

Results of Proficiency Test Brominated Flame retardants August 2015

Organised by: Institute for Interlaboratory Studies
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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 bio accumulate 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. Hexabromocyclododecane (HBCDD) has been under suspicion since 2008, when it was placed on the list of Substances of Very High Concern of the European Chemicals Agency. HBCDD is toxic to water-living organisms. It has been included in the EPA's List of Chemicals of Concern since 2010. In 2011 it was listed in the Annex XIV of REACH and hence is subject to Authorisation. HBCDD is slowly banned worldwide.

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. This year also HBCDD was added to the scheme. In the interlaboratory study of August 2015, 64 laboratories from 20 different countries participated (see appendix 3). In this report, the results of the 2015 proficiency test are presented and discussed. This report is also electronically available through the iis internet site www.iisnl.com.

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 #15152 and #15153 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 PT falls under the accredited scope. This ensures strict adherence to protocols for sample preparation and statistical evaluation and 100% confidentiality 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 (#15152) was a Poly Vinyl Chloride (PVC) in granulates, fortified with nonabromodiphenylether (Nona-BDE) and decabromodiphenylether (Deca-BDE). The second material (#15153) was a PVC that was fortified with hexabromocyclo-dodecane (HBCDD).

Sample #15152 and sample #15153 were both divided into 100 subsamples of approx. 3 grams. The homogeneity of subsamples #15152 and #15153 was checked by the determination of Deca-BDE and HBCDD content on 8 stratified randomly selected subsamples.

	Deca-BDE #15152 in mg/kg	HBCDD #15153 in mg/kg
Sample 1	2368	2090
Sample 2	2221	2010
Sample 3	2261	2147
Sample 4	2231	2088
Sample 5	2303	1986
Sample 6	2357	2048
Sample 7	2332	2110
Sample 8	2372	2036

Table 1: test results of the homogeneity study on the subsamples #15152 and #15153

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

	Deca-BDE #15152 in mg/kg	HBCDD #15153 in mg/kg
r (observed)	172	151
reference	IMEP-26*	IMEP-26*
0.3 x R (reference)	480	434

Table 2: evaluation of the observed repeatabilities of the subsamples

* See appendix 4: ref. 17.

Both observed repeatabilities were in agreement with 0.3 times the assigned target reproducibility. Therefore, homogeneity of the subsamples of #15152 and #15153 was assumed.

To each of the participating laboratories one set of samples (1* sample #15152 and 1* sample #15153, both 3 grams each) was sent on August 12, 2015.

2.5 ANALYSIS

The participants were requested to determine on both samples: octa-BDE, nona-BDE, deca-BDE and HBCDD. 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 as well as the required standards and a letter of instructions were prepared and made available on the data entry portal www.kpmd.co.uk/sgs-iis-cts/. A SDS, a form to confirm receipt of the samples and a letter of instructions were added to the samples.

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:

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

The $z_{(\text{target})}$ 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. Seven participants reported results after the final reporting date and six participants did not report any results at all. Not all laboratories were able to report all analytes requested. Finally, the 58 reporting laboratories reported 165 numerical test results. Observed were 10 outlying results, which is 5.7% of all reported numerical test results. In proficiency studies, outlier percentages of 3% - 7.5% are quite normal.

All original data sets proved to have a normal Gaussian distribution.

For the determination of PBB and PBDE, the IEC62321 method is considered to be the official EC test method. Regretfully, the 2008 version of IEC62321 does not mention precision data.

Normally, when no (suitable) reproducibility requirements from a test method are available, target requirements are estimated from the Horwitz equation. Fortunately, an Interlaboratory Comparison report is available: IMEP-26 Determination of brominated flame retardants in plastic. 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). The reproducibility is calculated to be 2.8 times the standard deviation of 25% of the assigned value.

However, during the evaluation of the data for this PT, the updated IEC62321-6:2015 was published, including precision data. Analyzing the precision data of this new method for all measured poly-BDE, a general reproducibility of 50% of the assigned value was determined. This new method will have to be implemented in the next year by all countries concerned. Therefore this

reproducibility value of 50% of the assigned value has not yet been used in this report, but has been mentioned for comparison in the tables (see appendix 1).

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-BDE as well as HBCDD. The majority of participants did not detect Octa-BDE and HBCDD for sample #15152 and Octa-, Nona- and Deca-BDE for sample #15153. This means that for #15152 only Nona- and Deca-BDE were statistically evaluated and for #15153 only HBCDD.

The participants were also requested to report the analytical details of the methods. The analytical details are listed in Appendix 2.

The test results reported by laboratory 551 for Nona- and Deca-BDE (#15152) appeared to be outliers, while for HBCDD “not detected” was reported, when the majority of laboratories reported HBCDD present in the sample. The test results of laboratory 2612 appeared to be outliers for all three of the evaluated brominated flame retardants.

sample #15152:

Nona-BDE: This determination was problematic. Three statistical outliers were observed. The calculated reproducibility after rejection of the statistical outliers is not in agreement with the target reproducibility from IMEP-26 and not at all in agreement with the more strict requirements of method IEC62321-6:2015.

Deca-BDE: This determination was not problematic. Six statistical outliers were observed. However, the calculated reproducibility after rejection of the statistical outliers is in good agreement with the target reproducibility from IMEP-26 and also in agreement with the more strict requirements of method IEC62321-6:2015.

