**Institute for
Interlaboratory Studies**

Results of Proficiency Test
Chlorinated Phenols
in Leather/Footwear
April 2022

CONTENTS

Appendices:

1   INTRODUCTION

Products containing Pentachlorophenol (PCP) may form highly toxic substances when they are incinerated. PCP is also a suspected 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 OEKO-TEX® and Bluesign®.

Since 2016 the Institute for Interlaboratory Studies (iis) organizes a proficiency scheme for the determination of Chlorinated Phenols in Leather/Footwear every year. During the annual proficiency testing program 2021/2022 it was decided to continue the proficiency test for the determination of Chlorinated Phenols in Leather/Footwear.

In this interlaboratory study 70 laboratories in 23 countries registered for participation, see appendix 4 for the number of participants per country. In this report the results of the Chlorinated Phenols in Leather/Footwear 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 (PT). 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 containing some Chlorinated Phenols of 3 grams labelled #22585.
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 green leather containing some Chlorinated Phenols was selected. The batch was cut into small pieces and after homogenization 100 small plastics bags were filled with approximately 3 grams each and labelled #22585.
The homogeneity of the subsamples was checked by determination of 2,4,6-Trichlorophenol in accordance with ISO17070 on 8 stratified randomly selected subsamples.

	2,4,6-Trichlorophenol in mg/kg
sample #22585-1	1.327
sample #22585-2	1.325
sample #22585-3	1.256
sample #22585-4	1.191
sample #22585-5	1.257
sample #22585-6	1.323
sample #22585-7	1.241
sample #22585-8	1.470

Table 1: homogeneity test result of subsamples #22585

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

	2,4,6-Trichlorophenol in mg/kg
r (observed)	0.236
reference method	iis memo 1601
0.3 x R (reference method)	0.383

Table 2: evaluation of the repeatability of subsamples #22585

The calculated repeatability is 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 of #22585 was sent on March 30, 2022.

2.5 ANALYZES

The participants were requested to determine Pentachlorophenol, all isomers of Tetra-, Tri-, Di- and Monochlorinated Phenols.
To ensure homogeneity it was requested not to use less than 0.5 gram per determination.
It was also requested to report if the laboratory was accredited for the determination of Chlorinated Phenols in Leather/Footwear 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 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 per determination in appendices 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 reanalyzes). Additional or corrected test results are used for data analysis and the original test results are placed under 'Remarks' in the result tables in appendices 1 and 2. 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 for proficiency testing in the report 'iis Interlaboratory Studies: Protocol for the Organisation, 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 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.
The assigned value is determined by consensus based on the test results of the group of participants after rejection of the statistical outliers and/or suspect data.

According to ISO13528 all (original received or corrected) results per determination were submitted to outlier tests. In the iis procedure for proficiency tests, outliers are detected prior to calculation of the mean, standard deviation and reproducibility. For small data sets, Dixon (up to 20 test results) or Grubbs (up to 40 test results) outlier tests can be used. For larger data sets (above 20 test results) Rosner's outlier test can be used. 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 averages and standard deviations.

For each assigned value the uncertainty was determined in accordance with ISO13528. Subsequently the calculated uncertainty was evaluated against the respective requirement based on the target reproducibility in accordance with ISO13528. 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. This 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 (dotted line) was projected over the Kernel Density Graph (smooth line) for reference. The Gauss curve is calculated from the consensus value and the corresponding standard deviation.

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 (derived from e.g. ISO or ASTM test methods), 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 were 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 result 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 test result tables in appendix 1.

Absolute values for z<2 are very common and absolute values for z>3 are very rare. Therefore, the usual interpretation of z-scores is as follows:

$$|z| < 1 \quad \text{good}$$
$$1 < |z| < 2 \quad \text{satisfactory}$$
$$2 < |z| < 3 \quad \text{questionable}$$
$$3 < |z| \quad \text{unsatisfactory}$$

4   EVALUATION

In this proficiency test some problems were encountered with the dispatch of the samples due to COVID-19 pandemic. Therefore, the reporting time on the data entry portal was extended with another week. Twelve participants reported test results after the extended reporting date and two other participants did not report any test results. Not all participants were able to report all tests requested.
In total 68 participants reported 119 numerical test results. Observed were 5 outlying test results, which is 4.2%. In proficiency tests, outlier percentages of 3% - 7.5% are quite normal.

Both data sets proved to have a normal Gaussian 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 in together with the original data in appendix 1. The abbreviations, used in these tables, are explained in appendix 5.

Test methods ISO17070:15 and LFGB 82.02-8 mention precision data for Pentachlorophenol. In 2016 iis investigated the reproducibilities of the determination of Pentachlorophenol in textile over 18 determinations in iis PTs conducted from 2004 until 2014. It was observed that the reproducibility as mentioned in ISO17070 is very strict. Therefore, a new target reproducibility on base of the iis PTs was determined and described in iis memo 1601. Although iis memo 1601 is based on iis PTs of Pentachlorophenol in Textile it is decided to use the estimated iis target reproducibility also for the determination of Pentachlorophenol in Leather. Furthermore, it is decided to use the estimated iis target reproducibility for other Chlorinated Phenol components determined in Leather as well.

