Results of Proficiency Test
SCCP&MCCP content in Polymer
September 2015

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. In this first interlaboratory study organized in August 2015, 64 laboratories from 19 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 one plastic sample (approximately 3 gram), positive (artificially fortified) on MCCP and SCCP and was labelled #15076. Sample analyses for fit-for-use and homogeneity testing were subcontracted. 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/IEC17043:2010 (R007). This ensures strict adherence to protocols for sample preparation and statistical evaluation and 100% confidentially 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 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). This protocol is electronically available through the iis internet site 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

A batch of PVC artificially fortified to be positive on MCCP/SCCP was selected. The batch of approximately 5 kg of PVC mixture (55% PVC, 7% $CaCO_3$, 33% DOTP and 5% Ca-Zn stabilizer) was enriched with 25 gram of a MCCP/SCCP mixture. After homogenisation, 100 sub samples were prepared of approx. 3 gram each and labelled #15076. The homogeneity of the subsamples was checked by determination of SCCP content on a number of stratified randomly selected subsamples. The test results varied for SCCP between 1226 and 1397 mg/kg.
From the results of the homogeneity test, the relative, in between sample, standard deviation RSD_r was 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:

	SCCP in #15076
RSD_r (observed)	4.8%
reference method	Horwitz
0.3 x RSD_R (reference method)	4.9%

Table 1: relative repeatability standard deviation of SCCP content of the subsamples #15076

The calculated variation coefficient RSDr is in full agreement with the estimated target, calculated using the Horwitz equation. Therefore, homogeneity of the subsamples was assumed.

To each of the participating laboratories one sample (#15076) was sent on August 12, 2015.

2.5 ANALYSIS

The participants were requested to determine MCCP and SCCP content. It was explicitly requested to treat the sample as a routine sample 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 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 form to confirm receipt of the sample and a letter of instructions were added to the sample. The laboratories were requested to complete the tests within a time frame of one month.

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. 14]. 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 [ref. 12 & 13]. Also a normal Gauss curve was projected over the Kernel Density Graph for reference.

3.3 Z-SCORES

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

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

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

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

When a laboratory did use a test method with a reproducibility that is significantly different from the reproducibility of the reference test method used in this report, it is strongly advised to recalculate the z-score, while using the reproducibility of the actual test method used this in order to evaluate the fit-for-useness of the reported test result [ref. 15].

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. Three participants reported test results after the final reporting date and six other participants did not report any test results at all.
Finally, the 58 reporting laboratories reported 110 numerical results. Observed were 3 outlying results, which is 2.7%. 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 MCCP/SCCP in Polymer the ISO/DIS 18219 method [ref. 15] is considered to be the official test method. However the scope of this method is more for extractable SCCP and not for total SCCP content, see also the discussion in paragraph 4.3. Regretfully, for the determination of total MCCP/SCCP content in Polymers no official test method is available. Therefore, the target requirements in this study were estimated using the Horwitz equation (for n=9).

Furthermore, it was decided to use assigned consensus values for the MCCP and SCCP determination based on a sub set of test results to calculate the z(target), determined after exploring the effect of sample pre-treatment as reported by the participants. It appears that the amount of MCCP and SCCP determined is higher or increases and the variation between test results decreases when the samples were reduced by using THF as extraction solvent, see paragraphs 4.3 and 5 for more discussion.

One participant reported the presence of an extra peak on top of MCCP chromatogram. The extra peak present was correctly identified as Dioctyl Terephthalate (DOTP). This component was added during the preparation of the PVC sample material as plasticizer to a concentration of 33%M/M.

4.1 PERFORMANCE EVALUATION OF THE GROUP OF LABORATORIES

The calculated reproducibilities and the target reproducibilities derived from the literature standards, here Horwitz, and based on all received test results and THF only, are compared in the next table.

	unit	n	Average	2.8 * sd	R(Horwitz)
MCCP (All)	mg/kg	51	1871	2640	809
SCCP (All)	mg/kg	56	1053	2071	497
MCCP (THF only)	mg/kg	9	2064	1102	880
SCCP (THF only)	mg/kg	10	1658	1363	730

Table 2: performance overview for all and THF only received test results on samples #15076

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

4.2 EVALUATION PER COMPONENT

In this section the results are discussed per sample (see also discussion in 4, 4.3 and 5).

MCCP: This determination was problematic. No statistical outliers were observed after the exclusion of 43 test results (without the excluded test results the data set showed one statistical outlier). The observed reproducibility after rejection of the suspect data was not in agreement with the estimated reproducibility calculated using the Horwitz equation (n=9).

