

Results of Proficiency Test OPP, PCP and TeCP in textile November 2013

Organised by: Institute for Interlaboratory Studies
Spijkenisse, the Netherlands

Author: ing. R.J. Starink
Corrector: dr. R.G. Visser & ing. N. Boelhouwer
Report: iis13A06

January 2014

-- Empty page --

CONTENTS

1	INTRODUCTION	4
2	SET UP	4
2.1	QUALITY SYSTEM.....	4
2.2	PROTOCOL.....	4
2.3	CONFIDENTIALITY STATEMENT	5
2.4	SAMPLES	5
2.5	ANALYSES	6
3	RESULTS.....	6
3.1	STATISTICS	7
3.2	GRAPHICS	7
3.3	Z-SCORES.....	8
4	EVALUATION	8
4.1	EVALUATION PER DETERMINATION	8
4.2	PERFORMANCE EVALUATION FOR THE GROUP OF LABORATORIES.....	10
5	COMPARISON WITH PREVIOUS INTERLABORATORY STUDIES.....	10
6	DISCUSSION.....	11

Appendices:

1.	Data and statistical results	12
2.	Details of the methods used by the participants	22
3.	Number of participants per country	24
4.	Abbreviations and literature	25

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 2013/2014, this proficiency test was continued.

In this interlaboratory study 102 laboratories in 21 different countries participated. See appendix 3 for the number of participants per country. In this report, the results of the 2013 proficiency test are presented and discussed.

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: one spiked with OPP and another spiked with PCP. A third party laboratory prepared the samples and another (accredited) third party laboratory was subcontracted to perform the homogeneity tests. Participants were requested to report results with one extra figure. These results with an extra figure are 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% confidentiality 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 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 January 2010 (iis-protocol, version 3.2).

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 batches of textile were obtained from a third party laboratory. The first bulk sample a hosiery fabric, positive on OPP, was cut into pieces. The pieces were well mixed and divided over 112 subsamples of 3 grams each and labelled #13234. The second bulk sample, another hosiery fabric, positive on PCP, was also cut into pieces. The pieces were well mixed and divided over 135 subsamples of 3 grams each and subsequently labelled #13235. The homogeneities of 4 stratified randomly selected samples of each batch were checked by determination of OPP (on samples #13234) and PCP (on samples #13235) by an accredited third party laboratory. The determination is performed in accordance with an in-house test method for OPP and in accordance with LFGB 82.02.8 for PCP. See the following table for the test results.

	<i>OPP in mg/kg</i>
Sample #13234-1	24.6
Sample #13234-2	24.3
Sample #13234-3	24.6
Sample #13234-4	24.5

Table 1: homogeneity test results of subsample #13234

	<i>PCP in mg/kg</i>
Sample #13235-1	19.2
Sample #13235-2	19.0
Sample #13235-3	19.4
Sample #13235-4	19.2

Table 2: homogeneity test results of subsample #13235

From the above results of the homogeneity test, the repeatabilities were 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:

	<i>OPP in mg/kg</i>
r (samples #13234)	0.4
Reference method	Horwitz
0.3 x R (reference method)	2.0

Table 3: repeatabilities of subsamples #13234.

	<i>PCP in mg/kg</i>
r (samples #13235)	0.5
Reference method	LFGB 82.02.8
0.3 x R (reference method)	2.0

Table 4: repeatabilities of subsamples #13235

The repeatabilities of Pentachlorophenol (PCP) and Orthophenylphenol (OPP) were in agreement with 0.3 times the target requirements. Therefore, homogeneity of the subsamples was assumed.

To each participating laboratory one sample of approx. 3 grams (labelled #13234) and one sample of approx. 3 grams (labelled #13235) was sent on November 6, 2013.

2.5 ANALYSES

The participants were asked to determine the concentrations of Orthophenylphenol (OPP) on sample #13234 and Pentachlorophenol (PCP), 2,3,4,5-Tetrachlorophenol, 2,3,4,6-Tetrachlorophenol and 2,3,5,6-Tetrachlorophenol on sample #13235 applying the analysis procedure that is routinely used in the laboratory. To get comparable results a detailed report form, was sent together with each set of samples. On the report forms the requested phenols including the units and questions about the analytical details were printed. In addition, a letter of instructions was sent along.

3 RESULTS

During four weeks after sample despatch, the results of the individual laboratories were gathered. The original data are tabulated in the appendices of this report. The laboratories are presented by their code numbers.

Directly after the deadline, a reminder fax was sent to those laboratories that had not yet reported. 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, see lit.5) found it to be an outlier. The laboratories that produced these suspect data were asked to check the results. Additional or corrected data are placed under 'Remarks' in the result tables in appendix 1. A list of abbreviations used in the tables can be found in appendix 4.

3.1 STATISTICS

Statistical calculations were performed as described in the report 'iis Interlaboratory Studies: Protocol for the Organisation, Statistics and Evaluation' of January 2010 (iis-protocol, version 3.2)

For the statistical evaluation the *unrounded* (when available) figures were used instead of the rounded results. Results reported as '<...' or '>..."' were not used in the statistical evaluation. Before further calculations, the normality of the distribution of the various data sets per determination was checked by means of the Lilliefors-test. In the case of an abnormal distribution, the statistical evaluation should be used with care.

According to ISO 5725 (1986 and 1994, lit.7 and 8) the original results per determination were submitted subsequently to Dixon's and Grubbs' outlier tests. Outliers are marked by D(0.01) for the Dixon's test, by G(0.01) or DG(0.01) for the Grubbs' test. Stragglers are marked by D(0.05) for the Dixon's test, by G(0.05) or DG(0.05) for the Grubbs' 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 visualize the data against the reproducibilities from literature, Gauss plots were made, using the sorted data for one determination (see appendix 1). On the Y-axis the reported 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, nos.14-15).

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, e.g. ISO reproducibilities, 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 literature reproducibility by division with 2.8. The z-scores were calculated in accordance with:

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

When a laboratory did use a test method with a reproducibility that is significantly different from the reproducibility of the reference test method used in this report, it is strongly advised to recalculate the z-score, while using the reproducibility of the actual test method used, this in order to evaluate the fit-for-useness of the reported test result.

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

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

4 EVALUATION

During the execution of this proficiency test no serious problems occurred. In total 97 of the 102 participants reported 248 numerical results. Observed in all reported results were 14 statistical outlying results, which is 5.6%. In proficiency studies, outlier percentages of 3% - 7.5% are quite normal.

All original data sets proved to have a normal distribution.

