Results of Proficiency Test OPP, PCP and TeCP in textile December 2015

Organised by: Institute for Interlaboratory Studies
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1 INTRODUCTION

Since the 1990's, many countries have adopted environmental standards and requirements restricting the use of harmful chemicals in the production of textiles and clothing. Laws and regulations impose some of these standards and requirements. In addition to mandatory environmental standards and requirements for textiles, some Eco-labelling schemes are imposing environmental requirements for textile products on a voluntary basis, e.g. Milieukeur (Netherlands) and Öko-Tex Standard 100 (Germany).
The Institute for Interlaboratory Studies organizes since 2004 a scheme of proficiency test for Orthophenylphenol (OPP), Pentachlorophenol (PCP) and Tetrachlorophenols (TeCP) in textile. In the annual proficiency test program of 2015/2016, this proficiency test was continued.
In this interlaboratory study 93 laboratories in 22 different countries participated. See appendix 3 for the number of participants per country. In this report, the results of the 2015 proficiency test are presented and discussed. This report is also electronically available through the iis internet site www.iisnl.com.

2 SET UP

The Institute for Interlaboratory Studies in Spijkenisse was the organiser of the proficiency test. It was decided to use two different samples which were positive on OPP or PCP. Sample analyses for fit-for-use and homogeneity testing were subcontracted to an accredited laboratory. The participants were requested to report the analytical results using the indicated units and to report rounded and unrounded results. The unrounded 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 IEC/ISO17043:2010. This ensures strict adherence to protocols for sample preparation and statistical evaluation and 100% confidentially of participant's data. Feedback from the participants on the reported data is encouraged and customer's satisfaction is measured on regular basis by sending out questionnaires.

2.2 PROTOCOL

The protocol followed in the organisation was the one as described for proficiency testing in the report 'iis Interlaboratory Studies: Protocol for the Organisation, Statistics and Evaluation' of April 2014 (iis-protocol, version 3.3). This protocol is electronically available through the iis internet site 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

Two different batches of textile were obtained from third party laboratories. The first bulk sample a hosiery fabric, positive on OPP, was cut into pieces. Out of this batch, after mixing well, 120 subsamples of 3 grams each were packed and labelled #15243.
The homogeneity of 8 stratified randomly selected samples was checked by determination of OPP by an accredited third party laboratory. The determination is performed in accordance with an in-house test method for OPP. See the following table for the test results.

	OPP in mg/kg
Sample #15243-1	12.3
Sample #15243-2	12.1
Sample #15243-3	11.2
Sample #15243-4	12.8
Sample #15243-5	10.6
Sample #15243-6	10.9
Sample #15243-7	12.1
Sample #15243-8	11.9

Table 1: homogeneity test results of subsample #15243

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

	OPP in mg/kg
r (samples #15243)	2.1
Reference method	iis-memo (see lit.18)
0.3 x R (reference method)	2.5

Table 2: repeatability of subsamples #15243.

The second bulk sample a hosiery fabric, positive on PCP, was cut into pieces. Out of this batch, after mixing well, 109 subsamples of 3 grams each were filled and labelled #15244. The homogeneity of 4 stratified randomly selected samples was checked by determination of PCP by an accredited third party laboratory. The determination is performed in accordance with LFBG82.02.8 for PCP. See the following table for the test results.

	PCP in mg/kg
Sample #15244-1	25.7
Sample #15244-2	24.6
Sample #15244-3	25.3
Sample #15244-4	25.4

Table 3: homogeneity test results of subsample #15244

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

	PCP in mg/kg
r (samples #15244)	1.3
Reference method	iis-memo (see lit.18)
0.3 x R (reference method)	4.8

Table 4: repeatability of subsamples #15244.

The repeatabilities of Orthophenylphenol (OPP) and Pentachlorophenol (PCP) were in agreement with 0.3 times the target requirements. Therefore, homogeneity of the subsamples was assumed.
To each participating laboratory one samples of approx. 3 grams, labelled #15243 and one sample of approx. 3 grams, labelled #15244 were sent on November 18, 2015.

2.5 ANALYSES

The participants were asked to determine the concentration of Orthophenylphenol (OPP) on sample #15243 and the concentration of Pentachlorophenol (PCP), 2,3,4,5-Tetrachlorophenol, 2,3,4,6-Tetrachlorophenol and 2,3,5,6-Tetrachlorophenol on sample #15244 applying the analysis procedure that is routinely used in the laboratory.
To get comparable results a detailed report form, on which the units were prescribed as well as the required standards and a letter of instructions were prepared and made available on the data entry portal www.kpmd.co.uk/sgs-iis-cts/. A form to confirm receipt of the samples and a letter of instructions were added to the samples.

3 RESULTS

During four weeks after sample despatch, the results of the individual laboratories were gathered via the data entry portal www.kmpd.co.uk/sgs-iis-cts/. The original data are tabulated per sample in the appendix 1 of this report. The laboratories are represented by the code numbers.
Directly after the deadline, a reminder was sent to those laboratories that did not report results at that moment.
Shortly after the deadline, the available results were screened for suspect data. A 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 results. Additional or corrected results are used for the data analysis and the original results are placed under 'Remarks' in the result tables in appendix 1.

3.1 STATISTICS

The statistical calculations were performed as described in the procedures in the report ‘iis Interlaboratory Studies, Protocol for the Organisation, Statistics and Evaluation’ of April 2014 (iis-protocol, version 3.3).

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. Not all data sets proved to have a normal distribution, in which cases the statistical evaluation of the results should be used with due care.

In accordance to ISO 5725 (1986 and 1994) the original results per determination were submitted subsequently to Dixon, Grubbs and or Rosner General ESD outlier tests. Outliers are marked by D(0.01) for the Dixon test, by G(0.01) or DG(0.01) for the Grubbs test and by R(0.01) for the Rosner General ESD test. Stragglers are marked by D(0.05) for the Dixon test, by G(0.05) or DG(0.05) for the Grubbs test and by R(0.05) for the Rosner General ESD test (ref. 17). Both outliers and stragglers were not included in the calculations of averages and standard deviations.
Finally, the reproducibilities were calculated from the standard deviations by multiplying them with a factor of 2.8.

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 significant consequences for the evaluation of the test results.

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 under 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. This is a method for producing a smooth density approximation to a set of data that avoids some problems associated with histograms (see appendix 4; nr.14 and 15). 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 spread of this interlaboratory study.

The target standard deviation was calculated from the target reproducibility (preferably taken from a standardized test method) by division with 2.8.
The z-scores were calculated in accordance with:

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

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

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.

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 5 participants reported the test results after the final reporting date and 7 participants did not report any results at all. In total 85 of the 92 participants reported 286 numerical results. Observed in all reported results were 9 statistical outlying results, which is 3.1%. In proficiency studies, outlier percentages of 3% - 7.5% are quite normal.

