Results of Proficiency Test
SCCP & MCCP in Polymer
May 2017

Organised by: Institute for Interlaboratory Studies
Spijkenisse, the Netherlands

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1 INTRODUCTION

Commercially produced chlorinated paraffins (CPs) are classified according to their carbon chain length into Short Chain CPs (SCCP C_{10}-C_{13}) , Medium Chain CPs (MCCP C_{14}-C_{17}) and Long Chain CPs (LCCP >C_{17}). The chlorine content of these mixtures can vary from 30-70% depending on the application. Technical CPs are used in plasticizers and fire retardants. CPs are classified as persistent and non-biodegradable and they accumulate in the food chain. SCCPs were categorized in group 2B as possibly carcinogenic to humans from the International Agency for Research on Cancer (IARC). A global ban on SCCPs is being considered under the Stockholm Convention on Persistent Organic Pollutants.
On request of several participants, the Institute for Interlaboratory Studies decided to organise an interlaboratory study for the determination of MCCP/SCCP content in polymers in the 2015 PT program. This PT was continued in 2017. In this interlaboratory study 64 laboratories from 21 different countries registered for participation (see appendix 3).
In this report, the results of the 2017 proficiency test are presented and discussed. This report is also electronically available through the iis website www.iisnl.com.

2 SET-UP

The Institute for Interlaboratory Studies (iis) in Spijkenisse, the Netherlands, was the organiser of this proficiency test. Sample analyses for fit-for-use and homogeneity testing were subcontracted to an ISO/IEC17025 accredited laboratory. It was decided to send two different plastic samples (approximately 3 grams each), artificially fortified with MCCP and SCCP. The participants were requested to report rounded and unrounded test results. The unrounded test results were preferably used for statistical evaluation. Participants were also requested to report a number of details of the test method used.

2.1 QUALITY SYSTEM

The Institute for Interlaboratory Studies in Spijkenisse, the Netherlands, has implemented a quality system based on ISO/IEC17043. This ensures strict adherence to protocols for sample preparation and statistical evaluation and 100% confidentiality of participant's data. Also customer's satisfaction is measured on regular basis by the distribution of questionnaires.

2.2 PROTOCOL

The protocol followed in the organisation of this proficiency test was the one as described for proficiency testing in the report 'iis Interlaboratory Studies: Protocol for the Organization, Statistics and Evaluation' of March 2017 (iis-protocol, version 3.4). This protocol can be downloaded from the iis website www.iisnl.com, from the FAQ page.

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 PVC materials, both artificially fortified with a commercial mixture of SCCP and MCCP were selected. One existed of tube-shaped pieces (approx 3x4mm, 30 mg on average each) and the other of solid square pieces (approx 2x4x4mm, 45 mg on average each). Both materials were divided after homogenisation over plastic bags, approx. 3 grams for each sample. The homogeneity of the subsamples #17570 was checked by determination of the SCCP content on 8 stratified randomly selected subsamples.

	SCCP in mg/kg
Sample #17570-1	950
Sample #17570-2	982
Sample #17570-3	983
Sample #17570-4	953
Sample #17570-5	948
Sample #17570-6	970
Sample #17570-7	938
Sample #17570-8	938

Table 1: homogeneity test results of the subsamples #17570

From the above test results the repeatabilities were calculated and compared with 0.3 times the target reproducibility, estimated from the Horwitz equation, in agreement with the procedure of ISO 13528, Annex B2. See the next table;

	SCCP in mg/kg
r (observed) #17570	56
reference method	Horwitz
0.3 x R (reference method)	137

Table 2: evaluation of repeatability of SCCP contents of the subsamples #17570

As the observed repeatability of the test results of the homogeneity test was in full agreement with the target precision data estimated from the Horwitz equation, the homogeneity of subsamples #17570 was assumed.

The second batch was used in the previous proficiency test iis16P06 as sample #16571. Therefore, homogeneity was already proven.

To each of the participating laboratories one sample #17570 and one sample #17571 was sent on April 19, 2017.

2.5 ANALYSES

The participants were requested to determine on both samples: MCCP and SCCP content, applying the analysis procedure that is routinely used in the laboratory. Also some method details were requested to be reported.

It was explicitly requested to treat the samples as if they were routine samples and to report the test results using the indicated units on the report form and not to round the test 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 test results, a detailed report form and a letter of instructions are prepared. On the report form, the reporting units are given as well as the reference test methods that will be used during the evaluation. The detailed report form and the letter of instructions are both made available on the data entry portal www.kpmd.co.uk/sgs-iis-cts/. The participating laboratories are also requested to confirm the sample receipt on this data entry portal. The letter of instructions can also be downloaded from the iis website www.iisnl.com.

3 RESULTS

During five weeks after sample dispatch, the test results of the individual laboratories were gathered via the data entry portal www.kpmd.co.uk/sgs-iis-cts/. The reported test results are tabulated per determination in appendix 1 of this report. The laboratories are presented by their code numbers.

Directly after the deadline, a reminder was sent to those laboratories that had not reported test results at that moment.
Shortly after the deadline, the available test results were screened for suspect data. A test 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 reported test results (no reanalysis). Additional or corrected test results are used for data analysis and the original reported test results placed under 'Remarks' in the result tables in appendix 1. Test results that came in after the deadline were not taken into account in this screening for suspect data and thus these participants were not requested for checks.

3.1 STATISTICS

The protocol followed in the organisation of this proficiency test was the one as described for proficiency testing in the report ‘’iis Interlaboratory Studies: Protocol for the Organisation, Statistics and Evaluation’ of March 2017 (iis-protocol, version 3.4).

For the statistical evaluation the unrounded (when available) figures were used instead of the rounded results. Test 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. If a data set does not have a normal distribution, the (results of the) statistical evaluation should be used with due care.

According to ISO 5725 the original test results per determination were submitted subsequently to Dixon's and 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. 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 the averages and the 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 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 reference test method. 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. The Kernel Density Graph is a method for producing a smooth density approximation to a set of data that avoids some problems associated with histograms. 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 variation in 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. In case no literature reproducibility was available, other target values were used. In some cases, a reproducibility based on former iis proficiency tests could be used.

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 whether the reported test results is fit-for-use.

The z-scores were calculated in according to:

$z_{(target)}$ = (test result – average of proficiency test) / target standard deviation

The $z_{(target)}$ scores are listed in the result tables of 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:

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

4 EVALUATION

In this interlaboratory study, several problems were encountered. Nine participants decided not report any test results and three participants reported test results after the final reporting date.
Finally, the 55 reporting laboratories reported 198 numerical results. In the reported test results 10 statistical outliers were observed, which is 4.8%. In proficiency studies, outlier percentages of 3% - 7.5% are quite normal.

Not all original data sets proved to have a normal Gaussian distribution. These are referred to as “not OK” or “suspect”. The statistical evaluation of these data sets should be used with due care, see also paragraph 3.1.