Pentachlorophenol: The determination of this component was problematic for a number of laboratories. Five statistical outliers were observed. The calculated reproducibility after rejection of the statistical outliers is in agreement with the target reproducibility as derived from iis memo 1601.

2,4,6-Trichlorophenol: 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 as derived from iis memo 1601.

The majority of the participants agreed on a concentration near or below the limit of detection for all other Chlorinated Phenols mentioned in paragraph 2.5. Therefore, no z-scores were calculated for these Chlorinated Phenols. The reported 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 declared by the reference test method and the reproducibility as found for the group of participating laboratories. The number of significant test results, the average, the calculated reproducibility (2.8 * standard deviation) and the target reproducibility from reference methods are presented in the next table.

Component	unit	n	average	2.8 * sd	R(target)
Pentachlorinatedphenol	mg/kg	50	0.18	0.18	0.24
2,4,6-Trichlorophenol	mg/kg	64	0.90	0.75	0.93

Table 3: reproducibility of tests on sample #22585

Without further statistical calculations it can be concluded that there is a good compliance of the group of participating laboratories with the target reproducibilities.

4.3 COMPARISON OF THE PROFICIENCY TEST OF APRIL 2022 WITH PREVIOUS PTS

	April 2022	May 2021	May 2020	May 2019	April 2018
Number of reporting laboratories	68	70	65	73	72
Number of test results	119	70	125	205	127
Number of statistical outliers	5	1	2	4	4
Percentage of statistical outliers	4.2%	1.4%	1.6%	2.0%	3.1%

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.

	April 2022	May 2021	May 2020	2016 – 2019	Target *)
PCP	35%	31%	21%	26 - 41%	35 – 25%
2,3,4,5-TeCP	n.e.	n.e.	18%	n.e.	35 – 25%
2,3,5,6-TeCP	n.e.	n.e.	n.e.	26%	35 – 25%
2,4,6-TCP	30%	n.e.	n.e.	29 - 34%	35 – 25%

Table 5: development of the uncertainties over the years

* Concentration range 0.5 – 13 mg/kg respectively

The uncertainties observed in this PT are in line with previous PTs.

4.4 EVALUATION OF THE ANALYTICAL DETAILS

Test method ISO17070 is used by about 60% of the reporting participants and test method LFGB B82.02.8 is used by about 5% of the participants. Test methods ISO17070 and LFGB 82.02-8 describe a similar sample pathway to determine PCP. About 20% of the reporting participants mentioned to have used an in-house test method.

For this PT also some analytical details were requested, see appendix 3 for the reported details. Based on the answers given by the participants the following can be summarized:
- About 75% of the participants mentioned that they are accredited for the determination of the reported components.
- About 40% of the participants used the sample as received and about 60% did further cut or grind the sample.
- About 80% of the participants used a sample intake between 0.5 - 1 grams and about 10% used more than 1 grams as sample intake.
- About 60% of the participants used steam distillation as technique to release the Chlorinated Phenols and about 20% used KOH as extraction technique.

- About 20% of the participants used Ultrasonic extraction and about 50% used Mechanical Shaking as technique to extract the Chlorinated Phenols.

The calculated reproducibilities are in agreement with the estimated reproducibilities of the reference method, therefore no separate statistical analysis has been performed.

5   DISCUSSION

When the results of this proficiency test were compared to the OEKO-TEX® Leather Standard (see Table 6) it was noticed that not all participants would make identical decisions about the acceptability of the leather for Chlorophenols.

	Baby in mg/kg	Direct skin contact in mg/kg	No direct skin contact in mg/kg	Decoration material in mg/kg
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: Oeko-Tex® Leather Standard specific limits for Chlorophenols

For Pentachlorophenol almost all participants would have accepted the leather for all classes. However, five participants would have rejected the leather for the class of Baby. For Trichlorophenol seven participants would have accepted the leather for all classes, while twenty-one participants would have rejected the leather for all classes.

6   CONCLUSION

The majority of the participants has no problem with the determination of Pentachlorophenol and 2,4,6-Trichlorophenol in Leather/Footwear.

