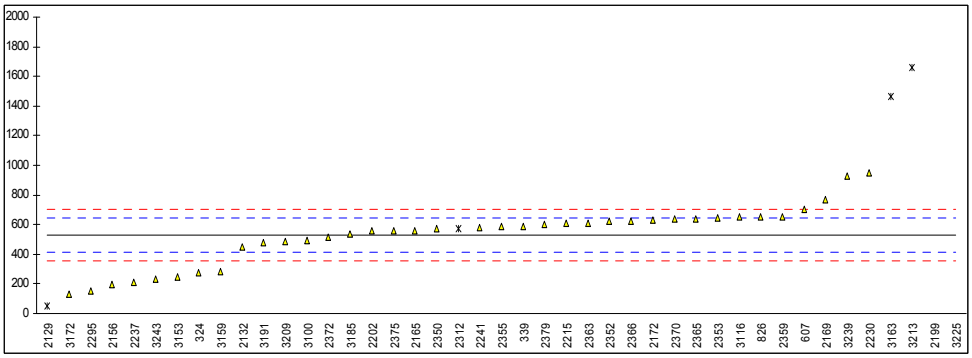
lab	method	value	mark	z(targ)	remarks
324	IEC62321	<5		<-3.05	false negative?
339	IEC62321	36.2		0.12	
551		-----		-----	
607	EPA3540C/3550C	45.2		1.04	
826	IEC62321	24.76		-1.04	
2129	EN62321	<40		-----	
2132	in house	n.d.		-----	
2156	IEC62321	5		-3.05	
2165	IEC62321	49		1.42	
2169	IEC62321	14.1446		-2.12	
2172	IEC62321	31.17		-0.39	
2199	EPA3540C/GCMS	<5		<-3.05	false negative?
2202	in house	20		-1.52	
2215	in house	31.93		-0.31	
2216		-----		-----	
2230	IEC62321	54.4		1.97	
2237	EN62321	1.46	D(0.05)	-3.41	
2241	IEC62321	33		-0.20	
2295	in house	0	ex	-3.56	Result excluded, zero is not a real result
2312	IEC62321	n.d.		-----	
2350	IEC62321	27.70		-0.74	
2352	EPA3540C/8270D	37.12		0.22	
2353	IEC62321	41.07		0.62	
2355	IEC62321	33.00		-0.20	
2359	IEC62321	35.0		0.00	
2363	IEC62321	35.7		0.07	
2365	IEC62321	45.7		1.09	
2366	IEC62321	44.6		0.98	
2370	IEC62321	34.0		-0.10	
2372	IEC62321	11.7		-2.37	
2375	IEC62321	35		0.00	
2379	IEC62321	35.60		0.06	
3100	IEC62321	54.3		1.96	
3116		-----		-----	
3153	IEC62321	47.5		1.27	
3154		-----		-----	
3159	IEC62321	7.15		-2.83	
3163	GC/MS	608	G(0.01)	58.25	
3172	in house	<100		-----	
3185	IEC62321	50.56		1.58	
3191	IEC62321	43		0.81	
3209	in house	n.d.		-----	
3213	IEC62321	51.3	ex	1.66	Result excluded, see paragraph 4.2
3225	IEC62321	736.85	G(0.01)	71.35	
3239	IEC62321	51.32		1.66	
3243	EN62321	n.d.		-----	
	normality	OK			
	n	29			
	outliers	3	(+2 excl.)		
	mean (n)	34.99			
	st.dev. (n)	13.493			
	R(calc.)	37.78			
	R(Horwitz)	27.54			

