Results of Proficiency Test
Chlorinated Phenols in Leather
May 2020

Organized by: Institute for Interlaboratory Studies
Spijkenisse, the Netherlands

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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 and leather products on a voluntary basis. Well-known Ecolabelling organizations are OekoTex® and Bluesign®.

Since 2016 the Institute for Interlaboratory Studies (iis) organizes a proficiency test for the determination of 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 2019/2020 it was decided to continue the proficiency test for the analysis of Chlorinated Phenols in Leather.

In this interlaboratory study 70 laboratories in 20 different countries registered for participation. See appendix 4 for the number of participating participants per country. In this report, the results of this 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 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 which is positive on some Chlorophenols and labelled #20590. 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 brown leather positive on Chlorophenols was obtained from a third-party laboratory. After cutting and homogenization 100 small bags were filled with approximately 3 grams each and labelled #20590.
The homogeneity of the subsamples was checked by the determination of PCP and 2,3,4,5-TeCP in accordance with an in-house test method on ten stratified randomly selected subsamples.

	PCP in mg/kg	2,3,4,5-TeCP in mg/kg
Sample #20590-1	18.0	17.3
Sample #20590-2	16.7	16.3
Sample #20590-3	17.5	16.7
Sample #20590-4	18.4	16.5
Sample #20590-5	16.9	17.0
Sample #20590-6	18.3	15.9
Sample #20590-7	17.8	16.6
Sample #20590-8	18.4	17.2
Sample #20590-9	17.2	15.8
Sample #20590-10	17.4	16.2

Table 1: homogeneity test results of subsamples #20590

From the above test results the repeatabilities were 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	2,3,4,5-TeCP in mg/kg
r (observed)	1.7	1.4
reference method	iis memo 1601	iis memo 1601
0.3 * R (reference method)	2.7	3.3

Table 2: evaluation of the repeatabilities of subsamples #20590.

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

To each of the participating laboratories one sample labelled #20590 was sent on April 15, 2020.

2.5 ANALYZES

The participants were requested to determine on sample #20590: 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 ISO5725, 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 some problems were encountered with the dispatch of the samples due to the COVID-19 pandemic. Ten participants reported after the final reporting date and five participants did not report any test results at all.
In total 65 participants reported 125 numerical results. Observed were 2 outlying test results, which is 1.6% of the numerical results. 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 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.

The test methods LFGB 82.02-8 and ISO17070:15 mention identical precision data for Pentachlorophenol (PCP). 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. No statistical outliers were observed. The calculated reproducibility is in agreement with the target reproducibility derived from the reproducibilities observed in previous iis PTs, iis memo 1601.

2,3,4,5-TeCP: The determination of this component was not problematic. Two statistical outliers were observed. However, the calculated reproducibility after rejection of the statistical outliers is in good 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 all other TeCPs and TCPs mentioned in paragraph 2.5. Therefore, no z-scores were calculated for these Chlorinated Phenols. The test results of these components are given in appendix 2.

4.2 PERFORMANCE EVALUATION FOR THE GROUP OF LABORATORIES

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

Component	unit	n	average	2.8 * sd	R(target)
PCP	mg/kg	64	14.82	8.81	10.12
2,3,4,5-TeCP	mg/kg	59	13.12	6.68	9.12

Table 3: reproducibilities of tests on sample #20590

Without further statistical calculations, it could be concluded that for PCP and 2,3,4,5-TeCP there is a good compliance of the group of participating laboratories with the target.

4.3 COMPARISON OF THE PROFICIENCY TEST OF MAY 2020 WITH PREVIOUS PTS

	May 2020	May 2019	April 2018	April 2017	April 2016
Number of reporting laboratories	65	73	72	72	74
Number of test results	125	205	127	107	110
Number of statistical outliers	2	4	4	2	3
Percentage of statistical outliers	1.6%	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 2020	May 2019	April 2018	2016 – 2017	Target 1.3 – 13 mg/kg
PCP	21%	26%	26%	36 - 41%	35 - 25%
2,3,4,5-TeCP	18%	n.e.	n.e.	n.e.	35 – 25%
2,3,5,6-TeCP	n.e.	26%	n.e.	n.e.	35 - 25%
2,4,6-TCP	n.e.	34%	29%	n.e.	35 - 25%

Table 5: developmement of the uncertainties over the years

The uncertainty for PCP observed in this PT has improved when compared with the previous PTs. The uncertainty for 2,3,4,5-TeCP is small in comparison with the uncertainties of the other components.