For the determination of MCCP/SCCP, ISO/DIS 18219 is considered to be the official test method. However this method is developed for the determination of MCCP/SCCP in leather and therefore it is unknown if it is applicable for other matrices like plastics. Regretfully, for the determination of MCCP/SCCP content in plastics no official test method is available. Therefore, the target requirements in this study were estimated using the Horwitz equation (for n=9).

It was decided to use assigned consensus values for the MCCP and SCCP determination, after exploring the effect of sample pre-treatment as reported by the participants. It appears that the values of the test results increase and the variation between test results decreases when the samples were cut or grinded or when toluene or THF was used as solvent see paragraph and 5 for more discussion. Therefore, based on the analytical details reported by the participants, samples that were not cut or grinded and where hexane was used as solvent were excluded from statistical calculations.

4.1 EVALUATION PER SAMPLE AND PER COMPONENT

In this section the results are discussed per sample (see also discussion in paragraph 5).

sample #17570:

SCCP: This determination may be problematic for a number of laboratories. Five statistical outliers were observed and nine other test results were excluded from the statistical evaluations. However, the observed reproducibility after rejection of the suspect data is in good agreement with the estimated reproducibility calculated using the Horwitz equation (n=9).

MCCP: This determination may be problematic. Two statistical outliers were observed and five test results were excluded from the statistical evaluations. The observed reproducibility after rejection of the suspect data is not in agreement with the estimated reproducibility calculated using the Horwitz equation (n=9).

sample #17571:

SCCP: This determination may be problematic. Three statistical outliers were observed and nine other test results were excluded from the statistical evaluations. The observed reproducibility after rejection of the suspect data is not in agreement with the estimated reproducibility calculated using the Horwitz equation (n=9).

MCCP: This determination may be problematic. No statistical outliers were observed, but five test results were excluded from the statistical evaluations. The observed reproducibility after rejection of the suspect data is not in agreement with the estimated reproducibility calculated using the Horwitz equation (n=9).

4.2 PERFORMANCE EVALUATION OF THE GROUP OF LABORATORIES

A comparison has been made between the reproducibility as declared by the estimated target reproducibility using the Horwitz equation and the reproducibility as found for the group of participating laboratories.

The number of significant test results, the average result, the calculated reproducibility (standard deviation*2.8) and the estimated target reproducibility are presented in the next tables.

	unit	n	Average	2.8 * sd	R(Horwitz)
SCCP	mg/kg	42	1291	552	591
MCCP	mg/kg	37	3281	1759	1304

Table 3: performance overview on samples #17570

	unit	n	Average	2.8 * sd	R(Horwitz)
SCCP	mg/kg	43	844	552	411
MCCP	mg/kg	38	2184	1198	923

Table 4: performance overview on samples #17571

Without further statistical calculations, it can be concluded that there is not a good compliance of the group of participating laboratories with the target reproducibilities, except for the determination of SCCP in sample #17570.

4.3 COMPARISON OF THE PROFICIENCY TEST OF MAY 2017 WITH PREVIOUS PTS

	May 2017	*May 2016*	*May 2015*
Number of reporting labs	55	51	58
Number of results reported	198	184	110
Statistical outliers	10	4	3
Percentage outliers	4.8%	2.1%	2.7%

Table 5: comparison with previous proficiency tests

In proficiency tests, outlier percentages of 3% - 7.5% are quite normal.

The uncertainties determined in this PT are compared with the relative standard deviations as found in previous year and with the target requirements based on the Horwitz equation in the next table:

component	*May 2017*	*April 2016*	*April 2015*	*Target*
SCCP	15-23%	23-33%	29%	16-18%
MCCP	19-20%	31-39%	19%	14-15%

Table 6: comparison of the observed uncertainties

For the investigated components the performance of the group has improved and is good in comparison with previous years.

5 DISCUSSION

About half of the participants (29 = 52%) reported to have used ISO/DIS18219 as test method and 26 other participants reported to have used an 'in house' test method.
The details of the methods that were reported by the participants are listed in appendix 2.
ISO/DIS18219 mentions a number of essential steps that is necessary to follow in order to get reproducible test results. Therefore it is remarkable to note that 11 of the 29 laboratories that reported to have used ISO/DIS18219 did not cut or grind the samples, but tested the samples as received.

In the previous PTs iis15P05 and iis16P06, it became clear that the ultrasonic extraction with n-hexane at 60°C during 60 min. (the conditions as per ISO/DIS18219) will give low recoveries of SCCP/MCCP. In the current PT, in total 15 laboratories reported to have used n-hexane as extraction solvent, while 25 laboratories used toluene for the extraction and another 10 laboratories used THF to dissolve the samples completely. For SCCP the use of different extraction solvents results was investigated. Each solvent gives a different average concentration SCCP, but also a significantly different dispersion of these test results, see table 6:

SCCP	Solvent	n	Average in mg/kg	st.dev in mg/kg	RSD%
#17570	n-hexane *)	13	1275	776	61%
#17570	toluene *)	23	1250	160	13%
#17570	THF	9	1373	271	20%
#17571	n-hexane *)	13	659	384	58%
#17571	toluene *)	24	828	157	19%
#17571	THF	8	846	127	15%

Table 7: observed differences between different extraction solvents

*) Using ultrasonic extraction at 60ºC for 60 minutes

THF is able to dissolve the PVC sample completely and this gives the highest concentrations SCCP and MCCP.
The dispersion of the test results after extraction with THF or toluene is much smaller (13-20%) compared to hexane (58-61%).

The reduction of the grain size of the samples also has an effect on the test results. Contradictory to the expectations, after cutting or grinding the sample does release only slightly more SCCP and MCCP, but the dispersion of the test results is much smaller than the dispersion of the test results from the original sample. For sample #17570 the dispersion of the reported test SCCP results is reduced from 46% on the samples as received to 20% on the samples after cutting or grinding, see table 7.

SCCP	condition	n	Average in mg/kg	st.dev in mg/kg	RSD%
#17570	as received	22	1187	547	46%
#17570	cut/grinded	28	1257	250	20%
#17571	as received	22	722	311	43%
#17571	cut/grinded	30	859	290	34%

Table 8: observed differences between samples as received and samples after cutting/grinding

This same phenomenon was also found in the previous proficiency test “SCCP/MCCP in polymer” iis16P06.
Therefore it was decided to exclude test results where the sample was not cut or grinded and where n-hexane was used as extraction solvent.

Sample #17571 was already used in a previous PT; as sample #16571 in iis16P06. During PT iis16P06 the evaluation of SCCP in sample#16571 was quite problematic and 17 test results were excluded from the statistical evaluation in order to get a reliable estimate of the consensus value.