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 #22585; results in mg/kg

lab	method	value	mark	z(targ)	remarks
210	ISO17070	0.15		-0.38	
551	LFGB B82.02.8	0.2996		1.36	
623	ISO17070	0.272		1.04	
2115	ISO17070	0.174		-0.10	
2129	ISO17070	0.460	R(0.05)	3.23	
2131	In house	0.03		-1.77	
2165	ISO17070	not detected		-----	
2247	DIN50009	0.20		0.21	
2250	In house	0.20		0.21	
2255	ISO17070	0.18		-0.03	
2265	DIN50009	0.28		1.14	
2289	ISO17070	0.2		0.21	
2293		-----		-----	
2297	ISO17070	0.19		0.09	
2301	ISO17070	0.31281	C	1.52	First reported 216.91 mg/kg
2310	LFGB B82.02.8	0.1		-0.96	
2311	ISO17070	0.0941		-1.03	
2330	ISO17070	0.196		0.16	
2347	ISO17070	0.17		-0.14	
2350	ISO17070	0.16		-0.26	
2357	ISO17070	0.181		-0.02	
2358	ISO17070	0.124		-0.68	
2363		-----		-----	
2365	ISO17070	0.182		0.00	
2366	In house	<0.50		-----	
2370	ISO17070	0.170		-0.14	
2373	ISO17070	0.183		0.01	
2375	ISO17070	0.072		-1.28	
2379	ISO17070	0.2792		1.13	
2380	ISO17070	0.152		-0.35	
2382	ISO17070	0.180		-0.03	
2386	In house	0.447	R(0.05)	3.08	
2390	In house	0.217		0.40	
2452	ISO17070	not detected		-----	
2489	ISO17070	0.18		-0.03	
2495	In house	0.120		-0.72	
2504	In house	0.275		1.08	
2511	ISO17070	0.2366		0.63	
2514	In house	0.17		-0.14	
2520	ISO17070	Less than 0.1		-----	
2532	ISO17070	0.27		1.02	
2561	ISO17070	0.231		0.57	
2569	ISO17070	0.2		0.21	
2573	ISO17070	0.21		0.32	
2590		-----		-----	
2605	ISO17070	0.18		-0.03	
2668	ISO17070	0.18		-0.03	
2695	ISO17070	0.0708		-1.30	
2703	In house	Not detected		-----	
2711	ISO17070	0	R(0.05)	-2.12	
2713	In house	0.422	R(0.05)	2.79	
2723	In house	not detected		-----	
2727	ISO17070	0.156		-0.31	
2734	ISO17070	not detected		-----	
2737		-----		-----	
2756	ISO17070	1.83	C,R(0.01)	19.16	First reported 2.54
2806	In house	0.2		0.21	
2977		0.08105		-1.18	
2979	ISO17070	Not detected		-----	
2980		-----		-----	
3003	DIN50009	0.1598		-0.26	
3116	LFGB B82.02.8	0.086		-1.12	
3154	DIN50009	0.275		1.08	
3172	ISO17070	0.2713		1.03	
3210	In house	0.14		-0.49	
3218	ISO17070	<0.050		-----	
3228	In house	0.18		-0.03	
3237		-----		-----	
3250	LFGB B82.02.8	0.2		0.21	
8005	ISO17070	0.095		-1.02	

normality	OK	
n	50	
outliers	5	
mean (n)	0.1823	
st.dev. (n)	0.06433	RSD = 35%
R(calc.)	0.1801	
st.dev.(iis memo 1601)	0.08600	
R(iis memo 1601)	0.2408	

Kernel Density
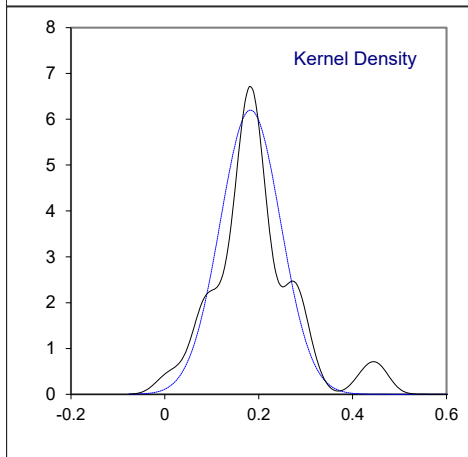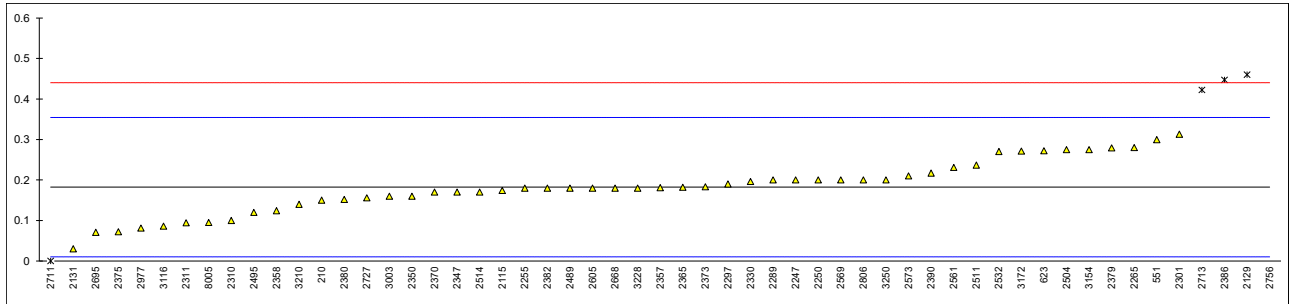
Determination of 2,4,6-Trichlorophenol on sample #22585; results in mg/kg

