

**Results of Proficiency Test
Brominated Flame retardants
September 2011**

Organised by: Institute for Interlaboratory Studies
Spijkenisse, the Netherlands

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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 it was decided to continue the interlaboratory study for the determination of PBB and PBDE in the 2010 and 2011 iis' PT programs.

In the interlaboratory study of September 2011, 67 laboratories from 16 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), of which one clearly positive on a number of brominated flame retardants and labelled #11052 and #11053 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, ILAC-G13:2007 and ISO/IEC 17043:2010. This ensures 100% confidentiality 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 (#11052) was a white coloured PP granulate fortified with deca-BDE. The second material (#11053) was a light yellowish coloured granulate that was positive on brominated components and did contain a small amount of Octa-BDE.

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 3 stratified randomly selected subsamples.

	Deca-BDE in #11052	Octa-BDE in #11053
Sample 1	2063 mg/kg	81 mg/kg
Sample 2	1989 mg/kg	76 mg/kg
Sample 3	2040 mg/kg	88 mg/kg

Table 1: test results of the homogeneity test on the subsamples #11052 and #11053

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 #11052	Octa-BDE in #11053
RSD_r (observed)	1.9%	7.4%
reference method	Horwitz	Horwitz
$0.3 \times RSD_R$ (reference method)	1.5%	7.4%

Table 2: evaluation of the observed relative repeatability standard deviations against the requirements

The calculated variation coefficient RSD_r for #11052 is almost in agreement and for #11053 in good agreement with the estimated target, calculated using the Horwitz equation. Therefore, homogeneity of all subsamples was assumed.

To each of the participating laboratories one set of samples, (1* sample #11052 and 1* sample #11053) was sent on August 17, 2011.

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, except for deca BDE in #11052 and octa BDE in #11053.

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.

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.

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; nos.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.

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; no. 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.

Seven participants reported results after the final reporting date and eight (!) participants did not report any results at all. Not all laboratories were able to report all analytes requested.

Finally, 59 of the 67 participants submitted analysis results. The 59 reporting laboratories reported 286 numerical results. Observed were 27 outlying results, which is 8.6%. 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. Regrettably 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)
Nona-BDE #11052	mg/kg	39	130.0	84.6	48.5
Deca-BDE #11052	mg/kg	47	2042	1165	290

Table 3: performance overview for sample #11052

Parameter	unit	n	Average	2.8 * sd	R (lit)
Hexa-BDE #11053	mg/kg	24	25.7	19.9	21.2
Hepta-BDE #11053	mg/kg	24	127.2	54.4	61.5
Octa-BDE #11053	mg/kg	50	81.7	57.0	56.6
Nona-BDE #11053	mg/kg	47	40.0	17.2	17.8
Deca-BDE #11053	mg/kg	25	9.3	6.4	3.0

Table 4: performance overview for sample #11053

Without further statistical calculations, it can be concluded that in some cases 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 for sample #11052 reported by these participants (2139, 2247, 2438) were excluded from the statistical evaluations.

Initially the participants were only requested to report octa-, nona-, and deca-BDE. However, several participants did report also to have found hexa- and hepta-BDE in sample #11053. Therefore, the other participants were asked whether they also did observe the presence of hexa- and hepta-BDE in sample #11053 and if this was the case to report also these test results. A number of participants reported to have observed the presence of hexa- and hepta-BDE in sample #11053, but regretfully several laboratories did not quantify these components because iis had not requested to do so explicitly. These cases are marked in the tables in appendix 2 as 'detected'.

PBB: In the samples #11052 and #11053 no PBB were detected by the participating laboratories. Therefore, no conclusions can be drawn about the determination of these components.

Hexa-BDE: No analytical problems were observed in general. In the sample #11052 no hexa-BDE was detected by the participating laboratories. For sample #11053 the calculated reproducibility after rejection of the two statistical outliers, is in full agreement with the target requirement estimated from the Horwitz equation.

Hepta-BDE: No analytical problems were observed in general. In the sample #11052 no hepta-BDE was detected by the participating laboratories. For sample #11053 the calculated reproducibility after rejection of the three statistical outliers, is in full agreement with the target requirement estimated from the Horwitz equation.

Octa-BDE: No analytical problems were observed in general. All participating laboratories agreed that the amount of Octa-BDE present in sample #11052 was below the detection limit. For sample #11053 the calculated reproducibility after rejection of the three statistical outliers, is in full agreement with the target requirement estimated from the Horwitz equation. Two participants reported a false negative result.

Nona-BDE: Analytical problems were observed for a number of individual laboratories. For sample #11052, the calculated reproducibility after rejection of the six statistical outliers is not in agreement with the target requirement estimated from the Horwitz equation. The reported test results vary over a large range (20 – 280 mg/kg). However, for sample #11053, the calculated reproducibility after rejection of the four statistical outliers is in good agreement with the target requirement estimated from the Horwitz equation. Here the reported test results vary over a smaller range (10.5 – 76.3 mg/kg). One participant may have reported a false negative test result.

Deca-BDE: Analytical problems were observed for a number of individual laboratories. For sample #11052, the calculated reproducibility after rejection of the 5 statistical outliers (and another 3 suspect test results) is not at all in agreement with the target requirement estimated from the Horwitz equation. The reported test results vary

over a very large range (160 – 22415 mg/kg). Three results were excluded from the statistical evaluation. Three other participants reported a false negative result. Also, for sample #11053, the calculated reproducibility after rejection of the four statistical outliers is not in agreement with the target requirement estimated from the Horwitz equation. However, the low concentration of Deca-BDE present in sample #11053 (9.3 mg/kg) may explain the above as this concentration will be near or below the limit of detection of most test procedures used.

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”, “3mm” or “<5mm”, 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 evolution of the relative reproducibilities for PBDE as observed in this proficiency scheme and the comparison with the findings in the previous iis' PTs is visualized in the next table.

	Hexa-BDE	Hepta-BDE	Octa-BDE	Nona-BDE	Deca-BDE
2009	---	---	60 – 102%	60 – 110%	36 – 103%
2010	---	---	97 – 108%	104 - 112%	29 – 39%
2011	78%	43%	70%	43 – 65%	57 – 69%

Table 5: comparison of the relative PBDE reproducibilities in the previous iis' PTs 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 is rather problematic.

