Results of Proficiency Test
Chlorinated Phenols in Leather
May 2019

Organised by: Institute for Interlaboratory Studies
Spijkenisse, the Netherlands

Author: ing. G.A. Oosterlaken-Buijs
Correctors: ing. A.S. Noordman-de Neef & ing. R.J. Starink

Report: iis19A09

July 2019

CONTENTS

1 INTRODUCTION

Products containing Pentachlorophenol (PCP) may form highly toxic substances when they are incinerated. PCP is also a suspected/probable carcinogen. Since the 1990's, many countries have adopted environmental standards and requirements restricting the use of harmful chemicals in the production of textiles and leather consumer products. Laws and regulations impose some of these standards and requirements. In addition to mandatory environmental standards and requirements for leather, there are some Ecolabelling schemes imposing environmental requirements for textile & leather products on a voluntary basis. Well-known organizations are Oeko-Tex® and Bluesign®, which has created a Bluesign® system substances list (BSSL).

Since 2016, the Institute for Interlaboratory Studies (iis) organizes a proficiency scheme for Pentachlorophenol (PCP) and Tetrachlorophenols (TeCPs) in Leather every year. In 2018 the scope of the scheme was extended with Trichlorophenols (TrCPs). During the annual proficiency testing program 2018/2019, it was decided to continue the proficiency test for the analysis Chlorinated Phenols in Leather.
In this interlaboratory study 75 laboratories in 25 different countries registered for participation. See appendix 4 for the number of participants per country. In this report, the results of the 2019 proficiency test for Chlorinated Phenols in Leather 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 organizer of this proficiency test. Sample analyzes for fit-for-use and homogeneity testing were subcontracted to an ISO/IEC17025 accredited laboratory. It was decided to send one leather sample of 3 grams, positive on some Chlorophenols, labelled #19541.
The participants were asked to report rounded and unrounded test results. The unrounded test results were preferably used for statistical evaluation.

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 organization 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 June 2018 (iis-protocol, version 3.5). 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

A batch of black colored leather positive on Chlorophenols (Pentachlorophenol (PCP), 2,3,5,6-Tetrachlorophenol (2,3,5,6-TeCP) and 2,4,6-Trichlorophenol (2,4,6-TrCP)) was obtained from a third-party laboratory. After cutting and homogenization, 100 plastic bags were filled with approximately 3 grams of leather and labelled #19541.
The homogeneity the subsamples was checked by the determination of PCP in accordance with an in-house test method on eight stratified randomly selected samples.

	PCP in mg/kg
Sample #19541-1	12.9
Sample #19541-2	13.6
Sample #19541-3	14.1
Sample #19541-4	13.6
Sample #19541-5	12.8
Sample #19541-6	12.6
Sample #19541-7	12.8
Sample #19541-8	12.1

Table 1: homogeneity test results of subsamples #19541

From the above test results, the repeatability was calculated and compared with 0.3 times the reproducibility of reference method in agreement with the procedure of ISO13528, Annex B2 in the next table.

	PCP in mg/kg
r (observed)	1.8
reference method	iis memo 1601
0.3 * R (reference method)	2.7

Table 2: evaluation of the repeatability of subsamples #19541.

The calculated repeatability was in agreement with 0.3 times the reproducibility of the reference method. Therefore, homogeneity of the subsamples was assumed.

To each of the participating laboratories one sample labelled #19541 was sent on April 17, 2019.

2.5 ANALYSES

The participants were requested to determine on sample #19541: Pentachlorophenol (PCP), 2,3,4,5-Tetrachlorophenol, 2,3,4,6-Tetrachlorophenol, 2,3,5,6-Tetrachlorophenol, 2,3,4-Trichlorophenol, 2,3,5-Trichlorophenol, 2,3,6-Trichlorophenol, 2,4,5-Trichlorophenol, 2,4,6-Trichlorophenol, 3,4,5-Trichlorophenol and other Chlorinated Phenols.
It was also requested to report if the laboratory was accredited for the determination of Chlorinated Phenols and to report some analytical details.

It was explicitly requested to treat the sample as if it was a routine sample, but not to age nor to dry the sample nor to determine volatile matter. The amount of sample was not sufficient to allow aging and/or determine the volatile matter content. It was also requested to report the test results using the indicated units on the report form and not to round the results, but report as much significant figures as possible and not to report ‘less than’ test results, which are above the detection limit, because such test results cannot be used for meaningful statistical evaluations.

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 appropriate reference test methods (when applicable) that will be used during the evaluation. The detailed report form and the letter of instructions are both made available on the data entry portal www.kpmd.co.uk/sgs-iis-cts/. The participating laboratories are also requested to confirm the sample receipt on this data entry portal. The letter of instructions can also be downloaded from the iis website www.iisnl.com.

3 RESULTS

During five weeks after sample dispatch, the test results of the individual laboratories were gathered via the data entry portal www.kpmd.co.uk/sgs-iis-cts/. The reported test results are tabulated in appendix 1 and 2 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 re-analyzes). Additional or corrected test results are used for data analysis and original test results are 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 organization of this proficiency test was the one as described in the report 'iis Interlaboratory Studies: Protocol for the Organization, Statistics and Evaluation' of June 2018 (iis-protocol, version 3.5).

For the statistical evaluation the *unrounded* (when available) figures were used instead of the rounded test results. Test results reported as '<…' or '>…" were in general 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 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. 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 test 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 proficienct 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 literature reproducibility by division with 2.8. In case no literature reproducibility was available, other target values may be used, like Horwitz or an estimated reproducibility based on former iis proficiency tests.

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 according to:

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

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

Absolute values for z<2 are very common and absolute values for z>3 are very rare. 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. Four participants reported test results after the final reporting date and two other participants did not report any test results at all. Not all laboratories were able to report all analyses requested. In total, 73 participants reported 205 numerical results. Observed were 4 outlying test results, which is 2.0% of the numerical results. In proficiency studies, outlier percentages of 3% - 7.5% are quite normal.

All original data sets given in appendix 1 proved to have a normal Gaussion distribution.