SCCP: This determination was problematic. No statistical outliers were observed after the exclusion of 48 test results (without the excluded test results the data set showed two statistical outliers). The observed reproducibility after rejection of the suspect data was not in agreement with the estimated reproducibility calculated using the Horwitz equation (n=9).

4.3 EVALUATION OF THE TEST METHODS USED

The majority of the participants (24) reported to have used the ISO/DIS18219 method, 15 participants reported to have used an ‘in house’ test method and 15 participants did not report the test method used. Another four participants reported to have used EPA3550C or 8082A methods. The reported details of the methods that were used by the participants are listed in appendix 2.

For MCCP, 20 participants and for SCCP, 21 participants reported to have used hexane as solvent and used ultrasonic at 60ºC for 1 hr as extraction method. Another, 7 (MCCP) and 9 (SCCP) participants reported to have used toluene instead of hexane as solvent but used the same extraction method. Nine (MCCP) and ten (SCCP) participants reported to have used THF as solvent.
Three participants reported to have used Soxhlet (or ASE) as extraction technique. These three laboratories found deviating results.

	Solvent	Unit	n	Average	st.dev.
MCCP	Hexane *)	mg/kg	20	1227	738
MCCP	Toluene *)	mg/kg	7	1824	795
MCCP	THF	mg/kg	9	2064	394
SCCP	Hexane *)	mg/kg	21	387	309
SCCP	Toluene *)	mg/kg	9	1055	506
SCCP	THF	mg/kg	10	1658	487

Table 3: observed differences between THF extraction and other extractions

*) Used Ultrasonic extraction at 60º for 1 hr

From table 3 it is clear that the type of solvent may have a significant effect on the MCCP and SCCP content found.
With THF the highest amount of CP was found. This was expected as the sample, a PVC polymer is complete soluble in THF and thus the maximum content of MCCP/SCCP will be found.
Also the use of toluene instead of hexane increased the average concentrations found for MCCP and SCCP, when using the same extraction technique, time and temperature.

When evaluating the grain size only, it is noticed that the majority of the participants (36) did not reduce the grain size of the sample and used a grain size “>1”mm. The other 19 participants reduced the initial grain size to either <1 mm or <0.5 mm, see the details in appendix 2.
The test results for MCCP and for SCCP of the laboratories that reduced the sample to fine powder (<1 or <0.5 mm) were significantly higher than the test results of the participants that did not reduce this sample (see also page 11 and 13).

	Grain size	Unit	n	Average	st.dev
MCCP	>1mm	mg/kg	32	1751	1031
MCCP	≤1mm	mg/kg	13	2009	866
MCCP	≤0.5mm	mg/kg	4	2034	456
SCCP	>1mm	mg/kg	35	933	697
SCCP	≤1mm	mg/kg	15	976	657
SCCP	≤0.5mm	mg/kg	4	1559	601

Table 4: observed differences between effect of grain size

From table 4 it is clear that the grain size reduction step may have a significant effect on the MCCP and SCCP content found, the smaller the grain size, the higher the test results. Also the uncertainty is getting smaller when a smaller grain size is used, even when less test results are available.

Furthermore the participants were requested to report the calibration solution used.
It appeared that almost all participants used the Dr. Ehrerstorfer calibration standards

	Calibration solvent	Unit	n	Average	st.dev
MCCP	52 % Chlorine	mg/kg	11	2026	1235
MCCP	55 % Chlorine	mg/kg	9	1544	1016
SCCP	55.5 % Chlorine	mg/kg	7	1085	730
SCCP	59 % Chlorine	mg/kg	20	900	799

Table 5: observed differences between Calibration solutions used

From results listed in table 5 it appears that the calibrations solution used has a significant effect on the MCCP and SCCP results found. When a calibration solvent with a smaller amount of Chlorine is used, the MCCP and SCCP concentrations reported are higher.
It is clear that the integration, the response and the choice of the characteristic ion-mass of MCCP and SCCP is of utmost importance [ref.16].

5 DISCUSSIONS

The final assigned value in sample #15076 is for SCCP 1658 mg/kg and for MCCP 2064 mg/kg. Thus the total concentration MCCP/SCCP in the sample will be approx. 3700 mg/kg. The concentration of the MCCP/SCCP mixture added to the PVC was approximately 5000 mg/kg. The total recovery is 75%, which is satisfactory. Regretfully, the actual ratio MCCP:SCCP in the added mixture is not known.