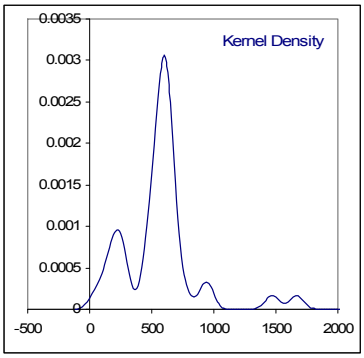




Determination of Nonabromo diphenyl ether on sample #1050; results in mg/kg

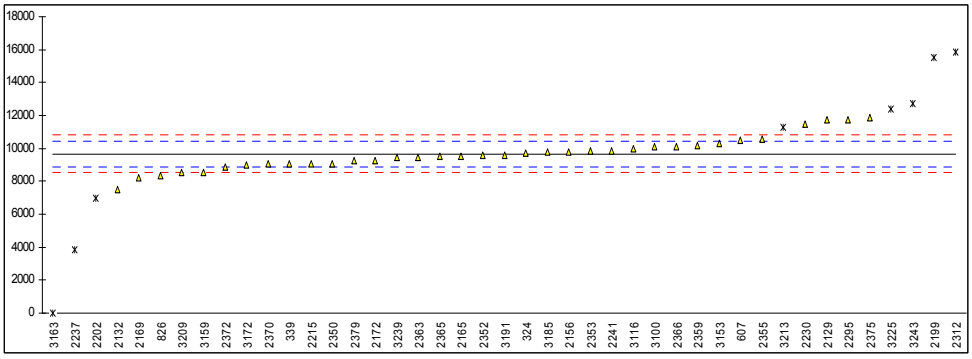
lab	method	value	mark	z(targ)	remarks
324	IEC62321	277		-4.43	
339	IEC62321	588		1.01	
551		-----		-----	
607	EPA3540C/3550C	699.5		2.96	
826	IEC62321	651.11		2.12	
2129	EN62321	48	D(0.05)	-8.44	
2132	in house	447.9		-1.44	
2156	IEC62321	197	C	-5.83	First reported 97
2165	IEC62321	559		0.51	
2169	IEC62321	766.7183		4.14	
2172	IEC62321	633.5		1.81	
2199	EPA3540C/GCMS	3190	G(0.01)	46.54	
2202	in house	557		0.47	
2215	in house	605.7		1.32	
2216		-----		-----	
2230	IEC62321	950		7.35	
2237	EN62321	213		-5.55	
2241	IEC62321	581		0.89	
2295	in house	151		-6.63	
2312	IEC62321	572.1	ex	0.73	Result excluded, see paragraph 4.2
2350	IEC62321	572.0		0.73	
2352	EPA3540C/8270D	623.94		1.64	
2353	IEC62321	648.29		2.07	
2355	IEC62321	588.00		1.01	
2359	IEC62321	652.3		2.14	
2363	IEC62321	609.6		1.39	
2365	IEC62321	639.7		1.92	
2366	IEC62321	625.9		1.68	
2370	IEC62321	635		1.84	
2372	IEC62321	511		-0.33	
2375	IEC62321	558		0.49	
2379	IEC62321	603		1.28	
3100	IEC62321	495.2		-0.61	
3116	IEC62321	650		2.10	
3153	IEC62321	250		-4.90	
3154		-----		-----	
3159	IEC62321	279.3		-4.39	
3163	GC/MS	1467	G(0.01)	16.39	
3172	in house	134		-6.93	
3185	IEC62321	538.2		0.14	
3191	IEC62321	477		-0.93	
3209	in house	486.8		-0.76	
3213	IEC62321	1662.9	G(0.01)	19.82	
3225	IEC62321	4796.6	G(0.01)	74.66	
3239	IEC62321	930.71		7.01	
3243	EN62321	229		-5.27	
	normality	not OK			
	n	37			
	outliers	5	(+1 excl.)		
	mean (n)	530.12			
	st.dev. (n)	196.011			
	R(calc.)	548.83			
	R(Horwitz)	160.01			