4.1 EVALUATION PER COMPONENT

In this section, the reported test results are discussed per component. The test methods, which were used by the various laboratories were taken into account for explaining the observed differences when possible and applicable. These methods are also in the tables together with the original data. The abbreviations, used in these tables, are listed in appendix 5.

For Pentachlorophenol (PCP), both existing test methods LFGB 82.02-8 and ISO17070:15, mention identical precision data. Most participating laboratories in this PT reported to have used one of these two test methods.

In iis memo 1601, in which the reproducibilities of the PCP determination on textile over 18 PTs from 2004 until 2014 were compared, it was concluded that the published reproducibility of these test methods is in practice too strict and a more realistic target reproducibility was determined. As it was assumed that the variation in the PT test results will be dependent on the concentration, this resulted in a Horwitz-like equation to estimate the target reproducibilities for the evaluation of the PT test results by iis from 2015 onwards (iis memo 1601, see lit.18).

Although iis memo 1601 is based on previous iis PTs of PCP in Textile and not based on iis PTs of PCP in Leather, it was decided to use the estimated iis target reproducibility of PCP both in textile PTs and leather PTs. It was also decided to use the estimated iis target reproducibility of PCP also for other Chlorinated Phenols components.

PCP: The determination of this component was not problematic. Three statistical outliers were observed. However, the calculated reproducibility after rejection of the statistical outliers is in full agreement with the target reproducibility derived from the reproducibilities observed in previous iis PTs, iis memo 1601.

2,3,5,6-TeCP: The determination of this component was not problematic. One statistical outlier was observed and one other test result was excluded. However, the calculated reproducibility after rejection of the suspect data is in full agreement with the target reproducibility derived from the reproducibilities observed in previous iis PTs, iis memo 1601.

2,4,6-TrCP: The determination of this component was problematic. No statistical outliers were observed but one test result was excluded. The calculated reproducibility after rejection of the suspect data is not in agreement with the target reproducibility derived from the reproducibilities observed in previous iis PTs, iis memo 1601.

The majority of the participants agreed on a concentration near or below the limit of detection for other TeCPs or TrCPs.

4.2 PERFORMANCE EVALUATION FOR THE GROUP OF LABORATORIES

A comparison has been made between the estimated target reproducibilities and the reproducibilities as found for the group of participating laboratories.
The number of significant test results, the average test results, the calculated reproducibilities (2.8 * standard deviation) and the target reproducibilities are presented in the next table.

Component	unit	n	average	2.8 * sd	R (target)
PCP	mg/kg	70	10.20	7.51	7.36
2,3,5,6-TeCP	mg/kg	63	8.44	6.07	6.27
2,4,6-TrCP	mg/kg	66	9.45	9.10	6.91

Table 3: reproducibilities of tests on sample #19541

Without further statistical calculations, it could be concluded that for PCP and 2,3,5,6-TeCP there is a good compliance of the group of participating laboratories with the target. For 2,4,6-TrCP the group of participating laboratories show to have more difficulty in this determination.

4.3 COMPARISON OF THE PROFICIENCY TEST OF MAY 2019 WITH PREVIOUS PTS

	May 2019	April 2018	April 2017	April 2016
Number of reporting labs	73	72	72	74
Number of test results	205	127	107	110
Number of statistical outliers	4	4	2	3
Percentage outliers	2.0%	3.1%	1.9%	2.7%

Table 4: comparison with previous proficiency tests

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

The performance of the determinations of the proficiency tests was compared, expressed as relative standard deviation (RSD) of the PTs, see next table.

	May 2019	April 2018	April 2017	April 2016	Target 1.3 – 13 mg/kg
PCP	26%	26%	36%	41%	35 - 25%
2,3,5,6-TeCP	26%	n.e.	n.e.	n.e.	35 - 25%
2,4,6-TrCP	34%	29%	n.e.	n.e.	35 - 25%

Table 5: developmement of the uncertainties over the years

The uncertainties for PCP and 2,3,5,6-TeCP observed in this PT are in line with the 2018 PT. The uncertainty for 2,4,6-TrCP is somewhat higher.

4.4 EVALUATION OF THE ANALYTICAL DETAILS

The test method ISO17070 is used by about 70% of the reporting participants and test method LFGB B82.02.8 is used by about 10% of the reporting participants. Test methods ISO17070 and LFGB 82.02-8 describe a similar sample pathway to determine PCP: steam distillation to extract the phenols from leather, liquid to liquid extraction to get the phenols in a hydrophobic solvent and acetylation of the phenols (with a mechanical shaker) to separate the phenols easier by the gas chromatograph.

For this PT also some analytical details were requested, see appendix 3. Based on the answers given by the participants the following can be summarized:

- About 80% of the reporting participants mentioned that they are accredited for the determination of the reported components.
- About 50% of the reporting participants used the sample as received and about 40% of the reporting participants did further cut the sample.
- About 55% of the reporting participants used Steam distillation as technique to release the Chlorinated Phenols and about 10% reported to have skipped the Steam distillation.
- About 30% of the reporting participants used Ultrasonic extraction and about 15% used Soxhlet/AES extraction as technique to extract the Chlorinated Phenols.
- About 75% of the reporting participants used a sample intake between 0.5 - 1 grams and about 10% used more than 1 grams as sample intake.

When the analytical details were investigated separately, it appeared that the effect on the determination of Chlorinated Phenols in Leather is negligible.

5 DISCUSSION

In table 6 the limits mentioned in Oeko-Tex® Leather Standard are mentioned. It was noticed that all participants would make identical decisions about the acceptability of the leather for Chlorophenols except one laboratory.

Chlorinated Phenols in mg/kg	Class I Baby	Class II Direct skin contact	Class III With no direct skin contact	Class IV Decoration material
Pentachlorophenol (PCP)	<0.3	<0.5	<0.5	<0.5
Tetrachlorophenols (TeCP), each isomer	<0.5	<0.5	<0.5	<0.5
Trichlorophenols (TrCP), each isomer	<0.5	<1.0	<1.0	<1.0

Table 6: Product classes specific limit values, Oeko-Tex® Leather Standard

For the determination of PCP, all participants would reject the sample for all classes.
For determination of TeCPs, all participants would reject the sample for all classes as all participants reported at least one TeCP isomer with a test result larger than 0.5 mg/kg.
For determination of TrCP, almost all participants would reject the sample for all classes as these participants reported at least one TrCP isomer with a test result larger than 0.5 mg/kg. However, one participant would accept the sample for classes II, III and IV.