For Octa-BDE forty-six participants reported a test result of <50 mg/kg and for HBCDD thirty-one participants reported a test result of <50 mg/kg.

sample #15153:

HBCDD: This determination was very problematic. One statistical outlier was observed. The calculated reproducibility after rejection of the statistical outlier is not at all in agreement with the target reproducibility from IMEP-26.

For Octa- and Nona-BDE a test result of <50 mg/kg was reported by more than forty participants. For Deca-BDE forty-nine participants reported a test result of <100 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)
Nona-BDE #15152	mg/kg	47	104.5	133.7	73.1
Deca-BDE #15152	mg/kg	51	2054	1006	1438

Table 3: performance overview for sample #15152

Analytes	unit	n	Average	2.8 * sd	R (target)
HBCDD #15153	mg/kg	30	2457	3400	1720

Table 4: performance overview for sample #15153

4.3 COMPARISON WITH PREVIOUS PROFICIENCY TESTS

The uncertainties in the test results of the determined Brominated Flame Retardants in the iis15P07 PT are listed in the next table and are comparable with previous proficiency tests.

	2015	2014	2013	2012	2011	2010	2009	est. IMEP-26
hexa-BDE	n.e.	n.e.	n.e.	n.e.	28%	n.e.	n.e.	25%
hepta-BDE	n.e.	n.e.	n.e.	n.e.	15%	n.e.	n.e.	25%
octa-BDE	n.e.	n.e.	n.e.	41%	25%	35 – 39%	21 – 36%	25%
nona-BDE	46%	32 - 33%	33 – 38%	40 - 51%	15 – 23%	37 - 40%	21 – 39%	25%
deca-BDE	17%	24%	14 – 21%	15 - 16%	20 – 25%	10 – 14%	13 – 37%	25%
HBCDD	49%	n.e.	n.e.	n.e.	n.e.	n.e.	n.e.	25%

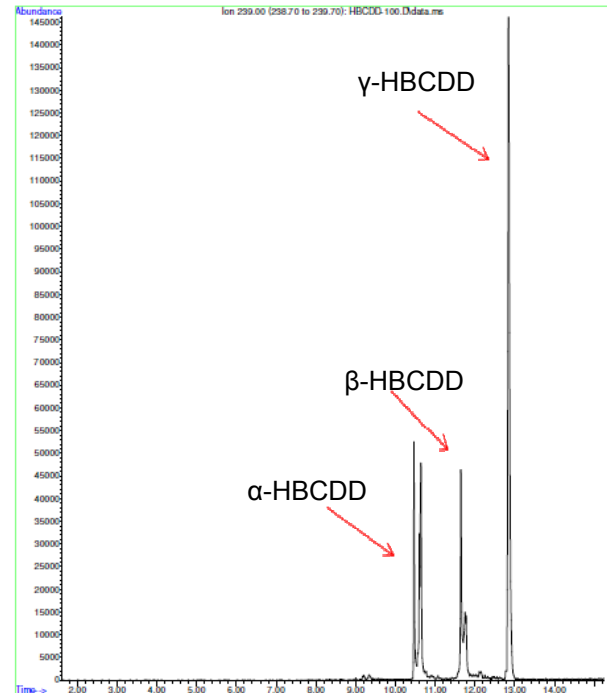
table 5: development of uncertainties over the last years

5 DISCUSSION

For the determination of PBB and PBDE, the IEC62321 method is considered to be the official EC test method. In this proficiency test almost all of the participants used a version of IEC62321 for the determination of Octa-, Nona- and Deca-BDE.

This year ninety percent of the participants reduced the sample size before testing and used toluene as the extraction solvent. Surprisingly only seventy percent of the participants used a Soxhlet extraction, as described in test method IEC62321. The other participants used the alternative ultrasonic technique (also mentioned in IEC62321), which is only applicable to soluble polymers, while PVC (like the samples of this PT) is not likely to be considered a soluble polymer, except for in THF. Most laboratories that used ultrasonic as extraction method, also used toluene as extraction solvent and toluene does not dissolve PVC. However, when evaluated separately, the effect of using two different extraction methods for these particular samples appears to be small.

In this PT, a sample with HBCDD was evaluated for the first time. The spread of this determination was large. Fifteen participants (=50%) reported to have used IEC62321, while three used EPA3550C and the other 12 participants used an in-house test or did not report a test method. Part of the spread may be explained by the fact that the HBCDD (CAS number 3194-55-6) does consist of three predominant isomers, α -, β - and γ -HBCDD, that will not coelute, but give a number of peaks in the chromatogram. Separation of these isomers may be easier with LC-MS than with GC-MS, due to the fact that higher temperatures HBCDD may re-arrange above 160°C and decompose above 220°C [5]. Another problem may be the fact that the plasticizer of the PVC may be interfering with the peak of β -HBCDD. Therefore quantification of HBCDD with GC-MS may be preferably done using either α - or γ -HBCDD or both α - and γ -HBCDD.



