Results of Proficiency Test
SCCP & MCCP in Polymer
April 2016

Organised by: Institute for Interlaboratory Studies
Spijkenisse, the Netherlands

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CONTENTS

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 2016. In this interlaboratory study 57 laboratories from 21 different countries participated (See appendix 3).
In this report, the results of the 2016 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. It was decided to send two different plastic samples (approximately 3 grams each), artificially fortified with MCCP and SCCP. Sample analyses for fit-for-use and homogeneity testing were subcontracted to an ISO/IEC17025 accredited laboratory. 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 (R007). 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 April 2014 (iis-protocol, version 3.3). 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 to be positive on SCCP (with respective approx. 3000 mg/kg and 1500 mg/kg), were selected. Both materials were divided over plastic bags, approx. 3 grams for each sample. The homogeneity of the subsamples was checked by determination of SCCP content on 8 stratified randomly selected subsamples.

	SCCP in mg/kg		SCCP in mg/kg
Sample #16570-1	2887	Sample #16571-1	1397
Sample #16570-2	2662	Sample #16571-2	1245
Sample #16570-3	2586	Sample #16571-3	1267
Sample #16570-4	2821	Sample #16571-4	1348
Sample #16570-5	2640	Sample #16571-5	1226
Sample #16570-6	2877	Sample #16571-6	1342
Sample #16570-7	2807	Sample #16571-7	1241
Sample #16570-8	2760	Sample #16571-8	1326

Table 1: homogeneity test results of the subsamples #16570 and #16571

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	SCCP in mg/kg
r (observed) #16570	175	---
r (observed) #16571	---	317
reference	Horwitz	Horwitz
0.3 x R (reference)	178	337

Table 2: evaluation of repeatabilities of SCCP contents of the subsamples #16570 and #16571

As the observed repeatabilities of the results of the homogeneity tests were both in full agreement with the target precision data estimated from the Horwitz equation, the homogeneity of subsamples #16570 and #16571 was assumed.

To each of the participating laboratories one sample #16570 and one sample #16571 was sent on April 20, 2016.

2.5 ANALYSES

The participants were requested to determine MCCP and SCCP content, applying the analysis procedure that is routinely used in the laboratory. To get comparable test results, a detailed report form, on which the analytes and the units were prescribed as well as the reference test method and a letter of instructions were prepared. Both were 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 package.

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. A list of abbreviations used in the tables can be found in appendix 3.

3.1 STATISTICS

Statistical calculations were performed as described in the report ’iis Interlaboratory Studies: Protocol for the Organisation, Statistics and Evaluation’ of April 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.
In accordance 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 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:

$z_{(target)}$ = (individual test result – average of proficiency test) / 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:

$\lvert z \rvert < 1$	good
$1 < \lvert z \rvert < 2$	satisfactory
$2 < \lvert z \rvert < 3$	questionable
$3 < \lvert z \rvert$	unsatisfactory

4 EVALUATION

In this interlaboratory study, no problems were encountered with the dispatch of the samples. Six participants did not report any test results at all, but all other participants reported test results before the final reporting date.
Finally, the 51 reporting laboratories reported 184 numerical results. In the reported test results four statistical outliers were observed, which is 2.1%. 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 [ref. 15] 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 based on a sub set of test results, 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, see paragraphs 4.4 and 5 for more discussion.

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 the test results of the laboratories that reported to have used ISO/DIS18219 (incl. cutting/grinding of the samples), are compared in the next tables.

	unit	n	Average	2.8 * sd	R(Horwitz)
SCCP	mg/kg	32	1666	1535	733
MCCP	mg/kg	28	3323	3611	1318

Table 3: performance overview on samples #16570

	unit	n	Average	2.8 * sd	R(Horwitz)
SCCP	mg/kg	29	698	441	350
MCCP	mg/kg	26	1850	1588	801

Table 4: performance overview on samples #16571

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 #16571.

4.2 EVALUATION PER COMPONENT AND PER SAMPLE

In this section the results are discussed per sample (see also discussion in 4.4 and 5).

sample #16570:

SCCP: This determination was problematic. Two statistical outliers were observed after the exclusion of 17 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).

MCCP: This determination was very problematic. No statistical outliers were observed after the exclusion of 15 test results (without the excluded test results the data set showed two statistical outliers). The observed reproducibility after rejection of the excluded data was not at all in agreement with the estimated reproducibility calculated using the Horwitz equation (n=9).

sample #16571:

SCCP: This determination was somewhat problematic. Three statistical outliers were observed after the exclusion of 17 test results (without the excluded test results the data set showed one statistical outlier). The observed reproducibility after rejection of the suspect data was almost in agreement with the estimated reproducibility calculated using the Horwitz equation (n=9).

MCCP: This determination was problematic. No statistical outliers were observed after the exclusion of 15 test results (without the excluded test results the data set showed two statistical outliers). The observed reproducibility after rejection of the excluded data was not in agreement with the estimated reproducibility calculated using the Horwitz equation (n=9).

4.3 COMPARISON OF THE PROFICIENCY TEST OF APRIL 2016 WITH PREVIOUS PTS

	April 2016	*Sept. 2015*
Number of reporting labs	51	58
Number of results reported	184	110
Statistical outliers	4	3
Percentage outliers	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	*April 2016*	*April 2015*	*Target*
SCCP	23-33%	29%	16-18%
MCCP	31-39%	19%	14-15%

Table 6: comparison of the observed uncertainties

5 DISCUSSION

About half of the participants (22 = 44%) reported to have used ISO/DIS18219 as test method and 25 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/DIS 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 4 of the 22 laboratories that reported to have used ISO/DIS18219 did not cut or grind the samples, but tested the samples as received.