6 CONCLUSION

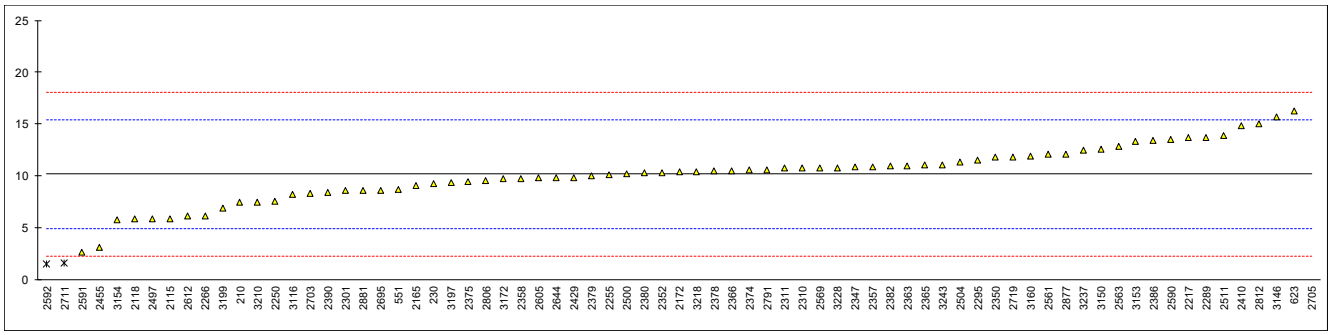
The majority of the participants has no problem with the determination of Pentachlorophenol (PCP) and 2,3,5,6-Tetrachlorophenol (2,3,5,6-TeCP) in leather. However, the determination of 2,4,6-Trichlorophenol (2,4,6-TrCP) was more problematic at the concentration level in this PT. Each participating laboratory will have to evaluate its performance in this study and decide about any corrective actions if necessary.
Therefore, participation on a regular basis in this scheme could be helpful to improve the performance and thus increase of the quality of the analytical results.

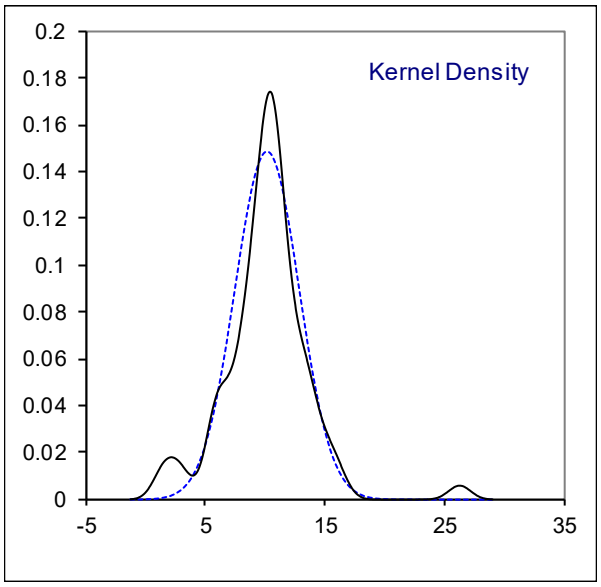
APPENDIX 1

Determination of Pentachlorophenol (PCP) on sample #19541; results in mg/kg

lab	method	value	mark	z(targ)	remarks
210	ISO17070	7.44		-1.05	
230	ISO17070	9.311		-0.34	
551	ISO17070	8.7423		-0.55	
623	ISO17070Mod.	16.225	C	2.29	first reported 19.343
2115	ISO17070	5.92		-1.63	
2118	ISO17070	5.905	C	-1.63	first reported 1.181
2165	ISO17070	9.04		-0.44	
2172	In house	10.392		0.07	
2217	ISO17070	13.69		1.33	
2250	In house	7.58		-0.99	
2255	ISO17070	10.1		-0.04	
2266	ISO17070	6.15		-1.54	
2289	ISO17070	13.72		1.34	
2295	In house	11.5		0.50	
2301	LFGB B82.02.8	8.6		-0.61	
2310	ISO17070	10.8		0.23	
2311	ISO17070	10.7775		0.22	
2347	LFGB B82.02.8	10.9		0.27	
2350	LFGB B82.02.8	11.8123		0.62	
2352	LFGB B82.02.8	10.36		0.06	
2357	ISO17070	10.927		0.28	
2358	ISO17070	9.765		-0.16	
2363	ISO17070	11.02		0.31	
2365	ISO17070	11.03		0.32	
2366	ISO17070	10.48		0.11	
2374	ISO17070	10.62		0.16	
2375	ISO17070	9.42		-0.29	
2378	LFGB B82.02.8	10.46		0.10	
2379	ISO17070	9.988		-0.08	
2380	ISO17070	10.31		0.04	
2382	ISO17070	11.0		0.31	
2386	In house	13.45		1.24	
2390	ISO17070	8.399		-0.68	
2410	ISO17070	14.87		1.78	
2429	ISO17070	9.8698		-0.12	
2455		3.161		-2.67	
2497	ISO17070	5.91		-1.63	
2500	ISO17070	10.21		0.01	
2504	In house	11.32		0.43	
2511	ISO17070	13.893		1.41	
2561	ISO17070	12.1348		0.74	
2563	ISO17070	12.9		1.03	
2569	ISO17070	10.8		0.23	
2590	ISO17070	13.538		1.27	
2591	In house	2.683		-2.86	
2592	ISO17070	1.53	C,R(0.05)	-3.30	first reported 0.74
2605	ISO17070	9.826		-0.14	
2612	ISO17070	6.1239		-1.55	
2644	ISO17070	9.83		-0.14	
2695	ISO17070	8.619		-0.60	
2703	ISO17070	8.319		-0.71	
2705	In house	26.3	R(0.01)	6.12	
2711	ISO17070	1.62	R(0.05)	-3.26	
2719	In house	11.86		0.63	
2734		-----		-----	
2756		-----		-----	
2791	ISO17070	10.62		0.16	
2806	ISO17070	9.6		-0.23	
2812	ISO17070	15.06		1.85	
2877	ISO17070	12.1436		0.74	
2881	In house	8.61		-0.60	
3116	LFGB B82.02.8	8.198		-0.76	
3146	In house	15.71		2.10	
3150	ISO17070	12.609		0.92	
3153	LFGB B82.02.8	13.37		1.21	
3154	In house	5.80		-1.67	
3160	ISO17070	11.894		0.65	
3172	In house	9.72		-0.18	
3197	ISO17070	9.38		-0.31	
3199	LFGB B82.02.8	6.91		-1.25	
3210	In house	7.45		-1.04	
3218	ISO17070	10.43		0.09	
3228	ISO17070	10.82		0.24	
3237	ISO17070	12.5		0.88	
3243	ISO17070	11.109		0.35	