Due to the lack of relevant standard test methods for the determination of OPP, calculated reproducibilities were compared with reproducibilities estimated from the Horwitz equation until now. For Pentachlorophenol (PCP), both existing methods (LFGB 82.02-8 and ISO17070:2006, the latter method superseding DIN53313:1996 and DIN14494:2003), mention identical precision data for leather only. These precision data for leather are in full agreement with the Horwitz equation and were used in the calculation of the z-scores due to lack of a better alternative. In other PTs for other determinations, a quality improvement is visible over the years as a decrease of the dispersion is observed. However, in the case of OPP and PCP a quality improvement is not clearly visible and therefore it is doubtful whether the target reproducibility based on the Horwitz equation will ever be met. This goal may be unreachable. Therefore it was now decided to use the iis PT data gathered since 2004, to estimate a more realistic target reproducibility. As it is assumed that the actual dispersion of the test results will be concentration dependent, a Horwitz like equation was prepared to estimate the target reproducibilities for OPP and PCP. For future PTs on OPP and PCP in textile, starting the 2015 PT iis15A07, iis will use this Horwitz-like equation to estimate the target reproducibilities to be used for the evaluation of the quality of the test results (see lit.18).

4.1 EVALUATION PER DETERMINATION

Not all original data sets proved to have a normal Gaussian distribution. These are referred to as “not OK” or “suspect”. The statistical evaluation of these data sets should be used with due care.

OPP: The determination of this component was problematic for a number of laboratories. Five statistical outliers were detected. The calculated reproducibility after rejection of the statistical outliers is in full agreement with the estimated reproducibility found in previous iis PTs (see lit 18).

PCP: The determination of this component was problematic. Two statistical outliers were detected. The calculated reproducibility after rejection of the statistical outliers is not in agreement with the estimated reproducibility found in previous iis PTs (see lit 18).

2,3,4,5-TeCP: Sample #15244 did contain very little of this component, which concentration was near or below the detection limit. Therefore no significant conclusions were drawn.

2,3,4,6-TeCP: The determination of this component may not be problematic. Two statistical outliers were detected. The calculated reproducibility after rejection of the statistical outliers is in agreement with the estimated reproducibility found in previous iis PTs (see lit 18).

2,3,5,6-TeCP: Sample #15244 did contain very little of this component, which concentration was 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 significant results, the average results, the calculated reproducibilities (standard deviation*2.8) and the target reproducibilities are compared in the next table:

	unit	*n*	*Average*	*2.8 * sd*	*R (target)*
OPP	mg/kg	70	14.9	10.1	10.2
PCP	mg/kg	83	16.5	17.5	11.1
2,3,4,5-TeCP	mg/kg	54	<0.1	unknown	unknown
2,3,4,6-TeCP	mg/kg	75	0.99	0.73	1.01
2,3,5,6-TeCP	mg/kg	54	<0.1	unknown	unknown

Table 5: reproducibility of phenols on textile sample #15243 and #15244

Without further statistical calculations, it can be concluded that for OPP and TCEP, the total group of participating laboratories may have no difficulties with the analysis. See also the discussion in paragraphs 4.1 and 6.

5 COMPARISON WITH PREVIOUS INTERLABORATORY STUDIES

The spreads, found during the present proficiency test when using all reported results, are similar to the spreads as observed in the previous rounds.

	Nov 2015	*Nov 2014*	*Nov 2013*	*Nov 2012*	*Nov 2011*	*Dec 2010*	*Feb 2010*	*Feb 2009*
OPP	24%	27%	29%	29%	21–24%	17-31%	17-19%	29–35%
PCP	38%	26%	20%	16-23%	19–20%	15-24%	18-20%	29–31%

Table 6: Comparison of uncertainties in iis proficiency tests

6 DISCUSSION

In this proficiency test for the determination of phenols in textile, it was noticed that the majority of the participants was able to detect OPP in sample #15243 and PCP and 2,3,4,6-TeCP in sample #15244.

When the results of this interlaboratory study were compared to the Ecolabelling Standards and Requirements for Textiles in EU (table 7), it could be noticed that for sample #15243 one laboratory would make a different decision about the acceptability of the textile. All reporting laboratories, except one, would accept the sample for all classes. One laboratory would reject this sample for class 1 (Baby clothes).
For sample #15244 all reporting laboratories would reject the sample for all classes for the determination on PCP.
For the determination on Tetrachlorophenols in sample #12544, all reporting laboratories, except one, would reject the sample for all classes. One laboratory would reject the sample only for class 1 (baby clothes)
A number of laboratories did report <0.1 or <0.5 mg/kg for one or more TCEP components, which is remarkable as these reported limits are above the lower limits of the OekoTex requirements of 0.05 mg/kg, see below table.

Ecolabel	Class 1 Baby clothes (mg/kg)	Class 2 Clothes direct skin contact (mg/kg)	Class 3 Clothes, no direct contact with skin (mg/kg)	Class 4 Decoration material (mg/kg)
Orthophenylphenol	50.0	100.0	100.0	100.0
Pentachlorophenol	0.05	0.5	0.5	0.5
Sum of Tetrachlorophenols	0.05	0.5	0.5	0.5

Table 7: Ecolabelling Standards and Requirements for Textiles in EU

APPENDIX 1

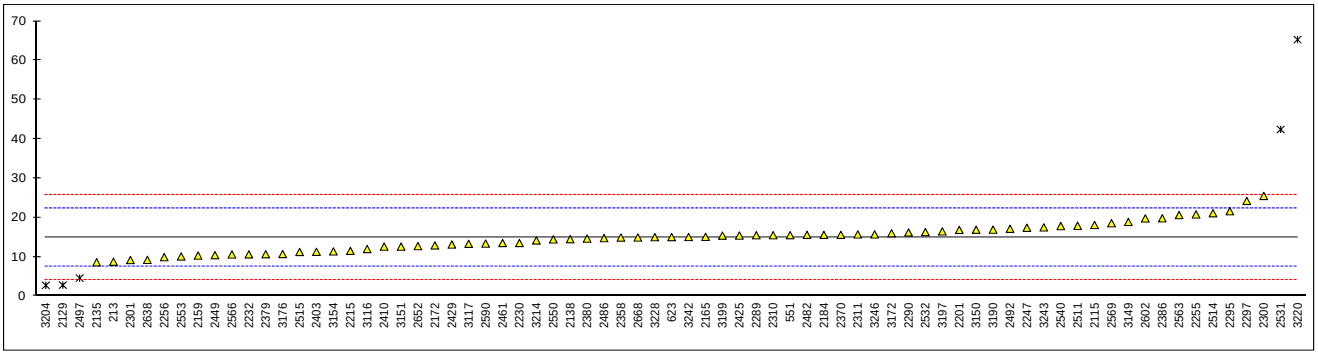
Determination of Orthophenylphenol (OPP) on sample #15243; results in mg/kg