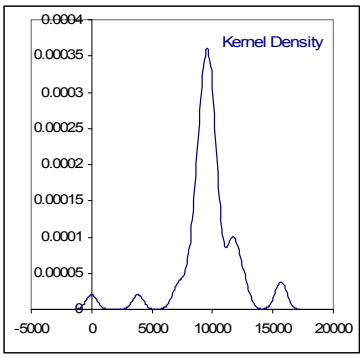




Determination of Decabromo diphenyl ether on sample #1050; results in mg/kg

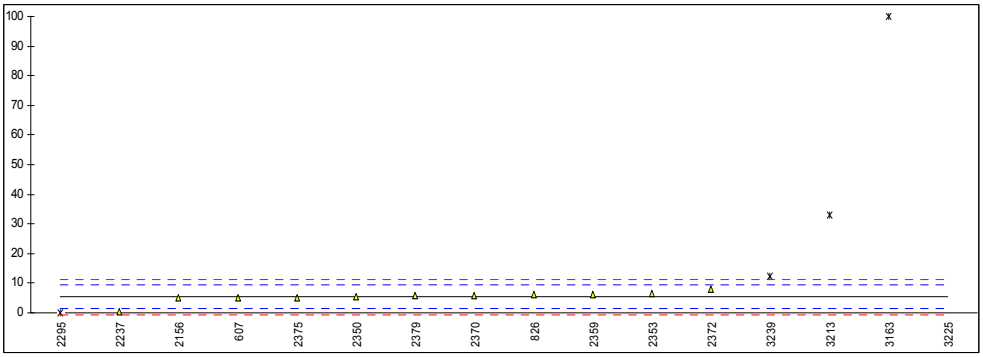
lab	method	value	mark	z(targ)	remarks
324	IEC62321	9721		0.11	
339	IEC62321	9070		-1.57	
551		-----		-----	
607	EPA3540C/3550C	10493.0		2.09	
826	IEC62321	8373.47		-3.36	
2129	EN62321	11750		5.32	
2132	in house	7476.4		-5.66	
2156	IEC62321	9799		0.31	
2165	IEC62321	9540		-0.36	
2169	IEC62321	8185.974		-3.84	
2172	IEC62321	9285		-1.01	
2199	EPA3540C/GCMS	15500	G(0.01)	14.96	
2202	in house	6992	G(0.05)	-6.91	
2215	in house	9083		-1.53	
2216		-----		-----	
2230	IEC62321	11485		4.64	
2237	EN62321	3820	G(0.05)	-15.06	
2241	IEC62321	9861		0.47	
2295	in house	11760		5.35	
2312	IEC62321	15827.8	G(0.05)	15.80	
2350	IEC62321	9097		-1.50	
2352	EPA3540C/8270D	9566.36		-0.29	
2353	IEC62321	9828.82		0.38	
2355	IEC62321	10576.07		2.31	
2359	IEC62321	10195.9		1.33	
2363	IEC62321	9464.1		-0.55	
2365	IEC62321	9525.4		-0.40	
2366	IEC62321	10126.4		1.15	
2370	IEC62321	9056		-1.60	
2372	IEC62321	8870		-2.08	
2375	IEC62321	11898		5.70	
2379	IEC62321	9283		-1.02	
3100	IEC62321	10117.6		1.13	
3116	IEC62321	10000		0.82	
3153	IEC62321	10300		1.60	
3154		-----		-----	
3159	IEC62321	8574		-2.84	
3163	GC/MS	0	G(0.01)	-24.88	
3172	in house	9011		-1.72	
3185	IEC62321	9784		0.27	
3191	IEC62321	9611		-0.18	
3209	in house	8566.8		-2.86	
3213	IEC62321	11288.4	ex	4.14	Result excluded, see paragraph 4.2
3225	IEC62321	12386.9	ex	6.96	Result excluded, see paragraph 4.2
3239	IEC62321	9434.01		-0.63	
3243	EN62321	12708	C, G(0.05)	7.79	First reported 20063
	normality	OK			
	n	35			
	outliers	6	(+2 excl.)		
	mean (n)	9679.1			
	st.dev. (n)	996.74			
	R(calc.)	2790.9			
	R(Horwitz)	1089.4			