normality	OK	
n	70	
outliers	3	
mean (n)	10.195	
st.dev. (n)	2.6829	RSD = 26.3%
R(calc.)	7.512	
st.dev.(iis memo 1601)	2.6295	
R(iis memo 1601)	7.363	
compare		
R(ISO17010:15)	3.449	
R(Horwitz)	3.220	

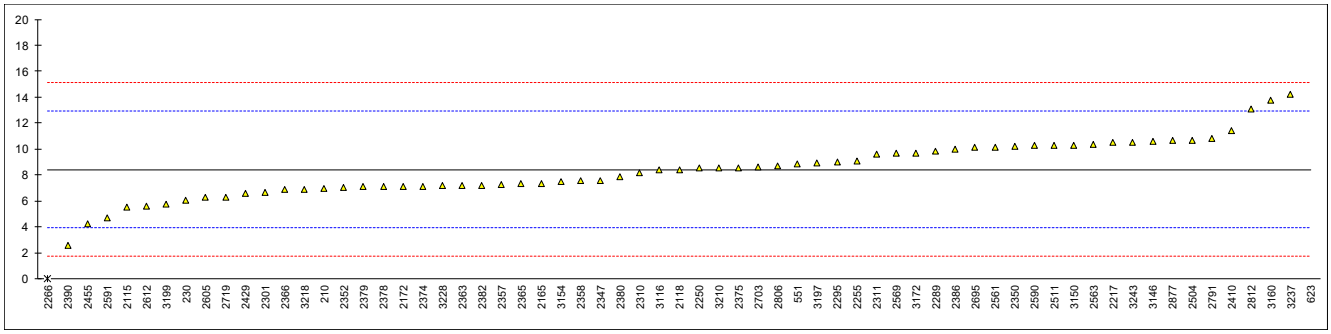


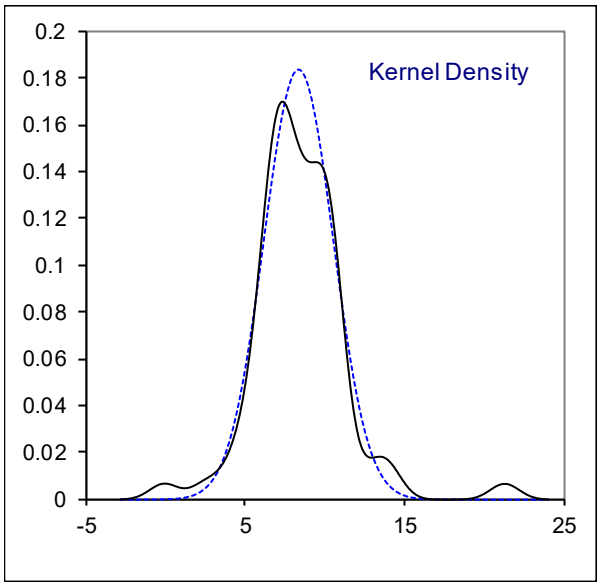


Determination of 2,3,5,6-Tetrachlorophenol (2,3,5,6-TeCP) on sample #19541; results in mg/kg

lab	method	value	mark	z(targ)	remarks
210	ISO17070	6.95		-0.66	
230	ISO17070	6.034		-1.07	
551	ISO17070	8.8917		0.20	
623	ISO17070Mod.	21.367	C,R(0.01)	5.78	first reported 24.639
2115	ISO17070	5.53		-1.30	
2118	ISO17070	8.379	C	-0.03	first reported 1.676
2165	ISO17070	7.36		-0.48	
2172	In house	7.131		-0.58	
2217	ISO17070	10.54		0.94	
2250	In house	8.53		0.04	
2255	ISO17070	9.1		0.30	
2266	ISO17070	0	ex	-3.77	excluded as 0 is not a real value, possibly reported as 2,3,4,5-TeCP?
2289	ISO17070	9.80		0.61	
2295	In house	9		0.25	
2301	LFGB B82.02.8	6.7		-0.78	
2310	ISO17070	8.2		-0.11	
2311	ISO17070	9.581		0.51	
2347	ISO17070	7.6		-0.37	
2350	LFGB B82.02.8	10.2193		0.80	
2352	LFGB B82.02.8	7.02		-0.63	
2357	ISO17070	7.302		-0.51	
2358	ISO17070	7.595		-0.38	
2363	ISO17070	7.21		-0.55	
2365	ISO17070	7.31		-0.50	
2366	ISO17070	6.86		-0.70	
2374	ISO17070	7.15		-0.57	
2375	ISO17070	8.58		0.06	
2378	LFGB B82.02.8	7.13		-0.58	
2379	ISO17070	7.101		-0.60	
2380	ISO17070	7.86		-0.26	
2382	ISO17070	7.21		-0.55	
2386	In house	10.01		0.70	
2390	ISO17070	2.62	C	-2.60	first reported 1.88
2410	ISO17070	11.43		1.34	
2429	ISO17070	6.6124		-0.81	
2455		4.242		-1.87	
2497		-----		-----	
2500		-----		-----	
2504	In house	10.70		1.01	
2511	ISO17070	10.286		0.83	
2561	ISO17070	10.1746		0.78	
2563	ISO17070	10.36		0.86	
2569	ISO17070	9.7		0.56	
2590	ISO17070	10.282		0.82	
2591	In house	4.690		-1.67	
2592		-----		-----	
2605	ISO17070	6.267		-0.97	
2612	ISO17070	5.6244	C	-1.26	first reported <0.5
2644		-----		-----	
2695	ISO17070	10.116		0.75	
2703	ISO17070	8.650		0.10	
2705		-----		-----	
2711	ISO17070	<1		<-3.32	possibly a false negative test result?
2719	In house	6.31		-0.95	
2734		-----		-----	
2756		-----		-----	
2791	ISO17070	10.81		1.06	
2806	ISO17070	8.7		0.12	
2812	ISO17070	13.05		2.06	
2877	ISO17070	10.6660		1.00	
2881		-----		-----	
3116	LFGB B82.02.8	8.378		-0.03	
3146	In house	10.56		0.95	
3150	ISO17070	10.315		0.84	
3153		-----		-----	
3154	In house	7.48		-0.43	
3160	ISO17070	13.762		2.38	
3172	In house	9.71		0.57	
3197	ISO17070	8.95		0.23	
3199	LFGB B82.02.8	5.73		-1.21	
3210	In house	8.57		0.06	
3218	ISO17070	6.91		-0.68	
3228	ISO17070	7.19		-0.56	
3237	ISO17070	14.2		2.57	
3243	ISO17070	10.554		0.95	