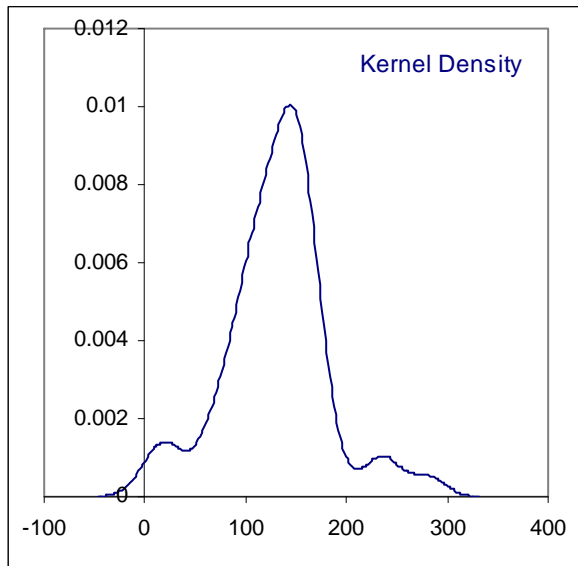
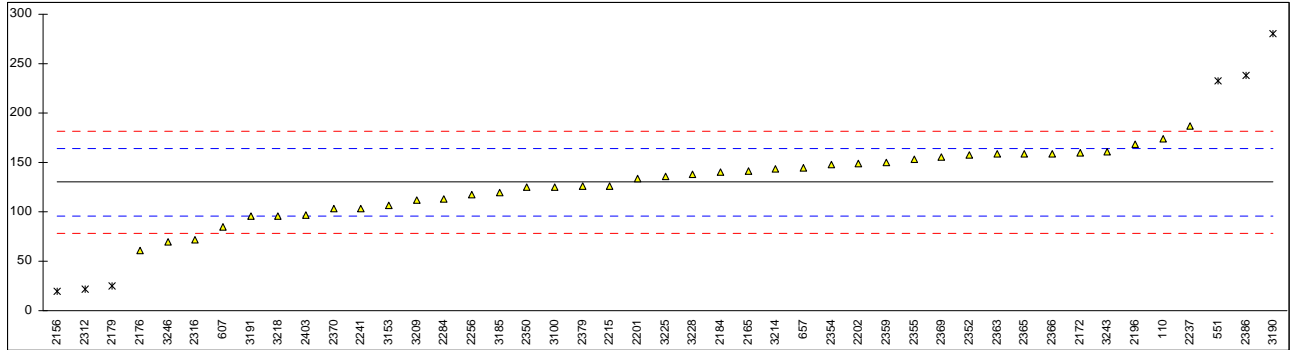
Each laboratory has to evaluate its performance in this study and make decisions about necessary corrective actions. Therefore, participation on a regular basis in this scheme could be helpful to improve the performance and the quality of the analytical results.

APPENDIX 1

Determination of Nonabromo diphenyl ether on sample #11052; results in mg/kg

lab	method	value	mark	z(targ)	remarks
110	IEC62321	174.25		2.55	
339	GC/MS	<25		<-6.06	false negative?
551	IEC62321	232.128	DG(0.05)	5.90	
607	IEC62321	85.29		-2.58	
657	IEC62321:2008	144.06		0.81	
1213	IEC62321	<25.0		<-6.06	false negative?
2115		----		----	
2129		----		----	
2139	IEC62321	n.d.		----	
2146		----		----	
2156	IEC62321	20	G(0.05)	-6.35	first reported 5
2165	IEC62321:2008	141.6		0.67	
2172	IEC62321	160.3		1.75	
2173	IEC62321	n.d.		----	
2176	in house	61.4		-3.96	
2179	IEC62321	25.33	C,DG(0.05)	-6.04	first reported 50.86
2184	IEC62321	140.1		0.58	
2196	IEC62321	168		2.19	
2201	IEC62321	134		0.23	
2202	in house	148.7		1.08	
2212		----		----	
2215	in house	126.3		-0.21	
2216		----		----	
2237	GC-MS/MS	187		3.29	
2241	IEC62321:2008	103.2		-1.55	
2247	IEC62321	*		----	unable to quantify due to high matrix effects
2256	IEC62321	117		-0.75	
2284	IEC62321	113.0		-0.98	
2312	IEC62321:2008	21.5	DG(0.05)	-6.27	
2316	IEC62321:2008	72.28		-3.33	
2350	IEC62321	124.67		-0.31	
2352	EPA3550C/8270D	157.13		1.57	
2354	IEC62321Mod.	147.90		1.03	
2355	IEC62321:2008	153.62		1.36	
2359	IEC62321:2008	150.0		1.15	
2363	IEC62321:2008	158.4		1.64	
2365	IEC62321:2008	158.7		1.66	
2366	IEC62321:2008	159.0		1.67	
2369	IEC62321:2008	155.429		1.47	
2370	IEC62321:2008	103		-1.56	
2372	IEC62321	n.d.		----	
2379	IEC62321	125.70		-0.25	
2386	IEC62321	238.5	DG(0.05)	6.27	
2403	IEC62321:2008	96.7		-1.92	
2410	IEC62321	<5		<-7.22	false negative?
2438	IEC62321	<0.3		<-7.49	false negative?
3100	IEC62321:2008	125.2		-0.28	
3126		----		----	
3146		----		----	
3151	IEC62321	n.d.		----	
3153	IEC62321:2008	107		-1.33	
3163		----		----	
3166	GC-MS	<100		----	
3172	IEC62321	<25		<-6.06	false negative?
3182	IEC62321	<50		<-4.62	false negative?
3185	IEC62321:2008	120		-0.58	
3190	IEC62321	280	G(0.05)	8.66	
3191	IEC62321:2008	95.6		-1.99	
3209	EPA3550C/GC-MS	112.12		-1.03	
3210		----		----	
3214	IEC62321	143.7		0.79	
3218	IEC62321	96		-1.96	
3225	IEC62321	135.6		0.32	
3228	in house	138		0.46	
3239		----		----	
3243	IEC62321	160.4	C	1.75	first reported 226
3246	IEC62321	70	C	-3.47	first reported 638