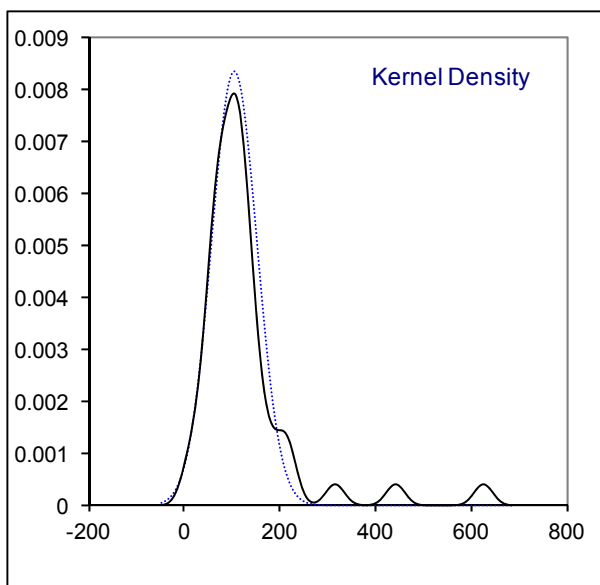
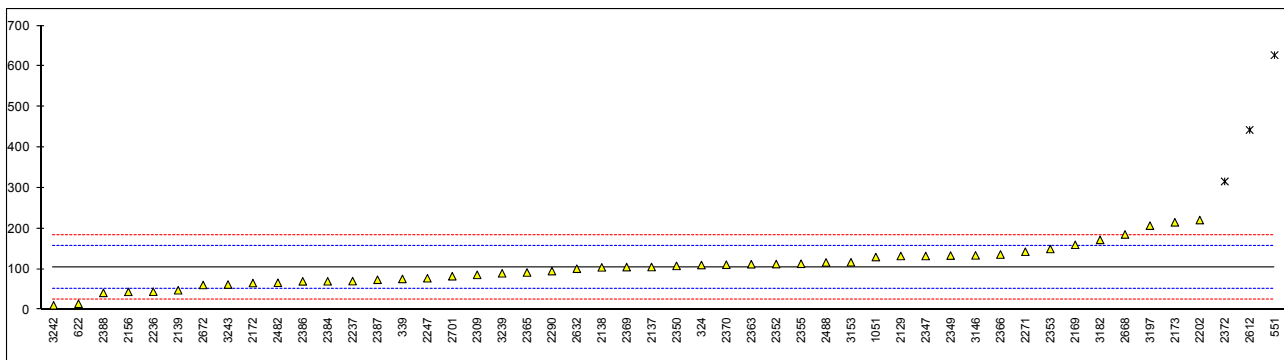
To avoid decomposition and/or debromination of the brominated components by UV light during extraction and analysis, glass equipment made from brown or amber glass shall be used. Also it should be noted that brominated flame retardants may undergo thermal decomposition. Decabromodiphenyl ether exhibits a threshold decomposition temperature that is close to polypropylene processing temperatures (130-170°C). In the presence of hydrocarbon polymer the loss of bromine leads to the formation of lower brominated by-products and hydrobromic acid.

When all participants would follow the above precautions, this may reduce the high spread found in this PT.

APPENDIX 1

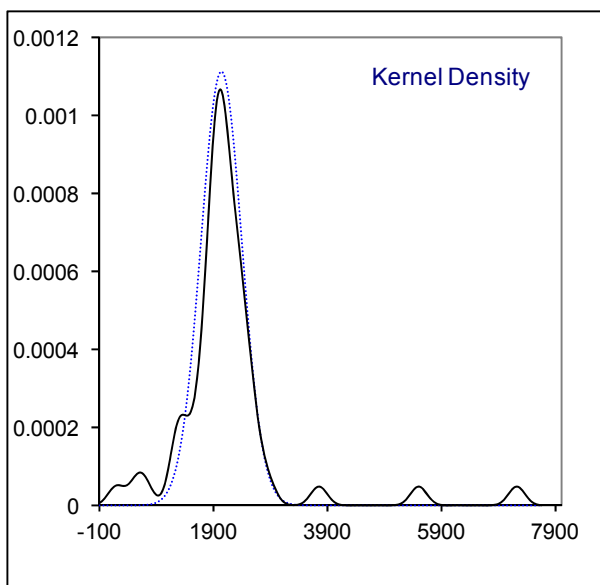
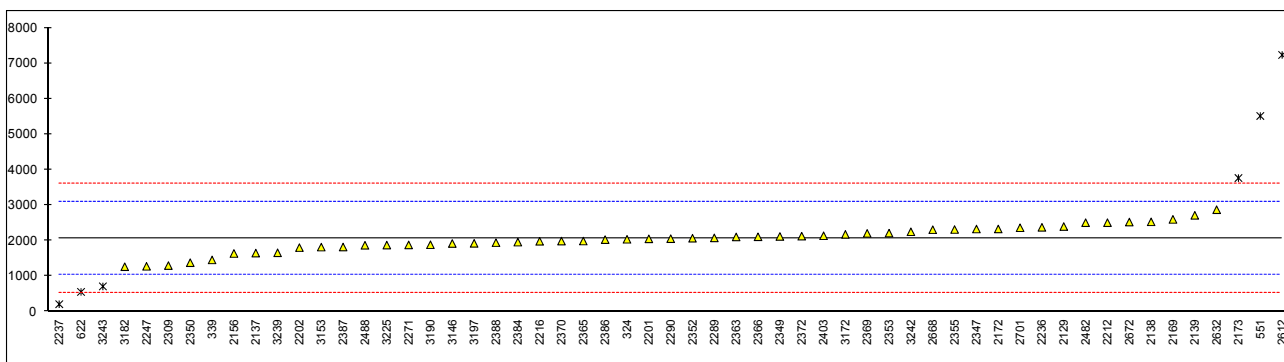
Determination Nonabromodiphenyl ether on sample #15152; results in mg/kg