After issue of the PT report iis16P06 an additional investigation was done and the findings were published in an addendum report (ref. 12). In this addendum report a fixed ratio SCCP/MCCP of 28/72 was used to recalculate values for SCCP and MCCP. The data distribution of the recalculated test results was much better than the data distribution of the originally reported test results. From this it was concluded that the influence of the identification and quantification procedures of SCCP and MCCP was significant. Therefore, it was decided to request the participants to report details about the identification and quantification. Twenty-nine participants (53%) reported to have used the m/z ions as mentioned in ISO18219:2015 for the identification and quantification. The other twenty-six reporting participants reported deviating ion masses (some only one or two) or did not report any details. No significant influence from the used ion masses was observed.

In this PT iis17P05 the evaluated samples both contained the same SCCP/MCCP mixture as in previous years. Therefore it would be interesting to look again at the ratio SCCP/MCCP as reported by the participating laboratories. It appears that the large majority of the participants did report a ratio very similar to last year; from 21/79 to 33/67. One laboratory (2723) reported a very low ratio of 5/95 and several other laboratories (2118, 2255 and 2293) a very high ratio of 47/53 or 51/49). The test results of these 4 participants were already excluded because hexane was used as solvent and the sample was not cut or grinded.

6 CONCLUSION

It is clear is that the majority of the participants is able to determine total SCCP and total MCCP in the polymer matrix, but a large variation is found between participants. This variation obviously is highly dependent on the chosen sample pre-treatment and the extraction solvent. Fortunately, the determination of MCCP and SCCP becomes more reproducible when sample pre-treatments are chosen that release SCCP and MCCP more effectively from the polymer. Such pathways could be cutting, milling or grinding the polymer prior the extraction or the use of toluene or THF as solvent.

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.

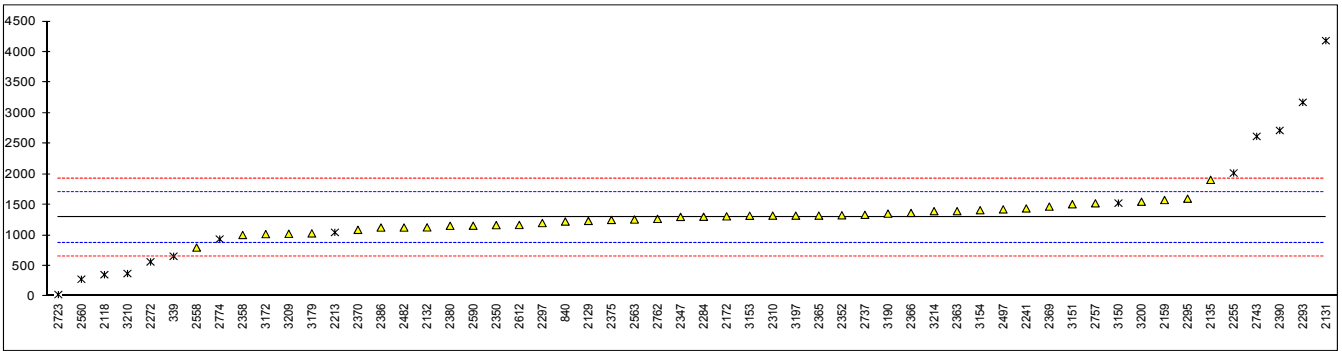
APPENDIX 1

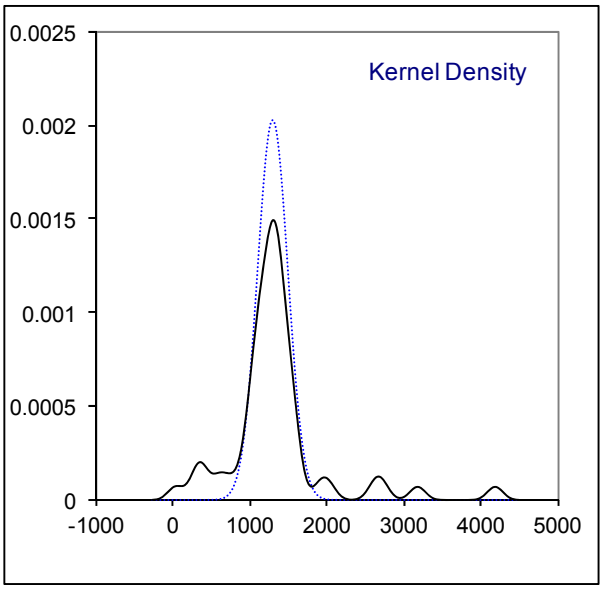
Determination of SCCP on sample #17570; results in mg/kg

lab	method	value	mark	z(targ)	Remarks
324		-----		-----	
339	In house	657	ex	-3.01	
551		-----		-----	
623		-----		-----	
840	In house	1226		-0.31	
1170		-----		-----	
2118	In house	355.34	ex	-4.44	
2129	ISO/DIS18219	1236		-0.26	
2131	In house	4186	ex	13.72	
2132	In house	1129.96		-0.77	
2135	In house	1908		2.92	
2159	ISO/DIS18219	1577.39		1.35	
2172	In house	1310.24		0.09	
2213	ISO/DIS18219	1048	ex	-1.16	
2241	In house	1440.376	C	0.71	First reported 2205.4861
2255	ISO/DIS18219	2020	R(0.05)	3.45	
2272	ISO/DIS18219	565.52	R(0.05)	-3.44	
2284	In house	1303.63		0.06	
2293	ISO/DIS18219	3176.78	C,R(0.01)	8.94	First reported 6837.76
2295	ISO/DIS18219	1600		1.46	
2297	ISO/DIS18219	1201.3		-0.43	
2301		-----		-----	
2310	ISO/DIS18219	1322		0.14	
2347	ISO/DIS18219	1302		0.05	
2350	ISO/DIS18219	1167.115		-0.59	
2352	In house	1328.0		0.17	
2358	INH-112015	1006.0		-1.35	
2363	In house	1395.8		0.49	
2365	In house	1322.8		0.15	
2366	In house	1367.1		0.36	
2369	ISO/DIS18219	1470		0.85	
2370	ISO/DIS18219	1090		-0.96	
2375	ISO/DIS18219	1252.0		-0.19	
2380	ISO/DIS18219	1155.7692		-0.64	
2386	ISO/DIS18219	1128		-0.78	
2390	ISO/DIS18219	2716.20	C,R(0.01)	6.75	First reported 3320.12
2482	ISO18219:2016Mod.	1128		-0.78	
2497	In house	1425.08		0.63	
2558	In house	799.4		-2.33	
2560	In house	280.8586	R(0.05)	-4.79	
2561		-----		-----	
2563	ISO/DIS18219	1259		-0.15	
2590	ISO/DIS18219	1157.4101		-0.64	
2612	In house	1169.86		-0.58	
2723	ISO/DIS18219	30	ex	-5.98	
2737	In house	1335.78		0.21	
2743	ISO/DIS18219	2619.59	ex	6.30	
2757		1524		1.10	
2762	In house	1269		-0.11	
2774	In house	938	ex	-1.68	
3146		-----		-----	
3150	ISO/DIS18219	1527	C,ex	1.12	First reported 454
3151	In house	1509		1.03	
3153	In house	1320.2		0.14	
3154	ISO/DIS18219	1411.383		0.57	
3163		-----		-----	
3172	ISO/DIS18219	1020		-1.29	
3179	ISO/DIS18219	1032		-1.23	
3190	In house	1355.8		0.30	
3197	In house	1322		0.14	
3200	ISO/DIS18219	1550.3		1.23	
3209	ISO/DIS18219	1025.2		-1.26	
3210	In house	375	ex	-4.35	
3214	ISO/DIS18219	1395.78		0.49	