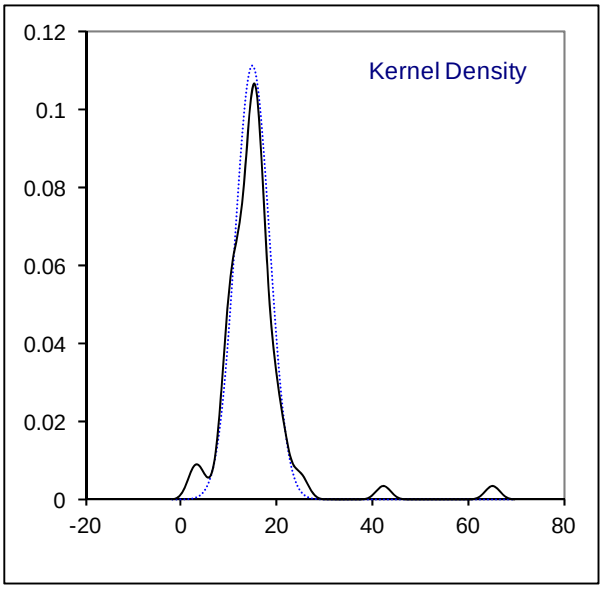
lab	method	value	mark	z(targ)	remarks
213	XP G 08-015	8.76	C	-1.70	First reported 1.4
551	In house	15.52		0.16	
623	In house	15.02		0.03	
2115	UNI11057	18.10		0.87	
2129		2.795	C,R(0.01)	-3.34	First reported 0.693
2135	In house	8.61		-1.74	
2138	In house	14.49		-0.12	
2159	LFGB §64 B82.02.8	10.33		-1.26	
2165	LFGB B82.02.8	15.10		0.05	
2172	In house	12.91		-0.55	
2184	LFGB B82.02.8	15.6		0.19	
2201	In house	16.86		0.53	
2215	In house	11.52		-0.94	
2230	In house	13.52		-0.39	
2232	In house	10.62		-1.18	
2241		-----		-----	
2247	In house	17.4		0.68	
2255	In house	20.8		1.62	
2256	In house	9.91		-1.38	
2289	LMBG 82.02.8	15.5		0.16	
2290	ISO17070	16.21		0.35	
2295	In house	21.6		1.84	
2296		-----		-----	
2297	ISO17070Mod.	24.23		2.56	
2300	In house	25.51		2.91	
2301	In house	9.18		-1.58	
2310	In house	15.5		0.16	
2311	In house	15.7		0.21	
2358	In house	14.913		0.00	
2369		-----		-----	
2370	In house	15.6		0.19	
2379	LFGB §64 B82.02.8	10.665		-1.17	
2380	In house	14.64		-0.08	
2386	In house	19.81		1.34	
2390		-----		-----	
2403	GB/T20386	11.28		-1.00	
2410	In house	12.6		-0.64	
2425	In house	15.42		0.14	
2429	ISO17070	13.13		-0.49	
2449	CPSD-AN-00094	10.42	C	-1.24	First reported 15.791
2461	GB/T20386	13.52		-0.39	
2482	In house	15.597		0.18	
2486	In house	14.76392		-0.04	
2492	In house	17.148		0.61	
2493		-----		-----	
2495		-----		-----	
2497	UNI11057	4.572	R(0.01)	-2.85	
2508		-----		-----	
2511	In house	17.9		0.82	
2514	In house	21.10		1.70	
2515	In house	11.23		-1.02	
2531	ISO17070	42.42	R(0.01)	7.56	
2532	LFGB B82.02.8	16.3		0.38	
2538		-----		-----	
2540	In house	17.831		0.80	
2550	GB/T20386	14.443		-0.13	
2553	In house	10.1		-1.33	
2563	ISO17070	20.642		1.57	
2566	LFGB82.02.8	10.6		-1.19	
2569	In house	18.56		1.00	
2590	ISO17070	13.37	C	-0.43	First reported 48.61
2601		-----		-----	
2602	In house	19.78		1.34	
2638	In house	9.227		-1.57	
2652	In house	12.72		-0.61	
2668	In house	14.92		0.00	
3116	In house	11.98		-0.81	
3117		13.320		-0.44	
3118		-----		-----	
3146		-----		-----	
3149	In house	18.88		1.09	
3150	In house	16.9		0.54	
3151	In house	12.6		-0.64	
3153		-----		-----	
3154	In house	11.375		-0.98	

3172	UNI11057	16.00		0.30
3176	In house	10.709		-1.16
3183		-----		-----
3186		-----		-----
3190	LFGB B82.02.8	16.93		0.55
3197	64 LFGB B82.02.8	16.47		0.43
3199	In house	15.4		0.13
3204	In house	2.75	R(0.01)	-3.35
3210	In house	<40		-----
3214	ISO17070	14.17		-0.21
3220	In house	65.3	R(0.01)	13.86
3228	LFGB B82.02.8	15.0		0.02
3233		-----		-----
3237		-----		-----
3242	ISO17070	15.05		0.03
3243	In house	17.5		0.71
3246	In house	15.71		0.22

	normality	OK
	n	70
	outliers	5
	mean (n)	14.925
	st.dev. (n)	3.5953
	R(calc.)	10.067
	R(iis, see lit 18).	10.180

Compare R(Horwitz) = 4.451





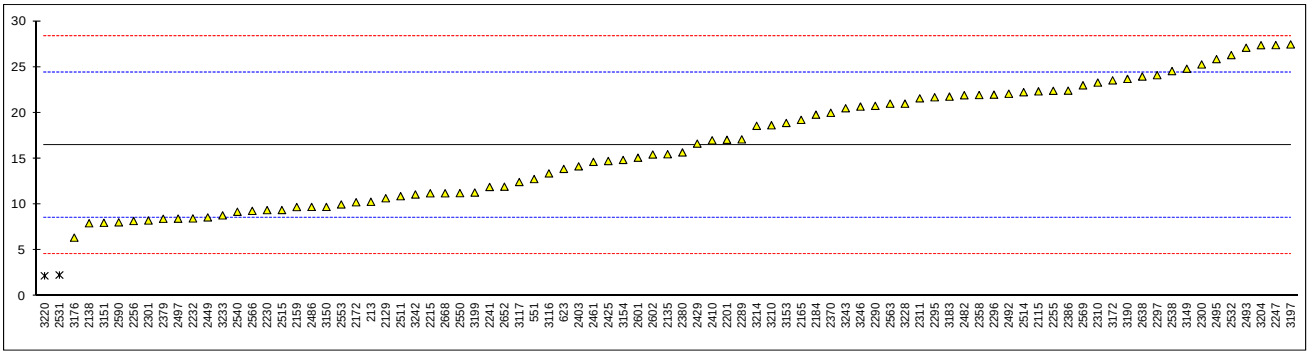
Determination of Pentachlorophenol (PCP) on sample #15244; results in mg/kg