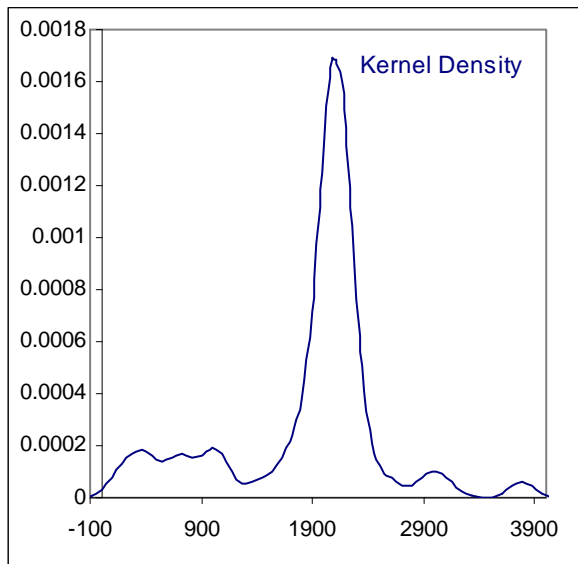
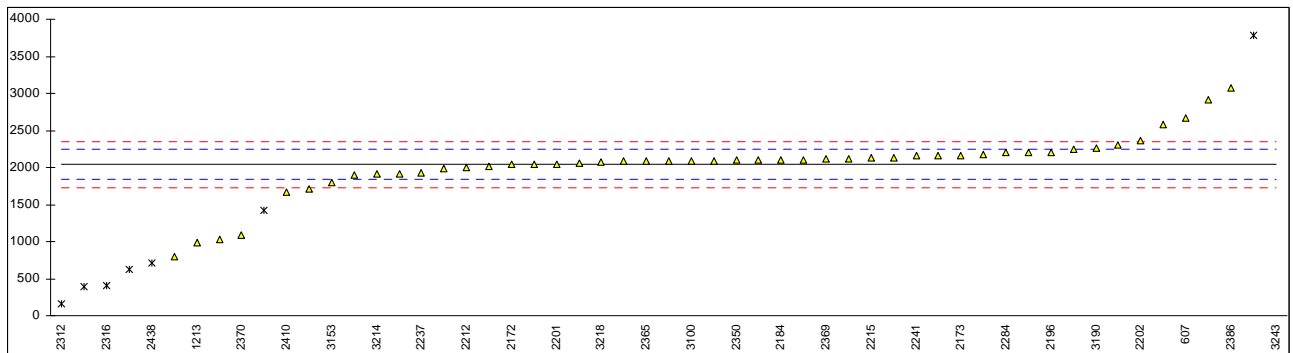
normality	OK
n	39
outliers	6
mean (n)	130.0
st.dev. (n)	30.232
R(calc.)	84.65
R(Horwitz)	48.49



Determination of Decabromo diphenyl ether on sample #11052; results in mg/kg

lab	method	value	mark	z(targ)	remarks
110	IEC62321	2584.67		5.23	
339	GC/MS	1710		-3.20	
551	IEC62321	2916.829		8.43	
607	IEC62321	2662.81	C	5.99	first reported 472.29
657	IEC62321:2008	2136.38		0.91	
1213	IEC62321	986.59		-10.17	
2115		----		----	
2129		----		----	
2139	IEC62321	1420.6	ex,C	-5.99	see §4.1, first reported 2834.8
2146		----		----	
2156	IEC62321	395	C,DG(0.05)	-15.88	first reported 270
2165	IEC62321:2008	2081		0.38	
2172	IEC62321	2037		-0.05	
2173	IEC62321	2165.4		1.19	
2176	in house	796.0		-12.01	
2179	IEC62321	n.d.		----	false negative?
2184	IEC62321	2104		0.60	
2196	IEC62321	2201		1.53	
2201	IEC62321	2050		0.08	
2202	in house	2361.8		3.08	
2212	in house	1999.8	C	-0.41	first reported 449.3
2215	in house	2128.3		0.83	
2216		----		----	
2237	GC-MS/MS	1926		-1.12	
2241	IEC62321:2008	2155.3		1.09	
2247	IEC62321	3778.63	ex,C	16.74	see §4.1, first reported 3186.39
2256	IEC62321	2087		0.44	
2284	IEC62321	2199.8		1.52	
2312	IEC62321:2008	160	DG(0.05)	-18.14	
2316	IEC62321:2008	410.72	DG(0.01)	-15.72	
2350	IEC62321	2097.33		0.53	
2352	EPA3550C/8270D	2171.99		1.25	
2354	IEC62321Mod.	1895.99		-1.41	
2355	IEC62321:2008	2240.21		1.91	
2359	IEC62321:2008	2010.0		-0.31	
2363	IEC62321:2008	2200.3		1.53	
2365	IEC62321:2008	2085.4		0.42	
2366	IEC62321:2008	2165.2		1.19	
2369	IEC62321:2008	2112.788		0.68	
2370	IEC62321:2008	1080		-9.27	
2372	IEC62321	1915		-1.22	
2379	IEC62321	1025.67		-9.80	
2386	IEC62321	3069		9.90	
2403	IEC62321:2008	2105.2		0.61	
2410	IEC62321	1660		-3.68	
2438	IEC62321	707.97	ex	-12.86	see §4.1
3100	IEC62321:2008	2089.9		0.46	
3126		----		----	
3146		----		----	
3151	IEC62321	n.d.		----	false negative?
3153	IEC62321:2008	1790		-2.43	
3163		----		----	
3166	GC-MS	<100		<-18.72	false negative?
3172	IEC62321	628.0	DG(0.01)	-13.63	
3182	IEC62321	2307.26		2.56	
3185	IEC62321:2008	2118		0.73	
3190	IEC62321	2267		2.17	
3191	IEC62321:2008	2090.4		0.47	
3209	EPA3550C/GC-MS	2061.40		0.19	
3210		----		----	
3214	IEC62321	1910.2		-1.27	
3218	IEC62321	2070		0.27	
3225	IEC62321	1988.6		-0.51	
3228	in house	2050		0.08	
3239		----		----	
3243	IEC62321	22415	C,G(0.01)	196.39	first reported 32428
3246	IEC62321	2100	C	0.56	first reported 2971