			All test results
normality	suspect		Suspect
n	42		51
outliers	5 (+9 excl)		5
mean (n)	1291.64		1215.99
st.dev. (n)	197.041	RSD=15%	338.788
R(calc.)	551.71		948.61
R(Horwitz n=9)	590.56		561.05

Ex = result excluded from statistical calculations, see §4 and §5



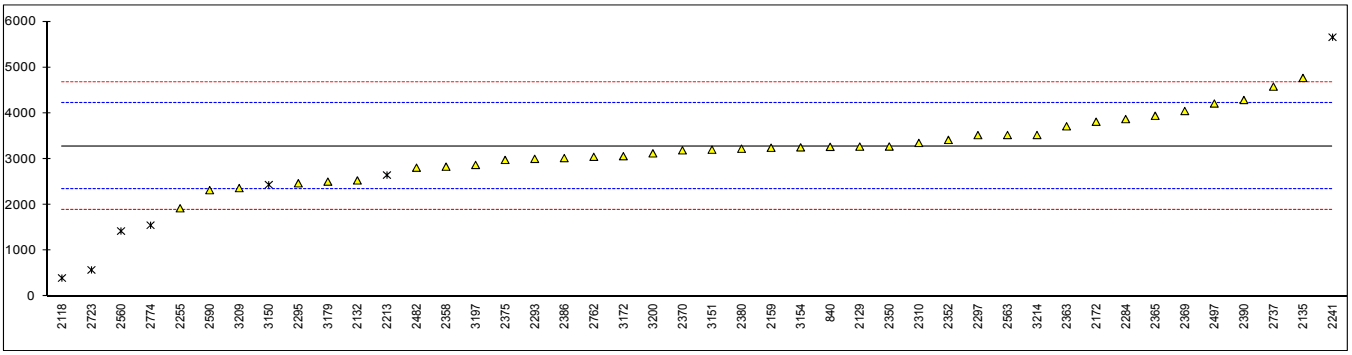


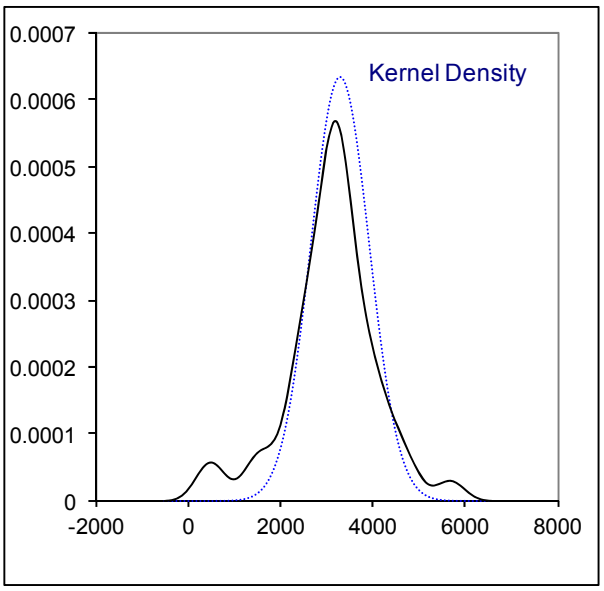
Determination of MCCP on sample #17570; results in mg/kg

lab	method	value	mark	z(targ)	remarks
324		-----		-----	
339		-----		-----	
551		-----		-----	
623		-----		-----	
840	In house	3266		-0.03	
1170		-----		-----	
2118	In house	403.16	ex	-6.18	
2129	ISO/DIS18219	3271		-0.02	
2131		-----		-----	
2132	In house	2532.99		-1.61	
2135	In house	4769		3.20	
2159	ISO/DIS18219	3245.81		-0.07	
2172	In house	3814.09		1.15	
2213	ISO/DIS18219	2650	ex	-1.35	
2241	In house	5657.976	C,R(0.05)	5.11	First reported 7932.0957
2255	ISO/DIS18219	1925.3		-2.91	
2272		-----		-----	
2284	In house	3871.73		1.27	
2293	ISO/DIS18219	3004.09	C	-0.59	First reported 462.87
2295	ISO/DIS18219	2471		-1.74	
2297	ISO/DIS18219	3521.1		0.52	
2301		-----		-----	
2310	ISO/DIS18219	3351.1		0.15	
2347		-----		-----	
2350	ISO/DIS18219	3272.849		-0.02	
2352	In house	3416.8		0.29	
2358	ISO18219:15	2833.1		-0.96	
2363	In house	3714.7		0.93	
2365	In house	3944.0		1.42	
2366		-----		-----	
2369	ISO/DIS18219	4048		1.65	
2370	ISO/DIS18219	3190		-0.19	
2375	ISO/DIS18219	2980.1		-0.65	
2380	ISO/DIS18219	3225.000		-0.12	
2386	ISO/DIS18219	3021		-0.56	
2390	ISO/DIS18219	4288.18		2.16	
2482	ISO18219:2016Mod	2811		-1.01	
2497	In house	4211.28		2.00	
2558		-----		-----	
2560	In house	1428.7638	R(0.05)	-3.98	
2561		-----		-----	
2563	ISO/DIS18219	3524		0.52	
2590	ISO/DIS18219	2321.2422		-2.06	
2612		-----		-----	
2723	ISO/DIS18219	580	ex	-5.80	
2737	In house	4580.34		2.79	
2743		-----		-----	
2757		-----		-----	
2762	In house	3048		-0.50	
2774	In house	1555	ex	-3.71	
3146		-----		-----	
3150	ISO/DIS18219	2439	ex	-1.81	
3151	In house	3204		-0.16	
3153		-----		-----	
3154	ISO/DIS18219	3254.446		-0.06	
3163		-----		-----	
3172	ISO/DIS18219	3062		-0.47	
3179	ISO/DIS18219	2507		-1.66	
3190		-----		-----	
3197	In house	2871		-0.88	
3200	ISO/DIS18219	3124.6		-0.34	
3209	ISO/DIS18219	2365.6		-1.97	
3210		-----		-----	
3214	ISO/DIS18219	3524.00		0.52	

