Results of Proficiency Test
SCCP & MCCP in Polymer
May 2018

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). Since 2017, SCCP is banned under the Stockholm Convention on Persistent Organic Pollutants (annex A).

Since 2015, the Institute for Interlaboratory Studies (iis) organizes a proficiency scheme for the determination of MCCP/SCCP content in polymers. During the annual proficiency testing program 2017/2018 it was decided to continue the proficiency test for the analysis of MCCP/SCCP in polymers. In this interlaboratory study 71 laboratories from 19 different countries registered for participation (see appendix 3).
In this report, the results of the 2018 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, one artificially fortified with MCCP and SCCP, the other sample was a real life sample (light tube) positive on 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/IEC17043:2010. 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 a regular basis by sending out 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 is electronically available through 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 were selected. The first batch contained solid green PVC square pieces (approx 2x4x4mm, 45 mg on average each), artificially fortified with a commercial mixture of SCCP and MCCP, labelled #18570. The second batch was a real life sample (light tube) (approx 2 cm, 3 g on average each), labelled #18571.
After homogenisation, both materials were divided over plastic bags, approx. 3 grams for each sample. The homogeneities of the subsamples #18570 and #18571 were checked by determination of the SCCP content on resp. 8 and 7 stratified randomly selected subsamples.

	SCCP in mg/kg sample #18570	SCCP in mg/kg sample #18571
Sample -1	2887	38394
Sample -2	2662	37550
Sample -3	2586	38039
Sample -4	2821	39373
Sample -5	2640	38813
Sample -6	2877	38263
Sample -7	2807	39061
Sample -8	2760	--

Table 1: homogeneity test results of the subsamples #18570 and #18571

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 Sample #18570	SCCP in mg/kg Sample #18571
r (observed)	317	1755
reference method	Horwitz (n=9)	Horwitz (n=9)
0.3 x R (reference method)	337	3168

Table 2: evaluation of repeatability of SCCP contents of the subsamples #18570 and #18571

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 (n=9), the homogeneities of subsamples #18570 and #18571 were assumed.

To each of the participating laboratories one sample #18570 and one sample #18571 was sent on April 18, 2018.

2.5 ANALYSES

The participants were requested to determine on both samples the 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. Extra instruction was given about sample #18571 in the letter of instructions.

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, 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. In this PT the criterion of ISO13528, paragraph 9.2.1 was met for all evaluated tests, therefore, the uncertainty of all assigned values may be negligible and need not be included in the PT report.

Finally, the reproducibilities were calculated from the standard deviations by multiplying them with a factor of 2.8.

3.2 GRAPHICS

In order to visualize 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, some problems were encountered. Five participants decided not to report any test results and five other participants reported test results after the final reporting date.
Finally, the 66 reporting laboratories reported 216 numerical results. In the reported test results 8 statistical outliers were observed, which is 3.6%. 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.

4.1 EVALUATION PER SAMPLE AND PER COMPONENT

In this section, the results are discussed per sample and per component.

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 based on nine components (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 5 for more discussion. Therefore, based on the analytical details reported by the participants, samples where Hexane (or Pentane) was used as solvent were excluded from statistical calculations (and participants that did not report any details). Almost all reporting participants mentioned to cut the sample further into smaller pieces. Therefore, it was decided not to exclude the test results based on this analytical detail as in previous reports.

Sample #18570:

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

MCCP: This determination may be problematic. One statistical outlier was observed and eleven 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 #18571:

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

MCCP: This determination may be very problematic. Two statistical outliers were observed and ten test results were excluded from the statistical evaluations. The observed reproducibility after rejection of the suspect data is not at all 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 (n=9) 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 next tables.

component	unit	n	average	2.8 * sd	R(Horwitz)
SCCP	mg/kg	40	1755	660	766
MCCP	mg/kg	33	4064	2041	1564

Table 3: performance overview on samples #18570

component	unit	n	average	2.8 * sd	R(Horwitz)
SCCP	mg/kg	42	31298	24395	8857
MCCP	mg/kg	32	85329	43617	20763

Table 4: performance overview on samples #18571

Without further statistical calculations, it can be concluded that there is for sample #18570 a good compliance of the group of participating laboratories for the SCCP determination with the target reproducibility. Regretfully, for sample #18571 there is not a compliance with the target reproducibilities.

4.3 COMPARISON OF THE PROFICIENCY TEST OF MAY 2018 WITH PREVIOUS PTS

	May 2018	*May 2017*	*May 2016*	*May 2015*
Number of reporting labs	66	55	51	58
Number of results reported	216	198	184	110
Statistical outliers	8	10	4	3
Percentage outliers	3.6%	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 2018*	*May 2017*	*April 2016*	*April 2015*	*Target*
SCCP	13-28%	15-23%	23-33%	29%	16-18%
MCCP	18%	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 in comparison with previous years.

4.4 EVALUATION OF THE ANALYTICAL DETAILS

About half of the participants (41 = 58%) reported to have used ISO/DIS18219 as test method and 22 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.

Based on the answers given by the participants the following can be summarized:
Forty-three of the participants reported to have an ISO/IEC17025 accreditation for the determination of total MCCP/SCCP in polymers (= 58%).
Almost all participants cut both samples prior to analysis. The final estimated sample size reported was most often between 2mm x 2mm and 3mm x 3mm for both samples.
Almost all participants used a sample intake between 0.5 and 1.0 grams for both samples. Six of the reporting participants mentioned to have used <0.5 grams. Which is remarkable as in the letter of instruction it is advised not to use less than 0.5 grams per determination for homogeneity reasons.