It is clear is that the majority of the participants is able to determine total MCCP and total SCCP in the polymer matrix, but a huge variation is found between participants. This variation is highly dependent on the chosen sample pre-treatment, extraction and quantification. Fortunately, the determination of MCCP and SCCP becomes more reproducible when sample pre-treatments are chosen which releases 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 a solvent. However it is important to realize what kind of determination is requested by the applicant. In case of a migration request the cutting or grinding may not be appropriate and the material should probably best be treated as received. In the case of a total content determination request the polymer matrix should be reduced to facilitate the release of MCCP and SCCP from the matrix.

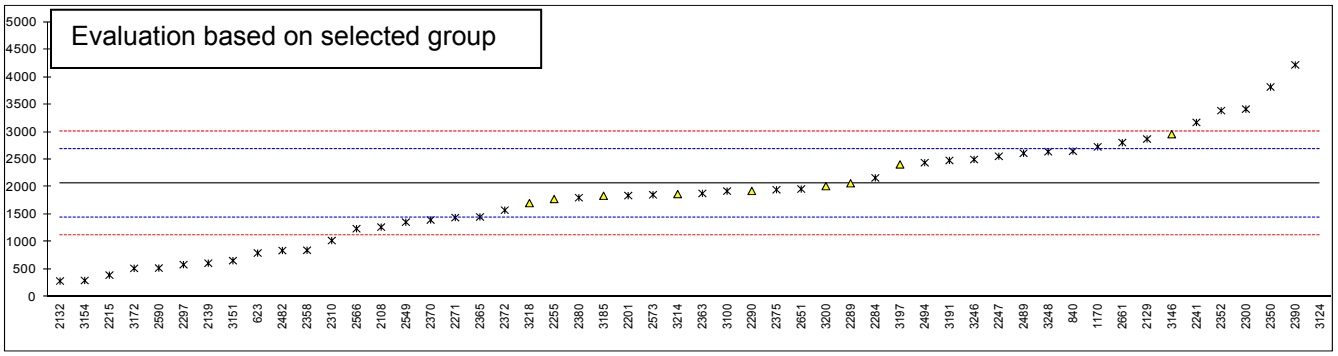
Each laboratory has to evaluate its performance in this study and make decisions about necessary corrective actions. Therefore, participation on a regular basis in this scheme could be helpful to improve the performance and the quality of the analytical results.