			All test results
normality	OK		OK
n	37		41
outliers	2 (+5 excl)		3
mean (n)	3280.69		3157.52
st.dev. (n)	628.335	RSD = 19%	726.375
R(calc.)	1759.34		2033.85
R(Horwitz n=9)	1303.64		1261.95

Ex = result excluded from statistical calculations, see §4 and §5



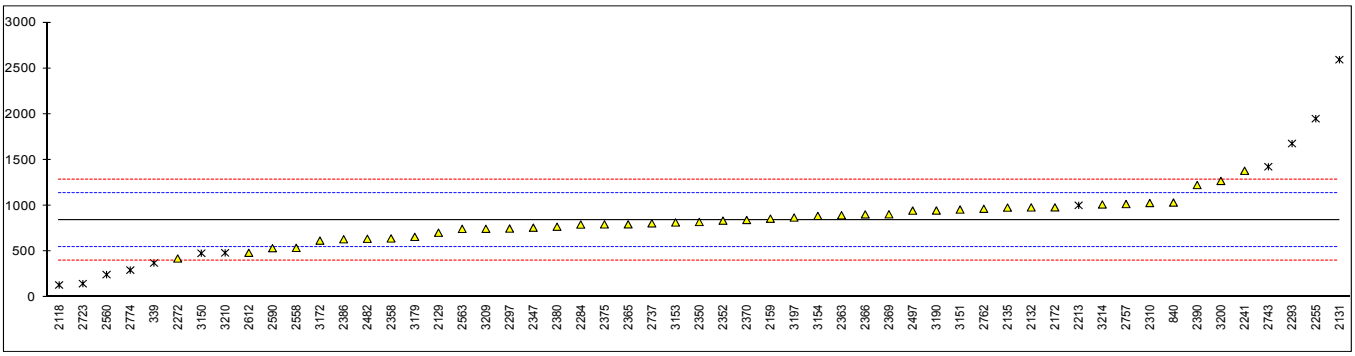


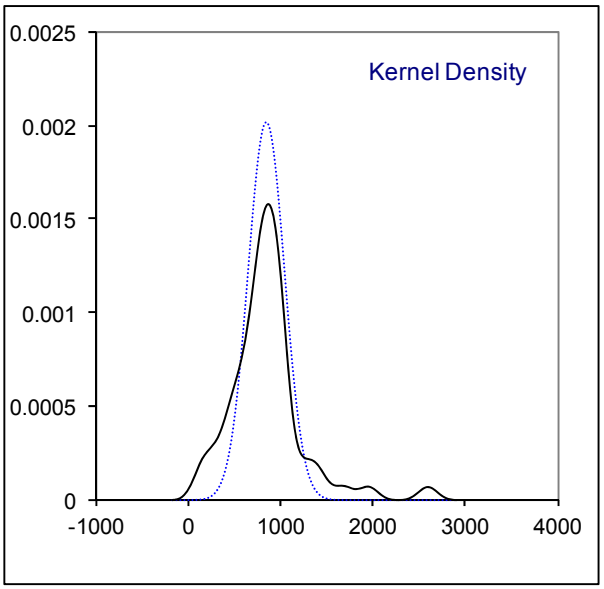
Determination of SCCP on sample #17571; results in mg/kg

lab	method	value	mark	z(targ)	remarks
324		-----		-----	
339	ISO18219 mod.	376	ex	-3.18	
551		-----		-----	
623		-----		-----	
840	In house	1035		1.30	
1170		-----		-----	
2118	In house	135.81	ex	-4.82	
2129	ISO/DIS18219	706		-0.94	
2131	In house	2594	ex	11.92	
2132	In house	982.18		0.94	
2135	In house	980		0.93	
2159	ISO/DIS18219	859.29		0.11	
2172	In house	982.81		0.95	
2213	ISO/DIS18219	1005	ex	1.10	
2241	In house	1382.2009		3.67	
2255	ISO/DIS18219	1950.4	R(0.01)	7.54	
2272	ISO/DIS18219	424.73		-2.85	
2284	In house	795.46		-0.33	
2293	ISO/DIS18219	1679.09	C,R(0.05)	5.69	First reported 4454.20
2295		-----		-----	
2297	ISO/DIS18219	751.5		-0.63	
2301		-----		-----	
2310	ISO/DIS18219	1030.3		1.27	
2347	ISO/DIS18219	761		-0.56	
2350	ISO/DIS18219	823.241		-0.14	
2352	In house	837.8		-0.04	
2358	INH-112015	643.7		-1.36	
2363	In house	896.5		0.36	
2365	In house	797.8		-0.31	
2366	In house	906.2		0.43	
2369	ISO/DIS18219	907		0.43	
2370	ISO/DIS18219	845		0.01	
2375	ISO/DIS18219	797.0		-0.32	
2380	ISO/DIS18219	771.3615		-0.49	
2386	ISO/DIS18219	635		-1.42	
2390	ISO/DIS18219	1226.30	C	2.61	First reported 1943.95
2482	ISO18219:2016Mod	640.2		-1.38	
2497	In house	947.28		0.71	
2558	In house	540.3		-2.06	
2560	In house	248.9071	R(0.05)	-4.05	
2561		-----		-----	
2563	ISO/DIS18219	748		-0.65	
2590	ISO/DIS18219	537.4511		-2.08	
2612	In house	486.9		-2.43	
2723	ISO/DIS18219	150	ex	-4.72	
2737	In house	808.13		-0.24	
2743	ISO/DIS18219	1425.74	ex	3.96	
2757		1019		1.19	
2762	In house	967.0		0.84	
2774	In house	298	ex	-3.71	
3146		-----		-----	
3150	ISO/DIS18219	482	ex	-2.46	
3151	In house	959		0.79	
3153	In house	818.2		-0.17	
3154	ISO/DIS18219	889.150		0.31	
3163		-----		-----	
3172	ISO/DIS18219	620		-1.52	
3179	ISO/DIS18219	661		-1.24	
3190	In house	948.4		0.71	
3197	In house	872		0.19	
3200	ISO/DIS18219	1270.8		2.91	
3209	ISO/DIS18219	748.6		-0.65	
3210	In house	486	ex	-2.43	
3214	ISO/DIS18219	1014.4		1.16	

			All test results
normality	OK		OK
n	43		53
outliers	3 (+9 excl)		2
mean (n)	843.56		803.01
st.dev. (n)	197.301	RSD=23%	301.321
R(calc.)	552.44		843.70
R(Horwitz n=9)	411.24		394.38