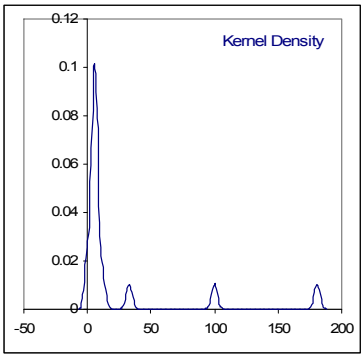




Determination of Octabromo diphenyl ether on sample #1051; results in mg/kg

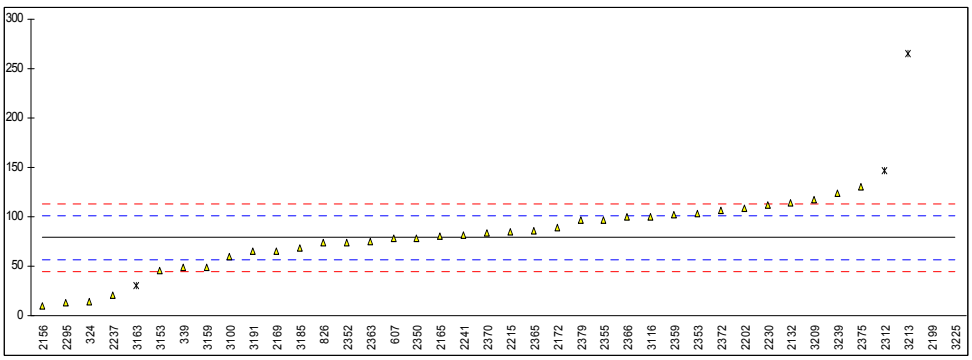
lab	method	value	mark	z(targ)	remarks
324	IEC62321	<5		-----	
339	IEC62321	<25		-----	
551		-----		-----	
607	EPA3540C/3550C	5.1		-0.14	
826	IEC62321	6.02		0.32	
2129	EN62321	<40		-----	
2132	in house	n.d.		-----	
2156	IEC62321	5		-0.19	
2165	IEC62321	n.d.		-----	
2169	IEC62321	<5		-----	
2172	IEC62321	<5.00		-----	
2199	EPA3540C/GCMS	<5		-----	
2202	in house	n.d.		-----	
2215	in house	n.d.		-----	
2216		-----		-----	
2230	IEC62321	<50		-----	
2237	EN62321	0.327		-2.52	
2241	IEC62321	n.d.		-----	
2295	in house	0	ex	-2.68	Result excluded, zero is not a real result
2312	IEC62321	n.d.		-----	
2350	IEC62321	5.30		-0.04	
2352	EPA3540C/8270D	<5		-----	
2353	IEC62321	6.42		0.52	
2355	IEC62321	n.d.		-----	
2359	IEC62321	6.3		0.46	
2363	IEC62321	<5		-----	
2365	IEC62321	n.d.		-----	
2366	IEC62321	n.d.		-----	
2370	IEC62321	5.93		0.28	
2372	IEC62321	7.79		1.21	
2375	IEC62321	5.2		-0.09	
2379	IEC62321	5.70		0.16	
3100	IEC62321	n.d.		-----	
3116		-----		-----	
3153	IEC62321	<20		-----	
3154		-----		-----	
3159	IEC62321	<5.0		-----	
3163	GC/MS	100	G(0.01)	47.27	
3172	in house	<100		-----	
3185	IEC62321	n.d.		-----	
3191	IEC62321	<10		-----	
3209	in house	n.d.		-----	
3213	IEC62321	32.9	G(0.01)	13.75	
3225	IEC62321	180.7	G(0.01)	87.58	
3239	IEC62321	12.41	D(0.01)	3.52	
3243	EN62321	n.d.		-----	
	normality	not OK			
	n	11			
	outliers	4	(+1 excl.)		
	mean (n)	5.37			
	st.dev. (n)	1.853			
	R(calc.)	5.19			
	R(Horwitz)	5.61			

