Results of Proficiency Test
Chlorinated Phenols in leather
April 2018

Organised by: Institute for Interlaboratory Studies
Spijkenisse, the Netherlands

Author: ing. R.J. Starink
Corrector: dr. R.G. Visser

Report: iis18A07Cl

July 2018

CONTENTS

Appendices:

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.
Pentachlorophenol is an anti-fungal agent that has been restricted for sale in preparations since 1991, with a maximum permissible amount of 1000 mg/kg. However, in some regions (such as Germany), more stringent limits (a maximum of 5 mg/kg) are placed on its inclusion in finished materials and this lower limit is found in 94/783/EC.

Since 2016, theThe Institute for Interlaboratory Studies organizes a proficiency scheme Pentachlorophenol (PCP) and Tetrachlorophenols (TeCP) in Leather. In the annual proficiency test program of 2017/2018, it was decided to continue the PT on PCP and TeCP in Leather and extend it with TCP (Trichlorophenols).

In this interlaboratory study 80 laboratories in 26 different countries registered for participation. See appendix 3 for the number of participants per country. In this report, the results of the 2018 proficiency test are presented and discussed. This report is also available through the iis website www.iisnl.com.

2 SET UP

The Institute for Interlaboratory Studies in Spijkenisse was the organiser of the proficiency test. Sample analyses for fit-for-use and homogeneity testing were subcontracted to an ISO/IEC 17025 accredited laboratory. Due to limited availability of samples positive on PCP, TCEP and/or TCP on leather, it was decided to send one leather sample which was positive on PCP and TCP. The participants were requested 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/IEC 17043:2010. This ensures strict adherence to protocols for sample preparation and statistical evaluation and 100% confidentiality of participant's data. Feedback from the participants on the reported data is encouraged and customer's satisfaction is measured on a regular basis by sending out questionnaires.

2.2 PROTOCOL

The protocol followed in the organisation of this proficiency test was the one as described for proficiency testing in the report 'iis Interlaboratory Studies: Protocol for the Organisation, Statistics and Evaluation' of March 2017 (iis-protocol, version 3.4). This protocol is electronically available through the iis website www.iisnl.com, from the FAQ page.

2.3 CONFIDENTIALITY STATEMENT

All data presented in this report must be regarded as confidential and for use by the participating companies only. Disclosure of the information in this report is only allowed by means of the entire report. Use of the contents of this report for third parties is only allowed by written permission of the Institute for Interlaboratory Studies. Disclosure of the identity of one or more of the participating companies will be done only after receipt of a written agreement of the companies involved.

2.4 SAMPLES

A batch of brown leather positive on Chlorophenols (PCP and 2,4,6-TCP) was obtained from a third party laboratory. The bulk was cut into pieces. Out of this batch, after mixing well, 100 subsamples of 3 grams each were packed and labelled #18550.
The homogeneity the subsamples #18550 was checked by the determination of PCP on eight stratified randomly selected samples. The determination is performed in accordance with an in-house test method for PCP. See the following table for the test results.

	PCP in mg/kg
Sample #18550-1	7.35
Sample #18550-2	7.45
Sample #18550-3	7.63
Sample #18550-4	7.75
Sample #18550-5	7.25
Sample #18550-6	7.43
Sample #18550-7	7.42
Sample #18550-8	7.25

Table 1: homogeneity test results of subsamples #18550

From the above test results of the homogeneity test, the repeatability was calculated and compared with 0.3 times the target reproducibility in agreement with the procedure of ISO 13528, Annex B2 in the next table:

	PCP in mg/kg
r (observed)	0.49
Target	iis-memo (lit.18)
0.3 x R (Target)	1.69

Table 2: evaluation of the repeatability of subsamples #18550.

The calculated repeatability of Pentachlorophenol (PCP) was in agreement with 0.3 times the target reproducibility. Therefore, homogeneity of the subsamples was assumed.

To each of the participating laboratories one sample of approx. 3 grams, labelled #18550 was sent on April 4, 2018.

2.5 ANALYSES

The participants were asked to determine the concentration of 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 on sample #18550 applying the analysis procedure that is routinely used in the laboratory.

It was explicitly requested to treat the samples as if they were routine samples and to report the test results using the indicated units on the report form and not to round the results, but report as much significant figures as possible. It was also requested not to report ‘less than’ results, which are above the detection limit, because such 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 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 results of the individual laboratories were gathered via the data entry portal www.kmpd.co.uk/sgs-iis-cts/. The reported test results are tabulated per sample and determination in appendix 1 of this report. The laboratories are presented by the 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 reanalyses). Additional or corrected test results are used for the data analysis and the original 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 organisation of this proficiency test wast the one as described for proficiency testing in the report 'iis Interlaboratory Studies: Protocol for the Organisation, Statistics and Evaluation' of March 2017 (iis-protocol, version 3.4).

For the statistical evaluation, the *unrounded* (when available) figures were used instead of the rounded 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.

According to ISO 5725 the original test results per determination were submitted subsequently to Dixon's, Grubbs' and/or Rosner's outlier tests. Outliers are marked by D(0.01) for the Dixon's test, by G(0.01) or DG(0.01) for the Grubbs's test and by R(0.01) for the Rosner's. 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. When the uncertainty passed the evaluation no remarks are made in the report. However, when the uncertainty failed the evaluation it is mentioned in the report and it will have consequences for the evaluation of the test results.

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

3.2 GRAPHICS

In order to visualise the data against the reproducibilities from literature, Gauss plots were made, using the sorted data for one determination (see appendix 1). On the Y-axis the reported analysis results are plotted. The corresponding laboratory numbers are on the X-axis.