Ex = result excluded from statistical calculations, see §4 and §5



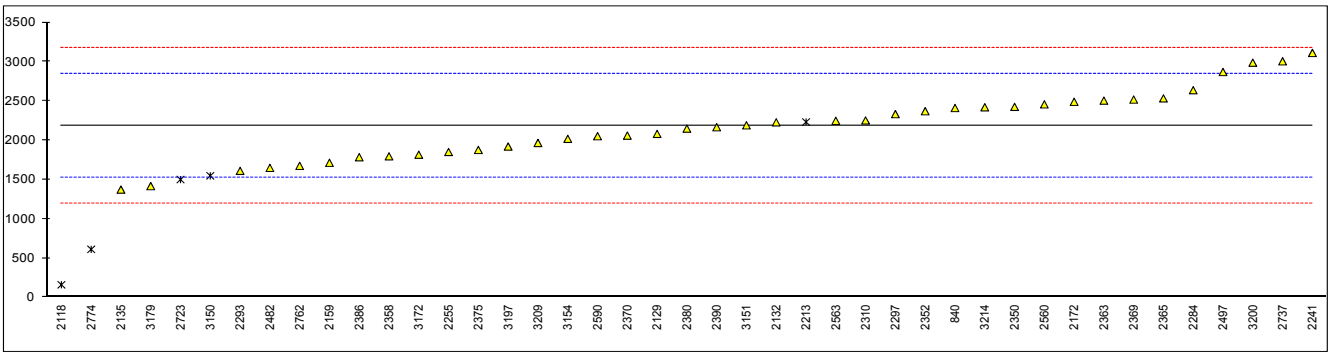


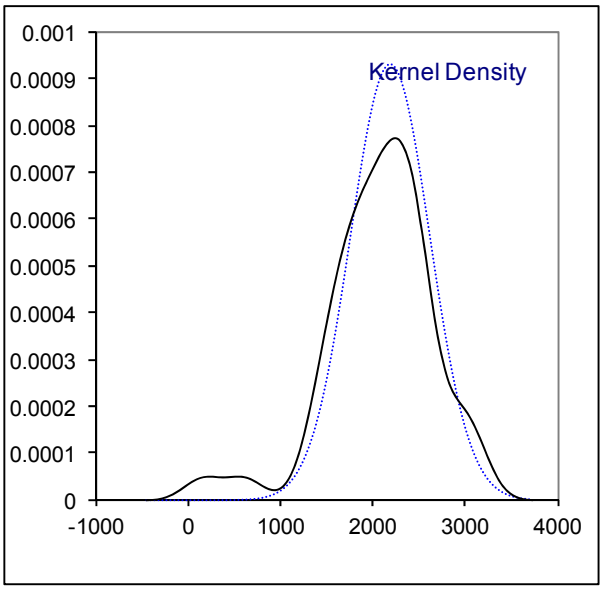
Determination of MCCP on sample #17571; results in mg/kg

lab	method	value	mark	z(targ)	remarks
324		-----		-----	
339		-----		-----	
551		-----		-----	
623		-----		-----	
840	In house	2411		0.69	
1170		-----		-----	
2118	In house	160.86	ex	-6.14	
2129	ISO/DIS18219	2082		-0.31	
2131		-----		-----	
2132	In house	2228.88		0.14	
2135	In house	1373		-2.46	
2159	ISO/DIS18219	1714.06		-1.43	
2172	In house	2490.79		0.93	
2213	ISO/DIS18219	2233	ex	0.15	
2241	In house	3112.118	C	2.82	First reported 4376.2664
2255	ISO/DIS18219	1851.7		-1.01	
2272		-----		-----	
2284	In house	2638.27		1.38	
2293	ISO/DIS18219	1611.270	C	-1.74	First reported 300.889
2295		-----		-----	
2297	ISO/DIS18219	2333.3		0.45	
2301		-----		-----	
2310	ISO/DIS18219	2253		0.21	
2347		-----		-----	
2350	ISO/DIS18219	2426.091		0.74	
2352	In house	2370.1		0.57	
2358	ISO18219:15	1796.5		-1.18	
2363	In house	2505.8		0.98	
2365	In house	2534.3		1.06	
2366		-----		-----	
2369	ISO/DIS18219	2519		1.02	
2370	ISO/DIS18219	2060		-0.38	
2375	ISO/DIS18219	1877.5		-0.93	
2380	ISO/DIS18219	2148.8262		-0.11	
2386	ISO/DIS18219	1785		-1.21	
2390	ISO/DIS18219	2166.77		-0.05	
2482	ISO18219:2016Mod	1649		-1.62	
2497	In house	2869.51		2.08	
2558		-----		-----	
2560	In house	2457.6250		0.83	
2561		-----		-----	
2563	ISO/DIS18219	2248		0.19	
2590	ISO/DIS18219	2052.5732		-0.40	
2612		-----		-----	
2723	ISO/DIS18219	1500	ex	-2.08	
2737	In house	3005.94		2.49	
2743		-----		-----	
2757		-----		-----	
2762	In house	1675		-1.54	
2774	In house	612	ex	-4.77	
3146		-----		-----	
3150	ISO/DIS18219	1548	ex	-1.93	
3151	In house	2191		0.02	
3153		-----		-----	
3154	ISO/DIS18219	2018.761		-0.50	
3163		-----		-----	
3172	ISO/DIS18219	1817		-1.11	
3179	ISO/DIS18219	1417		-2.33	
3190		-----		-----	
3197	In house	1921		-0.80	
3200	ISO/DIS18219	2988.1		2.44	
3209	ISO/DIS18219	1966.2		-0.66	
3210		-----		-----	
3214	ISO/DIS18219	2420.6		0.72	

			All test results
normality	OK		OK
n	38		41
outliers	0 (+5 excl)		2
mean (n)	2183.86		2152.87
st.dev. (n)	428.018	RSD= 20%	436.274
R(calc.)	1198.45		1221.57
R(Horwitz n=9)	922.61		911.48