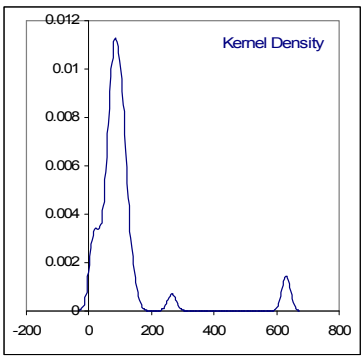




Determination of Nonabromo diphenyl ether on sample #1051; results in mg/kg

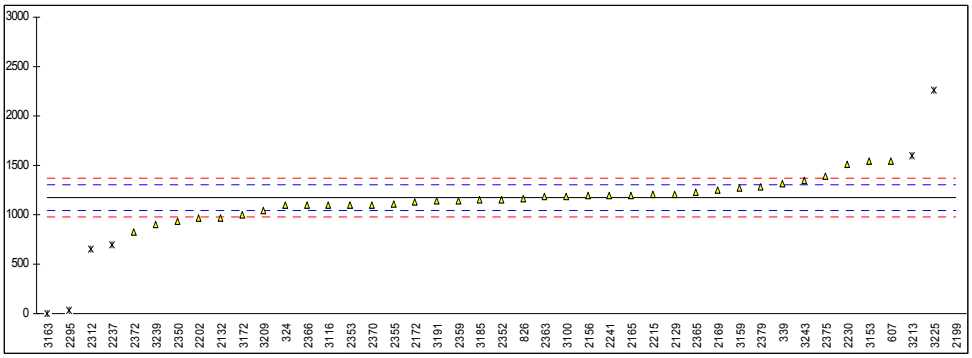
lab	method	value	mark	z(targ)	remarks
324	IEC62321	14.4		-5.69	
339	IEC62321	48.4		-2.69	
551		-----		-----	
607	EPA3540C/3550C	78.5		-0.03	
826	IEC62321	74.27		-0.40	
2129	EN62321	<40		<-3.43	false negative?
2132	in house	113.9		3.09	
2156	IEC62321	10		-6.08	
2165	IEC62321	80		0.10	
2169	IEC62321	65.5700		-1.17	
2172	IEC62321	88.90		0.89	
2199	EPA3540C/GCMS	630	G(0.01)	48.67	
2202	in house	109		2.66	
2215	in house	84.42		0.49	
2216		-----		-----	
2230	IEC62321	112		2.93	
2237	EN62321	21.1		-5.10	
2241	IEC62321	82		0.28	
2295	in house	13		-5.82	
2312	IEC62321	146.2	D(0.05)	5.95	
2350	IEC62321	78.70		-0.01	
2352	EPA3540C/8270D	74.30		-0.40	
2353	IEC62321	103.56		2.18	
2355	IEC62321	96.39		1.55	
2359	IEC62321	102.5		2.09	
2363	IEC62321	74.6		-0.38	
2365	IEC62321	85.8		0.61	
2366	IEC62321	99.8		1.85	
2370	IEC62321	83.4		0.40	
2372	IEC62321	107		2.49	
2375	IEC62321	130.9		4.60	
2379	IEC62321	96.20		1.53	
3100	IEC62321	60.3		-1.64	
3116	IEC62321	100		1.87	
3153	IEC62321	45.6		-2.94	
3154		-----		-----	
3159	IEC62321	49.44		-2.60	
3163	GC/MS	30	ex	-4.31	Result excluded, see paragraph 4.2
3172	in house	<100		-----	
3185	IEC62321	68.92		-0.88	
3191	IEC62321	65		-1.22	
3209	in house	117.6		3.42	
3213	IEC62321	265.3	G(0.01)	16.46	
3225	IEC62321	631.2	G(0.01)	48.78	
3239	IEC62321	124.40		4.02	
3243	EN62321	n.d.		-----	false negative?
	normality	OK			
	n	35			
	outliers	4	(+1 excl.)		
	mean (n)	78.85			
	st.dev. (n)	31.401			
	R(calc.)	87.92			
	R(Horwitz)	31.71			