lab	method	value	mark	z(targ)	remarks
210	ISO17070	0.65		-0.74	
551	LFGB B82.02.8	0.8987		0.00	
623	ISO17070	0.657		-0.72	
2115	ISO17070	1.41		1.54	
2129	ISO17070	1.310		1.24	
2131	In house	0.31		-1.76	
2165	ISO17070	0.83		-0.20	
2247	DIN50009	0.87		-0.08	
2250	In house	1.02		0.37	
2255	ISO17070	0.81		-0.26	
2265	DIN50009	1.11		0.64	
2289	ISO17070	1.08		0.55	
2293		-----		-----	
2297	ISO17070	1.02		0.37	
2301	ISO17070	0.93		0.10	
2310	LFGB B82.02.8	0.65		-0.74	
2311	ISO17070	0.6126		-0.85	
2330	ISO17070	0.843		-0.16	
2347	ISO17070	0.95		0.16	
2350	ISO17070	0.71		-0.56	
2357	ISO17070	0.950		0.16	
2358	ISO17070	1.1235		0.68	
2363		-----		-----	
2365	ISO17070	0.993		0.29	
2366	In house	0.94		0.13	
2370	ISO17070	1.04		0.43	
2373	ISO17070	0.982		0.25	
2375	ISO17070	0.60		-0.89	
2379	ISO17070	1.2076		0.93	
2380	ISO17070	0.747		-0.45	
2382	ISO17070	0.980		0.25	
2386	In house	0.932		0.10	
2390	In house	1.04		0.43	
2452	ISO17070	0.134		-2.29	
2489	ISO17070	0.83		-0.20	
2495	In house	<0.05		-----	
2504	In house	1.215	C	0.95	First reported 2.322
2511		-----		-----	
2514	In house	0.84		-0.17	
2520	ISO17070	1.21		0.94	
2532	ISO17070	0.95		0.16	
2561	ISO17070	0.94159		0.13	
2569	ISO17070	0.86		-0.11	
2573	ISO17070	0.98		0.25	
2590	ISO17070	0.420		-1.43	
2605	ISO17070	0.98		0.25	
2668	ISO17070	0.77		-0.38	
2695	ISO17070	0.7795		-0.35	
2703	In house	0.7616		-0.41	
2711	ISO17070	0.6844		-0.64	
2713	In house	1.044		0.44	
2723	In house	1.4		1.51	
2727	ISO17070	1.041		0.43	
2734	ISO17070	0.375		-1.57	
2737	GB/T22808	1.333		1.31	
2756		-----		-----	
2806	In house	1.3		1.21	
2977		Not Determined		-----	
2979	ISO17070	1.2		0.91	
2980	ISO17070	1.2	C	0.91	First reported 1.8
3003	DIN50009	0.78		-0.35	
3116	LFGB B82.02.8	0.437		-1.38	
3154	DIN50009	1.189		0.88	
3172	ISO17070	0.9079		0.03	
3210	In house	1.01		0.34	
3218	ISO17070	0.953		0.17	
3228	In house	0.86		-0.11	
3237	ISO17070	0.42		-1.43	
3250	LFGB B82.02.8	0.992		0.28	
8005	ISO17070	0.419		-1.44	

normality	OK	
n	64	
outliers	0	
mean (n)	0.8972	
st.dev. (n)	0.26898	RSD = 30%
R(calc.)	0.7531	
st.dev.(iis memo 1601)	0.33322	
R(iis memo 1601)	0.9330	
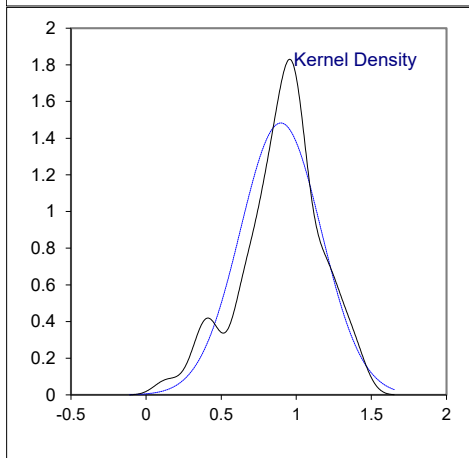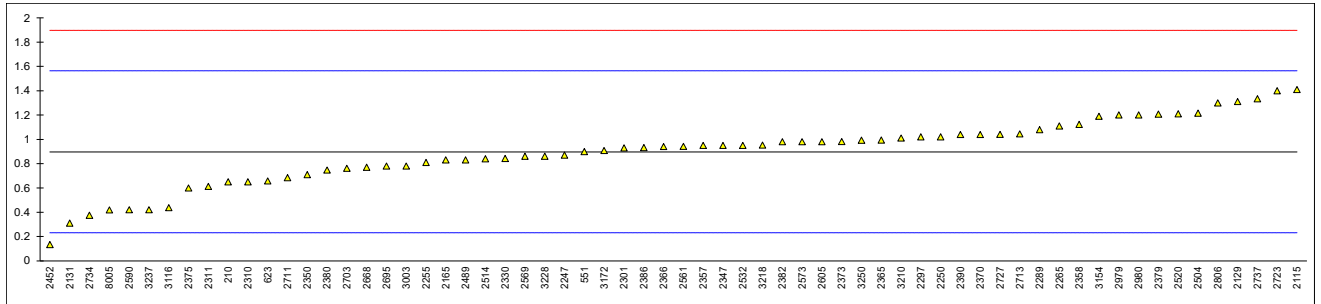
APPENDIX 2
Summary of other reported Chlorinated Phenols on sample #22585; results in mg/kg

