

**Results of Proficiency Test  
PCP / TeCP in leather  
April 2017**

**Organised by:** Institute for Interlaboratory Studies  
Spijkenisse, the Netherlands

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## 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.

The Institute for Interlaboratory Studies organizes since 2004 a scheme of proficiency test for Orthophenylphenol (OPP), Pentachlorophenol (PCP) and Tetrachlorophenols (TeCP) in textile. In last year's program, iis organised a proficiency test of Pentachlorophenol (PCP) and Tetrachlorophenols (TeCP) on Leather. In the annual proficiency test program of 2016/2017, it was decided to continue the PT on PCP and TeCP in Leather.

In this interlaboratory study 77 laboratories in 24 different countries registered for participation. See appendix 3 for the number of participants per country. In this report, the results of the 2017 proficiency test are presented and discussed. This report is also available through the iis website [www.iisnl.com](http://www.iisnl.com).

## 2 SET UP

The Institute for Interlaboratory Studies in Spijkensisse 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 and/or TeCP on leather, it was decided to send one leather sample which was positive on PCP. 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 Spijkensisse, 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](http://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 yellow leather positive on PCP was obtained from a third party laboratory. The bulk was cut into pieces. Out of this batch, after mixing well, 90 subsamples of 5 grams each were packed and labelled #17545.

The homogeneity the subsamples #17545 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.

	<i>PCP in mg/kg</i>
Sample #17545-1	8.30
Sample #17545-2	8.25
Sample #17545-3	7.88
Sample #17545-4	8.65
Sample #17545-5	7.85
Sample #17545-6	8.75
Sample #17545-7	7.85
Sample #17545-8	7.15

Table 1: homogeneity test results of subsamples #17545

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:

	<i>PCP in mg/kg</i>
r (observed)	1.44
Target	iis-memo (lit.18)
0.3 x R (Target)	1.81

Table 2: evaluation of the repeatability of subsamples #17545.

As target reproducibility, the reproducibility of PCP on textile (lit. 18) was taken as it was concluded that the determination of PCP in leather is quite similar to PCP in textile.

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 participating laboratory one sample of approx. 3 grams, labelled #17545 was sent on March 22, 2017.

## 2.5 ANALYSES

The participants were asked to determine the concentration of Pentachlorophenol (PCP), 2,3,4,5-Tetrachlorophenol, 2,3,4,6-Tetrachlorophenol and 2,3,5,6-Tetrachlorophenol on sample #17545 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/](http://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](http://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.kpmd.co.uk/sgs-iis-cts/](http://www.kpmd.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 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).

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:

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

The  $z_{(\text{target})}$  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 no serious problems occurred, although one participant reported the test results after the final reporting date and five participants did not report any test results at all. In total 72 laboratories reported 107 numerical test results. Observed were 2 statistical outlying test results, which is 1.9%. 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. These precision data for leather are in full agreement with the Horwitz equation and were used in the calculation of the z-scores. In the proficiency tests of PCP on textile most participating laboratories reported to use the same two test methods for the determination of PCP. In a recent study (lit. 18), in which reproducibilities of this 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 #17545 and to calculate the z-scores.

#### 4.1 EVALUATION PER DETERMINATION

PCP: The determination of this component was problematic. Two statistical outliers were observed. The calculated reproducibility after rejection of the statistical outliers is not in agreement with the estimated reproducibility calculated from the iis memo (lit. 18).

TeCPs: Sample #17545 did contain very little of the components 2,3,4,5-TeCP, 2,3,4,6-TeCP and 2,3,5,6-TeCP, 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:

	<i>unit</i>	<i>n</i>	<i>average</i>	<i>2.8 x sd</i>	<i>R (target)</i>
PCP	mg/kg	70	9.76	9.92	7.09
2,3,4,5-TeCP	mg/kg	51	<0.5 or n.d.	n.a.	n.a.
2,3,4,6-TeCP	mg/kg	52	<0.5 or n.d.	n.a.	n.a.
2,3,5,6-TeCP	mg/kg	51	<0.5 or n.d.	n.a.	n.a.