In the previous PT iis15P05, 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 10 laboratories reported to have used n-hexane as extraction solvent, while 20 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 7:

SCCP	Solvent	n	Average in mg/kg	st.dev in mg/kg	RSD%
#16570	n-hexane *)	10	1538	699	45%
#16570	toluene *)	20	1463	297	20%
#16570	THF	10	1665	852	51%
#16571	n-hexane *)	9	631	238	38%
#16571	toluene *)	20	677	97	14%
#16571	THF	10	954	457	48%

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. The dispersion is regretfully rather high (48-51%). The dispersion of the test results after extraction with toluene is much smaller (14-20%), but the recovery of SCCP is much less than after the THF dissolution (71-88%).

Regretfully, too little information on the calibration solutions was reported by the participating laboratories to allow investigation of the effect of the calibration on the test results.

The reduction of the grain size of the samples also has an effect on the test results. Strangely, the amount of SCCP and MCCP extracted is not very different contradictory to the expectations, but the dispersion of the test results is very different. For sample #16571 the dispersion of the reported test SCCP results is reduced from 44% on the samples as received to 22% on the samples after cutting or grinding, see table 8.

SCCP	condition	n	Average in mg/kg	st.dev in mg/kg	RSD%
#16570	as received	15	1629	746	46%
#16570	cut/grinded	32	1666	548	33%
#16571	as received	15	865	417	48%
#16571	cut/grinded	29	698	157	22%

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

*) Using ultrasonic extraction at 60ºC for 60 minutes

The averages from the SCCP test results after cutting or grinding show a large resemblance with the averages of the reported ISO18219 test results. And for sample #16570 the resemblance with the average of the reported THF test results is striking, see page 12. Therefore it was decided to use averages of the test results after cutting or grinding as assigned values. The selected test results represent a large part of the participating laboratories (67%) and also have an acceptable standard deviation in comparison with the other test results.

The final assigned value in sample #16570 is for SCCP 1666 mg/kg and for MCCP 3323 mg/kg. Thus the total concentration SCCP/MCCP in sample#16570 will be approx. 5000 mg/kg. The values for sample #16571 are SCCP 698 mg/kg and MCCP 1850 mg/kg. Thus the total concentration SCCP/MCCP in sample #16571 will be approx. 2550 mg/kg.
The concentrations of the SCCP/MCCP mixtures added to the PVC were approximately 8000 mg/kg and 4000 mg/kg. The total recovery is approx 65% for each of the samples, which is lower than last year when the recovery was 75%, but then the average of the THF result was used as consensus value, see report iis15P05.

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 large variation is found between participants. This variation 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 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.

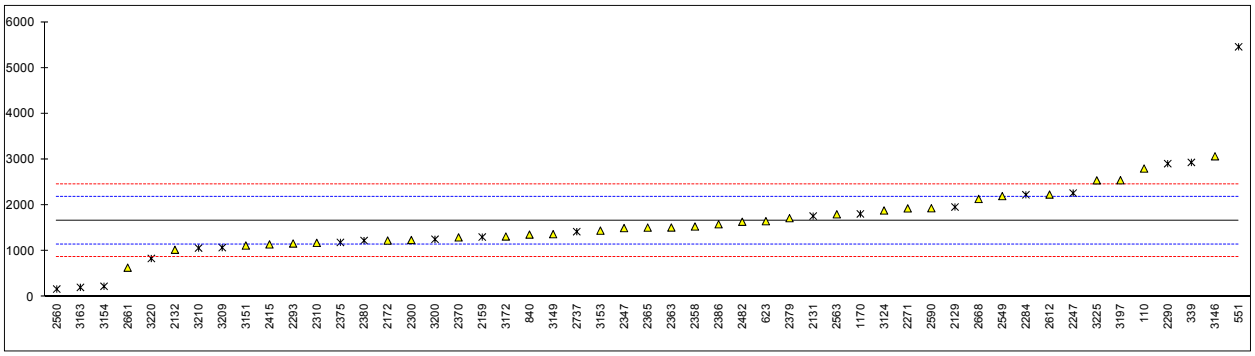
Each laboratory has to evaluate its performance in this study and make decisions about necessary corrective actions. Therefore, participation on a regular basis in this scheme could be helpful to improve the performance and the quality of the analytical results.