2345TeCP	= 2,3,4,5-Tetrachlorophenol	
2346TeCP	= 2,3,4,6-Tetrachlorophenol	
2356TeCP	= 2,3,5,6-Tetrachlorophenol	
234TCP	= 2,3,4-Trichlorophenol	
235TCP	= 2,3,5-Trichlorophenol	
236TCP	= 2,3,6-Trichlorophenol	
245TCP	= 2,4,5-Trichlorophenol	
345TCP	= 3,4,5-Trichlorophenol	
23DCP	= 2,3-Dichlorophenol	
24DCP	= 2,4-Dichlorophenol	
25DCP	= 2,5-Dichlorophenol	
26DCP	= 2,6-Dichlorophenol	
34DCP	= 3,4-Dichlorophenol	
35DCP	= 3,5-Dichlorophenol	
2CP	= 2-Chlorophenol	
3CP	= 3-Chlorophenol	
4CP	= 4-Chlorophenol	

lab	2345TeCP	2346TeCP	2356TeCP	234TCP	235TCP	236TCP	245TCP	345TCP
210	0.15	nd	nd	nd	nd	nd	nd	nd
551	-----	0.1997	-----	-----	-----	-----	0.1997	-----
623	not detected	not detected	not detected	not detected	not detected	not detected	not detected	not detected
2115	-----	0.094	-----	0.055	-----	-----	-----	-----
2129	<0,1	0.341	<0,1	<0,1	<0,1	<0,1	<0,1	<0,1
2131	not detected	not detected	not detected	not detected	not detected	not detected	not detected	not detected
2165	not detected	not detected	not detected	not detected	not detected	not detected	not detected	not detected
2247	not detected	not detected	not detected	not detected	not detected	not detected	not detected	not detected
2250	-----	0.10	-----	-----	-----	-----	-----	-----
2255	not detected	not detected	not detected	not detected	not detected	not detected	not detected	not detected
2265	< 0,05	< 0,05	< 0,05	< 0,05	< 0,05	< 0,05	< 0,05	< 0,05
2289	-----	0.09	-----	-----	-----	-----	-----	-----
2293	-----	-----	-----	-----	-----	-----	-----	-----
2297	<0.05	0.07	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05
2301	-----	-----	-----	-----	-----	-----	-----	-----
2310	not detected	0.08	not detected	not detected	not detected	not detected	not detected	not detected
2311	not detected	0.07038	not detected	not detected	not detected	not detected	not detected	not detected
2330	ND	ND	ND	ND	ND	ND	ND	ND
2347	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
2350	< 0.125	< 0.125	< 0.125	< 0.125	< 0.125	< 0.125	< 0.125	< 0.125
2357	-----	-----	-----	-----	-----	-----	-----	-----
2358	not detected	not detected	not detected	not detected	not detected	not detected	not detected	not detected
2363	-----	-----	-----	-----	-----	-----	-----	-----
2365	<0.05	0.071	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05
2366	<0.50	<0.50	<0.50	<0.50	<0.50	<0.50	<0.50	<0.50
2370	<0.05	0.0740	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05
2373	not detected	not detected	not detected	not detected	not detected	not detected	not detected	not detected
2375	-----	-----	-----	-----	-----	-----	-----	-----
2379	not detected	not detected	not detected	not detected	not detected	not detected	not detected	not detected
2380	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05
2382	<0.100	<0.100	<0.100	<0.100	<0.100	<0.100	<0.100	<0.100
2386	<0,10	<0,20	<0,10	<0,10	<0,10	<0,10	<0,10	<0,10
2390	not detected	0.0985	not detected	not detected	not detected	not detected	not detected	not detected
2452	not detected	not detected	not detected	not detected	not detected	not detected	not detected	not detected
2489	not detected	-----	not detected	not detected	not detected	not detected	not detected	not detected
2495	<0.05	0.320	<0.05	0.951	<0.05	<0.05	<0.05	<0.05
2504	-----	-----	-----	not detected	not detected	not detected	< 0.1	not detected
2511	-----	-----	-----	-----	-----	-----	-----	-----
2514	-----	-----	-----	-----	-----	-----	-----	-----
2520	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
2532	not detected	-----	not detected	not detected	not detected	not detected	not detected	not detected
2561	-----	0.11498	-----	0.06919	-----	-----	-----	-----
2569	not detected	-----	not detected	not detected	not detected	not detected	not detected	not detected
2573	not detected	0.08	not detected	not detected	not detected	not detected	not detected	not detected
2590	-----	-----	-----	-----	-----	-----	-----	-----
2605	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
2668	not detected	0.09	not detected	not detected	not detected	not detected	not detected	not detected
2695	not detected	not detected	not detected	not detected	not detected	not detected	not detected	not detected
2703	Not detected	0.0417	Not detected	Not detected	Not detected	Not detected	Not detected	Not detected
2711	0	0	0	0	0	0	0	0
2713	<0,05	<0,05	<0,05	<0,05	<0,05	<0,05	<0,05	<0,05