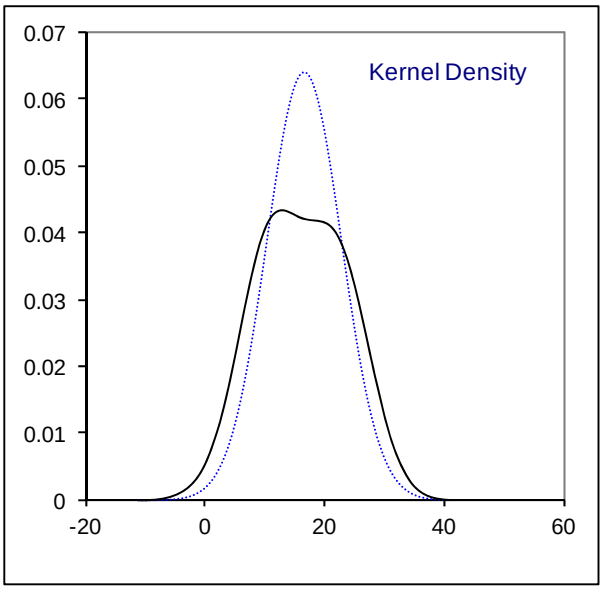
lab	method	value	mark	z(targ)	remarks
213	XP G 08-015	10.29	C	-1.56	First reported 1.22
551	In house	12.77		-0.94	
623	LFGB B82.02.8	13.88		-0.66	
2115	UNI11057	22.34		1.48	
2129	ISO17070	10.68	C	-1.47	First reported 2.69
2135	In house	15.48		-0.25	
2138	In house	7.95		-2.16	
2159	LFGB B82.02.8	9.72		-1.71	
2165	LFGB B82.02.8	19.23		0.70	
2172	LFGB B82.02.8	10.24		-1.58	
2184	LFGB B82.02.8	19.8		0.84	
2201	In house	17.06		0.15	
2215	In house	11.22		-1.33	
2230	LFGB B82.02.8	9.38		-1.79	
2232	LFGB B82.02.8	8.48		-2.02	
2241	ISO17070	11.911		-1.15	
2247	LFGB B82.02.8	27.39		2.76	
2255	In house	22.4		1.50	
2256	LFGB B82.02.8	8.20		-2.09	
2289	LFGB B82.02.8	17.1		0.16	
2290	ISO17070	20.76		1.08	
2295	In house	21.7		1.32	
2296	ISO17070	21.98		1.39	
2297	ISO17070	24.11		1.93	
2300	In house	25.28		2.23	
2301	In house	8.252		-2.08	
2310	LFGB B82.02.8	23.3		1.72	
2311	LFGB B82.02.8	21.58		1.29	
2358	In house	21.937		1.38	
2369		-----		-----	
2370	In house	20.0		0.89	
2379	LFGB B82.02.8	8.437		-2.03	
2380	In house	15.68		-0.20	
2386	In house	22.42		1.50	
2390		-----		-----	
2403	ISO17070	14.16		-0.59	
2410	ISO17070	17.0		0.13	
2425	In house	14.74		-0.44	
2429	ISO17070	16.64		0.04	
2449	CPSD-AN-00094	8.59	C	-1.99	First reported 9.9331
2461	GB/T18414.1	14.65		-0.46	
2482	In house	21.917		1.38	
2486	In house	9.729254		-1.71	
2492	In house	22.084		1.42	
2493	ISO17070	27.1		2.69	
2495	ISO17070	25.86		2.37	
2497	ISO17070	8.453		-2.03	
2508		-----		-----	
2511	In house	10.9		-1.41	
2514	In house	22.25		1.46	
2515	In house	9.391		-1.79	
2531	ISO17070	2.30	R(0.01)	-3.59	
2532	LFGB B82.02.8	26.3		2.48	
2538	LFGB B82.02.8	24.554		2.04	
2540	LFGB B82.02.8	9.203		-1.84	
2550	GB/T18414.1	11.236		-1.33	
2553	In house	10.0		-1.64	
2563	ISO17070	21	C	1.14	First reported 30.44
2566	LFGB82.02.8	9.3		-1.82	
2569	In house	23.0		1.65	
2590	ISO17070	8.05		-2.13	
2601	In house	15.1		-0.35	
2602	In house	15.45		-0.26	
2638	In house	23.961		1.89	
2652	In house	11.94		-1.15	
2668	In house	11.22		-1.33	
3116	In house	13.39		-0.78	
3117		12.448		-1.02	
3118		-----		-----	
3146		-----		-----	
3149	In house	24.81		2.11	
3150	ISO17070	9.73		-1.71	
3151	In house	8.0		-2.14	
3153	LFGB B82.02.8	18.89		0.61	
3154	In house	14.855		-0.41	

3172	UNI11057	23.54		1.79
3176	LFGB B82.02.8	6.376		-2.55
3183	LFGB B82.02.8Mod.	21.77		1.34
3186		-----		-----
3190	LFGB B82.02.8	23.70		1.83
3197	LFGB B82.02.8	27.46		2.78
3199	In house	11.3		-1.31
3204	In house	27.38		2.76
3210	In house	18.642		0.55
3214	ISO17070	18.58		0.53
3220	In house	2.21	R(0.01)	-3.61
3228	LFGB B82.02.8	21.0		1.14
3233	In house	8.81		-1.94
3237		-----		-----
3242	LFGB B82.02.8	11.09		-1.36
3243	LFGB B82.02.8	20.5		1.02
3246	In house	20.68		1.06

normality	OK
n	83
outliers	2
mean (n)	16.478
st.dev. (n)	6.2398
R(calc.)	17.472
R(iis, see lit 18).	11.074