normality	OK	
n	63	
outliers	1 (+1 ex)	
mean (n)	8.436	
st.dev. (n)	2.1689	RSD= 25.7%
R(calc.)	6.073	
st.dev.(iis memo 1601)	2.2386	
R(iis memo 1601)	6.268	
compare		
R(ISO17010:15)	2.819	
R(Horwitz)	2.742	

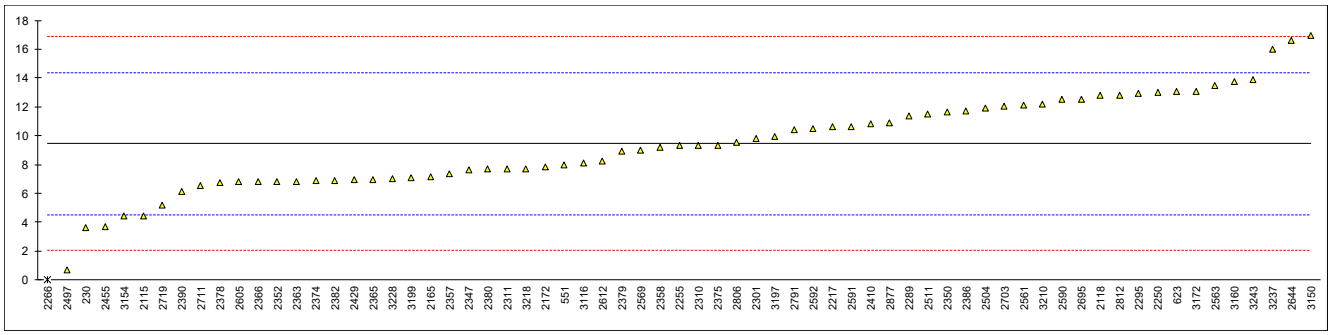


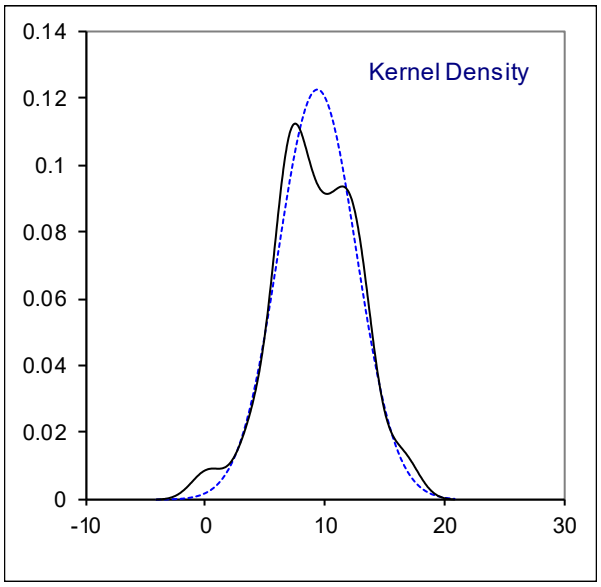


Determination of 2,4,6-Trichlorophenol (2,4,6-TrCP) on sample #19541; results in mg/kg