Ex = result excluded from statistical calculations, see §4 and §5





APPENDIX 2

Analytical details

lab	Was the grain size reduced before use?	reduced to particle size	Technique used for release	Extraction solvent used	Extraction time and temperature used
324	---		---		
339	Used as received	5x5 mm	Ultrasonic	Hexane-DCM 50/50	1 hour at 60 °C
551	---		---		
623	---		---		
840	Cut	1mm x 2mm	Ultrasonic	n-Hexane	60min, 50oC
1170	---		---		
2118	Used as received	3 mm	ASE	Hexane	5 min-100°C
2129	Used as received		Ultrasonic	Toluene	60 min / 60 °C
2131	Used as received		Ultrasonic	n-hexane	60 60
2132	Grinded	< 1mm x 1mm	Ultrasonic	Toluene	60 min, 60C
2135	Used as received		Ultrasonic	Acetone; n-Hexane.	60 Min , 70°C
2159	Used as received	5x5 mm	Ultrasonic	Toluene	60 minutes, 60°C
2172	Grinded	smaller than 1 mm	Ultrasonic	Toluene	60min 70°C
2213	Used as received	5X5 mm	Ultrasonic	50:50 Hexane:DCM	60 mins at 60°C
2241	Cut	1mm*1mm	Ultrasonic	Hexane	30min 40°C
2255	Cut	as small as possible	Ultrasonic	THF	30 minutes & 70°C
2272	Cut	<5mm	Ultrasonic	Hexane	60min, 60°C
2284	Cut	1mm*1mm	Ultrasonic	THF	60 min; 60°C
2293	Cut	2 x 2 mm	Ultrasonic	THF:ACN 5:10	30 minutes at 70°C
2295	---		---		
2297	Used as received	2mm-3mm	Ultrasonic	THF+Toluene	at 40 °C for 1hr
2301	---		---		
2310	Cut	2 mm*2 mm	Ultrasonic	Toluene	60 min and 60°C
2347	Cut	2mm*2mm	Ultrasonic	n-Hexane	60°C, 60min
2350	Used as received	5 mm	Ultrasonic	Toluene; hexane	60 Celsius and 60min
2352	Cut	2mm*2mm	Ultrasonic	Toluene	60min ,60°C
2358	Used as received	5mmx5mm	Ultrasonic	Toluene	60 min and 60 degree C
2363	Cut	1*1*1mm	Ultrasonic	Toluene	1hr 60°C
2365	Cut	1mm*1mm*1mm	Ultrasonic	Toluene	60 min
2366	Cut	2mm*2mm*2mm	Ultrasonic	Toluene	60°C 60min
2369	---		---		
2370	Cut	3mm x 3mm	Ultrasonic	Toluene	time : 60 min, temperature : 60 C
2375	Cut	2X 2 mm	Ultrasonic	Toluene	60 min ,60 C
2380	Used as received	2X3 mm	Ultrasonic	Toluene	60 Minutes & 60 °C
2386	Cut	3 * 3 mm	Ultrasonic	Toluene	60 min, 60 °C
2390	Cut		Ultrasonic	Toluene	60 minutes at 60 C
2482	Used as received		Ultrasonic	Toluene	60 °C for 60 min
2497	Used as received		Ultrasonic	THF	70 – 70
2558	Cut	3 mm	Ultrasonic	Hexane	60 min; 30°C
2560	Cut	2-3 mm	Ultrasonic	n-Hexane, ACN	60 min and 60°C
2561	---		---		
2563	Cut	~4x4 mm	Ultrasonic	Toluene	60 Min. | 60°C
2590	Cut	2mm x 2mm	Ultrasonic	Toluene	60 minutes and 60 °C
2612	Cut	3 mm	Ultrasonic	--	--
2723	Used as received	5 x 5mm	Ultrasonic	Hexane	60 minutes à 50°C
2737	Used as received	use as received	Ultrasonic	Toluene	60min; 60°C
2743	Used as received	not applicable	Ultrasonic	n-hexane	60 minutes 60°C
2757	Used as received		Ultrasonic	Toluene	60 min, 60 °C
2762	Grinded	1 mm	Mechanical Shaking	cyclohexane:acetone	10 min, 22 °C
2774	Used as received		Ultrasonic	Hexane	60min; 60°C
3146	---		---		
3150	Used as received		Ultrasonic	Hexane	60
3151	Used as received	3 x 3 mm	Ultrasonic	Toluene	60 min 60°C
3153	Cut	2 mm x 2 mm	Ultrasonic	Tetrahydrofuran	70oC 30 min
3154	Cut		Ultrasonic	Hexane	60 min at 60 °C
3163	---		---		
3172	Cut	3x3mm	Ultrasonic	THF-Hexane	60min - room temperature
3179	Used as received		Ultrasonic	Toluene	60 min at 60 °C
3190	Used as received	/	Ultrasonic	THF+Acetonitrile	60min ,70℃
3197	Cut	2 mm * 2 mm	Ultrasonic	THF/ACN	30 min 70 °C (performed twice)
3200	Cut		---		
3209	Cut	2mm X 2mm	Ultrasonic	Toluene	60 minutes at 60°C
3210	Used as received		Ultrasonic	n hexane	60 min at 60°C
3214	Grinded	< (2 mmx 2mm)	Ultrasonic	THF and ACN	each 30 min, 70°C

Analytical details -- continued –

lab	Analytical technique used	Ion masses used for Quantification	Ion masses used for Qualification	Internal standard used	Laboratory is accredited for ISO17025?
324					---
339	CI-GC/MS	349 SCCP 59%Cl C10 ; 361 SCCP 59%Cl C11 ; 375 SCCP 59%Cl C12 ; 395 SCCP 59%Cl C13	-	Lindane	No
551					---
623					---
840	GCMS	89			Yes
1170					---
2118	CI-GC/MS	279,313,347,418,292, 327,361,395,306,375, 445,355,389.423,403, 473,451,487,501	89,102,115	trans-chlordane	No
2129	GC/MS with NCI	SCCP: 347, 361, 375, 389; MCCP: 403, 417, 431, 445	SCCP: 349, 363, 377, 391; MCCP: 405, 419, 433, 447	PCB 209	Yes
2131	GC-CI/MS				No
2132	HPLC-LCMSMS	SCCP: m/z 455->59, 457 -> 59, 469 -> 59, 471 -> 59, 483 -> 59, 485 -> 59	NA	No	No
2135	GC/MS	91	115 , 81	--	No
2159	GC-CI-MS	SCCP: 347, 361, 375, 389 / MCCP: 403, 417, 431,445	SCCP: 349, 363, 377, 391 / MCCP: 405, 419, 433, 447	no internal standard	Yes
2172	GC-MS	SCCP:347,361,375,389,349,363,377,391	MCCP:403,417,431,445,405,419,433,447	NO	Yes
2213	GC-ECD/LC-MS/MS				Yes
2241	GC	/	/	no	Yes
2255	GC-ECD	NA	NA	NA	Yes
2272	GC-MS NCI	347/361/375/389	349/363/377/391	HCNN	Yes
2284	GC-MS-NCI	SCCP:347,361,377,389;MCCP:403,417,431,445	SCCP:349,363,375,391;MCCP:403,417,431, 445	Lindan	Yes
2293	LCMSMS			1,2,3,5 - tetra-chloro benzene (tetraCB) CAS 634-90-2	No
2295					---
2297	GCMS-NCI	347,361,375,389 for SCCP; 403,417,431,445 for MCCP	349,363,377,391for SCCP; 405,419,433,447 for MCCP	1,1,1,3,10,11-hexachloroundecane	Yes
2301					---
2310	GC-MS-NCI	SCCP(sum of all m/z) - 347,361,375,389 MCCP(sum of all m/z) - 403,417	SCCP(m/z) - 347/349,361/363,375/ 377,389/391 MCCP(m/z) - 403/405,417/419	Lindane	Yes
2347					Yes
2350	GC-NCI-MS	347, 361, 375, 389	403, 417	Lindane	Yes
2352	GC-NCI-MS	C10Cl7,347;C11Cl7,361;C12Cl7,375;C13Cl7,389;C14Cl7,403;C15Cl7,417	C10Cl7,349;C11Cl7,363;C12Cl7,377;C13Cl7,391;C14Cl7,405;C15Cl7,419	hexachlorocyclohexane(Lindane)	Yes
2358	ac/MS-NCI	C10Cl7 347,C11Cl7 361, C12Cl7 375, C13Cl7 389, C14Cl7 403, C15Cl7 417	C10Cl7 349,C11Cl7 363, C12Cl7 377, C13Cl7 391, C14Cl7 405, C15Cl7 419	Lindane	Yes
2363	GC-NCI-MS	SCCP£º347,361,375,389£»MCCP£º403,417	SCCP:349,363,377,391,MCCP:405,419	lindane	No
2365	GC-MS-NCI	SCCP:M/Z347,M/Z361,M/Z375,M/Z389; MCCP:M/Z403,M/Z417	SCCP:M/Z349,M/Z363,M/Z377,M/Z391; MCCP:M/Z405,M/Z419	Lindane (CAS No. 58-89-9)	Yes
2366	GC-NCI-MS	347,361,375,389	347,361,375,389,349, 363,377,391	Lindane	Yes
2369					Yes
2370	Ultrasonic	SCCP : 347, 361, 375, 389, MCCP : 403, 417	SCCP : 349, 363, 377, 391, MCCP : 405, 419	NO	Yes