Compare R(LFBG82.02.8) = 5.767



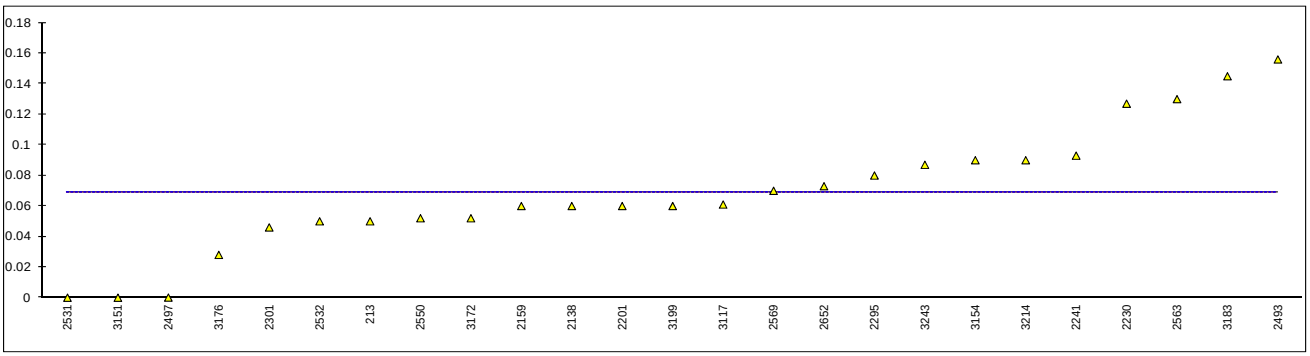


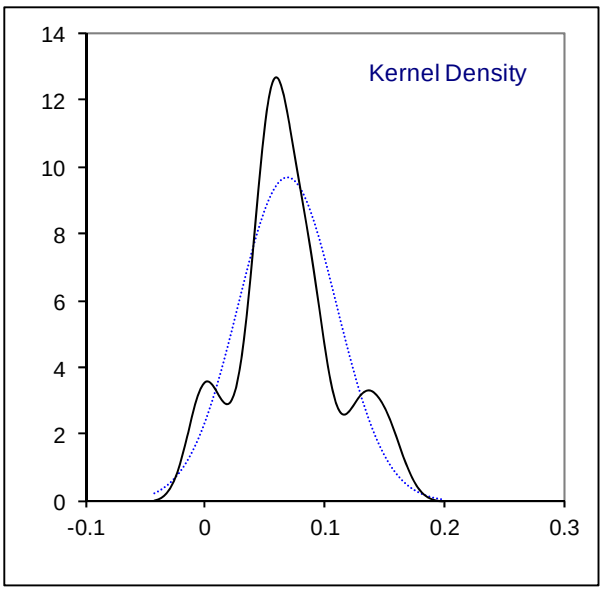
Determination of 2,3,4,5-Tetrachlorophenol on sample #15244; results in mg/kg

lab	method	value	mark	z(targ)	remarks
213	XP G 08-015	0.05		-----	
551		-----		-----	
623	LFGB B82.02.8	n.d.		-----	
2115		-----		-----	
2129	ISO17070	<0.05		-----	
2135		-----		-----	
2138	In house	0.06		-----	
2159	LFGB B82.02.8	0.06		-----	
2165	LFGB B82.02.8	N.D.		-----	
2172	LFGB B82.02.8	ND		-----	
2184	LFGB B82.02.8	Not detected		-----	
2201	In house	0.06		-----	
2215	In house	<0.05		-----	
2230	LFGB B82.02.8	0.127		-----	False positive result?
2232		-----		-----	
2241	ISO17070	0.093		-----	
2247	LFGB B82.02.8	ND		-----	
2255		-----		-----	
2256	LFGB B82.02.8	ND		-----	
2289	LFGB B82.02.8	ND		-----	
2290	ISO17070	<0.5		-----	
2295	In house	0.08		-----	
2296		-----		-----	
2297	ISO17070	nd		-----	
2300	In house	n.d		-----	
2301	In house	0.046		-----	
2310	LFGB B82.02.8	Not detected		-----	
2311	LFGB B82.02.8	Not detected		-----	
2358		-----		-----	
2369		-----		-----	
2370	In house	n.d.		-----	
2379	LFGB B82.02.8	ND		-----	
2380	In house	nd		-----	
2386	In house	<0.1		-----	
2390		-----		-----	
2403	ISO17070	ND		-----	
2410		-----		-----	
2425	In house	Not detected		-----	
2429	ISO17070	<0.05		-----	
2449	LFGB B82.02.8	Not detected		-----	
2461		-----		-----	
2482		-----		-----	
2486	In house	<0.05		-----	
2492		-----		-----	
2493	ISO17070	0.156		-----	False positive result?
2495		-----		-----	
2497	ISO17070	0.0001		-----	
2508		-----		-----	
2511		-----		-----	
2514		-----		-----	
2515	In house	ND		-----	
2531	ISO17070	0		-----	
2532	LFGB B82.02.8	0.05		-----	
2538		-----		-----	
2540		-----		-----	
2550	GB/T18414.1	0.052		-----	
2553	In house	ND		-----	
2563	ISO17070	0.13		-----	False positive result?
2566	LFGB82.02.8	nd		-----	
2569	In house	0.07		-----	
2590		-----		-----	
2601		-----		-----	
2602		-----		-----	
2638		-----		-----	
2652	In house	0.073		-----	
2668	In house	ND		-----	
3116	In house	<0.05		-----	
3117		0.061		-----	
3118		-----		-----	
3146		-----		-----	
3149	In house	<0.1		-----	
3150		-----		-----	
3151	In house	0		-----	
3153		-----		-----	
3154	In house	0.090		-----	

3172	UNI11057	0.052	-----	
3176	LFGB B82.02.8	0.028	-----	
3183	LFGB B82.02.8Mod.	0.145	-----	False positive result?
3186		-----	-----	
3190	LFGB B82.02.8	ND	-----	
3197	LFGB B82.02.8	ND	-----	
3199	In house	0.060	-----	
3204		-----	-----	
3210	In house	<0.500	-----	
3214	ISO17070	0.09	-----	
3220		-----	-----	
3228	LFGB B82.02.8	Not detected	-----	
3233		-----	-----	
3237		-----	-----	
3242	LFGB B82.02.8	Not detected	-----	
3243	LFGB B82.02.8	0.087	-----	
3246	In house	n.d.	-----	

normality	OK
n	54
outliers	n.a.
mean (n)	<0.1
st.dev. (n)	n.a.
R(calc.)	n.a.
R(lit)	n.a.





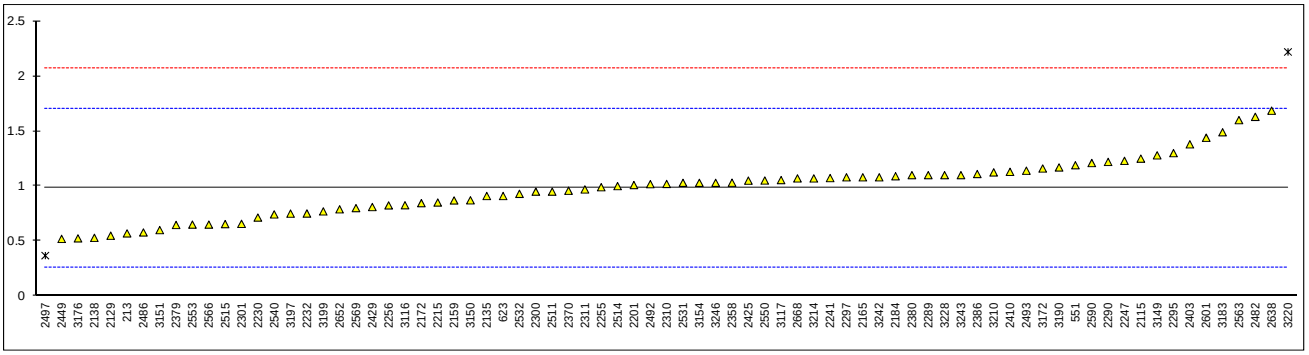
Determination of 2,3,4,6-Tetrachlorophenol on sample #15244; results in mg/kg