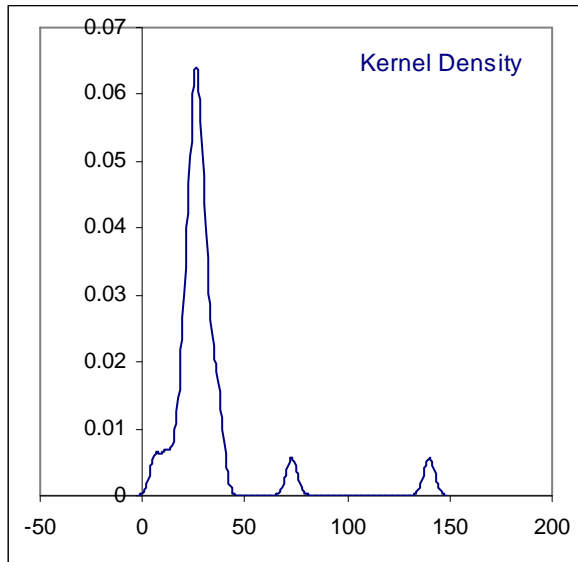
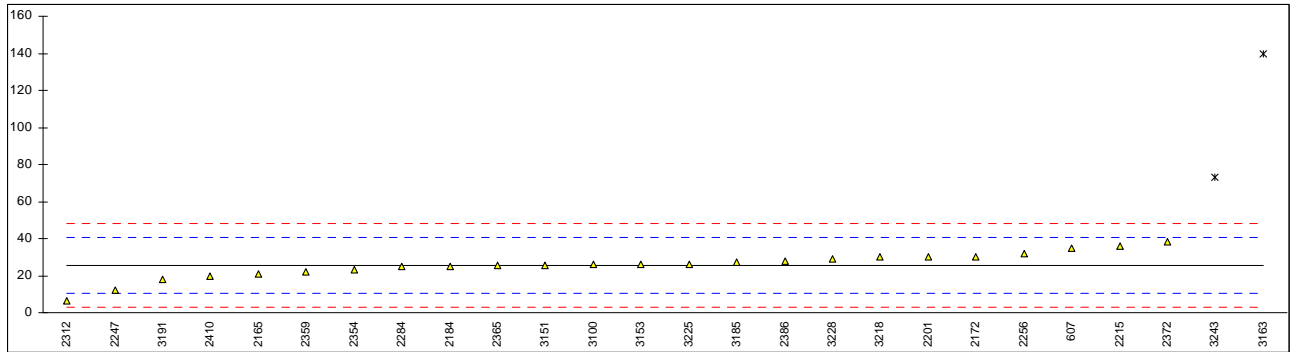
normality	not OK
n	47
outliers	5
mean (n)	2041.84
st.dev. (n)	416.221
R(calc.)	1165.42
R(Horwitz)	290.46



Determination of Hexabromo diphenyl ether on sample #11053; results in mg/kg

lab	method	value	mark	z(targ)	remarks
110		----		----	
339		----		----	
551		----		----	
607	EPA3540C/3550C	35		1.23	
657		----		----	
1213		----		----	
2115		----		----	
2129		----		----	
2139		----		----	
2146		----		----	
2156		----		----	
2165	IEC62321:2008	21		-0.62	
2172	IEC62321	30.09		0.58	
2173		----		----	
2176		----		----	
2179		----		----	
2184	IEC62321	25		-0.09	
2196	IEC62321	detected		----	
2201	IEC62321	30		0.57	
2202		----		----	
2212		----		----	
2215	in house	36		1.37	
2216		----		----	
2237		----		----	
2241		----		----	
2247	IEC62321	12		-1.81	
2256	IEC62321	32		0.84	
2284	IEC62321	25		-0.09	
2312	IEC62321:2008	6.167		-2.58	
2316		----		----	
2350		----		----	
2352		----		----	
2354	IEC62321Mod.	23		-0.35	
2355	IEC62321:2008	detected		----	
2359	IEC62321:2008	22		-0.49	
2363	IEC62321:2008	detected		----	
2365	IEC62321:2008	25.4		-0.04	
2366		----		----	
2369		----		----	
2370		----		----	
2372	IEC62321	38		1.63	
2379	IEC62321	detected		----	
2386	IEC62321	28		0.31	
2403	IEC62321:2008	detected		----	
2410	IEC62321	20		-0.75	
2438	IEC62321	detected		----	
3100	IEC62321:2008	26		0.04	
3126		----		----	
3146		----		----	
3151	IEC62321	25.5		-0.02	
3153	IEC62321:2008	26.0		0.04	
3163		140	G(0.01)	15.12	
3166		----		----	
3172		----		----	
3182	IEC62321	<50		----	
3185	IEC62321:2008	27		0.18	
3190	IEC62321	detected		----	
3191	IEC62321:2008	18		-1.01	
3209	EPA3550C/GC-MS	detected		----	
3210		----		----	
3214		----		----	
3218	IEC62321	30		0.57	
3225	IEC62321	26		0.04	
3228	in house	29		0.44	
3239		----		----	
3243	IEC62321	72.8	G(0.01)	6.23	
3246		----		----	

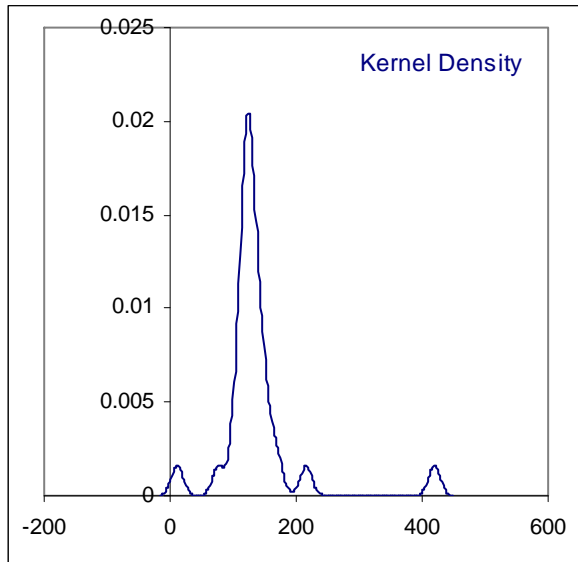
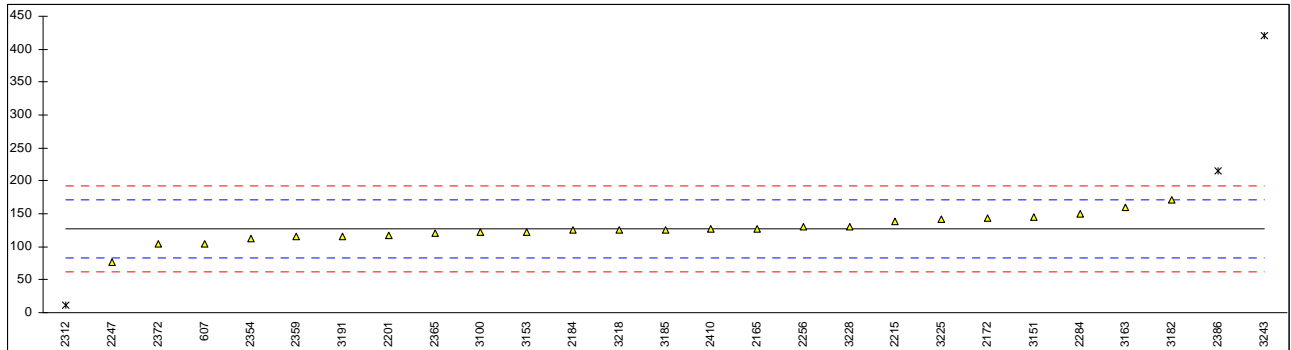
normality	OK
n	24
outliers	2
mean (n)	25.67
st.dev. (n)	7.111
R(calc.)	19.91
R(Horwitz)	21.17