APPENDIX 1

Determination of SCCP on sample #16570; results in mg/kg

lab	method	value	mark	z(targ)	remarks
110	In house	2803.0431		4.34	
339	In house	2936	ex	4.85	
551	In house	5458.70	ex, C	14.48	first reported 6941.49
623	ISO18219	1653.44		-0.05	
840	In house	1361		-1.17	
1170	In house	1813	ex	0.56	
2115		-----		-----	
2129	ISO/DIS18219	1963	ex	1.13	
2131	In house	1765	ex	0.38	
2132	ISO/DIS18219	1030		-2.43	
2159	In house	1307.66	ex	-1.37	
2172	In house	1231.40		-1.66	
2247	In house	2266.43	ex	2.29	
2255		-----		-----	
2271	ISO/DIS18219	1933		1.02	
2284	ISO/DIS18219	2229.58	ex	2.15	
2290	ISO/DIS18219	2909	ex	4.74	
2293	ISO/DIS18219	1166.72		-1.91	
2300	In house	1242.08	C	-1.62	first reported 3528.50
2310	ISO/DIS18219	1181		-1.85	
2347	ISO/DIS18219	1503.50		-0.62	
2350		-----		-----	
2358	ISO/DIS18219	1537.1		-0.49	
2363	ISO/DIS18219	1515.5		-0.58	
2365	ISO/DIS18219	1513.5		-0.58	
2369		-----		-----	
2370	EPA8082A	1300		-1.40	
2375	ISO/DIS18219	1190.51	ex	-1.82	
2379	ISO/DIS18219	1719.8		0.20	
2380	CADS v4:112015	1230.15	ex	-1.67	
2386	ISO/DIS18219	1586		-0.31	
2390		-----		-----	
2415	In house	1147		-1.98	
2482	CADS v1:072015	1641		-0.10	
2549	ISO/DIS18219	2201.0		2.04	
2560	In house	173	R(0.05)	-5.70	
2563	ISO/DIS18219	1804		0.53	
2590	ISO/DIS18219	1936.56		1.03	
2612	In house	2233.95		2.17	
2661		639		-3.92	
2668	ISO/DIS18219	2138.57		1.80	
2737	In house	1425.0	ex	-0.92	
3124	In house	1887		0.84	
3146	In house	3070.08		5.36	
3149	In house	1370		-1.13	
3151	In house	1121.9		-2.08	
3153	In house	1447		-0.84	
3154	In house	232.49	ex	-5.48	
3163	In house	210	R(0.05)	-5.56	
3172	ISO/DIS18219	1319		-1.33	
3197	In house	2547		3.36	
3200	In house	1258.3	ex	-1.56	
3209	ISO18219	1077.3	ex	-2.25	
3210	In house	1067.41	ex	-2.29	
3220	In house	839.1	ex	-3.16	
3225	ISO/DIS18219	2545.83		3.36	
3237		-----		-----	

		cut/grinded:		All test results:	using THF:	ISO18219 + cutting/grinding:
	normality	OK		OK	OK	OK
	n	32		50	10	17
	outliers	2	+ 17 excl	1	0	1
	mean (n)	1666.44		1584.38	1665.05	1663.80
	st.dev. (n)	548.274		662.443	852.098	399.601
	R(calc.)	1535.17		1854.84	2385.87	1118.88
	R(Horwitz n=9)	733.26		702.48	732.75	732.28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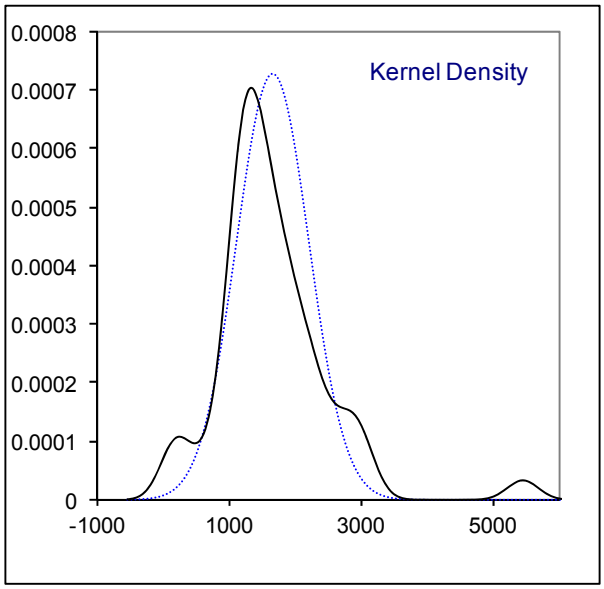
Kernel Density
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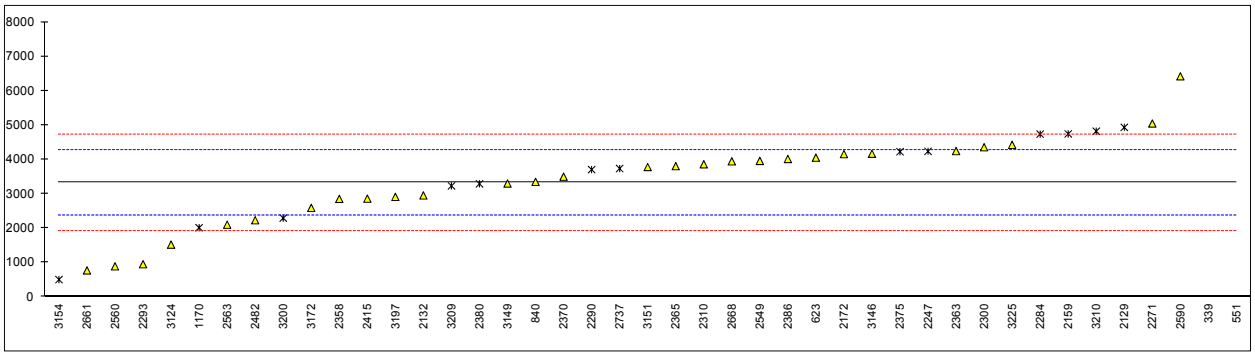
0.0007
0.0006
0.0005
0.0004
0.0003
0.0002
0.0001
0
-1000
1000
3000
5000