Table 3: reproducibility of phenols on sample #17545

Without further statistical calculations, it can be concluded that for PCP the total group of participating laboratories may have difficulties with the analysis. See also the discussion in paragraphs 4.1 and 6.

#### 5 COMPARISON OF THE PROFICIENCY TEST OF APRIL 2017 WITH THE PREVIOUS PT

	April 2017	April 2016
Number of reporting labs	72	74
Number of results reported	107	110
Number of statistical outliers	2	3
Percentage outliers	1.9%	2.7%

Table 4: Comparison with previous proficiency test

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.

	<i>PCP in Leather</i>		<i>PCP in Textile</i>					<i>Period 2011-2004</i>	<i>RSD(iis) see lit. 18</i>
	<i>April 2017</i>	<i>April 2016</i>	<i>Nov 2016</i>	<i>Nov 2015</i>	<i>Nov 2014</i>	<i>Nov 2013</i>	<i>Nov 2012</i>		
PCP	36%	41%	28%	38%	26%	20%	16-23%	15-38%	25%

Table 5: Comparison of uncertainties in iis proficiency tests



## 6 DISCUSSION

The limit for PCP mentioned in standard 100 by OEKO-TEX is 0.05 mg/kg for baby's and 0.5 mg/kg for all other applications. All laboratories except one (lab 2727) would reject this sample based on the limit of 0.5 mg/kg.

In this proficiency test for the determination of phenols in leather, it was noticed that the participants were able to detect PCP in sample #17545. Regretfully, the observed reproducibility was not in agreement with the target reproducibility.

It was observed that not all laboratories followed the same procedure for extracting the PCP from the leather. The majority of laboratories performed ISO17070 or LFGB B82.02.8 (53 participants), the others did an in house method or did not report any details. 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 37 of the 53 laboratories, which reported to have used ISO17070 or LFGB B82.02.8, used steam distillation. In addition, although there is no mention of the use of an ultrasonic device in the method, 5 laboratories used this in combination with steam distillation. The latter group (steam distillation without or with the aid of ultrasonic) was evaluated separately (see table 5).

Next to this, 5 laboratories used a steam distillation together with a soxhlet/ASE extraction, when the soxhlet/ASE extraction is not mentioned in the methods above. The question is what the benefit of this pathway is. The other 17 laboratories used only an ultrasonic device, this group was evaluated separately also (see table 5).

<i>PCP Determination pathway, first step</i>	<i>unit</i>	<i>n</i>	<i>average</i>	<i>st.dev</i>	<i>RSD%</i>
Overall (all test results)	mg/kg	70	9.76	3.54	36%
ISO17070, LFGB B82.02.8 and KS K 0733 only	mg/kg	52	9.45	3.23	34%
Steam Distillation (without or with ultrasonic extr.)	mg/kg	32	8.16	3.21	39%
Ultrasonic extraction only	mg/kg	17	11.16	3.64	33%

Table 6: Comparison of different sample pathways on the PCP determination

As can be seen in the table above, the laboratories that followed the pathway of ISO17070/LFGB 82.02.8 for the first step (Steam distillation) on average found a significantly lower result than the group using only an ultrasonic extraction. Not following the method to the letter will have an influence on the test results. In a sample like this, where the amount of PCP is well above the limit, it will have little consequence to acceptance/rejection of the sample. However, when the amount of PCP is close to the limit, not following the method may lead to false positive or false negative test results.