It appeared that different solvents or mixtures to release/extract the MCCP/SCCP are reported. About 24% of the participants used Hexane to release/extract the components. Toluene was used by 38% of the participants and about 14% of the participants used THF/ACN as release/extraction solvent.
Almost all participants used an extraction time of 60 minutes and an extraction temperature of 60°C.

5 DISCUSSION

ISO/DIS18219 mentions some essential steps to follow in order to get reproducible test results. One of these is about the sample pre-treatment (e.g. further grinding, cutting to reduce the sample size). Therefore, it is remarkable that 11 of the 29 laboratories reported to have used ISO/DIS18219 but did not cut or grind the samples further and tested the samples as received.
In earlier PTs on the determination of SCCP and MCCP (iis15P05 in 2015 and iis16P06 in 2016), it was concluded that the ultrasonic extraction with n-Hexane at 60°C during 60 min. (the conditions as per ISO/DIS18219) gives lower recoveries of SCCP/MCCP.
The effect of different extraction solvents was investigated for the determination of SCCP in this PT, see table 7. Again, it is observed that for sample #18571 n-Hexane yields a lower concentration for SCCP on average than with Toluene or THF. Furthermore, it is observed that the variation in the group of n-Hexane users is much larger. For sample #18570 the effect on the average was less profound. This can be explained that the reproducibility of the whole group was already in agreement with the target reproducibility. However, the variation was still lower in the group of Toluene or THF users.

sample	solvent	n	average in mg/kg	st.dev in mg/kg	RSD%
#18570	n-Hexane	10	1635	679	42%
#18570	Toluene	30	1781	253	14%
#18570	THF	9	1621	200	12%
#18571	n-Hexane	10	21907	17651	80%
#18571	Toluene	32	32092	9622	30%
#18571	THF	8	27049	1448	5%

Table 7: effect of extraction solvent on the determination of SCCP

Sample #18570 was used earlier as PT sample #16570 in iis16P06 (2016). In PT iis16P06, the determination of SCCP in sample #16570 was problematic and 17 test results (Hexane was used as solvent and the sample was not cut into smaller parts) were excluded from the statistical evaluation to obtain a better estimate for the consensus value. In the 2018 PT, as explained in paragraph 4, only the test results of laboratories were excluded that have reported to use Hexane (or Pentane) as solvent or did not report an extraction solvent. In table 8 a comparison is given over the two proficiency tests. It was observed that the reproducibility (R(calc)) has significantly improved in 2018. Also, the recovery of SCCP/MCCP improved on average.

	Sample #18570				Sample #16570			
	unit	n	average	R(calc)	unit	n	average	R(calc)
SCCP	mg/kg	40	1755	660	mg/kg	32	1666	1535
MCCP	mg/kg	33	4064	2041	mg/kg	28	3323	3611

Table 8: comparison of sample #18570 with #16570

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 still be 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 and/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.

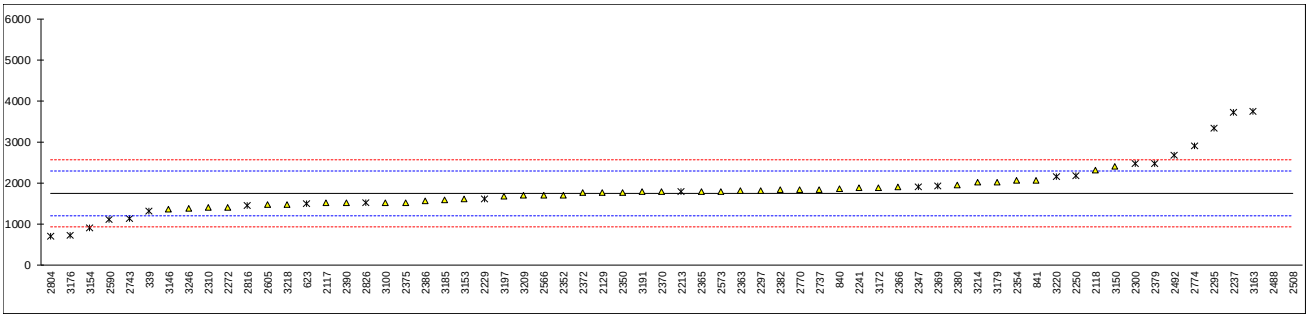
APPENDIX 1

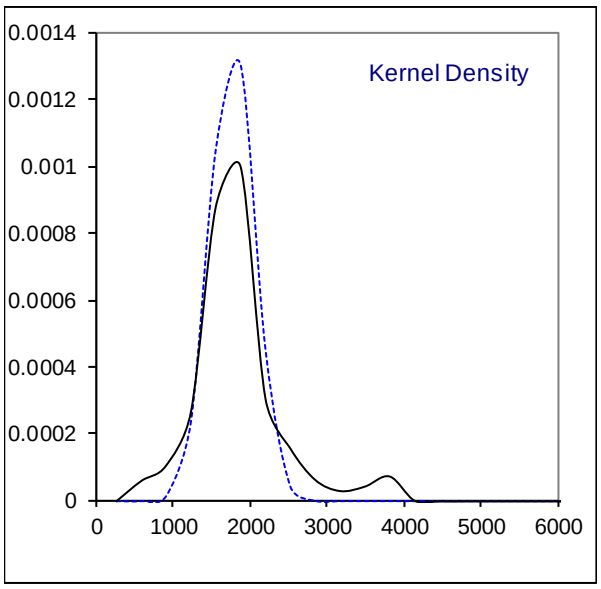
Determination of SCCP on sample #18570; results in mg/kg