4.1 EVALUATION PER DETERMINATION

Due to the lack of relevant standard test methods for the determination of OPP, the calculated reproducibility was compared with the reproducibility estimated using the Horwitz equation. For PCP, both existing methods (LFGB 82.02-8 and ISO17070:2006, the latter method superseding DIN53313:1996 and DIN14494:2003), mention the same precision data for leather only. Both methods are also applicable for isomers of Tri- and Tetrachlorophenols, but as no reproducibilities for these compounds are mentioned, again estimates using the Horwitz equation were used as target reproducibilities.

OPP: The determination of this component may be problematic at the levels of 14.3 mg/kg. Six statistical outliers were detected. The calculated reproducibility after rejection of the statistical outliers is not in agreement with the strict estimated reproducibility calculated using the Horwitz equation.

PCP: The determination of this component was problematic at the level of 15.0 mg/kg. Four statistical outliers were detected. The calculated reproducibility after rejection of the statistical outliers is not in agreement with the precision requirements of LFGB 82.02.8

2,3,4,5-TeCP: Sample #13235 did contain very little of this component (0.025 mg/kg), which is near or below the detection limit.
Therefore no significant conclusions were drawn.

2,3,4,6-TeCP: The determination of this component may be problematic at a concentration level of 0.084 mg/kg. In total 2 statistical outliers were detected. The calculated reproducibility after rejection of the statistical outliers is not in agreement with the estimated reproducibility calculated using the Horwitz equation.

2,3,5,6-TeCP: Sample #13235 did contain very little of this component (0.035 mg/kg), which is 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:

	<i>unit</i>	<i>n</i>	<i>Average</i>	<i>2.8 * sd</i>	<i>R (target)</i>
OPP	mg/kg	84	14.30	11.57	4.29

Table 5: reproducibility of phenyl phenols on textile sample #13234

	<i>unit</i>	<i>n</i>	<i>average</i>	<i>2.8 * sd</i>	<i>R (target)</i>
PCP	mg/kg	93	14.96	8.29	5.23
2,3,4,5-TeCP	mg/kg	12	0.025	unknown	unknown
2,3,4,6-TeCP	mg/kg	34	0.084	0.077	0.055
2,3,5,6-TeCP	mg/kg	11	0.035	unknown	unknown

Table 6: reproducibilities of chlorinated phenols on textile sample #13235

Without further statistical calculations, it can be concluded that for OPP and PCP, the total group of participating laboratories has 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.

	<i>November 2013</i>	<i>November 2012</i>	<i>November 2011</i>	<i>December 2010</i>	<i>February 2010</i>	<i>February 2009</i>
OPP	81%	80 - 81%	60 - 68%	47 - 88%	47 - 53%	82 - 98%
PCP	55%	45 - 65%	53 - 55%	41 - 66%	51 - 55%	82 - 88%

Table 7: Comparison of relative standard deviations (RSDs) in iis proficiency tests

Sample #13235 was already used before, in PT iis11A06. When the data of both PTs are compared it is good to see that the consensus values for both rounds differ not significantly, which proves that the samples were quite stable on PCP for this 2-year period and thus sufficiently stable for PT use and re-use.

	<i>iis11A06</i>	<i>iis13A06</i>
number of results	68	93
average	15.78	14.96
2.8 * st.dev.	8.74	8.29
R (LFBG82.02.8)	5.53	5.23

table 8: Comparison of PCP in samples #11136 (in iis11A06) and #13235 (in iis13A06)

6 DISCUSSION

In this proficiency test for the determination of phenols in textile, it was noticed that the majority of the participants detected OPP in sample #13234 and PCP and 2,3,4,6-TeCP in sample #13235.

When the results of this interlaboratory study were compared to the Ecolabelling Standards and Requirements for Textiles in EU (table 9), it could be noticed that for sample #13234 (OPP), only one laboratory would make a different decision about the acceptability of the textile. This laboratory should have rejected the textile for all classes, while all other laboratories would have accepted the textile for all classes.

For the determination on PCP all reporting laboratories would reject the sample for all classes, except one laboratory. This laboratory would only reject the sample for class 1.

For the determination on Tetrachlorophenols, 34 reporting laboratories would reject the sample only for class 1.

Many laboratories did report <0.1 or <0.5 mg/kg for one or more 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.

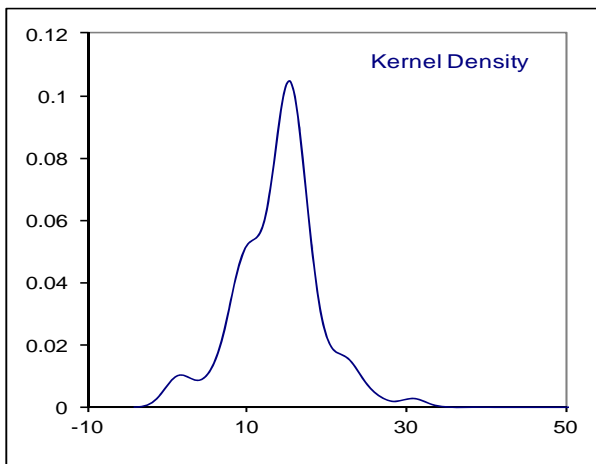
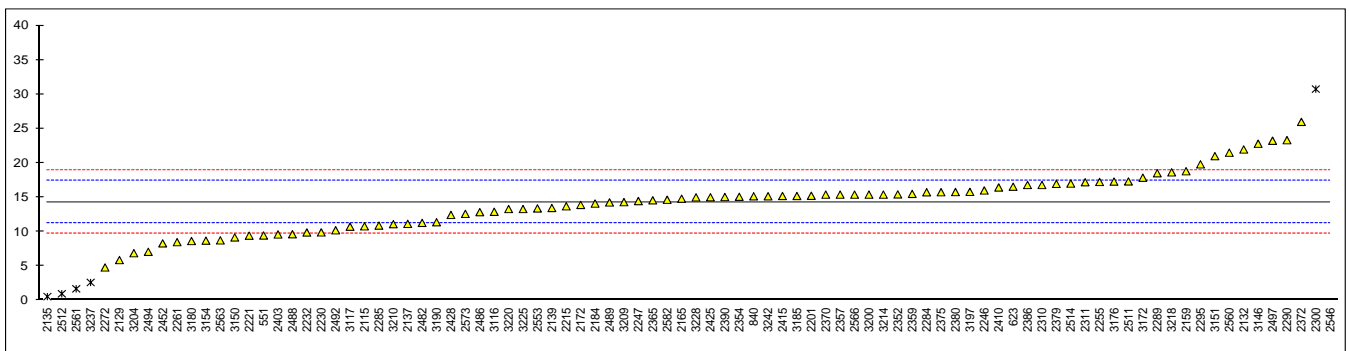
<i>Ecolabel</i>	Class 1 Baby clothes (mg/kg)	Class 2 Clothes direct skin contact (mg/kg)	Class 3 Clothes, no direct contact with skin (mg/kg)	Class 4 Decoration material (mg/kg)
Orthophenylphenol	50.0	100.0	100.0	100.0
Pentachlorophenol	0.05	0.5	0.5	0.5
Sum of Tetrachlorophenols	0.05	0.5	0.5	0.5