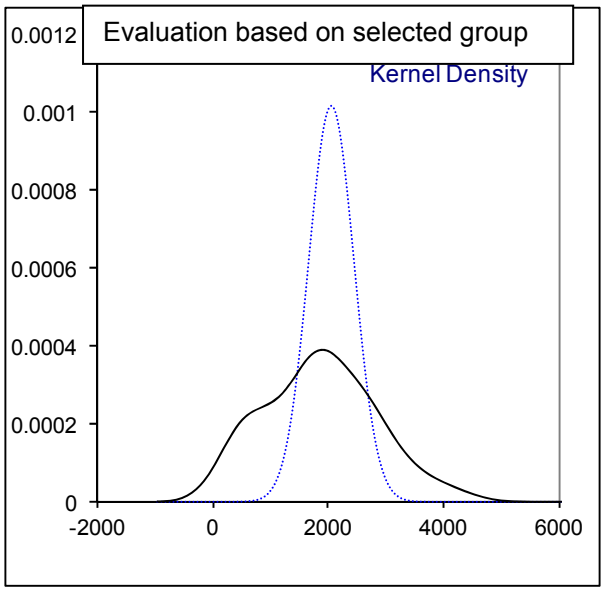
APPENDIX 1

Determination of MCCP on sample #15076; results in mg/kg

lab	method	value	mark	z(targ)	remarks
110		-----		-----	
623	ISO/DIS18219	798.69		-4.03	
840	EPA8082A	2651.2		1.87	
1170		2730.4		2.12	
2108	in house	1270		-2.53	
2115		-----		-----	
2129	ISO18219Mod.	2872		2.57	
2132	ISO18219	289		-5.65	
2139	ISO18219:12	614.42		-4.62	
2169		-----		-----	
2201		1843		-0.70	
2215		396.9		-5.31	
2237		-----		-----	
2241	in house	3173.4		3.53	
2247	in house	2558		1.57	
2255	in house	1780.9		-0.90	
2271		1444		-1.97	
2284	in house	2165.65		0.32	
2289		2067		0.01	
2290		1927.6		-0.44	
2297	ISO18219:14Mod.	588.2		-4.70	
2300	ISO/FDIS18219Mod.	3415.72		4.30	
2310	ISO/DIS18219:14	1025		-3.31	
2350	in house	3818.2		5.58	
2352	ISO/DIS18219:13	3388.37		4.22	
2358	ISO/DIS18219:14	849		-3.87	
2363	ISO/FDIS18219:15	1882.50		-0.58	
2365	ISO/FDIS18219:15	1455.5		-1.94	
2370	ISO18219	1400		-2.11	
2372	EPA3550C	1578		-1.55	
2375		1950.1		-0.36	
2380	ISO/DIS18219:14	1805		-0.83	
2386		-----		-----	
2390	EPA8082A	4220.216	C	6.86	First reported 5861.138
2410		-----		-----	
2482		844.24		-3.88	
2489	in house	2614		1.75	
2493		-----		-----	
2494	in house	2441.8	C	1.20	First reported 5167.9
2549	in house	1360		-2.24	
2563		-----		-----	
2566	ISO18219	1240.5		-2.62	
2573	ISO18219:15Mod.	1857.7		-0.66	
2590	ISO/FDIS18219:15	524.65		-4.90	
2651		1962.3		-0.32	
2661		2807	C	2.36	First reported 7807
2672		-----		-----	
3100	ISO/FDIS18219:14	1925		-0.44	
3124		8350		20.01	
3146	in house	2960		2.85	
3151	ISO/FDIS18219:15Mod	659.4		-4.47	
3154		300		-5.62	
3163		-----		-----	
3172	ISO18219:14	520		-4.92	
3185		1840		-0.71	
3191	in house	2482.7		1.33	
3197	ISO18219	2410		1.10	
3200	EPA3550C	2015.4		-0.16	
3210		-----		-----	
3214	IEC62321/ISO18219	1870.37		-0.62	
3218	in house	1707		-1.14	
3220		-----		-----	
3246	in house	2500		1.39	
3248		2641		1.84	

	Selection only THF		All reported results	
normality	not OK		OK	
n	9		51	
outliers	0		1	
mean (n)	2064.25		1871.39	
st.dev. (n)	393.505	RSD% = 19%	942.749	RSD% = 50%
R(calc.)	1101.81		2639.70	
R(Horwitz n=9)	879.51		809.20	





Separate evaluations:

Evaluation by Calibration solutions used:

	Calibration 52% Cl	Calibration 55% Cl
normality	OK	OK
n	11	9
outliers	0	0
mean (n)	2026.08	1544.32
st.dev. (n)	1235.179	1016.085
R(calc.)	3458.50	2845.04
R(Horwitz n=9)	865.67	687.36
RSD%	61%	66%

Evaluation by Solvent (ultrasonic extraction)

	Used hexane (60ºC/1hr)	Used Toluene (60ºC/1hr)	Used THF only
normality	OK	not OK	not OK
n	20	7	9
outliers	0	0	0
mean (n)	1226.86	1823.84	2064.25
st.dev. (n)	737.503	795.463	393.505
R(calc.)	2065.01	2227.30	1101.81
R(Horwitz n=9)	565.31	791.70	879.51
RSD%	60%	44%	19%