lab	method	value	mark	z(targ)	remarks
339	In house	1310	ex	-1.63	
623	ISO/DIS18219	1496.67	ex	-0.94	
840	ISO/DIS18219	1870		0.42	
841	ISO/DIS18219	2066.542		1.14	
2117	ISO/DIS18219	1513.5		-0.88	
2118	ISO/DIS18219	2307.54		2.02	
2129	ISO/DIS18219	1764		0.03	
2213	ISO/DIS18219	1790	ex	0.13	
2229	In house	1618.615	C,ex	-0.50	First reported 3544.554
2237	In house	3725	R(0.01)	7.20	
2241	ISO/DIS18219	1892.4		0.50	
2250	In house	2178	ex	1.55	
2255		-----		-----	
2266	ISO/DIS18219	< 100		<-6.05	False negative test result?
2272	ISO/DIS18219	1419.7		-1.23	
2293	ISO/DIS18219	Detected		-----	
2295	ISO/DIS18219	3332	R(0.01)	5.76	
2297	ISO/DIS18219	1828.84		0.27	
2300	CADS V8 2017	2464.4	ex	2.59	
2310	ISO/DIS18219	1412		-1.25	
2347	ISO/DIS18219	1912	ex	0.57	
2350	ISO/DIS18219	1772.011		0.06	
2352	In house	1709.2		-0.17	
2354	ISO/DIS18219	2056.139		1.10	
2363	ISO/DIS18219	1813		0.21	
2365	ISO/DIS18219	1800.8		0.17	
2366	ISO/DIS18219	1907.3		0.56	
2369	ISO/DIS18219	1938	ex	0.67	
2370	ISO/DIS18219	1785		0.11	
2372	ISO/DIS18219	1763.3		0.03	
2375	ISO/DIS18219	1530		-0.82	
2379	INH-209	2475.4	ex	2.63	
2380	ISO/DIS18219	1950.277		0.71	
2382	ISO/DIS18219	1831.2		0.28	
2386	ISO/DIS18219	1569		-0.68	
2390	ISO/DIS18219	1515.3		-0.88	
2488		20578.2	ex	68.78	
2492	In house	2670	C,ex	3.34	First reported 0.267
2495		-----		-----	
2508	ISO/DIS18219	82212.81	ex	293.99	
2566	ISO/DIS18219	1700.77		-0.20	
2573	ISO/DIS18219	1805.23		0.18	
2590	ISO/DIS18219	1112.97	ex	-2.35	
2605	ISO/DIS18219	1477.4		-1.01	
2612		-----		-----	
2737	In house	1835.35		0.29	
2743	ISO/DIS18219	1133.743	ex	-2.27	
2770	In house	1834		0.29	
2774	In house	2902	R(0.05)	4.19	
2788		-----		-----	
2804	In house	697.62	ex	-3.86	
2816	In house	1457.918	ex	-1.09	
2826	In house	1517	ex	-0.87	
3100	In house	1525.029		-0.84	
3146	In house	1367		-1.42	
3150	ISO/DIS18219	2399		2.35	
3153	In house	1609		-0.53	
3154	ISO/DIS18219	903.170	ex	-3.11	
3163		3750	R(0.01)	7.29	
3172	ISO/DIS18219	1896		0.51	
3176	ISO/DIS18219	721.00	ex	-3.78	
3179	ISO/DIS18219	2019.0		0.96	
3185	ISO/DIS18219	1585.84		-0.62	
3191	In house	1784.32		0.11	
3197	In house	1689.2		-0.24	
3209	In house	1700.01		-0.20	
3210		-----		-----	
3214	ISO/DIS18219	2016.9		0.96	
3218	In house	1486.667		-0.98	
3220	In house	2163.665	ex	1.49	
3246	In house	1397		-1.31	

			All test results	
normality	OK		suspect	
n	40		59	
outliers	4 (+20 excl)		5	
mean (n)	1755.12		1740.12	
st.dev. (n)	235.752	RSD=13%	412.606	RSD = 24%
R(calc.)	660.10		1155.30	
st.dev.(Horwitz n=9)	273.672		271.684	
R(Horwitz n=9)	766.28		760.72	

ex = test results were excluded as Hexane (or Pentane) was used as solvent or did not report any analytical details, see also chapter 4 and previous PT reports of iis17P05 and iis16P06.