lab	method	value	mark	z(targ)	remarks
110		----		----	
324	IEC62321	110		0.21	
339	IEC62321Mod.	75.9		-1.09	
551	IEC62321	627.4	R(0.01)	20.03	
622	IEC62321	14.58		-3.44	
632		----		----	
1051	GB/T26125	129.7	C	0.97	first reported: 335.88
2115		----		----	
2129	in house	132.4		1.07	
2137	IEC62321	105.23		0.03	
2138	IEC62321	104.4		0.00	
2139	INH-2130	48.0		-2.16	
2156	IEC62321	44.0		-2.32	
2169	IEC62321	160	C	2.13	first reported: 304
2172	IEC62321	65.7		-1.48	
2173	IEC62321	215.395		4.25	
2201	IEC62321	n.d.		----	
2202	IEC62321	221		4.46	
2212		----		----	
2216		----		----	
2236	IEC62321	44.453		-2.30	
2237	IEC62321	70.515		-1.30	
2247	IEC62321	77.62		-1.03	
2271	IEC62321	143.0		1.48	
2289	IEC62321	n.d.		----	
2290	IEC62321	95.2		-0.35	
2301		----		----	
2309	IEC62321	85.91		-0.71	
2347	IEC62321	132.4		1.07	
2349	IEC62321	133.3		1.10	
2350	IEC62321	108		0.14	
2352	IEC62321	112.4		0.30	
2353	IEC62321	149.7175		1.73	
2355	IEC62321	113.2		0.34	
2363	IEC62321	112		0.29	
2365	IEC62321	91.8155		-0.48	
2366	IEC62321	136		1.21	
2369	IEC62321	105		0.02	
2370	IEC62321	111		0.25	
2372	IEC62321	316.1	R(0.01)	8.11	
2384	IEC62321	70.07		-1.32	
2386	IEC62321	70		-1.32	
2387	IEC62321	73.93		-1.17	
2388	IEC62321	41.51		-2.41	
2403	IEC62321	n.d.		----	
2482	IEC62321	66.5	C	-1.45	first reported: 687.58
2488	IEC62321	116.499		0.46	
2492		----		----	
2612	IEC62321	443	R(0.01)	12.96	
2632	IEC62321	101.1	C	-0.13	first reported: 10.1
2668	IEC62321	185.44		3.10	
2672	IEC62321	61.00		-1.66	
2701	IEC62321	82.61		-0.84	
3146	IEC62321	134		1.13	
3153	IEC62321	117		0.48	
3163		----		----	
3172		----		----	
3182	IEC62321	172.0		2.59	
3190	IEC62321	n.d.		----	
3197	IEC62321	207.2		3.93	
3225	IEC62321	<250		----	
3239	IEC62321	89.765		-0.56	
3242	IEC62321	10.74		-3.59	
3243	IEC62321	62		-1.63	
	normality	OK			
	n	47			
	outliers	3			
	mean (n)	104.451			
	st.dev. (n)	47.7431			
	R(calc.)	133.681			
	R(IMEP-26)	73.116			Compare R(IEC62321-6:2015) = 52.226



Determination of Decabromodiphenyl ether on sample #15152; results in mg/kg

lab	method	value	mark	z(targ)	remarks
110		----		----	
324	IEC62321	2040		-0.03	
339	IEC62321Mod.	1459		-1.16	
551	IEC62321	5512	R(0.01)	6.73	
622	IEC62321	557.74	R(0.05)	-2.91	
632		----		----	
1051		----		----	
2115		----		----	
2129	in house	2400	C	0.67	first reported: 4448.7
2137	IEC62321	1650.55		-0.79	
2138	IEC62321	2531.9		0.93	
2139	INH-2130	2714.9		1.29	
2156	IEC62321	1640.0		-0.81	
2169	IEC62321	2600	C	1.06	first reported: 3200
2172	IEC62321	2330		0.54	
2173	IEC62321	3764.517	R(0.05)	3.33	
2201	IEC62321	2052		0.00	
2202	IEC62321	1806		-0.48	
2212	IEC62321	2507		0.88	
2216	INH-62321	1982.6		-0.14	
2236	IEC62321	2377.271		0.63	
2237	IEC62321	211.085	R(0.05)	-3.59	
2247	IEC62321	1278.83		-1.51	
2271	IEC62321	1881.1		-0.34	
2289	IEC62321	2079		0.05	
2290	IEC62321	2055.4		0.00	
2301		----		----	
2309	IEC62321	1298.53		-1.47	
2347	IEC62321	2329.2		0.54	
2349	IEC62321	2118.3		0.12	
2350	IEC62321	1380		-1.31	
2352	IEC62321	2069.1		0.03	
2353	IEC62321	2212.8060		0.31	
2355	IEC62321	2315.9		0.51	
2363	IEC62321	2105		0.10	
2365	IEC62321	1990.7095		-0.12	
2366	IEC62321	2109		0.11	
2369	IEC62321	2207		0.30	
2370	IEC62321	1990		-0.13	
2372	IEC62321	2127		0.14	
2384	IEC62321	1959.96		-0.18	
2386	IEC62321	2030		-0.05	
2387	IEC62321	1821.01		-0.45	
2388	IEC62321	1945.75		-0.21	
2403	IEC62321	2140		0.17	
2482	IEC62321	2506.43		0.88	
2488	IEC62321	1870.398		-0.36	
2492		----		----	
2612	IEC62321	7231	R(0.01)	10.08	
2632	IEC62321	2873.6	C	1.60	first reported: 35.0
2668	IEC62321	2310.33		0.50	
2672	IEC62321	2525		0.92	
2701	IEC62321	2365.28		0.61	
3146	IEC62321	1920		-0.26	
3153	IEC62321	1820		-0.46	
3163		----		----	
3172	IEC62321	2178		0.24	
3182	IEC62321	1266.3		-1.53	
3190	IEC62321	1887		-0.33	
3197	IEC62321	1925.4		-0.25	
3225	IEC62321	1875.646		-0.35	
3239	IEC62321	1658.698		-0.77	
3242	IEC62321	2251.97		0.38	
3243	IEC62321	713	R(0.05)	-2.61	
	normality	OK			
	n	51			
	outliers	6			
	mean (n)	2054.292			
	st.dev. (n)	359.2866			
	R(calc.)	1006.002			
	R(IMEP-26)	1438.004			Compare R(IEC62321-6:2015) = 1027.146