Determination of MCCP on sample #16570; results in mg/kg

lab	method	value	mark	z(targ)	remarks
110		-----		-----	
339	In house	11920	ex	18.27	
551	In house	31117.64	ex, C	59.06	first reported 9121.87
623	ISO18219	4052.77		1.55	
840	In house	3349		0.06	
1170	In house	2015	ex	-2.78	
2115		-----		-----	
2129	ISO/DIS18219	4935	ex	3.43	
2131		-----		-----	
2132	ISO/DIS18219	2954		-0.78	
2159	In house	4744.4	ex, C	3.02	first reported 6777.7
2172	In house	4156.67		1.77	
2247	In house	4237.72	ex	1.94	
2255		-----		-----	
2271	ISO/DIS18219	5047		3.66	
2284	ISO/DIS18219	4737.03	ex	3.01	
2290	ISO/DIS18219	3705	ex	0.81	
2293	ISO/DIS18219	952.00		-5.04	
2300	In house	4355.74		2.20	
2310	ISO/DIS18219	3861		1.14	
2347		-----		-----	
2350		-----		-----	
2358	ISO/DIS18219	2854.7		-0.99	
2363	ISO/DIS18219	4244.7		1.96	
2365	ISO/DIS18219	3806.0		1.03	
2369		-----		-----	
2370	EPA8082A	3500		0.38	
2375	ISO/DIS18219	4226.32	ex	1.92	
2379		-----		-----	
2380	CADS v4:112015	3292.34	ex	-0.06	
2386	ISO/DIS18219	4014		1.47	
2390		-----		-----	
2415	In house	2861		-0.98	
2482	CADS v1:072015	2232		-2.32	
2549	ISO/DIS18219	3958.7		1.35	
2560	In house	890		-5.17	
2563	ISO/DIS18219	2103		-2.59	
2590	ISO/DIS18219	6420.77	C	6.58	first reported 24025.02
2612		-----		-----	
2661		772		-5.42	
2668	ISO/DIS18219	3946.52		1.33	
2737	In house	3736.0	ex	0.88	
3124	In house	1523		-3.82	
3146	In house	4166.82		1.79	
3149	In house	3300		-0.05	
3151	In house	3780.63		0.97	
3153		-----		-----	
3154	In house	504.28	ex	-5.99	
3163		-----		-----	
3172	ISO/DIS18219	2592		-1.55	
3197	In house	2912		-0.87	
3200	In house	2294.3	ex	-2.18	
3209	ISO18219	3232.1	ex	-0.19	
3210	In house	4823.07	ex	3.19	
3220		-----		-----	
3225	ISO/DIS18219	4426.50		2.35	
3237		-----		-----	

	cut/grinded:		All test results:	using THF:	ISO18219 + cutting/grinding:
normality	OK		OK	OK	OK
n	28		41	9	16
outliers	0	+15 excl	2	0	0
mean (n)	3322.59		3402.81	3194.33	3507.73
st.dev. (n)	1289.795		1286.629	1524.314	1422.079
R(calc.)	3611.43		3602.56	4268.08	3981.82
R(Horwitz n=9)	1317.77		1344.75	1274.43	1379.89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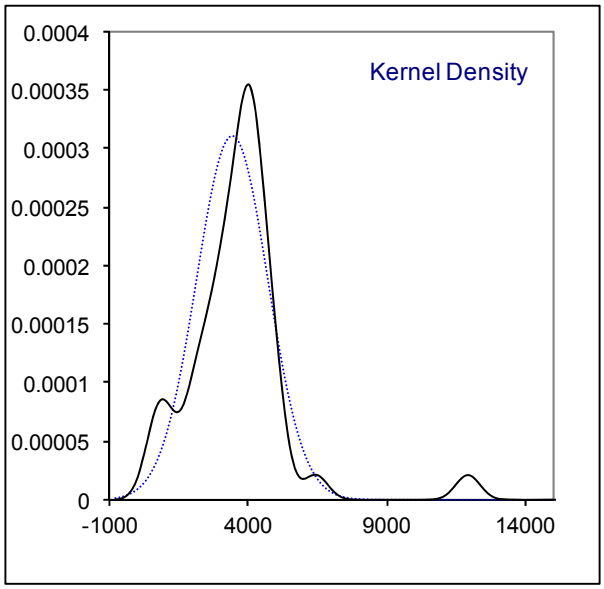
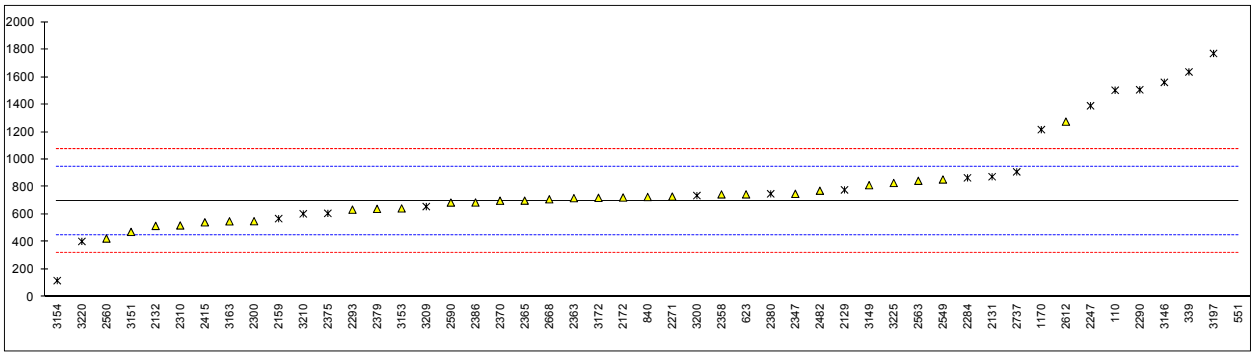
1000
0
3154 2661 2560 2293 3124 1170 2563 2482 3200 3172 2358 2415 3197 2132 3209 2380 3149 840 2370 2290 2737 3151 2365 2310 2668 2549 2386 623 2172 3146 2375 2247 2363 2300 3225 2284 2159 3210 2129 2271 2590 339 551