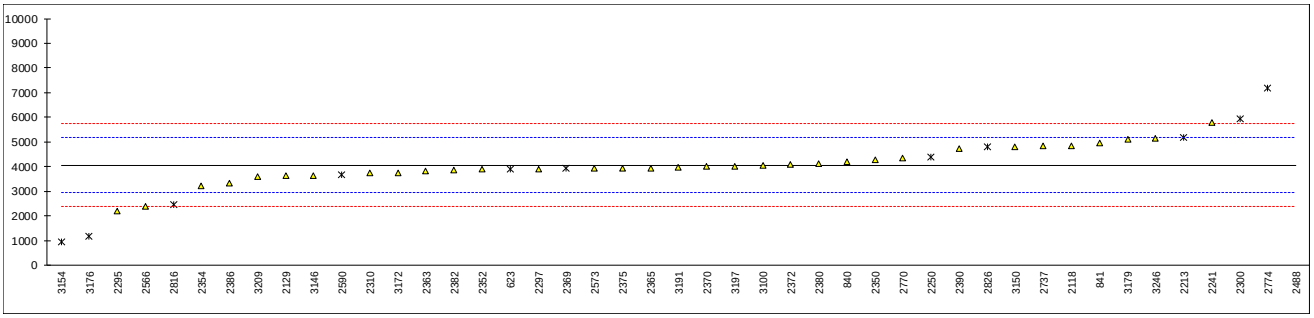


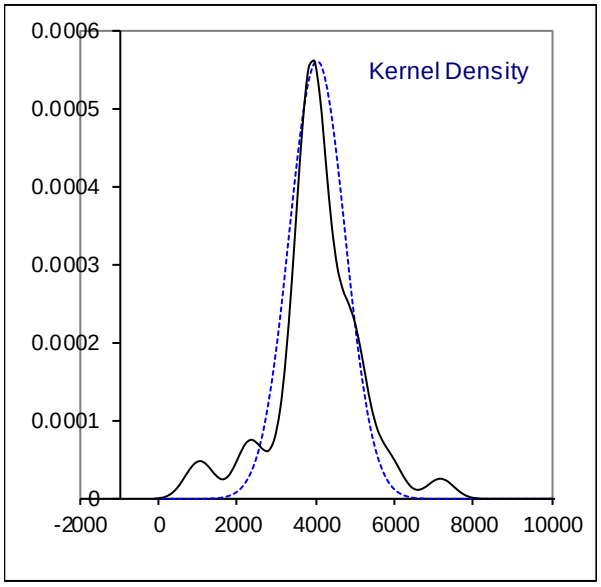
Determination of MCCP on sample #18570; results in mg/kg

lab	method	value	mark	z(targ)	remarks
339		-----		-----	
623	ISO/DIS18219	3896.35	ex	-0.30	
840	ISO/DIS18219	4200		0.24	
841	ISO/DIS18219	4972.970		1.63	
2117		-----		-----	
2118	ISO/DIS18219	4857.80	C	1.42	First reported 7626.08
2129	ISO/DIS18219	3630		-0.78	
2213	ISO/DIS18219	5188	ex	2.01	
2229		-----		-----	
2237		-----		-----	
2241	ISO/DIS18219	5784.0		3.08	
2250	In house	4399	ex	0.60	
2255		-----		-----	
2266	ISO/DIS18219	< 100		<-7.10	False negative test result?
2272		-----		-----	
2293	ISO/DIS18219	Detected		-----	
2295	ISO/DIS18219	2205		-3.33	
2297	ISO/DIS18219	3901.56		-0.29	
2300	CADS V8 2017	5932.9	ex	3.35	
2310	ISO/DIS18219	3738		-0.58	
2347		-----		-----	
2350	ISO/DIS18219	4272.475		0.37	
2352	In house	3883.8		-0.32	
2354	ISO/DIS18219	3235.436		-1.48	
2363	ISO/DIS18219	3828		-0.42	
2365	ISO/DIS18219	3945.8		-0.21	
2366	ISO/DIS18219	-----		-----	Out of capacity
2369	ISO/DIS18219	3919	ex	-0.26	
2370	ISO/DIS18219	4000		-0.12	
2372	ISO/DIS18219	4082.7		0.03	
2375	ISO/DIS18219	3930		-0.24	
2379	INH-209	Not tested		-----	
2380	ISO/DIS18219	4110.211		0.08	
2382	ISO/DIS18219	3866.3		-0.35	
2386	ISO/DIS18219	3325		-1.32	
2390	ISO/DIS18219	4747.2		1.22	
2488		35951.2	ex	57.09	
2492		-----		-----	
2495		-----		-----	
2508		-----		-----	
2566	ISO/DIS18219	2390.16		-3.00	
2573	ISO/DIS18219	3923.41		-0.25	
2590	ISO/DIS18219	3690.61	ex	-0.67	
2605		-----		-----	
2612		-----		-----	
2737	In house	4841.98		1.39	
2743		-----		-----	
2770	In house	4335		0.48	
2774	In house	7182	R(0.05)	5.58	
2788		-----		-----	
2804		-----		-----	
2816	In house	2448.802	C,ex	-2.89	First reported 1817.036
2826	In house	4802	ex	1.32	
3100	In house	4045.390		-0.03	
3146	In house	3647		-0.75	
3150	ISO/DIS18219	4818		1.35	
3153		-----		-----	
3154	ISO/DIS18219	942.710	ex	-5.59	
3163		-----		-----	
3172	ISO/DIS18219	3748		-0.57	
3176	ISO/DIS18219	1192	C,ex	-5.14	First reported 1550
3179	ISO/DIS18219	5117.0		1.88	
3185		-----		-----	
3191	In house	3966.40		-0.18	
3197	In house	4018.3		-0.08	
3209	In house	3600.01		-0.83	
3210		-----		-----	
3214		-----		-----	
3218		-----		-----	
3220		NT		-----	
3246	In house	5161		1.96	

			All test results	
normality	suspect		OK	
n	33		41	
outliers	1 (+11 excl)		4	
mean (n)	4064.48		4107.43	
st.dev. (n)	728.884	RSD=18%	792.682	RSD = 19%
R(calc.)	2040.87		2219.51	
st.dev.(Horwitz n=9)	558.518		563.527	
R(Horwitz n=9)	1563.85		1577.88	

ex = test results were excluded as Hexane (or Pentane) was used as solvent or did not report any analytical details, see also chapter 4 and previous PT reports of iis17P05 and iis16P06.