Table 9: Ecolabelling Standards and Requirements for Textiles in EU

APPENDIX 1**Determination of Orthophenylphenol (OPP) on sample #13234; results in mg/kg**

lab	Method	value	mark	z(targ)	remarks
551	in house	9.455		-3.16	
623	in house	16.55		1.47	
840	in house	15.157		0.56	
2115	Oeko-Tex	10.79		-2.29	
2127		-----		-----	
2129	in house	5.88		-5.49	
2132	in house	21.97		5.00	
2135	in house	0.56	DG(0.05)	-8.96	
2137	KS K0733Mod.	11.14		-2.06	
2139	in house	13.45		-0.55	
2159	64LFGB B82.02-8	18.8		2.94	
2165	64LFGB B82.02-8	14.80		0.33	
2172	in house	13.9		-0.26	
2184	64LFGB B82.02-8	14.10		-0.13	
2201	ISO17070	15.23		0.61	
2215	ISO17070	13.7		-0.39	
2221	GB/T20386	9.43		-3.18	
2230	in house	9.90		-2.87	
2232	LFGB B82.02-8	9.889		-2.88	
2246	ISO17070	16		1.11	
2247	64LFGB 82.02-8	14.46		0.10	
2255	in house	17.24		1.92	
2261	GB/T20386	8.48		-3.80	
2272	XP G 08-015	4.8		-6.20	
2284	ISO17070	15.74		0.94	
2285	GB/T20386	10.893		-2.22	
2289	ISO17070	18.51		2.75	
2290	in house	23.32		5.88	
2295	in house	19.8	C	3.59	First reported 24.3
2296		-----		-----	
2300	ISO17070	30.75	G(0.05)	10.73	
2310	64LFGB B82.02-8	16.8		1.63	
2311	64LFGB B82.02-8	17.2		1.89	
2352	in house	15.43		0.74	
2354	in house	15.086		0.51	
2357	64LFGB B82.02-8	15.40		0.72	
2359	64LFGB B82.02-8	15.5		0.78	
2365	GB20386	14.570		0.18	
2370	LFGB 82.02-8	15.4		0.72	
2372	EPA3055C	25.98		7.62	
2375	in house	15.743		0.94	
2379	in house	16.96		1.73	
2380	in house	15.77		0.96	
2386	LFGB 82.02-8	16.8		1.63	
2390	64LFGB B82.02-8	15.0510		0.49	
2403	GB/T20386	9.6		-3.07	
2410	LFGB B82.02-8	16.44		1.40	
2415	in house	15.2		0.59	
2425	in house	15.01		0.46	
2428	GB/T20386	12.44		-1.21	
2452	XP G 08-015	8.306		-3.91	
2453		-----		-----	
2482	in house	11.29		-1.96	
2486	64LFGB B82.02-8	12.85		-0.95	
2488	64LFGB B82.02-8	9.6327		-3.04	
2489	64LFGB 82.02-8	14.26		-0.03	
2492	in house	10.21		-2.67	
2494	ISO17070	7.0769		-4.71	
2495		-----		-----	
2497	UNI11057	23.24		5.83	
2508		-----		-----	
2511		17.32		1.97	
2512	GB/T20386	0.97	DG(0.05)	-8.70	
2514	LFGB B82.02-8	17.01		1.77	
2515		-----		-----	
2546	in house	112.35	G(0.01)	63.96	
2553	CPSD-AN-00094	13.39		-0.59	
2560	64LFGB B82.02-8	21.50		4.70	
2561	INH-2	1.69	G(0.05)	-8.23	
2563	DIN17070	8.74		-3.63	
2566	64LFGB B82.02-8	15.40		0.72	

2573	ISO17070	12.60	-1.11	
2582	LMBG 82.02-8	14.65	0.23	
2583		-----	-----	
3100		-----	-----	
3116	in house	12.9	-0.91	
3117	Oeko-Tex Std 200	10.73	-2.33	
3146	in house	22.8	5.54	
3150	in house	9.173	-3.34	
3151	in house	21	4.37	
3153		-----	-----	
3154	DIN13365	8.70	-3.65	
3172	in house	17.86	2.32	
3176	in house	17.3	1.96	
3180	in house	8.65	-3.69	
3182		-----	-----	
3185	ISO17070	15.2	0.59	
3190	DIN53313	11.38	-1.90	
3192		-----	-----	
3197	in house	15.8	0.98	
3200	64LFGB B82.02-8	15.40	0.72	
3204	64LFGB B82.02-8	6.88	-4.84	
3209	in house	14.299	0.00	
3210	in house	11.1	-2.09	
3214	ISO17070	15.40	0.72	
3218	ISO17070	18.64	2.83	
3220	in house	13.3	-0.65	
3225	in house	13.3	-0.65	
3228	64LFGB B82.02-8	15.00	0.46	
3233		-----	-----	
3237	in house	2.614	C,G(0.05) -7.62	First reported 3.972
3242	in house	15.16	0.56	
normality OK				
n 84				
outliers 6				
mean (n) 14.300				
st.dev. (n) 4.1335				
R(calc.) 11.574				
R(Horwitz) 4.293				