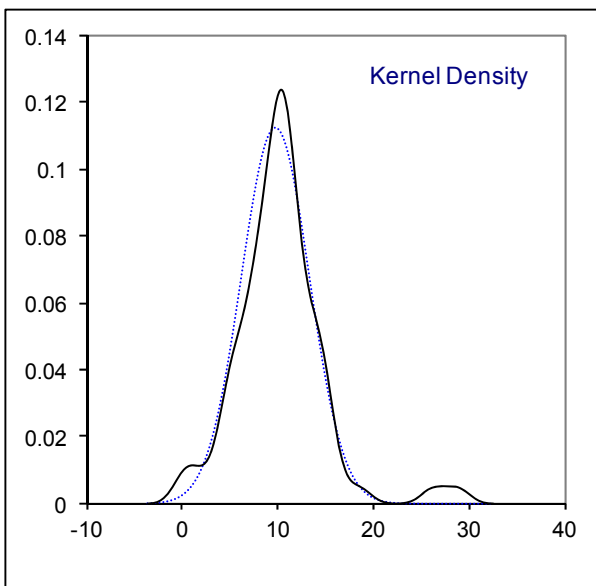
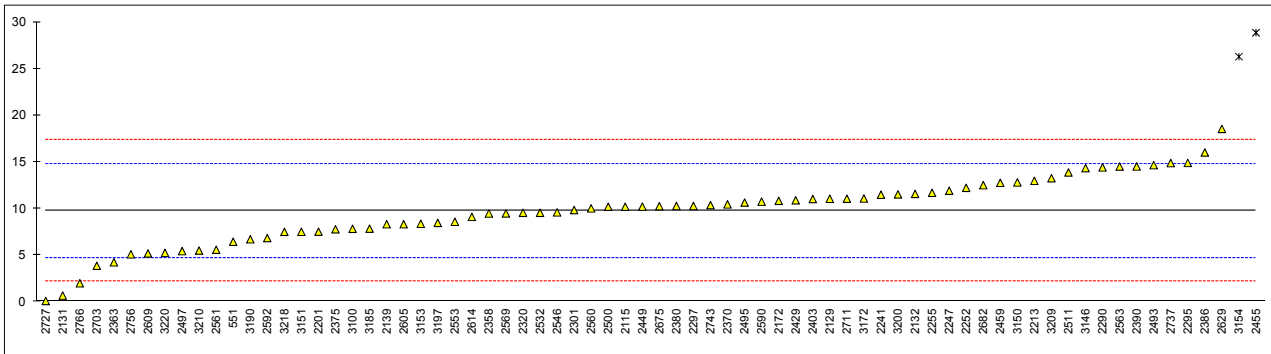
**APPENDIX 1****Determination of Pentachlorophenol (PCP) on sample #17545; results in mg/kg**

lab	method	value	mark	z(targ)	remarks
213		----		----	
230		----		----	
551	ISO17070	6.455		-1.30	
2115	ISO17070	10.21	C	0.18	first reported: 1.589
2129	ISO17070	11.06		0.51	
2131	In house	0.68		-3.58	
2132	In house	11.58		0.72	
2139	In house	8.33		-0.56	
2172	In house	10.846		0.43	
2201	ISO17070	7.534		-0.88	
2213	ISO17070	12.98		1.27	
2241	ISO17070	11.492		0.68	
2247	ISO17070	11.92		0.85	
2252	ISO17070	12.231		0.98	
2255	In house	11.7		0.77	
2290	ISO17070	14.42		1.84	
2295	ISO17070	14.9		2.03	
2297	ISO17070	10.29		0.21	
2301	In house	9.85		0.04	
2320	ISO17070	9.557		-0.08	
2358	ISO17070	9.480		-0.11	
2363	ISO17070	4.25		-2.17	
2370	ISO17070	10.46		0.28	
2375	ISO17070	7.79		-0.78	
2380	LFGB B82.02.8	10.29		0.21	
2386	In house	16.02		2.47	
2390	In house	14.5244		1.88	
2403	ISO17070	11.035		0.50	
2429	ISO17070	10.90		0.45	
2449	LFGB B82.02.8	10.219		0.18	
2455	ISO17070	28.86	C,R(0.01)	7.54	first reported: 0
2459	ISO17070	12.772		1.19	
2493	In house	14.663		1.94	
2495	ISO17070	10.659		0.36	
2497	In house	5.452		-1.70	
2500	In house	10.21		0.18	
2511	ISO17070	13.88		1.63	
2532	ISO17070	9.5585		-0.08	
2538		----		----	
2546	ISO17070	9.60		-0.06	
2553	In house	8.59		-0.46	
2560	ISO17070	10.029		0.11	
2561	ISO17070	5.5917		-1.64	
2563	ISO17070	14.52		1.88	
2569	ISO17070	9.49		-0.11	
2590	ISO17070	10.753		0.39	
2592	ISO17070	6.85		-1.15	
2605	ISO17070	8.33		-0.56	
2609	ISO17070	5.2		-1.80	
2614	LFGB B82.02.8	9.12		-0.25	
2629	In house	18.55		3.47	
2656		----		----	
2675	ISO17070	10.2588		0.20	
2682		12.52		1.09	
2703	ISO17070	3.882		-2.32	
2711	In house	11.07		0.52	
2727	ISO17070	0.11		-3.81	
2737	ISO17070	14.887		2.02	
2743	LFGB B82.02.8	10.38		0.24	
2756	ISO17070	5.106		-1.84	
2766	ISO17070	2.00		-3.06	
2773		----		----	
3100	ISO17070	7.841		-0.76	
3146	In house	14.349		1.81	
3150	ISO17070	12.81		1.20	
3151	In house	7.525		-0.88	
3153	LFGB B82.02.8	8.38		-0.54	
3154	ISO17070	26.29	C,R(0.01)	6.52	first reported: 23.05
3172	KS K 0733	11.09		0.53	
3185	ISO17070	7.856		-0.75	
3190	ISO17070	6.717		-1.20	
3197	ISO17070	8.48		-0.50	
3200	ISO17070	11.53		0.70	
3209	ISO17070	13.26		1.38	
3210	In house	5.51		-1.68	
3218	ISO17070	7.52		-0.88	
3220	ISO17070	5.26		-1.78	