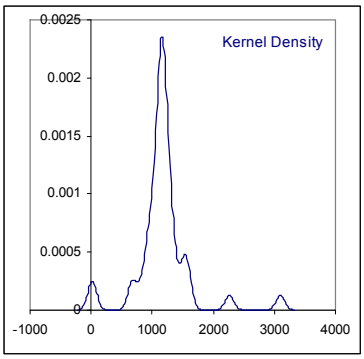




Determination of Decabromo diphenyl ether on sample #1051; results in mg/kg

lab	method	value	mark	z(targ)	remarks
324	IEC62321	1097		-1.16	
339	IEC62321	1310		2.13	
551		-----		-----	
607	EPA3540C/3550C	1545.5		5.77	
826	IEC62321	1162.26		-0.15	
2129	EN62321	1209		0.57	
2132	in house	971.0		-3.10	
2156	IEC62321	1196		0.37	
2165	IEC62321	1200		0.44	
2169	IEC62321	1254.638		1.28	
2172	IEC62321	1128		-0.68	
2199	EPA3540C/GCMS	3100	G(0.01)	29.79	
2202	in house	962		-3.24	
2215	in house	1204		0.50	
2216		-----		-----	
2230	IEC62321	1508		5.19	
2237	EN62321	699.9	DG(0.05)	-7.29	
2241	IEC62321	1197		0.39	
2295	in house	35	G(0.01)	-17.56	
2312	IEC62321	650.4	DG(0.05)	-8.06	
2350	IEC62321	939.0		-3.60	
2352	EPA3540C/8270D	1156.02		-0.24	
2353	IEC62321	1100.96		-1.10	
2355	IEC62321	1110.00		-0.96	
2359	IEC62321	1139.2		-0.50	
2363	IEC62321	1180.6		0.14	
2365	IEC62321	1224.9		0.82	
2366	IEC62321	1099.6		-1.12	
2370	IEC62321	1102		-1.08	
2372	IEC62321	824		-5.37	
2375	IEC62321	1386		3.31	
2379	IEC62321	1288		1.79	
3100	IEC62321	1186.7		0.23	
3116	IEC62321	1100		-1.11	
3153	IEC62321	1540		5.69	
3154		-----		-----	
3159	IEC62321	1273		1.56	
3163	GC/MS	0	G(0.05)	-18.10	
3172	in house	1005		-2.58	
3185	IEC62321	1156		-0.24	
3191	IEC62321	1139		-0.51	
3209	in house	1041.1		-2.02	
3213	IEC62321	1597.1	ex	6.57	Result excluded, see paragraph 4.2
3225	IEC62321	2262.45	G(0.05)	16.85	
3239	IEC62321	905.68		-4.11	
3243	EN62321	1345	C	2.68	First reported 2166
	normality	OK			
	n	36			
	outliers	6	(+1 excl.)		
	mean (n)	1171.8			
	st.dev. (n)	163.09			
	R(calc.)	456.7			
	R(Horwitz)	181.2			