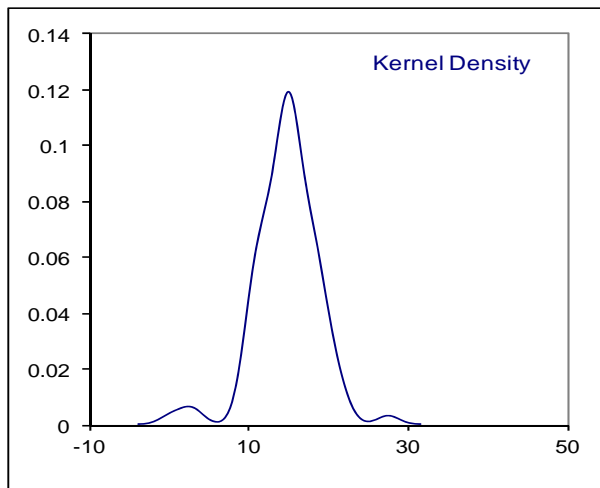
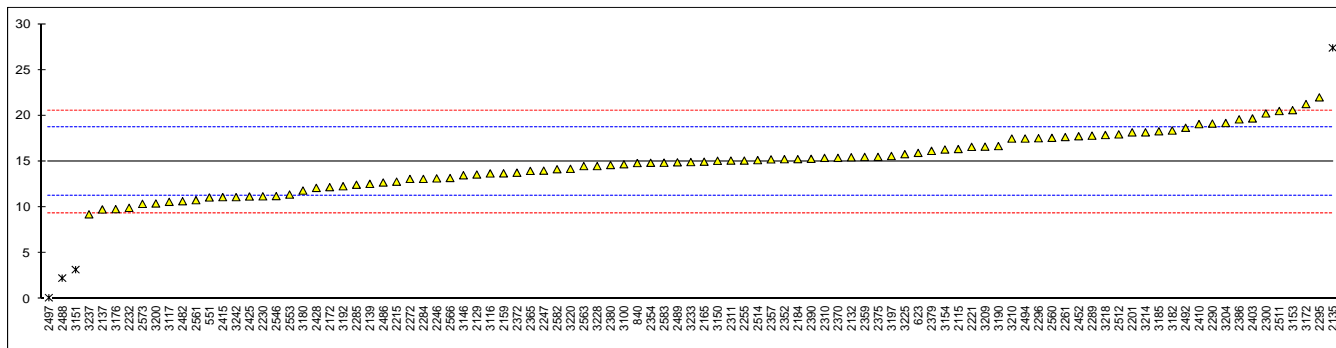
Determination of Pentachlorophenol (PCP) on sample #13235; results in mg/kg

lab	method	value	mark	z(targ)	remarks
551	in house	11.075		-2.08	
623	LFGB B82.02-8Mod.	15.94		0.53	
840	64LFGB B82.02-8	14.830		-0.07	
2115	Oeko-Tex	16.36		0.75	
2127		-----		-----	
2129	in house	13.58		-0.74	
2132	in house	15.46		0.27	
2135	in house	27.40	G(0.05)	6.66	
2137	KS K0733	9.77		-2.77	
2139	in house	12.56		-1.28	
2159	64LFGB B82.02-8	13.71		-0.67	
2165	64LFGB B82.02-8	14.98		0.01	
2172	in house	12.2		-1.47	
2184	64LFGB B82.02-8	15.26		0.16	
2201	ISO17070	18.18		1.73	
2215	ISO17070	12.8		-1.15	
2221	GB/T 18414	16.60		0.88	
2230	in house	11.2		-2.01	
2232	LFGB B82.02-8	9.942		-2.68	
2246	ISO17070	13.16		-0.96	
2247	64LFGB 82.02-8	14.00		-0.51	
2255	in house	15.1		0.08	
2261	GB/T18414	17.67		1.45	
2272	XP G 08-015	13.1		-0.99	
2284	ISO17070	13.10		-0.99	
2285	GB/T18414	12.463		-1.33	
2289	ISO17070	17.82		1.53	
2290	ISO17070	19.14		2.24	
2295	in house	22	C	3.77	First reported 0.22
2296	ISO17070	17.54		1.38	
2300	ISO17070	20.25		2.83	
2310	64LFGB B82.02-8	15.4		0.24	
2311	64LFGB B82.02-8	15.1		0.08	
2352	64LFGB B82.02-8	15.251		0.16	
2354	64LFGB B82.02-8	14.858		-0.05	
2357	64LFGB B82.02-8	15.23		0.15	
2359	ISO17070	15.5		0.29	
2365	GB18414	13.973		-0.53	
2370	LFGB 82.02-8	15.4		0.24	
2372	EPA3055C	13.78		-0.63	
2375	in house	15.5022		0.29	
2379	LFGB 82.02-8	16.16		0.64	
2380	64LFGB B82.02-8	14.61		-0.18	
2386	LFGB 82.02-8	19.6		2.48	
2390	64LFGB B82.02-8	15.2960		0.18	
2403	GB/T18414	19.7		2.54	
2410	LFGB B82.02-8	19.08		2.21	
2415	ISO17070	11.11		-2.06	
2425	64LFGB B82.02-8	11.18		-2.02	
2428	GB/T18414	12.12		-1.52	
2452	XP G 08-015	17.7557		1.50	
2453		-----		-----	
2482	in house	10.67		-2.29	
2486	64LFGB B82.02-8	12.71		-1.20	
2488	64LFGB B82.02-8	2.2761	G(0.05)	-6.78	
2489	64LFGB 82.02-8	14.91		-0.02	
2492	in house	18.68		1.99	
2494	ISO17070	17.5061		1.36	
2495		-----		-----	
2497	UNI11057	0.14	G(0.05)	-7.93	
2508		-----		-----	
2511		20.51		2.97	
2512	GB/T18414	17.96		1.61	
2514	LFGB B82.02-8	15.15		0.10	
2515		-----		-----	
2546	in house	11.226		-1.99	
2553	CPSD-AN-00094	11.39		-1.91	
2560	64LFGB B82.02-8	17.58		1.40	
2561	INH-11	10.78		-2.23	
2563	DIN17070	14.5		-0.24	
2566	64LFGB B82.02-8	13.20		-0.94	
2573	ISO17070	10.38		-2.45	

2582	LMBG 82.02-8	14.16	-0.43	
2583	in house	14.87	-0.05	
3100	ISO17070	14.7	-0.14	
3116	in house	13.7	-0.67	
3117	Oeko-Tex Std 200	10.60	-2.33	
3146	in house	13.5	-0.78	
3150	in house	15.08	0.07	
3151	in house	3.2	C,G(0.05)	First reported 6.4
3153	LFGB B82.02-8	20.6	3.02	
3154	ISO17070	16.31	0.72	
3172	in house	21.27	3.38	
3176	in house	9.8	-2.76	
3180	ISO17070	11.83	-1.67	
3182	LFGB 82.02-8	18.38	1.83	
3185	ISO17070	18.3	1.79	
3190	ISO17070	16.68	0.92	
3192	in house	12.3	-1.42	
3197	64LFGB 82.02-8	15.6	0.34	
3200	64LFGB B82.02-8	10.42	-2.43	
3204	64LFGB B82.02-8Mod.	19.2	2.27	
3209	in house	16.620	0.89	
3210	XP G 08-015	17.5	1.36	
3214	ISO17070	18.18	1.73	
3218	ISO17070	17.89	1.57	
3220	in house	14.2	C	First reported 7.86
3225	in house	15.8	0.45	
3228	64LFGB B82.02-8	14.50	-0.24	
3233	in house	14.94	-0.01	
3237	in house	9.237	-3.06	
3242	in house	11.11	-2.06	

normality OK
n 93
outliers 4
mean (n) 14.955
st.dev. (n) 2.9604
R(calc.) 8.289
R(LFGB82.02.8) 5.234