4.4 EVALUATION OF THE ANALYTICAL DETAILS

The test method ISO17070 is used by about 75% of the reporting participants and test method LFGB B82.02.8 is used by less than 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 for the reported answers. Based on the answers given by the participants the following can be summarized:

- About 85% of the reporting participants mentioned that they are accredited for the determination of the reported components.
- About 45% of the reporting participants used the sample as received and about 45% 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 25% of the reporting participants used Ultrasonic extraction and about 15% used Soxhlet/AES extraction as technique to extract the Chlorinated Phenols.
- About 80% of the reporting participants used a sample intake between 0.5 - 1 grams and less than 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 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 TeCP, 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.

6 CONCLUSION

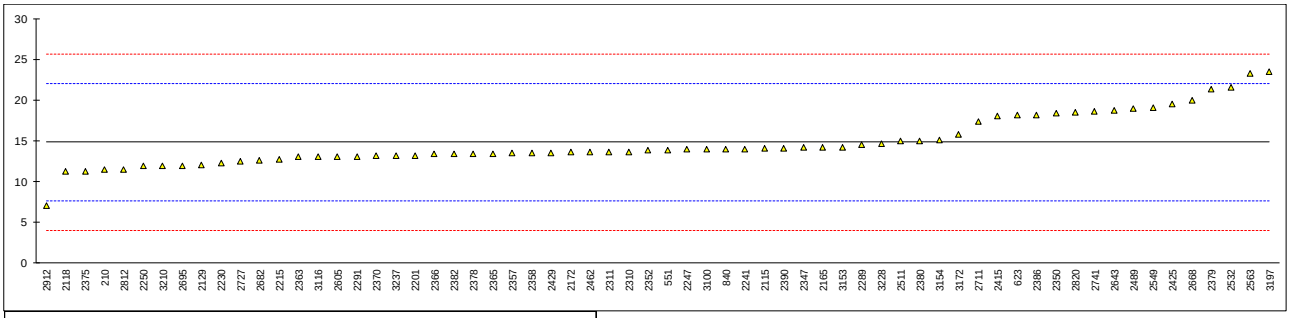
The majority of the participants has no problem with the determination of Pentachlorophenol and 2,3,4,5-Tetrachlorophenol in leather.
Each participating laboratory will have to evaluate its performance in this study and decide about any corrective actions if necessary.
Therefore, participation on a regular basis in this scheme could be helpful to improve the performance and thus increase of the quality of the analytical results.