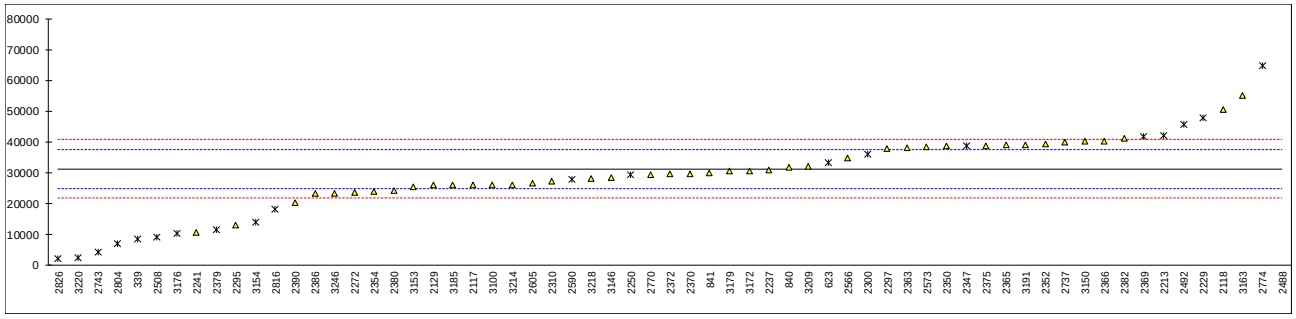


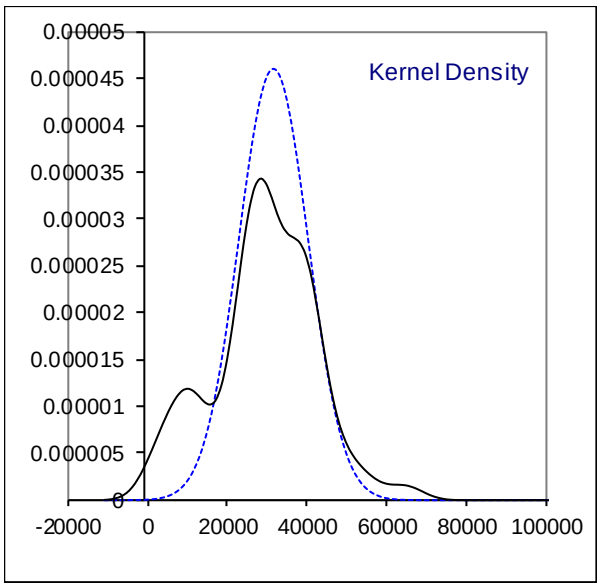
Determination of SCCP on sample #18571; results in mg/kg

lab	method	value	mark	z(targ)	remarks
339	In house	8660	ex	-7.16	
623	ISO/DIS18219	33387.66	ex	0.66	
840	ISO/DIS18219	31906		0.19	
841	ISO/DIS18219	29867.886		-0.45	
2117	ISO/DIS18219	25970.0		-1.68	
2118	ISO/DIS18219	50424.21		6.05	
2129	ISO/DIS18219	25906		-1.70	
2213	ISO/DIS18219	42058	ex	3.40	
2229	In house	47691.140	ex	5.18	
2237	In house	30848		-0.14	
2241	ISO/DIS18219	10632.1		-6.53	
2250	In house	29288	ex	-0.64	
2255		-----		-----	
2266	ISO/DIS18219	< 100		<-9.86	False negative test result?
2272	ISO/DIS18219	23771.5		-2.38	
2293	ISO/DIS18219	Detected		-----	
2295	ISO/DIS18219	13083		-5.76	
2297	ISO/DIS18219	37920.39		2.09	
2300	CADS V8 2017	35987.7	ex	1.48	
2310	ISO/DIS18219	27129.12		-1.32	
2347	ISO/DIS18219	38604	ex	2.31	
2350	ISO/DIS18219	38595.664		2.31	
2352	In house	39378.9		2.55	
2354	ISO/DIS18219	23915.706		-2.33	
2363	ISO/DIS18219	38080		2.14	
2365	ISO/DIS18219	39096.3		2.47	
2366	ISO/DIS18219	40167.5		2.80	
2369	ISO/DIS18219	41838	ex	3.33	
2370	ISO/DIS18219	29700		-0.51	
2372	ISO/DIS18219	29685		-0.51	
2375	ISO/DIS18219	38700		2.34	
2379	INH-209	11458.3	ex	-6.27	
2380	ISO/DIS18219	24251.771		-2.23	
2382	ISO/DIS18219	41014.4		3.07	
2386	ISO/DIS18219	23389		-2.50	
2390	ISO/DIS18219	20354.5		-3.46	
2488		332794.7	ex	95.32	
2492	In house	45600	C,ex	4.52	First reported 4.56
2495		-----		-----	
2508	ISO/DIS18219	9098.15	ex	-7.02	
2566	ISO/DIS18219	34915.2		1.14	
2573	ISO/DIS18219	38550.07		2.29	
2590	ISO/DIS18219	27882.92	ex	-1.08	
2605	ISO/DIS18219	26800.1		-1.42	
2612		-----		-----	
2737	In house	39936.82		2.73	
2743	ISO/DIS18219	4408.366	ex	-8.50	
2770	In house	29374		-0.61	
2774	In house	64649	R(0.05)	10.54	
2788		-----		-----	
2804	In house	6885.884	ex	-7.72	
2816	In house	18278.849	ex	-4.12	
2826	In house	2169	ex	-9.21	
3100	In house	26031.726		-1.66	
3146	In house	28580		-0.86	
3150	ISO/DIS18219	40112		2.79	
3153	In house	25471		-1.84	
3154	ISO/DIS18219	14012.567	ex	-5.46	
3163		55000		7.49	
3172	ISO/DIS18219	30704		-0.19	
3176	ISO/DIS18219	10321.00	ex	-6.63	
3179	ISO/DIS18219	30518.0		-0.25	
3185	ISO/DIS18219	25942.67		-1.69	
3191	In house	39184.76		2.49	
3197		-----		-----	
3209	In house	32012.01		0.23	
3210		-----		-----	
3214	ISO/DIS18219	26066.3		-1.65	
3218	In house	28125.373		-1.00	
3220	In house	2437.29	ex	-9.12	
3246	In house	23420		-2.49	