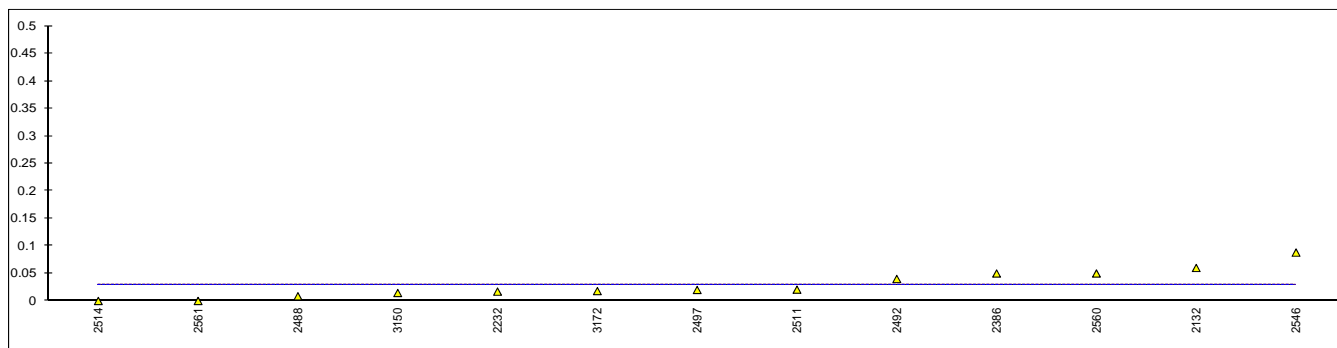
Compare R(Horwitz) = 4.459



Determination of 2,3,4,5-Tetrachlorophenol on sample #13235; results in mg/kg

lab	method	value	mark	z(targ)	remarks
551	in house	n.d.		----	
623	LFGB B82.02-8Mod.	n.d.		----	
840	64LFGB B82.02-8	n.d.		----	
2115				----	
2127				----	
2129	in house	<0.05		----	
2132	in house	0.06		----	
2135				----	
2137	KS K0733	<0.1		----	
2139				----	
2159	64LFGB B82.02-8	<0.05		----	
2165	64LFGB B82.02-8	n.d.		----	
2172	in house	n.d.		----	
2184	64LFGB B82.02-8	n.d.		----	
2201	ISO17070	<0.5		----	
2215				----	
2221				----	
2230	in house	<0.05		----	
2232	LFGB B82.02-8	0.0170		----	
2246	ISO17070	<0.05		----	
2247	64LFGB 82.02-8	<0.5		----	
2255	in house	n.d.		----	
2261				----	
2272				----	
2284	ISO17070	n.d.		----	
2285				----	
2289				----	
2290				----	
2295				----	
2296				----	
2300				----	
2310	64LFGB B82.02-8	n.d.		----	
2311	64LFGB B82.02-8	n.d.		----	
2352	64LFGB B82.02-8	n.d.		----	
2354	64LFGB B82.02-8	n.d.		----	
2357	64LFGB B82.02-8	n.d.		----	
2359	ISO17070	n.d.		----	
2365	GB18414	n.d.		----	
2370	LFGB 82.02-8	n.d.		----	
2372	EPA3055C	n.d.		----	
2375	in house	n.d.		----	
2379	LFGB 82.02-8	n.d.		----	
2380	64LFGB B82.02-8	n.d.		----	
2386	LFGB 82.02-8	0.05		----	
2390				----	
2403	GB/T18414	n.d.		----	
2410	LFGB B82.02-8	<0.5		----	
2415				----	
2425	64LFGB B82.02-8	n.d.		----	
2428	GB/T18414	n.d.		----	
2452				----	
2453				----	
2482	in house	<0.5	C	----	First reported 0.157
2486	64LFGB B82.02-8	<0.05		----	
2488	64LFGB B82.02-8	0.0085		----	
2489	64LFGB 82.02-8	<0.5		----	
2492	in house	0.04		----	
2494	ISO17070	n.d.		----	
2495				----	
2497	UNI11057	0.02		----	
2508				----	
2511		0.0206		----	
2512				----	
2514	LFGB B82.02-8	0.0		----	
2515				----	
2546	in house	0.088		----	
2553				----	
2560	64LFGB B82.02-8	0.05		----	
2561	INH-11	0		----	
2563				----	
2566	64LFGB B82.02-8	n.d.		----	
2573				----	

2582	LMBG 82.02-8	<0.5	----
2583		----	----
3100		----	----
3116	in house	<0.05	----
3117		----	----
3146	in house	<0.2	----
3150	in house	0.0145	----
3151	in house	<0.05	----
3153		----	----
3154		----	----
3172	in house	0.018	----
3176		----	----
3180		----	----
3182	LFGB 82.02-8	<0.5	----
3185		----	----
3190		----	----
3192		----	----
3197	64LFGB 82.02-8	<0.5	----
3200	64LFGB B82.02-8	n.d.	----
3204	64LFGB B82.02-8Mod.	n.d.	----
3209	in house	n.d.	----
3210		----	----
3214	ISO17070	n.d.	----
3218	ISO17070	<0.5	----
3220	in house	n.d.	----
3225	in house	n.d.	----
3228	64LFGB B82.02-8	n.d.	----
3233		----	----
3237		----	----
3242	in house	n.d.	----
	normality	n.a.	
	n	64	
	outliers	0	
	mean (n)	<0.5	
	st.dev. (n)	n.a.	
	R(calc.)	n.a.	
	R(lit)	n.a.	