Kernel Density
0.0004
0.00035
0.0003
0.00025
0.0002
0.00015
0.0001
0.00005
0
-1000
4000
9000
14000

Determination of SCCP on sample #16571; results in mg/kg

lab	method	value	mark	z(targ)	remarks
110	In house	1503.6404	R(0.01)	6.45	
339	In house	1637	ex	7.51	
551	In house	4062.74	ex, C	26.92	first reported 3984.99
623	ISO18219	746.21		0.39	
840	In house	727		0.23	
1170	In house	1217	ex	4.15	
2115		-----		-----	
2129	ISO/DIS18219	779	ex	0.65	
2131	In house	874.5	ex	1.41	
2132	ISO/DIS18219	517		-1.45	
2159	In house	569.56	ex	-1.03	
2172	In house	723.55		0.21	
2247	In house	1390.66	ex	5.54	
2255		-----		-----	
2271	ISO/DIS18219	730		0.26	
2284	ISO/DIS18219	866.37	ex	1.35	
2290	ISO/DIS18219	1507	ex	6.47	
2293	ISO/DIS18219	634.920		-0.50	
2300	In house	551.15	C	-1.17	first reported 1372.66
2310	ISO/DIS18219	520		-1.42	
2347	ISO/DIS18219	750.25		0.42	
2350		-----		-----	
2358	ISO/DIS18219	745.9		0.38	
2363	ISO/DIS18219	718.9		0.17	
2365	ISO/DIS18219	700.5		0.02	
2369		-----		-----	
2370	EPA8082A	700		0.02	
2375	ISO/DIS18219	607.93	ex	-0.72	
2379	ISO/DIS18219	640.6		-0.46	
2380	CADS v4:112015	750.16	ex	0.42	
2386	ISO/DIS18219	687		-0.09	
2390		-----		-----	
2415	In house	543		-1.24	
2482	CADS v1:072015	772.7		0.60	
2549	ISO/DIS18219	854.5		1.25	
2560	In house	425		-2.18	
2563	ISO/DIS18219	845		1.18	
2590	ISO/DIS18219	686.44		-0.09	
2612	In house	1275.45		4.62	
2661		-----		-----	
2668	ISO/DIS18219	710.37		0.10	
2737	In house	910.0	ex	1.70	
3124		-----		-----	
3146	In house	1561.2	R(0.01)	6.91	
3149	In house	813		0.92	
3151	In house	473.3		-1.80	
3153	In house	644		-0.43	
3154	In house	118.87	ex	-4.63	
3163	In house	550		-1.18	
3172	ISO/DIS18219	721		0.19	
3197	In house	1771	R(0.01)	8.59	
3200	In house	737.4	ex	0.32	
3209	ISO18219	657.3	ex	-0.32	
3210	In house	604.47	ex	-0.75	
3220	In house	403.9	ex	-2.35	
3225	ISO/DIS18219	829.04		1.05	
3237		-----		-----	