Only ISO17070, LFGB B82.02.8 and KS K 0733

normality	OK		OK	
n	70		52	
outliers	2		2	
mean (n)	9.76		9.45	
st.dev. (n)	3.543	RSD=36%	3.229	RSD=34%
R(calc.)	9.92		9.04	
R(iis, see lit 18)	7.09		6.90	

Compare R(ISO17070:15) = 3.29 and R(Horwitz) = 3.10



## Determination of Tetrachlorophenols on sample #17545; results in mg/kg

lab	method	2,3,4,5-TeCP	2,3,4,6-TeCP	2,3,5,6-TeCP	remarks
213		----	----	----	
230		----	----	----	
551	ISO17070	0.09978	ND	ND	
2115		0.0143	0.0290	----	
2129	ISO17070	<0,1	<0,1	<0,1	
2131	In house	0	0	0	
2132	In house	<0.05	<0.05	<0.05	
2139		----	----	----	
2172	In house	ND	ND	ND	
2201	ISO17070	ND[<0.5]	ND[<0.5]	ND[<0.5]	
2213	ISO17070	<0.05	<0.05	<0.05	
2241	ISO17070	<0.1	<0.1	<0.1	
2247	ISO17070	ND	ND	ND	
2252	ISO17070	nd	nd	nd	
2255	In house	nd	nd	nd	
2290	ISO17070	< 0.5	< 0.5	< 0.5	
2295		----	----	----	
2297	ISO17070	<0.1	<0.1	<0.1	
2301	In house	0.00 C	0.00 C	0.00 C	first reported: 0.03, 0.36 and 0.64
2320	ISO17070	N.D	0.113	N.D	
2358	ISO17070	< 0.05	< 0.05	< 0.05	
2363	ISO17070	ND	ND	ND	
2370	ISO17070	n.d.	n.d.	n.d.	
2375		----	----	----	
2380		----	----	----	
2386	In house	<0,1	<0,1	<0,1	
2390	In house	ND	ND	ND	
2403	ISO17070	ND	ND	ND	
2429	ISO17070	0	0	0	
2449		----	----	----	
2455	ISO17070	0	0	0	
2459	ISO17070	ND	ND	ND	
2493	In house	0	0	0	
2495	ISO17070	<0.5	<0.5	<0.5	
2497		----	----	0.0448	
2500	In house	ND	ND	ND	
2511		----	----	----	
2532	ISO17070	Not Detected	Not Detected	Not Detected	
2538		----	----	----	
2546	ISO17070	<0,1	<0,1	<0,1	
2553	In house	ND	ND	ND	
2560	ISO17070	ND	ND	ND	
2561	ISO17070	0.036 C	0.036 C	0.2379	first reported: 0.2499 and 0.2814
2563	ISO17070	0.066	0.0866	----	
2569	ISO17070	<0.05	<0.05	<0.05	
2590	ISO17070	< L.O.Q	< L.O.Q	< L.O.Q	
2592		----	----	----	
2605	ISO17070	Not Detected	Not Detected	Not Detected	
2609		----	----	----	
2614	LFGB B82.02.8	Not Detected	Not Detected	Not Detected	
2629		----	----	----	
2656		----	----	----	
2675	ISO17070	0.0229	0.0362	0	
2682		----	----	----	
2703	ISO17070	0	0	0	
2711		----	----	----	
2727	ISO17070	< 0.05	< 0.05	< 0.05	
2737	ISO17070	ND	ND	ND	
2743	LFGB B82.02.8	n.d. C	0.074	0.155	first reported: 0.368
2756	ISO17070	Not done	ND	Not done	
2766		----	----	----	
2773		----	----	----	
3100	ISO17070	<0.1	<0.1	<0.1	
3146	In house	<0,1	<0,1	<0,1	
3150		----	----	0.062	
3151		----	----	----	
3153		----	----	----	
3154		----	----	----	
3172	KS K 0733	< 0.05	< 0.05	< 0.05	
3185	ISO17070	ND	ND	ND	
3190		----	----	----	
3197	ISO17070	ND	ND	ND	
3200	ISO17070	<0.1	<0.1	<0.1	
3209	ISO17070	Not detected	Not detected	Not detected	
3210		----	----	----	
3218		----	----	----	
3220	ISO17070	ND	ND	0.203	