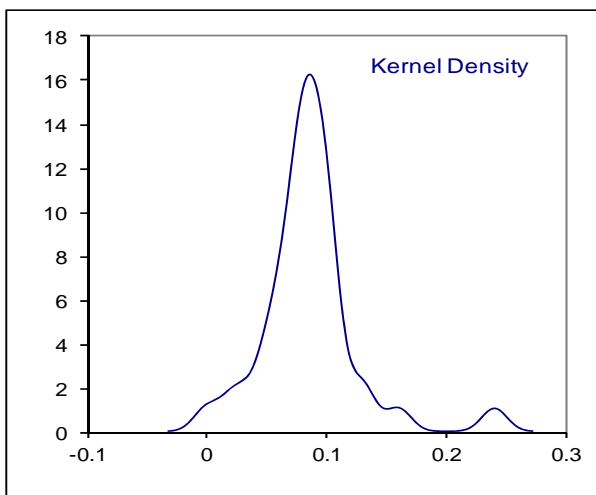
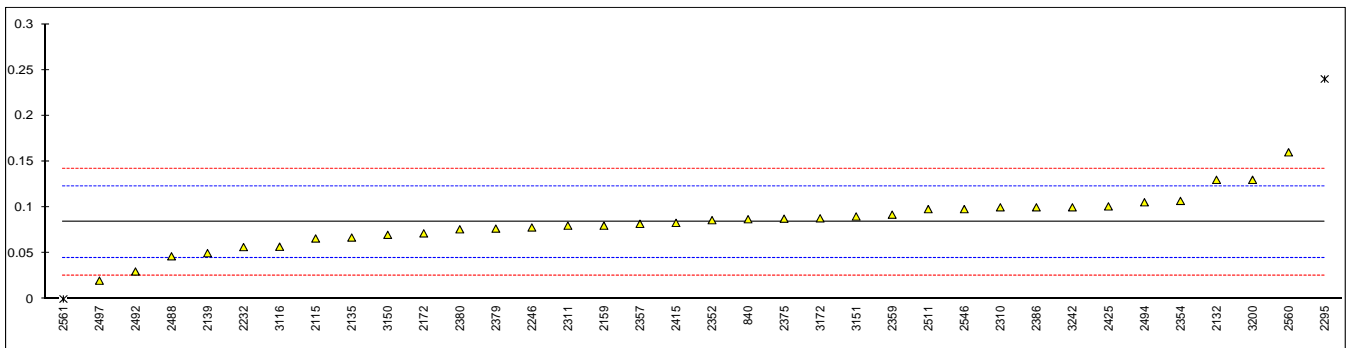


Determination of 2,3,4,6-Tetrachlorophenol on sample #13235; results in mg/kg

lab	method	value	mark	z(targ)	remarks
551	in house	n.d.		----	
623	LFGB B82.02-8Mod.	n.d.		----	
840	64LFGB B82.02-8	0.087		0.16	
2115	Oeko-Tex	0.066		-0.92	
2127		----		----	
2129	in house	<0.05		----	
2132	in house	0.13		2.37	
2135	in house	0.067		-0.86	
2137	KS K0733	<0.1		----	
2139	in house	0.05		-1.74	
2159	64LFGB B82.02-8	0.08		-0.20	
2165	64LFGB B82.02-8	n.d.		----	
2172	in house	0.0716		-0.63	
2184	64LFGB B82.02-8	n.d.		----	
2201	ISO17070	<0.5		----	
2215		----		----	
2221		----		----	
2230	in house	<0.05		----	
2232	LFGB B82.02-8	0.0566		-1.40	
2246	ISO17070	0.078		-0.30	
2247	64LFGB 82.02-8	<0.5		----	
2255	in house	n.d.		----	
2261		----		----	
2272		----		----	
2284	ISO17070	n.d.		----	
2285		----		----	
2289		----		----	
2290		----		----	
2295	in house	0.24	G(0.01)	8.02	
2296		----		----	
2300		----		----	
2310	64LFGB B82.02-8	0.1		0.83	
2311	64LFGB B82.02-8	0.08		-0.20	
2352	64LFGB B82.02-8	0.086		0.11	
2354	64LFGB B82.02-8	0.107		1.19	
2357	64LFGB B82.02-8	0.082		-0.09	
2359	ISO17070	0.092		0.42	
2365	GB18414	n.d.		----	
2370	LFGB 82.02-8	n.d.		----	
2372	EPA3055C	n.d.		----	
2375	in house	0.0876		0.19	
2379	LFGB 82.02-8	0.0768		-0.36	
2380	64LFGB B82.02-8	0.076		-0.40	
2386	LFGB 82.02-8	0.10		0.83	
2390		----		----	
2403	GB/T18414	n.d.		----	
2410	LFGB B82.02-8	<0.5		----	
2415	ISO17070	0.083		-0.04	
2425	64LFGB B82.02-8	0.101		0.88	
2428	GB/T18414	n.d.		----	
2452		----		----	
2453		----		----	
2482	in house	<0.5	C	----	First reported 0.356
2486	64LFGB B82.02-8	<0.05		----	
2488	64LFGB B82.02-8	0.0466		-1.91	
2489	64LFGB 82.02-8	<0.5		----	
2492	in house	0.03		-2.76	
2494	ISO17070	0.1055		1.11	
2495		----		----	
2497	UNI11057	0.02		-3.28	
2508		----		----	
2511		0.098		0.73	
2512		----		----	
2514	LFGB B82.02-8	n.d.	C	----	First reported 0.079
2515		----		----	
2546	in house	0.098		0.73	
2553		----		----	
2560	64LFGB B82.02-8	0.16	C	3.91	First reported 0.05
2561	INH-11	0	ex	-4.30	Result excluded zero is not a real result
2563		----		----	
2566	64LFGB B82.02-8	n.d.		----	
2573		----		----	

2582	LMBG 82.02-8	<0.5	----
2583		----	----
3100		----	----
3116	in house	0.057	-1.38
3117		----	----
3146	in house	<0.2	----
3150	in house	0.0700	-0.71
3151	in house	0.09	0.32
3153		----	----
3154		----	----
3172	in house	0.088	0.21
3176		----	----
3180		----	----
3182	LFGB 82.02-8	<0.5	----
3185		----	----
3190		----	----
3192		----	----
3197	64LFGB 82.02-8	<0.5	----
3200	64LFGB B82.02-8	0.13	2.37
3204		----	----
3209	in house	n.d.	----
3210		----	----
3214	ISO17070	n.d.	----
3218	ISO17070	<0.5	----
3220	in house	n.d.	----
3225	in house	n.d.	----
3228	64LFGB B82.02-8	n.d.	----
3233		----	----
3237		----	----
3242	in house	0.1	0.83