Determination of Heptabromo diphenyl ether on sample #11053; results in mg/kg

lab	method	value	mark	z(targ)	remarks
110		----		----	
339		----		----	
551		----		----	
607	EPA3540C/3550C	104		-1.06	
657		----		----	
1213		----		----	
2115		----		----	
2129		----		----	
2139		----		----	
2146		----		----	
2156		----		----	
2165	IEC62321:2008	127		-0.01	
2172	IEC62321	143.0		0.72	
2173		----		----	
2176		----		----	
2179		----		----	
2184	IEC62321	125		-0.10	
2196	IEC62321	detected		----	
2201	IEC62321	117		-0.47	
2202		----		----	
2212		----		----	
2215	in house	138		0.49	
2216		----		----	
2237		----		----	
2241		----		----	
2247	IEC62321	77	C	-2.29	
2256	IEC62321	130		0.13	
2284	IEC62321	150		1.04	
2312	IEC62321:2008	11.454	D(0.05)	-5.27	
2316		----		----	
2350		----		----	
2352		----		----	
2354	IEC62321Mod.	113		-0.65	
2355	IEC62321:2008	detected		----	
2359	IEC62321:2008	115		-0.56	
2363	IEC62321:2008	detected		----	
2365	IEC62321:2008	121.3		-0.27	
2366		----		----	
2369		----		----	
2370		----		----	
2372	IEC62321	104		-1.06	
2379	IEC62321	detected		----	
2386	IEC62321	216	G(0.05)	4.04	
2403	IEC62321:2008	detected		----	
2410	IEC62321	127		-0.01	
2438	IEC62321	detected		----	
3100	IEC62321:2008	123		-0.19	
3126		----		----	
3146		----		----	
3151	IEC62321	145		0.81	
3153	IEC62321:2008	123		-0.19	
3163		160		1.49	
3166		----		----	
3172		----		----	
3182	IEC62321	171.06		2.00	
3185	IEC62321:2008	126		-0.06	
3190	IEC62321	detected		----	
3191	IEC62321:2008	116		-0.51	
3209	EPA3550C/GC-MS	detected		----	
3210		----		----	
3214		----		----	
3218	IEC62321	126		-0.06	
3225	IEC62321	142		0.67	
3228	in house	130		0.13	
3239		----		----	
3243	IEC62321	420.0	G(0.01)	13.34	
3246		----		----	

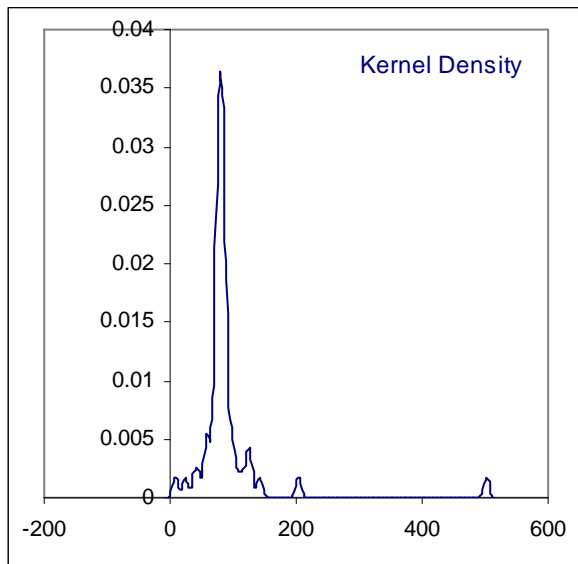
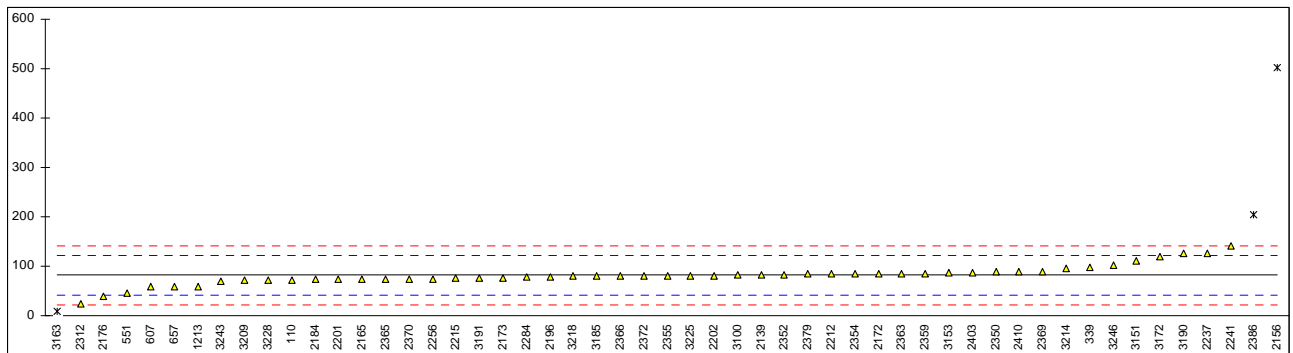
normality	OK
n	24
outliers	3
mean (n)	127.22
st.dev. (n)	19.440
R(calc.)	54.43
R(Horwitz)	61.46