n	51	52	51
mean (n)	<0.5 or n.d.	<0.5 or n.d.	<0.5 or n.d.

## APPENDIX 2 Details of the test methods used by the participants

lab		ISO17025 accr.?	Sample prep.?	Size	How to release the PCP?	How to extract the PCP?	How to shake the liquid/liquid extraction	Acetylation
213	ISO17070	---	---		---	---	---	---
230	ISO17070	---	---		---	---	---	---
551	ISO17070	Yes	Cut		Steam distillation	Ultrasonic extraction	Mechanical shaker	Yes
2115	In house	Yes	Cut	2mm x 2 mm	Steam distillation	---	Mechanical shaker	Yes
2129	In house	Yes	Cut	Ca 3*3 mm	ASE extraction with acetic acid / acetone	Soxhlet / AES extraction	Mechanical shaker	Yes
2131	In house	Yes	Used as received	Used as received	Steam distillation	---	Mechanical shaker	Yes
2132	In house	No	Cut	4 mm x 4 mm	Steam distillation was skipped	Stand over night	Mechanical shaker	Yes
2139	ISO17070	Yes	Cut	3~4 mm	---	---	Mechanical shaker	Yes
2172	ISO17070	Yes	Cut	3mm*3mm	Add 20 mL 2M potassium hydroxide in a vial, shake well and incubate in oven at 80oC for 12 hours (overnight).	---	Mechanical shaker	Yes
2201	ISO17070	No	Cut	4*4mm	Steam distillation	---	Mechanical shaker	Yes
2213	ISO17070	Yes	Cut		---	---	Mechanical shaker	Yes
2241	ISO17070	Yes	Cut	2mm*2mm	Steam distillation	---	Mechanical shaker	Yes
2247	In house	Yes	Used as received	4 X2 mm approx,	Steam distillation	---	Mechanical shaker	Yes
2252	ISO17070	Yes	Cut	1mm	Steam distillation	Soxhlet / AES extraction	Shaked by hand	Yes
2255	ISO17070	Yes	Cut	2 mm x 2 mm	KOH extraction	KOH extraction	Mechanical shaker	Yes
2290	ISO17070	---	---		---	---	---	---
2295	In house	Yes	Cut		---	Ultrasonic extraction	---	---
2297	ISO17070	Yes	Used as received		Steam distillation was skipped	Ultrasonic extraction	Mechanical shaker	Yes
2301	ISO17070	Yes	Cut	5mm x 5mm	---	Ultrasonic extraction	Mechanical shaker	Yes
2320	ISO17070	Yes	Cut	3mm*3mm	Steam distillation	---	Mechanical shaker	Yes
2358	ISO17070	Yes	Cut	< 5 mm x 5 mm	Steam distillation	---	Mechanical shaker	Yes
2363	ISO17070	Yes	Cut	3*3*3mm	Steam distillation	---	Mechanical shaker	Yes
2370	LFGB B82.02.8	Yes	Cut	3mm x 3mm	Steam distillation	Steam distillation	Mechanical shaker	Yes
2375	In house	No	Cut	2X2mm	Steam distillation	Ultrasonic extraction	Mechanical shaker	Yes
2380	In house	Yes	Used as received		---	---	Mechanical shaker	Yes
2386	ISO17070	Yes	Used as received	8*8mm	---	Ultrasonic extraction	Mechanical shaker	Yes
2390	ISO17070	Yes	Used as received	10 x 10 mm	---	Ultrasonic extraction	No liq/liq extraction was done	No
2403	LFGB B82.02.8	Yes	Cut	5*5 mm	Steam distillation	Soxhlet / AES extraction	Mechanical shaker	Yes
2429	ISO17070	Yes	Cut	3mm*2mm	Steam distillation	---	Mechanical shaker	Yes
2449	ISO17070	Yes	Cut	3x3	---	Ultrasonic extraction	Mechanical shaker	No
2455	In house	Yes	Grinded	ground fibers	Steam distillation was skipped	Ultrasonic extraction	No liq/liq extraction was done	No
2459	ISO17070	Yes	Used as received	5*5mm	Steam distillation	Ultrasonic extraction	Mechanical shaker	Yes
2493	In house	No	---	0,2 mm	---	Ultrasonic extraction	Mechanical shaker	No, methylation
2495	In house	Yes	Cut	3mm	Steam distillation	---	Mechanical shaker	Yes
2497	ISO17070	---	Used as received		---	Ultrasonic extraction	---	No
2500	ISO17070	Yes	Used as received	5mm x 5mm	---	Ultrasonic extraction	Mechanical shaker	Yes
2511		No	Cut		Steam distillation was skipped	---	Mechanical shaker	Yes
2532	ISO17070	Yes	Cut	3-5 mm	Steam distillation	Soxhlet / AES extraction	Mechanical shaker	Yes
2538	In house	---	---		---	---	---	---