The straight horizontal line presents the consensus value (a trimmed mean). The four striped lines, parallel to the consensus value line, are the +3s, +2s, -2s and -3s target reproducibility limits of the selected standard. Outliers and other data, which were excluded from the calculations, are represented as a cross. Accepted data are represented as a triangle.

Furthermore, Kernel Density Graphs were made. The Kernel Density Graph is a method for producing a smooth density approximation to a set of data that avoids some problems associated with histograms. Also, a normal Gauss curve was projected over the Kernel Density Graph for reference.

3.3 z-scores

To evaluate the performance of the participating laboratories the z-scores were calculated. As it was decided to evaluate the performance of the participants in this proficiency test (PT) against the literature requirements, the z-scores were calculated using a target standard deviation. This results in an evaluation independent of the variation in this interlaboratory study.

The target standard deviation was calculated from the target reproducibility by division with 2.8. In case no literature reproducibility was available, other target values are used.

When a laboratory did use a test method with a reproducibility that is significantly different from the reproducibility of the reference test method used in this report, it is strongly advised to recalculate the z-score, while using the reproducibility of the actual test method used. This should be done in order to evaluate whether the reported test results are fit-for-purpose.

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 of appendix 1.

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

|z| < 1 good
1 < |z| < 2 satisfactory
2 < |z| < 3 questionable
3 < |z| unsatisfactory

4 Evaluation

During the execution of this proficiency test some serious problems occurred with the dispatch of the samples. A number of participants was not able to report the test results before the final reporting date. Finally, eight participants reported the test results after the final reporting date and eight other participants did not report any test results at all.
In total 72 laboratories reported 127 numerical test results. Observed were 4 statistical outlying test results, which is 3.1%. In proficiency studies, outlier percentages of 3% - 7.5% are quite normal.

For Pentachlorophenol (PCP), both existing test methods (LFGB 82.02-8 and ISO17070, the latter test method superseding DIN53313:1996 and DIN14494:2003), mention identical precision data. Most participating laboratories in this PT reported to have used one of these two test methods. In a recent study (lit. 18), in which reproducibilities of the PCP determination on textile over 18 PTs over 10 years 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. This target reproducibility has been used in this PT to check the homogeneity of the sub samples of #18550 and to calculate the z-scores of the reported test results.

For Trichlorophenols no precision data are available. Therefore, also for 2,4,6-trichlorophenol the reproducibility from the iis memo on PCP is used as target reproducibility.

4.1 EVALUATION PER DETERMINATION

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 agreement with the estimated reproducibility calculated from the iis memo (lit.18).

2,4,6-TCP: The determination of this component was not problematic. One statistical outlier was observed. However, the calculated reproducibility after rejection of the statistical outlier is in agreement with the estimated reproducibility calculated from the iis memo (lit.18).

TeCPs and TCPs: Sample #18550 did contain very little of the other requested components, which concentrations were near or below the detection limit. Therefore, no significant conclusions were drawn.

4.2 PERFORMANCE EVALUATION FOR THE GROUP OF LABORATORIES

A comparison has been made between the estimated target reproducibilities (see § 4.1) and the reproducibilities as found for the group of participating laboratories.
The number of test results, the average test results, the calculated reproducibilities (standard deviation*2.8) and the target reproducibilities are compared in the next table:

	unit	*n*	*average*	*2.8 x sd*	*R (target)*
PCP	mg/kg	67	5.69	4.14	4.48
2,4,6-TCP	mg/kg	56	1.37	1.10	1.34

Table 3: reproducibility of chloro phenols on sample #18550

Without further statistical calculations, it can be concluded that the group of participating laboratories has no difficulties with the determination of PCP and 2,4,6-TCP. See also the discussion in paragraphs 4.1 and 6.

4.3 COMPARISON OF THE PROFICIENCY TEST OF APRIL 2018 WITH THE PREVIOUS PT

	April 2018	April 2017	April 2016
Number of reporting labs	72	72	74
Number of results reported	127	107	110
Number of statistical outliers	4	2	3
Percentage outliers	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 proficiency test was compared expressed as uncertainty of the PTs, see table below.

	April 2018	April 2017	April 2016	RSD (iis) see lit 18
PCP	26%	36%	41%	25%-35%
2,4,6-TCP	29%	n.e.	n.e.	25%-35%

Table 5: Comparison of uncertainties in iis proficiency tests

4.4 EVALUATION ANALYTICAL DETAILS

For this Proficiency Test some analytical details were requested (see appendix 2).
Based on the answers given by the participants the following can be summarized:
Fifty-four of the participants answered to be ISO/IEC17025 accredited for the determination of Chlorophenols in leather.
Fifty-six participants tested the leather samples according to the test method ISO17070 or LFGB B82.02.8, nine participants used an in house method and fourteen did not report the test method.
Almost all reporting laboratories did use a test portion between 0.5 - 2.0 grams. One mentioned to have use less material (0.3 gram) and another used more testing material for intake (2.5 gram).
Most of the laboratories mentioned to have cut the sample in smaller pieces before use.
Thirthy-four reported to have used steam distillation to release the Chlorophenols from the leather. Twenty-two used an extraction method (with or without KOH)

Not all laboratories followed identical procedures for extracting the PCP from the leather. 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.
Remarkably only 34 of the 56 laboratories, which reported to have used ISO17070 or LFGB B82.02.8, used steam distillation.