Determination of Octabromo diphenyl ether on sample #11053; results in mg/kg

lab	method	value	mark	z(targ)	remarks
110	IEC62321	72.37		-0.46	
339	GC/MS	98.1		0.81	
551	IEC62321	45.548		-1.79	
607	EPA3540C/3550C	58.2		-1.16	
657	IEC62321:2008	58.65		-1.14	
1213	IEC62321	58.78		-1.13	
2115		-----		-----	
2129		-----		-----	
2139	IEC62321	82.5	C	0.04	first reported 44.3
2146		-----		-----	
2156	IEC62321	502	C,G(0.01)	20.79	first reported 342
2165	IEC62321:2008	74.0		-0.38	
2172	IEC62321	84.63		0.14	
2173	IEC62321	76.873		-0.24	
2176	in house	38.7		-2.13	
2179	IEC62321	n.d.		-----	
2184	IEC62321	73.5		-0.41	
2196	IEC62321	78.7		-0.15	
2201	IEC62321	74		-0.38	
2202	in house	81.5		-0.01	
2212	in house	84.5		0.14	
2215	in house	75.33		-0.32	
2216		-----		-----	
2237	GC-MS/MS	127		2.24	
2241	IEC62321:2008	142.2		2.99	
2247	IEC62321	<5		<-3.79	false negative?
2256	IEC62321	75		-0.33	
2284	IEC62321	78.3		-0.17	
2312	IEC62321:2008	23.788		-2.87	
2316	IEC62321:2008	<50		-----	
2350	IEC62321	88.6		0.34	
2352	EPA3550C/8270D	82.56		0.04	
2354	IEC62321Mod.	84.54		0.14	
2355	IEC62321:2008	80.91		-0.04	
2359	IEC62321:2008	84.8		0.15	
2363	IEC62321:2008	84.8		0.15	
2365	IEC62321:2008	74.2		-0.37	
2366	IEC62321:2008	80.7		-0.05	
2369	IEC62321:2008	90.123		0.42	
2370	IEC62321:2008	75.0		-0.33	
2372	IEC62321	80.8		-0.05	
2379	IEC62321	84.10		0.12	
2386	IEC62321	203.5	G(0.01)	6.02	
2403	IEC62321:2008	87.2		0.27	
2410	IEC62321	90		0.41	
2438	IEC62321	<0.3		<-4.03	false negative?
3100	IEC62321:2008	81.6		-0.01	
3126		-----		-----	
3146		-----		-----	
3151	IEC62321	111.5		1.47	
3153	IEC62321:2008	86.6		0.24	
3163		8	G(0.05)	-3.65	
3166	GC-MS	<100		-----	
3172	IEC62321	120.2		1.90	
3182	IEC62321	<50		-----	
3185	IEC62321:2008	80.6		-0.06	
3190	IEC62321	126		2.19	
3191	IEC62321:2008	76.1		-0.28	
3209	EPA3550C/GC-MS	71.07		-0.53	
3210		-----		-----	
3214	IEC62321	96.7		0.74	
3218	IEC62321	80		-0.09	
3225	IEC62321	81.3		-0.02	
3228	in house	72		-0.48	
3239		-----		-----	
3243	IEC62321	69		-0.63	
3246	IEC62321	103		1.05	

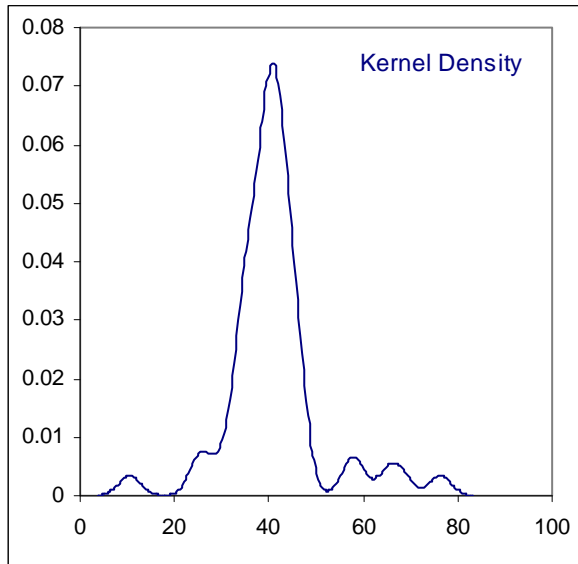
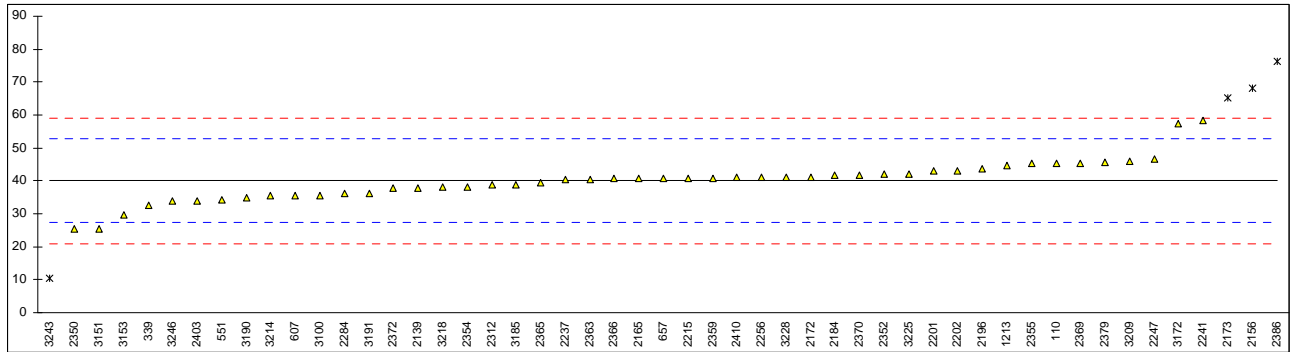
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n	50
outliers	3
mean (n)	81.72
st.dev. (n)	20.361
R(calc.)	57.01
R(Horwitz)	56.61



Determination of Nonabromo diphenyl ether on sample #11053; results in mg/kg

lab	method	value	mark	z(targ)	remarks
110	IEC62321	45.28		0.83	
339	GC/MS	32.7		-1.15	
551	IEC62321	34.305		-0.90	
607	EPA3540C/3550C	35.7		-0.68	
657	IEC62321:2008	40.80		0.13	
1213	IEC62321	44.72		0.74	
2115		----		----	
2129		----		----	
2139	IEC62321	37.8	C	-0.35	first reported 21.5
2146		----		----	
2156	IEC62321	68	C,G(0.05)	4.40	first reported 47
2165	IEC62321:2008	40.8		0.13	
2172	IEC62321	41.18		0.18	
2173	IEC62321	65.094	G(0.01)	3.94	
2176	in house	n.d.		----	
2179	IEC62321	n.d.		----	
2184	IEC62321	41.7		0.27	
2196	IEC62321	43.8		0.60	
2201	IEC62321	43		0.47	
2202	in house	43.2		0.50	
2212		----		----	
2215	in house	40.81		0.13	
2216		----		----	
2237	GC-MS/MS	40.3		0.05	
2241	IEC62321:2008	58.4		2.89	
2247	IEC62321	46.54	C	1.03	first reported <5
2256	IEC62321	41		0.16	
2284	IEC62321	36.3		-0.58	
2312	IEC62321:2008	38.767		-0.19	
2316	IEC62321:2008	<50		----	
2350	IEC62321	25.33		-2.31	
2352	EPA3550C/8270D	42.18		0.34	
2354	IEC62321Mod.	38.19		-0.29	
2355	IEC62321:2008	45.24		0.82	
2359	IEC62321:2008	40.9		0.14	
2363	IEC62321:2008	40.5		0.08	
2365	IEC62321:2008	39.5		-0.08	
2366	IEC62321:2008	40.6		0.09	
2369	IEC62321:2008	45.374		0.84	
2370	IEC62321:2008	41.7		0.27	
2372	IEC62321	37.8		-0.35	
2379	IEC62321	45.59		0.88	
2386	IEC62321	76.3	G(0.05)	5.70	
2403	IEC62321:2008	34.0		-0.94	
2410	IEC62321	41		0.16	
2438	IEC62321	<0.3		<-6.24	false negative?
3100	IEC62321:2008	35.7		-0.68	
3126		----		----	
3146		----		----	
3151	IEC62321	25.5		-2.28	
3153	IEC62321:2008	29.7	C	-1.62	first reported 25.2
3163	0	n.d.		----	
3166	GC-MS	<100		----	
3172	IEC62321	57.3		2.72	
3182	IEC62321	<50		----	
3185	IEC62321:2008	38.9		-0.17	
3190	IEC62321	35		-0.79	
3191	IEC62321:2008	36.3		-0.58	
3209	EPA3550C/GC-MS	45.99		0.94	
3210		----		----	
3214	IEC62321	35.6		-0.69	
3218	IEC62321	38		-0.31	
3225	IEC62321	42.2		0.35	
3228	in house	41		0.16	
3239		----		----	
3243	IEC62321	10.5	G(0.05)	-4.64	
3246	IEC62321	34		-0.94	