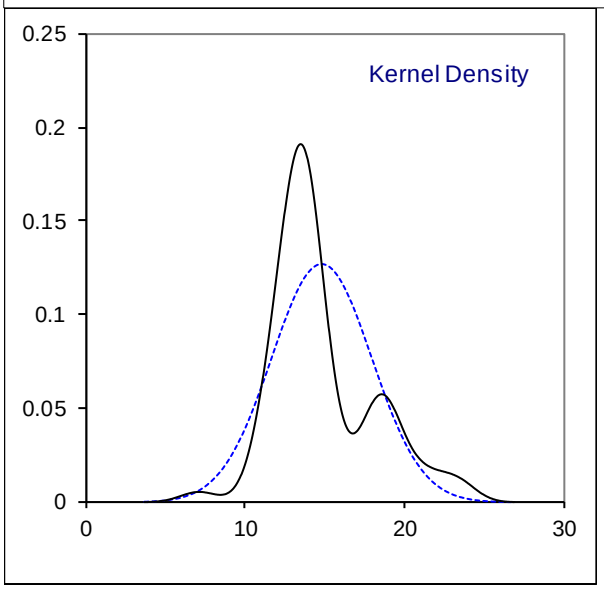
APPENDIX 1

Determination of Pentachlorophenol (PCP) on sample #20590; results in mg/kg

lab	method	value	mark	z(targ)	remarks
210	ISO17070	11.47		-0.93	
551	ISO17070	13.884		-0.26	
623	In house	18.17		0.93	
840	ISO17070	13.98		-0.23	
2115	ISO17070	14.12		-0.19	
2118	ISO17070	11.188		-1.00	
2129	In house	11.98		-0.79	
2165	ISO17070	14.2		-0.17	
2172	In house	13.63		-0.33	
2201	ISO17070	13.22		-0.44	
2215	ISO17070	12.7		-0.59	
2230	ISO17070	12.288		-0.70	
2241	ISO17070	13.99		-0.23	
2247	In house	13.92		-0.25	
2250	In house	11.9		-0.81	
2289	ISO17070	14.58		-0.07	
2291	ISO17070	13.1		-0.48	
2310	ISO17070	13.67		-0.32	
2311	ISO17070	13.66		-0.32	
2347	ISO17070	14.18		-0.18	
2350	LFGB B82.02.8	18.3359		0.97	
2352	ISO17070	13.82		-0.28	
2357	ISO17070	13.48		-0.37	
2358	ISO17070	13.515		-0.36	
2363	ISO17070	13.00		-0.50	
2365	ISO17070	13.43		-0.38	
2366	ISO17070	13.39		-0.40	
2370	In house	13.2		-0.45	
2375	ISO17070	11.2		-1.00	
2378	ISO17070	13.43		-0.38	
2379	ISO17070	21.3415		1.81	
2380	ISO17070	14.952		0.04	
2382	ISO17070	13.41		-0.39	
2386	In house	18.21		0.94	
2390	ISO17070	14.12		-0.19	
2415	ISO17070	18.07		0.90	
2425	In house	19.51		1.30	
2429	LFGB B82.02.8	13.56		-0.35	
2462	ISO17070	13.64		-0.33	
2489	ISO17070	19.0		1.16	
2511	ISO17070	14.935		0.03	
2532	ISO17070	21.57		1.87	
2538		-----		-----	
2549	ISO17070	19.01		1.16	
2561		-----		-----	
2563	ISO17070	23.2		2.32	
2590		-----		-----	
2605	ISO17070	13.08		-0.48	
2643	KS K0733	18.7		1.07	
2644		-----		-----	
2668	ISO17070	20.01		1.44	
2682	ISO17070	12.57		-0.62	
2695	ISO17070	11.95855		-0.79	
2711	ISO17070	17.4		0.71	
2713		-----		-----	
2727	ISO17070	12.4776		-0.65	
2741	In house	18.640		1.06	
2806		-----		-----	
2812	ISO17070	11.47		-0.93	
2820	ISO17070	18.5		1.02	
2912	ISO17070	7.1		-2.14	
3100	ISO17070	13.9333		-0.24	
3116	LFGB B82.02.8	13.00		-0.50	
3153	LFGB B82.02.8	14.22		-0.17	
3154	ISO17070	15.12		0.08	
3172	ISO17070	15.790		0.27	
3197	ISO17070	23.5		2.40	
3210	In house	11.9		-0.81	
3228	ISO17070	14.59		-0.06	
3237	ISO17070	13.2		-0.45	

normality	OK	
n	64	
outliers	0	
mean (n)	14.8175	
st.dev. (n)	3.14531	RSD = 21%
R(calc.)	8.8069	
st.dev.(iis memo 1601)	3.61340	
R(iis memo 1601)	10.1175	