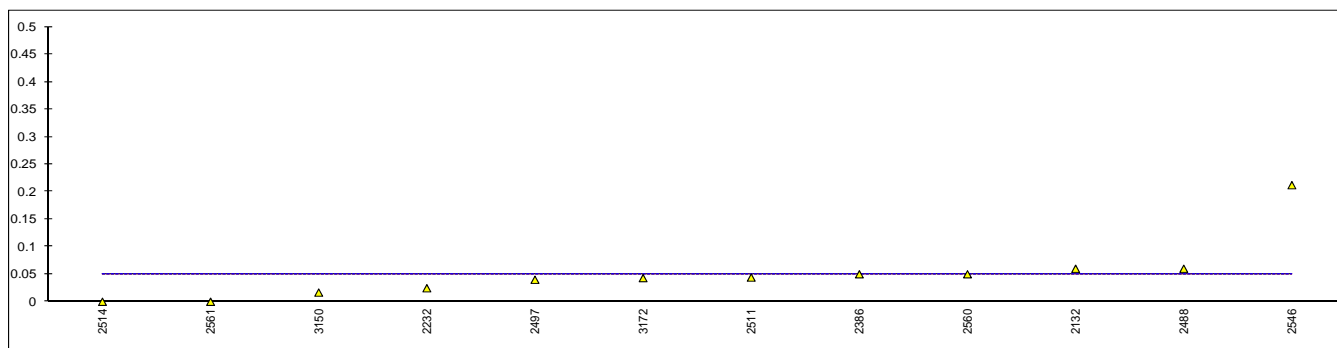
normality OK
n 34
outliers 2
mean (n) 0.084
st.dev. (n) 0.0274
R(calc.) 0.077
R(Horwitz) 0.055



Determination of 2,3,5,6-Tetrachlorophenol on sample #13235; results in mg/kg

lab	method	value	mark	z(targ)	remarks
551	in house	n.d.		----	
623	LFGB B82.02-8Mod.	n.d.		----	
840	64LFGB B82.02-8	n.d.		----	
2115		----		----	
2127		----		----	
2129	in house	<0.05		----	
2132	in house	0.06		----	
2135		----		----	
2137	KS K0733	<0.1		----	
2139		----		----	
2159	64LFGB B82.02-8	<0.05		----	
2165	64LFGB B82.02-8	n.d.		----	
2172	in house	n.d.		----	
2184	64LFGB B82.02-8	n.d.		----	
2201	ISO17070	<0.5		----	
2215		----		----	
2221		----		----	
2230	in house	<0.05		----	
2232	LFGB B82.02-8	0.0246		----	
2246	ISO17070	<0.05		----	
2247	64LFGB 82.02-8	<0.5		----	
2255	in house	n.d.		----	
2261		----		----	
2272		----		----	
2284	ISO17070	n.d.		----	
2285		----		----	
2289		----		----	
2290		----		----	
2295		----		----	
2296		----		----	
2300		----		----	
2310	64LFGB B82.02-8	n.d.		----	
2311	64LFGB B82.02-8	n.d.		----	
2352	64LFGB B82.02-8	n.d.		----	
2354	64LFGB B82.02-8	n.d.		----	
2357	64LFGB B82.02-8	n.d.		----	
2359	ISO17070	n.d.		----	
2365	GB18414	n.d.		----	
2370	LFGB 82.02-8	n.d.		----	
2372	EPA3055C	n.d.		----	
2375	in house	n.d.		----	
2379	LFGB 82.02-8	n.d.		----	
2380	64LFGB B82.02-8	n.d.		----	
2386	LFGB 82.02-8	0.05		----	
2390		----		----	
2403	GB/T18414	n.d.		----	
2410	LFGB B82.02-8	<0.5		----	
2415		----		----	
2425	64LFGB B82.02-8	n.d.		----	
2428	GB/T18414	n.d.		----	
2452		----		----	
2453		----		----	
2482	in house	<0.5	C	----	First reported <0.151
2486	64LFGB B82.02-8	<0.05		----	
2488	64LFGB B82.02-8	0.0600		----	
2489	64LFGB 82.02-8	<0.5		----	
2492		----		----	
2494	ISO17070	n.d.		----	
2495		----		----	
2497	UNI11057	0.04		----	
2508		----		----	
2511		0.044		----	
2512		----		----	
2514	LFGB B82.02-8	0.0		----	
2515		----		----	
2546	in house	0.212		----	
2553		----		----	
2560	64LFGB B82.02-8	0.05	C	----	First reported 0.16
2561	INH-11	0		----	
2563		----		----	
2566	64LFGB B82.02-8	n.d.		----	
2573		----		----	

2582	LMBG 82.02-8	<0.5	----
2583		----	----
3100		----	----
3116	in house	<0.05	----
3117		----	----
3146	in house	<0.2	----
3150	in house	0.0167	----
3151	in house	<0.05	----
3153		----	----
3154		----	----
3172	in house	0.043	----
3176		----	----
3180		----	----
3182	LFGB 82.02-8	<0.5	----
3185		----	----
3190		----	----
3192		----	----
3197	64LFGB 82.02-8	<0.5	----
3200	64LFGB B82.02-8	n.d.	----
3204		----	----
3209	in house	n.d.	----
3210		----	----
3214	ISO17070	n.d.	----
3218	ISO17070	<0.5	----
3220	in house	n.d.	----
3225	in house	n.d.	----
3228	64LFGB B82.02-8	n.d.	----
3233		----	----
3237		----	----
3242	in house	n.d.	----
	normality	n.a.	
	n	62	
	outliers	0	
	mean (n)	<0.5	
	st.dev. (n)	n.a.	
	R(calc.)	n.a.	
	R(lit)	n.a.	