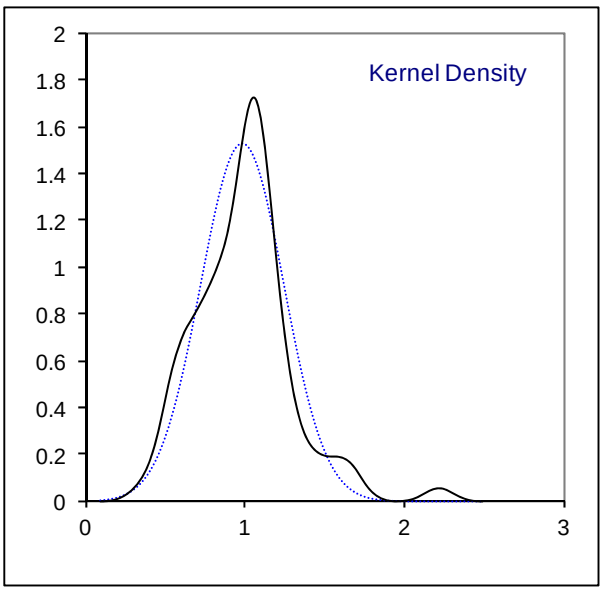
lab	method	value	mark	z(targ)	remarks
213	XP G 08-015	0.57	C	-1.15	First reported 0.08
551	In house	1.19		0.57	
623	LFGB B82.02.8	0.91		-0.21	
2115	UNI11057	1.25		0.73	
2129	ISO17070	0.549	C	-1.21	First reported 0.138
2135	In house	0.91		-0.21	
2138	In house	0.53		-1.26	
2159	LFGB B82.02.8	0.87		-0.32	
2165	LFGB B82.02.8	1.08		0.26	
2172	LFGB B82.02.8	0.8453		-0.39	
2184	LFGB B82.02.8	1.09		0.29	
2201	In house	1.01		0.07	
2215	In house	0.851		-0.37	
2230	LFGB B82.02.8	0.714		-0.75	
2232	LFGB B82.02.8	0.751		-0.65	
2241	ISO17070	1.073		0.24	
2247	LFGB B82.02.8	1.23		0.68	
2255	In house	0.99		0.01	
2256	LFGB B82.02.8	0.825		-0.45	
2289	LFGB B82.02.8	1.1		0.32	
2290	ISO17070	1.22		0.65	
2295	In house	1.3		0.87	
2296		-----		-----	
2297	ISO17070	1.08		0.26	
2300	In house	0.95		-0.10	
2301	In house	0.657		-0.91	
2310	LFGB B82.02.8	1.02		0.10	
2311	LFGB B82.02.8	0.97		-0.04	
2358	In house	1.031		0.13	
2369		-----		-----	
2370	In house	0.958		-0.08	
2379	LFGB B82.02.8	0.647		-0.94	
2380	In house	1.1		0.32	
2386	In house	1.11		0.34	
2390		-----		-----	
2403	ISO17070	1.38		1.09	
2410	ISO17070	1.13		0.40	
2425	In house	1.05		0.18	
2429	ISO17070	0.81		-0.49	
2449	CPSD-AN-00094	0.52	C	-1.29	First reported 0.5311
2461		-----		-----	
2482	In house	1.630		1.79	
2486	In house	0.578844		-1.13	
2492	In house	1.018		0.09	
2493	ISO17070	1.14		0.43	
2495		-----		-----	
2497	ISO17070	0.368	R(0.05)	-1.71	
2508		-----		-----	
2511	In house	0.95		-0.10	
2514	In house	1.0		0.04	
2515	In house	0.655		-0.92	
2531	ISO17070	1.03	C	0.12	First reported 0
2532	LFGB B82.02.8	0.93		-0.15	
2538		-----		-----	
2540	LFGB B82.02.8	0.743		-0.67	
2550	GB/T18414.1	1.051		0.18	
2553	In house	0.65		-0.93	
2563	ISO17070	1.6		1.70	
2566	LFGB82.02.8	0.65		-0.93	
2569	In house	0.8		-0.51	
2590	ISO17070	1.21		0.62	
2601	In house	1.44		1.26	
2602		-----		-----	
2638	In house	1.686		1.94	
2652	In house	0.789		-0.54	
2668	In house	1.07		0.23	
3116	In house	0.8262		-0.44	
3117		1.055		0.19	
3118		-----		-----	
3146		-----		-----	
3149	In house	1.28		0.82	
3150	ISO17070	0.871		-0.32	
3151	In house	0.60		-1.07	
3153		-----		-----	
3154	In house	1.030		0.12	

3172	UNI11057	1.16		0.48
3176	LFGB B82.02.8	0.525		-1.28
3183	LFGB B82.02.8Mod.	1.49		1.40
3186		-----		-----
3190	LFGB B82.02.8	1.17		0.51
3197	LFGB B82.02.8	0.75		-0.65
3199	In house	0.77		-0.60
3204		-----		-----
3210	In house	1.125		0.39
3214	ISO17070	1.07		0.23
3220	In house	2.22	R(0.01)	3.42
3228	LFGB B82.02.8	1.1		0.32
3233		-----		-----
3237		-----		-----
3242	LFGB B82.02.8	1.08		0.26
3243	LFGB B82.02.8	1.1		0.32
3246	In house	1.03		0.12

normality	OK
n	75
outliers	2
mean (n)	0.986
st.dev. (n)	0.2610
R(calc.)	0.731
R(iis, see lit 18).	1.011