lab	method	value	mark	z(targ)	remarks
210		-----		-----	
230	ISO17070	3.625		-2.36	
551	ISO17070	7.9480		-0.61	
623	ISO17070Mod.	13.044		1.46	
2115	ISO17070	4.43		-2.04	
2118	ISO17070	12.787	C	1.35	first reported 2.557
2165	ISO17070	7.17		-0.93	
2172	In house	7.834		-0.66	
2217	ISO17070	10.59		0.46	
2250	In house	13.0		1.44	
2255	ISO17070	9.3		-0.06	
2266	ISO17070	0	ex	-3.83	excluded as 0 is not a real value, possibly reported as 2,3,4-TrCP?
2289	ISO17070	11.39		0.79	
2295	In house	12.9		1.40	
2301	LFGB B82.02.8	9.8		0.14	
2310	ISO17070	9.3		-0.06	
2311	ISO17070	7.689		-0.72	
2347	ISO17070	7.6		-0.75	
2350	LFGB B82.02.8	11.6671		0.90	
2352	LFGB B82.02.8	6.82		-1.07	
2357	ISO17070	7.358		-0.85	
2358	ISO17070	9.195		-0.10	
2363	ISO17070	6.83		-1.06	
2365	ISO17070	6.95		-1.01	
2366	ISO17070	6.81		-1.07	
2374	ISO17070	6.85		-1.06	
2375	ISO17070	9.34		-0.05	
2378	LFGB B82.02.8	6.75		-1.10	
2379	ISO17070	8.900		-0.22	
2380	ISO17070	7.67		-0.72	
2382	ISO17070	6.89		-1.04	
2386	In house	11.74		0.93	
2390	ISO17070	6.13		-1.35	
2410	ISO17070	10.84		0.56	
2429	ISO17070	6.9273		-1.02	
2455		3.704		-2.33	
2497	ISO17070	0.678		-3.56	
2500		-----		-----	
2504	In house	11.90		0.99	
2511	ISO17070	11.520		0.84	
2561	ISO17070	12.0881		1.07	
2563	ISO17070	13.47		1.63	
2569	ISO17070	9		-0.18	
2590	ISO17070	12.545		1.25	
2591	In house	10.616		0.47	
2592	ISO17070	10.5		0.42	
2605	ISO17070	6.809		-1.07	
2612	ISO17070	8.2597		-0.48	
2644	ISO17070	16.60		2.90	
2695	ISO17070	12.555		1.26	
2703	ISO17070	12.026		1.04	
2705		-----		-----	
2711	ISO17070	6.54		-1.18	
2719	In house	5.16		-1.74	
2734		-----		-----	
2756		-----		-----	
2791	ISO17070	10.44		0.40	
2806	ISO17070	9.5		0.02	
2812	ISO17070	12.79	C	1.35	first reported 17.40
2877	ISO17070	10.9213		0.60	
2881		-----		-----	
3116	LFGB B82.02.8	8.126		-0.54	
3146		-----		-----	
3150	ISO17070	16.928		3.03	
3153		-----		-----	
3154	In house	4.40		-2.05	
3160	ISO17070	13.770		1.75	
3172	In house	13.09		1.47	
3197	ISO17070	9.95		0.20	
3199	LFGB B82.02.8	7.11		-0.95	
3210	In house	12.18		1.11	
3218	ISO17070	7.69		-0.71	
3228	ISO17070	7.03		-0.98	
3237	ISO17070	16		2.66	
3243	ISO17070	13.917		1.81	

normality	OK	
n	66	
outliers	0 (+ 1ex)	
mean (n)	9.453	
st.dev. (n)	3.2514	RSD= 34.4%
R(calc.)	9.104	
st.dev.(iis memo 1601)	2.4660	
R(iis memo 1601)	6.905	
compare		
R(ISO17010:15)	3.183	
R(Horwitz)	3.020	





APPENDIX 2
Other reported test results

Abbreviations of components:
2,3,4,5-TeCP = 2,3,4,5-Tetrachlorophenol
2,3,4,6-TeCP = 2,3,4,6-Tetrachlorophenol
2,3,4-TrCP = 2,3,4-Trichlorophenol
2,3,5-TrCP = 2,3,5-Trichlorophenol
2,3,6-TrCP = 2,3,6-Trichlorophenol
2,4,5-TrCP = 2,4,5-Trichlorophenol
3,4,5-TrCP = 3,4,5-Trichlorophenol
Other CP = Other Chlorinated Phenols
PCMC = 4-Chloro-3-Methylphenol
OPP = ortho-Phenylphenol

Determination of Other Chlorinated Phenols on sample #19541; results in mg/kg

lab	2,3,4,5-TeCP	2,3,4,6-TeCP	2,3,4-TrCP	2,3,5-TrCP	2,3,6-TrCP	2,4,5-TrCP	3,4,5-TrCP	Other CP
210	-----	-----	-----	-----	-----	-----	-----	-----
230	-----	2.742	-----	-----	-----	-----	-----	-----
551	ND	ND	ND	ND	ND	ND	ND	-----
623	n.d.	n.d.	n.d.	n.d.	n.d.	0.101	n.d.	n.d.
2115	-----	-----	-----	-----	-----	-----	-----	PCMC = 39.90 OPP = 133.66
2118	0	0	0	0	0	0	0	0
2165	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	-----
2172	-----	-----	-----	-----	-----	-----	-----	-----
2217	-----	-----	-----	-----	-----	-----	-----	-----
2250	-----	0.10	-----	-----	-----	0.04	-----	PCMC = 79 OPP = 54
2255	nd	nd	nd	nd	nd	nd	nd	nd
2266	8.34	0	15.29	0	0	0	0	0
2289	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	-----
2295	-----	-----	-----	-----	-----	-----	-----	-----
2301	ND	ND	ND	ND	ND	ND	ND	-----
2310	Not detected	Not detected	Not detected	Not detected	Not detected	Not detected	Not detected	Not detected
2311	Not Detected	Not Detected	Not Detected	Not Detected	Not Detected	Not Detected	Not Detected	Not Detected
2347	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	-----
2350	< 0.125	< 0.125	< 0.125	< 0.125	< 0.125	< 0.125	< 0.125	< 0.125
2352	-----	-----	-----	-----	-----	-----	-----	-----
2357	ND	ND	ND	ND	ND	ND	ND	ND
2358	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	N/A
2363	ND	ND	ND	ND	ND	ND	ND	ND
2365	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	-----
2366	-----	-----	-----	-----	-----	-----	-----	-----
2374	-----	-----	-----	-----	-----	-----	-----	-----
2375	-----	-----	-----	-----	-----	-----	-----	-----
2378	-----	-----	-----	-----	-----	-----	-----	-----
2379	Not detected	Not detected	Not detected	Not detected	Not detected	Not detected	Not detected	Not tested
2380	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	-----
2382	-----	-----	-----	-----	-----	-----	-----	-----
2386	<0,1	<0,1	<0,1	<0,1	<0,1	<0,1	<0,1	<0,1
2390	-----	-----	-----	-----	-----	-----	-----	PCMC = 51.68
2410	-----	-----	-----	-----	-----	-----	-----	-----
2429	ND	ND	ND	ND	ND	ND	ND	ND
2455	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	-----
2497	-----	2.387	-----	-----	-----	-----	-----	-----
2500	-----	-----	-----	-----	-----	-----	-----	-----
2504	n.d.	n.d.	n.d.	n.d.	n.d.	<0.10	n.d.	n.d.
2511	-----	-----	-----	-----	-----	-----	-----	-----
2561	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05
2563	ND	ND	ND	ND	ND	ND	ND	ND
2569	ND (<0.5)	ND (<0.5)	ND (<0.5)	ND (<0.5)	ND (<0.5)	ND (<0.5)	ND (<0.5)	ND (<0.5)
2590	-----	-----	-----	-----	-----	-----	-----	-----
2591	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	OPP = 12.275
2592	-----	-----	-----	-----	-----	-----	-----	-----
2605	ND	ND	ND	ND	ND	ND	ND	ND
2612	< 0.5	5.8817	< 0.5	< 0.5	< 0.5	< 0.5	< 0.5	----- PCMC = 117.50
2644	-----	-----	-----	-----	-----	-----	-----	OPP = 95.95
2695	-----	-----	-----	-----	-----	-----	-----	-----
2703	0	5.207	0	0	0	0	0	0
2705	-----	-----	-----	-----	-----	-----	-----	-----
2711	<1	<1	<1	2.08	<1	<1	<1	<1
2719	-----	-----	-----	-----	-----	-----	-----	-----