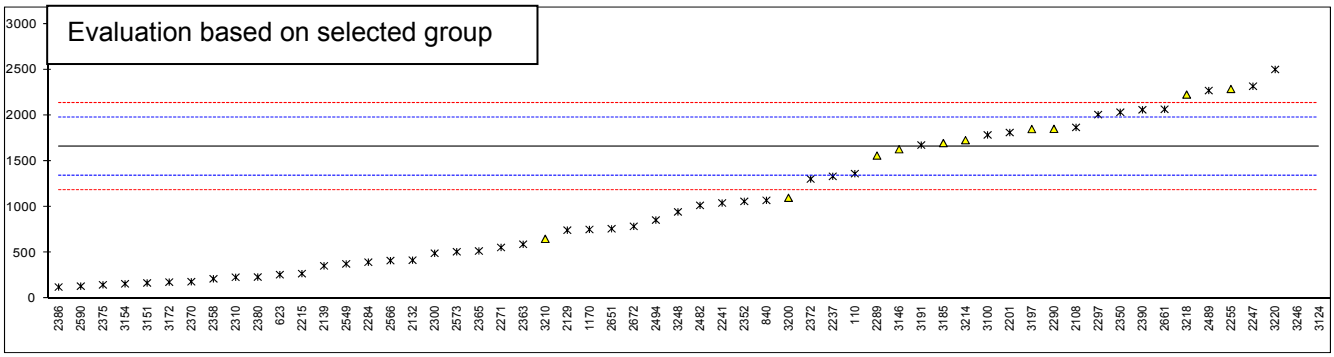
Evaluation by Particle size

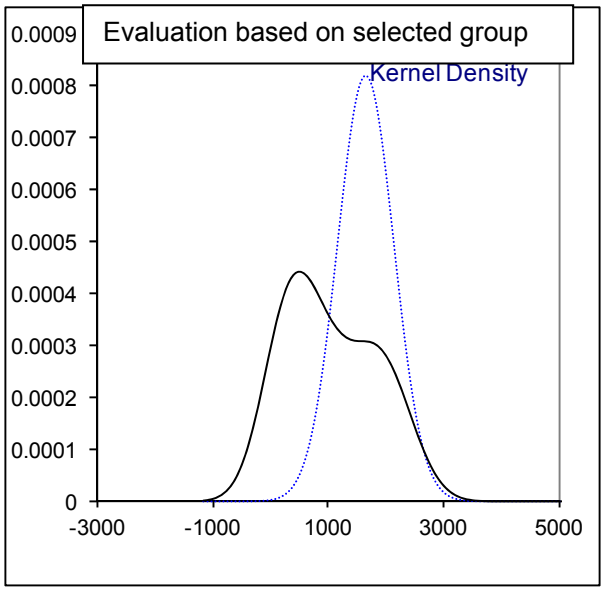
	Only >1 mm	Only ≤1 mm	Only ≤0.5 mm
normality	OK	OK	n.a.
n	32	13	4
outliers	1	0	n.a.
mean (n)	1750.57	2008.78	2034.20
st.dev. (n)	1031.302	866.201	455.537
R(calc.)	2887.65	2425.36	1275.50
R(Horwitz n=9)	764.60	859.39	868.62
RSD%	60%	43%	22%

Determination of SCCP on sample #15076; results in mg/kg

lab	method	value	mark	z(targ)	remarks
110		1363.3273		-1.13	
623	ISO/DIS18219	261.07		-5.36	
840	EPA8082A	1072.3		-2.25	
1170		754.3		-3.47	
2108	in house	1868		0.80	
2115		-----		-----	
2129	ISO18219Mod.	746.5		-3.50	
2132	ISO18219	419		-4.75	
2139	ISO18219:12	357.19		-4.99	
2169		-----		-----	
2201		1812		0.59	
2215		272.2		-5.31	
2237	in house	1334.38		-1.24	
2241	in house	1043.0		-2.36	
2247	in house	2317		2.53	
2255	in house	2287.3		2.41	
2271		558		-4.22	
2284	in house	397.33		-4.84	
2289		1561		-0.37	
2290		1851.7		0.74	
2297	ISO18219:14Mod.	2007		1.34	
2300	ISO/FDIS18219Mod.	494.77		-4.46	
2310	ISO/DIS18219:14	233		-5.47	
2350	in house	2033.5		1.44	
2352	ISO/DIS18219:13	1060.96		-2.29	
2358	ISO/DIS18219:14	216		-5.53	
2363	ISO/FDIS18219:15	592.60		-4.09	
2365	ISO/FDIS18219:15	519.5		-4.37	
2370	ISO18219	184		-5.65	
2372	EPA3550C	1305		-1.35	
2375		150.4		-5.78	
2380	ISO/DIS18219:14	235		-5.46	
2386	ISO18219	126		-5.88	
2390	EPA8082A	2060.190		1.54	
2410		-----		-----	
2482		1016.74		-2.46	
2489	in house	2270		2.35	
2493		-----		-----	
2494	in house	856.9		-3.07	
2549	in house	379		-4.91	
2563		-----		-----	
2566	ISO18219	414.2		-4.77	
2573	ISO18219:15Mod.	510.9		-4.40	
2590	ISO/FDIS18219:15	135.42		-5.84	
2651		762.1		-3.44	
2661		2066		1.56	
2672	ISO18219:15.	788.0		-3.34	
3100	ISO/FDIS18219:14	1786		0.49	
3124		20650		72.82	
3146	in house	1630		-0.11	
3151	ISO/FDIS18219:15Mod	170.5		-5.70	
3154		161		-5.74	
3163		-----		-----	
3172	ISO18219:14	180		-5.67	
3185		1697		0.15	
3191	in house	1675.3		0.07	
3197	ISO18219	1850		0.73	
3200	EPA3550C	1099.7		-2.14	
3210	ISO18219	651.85		-3.86	
3214	IEC62321/ISO18219	1728.89		0.27	
3218	in house	2226		2.18	
3220	in house	2500		3.23	
3246	in house	12000		39.65	
3248		946		-2.73	

	Selection only THF			All reported results	
normality	suspect			OK	
n	10			56	
outliers	0			2	
mean (n)	1658.34			1053.48	
st.dev. (n)	486.918	RSD%=	29%	739.638	RSD% = 70%
R(calc.)	1363.37			2070.99	
R(Horwitz n=9)	730.24			496.68	





Separate evaluations:

Evaluation by Calibration solutions used:

	Calibration 55.5% CI	Calibration 59% CI
normality	OK	OK
n	7	20
outliers	0	0
mean (n)	1085.47	900.31
st.dev. (n)	729.571	799.267
R(calc.)	2042.80	2237.95
R(Horwitz n=9)	509.46	434.62
RSD%	67%	89%

Evaluation by Solvent (ultrasonic extraction)

	Used hexane (60ºC/1hr)	Used Toluene (60ºC/1hr)	Used THF only
normality	not OK	OK	suspect
n	21	9	10
outliers	0	0	0
mean (n)	387.25	1055.24	1658.34
st.dev. (n)	309.281	505.968	486.918
R(calc.)	865.99	1416.71	1363.37
R(Horwitz n=9)	212.26	497.38	730.24
RSD%	80%	48%	29%

Evaluation by Particle size

	Only >1 mm	Only ≤1 mm	Only ≤0.5 mm
normality	OK	OK	not OK
n	35	15	4
outliers	1	1	0
mean (n)	932.95	976.45	1559.47
st.dev. (n)	696.591	657.126	601.949
R(calc.)	1950.45	1839.95	1685.46
R(Horwitz n=9)	447.97	465.65	693.08
RSD%	75%	67%	39%

APPENDIX 2
Analytical details

lab	Was granulate reduced?	reduced to maximum particle size	Particle size checked	Technique for release used	Extraction solvent used	Extraction time and temperature used
110	No	---	---	Ultrasonic	DCM: Hexane	50 ºC
623	Cut	>1 mm	By capiler	Ultrasonic	Hexane	60 °C for 1 hr
840	Cut	>1 mm	---	Ultrasonic	Hexane:Acetone 1:1	50 ºC
1170	Milled (cryo)	---	not checked	ASE	Dichloromethane	1 hour ,150 ºC
2108	No	>1 mm	---	Soxhlet	Hexane	---
2115	---	---	---	---	---	---
2129	No	---	---	Ultrasonic	Dichloromethane	30 min / room temperature
2132	Cut	=<1mm	---	Ultrasonic	Hexane	60 ºC, 1 hr
2139	No	>1 mm	vernier calipers	Ultrasonic	Hexane	1h /, 60 ºC
2169	---	---	---	---	---	---
2201	Grinded	---	1mm sieve	Ultrasonic	Toluene and DCM	60℃ for 1h.
2215	No	>1 mm	by ruler	Ultrasonic	Hexane	60min at 60 ℃
2237	Milled (cryo)	=<1 mm	---	Ultrasonic	DMF, Toluene	60 Min, room temperature
2241	Cut	>1 mm	2mm-3mm	Ultrasonic	Acetone: Hexane	30min at 50 ºC
2247	---	---	---	---	---	---
2255	Cut	=<1 mm	---	Ultrasonic	THF and acetonitirle	30 min at 70ºC
2271	Cut	=<1 mm	---	Ultrasonic	Toluene	60 min 60 ºC
2284	No	>1 mm	---	Ultrasonic	Hexane	60 minutes; 60 ºC
2289	Cut	>1 mm	2*2mm	Ultrasonic	THF and acetonitrile	70 ºC for 60min
2290	Cut	=<1 mm	---	Ultrasonic	THF	30min, 70oC
2297	Cut	>1 mm	---	Ultrasonic	Dichloromethane	at Room temperature for 30mins
2300	Cut	=<1 mm	scale/ruler	Ultrasonic	Dichloromethane	30 min
2310	Cut	=<1 mm	Vernier caliper	Ultrasonic	Hexane	1hr & 60± 2ºC