lab	Analytical technique used	Ion masses used for Quantification	Ion masses used for Qualification	Internal standard used	Laboratory is accredited for ISO17025?
2375	GC-NCI	-	-	G-BHC (Lindane)	No
2380	GC-MS-NCI	SCCP-347, 361, 375, 389 & MCCP-403, 417	SCCP-349, 363, 377, 391 & MCCP-405, 419	Lindane	No
2386	GC-MS (NCI)	347, 361, 375, 389, 403, 417	349, 363, 377, 391, 405, 419	Lindane	Yes
2390	GC-NCI-MS	MCCP m/z = 403, 417 SCCP m/z = 347, 361, 375 & 389	MCCP m/z = 405, 409 SCCP m/z = 349, 363, 377 & 391	Lindane	No
2482	GC-ECNI-MSD	SCCP: 347, 361, 375, 389; MCCP: 403, 417	SCCP: 349, 363, 377, 391; MCCP: 405, 419	Lindane	Yes
2497	LC-MSMS				Yes
2558	GC-ECD			PCB209	No
2560	LC MSMS	For SCCP: 472.1>62.1 and 556.0>62.0 For MCCP: 500.1>62.1 and 536.1>62.1	n/a	n/a	No
2561					---
2563	GC-MS-NCI	SCCP: 347 | 361 | 375 | 389 MCCP: 403 | 417 | 431 | 445	SCCP: 349 | 363 | 377 | 3941 MCCP: 405 |419 | 433 | 447	Lindane	Yes
2590	GC-MS-NCI	SCCP: 347-361-375-389 MCCP: 403-417-431-445	SCCP: 349-363-377-391 MCCP: 405-419-433-447	No internal standard was used	Yes
2612	GC-MSD			Toulol-d8	Yes
2723	GC-MS	375 pour SCCP - 403 pour MCCP	327, 409 pour SCCP - 369, 453 pour MCCP	non	Yes
2737	GC-NCI	SCCP F347,361,377 ,389 GMCCP:403,41 7,431	SCCP:349,364,375,39 1 GMCCP:405,419,4 33	Hexachlorobenzene	Yes
2743	GCMS	102-67	91-53 / 102-65	no	No
2757	CADS v4:112015	347, 361, 375, 389	349, 362, 377, 391	Lindane	No
2762	GC-NCI-MS	MCCP - 369, 367, 371, 465, 467; SCCP - 327, 423		beta-HCH	Yes
2774	GC-MS-CI	312.9 - 514.9	312.9 - 514.9	no	Yes
3146					---
3150	GC/MS NCI	403, 417, 431, 445, 347, 361, 375, 389	405, 419, 433, 447, 349, 363, 377, 391	gamma-HCH	Yes
3151	GCMS	SCCP: 347/361/375/389 MCCP: 403/417/431/445	SCCP: 349/363/377/391 MCCP: 405/419/433/447	no	Yes
3153	GC-NCI-MS	347, 361, 375, 389	349, 363, 377, 391	Lindane	No
3154	GC-NCI	SCCP: 347 361 375 389	MCCP: 403 417 431 445		Yes
3163					---
3172	GC-NCI-MS	347-361-375-389-403-417	349-363-377-391-405-419	Lindane	Yes
3179	GC/MS-NCI	SCCP: 347, 361, 375, 389 - MCCP: 403, 417, 431, 445	SCCP: 349, 363, 377, 391 - MCCP: 405, 419, 433, 447	Lindane (CAS 58-89-9)	Yes
3190	GC-ECNI-MS	347, 361, 375, 389	349, 363, 377, 391	none	Yes
3197	TIC			1,2,3,5-Tetrachlorobenzene	Yes
3200					Yes
3209	GC-ECD+LC-MS/MS			No	No
3210	GC/NCI/MS	409 + 375 + 327 + 423		1,1,1,3,8,9 Hexachlorononane	No
3214	LC/MS/MS	SCCP: TIC(360/324, 374/68,Etc) ; MCCP:TIC(400/365, 402/367, Etc.)	SCCP: (360/324, 374/68,Etc) ; MCCP: (400/365, 402/367, Etc.)	PCB 209	No

APPENDIX 3

Number of participating laboratories per country

3 labs in	BANGLADESH
2 labs in	BELGIUM
1 lab in	BRAZIL
1 lab in	CZECH REPUBLIC
2 labs in	FRANCE
14 labs in	GERMANY
1 lab in	GUATEMALA
3 labs in	HONG KONG
2 labs in	INDIA
2 labs in	INDONESIA
4 labs in	ITALY
1 lab in	NETHERLANDS
1 lab in	NORWAY
15 labs in	P.R. of CHINA
1 lab in	PAKISTAN
1 lab in	SOUTH KOREA
2 labs in	SWITZERLAND
2 labs in	TAIWAN R.O.C.
4 labs in	TURKEY
1 lab in	VIETNAM
1 lab in	UNITED KINGDOM

APPENDIX 4

Abbreviations:

C = final test result after checking of first reported suspect test 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's outlier test
R(0.05) = straggler in Rosner's outlier test
n.a. = not applicable
n.d. = not detected
ex = test results excluded from the statistical evaluation

Literature:

1 iis Interlaboratory Studies, Protocol for the Organisation, Statistics & Evaluation, March 2017
2 ASTM E178:02
3 ASTM E1301:03
4 ISO 5725:86
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