		cut/grinded:		All test results:	using THF:	ISO18219 + cutting/grinding:
	normality	not OK		not OK	OK	OK
	n	29		48	10	18
	outliers	3	+17 excl	1	0	0
	mean (n)	697.79		806.31	954.50	692.37
	st.dev. (n)	157.426		343.136	457.445	113.423
	R(calc.)	440.79		960.78	1280.85	317.59
	R(Horwitz n=9)	350.02		395.76	456.75	347.71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1800
1600
1400
1200
1000
800
600
400
200
0
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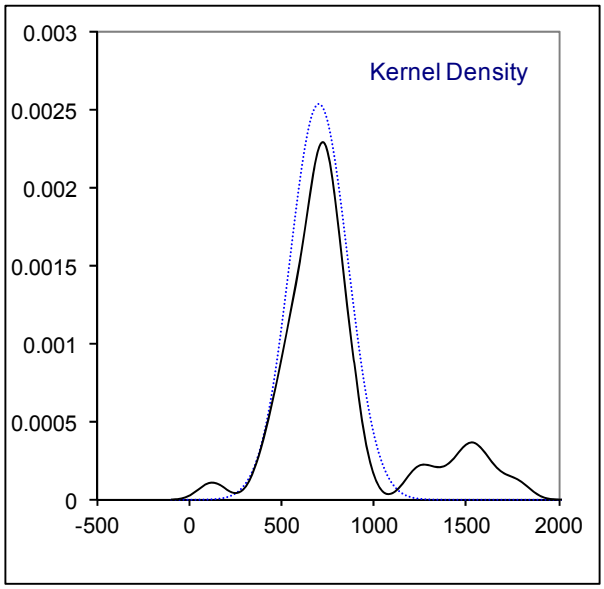
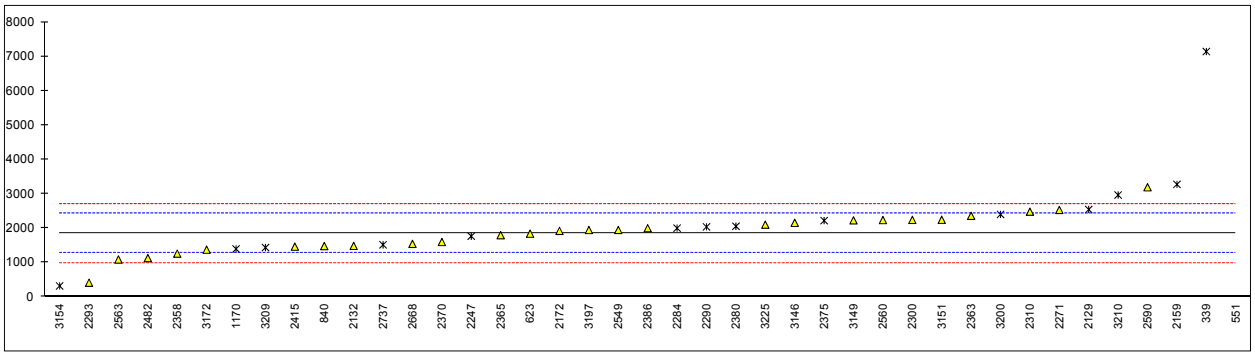
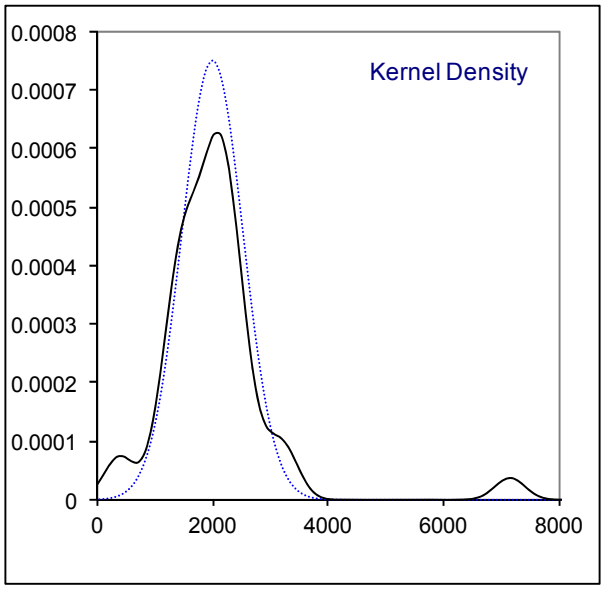

Kernel Density
0.003
0.0025
0.002
0.0015
0.001
0.0005
0
-500
0
500
1000
1500
2000

Determination of MCCP on sample #16571; results in mg/kg

lab	method	value	mark	z(targ)	remarks
110		-----		-----	
339	In house	7140	ex	18.49	
551	In house	31805.80	ex, C	104.69	first reported 6217.16
623	ISO18219	1841.58		-0.03	
840	In house	1481		-1.29	
1170	In house	1396	ex, C	-1.59	first reported 4251
2115		-----		-----	
2129	ISO/DIS18219	2545	ex	2.43	
2131		-----		-----	
2132	ISO/DIS18219	1486		-1.27	
2159	In house	3275.85	ex	4.98	
2172	In house	1923.01		0.26	
2247	In house	1768.12	ex	-0.28	
2255		-----		-----	
2271	ISO/DIS18219	2532		2.38	
2284	ISO/DIS18219	2001.96	ex	0.53	
2290	ISO/DIS18219	2039	ex	0.66	
2293	ISO/DIS18219	414.40		-5.02	
2300	In house	2241.38		1.37	
2310	ISO/DIS18219	2481		2.21	
2347		-----		-----	
2350		-----		-----	
2358	ISO/DIS18219	1261.6		-2.05	
2363	ISO/DIS18219	2359.5		1.78	
2365	ISO/DIS18219	1797.5		-0.18	
2369		-----		-----	
2370	EPA8082A	1600		-0.87	
2375	ISO/DIS18219	2221.62	ex	1.30	
2379		-----		-----	
2380	CADS v4:112015	2056.25	ex	0.72	
2386	ISO/DIS18219	2001		0.53	
2390		-----		-----	
2415	In house	1465		-1.34	
2482	CADS v1:072015	1130		-2.51	
2549	ISO/DIS18219	1950.6		0.35	
2560	In house	2237		1.35	
2563	ISO/DIS18219	1090		-2.65	
2590	ISO/DIS18219	3192.44	C	4.69	first reported 8383.41
2612		-----		-----	
2661		-----		-----	
2668	ISO/DIS18219	1544.22		-1.07	
2737	In house	1517.0	ex	-1.16	
3124		-----		-----	
3146	In house	2158.7		1.08	
3149	In house	2230		1.33	
3151	In house	2245.65		1.38	
3153		-----		-----	
3154	In house	321.10	ex	-5.34	
3163		-----		-----	
3172	ISO/DIS18219	1375		-1.66	
3197	In house	1947		0.34	
3200	In house	2403.2	ex	1.93	
3209	ISO18219	1437.8	ex	-1.44	
3210	In house	2966.53	ex	3.90	
3220		-----		-----	
3225	ISO/DIS18219	2103.96		0.89	
3237		-----		-----	

	cut/grinded:		All test results:	using THF:	ISO18219 + cutting/grinding:
normality	OK		OK	not OK	OK
n	26		39	9	16
outliers	0	+15 excl	2	32	0
mean (n)	1849.60		1898.44	1934.88	1854.24
st.dev. (n)	567.128		630.136	702.134	663.884
R(calc.)	1587.96		1764.38	1965.97	1858.88
R(Horwitz n=9)	801.18		819.12	832.46	802.89