The observed variation in this PT could not be explained from the reported analytical details. It is remarkable that for the leather sample used in this proficiency test, none of the reported analytical details appears to have a significant influence on the test results.

5 DISCUSSION

In table 6 the limits mentioned in standard 100 by OEKO-TEX are mentioned. It was noticed that not all participants would make identical decisions about the acceptability of the leather for Chlorophenols.

Chlorinated phenols, mg/kg	Baby clothes	In direct skin contact	With no direct skin contact	Decoration material
Pentachlorophenol PCP	0.05	0.5	0.5	0.5
Tetrachlorophenols (TeCP), sum	0.05	0.5	0.5	0.5
Trichlorophenols (TCP), sum	0.2	2.0	2.0	2.0

Table 6: Ecolabelling Standard and Requirements Oko-tex for Textiles in EU

For the determination of PCP, three participants would accept the sample for all categories except for baby clothes. Two laboratories reported a test result smaller than 0.5 mg/kg and the third reported ‘nd’. All other laboratories would reject the sample for containing too much PCP.
For the determination of TCPs, four participants would accept the sample for all categories. One laboratory reported a test result smaller than 0.2 mg/kg and three others reported ‘nd’. Five participants would reject this sample for all categories as they reported a test result larger than 2.0 mg/kg. All other participants would accept the sample for all categories except for baby clothes.

6 CONCLUSION

Although, it can be concluded that the majority of the participants has no problem with the determination of PCP or 2,4,6-TCP in the sample of 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.

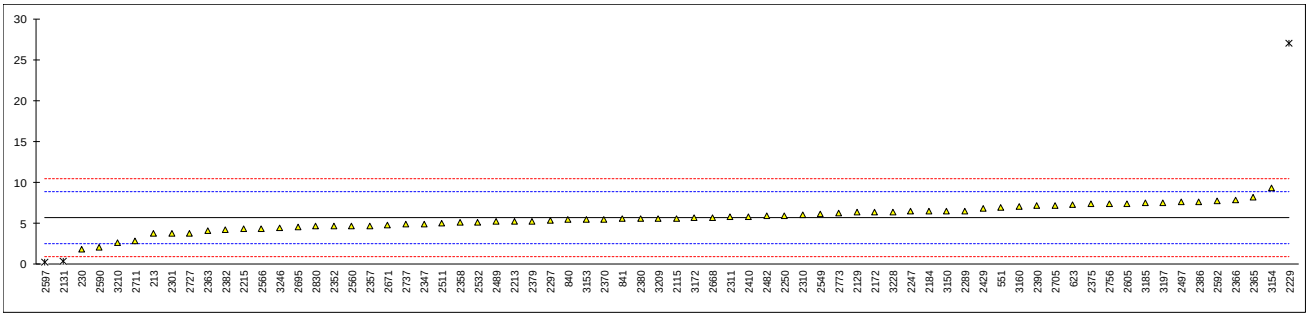
APPENDIX 1

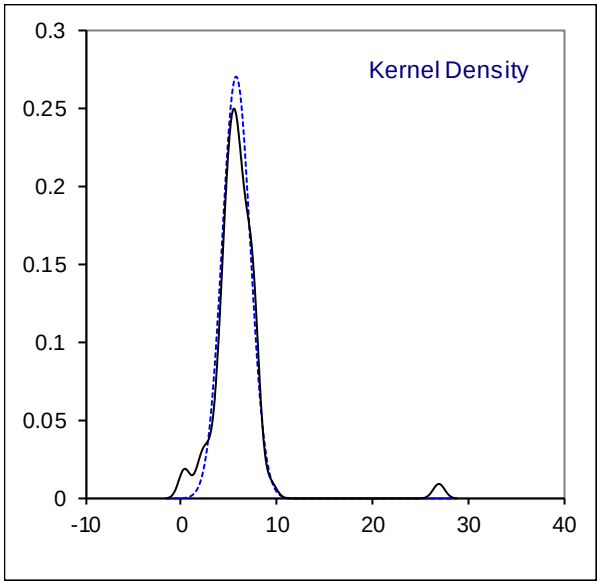
Determination of Pentachlorophenol (PCP) on sample #18550; results in mg/kg