2350	No	>1 mm	---	Ultrasonic	Hexane:acetone (1:1)	Sonicate at 50 ºC for 30 min
2352	Cut	=<1 mm	---	Ultrasonic	Toluene	60 ºC 60min
2358	Cut	Other	2*2mm	Ultrasonic	Hexane	60 minutes at 60 ºC
2363	Cut	>1 mm	---	Ultrasonic	Hexane	60 minutes at 60 ºC
2365	Cut	Other	2*2*2mm	Ultrasonic	Hexane	60min 60 ºC
2370	Cut	>1 mm	by ruler	Ultrasonic	Hexane	60 ºC /1hr
2372	Milled (cryo)	=< 0.5 mm	Visual	Ultrasonic	Hexane	60 ºC /1hr
2375	Cut	=<1 mm	---	Ultrasonic	Hexane	60 mins, 60 ºC
2380	No	---	---	Ultrasonic	Hexane	60 mins, 60 ºC
2386	No	---	---	Ultrasonic	Hexane	1h 60°C
2390	Cut	>1 mm	Vernier Caliper	Ultrasonic	Hexane and Acetone	30 mins and 50 ºC
2410	---	---	---	---	---	---
2482	No	---	---	Ultrasonic	Toluene	1 hour and 60 °C
2489	---	---	---	---	---	---
2493	---	---	---	---	---	---
2494	Cut	=< 0.5 mm	---	Ultrasonic	Hexane	1 hour at 60 ºC
2549	Cut	>1 mm	by ruler	Ultrasonic	Toluene	60°C for 1 hr + 60°C for 60min
2563	---	---	---	---	---	---
2566	No	---	---	Ultrasonic	Hexane	60C and 60min
2573	Cut	=<1 mm	sifting	Ultrasonic	Dichloromethane	30min room temperature
2590	No	---	---	Ultrasonic	Hexane	60 C for 60 minutes
2651	Cut	=<1 mm	---	Ultrasonic	Toluene	60min /room temperature
2661	Milled (cryo)	>1 mm	---	Soxhlet	Dichloromethane	1h at 150 degrees
2672	Milled (cryo)	=<1 mm	visual	Ultrasonic	Toluene	1 h / 60 °C
3100	Cut	>1 mm	2*2mm	Ultrasonic	Toluene	1 h / 70 ºC
3124	Cut	>1 mm	---	Ultrasonic	Hexane	---
3146	Cut	>1 mm	measured	Ultrasonic	THF	30 mIn 70 °C
3151	No	---	3*3mm	Ultrasonic	Hexane	60°C 1 hour
3154	No	>1 mm	---	Ultrasonic	Hexane	60 min / 60°C
3163	---	---	---	---	---	---
3172	Cut	>1 mm	2*2mm	Ultrasonic	Hexane	60min - 60°C
3185	Cut	>1 mm	---	Ultrasonic	THF and Acetonitrile	1hour 60 ºC
3191	No	>1 mm	by ruler	Microwave	DCM, Acetone	30min, 100 ºC
3197	Cut	=<0.5 mm	a 0.5 mm sieve	Ultrasonic	THF and Acrylonitrile	30 min, 70°C
3200	No	---	---	Mechanical Shaking	THF and Acetonitrile	room temperature hour
3210	No	>1 mm	---	Ultrasonic	THF/Hexane	30 minutes at 50°C
3214	Cut	>1 mm	---	See note	THF and Acetonitrile	30 min at 70 ºC Twice
3218	No	=< 0.5 mm	---	Ultrasonic	THF and Acetonitrile	30 min for each solvent at 70ºC
3220	---	---	---	---	---	---
3246	Cut	=<1mm	---	Ultrasonic	Hexane	2 hours, 70°C
3248	Cut	>1 mm	---	Ultrasonic	Hexane	60mins, 60oC