			All test results	
normality	OK		OK	
n	42		62	
outliers	1 (+20 excl)		1	
mean (n)	31298.36		29181.40	
st.dev. (n)	8712.374	RSD =28%	12835.613	RSD = 44%
R(calc.)	24394.65		35939.72	
st.dev.(Horwitz n=9)	3163.147		3177.042	
R(Horwitz n=9)	8856.81		8895.72	

ex = test results were excluded as Hexane (or Pentane) was used as solvent or did not report any analytical details, see also chapter 4 and previous PT reports of iis17P05 and iis16P06.



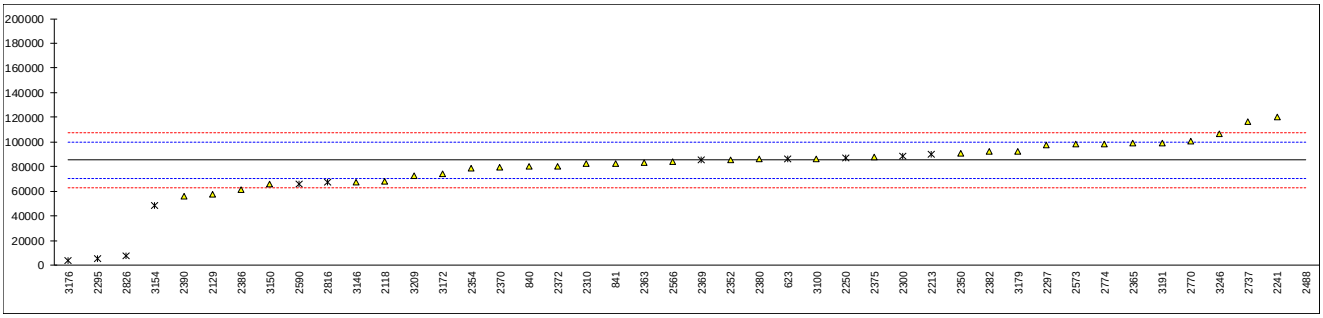


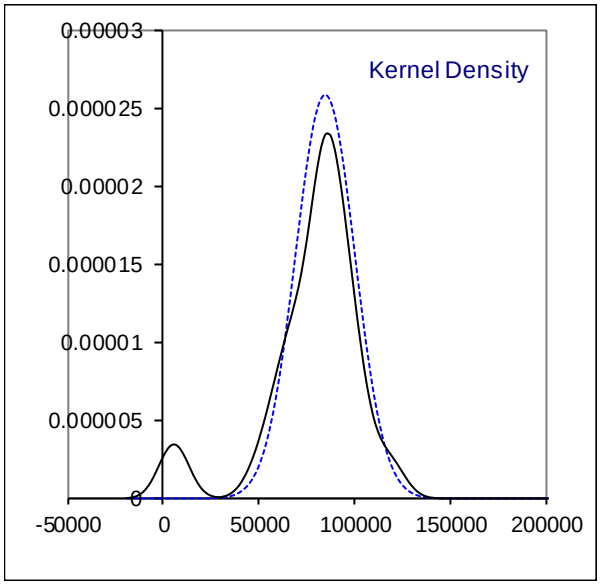
Determination of MCCP on sample #18571; results in mg/kg