lab	2,3,4,5-TeCP	2,3,4,6-TeCP	2,3,4-TrCP	2,3,5-TrCP	2,3,6-TrCP	2,4,5-TrCP	3,4,5-TrCP	Other CP
2734	-----	-----	-----	-----	-----	-----	-----	-----
2756	-----	-----	-----	-----	-----	-----	-----	-----
2791	ND	ND	ND	ND	ND	ND	ND	-----
2806	-----	-----	-----	-----	-----	-----	-----	-----
2812	-----	-----	-----	-----	-----	-----	-----	-----
2877	-----	0.4241	-----	0.6446	0.6847	-----	0.6034	-----
2881	-----	-----	-----	-----	-----	-----	-----	-----
3116	-----	-----	-----	-----	-----	-----	-----	-----
3146	-----	-----	-----	-----	-----	12.20	-----	-----
3150	<0,1	<0,1	<0,1	<0,1	<0,1	<0,1	<0,1	<0,1
3153	-----	-----	-----	-----	-----	-----	-----	-----
3154	-----	-----	-----	-----	-----	-----	-----	-----
3160	-----	-----	-----	-----	-----	-----	-----	-----
3172	< 0.05	< 0.05	< 0.05	< 0.05	< 0.05	< 0.05	< 0.05	< 0.05
3197	ND	ND	ND	ND	ND	ND	ND	ND
3199	-----	-----	-----	-----	-----	-----	-----	OPP = 31.6
3210	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
3218	-----	-----	-----	-----	-----	-----	-----	-----
3228	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	na
3237	-----	-----	-----	-----	-----	-----	-----	OPP = 95.3
3243	n.d.	0.063	0.09	n.d.	n.d.	n.d.	n.d.	n.d.

Lab 2266: possibly reported as 2,3,5,6-TeCP and 2,4,6-TrCP respectively?

APPENDIX 3
Analytical Details

lab	ISO17025 accr.	Sample preparation	Final estimated particle size	Release technique	Extraction technique	Sample intake (g)
210	No	Further Cut		Steam distillation	---	
230	Yes	Further Cut		Steam distillation	---	1 g
551	---	---		---	---	
623	Yes	Used as received		Ultrasonic extraction	Ultrasonic extraction	1 gram
2115	Yes	Used as received	0.5cm x0.5cm	Steam distillation	---	0.5
2118	No	Further Cut	2 mm	Steam distillation	---	0.6
2165	Yes	Used as received	1g, 5mm*5mm	Steam distillation	Liquid-liquid extraction.	1
2172	Yes	Further Cut	3mm*3mm	acetone extract	Ultrasonic extraction	1g
2217	Yes	Further Cut	2 x 3 mm	KOH extraction	Ultrasonic extraction	1 g
2250	Yes	Used as received	5 x 5 mm	Other	Ultrasonic extraction	0.5 g
2255	Yes	Further Cut	2x3 mm	KOH Extraction	Ultrasonic extraction	0.5
2266	Yes	Used as received		Steam distillation	Soxhlet / AES extraction	1g
2289	Yes	Further Cut	2mm*2mm	Steam distillation	---	1.0g
2295	Yes	Further Cut		Other	Ultrasonic extraction	1 gram
2301	Yes	Used as received	0.5cm x 0.5cm	Other	Ultrasonic extraction	1
2310	Yes	Further Cut	3mm x 3mm	Steam distillation	Other	1 gram
2311	Yes	Further Cut	3mm x 3mm	Steam distillation	Soxhlet / AES extraction	0.5
2347	Yes	---		---	---	
2350	No	Further Cut	about 3 X 3	Steam distillation	---	2 g
2352	Yes	Further Cut	3mm*3mm	Steam distillation	Derivative	0.5g
2357	Yes	Further Cut	3mm*3mm	Steam distillation	Other	0.5g
2358	Yes	---		---	---	
2363	Yes	Used as received	5*5mm	Steam distillation	Other	1g
2365	Yes	Used as received	Used as received	Steam distillation	No more treatment	1 g
2366	Yes	Further Grinded	3mm*3mm	Steam distillation	two-phase extraction by liquid separation funnel	0.5g
2374	Yes	Used as received	0.5-08mm	Steam distillation	Soxhlet / AES extraction	0.5g
2375	Yes	Further Cut	2 mm x 2 mm	Steam distillation	Soxhlet / AES extraction	1 gr
2378	Yes	Further Cut	3mm*3mm	Steam distillation	Derivative	0.5g
2379	No	Further Cut	3 x 3 mm.	Steam distillation	Liquid Liquid Extraction	1 g
2380	Yes	Used as received	3X3 mm	Steam distillation	Liquid-Liquid Extraction	0.2 g
2382	Yes	Further Cut	less than 5*5mm	Steam distillation	Other	0.5g
2386	Yes	Further Cut	3x3mm	KOH extraction	Ultrasonic extraction	0,5
2390	Yes	Used as received	3x3mm	Alkaline digestion	Ultrasonic extraction	1.0069 g
2410	Yes	Further Cut	2 mm x 2 mm	Steam distillation	Other	1 g
2429	Yes	Used as received	5mm*5mm	Steam distillation	liquid-liquid extraction	2.0000
2455	Yes	Further Cut		Steam distillation was skipped	Ultrasonic extraction	1.0084 & 1.0269 g
2497	Yes	Used as received		Steam distillation was skipped	Ultrasonic extraction	0.5
2500	Yes	Used as received	5mm x 5mm	Steam distillation was skipped	Ultrasonic extraction	2g
2504	Yes	Further Cut	2 x 2 mm	Heating block	Heating block	0.5 grams
2511	---	---		---	---	
2561	Yes	Further Cut	2 x 2 mm in size	Steam distillation	liquid liquid extraction	1 g
2563	Yes	Used as received		Steam distillation was skipped	Soxhlet / AES extraction	1.5g
2569	Yes	Further Cut	3X3 mm	Steam distillation	Soxhlet / AES extraction	1gm
2590	Yes	Used as received		Steam distillation	---	1 g
2591	No	Further Cut		ultrasonic extraction	Ultrasonic extraction	1 gram
2592	---	---		---	---	
2605	Yes	Used as received		Steam distillation	Liquid Liquid extraction	1.000g
2612	Yes	Used as received	5x5 mm	Steam distillation	Soxhlet / AES extraction	approx. 1 g
2644	No	Used as received		Steam distillation was skipped	Ultrasonic extraction	1 g
2695	Yes: PCP only	Used as received	about 3-5 mm	Steam distillation	---	1 gram
2703	Yes	Used as received	about 7mm square	Steam distillation	Other	1g
2705	Yes	Used as received		Other	Soxhlet / AES extraction	0.265
2711	Yes	Used as received	5 mm ca	aqueous KOH 1M	Ultrasonic extraction	1.03
2719	Yes	Further Cut	< 2 mm	Other	Other	0.5g
2734	---	---		---	---	
2756	---	---		---	---	
2791	Yes	Used as received	as received	Steam distillation	Acetylation followed by Liquid liquid extraction	1
2806	No	---		---	---	
2812	No	Further Cut	5x5	Steam distillation	Ultrasonic extraction	2 gr
2877	No	Used as received		Steam distillation	Liquid liquid extraction	
2881	Yes	Used as received		Steam distillation	Ultrasonic extraction	1.6981g
3116	Yes	Used as received	5mm x 5mm	Other	Ultrasonic extraction	1 gram