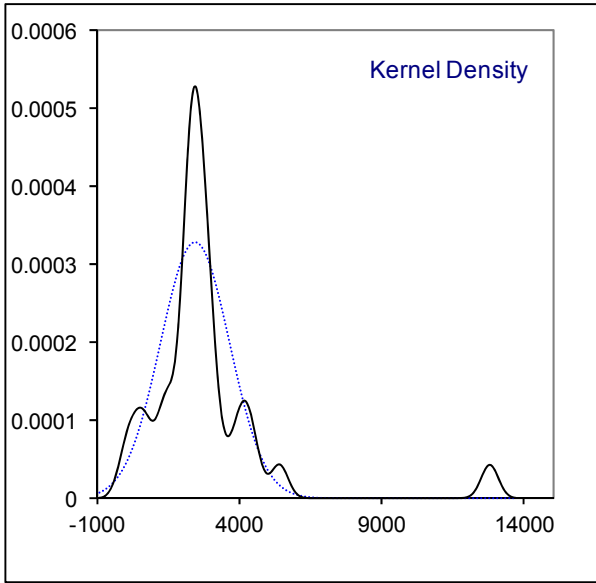
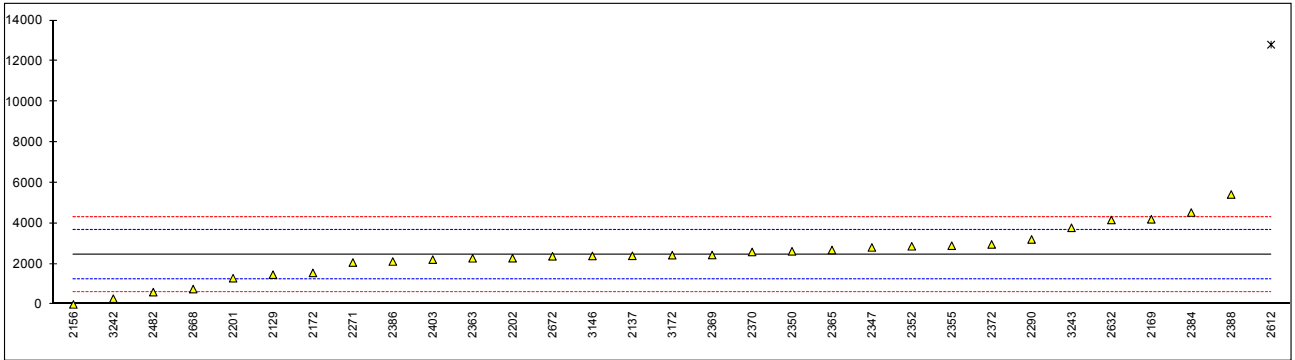