lab	2345TeCP	2346TeCP	2356TeCP	234TCP	235TCP	236TCP	245TCP	345TCP
2723	not detected	not detected	not detected	not analyzed	not analyzed	not analyzed	not analyzed	not analyzed
2727	not detected	not detected	not detected	not detected	not detected	not detected	not detected	not detected
2734	not detected	not detected	not detected	not detected	not detected	not detected	not detected	not detected
2737	-----	-----	-----	-----	-----	-----	-----	-----
2756	-----	-----	-----	-----	-----	-----	-----	-----
2806	< 0,1	0.1	< 0,1	< 0,1	< 0,1	< 0,1	< 0,1	< 0,1
2977	0.21704	not detected	not detected	-----	-----	-----	-----	-----
2979	not detected	not detected	not detected	not detected	not detected	not detected	not detected	not detected
2980	-----	-----	-----	-----	-----	-----	-----	-----
3003	-----	0.1	-----	-----	-----	-----	-----	-----
3116	-----	-----	-----	-----	-----	-----	-----	-----
3154	not detected	0.163	not detected	not detected	not detected	not detected	0.11	not detected
3172	< 0.05	< 0.05	< 0.05	< 0.05	< 0.05	< 0.05	< 0.05	< 0.05
3210	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05
3218	<0.050	<0.050	<0.050	<0.050	<0.050	<0.050	<0.050	<0.050
3228	not detected	not detected	not detected	not detected	not detected	not detected	not detected	not detected
3237	-----	-----	-----	-----	-----	-----	-----	-----
3250	-----	-----	-----	-----	-----	-----	-----	-----
8005	-----	-----	-----	-----	-----	-----	-----	-----

-- continued --

lab	23DCP	24DCP	25DCP	26DCP	34DCP	35DCP	2CP	3CP	4CP
210	nd	nd	nd	nd	nd	nd	nd	nd	nd
551	-----	0.2996	0.2996	-----	-----	-----	-----	-----	-----
623	not detected	not detected	not detected	not detected	not detected	not detected	not detected	not detected	not detected
2115	-----	-----	0.075	-----	-----	-----	-----	-----	0.131
2129	<0,1	<0,1	<0,1	<0,1	<0,1	<0,1	<0,1	<0,1	0.219
2131	not detected	not detected	not detected	not detected	not detected	not detected	not detected	not detected	not detected
2165	not detected	not detected	not detected	not detected	not detected	not detected	not detected	not detected	not detected
2247	not detected	not detected	not detected	not detected	not detected	not detected	not detected	not detected	not detected
2250	-----	-----	-----	-----	-----	-----	-----	-----	0.12
2255	not detected	not detected	not detected	not detected	not detected	not detected	not detected	not detected	0.10
2265	< 0,05	0.29	0.29	< 0,05	< 0,05	< 0,05	< 0,05	< 0,05	< 0,05
2289	-----	-----	-----	-----	-----	-----	-----	-----	-----
2293	-----	-----	-----	-----	-----	-----	-----	-----	-----
2297	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	-----	-----	-----
2301	-----	-----	-----	-----	-----	-----	-----	-----	-----
2310	not detected	not detected	not detected	not detected	not detected	not detected	not detected	not detected	not detected
2311	not detected	<0.01	<0.01	not detected	not detected	not detected	not detected	not detected	not detected
2330	ND	3.668	3.668	ND	ND	ND	ND	ND	0.134
2347	-----	-----	-----	-----	-----	-----	-----	-----	-----
2350	< 0.125	< 0.125	< 0.125	< 0.125	< 0.125	< 0.125	< 0.125	< 0.125	< 0.125
2357	-----	-----	-----	-----	-----	-----	-----	-----	-----
2358	not detected	not detected	not detected	not detected	not detected	not detected	not detected	not detected	0.134
2363	-----	-----	-----	-----	-----	-----	-----	-----	-----
2365	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	0.124
2366	-----	-----	-----	-----	-----	-----	-----	-----	-----
2370	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	0.126
2373	not detected	not detected	not detected	not detected	not detected	not detected	not detected	not detected	not detected
2375	-----	-----	-----	-----	-----	-----	-----	-----	-----
2379	not detected	-----	-----	not detected	not detected	not detected	not detected	not detected	0.1129
2380	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	0.100
2382	<0.100	<0.100	<0.100	<0.100	<0.100	<0.100	<0.100	<0.100	<0.100
2386	<0,50	0.706	see comment	<0,50	<0,50	<0,50	<0,50	<0,50	<0,50
2390	not detected	not detected	0.217	not detected	not detected	not detected	not detected	not detected	not detected
2452	not detected	-----	not detected	not detected	not detected	not detected	not detected	not detected	not detected
2489	not detected	-----	-----	not detected	not detected	not detected	not detected	not detected	not detected
2495	<0.05	-----	-----	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05
2504	-----	-----	-----	-----	-----	-----	-----	-----	-----
2511	-----	-----	-----	-----	-----	-----	-----	-----	-----
2514	-----	-----	-----	-----	-----	-----	-----	-----	0.10
2520	<0.1	0.59	0.61	16.35	<0.1	<0.1	<0.1	<0.1	<0.1
2532	not detected	-----	-----	not detected	not detected	not detected	not detected	not detected	not detected
2561	-----	-----	-----	-----	-----	-----	-----	-----	-----
2569	not detected	-----	-----	not detected	not detected	not detected	not detected	not detected	not detected
2573	not detected	not detected	not detected	not detected	not detected	not detected	not detected	not detected	not detected
2590	-----	-----	-----	-----	-----	-----	-----	-----	-----
2605	<0.1	-----	-----	-----	-----	-----	-----	-----	-----
2668	not detected	not detected	not detected	not detected	not detected	not detected	not detected	not detected	not detected
2695	not detected	not detected	not detected	not detected	not detected	not detected	0.1571	not detected	0.1222
2703	not detected	-----	0.1619	not detected	not detected	not detected	not detected	not detected	not detected
2711	-----	-----	-----	-----	-----	-----	-----	-----	-----
2713	-----	-----	-----	-----	-----	-----	-----	-----	-----
2723	-----	-----	-----	-----	-----	-----	-----	-----	-----
2727	-----	-----	-----	-----	-----	-----	-----	-----	-----