lab		ISO17025 accr.?	Sample prep.?	Size	How to release the PCP?	How to extract the PCP?	How to shake the liquid/liquid extraction	Acetylation
2546	ISO17070	Yes	Cut	3-4 mm	Steam distillation	---	Mechanical shaker	Yes
2553	ISO17070	Yes	Cut	5 mm*5 mm	Steam distillation was skipped	Ultrasonic extraction	Mechanical shaker	Yes
2560	ISO17070	Yes	Used as received	6mmX6mm	---	---	Mechanical shaker	No
2561	ISO17070	Yes	Cut		Steam distillation	---	Mechanical shaker	Yes
2563	ISO17070	Yes	Cut	approx. 5x5 mm	---	Soxhlet / AES extraction	Mechanical shaker	Yes
2569	ISO17070	Yes	Cut		Steam distillation	---	Mechanical shaker	Yes
2590	ISO17070	Yes	Cut		Steam distillation	---	Mechanical shaker	Yes
2592	ISO17070	Yes	Used as received		Steam distillation	Ultrasonic extraction	Mechanical shaker	Yes
2605	LFGB B82.02.8	Yes	Cut	2*3mm	Steam distillation	---	Mechanical shaker	Yes
2609	In house	Yes	Cut	2-3mm	Steam distillation	---	Mechanical shaker	Yes
2614		Yes	Cut	2MM*2MM	---	Ultrasonic extraction	Mechanical shaker	Yes
2629	ISO17070	No	Cut		in Acetone by ultrasonic extraction at 40 ±2 0C for 30 minutes then alkaline with KOH 2M	Ultrasonic extraction	Mechanical shaker	Yes
2656		---	---				---	---
2675	ISO17070	Yes	Cut	about 4 x 4 mm	Steam distillation	---	Mechanical shaker	Yes
2682	In house	---	---		---	---	---	---
2703	ISO17070	Yes	Used as received	1cm^2	Steam distillation	---	Mechanical shaker	Yes
2711	ISO17070	No	Used as received	As received	Phenols extracted from leather with an aqueous solution of sodium carbonate 0,1 M.		Mechanical shaker	Yes
2727	LFGB B82.02.8	Yes	Cut	3-5 mm	Steam distillation	---	Mechanical shaker	Yes
2737	ISO17070	Yes	Used as received		---	---	Mechanical shaker	Yes
2743	ISO17070	Yes	Used as received	already grinded	---	Ultrasonic extraction	Shaked by hand	Yes
2756		No	Cut		Steam distillation	---	Mechanical shaker	Yes
2766	ISO17070	Yes	Cut	1 mm	We extracted sample in acetone acetic acid solution and then further in hexane. Then transferred it to K2CO3 solution. The K2CO3 solution was separated and derivatised with acetic		Mechanical shaker	Yes
2773	In house	---	---		---	---	---	---
3100	ISO17070	Yes	Cut	2mm*3mm	Steam distillation	---	Mechanical shaker	Yes
3146	In house	Yes	Cut	2mm x 2mm	Method: KOH-Method - Sample + 1m KOH 12-16h 90°C in the oven - cool down to room temperature - an aliquot of the extract + Acetic anhydride + Hexane - shake 1h at 350 rpm		Mechanical shaker	Yes
3150	LFGB B82.02.8	Yes	Cut	(3 x 3) mm	---	Ultrasonic extraction	Mechanical shaker	Yes
3151	ISO17070	Yes	Used as received	8x8 mm	---	Ultrasonic extraction	Mechanical shaker	Yes
3153	KS K 0733	Yes	Cut	3mm x 3mm	Steam distillation	---	Mechanical shaker	Yes
3154	ISO17070	Yes	Used as received		---	---	---	---
3172	ISO17070	Yes	Cut	5mm x 5mm	---	Ultrasonic extraction	Mechanical shaker	No
3185	ISO17070	Yes	Cut	5mm*5mm	Steam distillation	---	Mechanical shaker	Yes
3190	ISO17070	Yes	Used as received	Original size	Steam distillation	Soxhlet / AES extraction	Mechanical shaker	Yes
3197	ISO17070	Yes	Used as received		Steam distillation	Soxhlet / AES extraction	Mechanical shaker	Yes
3200	In house	No	Cut	5mm	Steam distillation	---	Mechanical shaker	Yes
3209	ISO17070	Yes	Cut	2mm X 2mm	Steam distillation	Ultrasonic extraction	Mechanical shaker	Yes
3210	ISO17070	Yes	Used as received		---	Ultrasonic extraction	Mechanical shaker	Yes
3218		Yes	Used as received	80*90mm	Steam distillation	---	Mechanical shaker	Yes
3220		Yes	Cut	0.5 sq.cm	Steam distillation	---	Mechanical shaker	Yes