Determination of Octa-BDE, HBCDD and Other on sample #15152; results in mg/kg

lab	method	Octa-BDE	method	HBCDD	method	Other	remarks
110		----		----		----	
324	IEC62321	<5.0		----		----	
339	IEC62321Mod.	<1.0		----		----	
551	IEC62321	10.5		----		----	
622	IEC62321	<10		----		----	
632		----		----		----	
1051	GB/T26125	21.47		----		----	
2115		----		----		----	
2129		----		----		----	
2137	IEC62321	<1	in house	<10	in house	<1	
2138	IEC62321	n.d.		----		----	
2139		----		----		----	
2156	IEC62321	5.0	IEC62321	5.0		----	
2169	IEC62321	<10		<50		----	first reported for Octa-BDE: 16.4
2172	IEC62321	<5	IEC62321	<5		n.d.	
2173	IEC62321	37.474		----		n.d.	first reported for Octa-BdE: 88.832
2201	IEC62321	n.d.		n.d.		----	
2202	IEC62321	23		n.d.		----	
2212	IEC62321	<100		----		----	
2216	INH-62321	<100		----		----	
2236		----		----		----	
2237	IEC62321	<10	IEC62321	<10		----	
2247	IEC62321	n.d.		----		----	HBCDD: no traceable Reference Material
2271	IEC62321	29.4		<5		<5	
2289	IEC62321	n.d.		1391		----	HBCDD: false positive?
2290	IEC62321	<5.0		<5.0		<5.0	
2301		----		----		----	
2309	IEC62321	<50		----		----	
2347	IEC62321	<5	EPA3550C	<5		<5	
2349	IEC62321	n.d.		----		----	
2350		----		----		----	
2352	IEC62321	n.d.	in house	n.d.		n.d.	
2353	IEC62321	n.d.		----		----	
2355	IEC62321	<5	EPA3550C	<10		----	
2363	IEC62321	<5	INH-280	<10		----	
2365	IEC62321	<5	EPA3550C	<10	EPA3550C	<5	
2366	IEC62321	<5		----		----	
2369	IEC62321	<5		<10		<5	
2370	IEC62321	n.d.	IEC62321	n.d.	IEC62321	n.d.	
2372	IEC62321	11.63	IEC62321	n.d.		----	
2384	IEC62321	n.d.	IEC62321	n.d.		----	
2386	IEC62321	<50	in house	<50		----	
2387	IEC62321	n.d.		----		----	
2388	IEC62321	n.d.	INH-62321	n.d.		----	
2403	IEC62321	n.d.	IEC62321	n.d.	IEC62321	n.d.	
2482	IEC62321	<50		----		----	
2488	IEC62321	n.d.	IEC62321	n.d.	IEC62321	n.d.	
2492		----		----		----	
2612	IEC62321	162		<50		<50	
2632	IEC62321	3.9	IEC62321	<5	IEC62321	<5	
2668		----	IEC62321	n.d.	IEC62321	n.d.	Octa-BDE: reported BDE-203 10.7 mg/kg
2672	IEC62321	<50	IEC62321	<100		----	
2701	IEC62321	<50		----		----	
3146	IEC62321	<25	IEC62321	<25	IEC62321	<25	
3153	IEC62321	<20	IEC62321	<20	IEC62321	<20	
3163		----		----		----	
3172		----		----		----	
3182	IEC62321	n.d.		----		n.d.	HBCDD was not analyzed as no standard
3190	IEC62321	n.d.		n.d.		----	
3197	IEC62321	n.d.	IEC62321	n.d.	IEC62321	n.d.	
3225	IEC62321	<250	IEC62321	<250	IEC62321	<250	
3239		----		----		----	
3242		----	IEC62321	n.d.	IEC62321	n.d.	Octa-BDE: mentioned CAS no. not available
3243	IEC62321	n.d.		n.d.		n.d.	
	normality	n.a.		n.a.		n.a.	
	n	46		31		21	
	outliers	n.a.		n.a.		n.a.	
	mean (n)	<50		<50		<50	
	st.dev. (n)	n.a.		n.a.		n.a.	
	R(calc.)	n.a.		n.a.		n.a.	
	R(IMEP-26)	n.a.		n.a.		n.a.	

Determination of Hexabromocyclododecane on sample #15153; results in mg/kg

lab	method	value	mark	z(targ)	remarks
110		----		----	
324		----		----	
339		----		----	
551		n.d.		----	
622		----		----	
632		----		----	
1051		----		----	
2115		----		----	
2129	in house	1470		-1.61	
2137	in house	2400.45		-0.09	
2138		----		----	
2139		----		----	
2156	IEC62321	5.0		-3.99	
2169		4200	C	2.84	first reported: 4260
2172	IEC62321	1554.82		-1.47	
2173		----		----	HBCDD not determined because of no available test method
2201		1295		-1.89	HBCDD was quantified with LCMSMS
2202		2279		-0.29	
2212		----		----	
2216		----		----	
2236		----		----	
2237		----		----	
2247		----		----	
2271		2068.2		-0.63	no traceable Ref. Material, only detected in screening: approx. 495 ppm
2289		----		----	
2290		3205.1		1.22	
2301		----		----	
2309		----		----	
2347	EPA3550C	2814.0		0.58	
2349		----		----	
2350	in house	2622		0.27	
2352	in house	2868.9		0.67	
2353		----		----	
2355	EPA3550C	2896.5		0.72	
2363	INH-280	2278		-0.29	
2365	EPA3550C	2681.5875		0.37	
2366		----		----	
2369		2437		-0.03	
2370	IEC62321	2590		0.22	
2372	IEC62321	2961		0.82	
2384	IEC62321	4533.15		3.38	
2386	in house	2120		-0.55	
2387		----		----	
2388	INH-62321	5420.07		4.82	
2403	IEC62321	2210		-0.40	
2482		608.3		-3.01	
2488	IEC62321	n.d.		----	
2492		----		----	
2612		12806	R(0.01)	16.85	
2632	IEC62321	4164.4		2.78	
2668	IEC62321	757.96		-2.77	
2672	IEC62321	2375		-0.13	
2701		----		----	
3146	IEC62321	2390		-0.11	
3153	IEC62321	<20		----	
3163		----		----	
3172		2430.8		-0.04	
3182		----		----	HBCDD was not analyzed as no standard
3190		----		----	
3197	IEC62321	n.d.		----	
3225	IEC62321	<250		----	
3239		----		----	
3242	IEC62321	288.13		-3.53	
3243		3781.50		2.16	
	normality	OK			
	n	30			
	outliers	1			
	mean (n)	2456.862			
	st.dev. (n)	1214.2981			
	R(calc.)	3400.035			
	R(IMEP-26)	1719.804			