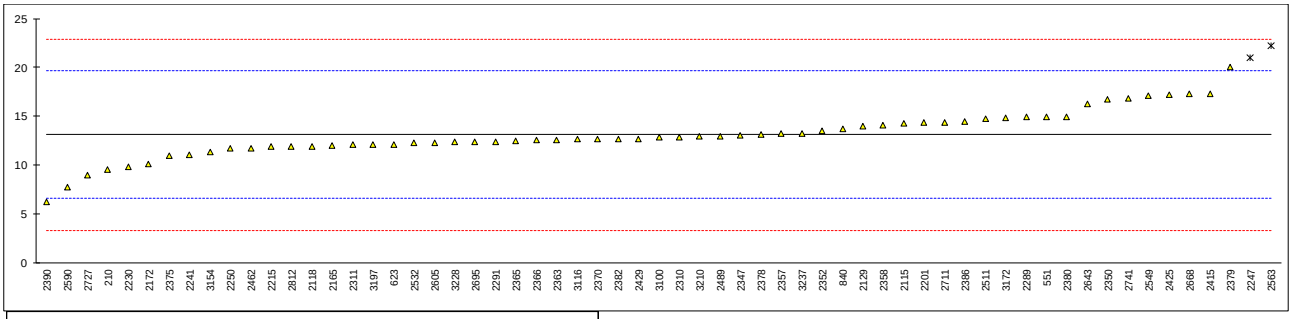


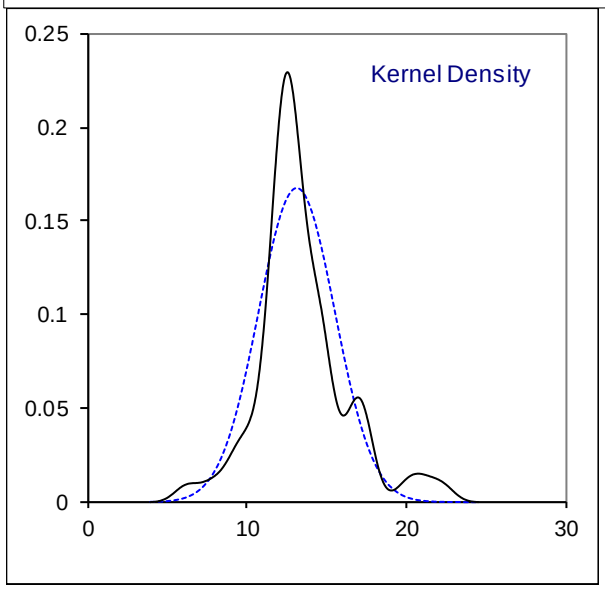


Determination of 2,3,4,5-Tetrachlorophenol (2,3,4,5-TeCP) on sample #20590; results in mg/kg

lab	method	value	mark	z(targ)	remarks
210	ISO17070	9.56		-1.09	
551	ISO17070	14.950		0.56	
623	In house	12.14		-0.30	
840	ISO17070	13.76		0.20	
2115	ISO17070	14.24		0.34	
2118	ISO17070	11.935		-0.36	
2129	In house	13.96		0.26	
2165	ISO17070	12.0		-0.34	
2172	In house	10.16		-0.91	
2201	ISO17070	14.34		0.37	
2215	ISO17070	11.9		-0.37	
2230	ISO17070	9.836		-1.01	
2241	ISO17070	11.11		-0.62	
2247	In house	20.96	DG(0.05)	2.41	
2250	In house	11.7		-0.44	
2289	ISO17070	14.93		0.56	
2291		12.4		-0.22	
2310	ISO17070	12.84		-0.09	
2311	ISO17070	12.08		-0.32	
2347	ISO17070	13.07		-0.01	
2350	LFGB B82.02.8	16.7131		1.10	
2352	ISO17070	13.50		0.12	
2357	ISO17070	13.20		0.03	
2358	ISO17070	14.065		0.29	
2363	ISO17070	12.60		-0.16	
2365	ISO17070	12.49		-0.19	
2366	ISO17070	12.57		-0.17	
2370	In house	12.7		-0.13	
2375	ISO17070	11.0		-0.65	
2378	ISO17070	13.13		0.00	
2379	ISO17070	20.0405		2.12	
2380	ISO17070	14.952		0.56	
2382	ISO17070	12.72		-0.12	
2386	In house	14.49		0.42	
2390	ISO17070	6.24		-2.11	
2415	ISO17070	17.30		1.28	
2425	In house	17.24		1.27	
2429	LFGB B82.02.8	12.72		-0.12	
2462	ISO17070	11.74		-0.42	
2489	ISO17070	13.0		-0.04	
2511	ISO17070	14.736		0.50	
2532	ISO17070	12.25		-0.27	
2538		-----		-----	
2549	ISO17070	17.11		1.23	
2561		-----		-----	
2563	ISO17070	22.2	DG(0.05)	2.79	
2590	ISO17070	7.81		-1.63	
2605	ISO17070	12.34		-0.24	
2643	KS K0733	16.3		0.98	
2644		-----		-----	
2668	ISO	17.28		1.28	
2682		-----		-----	
2695	ISO17070	12.38492		-0.23	
2711	ISO17070	14.4		0.39	
2713		-----		-----	
2727	ISO17070	9.0160		-1.26	
2741	In house	16.845		1.14	
2806		-----		-----	
2812	ISO17070	11.91		-0.37	
2820		-----		-----	
2912		-----		-----	
3100	ISO17070	12.8346		-0.09	
3116	LFGB B82.02.8	12.64		-0.15	
3153		-----		-----	
3154	ISO17070	11.34		-0.55	
3172	ISO17070	14.825		0.52	
3197	ISO17070	12.1		-0.31	
3210	In house	12.99		-0.04	
3228	ISO17070	12.36		-0.23	
3237	ISO17070	13.2		0.03	