## APPENDIX 3

### Number of participants per country

3 labs in BANGLADESH  
1 lab in BRAZIL  
1 lab in ETHIOPIA  
2 labs in FRANCE  
9 labs in GERMANY  
3 labs in HONG KONG  
1 lab in HUNGARY  
8 labs in INDIA  
1 lab in INDONESIA  
9 labs in ITALY  
1 lab in KOREA  
1 lab in MAURITIUS  
1 lab in MOROCCO  
18 labs in P.R. of CHINA  
4 labs in PAKISTAN  
1 lab in PORTUGAL  
2 labs in SRI LANKA  
1 lab in SWITZERLAND  
1 lab in TAIWAN R.O.C.  
1 lab in TUNISIA  
3 labs in TURKEY  
1 lab in U.S.A.  
2 labs in UNITED KINGDOM  
2 labs in VIETNAM



**APPENDIX 4****Abbreviations:**

C	= final test result after checking of first reported suspect test result
D(0.01)	= outlier in Dixon's outlier test
D(0.05)	= straggler in Dixon's outlier test
G(0.01)	= outlier in Grubbs' outlier test
G(0.05)	= straggler in Grubbs' outlier test
DG(0.01)	= outlier in Double Grubbs' outlier test
DG(0.05)	= straggler in Double Grubbs' outlier test
R(0.01)	= outlier in Rosner's outlier test
R(0.05)	= straggler in Rosner's outlier test
n.a.	= not applicable
n.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 result

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