lab	method	value	mark	z(targ)	remarks
339		-----		-----	
623	ISO/DIS18219	86147.47	ex	0.11	
840	ISO/DIS18219	79927		-0.73	
841	ISO/DIS18219	82459.350		-0.39	
2117		-----		-----	
2118	ISO/DIS18219	68092.50		-2.32	
2129	ISO/DIS18219	57338		-3.77	
2213	ISO/DIS18219	90065	ex	0.64	
2229		-----		-----	
2237		-----		-----	
2241	ISO/DIS18219	120661.4		4.76	
2250	In house	86856	ex	0.21	
2255		-----		-----	
2266	ISO/DIS18219	< 100		<-11.49	False negative test result?
2272		-----		-----	
2293	ISO/DIS18219	Detected		-----	
2295	ISO/DIS18219	5661	R(0.01)	-10.74	
2297	ISO/DIS18219	97656.78		1.66	
2300	CADS V8 2017	88373.8	ex	0.41	
2310	ISO/DIS18219	82224.32		-0.42	
2347		-----		-----	
2350	ISO/DIS18219	90480.679		0.69	
2352	In house	85692.5		0.05	
2354	ISO/DIS18219	78774.141		-0.88	
2363	ISO/DIS18219	83099		-0.30	
2365	ISO/DIS18219	98786.2		1.81	
2366	ISO/DIS18219	-----		-----	Out of capacity
2369	ISO/DIS18219	85647	ex	0.04	
2370	ISO/DIS18219	79415		-0.80	
2372	ISO/DIS18219	80013		-0.72	
2375	ISO/DIS18219	87900		0.35	
2379	INH-209	Not tested		-----	
2380	ISO/DIS18219	86142.841		0.11	
2382	ISO/DIS18219	92097.1		0.91	
2386	ISO/DIS18219	61152		-3.26	
2390	ISO/DIS18219	56285.1		-3.92	
2488		674893.8	ex	79.51	
2492		-----		-----	
2495		-----		-----	
2508		-----		-----	
2566	ISO/DIS18219	84190.85		-0.15	
2573	ISO/DIS18219	98333.19		1.75	
2590	ISO/DIS18219	65911.88	ex	-2.62	
2605		-----		-----	
2612		-----		-----	
2737	In house	116165.74		4.16	
2743		-----		-----	
2770	In house	100307		2.02	
2774	In house	98681		1.80	
2788		-----		-----	
2804		-----		-----	
2816	In house	67251.611	ex	-2.44	
2826	In house	7422	ex	-10.51	
3100	In house	86316.818		0.13	
3146	In house	67621		-2.39	
3150	ISO/DIS18219	65805		-2.63	
3153		-----		-----	
3154	ISO/DIS18219	48729.520	ex	-4.94	
3163		-----		-----	
3172	ISO/DIS18219	74344		-1.48	
3176	ISO/DIS18219	4018	C,R(0.01)	-10.97	First reported 3293.8
3179	ISO/DIS18219	92307.0		0.94	
3185		-----		-----	
3191	In house	98908.31		1.83	
3197		-----		-----	
3209	In house	72597.01		-1.72	
3210		-----		-----	
3214		-----		-----	
3218		-----		-----	
3220		NT		-----	
3246	In house	106746		2.89	

			All test results	
normality	OK		OK	
n	32		40	
outliers	2 (+10 excl)		4	
mean (n)	85328.75		83737.56	
st.dev. (n)	15577.395	RSD =18%	15606.659	RSD = 19%
R(calc.)	43616.70		43698.65	
st.dev.(Horwitz n=9)	7415.370		7297.736	
R(Horwitz n=9)	20763.04		20433.66	

ex = test results were excluded as Hexane (or Pentane) was used as solvent or did not report any analytical details, see also chapter 4 and previous PT reports of iis17P05 and iis16P06.