normality	suspect	
n	59	
outliers	2	
mean (n)	13.1185	
st.dev. (n)	2.38599	RSD = 18%
R(calc.)	6.6808	
st.dev.(iis memo 1601)	3.25807	
R(iis memo 1601)	9.1226	





APPENDIX 2
Determination of Other Chlorinated Phenols on sample #20590; results in mg/kg

Abbreviations of components
2,3,4,6-TeCP = 2,3,4,6-Tetrachlorophenol
2,3,5,6-TeCP = 2,3,5,6-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
2,4,6-TrCP = 2,4,6-Trichlorophenol
3,4,5-TrCP = 3,4,5-Trichlorophenol
Other CP = Other Chlorinated Phenols

lab	2,3,4,6-TeCP	2,3,5,6-TeCP	2,3,4-TrCP	2,3,5-TrCP	2,3,6-TrCP	2,4,5-TrCP	2,4,6-TrCP	3,4,5-TrCP	Other CP
210	-----	-----	-----	-----	-----	-----	-----	-----	-----
551	-----	-----	-----	-----	-----	-----	-----	-----	-----
623	0.07	0.16	ND	ND	ND	ND	ND	ND	ND
840	not detected	not detected	not detected	not detected	not detected	not detected	not detected	not detected	-----
2115	0.02	0.03	0.024	0.023	0.01	0.01	0.019	0.02	-----
2118	0	0.161	0	0	0	0	0	0	0
2129	<0,05	<0,05	<0,1	<0,1	<0,1	<0,1	<0,1	<0,1	<0,1
2165	<RL	<RL	<RL	<RL	<RL	<RL	<RL	<RL	-----
2172	-----	-----	-----	-----	-----	-----	-----	-----	-----
2201	ND	ND	ND	ND	ND	ND	ND	ND	ND
2215	ND	ND	ND	ND	ND	ND	ND	ND	ND
2230	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	1.215
2241	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
2247	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05
2250	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05
2289	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05
2291	ND	ND	ND	ND	ND	ND	ND	ND	ND
2310	not detected	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	not detected
2347	<0.5	<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	<0.125
2352	-----	-----	-----	-----	-----	-----	-----	-----	-----
2357	-----	-----	-----	-----	-----	-----	-----	-----	-----
2358	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
2363	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	NA
2365	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05
2366	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5
2370	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05
2375	-----	-----	-----	-----	-----	-----	-----	-----	-----
2378	-----	-----	-----	-----	-----	-----	-----	-----	-----
2379	-----	-----	-----	-----	-----	-----	-----	-----	-----
2380	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05
2382	£¼0.050	£¼0.050	£¼0.050	£¼0.050	£¼0.050	£¼0.050	£¼0.050	£¼0.050	£¼0.050
2386	<0,1	<0,1	<0,1	<0,1	<0,1	<0,1	<0,1	<0,1	<0,1
2390	-----	-----	-----	-----	-----	-----	-----	-----	1.796
2415	-----	-----	-----	-----	-----	-----	-----	-----	-----
2425	not detected	not detected	not detected	not detected	not detected	not detected	not detected	not detected	not detected
2429	ND	ND	ND	ND	ND	ND	ND	ND	ND
2462	<0.3	<0.3	<0.3	<0.3	<0.3	<0.3	<0.3	<0.3	-----
2489	-----	-----	-----	-----	-----	-----	-----	-----	-----
2511	-----	-----	-----	-----	-----	-----	-----	-----	-----
2532	-----	-----	-----	-----	-----	-----	-----	-----	-----
2538	-----	-----	-----	-----	-----	-----	-----	-----	-----
2549	-----	-----	-----	-----	-----	-----	-----	-----	-----
2561	-----	-----	-----	-----	-----	-----	-----	-----	-----
2563	0.19	0.18	<0,2	<0,2	n.d.	n.d	n.d	n.d.	-----
2590	-----	-----	-----	-----	-----	-----	-----	-----	-----
2605	<0.25	<0.25	<0.25	<0.25	<0.25	<0.25	<0.25	<0.25	<0.25
2643	-----	-----	-----	-----	-----	-----	-----	-----	-----
2644	-----	-----	-----	-----	-----	-----	-----	-----	-----
2668	not detected	not detected	not detected	not detected	not detected	not detected	not detected	not detected	not detected
2682	-----	-----	-----	-----	-----	-----	-----	-----	-----
2695	-----	-----	-----	-----	-----	-----	-----	-----	-----
2711	-----	-----	-----	-----	-----	-----	-----	-----	-----
2713	-----	-----	-----	-----	-----	-----	-----	-----	-----
2727	-----	-----	-----	-----	-----	-----	-----	-----	-----
2741	0.091	0.075	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05
2806	-----	-----	-----	-----	-----	-----	-----	-----	-----
2812	-----	-----	-----	-----	-----	-----	-----	-----	-----