lab	23DCP	24DCP	25DCP	26DCP	34DCP	35DCP	2CP	3CP	4CP
2734	not detected	not detected	not detected	not detected	not detected	not detected	not detected	not detected	not detected
2737	-----	-----	-----	-----	-----	-----	-----	-----	-----
2756	-----	-----	-----	-----	-----	-----	-----	-----	-----
2806	-----	-----	-----	-----	-----	-----	-----	-----	-----
2977	-----	-----	-----	-----	-----	-----	-----	-----	-----
2979	not detected	0.6	0.6	16.5	not detected	not detected	not detected	not detected	not detected
2980	-----	0.6	0.6	16.5	-----	-----	-----	-----	-----
3003	-----	-----	-----	-----	-----	-----	-----	-----	0.1
3116	-----	-----	-----	-----	-----	-----	-----	-----	-----
3154	not detected	not detected	0.1	not detected	not detected	not detected	not detected	not detected	0.25
3172	< 0.05	< 0.05	< 0.05	< 0.05	< 0.05	< 0.05	< 0.05	< 0.05	< 0.05
3210	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05
3218	<0.050	<0.050	<0.050	<0.050	<0.050	<0.050	<0.050	<0.050	<0.050
3228	not detected	not detected	not detected	not detected	not detected	not detected	not detected	not detected	not detected
3237	-----	-----	-----	-----	-----	-----	-----	-----	-----
3250	-----	-----	-----	-----	-----	-----	-----	-----	-----
8005	-----	-----	-----	-----	-----	-----	-----	-----	-----