Compare R(Horwitz) = 0.443



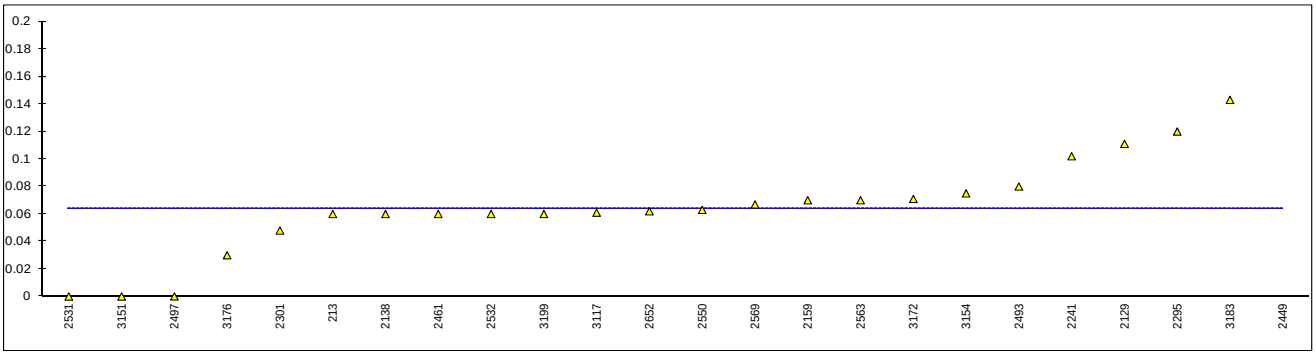


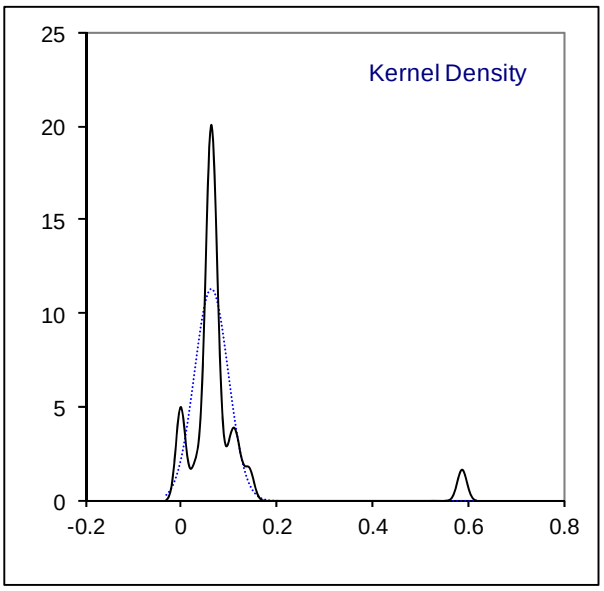
Determination of 2,3,5,6-Tetrachlorophenol on sample #15244; results in mg/kg

lab	method	value	mark	z(targ)	remarks
213	XP G 08-015	0.06		-----	
551		-----		-----	
623	LFGB B82.02.8	n.d.		-----	
2115		-----		-----	
2129	ISO17070	0.111	C	-----	First reported 0.028. False positive result?
2135		-----		-----	
2138	In house	0.06		-----	
2159	LFGB B82.02.8	0.07		-----	
2165	LFGB B82.02.8	N.D.		-----	
2172	LFGB B82.02.8	ND		-----	
2184	LFGB B82.02.8	Not detected		-----	
2201	In house	<0.05		-----	
2215	In house	<0.05		-----	
2230	LFGB B82.02.8	ND		-----	
2232		-----		-----	
2241	ISO17070	0.102		-----	
2247	LFGB B82.02.8	ND		-----	
2255		-----		-----	
2256	LFGB B82.02.8	ND		-----	
2289	LFGB B82.02.8	ND		-----	
2290	ISO17070	<0.5		-----	
2295	In house	0.12		-----	False positive result?
2296		-----		-----	
2297	ISO17070	nd		-----	
2300	In house	n.d		-----	
2301	In house	0.048		-----	
2310	LFGB B82.02.8	Not detected		-----	
2311	LFGB B82.02.8	Not detected		-----	
2358		-----		-----	
2369		-----		-----	
2370	In house	n.d.		-----	
2379	LFGB B82.02.8	<0.5		-----	
2380	In house	Nd		-----	
2386	In house	<0.1		-----	
2390		-----		-----	
2403	ISO17070	ND		-----	
2410		-----		-----	
2425	In house	Not Detected		-----	
2429	ISO17070	<0.05		-----	
2449	CPSD-AN-00094	0.588	C	-----	First reported 0.341. False positive result?
2461	GB/T18414.1	0.06	C	-----	First reported 1.89
2482		-----		-----	
2486	In house	<0.05		-----	
2492		-----		-----	
2493	ISO17070	0.08		-----	
2495		-----		-----	
2497	ISO17070	0.0001		-----	
2508		-----		-----	
2511		-----		-----	
2514		-----		-----	
2515	In house	ND		-----	
2531	ISO17070	0.00	C	-----	First reported 1.03
2532	LFGB B82.02.8	0.06		-----	
2538		-----		-----	
2540		-----		-----	
2550	GB/T18414.1	0.063		-----	
2553	In house	Nd		-----	
2563	ISO17070	0.07		-----	
2566	LFGB82.02.8	nd		-----	
2569	In house	0.067		-----	
2590		-----		-----	
2601		-----		-----	
2602		-----		-----	
2638		-----		-----	
2652	In house	0.062		-----	
2668	In house	ND		-----	
3116	In house	<0.05		-----	
3117		0.061		-----	
3118		-----		-----	
3146		-----		-----	
3149	In house	<0.1		-----	
3150		-----		-----	
3151	In house	0		-----	
3153		-----		-----	
3154	In house	0.075		-----	

3172	UNI11057	0.071	-----	
3176	LFGB B82.02.8	0.03	-----	
3183	LFGB B82.02.8Mod.	0.143	-----	False positive result?
3186		-----	-----	
3190	LFGB B82.02.8	ND	-----	
3197	LFGB B82.02.8	ND	-----	
3199	In house	0.060	-----	
3204		-----	-----	
3210	In house	<0.500	-----	
3214	ISO17070	<0.05	-----	
3220		-----	-----	
3228	LFGB B82.02.8	Not detected	-----	
3233		-----	-----	
3237		-----	-----	
3242	LFGB B82.02.8	Not Detected	-----	
3243	LFGB B82.02.8	<0.05	-----	
3246	In house	n.d.	-----	

normality	OK
n	54
outliers	n.a.
mean (n)	<0.1
st.dev. (n)	n.a.
R(calc.)	n.a.
R(Horwitz)	n.a.