APPENDIX 2

Analytical details

Lab	Max. particle size	Extraction	Detection	Corrected for rec.
324	<2mm	SOXHLET	GC-MS	NO
339	2mm	Extraction+ ultrawave 60°C 1hr	GC-MS	NO
551				
607	<0.5mm	Ultrasonic+SOXHLET	GC-MS	NO
826	Crushed by using LN2	IEC 32321	GC-MS	NO
2129	<100µm	Ultrasonic	GC-MS	NO
2132	Fine powder using cryogenic mill	Ultrasonic 50°C using Toluene 1 hr	GC-MSD	NO
2156	500µm	SOXHLET	GC-MS	NO
2165	Powder	Extract with organic solution	GC-MS	NO
2169	<500µm	SOXHLET	GC-MS	NO
2172	≤1x1x1mm	SOXHLET/Toluene	GC-MSD	NO
2199		SOXHLET	GC-MS	NO
2202	No pre-treatment	Dissolution + precipitation	GC-MS	NO
2215	1x1x1mm	Ultrasonic	GC-MS	NO
2216				
2230	Grinding into powder <5mm	SOXHLET 2 hr Toluene	GC-MSD	
2237	<0.5mm	Ultrasonic	GC-MS	NO
2241	Powder	SOXHLET	GC-MS	NO
2295	Used as it is	Ultrasonic 50°C 1 hr Toluene	GC analysis	NO
2312	<0.5mm	SOXHLET	SIM	
2350	Freezing grinding <500µm	SOXHLET	GC-MS	NO
2352	<0.5x0.5x0.5mm	SOXHLET 16 hr, 6 circles/hr	SIM	NO
2353	1x1x1mm	SOXHLET	GC-MS	NO
2355	1x1x1mm	SOXHLET	GC-MS	NO
2359	Powder	SOXHLET	GC-MS	NO
2363	0.5x0.5x0.5mm	SOXHLET	GC-MS	NO
2365	<0.5x0.5x0.5mm	SOXHLET	GC-MS	NO
2366	<500µm	SOXHLET	GC-MS	NO
2370	Powder	SOXHLET	GC-MS	NO
2372	<0.5mm	SOXHLET	GC-MS	NO
2375	0.5x0.5x0.5mm	SOXHLET	GC-MS	NO
2379	1x1x1mm	SOXHLET	GC-MS	NO
3100	<500µm	SOXHLET Toluene	SIM	NO
3116	500µm	SOXHLET	GC-MS	
3153	<500µm	SOXHLET	GC-MS	NO
3154				
3159	<1x1x1mm	SOXHLET	GC-MS	NO
3163		Dissolve in THF	GC-MS	NO
3172	<3mm	Extraction in Toluene, ultrasonic bath	GC-MS/MS	NO
3185	<500µm	SOXHLET	GC-MS/HPLC	NO
3191	<500µm	SOXHLET Toluene	GC-MS	NO
3209	<1mm	Extraction in Toluene, ultrasonic bath	GC-MS	NO
3213	Freeze mill	SOXHLET	GC-MS	NO
3225	~500µm	SOXHLET	GC-MSD	NO
3239	<500µm	SOXHLET	GC-MS	NO
3243	cooling and milling	SOXHLET	GC-MS	NO

APPENDIX 3

Number of participating laboratories per country

1 lab in	BELGIUM
1 lab in	BRASIL
1 lab in	FRANCE
4 labs in	GERMANY
6 labs in	HONG KONG
1 lab in	INDIA
1 lab in	ITALY
1 lab in	JAPAN
4 labs in	KOREA
2 labs in	MALAYSIA
14 labs in	P.R. of CHINA
2 labs in	SINGAPORE
3 labs in	TAIWAN R.O.C.
1 lab in	THAILAND
1 lab in	THE NETHERLANDS
2 labs in	TURKEY
1 lab in	U.S.A.

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
n.a. = not applicable

Literature:

1 iis Interlaboratory Studies, Protocol for the Organisation, Statistics & Evaluation, January 2010
2 EN 1122:2001, "Determination of Cadmium in plastics with the method of the wet decomposition".
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4 ASTM E178-02
5 ASTM E1301-03
6 ISO 5725-86
7 ISO 5725, parts 1-6, 1994
8 M. Thompson and R. Wood, J. AOAC Int, 76, 926, (1993)
9 W.J. Youden and E.H. Steiner, Statistical Manual of the AOAC, (1975)
10 IP 367/96
11 DIN 38402 T41/42
12 P.L. Davies, Fr. Z. Anal. Chem, 331, 513, (1988)
13 J.N. Miller, Analyst, 118, 455, (1993)
14 Analytical Methods Committee Technical Brief, No4 January 2001
15 The Royal Society of Chemistry 2002, Analyst 2002, 127 page1359-1364, P.J. Lowthian and M. Thompson. (see http://www.rsc.org/suppdata/an/b2/b205600n/)
16 R.G. Visser, Reliability of proficiency test results for metals and phthalates in plastics, Accred Qual Assur, 14:29-34 (2009)