lab	ISO17025 accr.	Sample preparation	Final estimated particle size	Release technique	Extraction technique	Sample intake (g)
				extract with KOH/Hexane	extract with KOH/Hexane	
3146	Yes	Used as received		16 h 90 °C	16 h 90 °C	0,5
3150	Yes	Used as received		KOH-extraction	Ultrasonic extraction	0,5
3153	Yes	Further Cut	3mm x 3mm	Steam distillation	Liquid-Liquid Extraction	0.5g
3154	Yes	Used as received		---	Ultrasonic extraction	1
3160	No	Further Cut	4mm	Steam distillation	liquid-liquid extraction	0,8g
3172	---	---		---	---	
3197	Yes	Used as received	5*5 mm	Steam distillation	Soxhlet / AES extraction	1 gram
3199	No	Used as received	6x6mm.	KOH/acetic anhydride	Ultrasonic extraction	1.0131g., 1.0032g.
3210	Yes	Further Cut	3 mmm	Steam distillation was skipped	Ultrasonic extraction	1 g
3218	Yes	Used as received	/	Steam distillation	mechanical shaker	0.5g
3228	Yes	Used as received	5mm*5mm	Steam distillation	liquid-liquid extraction	1g
3237	No	Used as received	Used as received	Steam distillation	Soxhlet / AES extraction	1 g
3243	Yes	Further Cut	0,5 cm x 0,5 cm	Other	Ultrasonic extraction	3 gram

Lab 2561 remarked: Sample extracted by steam distillation. Distillate concentrated onto SPE cartridge, eluted and then chlorinated phenols separated by liquid liquid extraction.

APPENDIX 4

Number of participants per country

2 labs in	BANGLADESH
1 lab in	BELGIUM
1 lab in	BRAZIL
1 lab in	ETHIOPIA
2 labs in	FRANCE
8 labs in	GERMANY
3 labs in	HONG KONG
1 lab in	HUNGARY
5 labs in	INDIA
2 labs in	INDONESIA
10 labs in	ITALY
2 labs in	KOREA
1 lab in	LUXEMBOURG
1 lab in	MAURITIUS
1 lab in	MOROCCO
17 labs in	P.R. of CHINA
1 lab in	PAKISTAN
1 lab in	POLAND
2 labs in	SPAIN
2 labs in	THAILAND
1 lab in	TUNISIA
5 labs in	TURKEY
2 labs in	U.S.A.
2 labs in	UNITED KINGDOM
1 lab in	VIETNAM

APPENDIX 5

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
W = test result withdrawn on request of participant
ex = test result excluded from statistical evaluation
n.a. = not applicable
n.e. = not evaluated
n.d. = not detected
fr. = first reported

Literature:

1 iis Interlaboratory Studies: Protocol for the Organisation, Statistics and Evaluation, June 2018
2 Oeko-Tex® Leather Standard; January 2019
3 Directive 94/783/EC
4 Impacts of Environmental Standards and requirements in EU Countries, August 1999
5 Horwitz, Journal of AOAC International, 79-3 (1996)
6 P.L. Davies, Fr Z. Anal. Chem., 351, 513, (1988)
7 W.J. Conover, Practical; Nonparametric Statistics, J. Wiley&Sons. NY,302, (1971)
8 ISO 5725:86
9 ISO 5725:94, parts 1-6
10 ISO105 E4:94
11 ISO14184-1:94
12 ISO13528:05
13 M. Thompson and R. Wood, J. AOAC Int., 76, 926, (1993)
14 Analytical Methods Committee, Technical brief, No 4, January 2001.
15 P.J. Lowthian and M. Thompson, The Royal Society of Chemistry, Analyst, 127, 1359-1364, (2002)
16 Official Journal of the European Communities L133/29: May 2002
17 Bernard Rosner, Percentage Points for a Generalized ESD Many-Outlier Procedure, Technometrics, 25(2), 165-172, (1983)
18 iis memo 1601, Precision data of OPP/PCP in textile (2016)