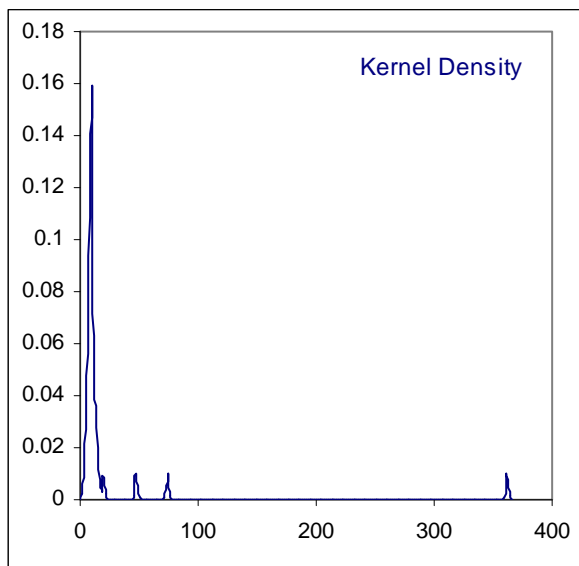
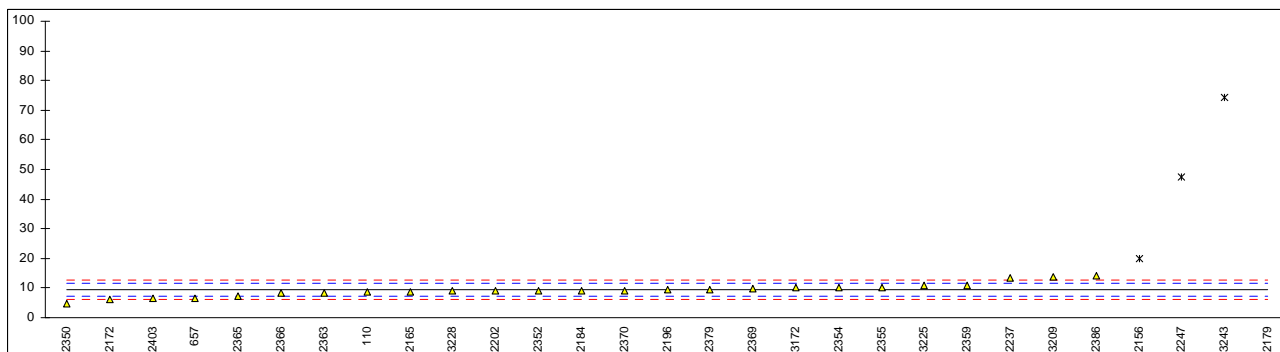
normality	OK
n	47
outliers	4
mean (n)	40.00
st.dev. (n)	6.131
R(calc.)	17.17
R(Horwitz)	17.82



Determination of Decabromo diphenyl ether on sample #11053; results in mg/kg

lab	method	value	mark	z(targ)	remarks
110	IEC62321	8.60		-0.67	
339	GC/MS	<50		----	
551	IEC62321	n.d.		----	
607	EPA3540C/3550C	<5		----	
657	IEC62321:2008	6.70		-2.46	
1213	IEC62321	<25.0		----	
2115		----		----	
2129		----		----	
2139	IEC62321	n.d.		----	
2146		----		----	
2156	IEC62321	20	C,G(0.01)	10.03	first reported 5
2165	IEC62321:2008	8.8		-0.48	
2172	IEC62321	6.006		-3.11	
2173	IEC62321	n.d.		----	
2176	in house	n.d.		----	
2179	IEC62321	362.28	C,G(0.01)	331.33	first reported 711.77
2184	IEC62321	9.1		-0.20	
2196	IEC62321	9.3		-0.02	
2201	IEC62321	<5		----	
2202	in house	9.0		-0.30	
2212	in house	<25		----	
2215	in house	n.d.		----	
2216		----		----	
2237	GC-MS/MS	13.5		3.93	
2241	IEC62321:2008	n.d.		----	
2247	IEC62321	47.61	C,G(0.01)	35.95	first reported <5
2256	IEC62321	n.d.		----	
2284	IEC62321	n.d.		----	
2312	IEC62321:2008	n.d.		----	
2316	IEC62321:2008	<50		----	
2350	IEC62321	4.6		-4.43	
2352	EPA3550C/8270D	9.01		-0.29	
2354	IEC62321Mod.	10.15		0.78	
2355	IEC62321:2008	10.25		0.88	
2359	IEC62321:2008	11.0		1.58	
2363	IEC62321:2008	8.4		-0.86	
2365	IEC62321:2008	7.1		-2.08	
2366	IEC62321:2008	8.4		-0.86	
2369	IEC62321:2008	9.700		0.36	
2370	IEC62321:2008	9.15		-0.16	
2372	IEC62321	n.d.		----	
2379	IEC62321	9.60		0.27	
2386	IEC62321	14.3		4.68	
2403	IEC62321:2008	6.4		-2.74	
2410	IEC62321	n.d.	C	----	first reported 25
2438	IEC62321	<0.6		<-8.18	false negative?
3100	IEC62321:2008	n.d.		----	
3126		----		----	
3146		----		----	
3151	IEC62321	n.d.		----	
3153	IEC62321:2008	<20		----	
3163		n.d.		----	
3166	GC-MS	<100		----	
3172	IEC62321	10.1		0.74	
3182	IEC62321	<50		----	
3185	IEC62321:2008	n.d.		----	
3190	IEC62321	<5		----	
3191	IEC62321:2008	<10		----	
3209	EPA3550C/GC-MS	13.74		4.15	
3210		----		----	
3214	IEC62321	n.d.		----	
3218	IEC62321	<5		----	
3225	IEC62321	11.0		1.58	
3228	in house	9		-0.30	
3239		----		----	
3243	IEC62321	74.2	G(0.01)	60.91	
3246	IEC62321	n.d.		----	

normality	OK
n	25
outliers	4
mean (n)	9.32
st.dev. (n)	2.294
R(calc.)	6.42
R(Horwitz)	2.98