APPENDIX 2**Details of the methods used by the participants:**

Lab	Used Method for extraction OPP	Used Method for extraction PCP/TECP
551	basic / ultrasonic extraction	basic / ultrasonic extraction
623	basic / ultrasonic extraction	basic / ultrasonic extraction
840	basic / ultrasonic extraction	steam distillation
2115	ASE extraction	ASE extraction
2127		
2129	soxhlet / AES extraction	soxhlet / AES extraction
2132	basic / ultrasonic extraction	basic / ultrasonic extraction
2135	basic / ultrasonic extraction	basic / ultrasonic extraction
2137	soxhlet / AES extraction	soxhlet / AES extraction
2139	soxhlet / AES extraction	soxhlet / AES extraction
2159		
2165	basic / ultrasonic extraction	basic / ultrasonic extraction
2172	basic / ultrasonic extraction	basic / ultrasonic extraction
2184	basic / ultrasonic extraction	basic / ultrasonic extraction
2201	steam distillation	steam distillation
2215	basic / ultrasonic extraction	basic / ultrasonic extraction
2221	basic / ultrasonic extraction	basic / ultrasonic extraction
2230	basic / ultrasonic extraction	basic / ultrasonic extraction
2232		
2246	steam distillation	steam distillation
2247	steam distillation	steam distillation
2255	basic extraction	basic extraction
2261	basic / ultrasonic extraction	basic / ultrasonic extraction
2272	basic / ultrasonic extraction	basic / ultrasonic extraction
2284	basic / ultrasonic extraction	basic / ultrasonic extraction
2285	basic / ultrasonic extraction	basic / ultrasonic extraction
2289	steam distillation	steam distillation
2290		steam distillation
2295	KOH Method	KOH Method
2296		steam distillation
2300	soxhlet / AES extraction	soxhlet / AES extraction
2310	basic / ultrasonic extraction	steam distillation
2311	basic / ultrasonic extraction	steam distillation
2352	basic / ultrasonic extraction	steam distillation
2354	basic / ultrasonic extraction	basic / ultrasonic extraction
2357	soxhlet / AES extraction	steam distillation
2359	basic / ultrasonic extraction	steam distillation
2365	basic / ultrasonic extraction	basic / ultrasonic extraction
2370	steam distillation	steam distillation
2372	basic / ultrasonic extraction	basic / ultrasonic extraction
2375	basic / ultrasonic extraction	basic / ultrasonic extraction
2379	basic / ultrasonic extraction	steam distillation
2380	alkaline digestion	alkaline digestion
2386	basic / ultrasonic extraction	steam distillation
2390	ultrasonic extraction	steam distillation
2403	basic / ultrasonic extraction	basic / ultrasonic extraction
2410	steam distillation	steam distillation
2415	basic / ultrasonic extraction	basic / ultrasonic extraction
2425	basic / ultrasonic extraction	basic / ultrasonic extraction
2428	basic / ultrasonic extraction	basic / ultrasonic extraction
2452	basic / ultrasonic extraction	basic / ultrasonic extraction
2453		
2482	basic / ultrasonic extraction	KOH method
2486	basic / ultrasonic extraction	basic / ultrasonic extraction
2488	basic / ultrasonic extraction	basic / ultrasonic extraction
2489	steam distillation	steam distillation

2492	soxhlet / AES extraction	soxhlet / AES extraction
2494	basic / ultrasonic extraction	basic / ultrasonic extraction
2495		
2497	steam distillation	basic / ultrasonic extraction
2508		
2511		
2512	basic / ultrasonic extraction	basic / ultrasonic extraction
2514	steam distillation	steam distillation
2515		
2546	steam distillation	steam distillation
2553	soxhlet / AES extraction	soxhlet / AES extraction
2560	AES extraction	AES extraction
2561	basic / ultrasonic extraction	steam distillation
2563	ASE extraction	ASE extraction
2566	basic / ultrasonic extraction	basic / ultrasonic extraction
2573	steam distillation	steam distillation
2582	steam distillation	steam distillation
2583		soxhlet / AES extraction
3100		steam distillation
3116	basic / ultrasonic extraction	basic / ultrasonic extraction
3117	basic / ultrasonic extraction	basic / ultrasonic extraction
3146	KOH extraction over night	KOH extraction over night
3150	basic / ultrasonic extraction	basic / ultrasonic extraction
3151	basic / ultrasonic extraction	basic / ultrasonic extraction
3153		steam distillation
3154	basic / ultrasonic extraction	steam distillation
3172	alcoholic digestion with KOH	alcoholic digestion with KOH
3176	basic / ultrasonic extraction	basic / ultrasonic extraction
3180	basic / ultrasonic extraction	
3182		steam distillation
3185	steam distillation	steam distillation
3190	soxhlet / AES extraction	steam distillation
3192		basic / ultrasonic extraction
3197	ultrasonic extraxtion	steam distillation
3200	steam distillation	steam distillation
3204	steam distillation	steam distillation
3209	basic / ultrasonic extraction	basic / ultrasonic extraction
3210	basic / ultrasonic extraction	basic / ultrasonic extraction
3214	steam distillation	steam distillation
3218	steam distillation	steam distillation
3220	basic / ultrasonic extraction	steam distillation
3225	basic / ultrasonic extraction	basic / ultrasonic extraction
3228	basic / ultrasonic extraction	basic / ultrasonic extraction
3233		basic / ultrasonic extraction
3237	basic / ultrasonic extraction	basic / ultrasonic extraction
3242	basic / ultrasonic extraction	basic / ultrasonic extraction

APPENDIX 3

Number of participants per country

6 labs in BANGLADESH
1 lab in BRAZIL
2 lab in FRANCE
14 labs in GERMANY
9 labs in HONG KONG
8 labs in INDIA
2 labs in INDONESIA
5 labs in ITALY
3 labs in KOREA
25 labs in P.R. of CHINA
1 lab in PAKISTAN
1 lab in PORTUGAL
1 lab in SINGAPORE
2 labs in SRI LANKA
1 lab in SWITZERLAND
4 labs in TAIWAN R.O.C.
2 labs in THAILAND
2 labs in TUNESIA
7 labs in TURKEY
2 labs in UNITED KINGDOM
4 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
n.a.	= not applicable
n.d.	= not detected
ex	= excluded
cfr.	= conform

Literature:

- 1 iis Interlaboratory Studies, Protocol for the Organisation, Statistics & Evaluation, January 2010
- 2 Official Journal of the European Communities L133/29 : May 2002
- 3 Öko-Tex Standard 100; February 2012
- 4 Thai Green label, TGL-16. July 2002
- 5 Impacts of Environmental Standards and requirements in EU Countries, Aug 99
- 6 Horwitz, Journal of AOAC International Vol. 79 No.3, 1996
- 7 P.L. Davies, Fr Z. Anal. Chem, 351, 513, (1988)
- 8 W.J. Conover, Practical; Nonparametric Statistics, J. Wiley&Sons, NY, p.302, (1971)
- 9 ISO 5725:1986
- 10 ISO 5725, parts 1-6, (1994)
- 11 ISO105 E4:1994
- 12 ISO14184-1:1994
- 13 M. Thompson and R. Wood, J. AOAC Int, 76, 926, (1993)
- 14 Analytical Methods Committee Technical brief, No4 February 2001.
- 15 The Royal Society of Chemistry 2002, Analyst 2002, 127 page 1359-1364, P.J. Lowthian and M. Thompson (see <http://www.rsc.org/suppdata/an/b2/b205600n/>)
- 16 ISO 13528:2005, Statistical methods for use in proficiency testing by interlaboratory comparisons