8000
7000
6000
5000
4000
3000
2000
1000
0
3154 2293 2563 2482 2358 3172 1170 3209 2415 840 2132 2737 2668 2370 2247 2365 623 2172 3197 2549 2386 2284 2290 2380 3225 3146 2375 3149 2560 2300 3151 2363 3200 2310 2271 2129 3210 2590 2159 339 551


Kernel Density
0.0008
0.0007
0.0006
0.0005
0.0004
0.0003
0.0002
0.0001
0
0
2000
4000
6000
8000

APPENDIX 2

Analytical details

lab	Was granulate reduced?	reduced to particle size	Technique for release used	Extraction solvent used	Extraction time and temperature used
110	Cut	2mm x 2mm	Ultrasonic	DCM:Hexane (1:1)	60 min at 50°C
339	Used as received		Ultrasonic	DCM:Hexane (1:1)	1 hour at 50°C
551	Used as received				
623	Cut	2 mm x 2 mm	Ultrasonic	Hexane	60 C for 60 minutes
840	Cut		Ultrasonic	Toluene	60min/ 60°C
1170	Used as received		ASE	DKM	1 hour /100°C
2115	---		---		
2129	Used as received		Ultrasonic	toluene	60 min / 60°C
2131	Used as received		SpeedExtractor	DCM/Hexane	
2132	Cut	1 mm	Ultrasonic	Toluene	60C, 60 mins
2159	Used as received	3 x 3 mm	Ultrasonic	Toluene	60 min 60°CC
2172	Grinded	powder	Ultrasonic	hexane	60°C,60 minutes
2247	Used as received		Ultrasonic	THF/ACN	30 min at 70°C
2255	---		---		
2271	Cut	2mmx2mm	Ultrasonic	Toluene	60
2284	Used as received	5mm*4mm	Ultrasonic	THF	60minutes, 60 °C
2290	Used as received				
2293	Cut	2 x 2 mm	Ultrasonic	THF	30 min at 70°C
2300	Cut	1 mm	Ultrasonic	Dichloromethane	Time-30 minutes and 32 °C
2310	Cut	2mm*2mm	Ultrasonic	Toluene	60 min & 60°C
2347	Cut	2*2*2mm	Ultrasonic	hexane	60 min, 60°C
2350	---		---		
2358	Cut	3mm x 3mm	Ultrasonic	Toluene	60 degree C, 1 hour
2363	Cut	2*2*2mm	Ultrasonic	Toluene	60 minutes temperature:65 °C
2365	Cut	2*2*2mm	Ultrasonic	toluene	60 min, 60°C
2369	---		---		
2370	Cut	2mm*2mm	Ultrasonic	Toluene	60°C;1h
2375	Used as received		Ultrasonic	Toluene	60 min - 60 C
2379	Cut	2X2 mm	Ultrasonic	Toluene	60 min
2380	Used as received	3X3 mm	Ultrasonic	Toluene	60 minute and 60 °C
2386	Cut	2-3mm	Ultrasonic	Toluene	60 min, 60 °C
2390	---		---		
2415	Cut	3 mm X 3mm	Ultrasonic	n hexane	60 min 60 C
2482	Cut	2-3mm	Ultrasonic	Toluene	60 minutes 60°C
2549	Cut	2 X 2 mm	Ultrasonic	Hexane	60 min at 60°C
2560	Cut	3mm x 3mm	Ultrasonic	THF, Hexane, ACN	60mins & 60^{0}C
2563	Grinded	< 1 x 1 mm	Ultrasonic	Toluene	60 minutes at 60°C
2590	Cut	2 mm x 2 mm	Ultrasonic	Toluene	60 min at 60 °C
2612	Cut	2 mm²	Ultrasonic	Acetone	2 x 15 min in 30 °C water bath
2661	Grinded	> 1 mm	Soxhlet	Dichloromethane	1 hour at 150°C
2668	Cut	2 mm X 2 mm	Ultrasonic	Hexane	60 °C for 60 minutes
2737	Used as received		Ultrasonic	THF+n-Hexane	60min, 60°C
3124	Cut		Mechanical Shaking	Hexane	1 hour
3146	Cut	2 x 2	Ultrasonic	THF/ACN	2 x 30 min, 70°C
3149	Cut	2 mm - 3 mm	Ultrasonic	isooctane	2,5 h
3151	Cut	2 x 2 mm	Ultrasonic	toluene	60 minutes, 60 °C
3153	Cut	2mm x 2mm	Ultrasonic	THF/ACN	70°C 30 min for each solvent
3154	Used as received		Ultrasonic	n-hexane	60 min 60 °C
3163	Cut	0.5mg	Thermal Desorption	none	none
3172	Cut	2x2cm	Ultrasonic	Toluene	60 min @ 60°C
3197	Cut	2 mm x 2 mm	Ultrasonic	THF/ACN	30 minutes / 70°C - twice
3200	Used as received	<5mm	Mechanical Shaking	THF	30 min
3209	Used as received	~3*3mm	Ultrasonic	Toluene	60°C 1hr
3210	Used as received		Ultrasonic	1) THF 2) hexane	60 minutes at 40°C
3220	Used as received		Ultrasonic	Hexane	30 minutes at Room temperature
3225	Cut	5mm x 5mm	Ultrasonic	n-hexane	1 hour and 60 °C
3237	---		---		