lab	method	value	mark	z(targ)	remarks
213	ISO17070	3.74		-1.22	
230	ISO17070	1.85		-2.40	
551	In house	6.94		0.78	
623	ISO17070	7.28		1.00	
840		5.42		-0.17	
841	LFGB B82.02.8	5.53		-0.10	
2115	ISO17070	5.623		-0.04	
2129	ISO17070	6.38		0.43	
2131	In house	0.335	R(0.05)	-3.34	
2137		-----		-----	
2172	In house	6.420		0.46	
2184	LFGB B82.02.8	6.51		0.51	
2213	ISO17070	5.2		-0.30	
2215	In house	4.33		-0.85	
2229	ISO17070	26.95	C,R(0.01)	13.28	First reported 19.39
2247	ISO17070	6.4695		0.49	
2250	ISO17070	5.9		0.13	
2289	ISO17070	6.53		0.53	
2297	ISO17070	5.31		-0.24	
2301	LFGB B82.02.8	3.75		-1.21	
2310	ISO17070	6.02		0.21	
2311	ISO17070	5.757		0.04	
2347	ISO17070	4.95		-0.46	
2350		-----		-----	
2352	ISO17070	4.637		-0.66	
2357	ISO17070	4.699		-0.62	
2358	ISO17070	5.122		-0.35	
2363	ISO17070	4.06		-1.02	
2365	ISO17070	8.136		1.53	
2366	ISO17070	7.890		1.38	
2369		-----		-----	
2370	ISO17070	5.495		-0.12	
2375	ISO17070	7.40		1.07	
2379	ISO17070	5.26		-0.27	
2380	LFGB B82.02.8	5.555		-0.08	
2382	ISO17070	4.181		-0.94	
2386	In house	7.62		1.21	
2390	ISO17070	7.120		0.90	
2410	ISO17070	5.84		0.10	
2429	In house	6.771		0.68	
2455	ISO17070	nd		-----	
2482	ISO17070	5.868		0.11	
2489	ISO17070	5.19		-0.31	
2492		-----		-----	
2497	ISO17070	7.561		1.17	
2511	LFGB B82.02.8	4.990		-0.43	
2532	ISO17070	5.148		-0.34	
2549		6.14		0.28	For KOH: 9.51 (z-score 2.27)
2560	ISO17070	4.695		-0.62	
2561		-----		-----	
2566	LFGB B82.02.8	4.36		-0.83	
2590	ISO17070	2.111		-2.23	
2592	ISO17070	7.72		1.27	
2597	ISO17070	0.21	R(0.05)	-3.42	
2605	ISO17070	7.431		1.09	
2656		-----		-----	
2668		5.74		0.03	For KOH 10.28 (z-score 2.75)
2671		4.82		-0.54	
2695	ISO17070	4.509		-0.74	
2703		-----		-----	
2705	In house	7.2		0.95	
2711	ISO17070	2.80		-1.80	
2727	ISO17070	3.75		-1.21	
2737	In house	4.896		-0.49	
2756	ISO17070	7.4	C	1.07	First reported 16.18
2773	ISO17070	6.2		0.32	
2830		4.621		-0.67	
3146		-----		-----	
3150	ISO17070	6.52		0.52	
3153	LFGB B82.02.8	5.46		-0.14	
3154	ISO17070	9.34		2.28	
3160	ISO17070	7.036		0.84	
3163		-----		-----	
3172	KS K0733	5.731		0.03	
3185	ISO17070	7.500		1.13	
3197	ISO17070	7.50		1.13	

lab	method	value	mark	z(targ)	remarks
3209	ISO17070	5.6020		-0.05	
3210	In house	2.58		-1.94	
3228	ISO17070	6.42		0.46	
3246	ISO17070	4.45		-0.77	

	normality	OK
	n	67
	outliers	3
	mean (n)	5.686
	st.dev. (n)	1.4766
	R(calc.)	4.135
	st.dev.(iis, see lit 18)	1.6009
	R(iis, see lit 18)	4.483
Compare		
	R(ISO17070:15)	1.834
	R(Horwitz)	1.961



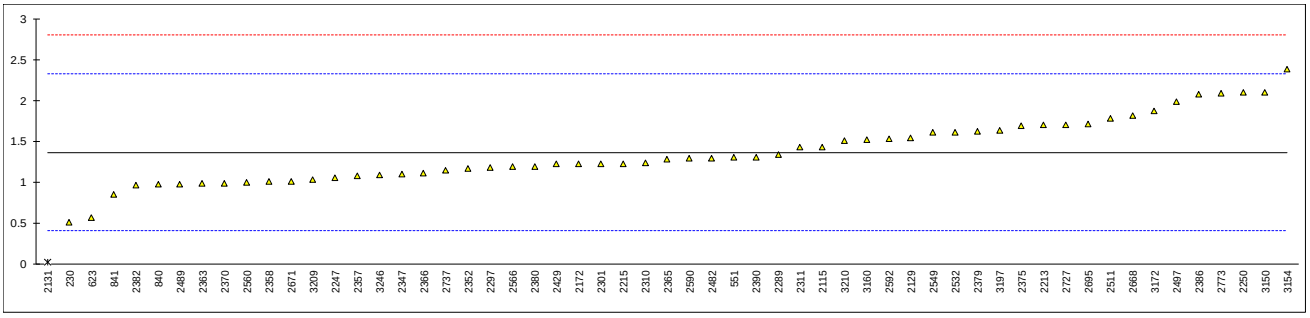


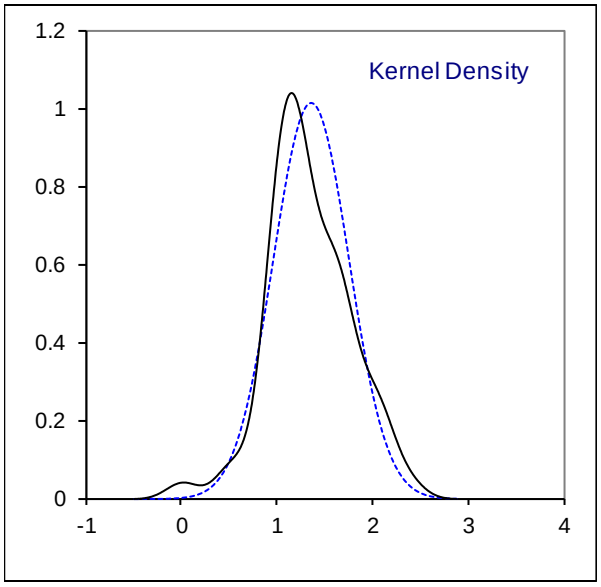
Determination of 2,4,6-Trichlorophenol (2,4,6-TCP) on sample #18550; results in mg/kg