APPENDIX 2

Details of the methods used by the participants

Lab	Used Method for extraction OPP	Used Method for extraction PCP/TCEP
213	Basic / Ultrasonic extraction	Basic / Ultrasonic extraction
551	Basic / Ultrasonic extraction	Basic / Ultrasonic extraction
623	Basic / Ultrasonic extraction	Basic / Ultrasonic extraction
2115	Basic / Ultrasonic extraction	Basic / Ultrasonic extraction
2129	Soxhlet / AES extraction	Soxhlet / AES extraction
2135	Basic / Ultrasonic extraction	Basic / Ultrasonic extraction
2138	Basic / Ultrasonic extraction	Basic / Ultrasonic extraction
2159	Basic / Ultrasonic extraction	Basic / Ultrasonic extraction
2165	Basic / Ultrasonic extraction	Basic / Ultrasonic extraction
2172	Basic / Ultrasonic extraction	Basic / Ultrasonic extraction
2184	Basic / Ultrasonic extraction	Basic / Ultrasonic extraction
2201	Basic / Ultrasonic extraction	Basic / Ultrasonic extraction
2215	Basic / Ultrasonic extraction	Basic / Ultrasonic extraction
2230	Basic / Ultrasonic extraction	Basic / Ultrasonic extraction
2232	Basic / Ultrasonic extraction	Basic / Ultrasonic extraction
2241	---	Basic / Ultrasonic extraction
2247	Steam distillation	Steam distillation
2255	Basic / Ultrasonic extraction	Basic / Ultrasonic extraction
2256	Soxhlet / AES extraction	Soxhlet / AES extraction
2289	Steam distillation	Steam distillation
2290	Steam distillation	Steam distillation
2295	---	---
2296	---	Steam distillation
2297	Steam distillation	Steam distillation
2300	Soxhlet / AES extraction	Soxhlet / AES extraction
2301	Soxhlet / AES extraction	Soxhlet / AES extraction
2310	Basic / Ultrasonic extraction	Steam distillation
2311	Basic / Ultrasonic extraction	Steam distillation
2357	---	---
2358	Basic / Ultrasonic extraction	Basic / Ultrasonic extraction
2369	---	---
2370	Basic / Ultrasonic extraction	Basic / Ultrasonic extraction
2379	Steam distillation	Steam distillation
2380	Basic / Ultrasonic extraction	Basic / Ultrasonic extraction
2386	Basic / Ultrasonic extraction	Basic / Ultrasonic extraction
2390	---	---
2403	Basic / Ultrasonic extraction	Steam distillation
2410	Basic / Ultrasonic extraction	Basic / Ultrasonic extraction
2425	Basic / Ultrasonic extraction	Basic / Ultrasonic extraction
2429	Steam distillation	Steam distillation
2449	Basic / Ultrasonic extraction	Basic / Ultrasonic extraction
2461	Basic / Ultrasonic extraction	Basic / Ultrasonic extraction
2482	Basic / Ultrasonic extraction	Basic / Ultrasonic extraction
2486	Basic / Ultrasonic extraction	Basic / Ultrasonic extraction
2492	Soxhlet / AES extraction	Soxhlet / AES extraction
2493	---	Basic / Ultrasonic extraction
2495	---	Steam distillation
2497	Basic / Ultrasonic extraction	Basic / Ultrasonic extraction
2508	---	---
2511	Basic / Ultrasonic extraction	Basic / Ultrasonic extraction
2514	---	---
2515	Steam distillation	Steam distillation
2531	Steam distillation	Steam distillation
2532	Steam distillation	Steam distillation
2538	---	Steam distillation
2540	Steam distillation	Steam distillation
2550	Basic / Ultrasonic extraction	Basic / Ultrasonic extraction

2553	Basic / Ultrasonic extraction	Basic / Ultrasonic extraction
2563	Soxhlet / AES extraction	Soxhlet / AES extraction
2566	---	---
2569	---	---
2590	Basic / Ultrasonic extraction	Basic / Ultrasonic extraction
2601	---	Basic / Ultrasonic extraction
2602	Basic / Ultrasonic extraction	Basic / Ultrasonic extraction
2638	Basic / Ultrasonic extraction	Basic / Ultrasonic extraction
2643	---	---
2652	Basic / Ultrasonic extraction	Basic / Ultrasonic extraction
2668	Basic / Ultrasonic extraction	Basic / Ultrasonic extraction
3116	Basic / Ultrasonic extraction	Basic / Ultrasonic extraction
3117	Basic / Ultrasonic extraction	Basic / Ultrasonic extraction
3118	---	---
3146	---	---
3149	Soxhlet / AES extraction	Soxhlet / AES extraction
3150	Basic / Ultrasonic extraction	Basic / Ultrasonic extraction
3151	Basic / Ultrasonic extraction	Basic / Ultrasonic extraction
3153	---	Steam distillation
3154	Basic / Ultrasonic extraction	Basic / Ultrasonic extraction
3172	Basic / Ultrasonic extraction	Basic / Ultrasonic extraction
3176	Basic / Ultrasonic extraction	Basic / Ultrasonic extraction
3183	---	Steam distillation
3186	---	---
3190	Steam distillation	Steam distillation
3197	Basic / Ultrasonic extraction	Steam distillation
3199	Basic / Ultrasonic extraction	Basic / Ultrasonic extraction
3204	Basic / Ultrasonic extraction	Basic / Ultrasonic extraction
3210	Basic / Ultrasonic extraction	Basic / Ultrasonic extraction
3214	Steam distillation	Steam distillation
3220	Basic / Ultrasonic extraction	Basic / Ultrasonic extraction
3228	Basic / Ultrasonic extraction	Basic / Ultrasonic extraction
3233	---	Basic / Ultrasonic extraction
3237	---	---
3242	Basic / Ultrasonic extraction	Basic / Ultrasonic extraction
3243	Basic / Ultrasonic extraction	Basic / Ultrasonic extraction
3246	---	---

APPENDIX 3

Number of participants per country

5 labs in	BANGLADESH
1 lab in	BRAZIL
2 labs in	FRANCE
17 labs in	GERMANY
6 labs in	HONG KONG
1 lab in	HUNGARY
11 labs in	INDIA
3 labs in	INDONESIA
6 labs in	ITALY
3 labs in	KOREA
1 lab in	MOROCCO
16 labs in	P.R. of CHINA
3 labs in	PAKISTAN
1 lab in	SINGAPORE
1 lab in	SRI LANKA
3 labs in	TAIWAN R.O.C.
1 lab in	THAILAND
1 lab in	TUNESIA
5 labs in	TURKEY
2 labs in	U.S.A.
1 lab in	UNITED KINGDOM
3 labs in	VIETNAM

APPENDIX 4

Abbreviations:

C = final result after checking of first reported suspect 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 outlier test
R(0.05) = straggler in Rosner outlier test
n.a. = not applicable
n.d. = not detected

Literature:

1 iis Interlaboratory Studies, Protocol for the Organisation, Statistics & Evaluation, April 2014
2 Öko-Tex Standard 100; January 2013
3 Thai Green label. TGL-16. July 2002
4 Impacts of Environmental Standards and requirements in EU Countries. Aug 99
5 Horwitz. Journal of AOAC International Vol. 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 ISO13528-05
13 M. Thompson and R. Wood. J. AOAC Int. 76. 926. (1993)
14 Analytical Methods Committee Technical brief, No4 January 2001.
15 The Royal Society of Chemistry 2002, Analyst 2002, 127 page 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), pp. 165-172, (1983)
18 MEMO iis: Precision data of OPP/PCP in textile, February 18, 2016