Calibration solutions used

lab	calibrants
110	10 ppm - 50 ppm, 55.5% Cl SCCP
339	Standard from Dr Ehrenstorfer with 55,5%Chloride.
551	
623	SCCP 59% and MCCP 52%
840	SCCP 59%, MCCP 55%
1170	100ng/µl MCCP 52%CL in cyclohexane ; 100ng/µl SCCP 55,5%CL in cyclohexane
2115	
2129	refer to ISO/DIS 18219
2131	SCCP (Cl contents of 51.5, 55.5 and 63.0%), MCCP (Cl content of 52%) from Ehrenstorfer GmbH
2132	SCCP: 59% Cl, MCCP: 55% Cl
2159	59% SCCP, 55% MCCP
2172	SCCP-59%Cl,MCCP-55%Cl
2247	Mixture of 52 & 57% Chloride
2255	
2271	59% for SCCP, 57% for MCCP
2284	SCCP: 59% Chloride; MCCP: 55% Chloride
2290	
2293	SCCP (Chloroparaffin C10-C13 55.5%Cl and 63%Cl); MCCP (Chloroparaffin C14-C17 52% and 57% Cl)
2300	SCCP-59% Chloride and MCCP-55% Chloride
2310	SCCP 59% MCCP 55%
2347	59%
2350	
2358	SCCP: 59% Chloride; MCCP: 55% Chloride
2363	SCCP:59% MCCP:55%
2365	59%SCCP;55%MCCP
2369	
2370	1.SCCP 55.5%Cl; SCCP 63%Cl 2. MCCP 52 %Cl; MCCP 57%Cl
2375	
2379	5 , 10 , 20 , 30
2380	For SCCP 59% Cl & for MCCP 55% Cl
2386	Ehrenstorfer-Standards mixture of 55,5% Cl and 63 % Cl to get 59 % Cl according to ISO 18219
2390	
2415	SCCP 59% chloride MCCP 55% chloride
2482	SCCP: 59% MCCP: 55%
2549	Single point calibration
2560	SCCP – 63% & 55.5%; MCCP – 57% & 52%.
2563	SCCP C10-13 59% chlorination MCCP C14-17 55% chlorination
2590	SCCP at 59%Chloride and MCCP 55%Chloride
2612	Chlorparaffin C10-C13 55,5 % Cl from LCG Standards
2661	C10-C13 55,5% og C14-C17 52%
2668	Single point calibration;59% chlorination degree for SCCP/ 55% chlorination degree for MCCP
2737	59% chlorination SCCP, 55% chlorination MCCP
3124	Mixture of 3 standards. App 50% chlorine
3146	0,5 µg/ml - 20 µg/ml SCCP 59%, MCCP 55%
3149	C10-C13: 55,5 % Cl, C14-C17: 52 % Cl
3151	SCCP 59% Chloride, MCCP 55% Chloride
3153	59% chlorine content
3154	SCCP: 59 % Chloride / MCCP: 54,5 % Chloride
3163	
3172	Dr. Ehrenstorfer 100 mg/L: 55% - 63% Cl mix for SCCP; 52%-57% Cl mix for MCCP
3197	SCCP %59 / MCCP %55 Chlorine Content
3200	59Cl% SCCP,54.5Cl% MCCP
3209	1mg/L, 2mg/L, 5mg/L, 55.5%Cl
3210	SCCP : 59% Ehrenstorfer C10-C13 : 55.5% and 63% chloride MCCP 55% Ehrenstorfer C14-C17 57% and 52% chloride
3220	Chloroparaffin C10-C13 51.5% Cl
3225	59%
3237	10 ppm - 50 ppm, 55.5% Cl SCCP

APPENDIX 3

Number of participating laboratories per country

3 labs in	BANGLADESH
1 lab in	BRAZIL
1 lab in	DENMARK
2 labs in	FRANCE
9 labs in	GERMANY
1 lab in	GUATEMALA
4 labs in	HONG KONG
6 labs in	INDIA
1 lab in	INDONESIA
3 labs in	ITALY
1 lab in	KOREA
2 labs in	NORWAY
10 labs in	P.R. of CHINA
1 lab in	PAKISTAN
1 lab in	SWITZERLAND
1 lab in	TAIWAN R.O.C.
1 lab in	THAILAND
1 lab in	THE NETHERLANDS
4 labs in	TURKEY
1 lab in	U.S.A.
3 labs in	VIETNAM

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

Literature:

1 iis Interlaboratory Studies, Protocol for the Organisation, Statistics & Evaluation, April 2014
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)
7 W.J. Youden and E.H. Steiner, Statistical Manual of the AOAC, (1975)
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 Brief, No4 January 2001
13 The Royal Society of Chemistry 2002, Analyst 2002, 127 page1359-1364, P.J. Lowthian and M. Thompson.
14 Bernard Rosner, Percentage Points for a Generalized ESD Many-Outlier Procedure, Technometrics, 25(2), pp. 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