lab	method	value	mark	z(targ)	remarks
213		-----		-----	
230	ISO17070	0.51		-1.80	
551	In house	1.30		-0.14	
623	ISO17070	0.57		-1.67	
840		0.98		-0.81	
841	LFGB B82.02.8	0.85		-1.09	
2115	ISO17070	1.431		0.13	
2129	ISO17070	1.54		0.36	
2131	In house	0.025	R(0.01)	-2.82	
2137		-----		-----	
2172	In house	1.222		-0.31	
2184		-----		-----	
2213	ISO17070	1.7		0.70	
2215	In house	1.23		-0.29	
2229		-----		-----	
2247	ISO17070	1.0524		-0.66	
2250	ISO17070	2.1		1.54	
2289	ISO17070	1.34		-0.06	
2297	ISO17070	1.18		-0.39	
2301	LFGB B82.02.8	1.23		-0.29	
2310	ISO17070	1.24		-0.27	
2311	ISO17070	1.426		0.12	
2347	ISO17070	1.1		-0.56	
2350		-----		-----	
2352	ISO17070	1.164		-0.43	
2357	ISO17070	1.075		-0.61	
2358	ISO17070	1.006		-0.76	
2363	ISO17070	0.99		-0.79	
2365	ISO17070	1.285		-0.17	
2366	ISO17070	1.110		-0.54	
2369		-----		-----	
2370	ISO17070	0.9928		-0.79	
2375	ISO17070	1.69		0.68	
2379	ISO17070	1.62		0.53	
2380	LFGB B82.02.8	1.1905		-0.37	
2382	ISO17070	0.962		-0.85	
2386	In house	2.08		1.49	
2390	ISO17070	1.307		-0.13	
2410		-----	W	-----	Result with drawn, reported 2.59
2429	In house	1.221		-0.31	
2455	ISO17070	nd		-----	
2482	ISO17070	1.299		-0.14	
2489	ISO17070	0.98		-0.81	
2492		-----		-----	
2497	ISO17070	1.982		1.29	
2511	LFGB B82.02.8	1.781		0.87	
2532	ISO17070	1.616		0.52	
2549		1.61	C	0.51	First reported ND. For KOH 2.28 (z-score 1.91)
2560	ISO17070	0.994		-0.78	
2561		-----		-----	
2566	LFGB B82.02.8	1.19		-0.37	
2590	ISO17070	1.296		-0.15	
2592	ISO17070	1.53		0.34	
2597		-----		-----	
2605		-----		-----	
2656		-----		-----	
2668		1.81		0.93	For KOH 2.31 (z-score 1.98)
2671		1.01		-0.75	
2695	ISO17070	1.712		0.72	
2703		-----		-----	
2705		-----		-----	
2711		-----		-----	
2727	ISO17070	1.70		0.70	
2737	In house	1.142		-0.47	
2756	ISO17070	ND		-----	
2773	ISO17070	2.09		1.52	
2830		ND		-----	
3146		-----		-----	
3150	ISO17070	2.10		1.54	
3153		-----		-----	
3154	ISO17070	2.38		2.12	
3160	ISO17070	1.519		0.32	
3163		-----		-----	
3172	KS K0733	1.877		1.07	
3185		-----		-----	
3197	ISO17070	1.63		0.55	

lab	method	value	mark	z(targ)	remarks
3209	ISO17070	1.0321		-0.70	
3210	In house	1.51		0.30	
3228		-----		-----	
3246	ISO17070	1.09		-0.58	

	normality	OK
	n	56
	outliers	1
	mean (n)	1.3674
	st.dev. (n)	0.39417
	R(calc.)	1.1037
	st.dev.(iis, see lit 18)	0.476732
	R(iis, see lit 18)	1.3348
Compare		
	R(ISO17070:15)	0.2869
	R(Horwitz)	0.5844