APPENDIX 3 Analytical Details

lab	ISO17025 accredited	Sample preparation	Sample intake (g)	Release technique	Extraction technique
210	Yes	Further cut		Steam distillation	Mechanical Shaking
551	Yes	Further cut	1 g	Steam distillation was skipped	Ultrasonic
623	Yes	Further cut	1 gram	Other	Ultrasonic
2115	Yes	Used as received	1g	Steam distillation	Ultrasonic
2129	Yes	Used as received	0,5g	Other	ASE
2131	Yes	Used as received	1g	Microwave extraction	Other
2165	Yes	Further cut	1.0g	Steam distillation	Mechanical Shaking
2247	Yes	Used as received	0.7gm	KOH extraction followed by 64 LFGB 82.02.8	Other
2250	Yes	Further cut	1	Other	Ultrasonic
2255	Yes	Further cut	0.5	Steam distillation	Ultrasonic
2265	No	Used as received	0,5	Other	Ultrasonic
2289	Yes	Further cut	1.0g	Steam distillation	Soxhlet
2293	---	---		---	---
2297	Yes	Used as received	1g	Steam distillation	Mechanical Shaking
2301	No	Used as received	1.0030	Steam distillation	Ultrasonic
2310	Yes	Further cut	2grams	Steam distillation	Mechanical Shaking
2311	Yes	Further cut	1	Steam distillation	Mechanical Shaking
2330	No	Further cut	1.0000g	Steam distillation	Mechanical Shaking
2347	Yes	Further cut	1.0g	---	---
2350	No	Further cut	2.0083 g	Steam distillation	ASE
2357	---	---		---	---
2358	Yes	Used as received	1 g	Steam distillation	---
2363	---	---		---	---
2365	Yes	Further cut	1.5g	Steam distillation	Mechanical Shaking
2366	No	Further cut	0.5g	Other	Ultrasonic
2370	Yes	Further cut	1 g	Steam distillation	Other
2373	---	---	2g	---	---
2375	Yes	Further cut	1 gr	Steam distillation	Mechanical Shaking
2379	No	Further cut	1 grams	Steam distillation	Other
2380	Yes	Further cut	1.0 g	Steam distillation	Mechanical Shaking
2382	Yes	Further cut	1.0g	Steam distillation	Steam distillation
2386	Yes	Further cut	0.500	extracted with 1 M KOH	Ultrasonic
2390	Yes	Further cut	0.5 gram	Alkaline digestion	Ultrasonic
2452	No	Used as received	1	Steam distillation	Soxhlet
2489	Yes	Further cut	1.0010g	Steam distillation	Mechanical Shaking
2495	Yes	Used as received	0.5	KOH method	Ultrasonic
2504	Yes	Further cut	0.5 grams	KOH extraction	Heating block
2511	Yes	Used as received	0.5 gram	---	---
2514	Yes	Further cut	0.3712 gm	KOH METHOD	Mechanical Shaking
2520	No	Further cut	1gm	Steam distillation	Mechanical Shaking
2532	Yes	Further cut	1 Gram	Steam distillation	Mechanical Shaking
2561	Yes	Used as received	1g	Steam distillation	Mechanical Shaking
2569	Yes	Further grinded	1 gm	Steam distillation	Mechanical Shaking
2573	Yes	Used as received	1g	Steam distillation	Mechanical Shaking
2590	Yes	Used as received	1g	Steam distillation	Mechanical Shaking
2605	Yes	Further cut	1.000 g	Steam distillation	---
2668	Yes	Further cut	0.5 gms	16 hrs KOH extraction at 90 C for 16 hrs	Mechanical Shaking
2695	Yes	Further cut	1g	Steam distillation	Mechanical Shaking
2703	Yes	Used as received	1g	Steam distillation	Other
2711	No	Further cut	1	Steam distillation	Mechanical Shaking
2713	Yes	Further cut	0,5 g	Ultrasonic Bath	Mechanical Shaking
2723	Yes	Used as received	2g	Extraction with EtOH/Toluene 34:16 under reflux	Other
2727	Yes	Further cut	0.5	Steam distillation	Other
2734	Yes	Used as received	3g	Steam distillation	Mechanical Shaking
2737	Yes	Used as received	1g	KOH extraction in oven 90 degree for 16 hours	---
2756	Yes	Used as received		---	Mechanical Shaking
2806	No	Further cut		---	Ultrasonic
2977	No	Used as received	3 g	Digestion with KOH	Thermal Desorption
2979	No	Further cut	1 g	Steam distillation	Mechanical Shaking
2980	No	Further cut	1 gram	Steam distillation	Mechanical Shaking
3003	No	Used as received	2.8 gm	Release Techniques: KOH,	Mechanical Shaking
3116	Yes	Used as received	1 gram	Steam distillation was skipped	Ultrasonic
3154	Yes	Further cut	0,5	KOH extracted in water for 16 h at 90 °C	Other
3172	---	---		---	---
3210	Yes	Used as received	1g	Ultrasonic, followed by Liq-Liq extraction.	Mechanical Shaking
3218	Yes	Used as received	1g	Steam distillation	Mechanical Shaking
3228	Yes	Further cut	1 g	---	---
3237	Yes	Further cut	2,5g	Steam distillation	Mechanical Shaking
3250	Yes	Used as received	1	KOH 16h at 90C (DIN50009	Mechanical Shaking
8005	No	Used as received	1 gram	Steam distillation	Mechanical Shaking

APPENDIX 4

Number of participants per country

    4 labs in BANGLADESH
    1 lab in BRAZIL
    2 labs in CAMBODIA
    3 labs in EGYPT
    1 lab in ETHIOPIA
    1 lab in FRANCE
    5 labs in GERMANY
    1 lab in GUATEMALA
    3 labs in HONG KONG
    7 labs in INDIA
    2 labs in INDONESIA
    9 labs in ITALY
    1 lab in KOREA, Republic of
    1 lab in MOROCCO
  15 labs in P.R. of CHINA
    1 lab in PAKISTAN
    1 lab in PORTUGAL
    2 labs in SWITZERLAND
    1 lab in TAIWAN
    2 labs in THAILAND
    2 labs in TUNISIA
    3 labs in TURKEY
    2 labs in UNITED KINGDOM

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 & Evaluation, June 2018
2		ISO5725:86
3		ISO5725 parts 1-6:94
4		ISO13528:05
5		M. Thompson and R. Wood, J. AOAC Int, 76, 926, (1993)
6		W.J. Youden and E.H. Steiner, Statistical Manual of the AOAC, (1975)
7		P.L. Davies, Fr. Z. Anal. Chem, 331, 513, (1988)
8		J.N. Miller, Analyst, 118, 455, (1993)
9		Analytical Methods Committee, Technical Brief, No 4, January 2001
10		P.J. Lowthian and M. Thompson, The Royal Society of Chemistry, Analyst, 127, 1359-1364, (2002)
11		W. Horwitz and R. Albert, J. AOAC Int, 79.3, 589-621, (1996)
12		Bernard Rosner, Percentage Points for a Generalized ESD Many-Outlier Procedure, Technometrics, 25(2), 165-172, (1983)
13		iis memo 1601, Precision data of OPP/PCP in textile (2016)