Determination of Octa-BDE, Nona-BDE, Deca-BDE and Other on sample #15153; results in mg/kg

lab	method	Octa-BDE	Nona-BDE	Deca-BDE	Other	remarks
110		----	----	----	----	
324	IEC62321	<5.0	<5.0	16.7	----	
339	IEC62321Mod.	<1.0	<2.0	<10.0	----	
551	IEC62321	n.d.	n.d.	n.d.	n.d.	
622	IEC62321	<10	<10	24.97	----	
632		----	----	----	----	
1051		----	----	----	----	
2115		----	----	----	----	
2129		----	----	----	----	
2137	IEC62321	<1	<1	<1	<1	reported in house method for Other Brom. Flame Ret.
2138	IEC62321	n.d.	n.d.	n.d.	----	
2139		----	----	14.8	----	
2156	IEC62321	5.0	5.0	75.0	----	
2169	IEC62321	<10	<10	<10	----	fr: Octa-BDE 17.46, Nona-BDE 281 and Deca-BDE 2940
2172	IEC62321	<5	<5	11.914	n.d.	
2173	IEC62321	n.d.	n.d.	n.d.	n.d.	
2201	IEC62321	n.d.	n.d.	n.d.	----	
2202	IEC62321	n.d.	n.d.	n.d.	----	Other Brom. Flame Ret. was not tested
2212	IEC62321	<100	----	<100	----	
2216	INH-62321	<100	----	<100	----	
2236		----	<25	44.565	----	
2237		----	----	----	----	
2247	IEC62321	n.d.	n.d.	n.d.	----	
2271	IEC62321	<5	<5	<5	<5	
2289		----	----	----	----	
2290	IEC62321	<5.0	<5.0	26.3	<5.0	
2301		----	----	----	----	
2309	IEC62321	<50	<50	<50	----	
2347	IEC62321	<5	<5	<5	<5	
2349	IEC62321	n.d.	n.d.	n.d.	----	
2350		----	----	----	----	
2352	IEC62321	n.d.	n.d.	n.d.	n.d.	
2353	IEC62321	n.d.	n.d.	n.d.	----	
2355	IEC62321	<5	<5	<5	----	
2363	IEC62321	<5	<5	<5	----	
2365	IEC62321	<5	<5	<5	<5	reported method EPA3550C for Other Brom. Flame Ret.
2366	IEC62321	<5	<5	<5	----	
2369	IEC62321	<5	<5	<5	<5	
2370	IEC62321	n.d.	n.d.	n.d.	n.d.	
2372	IEC62321	n.d.	n.d.	n.d.	----	
2384	IEC62321	n.d.	n.d.	n.d.	n.d.	
2386	IEC62321	<50	<50	<50	----	
2387	IEC62321	n.d.	n.d.	n.d.	----	
2388	IEC62321	n.d.	n.d.	n.d.	----	
2403	IEC62321	n.d.	n.d.	n.d.	n.d.	
2482		----	----	----	----	
2488	IEC62321	n.d.	n.d.	40.296	n.d.	
2492		----	----	----	----	
2612	IEC62321	<5	<5	<5	<50	
2632	IEC62321	<5	<5	13.0	<5	
2668	IEC62321	n.d.	n.d.	n.d.	n.d.	
2672	IEC62321	<50	<50	<500	~1300	Other: Pentabromocyclododecane
2701	IEC62321	<50	<50	<50	----	
3146	IEC62321	<25	<25	28.8	<25	
3153	IEC62321	<20	<20	<20	<20	
3163		----	----	----	----	
3172		----	----	----	----	
3182	IEC62321	n.d.	n.d.	10.9	n.d.	
3190	IEC62321	n.d.	n.d.	n.d.	----	
3197	IEC62321	n.d.	n.d.	52.2	n.d.	
3225	IEC62321	<250	<250	<250	<250	
3239		----	----	10.609	----	
3242		----	n.d.	n.d.	n.d.	Octa-BDE: mentioned CAS no. not available
3243	IEC62321	n.d.	n.d.	n.d.	n.d.	
	normality	n.a.	n.a.	n.a.	n.a.	
	n	44	46	49	22	
	outliers	n.a.	n.a.	n.a.	n.a.	
	mean (n)	<50	<50	<100	<25	
	st.dev. (n)	n.a.	n.a.	n.a.	n.a.	
	R(calc.)	n.a.	n.a.	n.a.	n.a.	
	R(IMEP-26)	n.a.	n.a.	n.a.	n.a.	

APPENDIX 2:

Lab	Was the grain size of the granulate reduced before analysis?	To what max. particle size was the granulate reduced before analysis?	How was the final particle size checked?	Which technique was used to release/extract the analytes?	What extraction solvent (mixture) was used?	What was the extraction time and temperature?
110	---	---		---		
324	Milled (cryogenic)	≤ 0.5 mm		Soxhlet	Toluene	24 hours
339	Not reduced, used sample as received	>1 mm	melted	Ultrasonic	Toluene	1 hour at 60°C
551	Grinded	≤ 1 mm		Ultrasonic	Toluene	50°C
622	Cut	≤ 1 mm		Soxhlet	Toluene	Two hours
632	---	---		---		
1051	Not reduced, used sample as received	To particle >0.1g, the granulate was reduced before analysis	By Balance	Ultrasonic	THF	30 min, room temperature
2115	---	---		---		
2129	Milled (cryogenic)	≤ 1 mm	optical	Ultrasonic	10 ml DCM, 1g sample	Roomtemperature, 30 minutes
2137	Milled (cryogenic)	≤ 0.5 mm	through a sieve of 0.5 mm	Ultrasonic	Toluene	3 Hrs, 50 celcius
2138	Milled (cryogenic)	≤0.5 mm		Soxhlet	Toluene	2 h
2139	Cut	>1 mm	< 1mm	Ultrasonic	Toluene	1hr , 60 °C
2156	Cut	≤1 mm		Soxhlet	Toluene	6 hours, 200°C
2169	Milled (cryogenic)	≤ 0.5 mm		Ultrasonic	THF	1hr
2172	Milled (cryogenic)	≤ 0.5 mm		Soxhlet	Toluene	8h
2173	Not reduced, used sample as received	>1 mm		Soxhlet	Toluene	2 hours, 215°C
2201	Grinded	≤ 0.5 mm	through 500um sieve	Soxhlet	Toluene	Soxhlet 4h
2202	Not reduced, used sample as received	other	-	Stirrer	THF/Toluene/Hexane, THF/Dichloromehane	2hr, 25 °C
2212	Grinded	≤ 1 mm		Ultrasonic	Toluene	60mins at 60C
2216	Milled (cryogenic)	≤ 1 mm	Sieve	Ultrasonic	Toluene	60min at 60C
2236	Cut	≤ 1 mm	with a ruler	Stirrer/reflux condenser	Chlorobenzene	30 minutes @ 370 degrees C
2237	Milled (cryogenic)	≤ 1 mm		Ultrasonic	DMF, Toluene	60 Min room temperature
2247	Milled (cryogenic)	≤ 0.5 mm	visual , fine material	Soxhlet	Toluene	time : 2 hrs. temp 60 digree