lab	2,3,4,6-TeCP	2,3,5,6-TeCP	2,3,4-TrCP	2,3,5-TrCP	2,3,6-TrCP	2,4,5-TrCP	2,4,6-TrCP	3,4,5-TrCP	Other CP
2820	-----	-----	-----	-----	-----	-----	-----	-----	-----
2912	-----	6.4	-----	-----	-----	-----	-----	-----	1
3100	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05
3116	-----	-----	-----	-----	-----	-----	-----	-----	-----
3153	-----	-----	-----	-----	-----	-----	-----	-----	-----
3154	-----	-----	-----	-----	-----	-----	-----	-----	-----
3172	< 0.05	< 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	ND
3210	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
3228	<RL	<RL.	<RL	<RL	<RL	<RL	<RL	<RL	-----
3237	-----	-----	-----	-----	-----	-----	-----	-----	-----

APPENDIX 3 Analytical Details

lab	ISO17025 accr.	Sample preparation	Final estimated particle size	Release technique	Extraction technique	Sample intake (g)
210	No	---	---	---	---	---
551	Yes	---	---	---	Ultrasonic extraction	---
623	Yes	Further Cut	3x3 mm	Other	Ultrasonic extraction	1
840	Yes	Further Cut	3x3 mm	Steam distillation	Other	0.5
2115	Yes	Used as received	1 mm	Steam distillation skipped	Soxhlet / AES extraction	1
2118	No	Used as received	---	Steam distillation	---	0.75
2129	Yes	Used as received	---	Other	Other	0.5
2165	Yes	Further Cut	3x3 mm	Steam distillation	Other	1
2172	Yes	Used as received	3x3 mm	Ultrasonic extraction	Ultrasonic extraction	1
2201	Yes	Further Cut	2x3 mm	Steam distillation	Shaker	1
2215	Yes	Used as received	---	Steam distillation	---	1
2230	Yes	Used as received	---	Steam distillation skipped	Ultrasonic extraction	1
2241	Yes	Used as received	0.5 - 1.0 mm	Steam distillation	Steam distillation	0.5
2247	Yes	Used as received	<5 mm	KOH extraction	Ultrasonic extraction	0.5
2250	Yes	Used as received	5 x 5 mm	Other	Ultrasonic extraction	0.5
2289	Yes	Further Cut	3 mm	Steam distillation	Liquid – Liquid extraction	1
2291	No	Used as received	---	Steam distillation	Other	---
2310	Yes	Further Cut	3x3 mm	Steam distillation	Shaker	1
2311	Yes	Further Cut	3x3 mm	Steam distillation	Soxhlet / AES extraction	0.5
2347	Yes	Further Cut	---	---	---	---
2350	No	Further Cut	---	Steam distillation	Soxhlet / AES extraction	0.5, 2
2352	Yes	Further Cut	3x3 mm	Steam distillation	Ultrasonic extraction	0.5
2357	---	---	---	---	---	---
2358	Yes	Used as received	---	Steam distillation	Other	---
2363	Yes	Further Cut	3x3 mm	Steam distillation	Steam distillation	1
2365	Yes	Used as received	3.5x3.5mm-	Steam distillation	---	1
2366	No	Further Cut	2x2 mm	Steam distillation	Other	0.5
2370	Yes	Further Cut	0.5 x 0.5 cm	KOH release	KOH release	1.5
2375	Yes	Used as received	4x4 mm	Steam distillation	---	0.5
2378	Yes	Used as received	4x4 mm	Steam distillation	Soxhlet / AES extraction	1
2379	No	Further Cut	3x3 mm	Steam distillation	Other	1
2380	Yes	Used as received	2-3 X 2-3 mm	Steam distillation	Other	1
2382	Yes	Further Cut	5x5 mm	Steam distillation	Shaker	0.5