Determination of Tetra- and Tri-Chlorophenols on sample #18550; results in mg/kg

lab	2,3,4,5TeCP	2,3,4,6TeCP	2,3,5,6TeCP	2,3,4-TCP	2,3,5-TCP	2,3,6-TCP	2,4,5-TCP	3,4,5-TCP
213	-----	-----	-----	-----	-----	-----	-----	-----
230	-----	-----	-----	-----	-----	-----	-----	-----
551	-----	-----	-----	-----	-----	-----	-----	-----
623	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
840	not detected	not detected	not detected	not netected	not detected	not detected	not detected	not detected
841	n.d	n.d	n.d	n.d	n.d	n.d	n.d	n.d
2115	-----	0.036	-----	-----	-----	-----	-----	-----
2129	-----	-----	-----	-----	-----	-----	-----	-----
2131	-----	-----	-----	0.08	-----	-----	-----	-----
2137	-----	-----	-----	-----	-----	-----	-----	-----
2172	-----	-----	-----	-----	-----	-----	-----	-----
2184	-----	-----	-----	-----	-----	-----	-----	-----
2213	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05
2215	ND	ND	ND	ND	ND	ND	ND	ND
2229	-----	-----	-----	-----	-----	-----	-----	-----
2247	ND	ND	ND	ND	ND	ND	ND	ND
2250	-----	-----	-----	-----	-----	-----	-----	-----
2289	ND	ND	ND	ND	ND	ND	ND	ND
2297	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5
2301	ND	ND	ND	ND	ND	ND	ND	ND
2310	not detected	not detected	not detected	not netected	not detected	not detected	not detected	not detected
2311	not detected	not detected	not detected	not netected	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	-----	-----	-----	-----	-----	-----	-----	-----
2352	-----	-----	-----	-----	-----	-----	-----	-----
2357	ND	ND	ND	ND	ND	ND	ND	ND
2358	< 0.05	< 0.05	< 0.05	< 0.05	< 0.05	< 0.05	< 0.05	< 0.05
2363	ND	ND	ND	ND	ND	ND	ND	ND
2365	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05
2366	ND	ND	ND	ND	ND	ND	ND	ND
2369	-----	-----	-----	-----	-----	-----	-----	-----
2370	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
2375	-----	-----	-----	-----	-----	-----	-----	-----
2379	not detected	not detected	not detected	not netected	not detected	not detected	not detected	not detected
2380	-----	-----	-----	-----	-----	-----	-----	-----
2382	-----	-----	-----	-----	-----	-----	-----	-----
2386	<0,1	<0,1	<0,1	<0,1	<0,1	<0,1	<0,1	<0,1
2390	N.D	N.D	N.D	N.D	0.299	N.D	N.D	N.D
2410	-----	-----	-----	-----	-----	-----	-----	-----
2429	ND	ND	ND	ND	ND	ND	ND	ND
2455	nd	nd	nd	nd	nd	nd	nd	nd
2482	-----	-----	-----	-----	-----	-----	-----	-----
2489	ND	ND	ND	ND	ND	ND	ND	ND
2492	-----	-----	-----	-----	-----	-----	-----	-----
2497	-----	-----	0.0281	-----	-----	-----	-----	0.0122
2511	-----	-----	-----	-----	-----	-----	-----	-----
2532	not detected	not detected	not detected	not netected	not detected	not detected	not detected	not detected
2549	ND	ND	ND	ND	ND	ND	ND	ND
2560	-----	-----	-----	-----	-----	-----	-----	-----
2561	-----	-----	-----	-----	-----	-----	-----	-----
2566	ND	ND	ND	ND	ND	ND	ND	ND
2590	-----	-----	-----	-----	-----	-----	-----	-----
2592	-----	-----	-----	-----	-----	-----	-----	-----
2597	-----	-----	-----	-----	-----	-----	-----	-----
2605	ND	ND	ND	ND	ND	ND	ND	ND
2656	-----	-----	-----	-----	-----	-----	-----	-----
2668	not detected	not detected	not detected	not netected	not detected	not detected	not detected	not detected
2671	-----	-----	-----	-----	-----	-----	-----	-----
2695	-----	-----	-----	-----	-----	-----	-----	-----
2703	-----	-----	-----	-----	-----	-----	-----	-----
2705	-----	-----	-----	-----	-----	-----	-----	-----
2711	-----	-----	-----	-----	-----	-----	-----	-----
2727	-----	-----	-----	-----	-----	-----	-----	-----
2737	-----	-----	-----	-----	-----	-----	-----	-----
2756	ND	-----	-----	-----	-----	-----	-----	-----
2773	ND	ND	ND	ND	ND	ND	ND	ND
2830	ND	ND	ND	ND	ND	ND	ND	ND
3146	-----	-----	-----	-----	-----	-----	-----	-----
3150	-----	-----	-----	-----	-----	-----	-----	-----
3153	-----	-----	-----	-----	-----	-----	-----	-----
3154	-----	-----	-----	-----	-----	-----	-----	-----
3160	-----	-----	-----	-----	-----	-----	-----	-----
3163	-----	-----	-----	-----	-----	-----	-----	-----
3172	< 0.05	< 0.05	< 0.05	< 0.05	< 0.05	< 0.05	< 0.05	< 0.05
3185	-----	-----	-----	-----	-----	-----	-----	-----
3197	ND	ND	ND	ND	ND	ND	ND	ND

lab	2,3,4,5TeCP	2,3,4,6TeCP	2,3,5,6TeCP	2,3,4-TCP	2,3,5-TCP	2,3,6-TCP	2,4,5-TCP	3,4,5-TCP
3209	-----	-----	-----	-----	-----	-----	-----	-----
3210	<0.50	<0.50	<0.50	<0.50	<0.50	<0.50	<0.50	<0.50
3228	-----	-----	-----	-----	-----	-----	-----	-----
3246	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.

Determination of Other Chlorophenols and Orthophenylphenol on sample #18550; results in mg/kg

lab	Other CP	OPP
213	-----	
230	-----	
551	-----	
623	n.d.	
840	-----	
841	n.d	
2115	-----	19.9
2129	-----	
2131	-----	
2137	-----	
2172	-----	
2184	-----	
2213	<0.05	
2215	ND	
2229	-----	
2247	ND	8.97
2250	-----	
2289	ND	
2297	-----	
2301	-----	
2310	-----	
2311	not detected	
2347	<0.5	
2350	-----	
2352	-----	
2357	ND	
2358	< 0.05	
2363	ND	
2365	-----	
2366	out of cap.	
2369	-----	
2370	n.d.	
2375	-----	
2379	Not tested	
2380	-----	
2382	-----	
2386	<0,5	
2390	-----	12.83
2410	-----	
2429	ND	
2455	nd	
2482	-----	
2489	-----	9.52
2492	-----	
2497	35.11	10.55
2511	-----	
2532	-----	11.31
2549	-----	19.78
2560	-----	
2561	-----	
2566	-----	
2590	-----	
2592	-----	
2597	-----	
2605	-----	
2656	-----	
2668	-----	25.83
2671	-----	OPP positive
2695	-----	
2703	13.8	
2705	-----	
2711	-----	
2727	4.38	
2737	-----	
2756	-----	
2773	ND	
2830	ND	
3146	-----	
3150	-----	
3153	-----	
3154	-----	
3160	-----	
3163	-----	
3172	-----	
3185	-----	
3197	-----	

lab	Other CP	OPP
3209	-----	
3210	-----	
3228	-----	
3246	n.d.	