Lab	Was the grain size of the granulate reduced before analysis?	To what max. particle size was the granulate reduced before analysis?	How was the final particle size checked?	Which technique was used to release/extract the analytes?	What extraction solvent (mixture) was used?	What was the extraction time and temperature?
2271	Cut	≤ 0.5 mm		Soxhlet	Toluene	2 hour
2289	Grinded	≤ 0.5 mm	through 500um griddle	Soxhlet	Toluene	extract for 2 hours
2290	Cut	≤ 1 mm		Soxhlet	Toluene	4h
2301	---	---		---		
2309	Grinded	≤ 0.5 mm		Soxhlet	Toluene	70degree & two & half hrs
2347	Cut	≤ 0.5 mm		Soxhlet	Toluene	6 hours
2349	Cut	≤ 0.5 mm		Soxhlet	Toluene	3H
2350	Cut	≤ 0.5 mm		Ultrasonic	Toluene	3 hours and 50degree
2352	Cut	≤ 1 mm		Soxhlet / Ultrasonic	Toluene	4h/180°C
2353	Cut	>1 mm	2mm	Soxhlet	Toluene	2hr, 250C
2355	Cut	≤ 0.5 mm		Soxhlet / Ultrasonic	Toluene	PBDE:16h HBCDD:60°C 1h
2363	Cut	≤ 0.5 mm		Soxhlet	Toluene	4 hours
2365	Cut	≤ 0.5 mm		Soxhlet	Toluene	8h
2366	Cut	≤ 0.5 mm		Soxhlet	Toluene	
2369	Cut	≤ 0.5 mm		Soxhlet	Toluene	16hr, 110°C
2370	Milled (cryogenic)	≤ 0.5 mm		Soxhlet	Toluene	2 hrs
2372	Milled (cryogenic)	≤ 0.5 mm	Visual	Ultrasonic	Toluene	60°C/1hr
2384	Cut	≤ 0.5 mm	Pass through 0.5mm sieve	Soxhlet	Toluene	16 hours, under reflux
2386	Milled (cryogenic)	≤ 1 mm		Soxhlet	Toluene	4 h
2387	Cut	≤ 0.5 mm	Passing through 0.5mm sieve	Soxhlet	Toluene	16hours, under reflux condition
2388	Cut	≤ 0.5 mm	pass through 0.5mm sieve	Soxhlet	Toluene	16hours, under reflux temperature
2403	Cut	>1 mm	By measurement	Soxhlet	Toluene	2 hours, 2-3 min per cycle; Room temperature
2482	Not reduced, used sample as received	other		Ultrasonic	Toluene	1 hour and 60 °C
2488	---	---		---		
2492	---	---		---		

Lab	Was the grain size of the granulate reduced before analysis?	To what max. particle size was the granulate reduced before analysis?	How was the final particle size checked?	Which technique was used to release/extract the analytes?	What extraction solvent (mixture) was used?	What was the extraction time and temperature?
2612	Cut	>1 mm		Soxhlet	Toluene	reflux for 4 hours
2632	Milled (cryogenic)	≤ 0.5 mm	500µm	Soxhlet	Toluene	At least 4 hr
2668	Cut	0.5 mm	not checked	Ultrasonic	Toluene	70°C
2672	Milled (cryogenic)	≤ 1 mm	visual	Ultrasonic	Toluene	1 h / 70 °C
2701	Milled (cryogenic)	≤ 0.5 mm	the sample was milled	Soxhlet	Toluene	150 degree celcius for 4 hours
3146	Cut	≤ 1 mm		Soxtec extraction	Toluene	285°C 3h => 45 min reflux
3153	Milled (cryogenic)	≤ 0.5 mm		Soxhlet	Toluene	4 hours reflux
3163	---	---		---		
3172	Milled (cryogenic)	≤ 0.5 mm		Soxhlet	Toluene	2-3 hours
3182	Milled (cryogenic)	≤ 0.5 mm	By using sieve	Soxhlet	Toluene	6 hrs at 110 degree Celcius
3190	Grinded	≤ 0.5 mm		Soxhlet	Toluene	350°C 2h
3197	Cut	≤0.5 mm	sieved through 0.5 mm sieve	Soxhlet	Toluene	2 hours, 80°C
3225	Grinded	≤ 0.5 mm		Soxhlet	Toluene	4 hours
3239	Milled (cryogenic)	≤ 1 mm		Soxhlet	Toluene	2 hours
3242	---	---		---		
3243	Milled (cryogenic)	≤ 0.5 mm		Soxhlet	Toluene	2 hours

APPENDIX 3

Number of participating laboratories per country

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