Note: Mechanical Shaking / Thermal Desorption / Ultrasonic

Calibration solutions used

		MCCP			SCCP		
Lab	Manufacturer	% Chloride	Lot nr.1	Lot nr.2	% Chloride	Lot nr.1	Lot nr.2
110	--	--	--	--	--	--	--
623	Dr Ehrerstorfer	--	--	--	59%	X23105500CY (55.5%)	X23106300CY (63%)
840	--	--	--	--	--	--	--
1170	Dr Ehrerstorfer	57%	X23145700CY (57%)	--	55.5%	X23105500CY (55.5%)	--
2108	--	--	--	--	--	--	--
2115	--	--	--	--	--	--	--
2129	Dr Ehrerstorfer	55%	X23145700CY (57%)	X23145200CY (52%)	59%	X23105500CY (55.5%)	X23106300CY (63%)
2132	--	--	--	--	--	--	--
2139	Dr Ehrerstorfer	52%	--	X23145200CY (52%)	55.5%	X23105500CY (55.5%)	--
2169	--	--	--	--	--	--	--
2201	--	--	--	--	--	--	--
2215	Dr Ehrerstorfer	55%	X23145700CY (57%)	X23145200CY (52%)	59%	X23105500CY (55.5%)	X23106300CY (63%)
2237	Dr Ehrerstorfer	--	--	--	57.3%	X23105500CY (55.5%)	X23106300CY (63%)
2241	Dr Ehrerstorfer	52%	--	X23145200CY (52%)	55.5%	Lot 30711	--
2247	Dr Ehrerstorfer	--	--	--	59%	--	--
2255	--	--	--	--	--	--	--
2271	Dr Ehrerstorfer	--	--	--	59%	X23105500CY (55.5%)	X23106300CY (63%)
2284	Dr Ehrerstorfer	52%	--	X23145200CY (52%)	59%	X23105500CY (55.5%)	X23106300CY (63%)
2289	--	--	--	--	--	--	--
2290	Dr Ehrerstorfer	55%	X23145700CY (57%)	X23145200CY (52%)	59%	Lot 40701CY (55.5%)	Lot 40702CY (63%)
2297	Dr Ehrerstorfer	55%	X23145700CY (57%)	X23145200CY (52%)	59%	X23105500CY (55.5%)	X23106300CY (63%)
2300	--	--	--	--	--	--	--
2310	Dr Ehrerstorfer	52%	--	X23145200CY (52%)	59%	X23105500CY (55.5%)	X23106300CY (63%)
2350	Dr Ehrerstorfer	52%	--	X23145200CY (52%)	55.5%	X23105500CY (55.5%)	--
2352	Dr. Ehrerstorfer	42%	21105CY	--	55.5%	50716CY	--
2358	--	--	--	--	--	--	--
2363	--	--	--	--	--	--	--
2365	--	--	--	--	--	--	--
2370	Dr Ehrerstorfer	52%	--	X23145200CY (52%)	59%	X23105500CY (55.5%)	X23106300CY (63%)
2372	Dr Ehrerstorfer	52%	--	X23145200CY (52%)	59%	X23105500CY (55.5%)	X23106300CY (63%)
2375	--	--	--	--	--	--	--
2380	Dr Ehrerstorfer	52%	--	X23145200CY (52%)	59%	X23105500CY (55.5%)	X23106300CY (63%)
2386	Dr Ehrerstorfer	--	--	--	59%	X23105500CY (55.5%)	X23106300CY (63%)
2390	Dr Ehrerstorfer	52%	--	X23145200CY (52%)	55.5%	X23105500CY (55.5%)	--
2410	--	--	--	--	--	--	--
2482	Dr Ehrerstorfer	55%	X23145700CY (57%)	X23145200CY (52%)	59%	X23105500CY (55.5%)	X23106300CY (63%)
2489	Dr Ehrerstorfer	--	--	--	59%	--	--
2493	--	--	--	--	--	--	--
2494	--	--	--	--	--	--	--
2549	--	--	--	--	--	--	--
2563	--	--	--	--	--	--	--
2566	Dr Ehrerstorfer	55%	X23145700CY (57%)	X23145200CY (52%)	59%	X23105500CY (55.5%)	X23106300CY (63%)
2573	Dr Ehrerstorfer	--	--	--	55.5%	X23105500CY (55.5%)	--
2590	Dr Ehrerstorfer	52%	--	X23145200CY (52%)	55.5%	X23105500CY (55.5%)	--
2651	Dr Ehrerstorfer	52%	--	X23145200CY (52%)	51.5%	--	--
2661	--	--	--	--	--	--	--
2672	--	--	--	--	--	--	--
3100	--	--	--	--	--	--	--
3124	--	--	--	--	--	--	--
3146	Dr Ehrerstorfer	55%	X23145700CY (57%)	X23145200CY (52%)	59%	X23105500CY (55.5%)	X23106300CY (63%)
3151	Dr Ehrerstorfer	55%	X23145700CY (57%)	X23145200CY (52%)	59%	X23105500CY (55.5%)	X23106300CY (63%)
3154	LGC std.	54.5%	--	--	59%	--	--
3163	--	--	--	--	--	--	--
3172	--	--	--	--	--	--	--
3185	--	--	--	--	--	--	--
3191	--	--	--	--	--	--	--
3197	Dr Ehrerstorfer	55%	X23145700CY (57%)	X23145200CY (52%)	59%	X23105500CY (55.5%)	X23106300CY (63%)
3200	--	--	--	--	--	--	--
3210	--	--	--	--	--	--	--
3214	--	--	--	--	--	--	--
3218	--	--	--	--	--	--	--
3220	--	--	--	--	--	--	--
3246	--	--	--	--	--	--	--
3248	--	--	--	--	--	--	--

APPENDIX 3

Number of participating laboratories per country

2 labs in	BANGLADESH
1 lab in	DENMARK
1 lab in	FRANCE
10 labs in	GERMANY
4 labs in	HONG KONG
1 lab in	HUNGARY
7 labs in	INDIA
2 labs in	INDONESIA
3 labs in	ITALY
1 lab in	JAPAN
3 labs in	KOREA
2 labs in	NORWAY
16 labs in	P.R. of CHINA
1 lab in	PAKISTAN
3 labs in	TAIWAN R.O.C.
1 lab in	THE NETHERLANDS
2 labs in	TURKEY
1 lab in	U.S.A.
3 labs in	VIETNAM

APPENDIX 4

Abbreviations:

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

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