APPENDIX 2 Details of the test methods used by the participants

lab	Test methd	ISO17025 accr.	Sample prep.	Grain size	Release technique	Extraction technique	Sample intake	Remarks
213	ISO17070	No	Further Cut		Steam distillation	---		
230	ISO17070	Yes	Used as received		Steam distillation	Liquid liquid extraction	1-2 g	
551	In house	---	---		---	---		
623	ISO17070	---	---		---	---		
840		Yes	Further Cut	3x3mm	Other	Ultrasonic extraction		
841	LFGB B82.02.8	---	---		---	---		
2115	ISO17070	Yes	Used as received		Steam distillation	Soxhlet / AES extraction	0.5 g	
2129	ISO17070	Yes	Further Cut	5x5 mm	Steam distillation was skipped	Soxhlet / AES extraction	1,0 g	
2131	In house	---	Used as received		Steam distillation	---	1	
2137		---	---		---	---		
2172	In house	Yes	Further Cut	3mm*3mm	Other	Ultrasonic extraction	0.3g	
2184	LFGB B82.02.8	Yes	Used as received	3mm x 3mm	Steam distillation was skipped	Ultrasonic extraction	0.5g	
2213	ISO17070	Yes	Further Cut	5 X 5 mm	Other	KOH extraction	0.5 gm	
2215	In house	Yes	Used as received		---	Ultrasonic extraction		
2229	ISO17070	No	Further Cut	2mm*2mm	Steam distillation was skipped	Ultrasonic extraction	1g	
2247	ISO17070	Yes	Further Cut	2mmx3mm	Steam distillation	Soxhlet / AES extraction	1.0010gm	
2250	ISO17070	Yes	Used as received		Other	Ultrasonic extraction	0,5	
2289	ISO17070	Yes	Further Cut	5mm*5mm	Steam distillation	---	1.0g	
2297	ISO17070	Yes	Further Cut	2*2	Steam distillation	Liquid-liquid-extraction	1.0022	
2301	LFGB B82.02.8	Yes	Further Cut	0.2 mmx0.2mm	Other	Ultrasonic extraction	1	
2310	ISO17070	Yes	Further Cut	3mm * 3mm	Steam distillation	---	1 gram	
2311	ISO17070	Yes	Further Cut	3mm x 3mm	Steam distillation	Soxhlet / AES extraction	0.5	
2347	ISO17070	Yes	Further Cut	3mm*3mm	Steam distillation	Ultrasonic extraction		
2350		No	Further Cut		Other	Ultrasonic extraction		
2352	ISO17070	Yes	Further Cut	2mm*2mm	Steam distillation	liquid-liquid extract	0.5g	
2357	ISO17070	Yes	Further Cut	3mm*3mm	Steam distillation	Soxhlet / AES extraction	1.0	
2358	ISO17070	Yes	Further Cut	3mm x 3mm	Steam distillation	Steam distillation	1.0 g	
2363	ISO17070	Yes	Further Cut	3mm*3mm	Steam distillation	Other (mention in remarks)	1g	
2365	ISO17070	Yes	Further Cut	3mm*3mm	Steam distillation	none	1g	
2366	ISO17070	Yes	Further Cut	2mm*2mm	Steam distillation	shake bath	0.5g	
2369		---	---		---	---		
2370	ISO17070	Yes	Further Cut	3x3 mm	Steam distillation	Steam distillation	1 g	
2375	ISO17070	Yes	Further Cut	6 x 6 mm	Steam distillation	Other (mention in remarks)	0.5 gr	
2379	ISO17070	No	Further Cut	3 mm x 3 mm	Steam distillation	Liquid Liquid Extraction	1 g	
2380	LFGB B82.02.8	Yes	Further Cut	3x3 mm	Other	Ultrasonic extraction	0.5040	
2382	ISO17070	No	Further Cut	5*5mm	Steam distillation	Other (mention in remarks)	2.500	
2386	In house	Yes	Further Cut	3mm x 3mm	Other	Ultrasonic extraction	0,5	
2390	ISO17070	Yes	Further Cut	3 mm x 3mm	Other	Other (mention in remarks)	0.5 gm	
2410	ISO17070	Yes	Used as received	NA	Steam distillation	Other (mention in remarks)	NA	
2429	In house	Yes	Further Cut	5mm ¡Á5mm	Other	Other (mention in remarks)	1	
2455	ISO17070	---	Used as received		Other	Ultrasonic extraction		
2482	ISO17070	Yes	Further Cut	< 5 mm	Other	Extraction with 1M KOH	0,5	
2489	ISO17070	Yes	Used as received		Steam distillation	Soxhlet / AES extraction	0.5029g	
2492		---	---		---	---		
2497	ISO17070	Yes	Further Cut		Other	Ultrasonic extraction	1	
2511	LFGB B82.02.8	---	---		---	---		