APPENDIX 2

Analytical details for samples #11052 & 11053

Lab	Max. particle size	Extraction	Detection	Other details
110	1 x1 x 1mm	extraction with toluene	GC/MS	
339	No Further grinding	ultrasonication (1 hr @60°C)	GC/MS	
551	<500µm	Soxhlet extraction	GC/MS	
607	<0.5mm	Soxhlet extraction	GC/MS	
657	<500µm	Soxhlet extraction	GC/MS	
1213	<100µm	extraction with hexane/acetone	GC/MS	
2115				
2129	cryogenic grinding	extraction in Dichloromethane	GC/MS	
2139	Powder	Soxhlet & Ultrasonic	GC/MS	
2146				
2156	<1mm (500µm)	Soxhlet extraction	GC/MS	
2165	3mmx3mmx3mm	Heating block	GC/MS	
2172	1mmx1mmx1mm	Soxhlet extraction with toluene	GC/MS	
2173	<5mm	Soxhlet extraction	GC/MS	
2176	90-250µm	Soxhlet extraction (6 hrs)	GC/MS	Use 0.3g sample
2179	Powder	ultrasonication	GC/MS	
2184	3mmx3mmx3mm	sonication	GC/MS	
2196	500µm	ultrasonic/50°C 1 hr/Toluene	GC/MS SIM	
2201	Grind to powder, 500µm	Soxhlet extraction	GC/MS	
2202	<500µm	Dissolution-precipitation	GC/MS	
2212	n.a.	Extraction with toluene	GC/MS	
2215	0.5 g sample	Sonicate	GC/MS	
2216				
2237	<0.2mm by Cryo milling		GC/MS	clean-up florisil
2241	Powder	Soxhlet extraction	GC/MS	
2247	Powder form by the help of cryomill	Soxhlet extraction with toluene	GC/MS	
2256	5mmx5mm	Soxhlet extraction	ISTD	
2284	1mmx1mm	Soxhlet extraction	GC/MS	
2312		Soxhlet extraction	GC/MS	
2316	500um	Soxhlet extraction	GC/MS	
2350	Freezing grinding	Soxhlet extraction	GC/MS	
2352	<0.5mmx0.5mmx0.5mm	Soxhlet extraction (16h, 6cycles/hr)	GC/MS	
2354	0.5mm x 0.5mm	Soxhlet extraction	GC/MS	
2355	<1mmx1mmx1mm	Soxhlet extraction	GC/MS	
2359	0.1g	Soxhlet extraction	GC/MS	
2363	0.5mm x 0.5mm	Soxhlet extraction	GC/MS	
2365	0.5mm x 0.5mm x 0.5mm	Soxhlet extraction with toluene	GC/MS	
2366	<500µm	Soxhlet extraction	GC/MS	
2369	1mmx1mmx1mm	Soxhlet extraction with toluene	GC/MS	
2370	Powder	Soxhlet extraction	GC/MS	
2372	<0.5mm	Soxhlet extraction	GC/MS	
2379	1x1x1mm	Soxhlet extraction	GC/MS	
2386	<1mm	Soxhlet extraction	GC/MS	
2403				
2410	Cryo-milling with nitrogen<500µm	Soxhlet extraction with toluene	GS/MS	

2438	1x1 mm	Soxhlet extraction	GC/MS ISTD	
3100	Grind to powder, 500µm	Soxhlet extraction with toluene		
3126				
3146				
3151	No further grinding	Soxhlet extraction with toluene	GC/MS	2hrs (0.5g / 50ml)
3153	<500µm	Soxhlet extraction	GC/MS	
3163				
3166		ultrasonic extract with hexane	GC/MS	
3172	<500µm	Soxhlet extraction with toluene	GC/MS	
3182	250µm	Soxhlet extraction with toluene	GC/MS	
3185	<500µm	Soxhlet extraction	GC/MS	
3190	Grinded	Soxhlet extraction	GC/MS	
3191	Grinded to pass through a 500µm sieve	Soxhlet extraction with toluene	GC/MS	
3209	Fine powder using cryogenic mill	ultrasonic with toluene	GC/MS	
3210				
3214	<500µm	Soxhlet extraction	GC/MS	
3218	<500µm	Soxhlet extraction	GC/MS	
3225	as received	Soxhlet extraction	GC/MS	
3228	<0.5mm	ultrasonic	GC/MS ISTD	
3239				
3243	<2mm	Soxhlet extraction with toluene	GC/MS	light exclusion
3246	1x1mm 0.200-0.500 gr for extraction	Liquid extraction with toluene/acetone	GC/MS	

Note that several laboratories reported deviating conditions for sample #11053:

Lab	Max. particle size	Extraction	Detection	Other details
2202	<500µm	Soxhlet extraction	GC/MS	
2350		ultrasonic	GC/MS	
2359	0.5g	Soxhlet extraction	GC/MS	
2438	1*1 mm	Soxhlet extraction with toluene	GC/MS ISTD	
3246	1x1mm 0.200-0.500 gr for extraction	Liquid extraction with toluene/acetone	GC/MS	precip. with MeOH

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APPENDIX 3

Number of participating laboratories per country

2 labs in BRAZIL
1 lab in FINLAND
2 labs in FRANCE
6 labs in GERMANY
6 labs in HONG KONG
3 labs in INDIA
2 labs in ITALY
4 labs in KOREA
2 labs in MALAYSIA
24 labs in P.R. of CHINA
2 labs in SINGAPORE
3 labs in TAIWAN R.O.C.
3 labs in THAILAND
2 labs in THE NETHERLANDS
3 labs in U.S.A.
2 labs in VIETNAM

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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
n.d.	= not detected

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