2386	Yes	Used as received	3x3 mm	KOH extraction	Ultrasonic extraction	0.334
2390	Yes	Further Cut	3x3 mm	Steam distillation skipped	Ultrasonic extraction	0.5
2415	Yes	Used as received	3x3 mm	Liquid-liquid extraction	Liquid-liquid extraction	0.5
2425	Yes	Further Cut	2x3 mm	Incubation 12 hrs at 90°C	Shaking 1 hr at 280 rpm	1
2429	Yes	Further Cut	5x5 mm	Steam distillation	Ultrasonic extraction	1
2462	Yes	Further Cut	2x2 mm	Steam distillation	Shaker	1
2489	Yes	Further Cut	2x2 mm	Steam distillation	Shaker	1
2511	---	---	---	---	---	---
2532	Yes	Further Cut	<3x3 mm	Steam distillation	Soxhlet / AES extraction	1
2538	---	---	---	---	---	---
2549	Yes	Used as received	<1 mm	KOH extraction	liquid/liquid extraction	1
2561	---	---	---	---	---	---
2563	Yes	Used as received		Other	Soxhlet / AES extraction	~1,5
2590	---	---	---	---	---	---
2605	Yes	Used as received	--	Steam distillation	Liquid-Liquid extraction	0.5
2643	Yes	Further Cut	about 1mm	Other	Ultrasonic extraction	0.5
2644	---	---	---	---	---	---
2668	Yes	Further Cut	---	KOH extraction 16 hrs	Solvent extraction	0.5
2682	Yes	Further Cut	2 - 3 mm	Soxhlet Extraction	Soxhlet / AES extraction	1
2695	Yes	Used as received	--	Steam distillation	Liquid-Liquid extraction	1
2711	No	Further Cut	ca. 3mm	Steam distillation	Liquid-Liquid extraction	1
2713	---	---	---	---	---	---
2727	Yes	Used as received	---	Steam distillation	---	---
2741	Yes	Further Cut	3x3 mm	KOH extraction	KOH extraction	0.5
2806	---	---	---	---	---	---
2812	Yes	---	---	Other	Ultrasonic extraction	1
2820	Yes	Used as received	5 mm	Steam distillation	---	0.5
2912	Yes	Used as received	---	Other	Ultrasonic extraction	1
3100	Yes	Used as received	3mm~5mm	Steam distillation	Other	0.5
3116	Yes	Used as received	5x5 mm	Steam distillation skipped	Ultrasonic extraction	1
3153	Yes	Further Cut	4x4 mm	Steam distillation	Other	0.2
3154	Yes	Used as received	---	Steam distillation	---	1
3172	Yes	Further Cut	2x2 mm	Acetone extraction	Ultrasonic extraction	0.5
3197	Yes	Used as received	5x5 mm	Steam distillation	Soxhlet / AES extraction	1
3210	Yes	Further Cut	2mm²	Steam distillation skipped	Ultrasonic extraction	1
3228	Yes	Used as received	5x5 mm	Steam distillation	liquid/liquid extraction	1
3237	Yes	Used as received	2mm	Steam distillation	liquid/liquid extraction	0.5

APPENDIX 4

Number of participants per country

2 labs in BANGLADESH
1 lab in BELGIUM
1 lab in BRAZIL
1 lab in FRANCE
6 labs in GERMANY
3 labs in HONG KONG
7 labs in INDIA
1 lab in INDONESIA
9 labs in ITALY
1 lab in MOROCCO
20 labs in P.R. of CHINA
2 labs in PAKISTAN
1 lab in PORTUGAL
2 labs in SOUTH KOREA
2 labs in TAIWAN
1 lab in THAILAND
1 lab in TUNISIA
5 labs in TURKEY
1 lab in UNITED KINGDOM
3 labs 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 OekoTex® 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 ISO5725:86
9 ISO5725:94, 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)