lab	Test methd	ISO17025 accr.	Sample prep.	Grain size	Release technique	Extraction technique	Sample intake	Remarks
2532	ISO17070	---	---		---	---		
2549		Yes	Further Cut	2 mm X 2mm	Other	KOH extraction	0.5	
2560	ISO17070	Yes	Further Cut	6mm X 6mm	Other	KOH extraction	0.503	
2561		---	---		---	---		
2566	LFGB B82.02.8	Yes	Further Cut	5mmx5mm	Other	Ultrasonic extraction	1.0077gm	
2590	ISO17070	Yes	Further Cut	5mm x 5mm	Steam distillation	Ultrasonic extraction	1 g	
2592	ISO17070	Yes	Used as received	4 mm	Steam distillation	Other (mention in remarks)	1 g	
2597	ISO17070	---	---		---	---		
2605	ISO17070	Yes	Further Cut	2mm*3mm	Steam distillation	Liquid-Liquid extraction	0.5grams	
2656		---	---		---	---		
2668		Yes	Further Cut	2 mm X 2 mm	Other	KOH extraction	0.5 grams	
2671		No	Further Cut	5x5 mm	Other	Ultrasonic extraction	2	
2695	ISO17070	No	Further Cut	1 mm	Steam distillation	Orbital Shaker	1 g	
2703		Yes	Further Grinded		Steam distillation	---		
2705	In house	Yes	Used as received		Steam distillation was skipped	Soxhlet / AES extraction	1 g	
2711	ISO17070	No	Further Cut	about 3 x 3 mm	Steam distillation	---	1	
2727	ISO17070	Yes	Further Cut	2x2mm	Steam distillation	---	1g	
2737	In house	Yes	Further Cut	3mm*3mm	KOH extraction in oven	1 gram	KOH extraction in oven	
2756	ISO17070	No	Used as received	AS IT IS	Steam distillation	Soxhlet / AES extraction	1.00	
2773	ISO17070	Yes	Further Cut		Steam distillation	---	1.0	
2830		---	---		---	---		
3146		---	---		---	---		
3150	ISO17070	Yes	Further Cut	3 * 3 mm	Other	Extraction with KOH (16h at 90°C)	0,5	
3153	LFGB B82.02.8	Yes	Further Cut	3mm X 3mm	Steam distillation	4b: Liquid-Liquid extraction	0.5g	
3154	ISO17070	Yes	Used as received		---	Ultrasonic extraction		
3160	ISO17070	No	Further Cut	3x3 mm	Steam distillation	4b. Liquid-liquid extraction	1	
3163		---	---		---	---		
3172	KS K0733	Yes	Further Cut	2x2mm	Other	Ultrasonic extraction	0.5	
3185	ISO17070	Yes	Further Cut	5mm * 5mm	Steam distillation	---	0.5g ~ 1.0g	
3197	ISO17070	Yes	Used as received	5 mm * 5 mm	Steam distillation	Soxhlet / AES extraction	1 g	
3209	ISO17070	Yes	Further Cut	<2*2mm	Steam distillation was skipped	Ultrasonic extraction	1g	
3210	In house	Yes	Further Cut	20 mm²	Steam distillation was skipped	Ultrasonic extraction	1.000	
3228	ISO17070	Yes	Further Cut	3mm*3mm	Steam distillation was skipped	Ultrasonic extraction	0.5g	
3246	ISO17070	Yes	Further Cut	4x4 mm	Other	Extraction by KOH/ Heat 90oC, 16h	0.5 g	

APPENDIX 3

Number of participants per country

2 labs in BANGLADESH

1 lab in BRAZIL

20 labs in CHINA, P.R. of

1 lab in ETHIOPIA

2 labs in FRANCE

7 labs in GERMANY

4 labs in HONG KONG

11 labs in INDIA

2 labs in INDONESIA

7 labs in ITALY

1 lab in LUXEMBOURG

1 lab in MAURITIUS

2 labs in MOROCCO

1 lab in NETHERLANDS

1 lab in PAKISTAN

1 lab in PORTUGAL

3 labs in SOUTH KOREA

1 lab in SPAIN

1 lab in SWITZERLAND

1 lab in TAIWAN R.O.C.

1 lab in THAILAND

1 lab in TUNISIA

2 labs in TURKEY

1 lab in U.S.A.

2 labs in UNITED KINGDOM

3 labs in VIETNAM

APPENDIX 4

Abbreviations:

C = final test result after checking of first reported suspect test result
D(0.01) = outlier in Dixon's outlier test
D(0.05) = straggler in Dixon's outlier test
G(0.01) = outlier in Grubbs' outlier test
G(0.05) = straggler in Grubbs' outlier test
DG(0.01) = utlier in Double Grubbs' outlier test
DG(0.05) = straggler in Double Grubbs' outlier test
R(0.01) = outlier in Rosner's outlier test
R(0.05) = straggler in Rosner's outlier test
n.a. = not applicable
n.e. = not evaluated
n.d. = not detected
W = test result withdrawn on request of participant
ex = test result excluded from statistical evaluation
fr. = first reported test result

Literature:

1 iis Interlaboratory Studies, Protocol for the Organisation, Statistics & Evaluation, March 2017
2 Öko-Tex Standard 100; January 2018
3 Directive 94/783/EC
4 Impacts of Environmental Standards and requirements in EU Countries, August 1999
5 Horwitz, Journal of AOAC International, 79 No.3 (1996)
6 P.L. Davies, Fr Z. Anal. Chem., 351. 513. (1988)
7 W.J. Conover, Practical; Nonparametric Statistics, J. Wiley&Sons. NY. p.302. (1971)
8 ISO 5725:1986
9 ISO 5725. parts 1-6:1994
10 ISO105 E4:1994
11 ISO14184-1:1994
12 ISO13528:2005
13 M. Thompson and R. Wood, J. AOAC Int., 76. 926. (1993)
14 Analytical Methods Committee Technical brief, No 4 January 2001.
15 The Royal Society of Chemistry 2002, *Analyst 2002*, 127, 1359-1364, P.J. Lowthian and M. Thompson
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 MEMO iis: Precision data of OPP/PCP in textile, February 18, 2016
19 ISO17070:2015