APPENDIX 2
Analytical details

lab	laboratory ISO/IEC17025 accredited	grain size reduced before use	reduced to particle size (mm)	Sample intake (g)	Extraction solvent used	Extraction time and temperature used
339	---	---	---	---	---	---
623	Yes	Further Cut	2 x 2	0.5	Hexane	60 min – 60°C
840	Yes	Further Cut	2 x 2	0.5	Toluene	60 min – 60°C
841	No	Further Cut	5 x 5	0.5	Toluene and Hexane	60 min – 60°C
2117	Yes	Further Cut	3 x 3		Toluene	60 min – 60°C
2118	No	Further Cut	2 x 2	0.5	Toluene	60 min – 60°C
2129	Yes	as received	--	0,5	Toluene	60 min – 60°C
2213	Yes	---	---	---	---	---
2229	Yes	Further Cut	3 x 3	0.5	Hexane	60 min – 60°C
2237	Yes	Other	<1	0,1	Toluene	60 min - room
2241	Yes	Further Cut	<1 x 1	0.2	Toluene	60 min – 60°C
2250	---	---	---	---	---	---
2255	---	---	---	---	---	---
2266	No	Further Cut	---	0.5	Hexane/DCM (50:50)	60 min – 60°C
2272	Yes	as received	---	0.5	Toluene	60 min – 60°C
2293	No	Further Cut	2 x 2	0.5	5 mL THF, 10 mL ACN	60 min – 70°C
2295	Yes	Further Cut	3 x 3	0.5	Toluene	60 min – room
2297	Yes	Further Cut	2	0.5	Toluene	60 min – 60°C
2300	---	---	---	---	---	---
2310	Yes	Further cut (#18571)	2 x 2	0.5	Toluene	60 min – 60°C
2347	Yes	Further Cut	2 x 2 x 2	0.5	Hexane	60 min – 60°C
2350	No	Further Cut	2 x 2	0.1	Toluene	60 min – 60°C
2352	Yes	Further Cut	2 x 2 x 2	0.5	Toluene	60 min – 60°C
2354	Yes	as received	5 x 5	~0.5	Toluene	60 min – 60°C
2363	No	Further Cut	2 x 2	0.5	Toluene	60 min – 60°C
2365	Yes	Further Cut	2 x 2 x 2	0.5	Toluene	60 min – 60°C
2366	No	Further Cut	2 x 2	0.5	Toluene	60 min – 60°C
2369	---	---	---	---	---	---
2370	Yes	Further Cut	3 x 3	0.5	Toluene	60 min – 60°C
2372	Yes	Further Cut	2	0.5	Toluene	60 min – 60°C
2375	Yes	Further Cut	Small piece	0.5	Toluene	60 min – 60°C
2379	No	Further Cut	5 ml	0.5	Hexane	60 min – 60°C
2380	Yes	Other	2.5 x 2.5	0.5	Toluene	60 min – 60°C
2382	No	Further Cut	2 x 2	0.5	Toluene	60 min – 60°C
2386	Yes	Further Cut	3 x 3	0,5	Toluene	60 min – 60°C
2390	Yes	Further Cut	2 x 2	0.5	Toluene	60 min – 60°C
2488	---	---	---	---	---	---
2492	No	as received	5	0.5	Hexane/DCM	60 min – 60°C
2495	---	---	---	---	---	---
2508	---	---	---	---	---	---
2566	Yes	Further Cut	2 x 2	0.1	Toluene	60 min – 60°C
2573	Yes	Further Cut	3 x 3	0.5	Toluene	60 min – 60°C
2590	---	---	---	---	---	---
2605	Yes	Further Cut	2 x 2	0.505	THF/ACN	60 min – 70°C
2612	---	---	---	---	---	---
2737	Yes	Further Cut	3 x 3	0.5	Toluene	60 min – 60°C
2743	No	Further Cut (#18571)	5 x 5	0.5	Hexane	60 min – 60°C
2770	Yes	Other	5	0.5373 / 0.4631	THF/ACN	35 min – room
2774	Yes	Further Cut	5 x 5	0.5	Toluene	60 min – 60°C
2788	---	---	---	---	---	---
2804	No	Further Cut	5 x 5	1	Hexane	60 min – 60°C
2816	No	Further Cut	2	0.5	Pentane	225 min – 25°C
2826	---	---	---	---	---	---
3100	Yes	Further Cut	2 x 2	0.5	THF/ACN	60 min – 70°C
3146	Yes	Further Cut (#18571)	2 x 3	0,5	THF/ACN	60 min – 70°C
3150	Yes	Further Cut	2.5 x 2.5	0,2	Toluene	60 min – 60°C
3153	Yes	Further Cut	3 x 3	0.5	THF/ACN	60 min – 70°C
3154	---	---	---	---	---	---
3163	No	as received	1	0.2	Toluene	60 min – 60°C
3172	Yes	Other	< 0.5 um	0.5	Toluene	60 min – 60°C
3176	Yes	Further Cut	0,2 x 0,2	0,5	Hexane/DCM	60 min – 60°C
3179	Yes	Further Cut	<1	---	Toluene	60 min – 60°C
3185	Yes	Further Cut	2 x 2	0.5	THF/CAN	60 min – 70°C
3191	Yes	Further Cut	>1		DCM/Acetone	30 min – 100°C
3197	Yes	Further Cut	2 x 2	0,5 g	THF/ACN	60 min – 70°C
3209	Yes	Further Cut	5 x 5	1	DCM	60 min – 40°C
3210	---	---	---	---	---	---
3214	Yes	Further Cut	3 x 3	0.5	THF	60 min – 70°C
3218	Yes	Further Cut	2 x 2	0.5	THF/ACN	60 min – 70°C
3220	Yes	Further Cut	< 1	0.5	Hexane	30 min - room
3246	Yes	Further Cut	2x2 to 5x5	0.50	Toluene	60 min – 60°C

APPENDIX 3

Number of participating laboratories per country

2 labs in	BANGLADESH
1 lab in	BELGIUM
1 lab in	DENMARK
3 labs in	FRANCE
12 labs in	GERMANY
1 lab in	GUATEMALA
5 labs in	HONG KONG
5 labs in	INDIA
1 lab in	INDONESIA
4 labs in	ITALY
1 lab in	NETHERLANDS
20 labs in	P.R. of CHINA
1 lab in	PAKISTAN
1 lab in	SOUTH KOREA
3 labs in	TAIWAN R.O.C.
1 lab in	THAILAND
5 labs in	TURKEY
3 labs in	VIETNAM
1 lab in	UNITED STATES OF AMERICA

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.e. = not evaluated
n.d. = not detected
W = result withdrawn on request of participant
ex = test result excluded from 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
5 ISO 5725, parts 1-6, 1994
6 M. Thompson and R. Wood, J. AOAC Int, 76, 926, (1993)
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8 IP 367:96
9 DIN 38402 T41/42
10 P.L. Davies, Fr. Z. Anal. Chem, 331, 513, (1988)
11 J.N. Miller, Analyst, 118, 455, (1993)
12 Analytical Methods Committee Technical Briefs, No 4 January 2001
13 P.J. Lowthian and M. Thompson, The Royal Society of Chemistry 2002, Analyst 2002, 127, 1359-1364
14 Bernard Rosner, Percentage Points for a Generalized ESD Many-Outlier Procedure, Technometrics, 25(2), 165-172, (1983)
15 ISO/DIS 18219 IUC (2012), Determination of chlorinated hydrocarbons in leather – Chromatographic method for short-chain chlorinated paraffins (SCCP).
16 Mise au point de methodes pour l'analyse de substances critiques issues des rejets industriels et de la fabrication des produits de la filiere cuir, Aurelien Rey, September 26, 2014
17 Addendum to PT report "SCCP&MCCP in polymer, April 2016", Dr. R.G. Visser, September 2016