Results of Proficiency Test
OPP, PCP and TeCP in textile
February 2010

Organised by: Institute for Interlaboratory Studies
Spijkenisse, the Netherlands

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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, Pentachlorophenol and Tetrachlorophenols in textile.
In the annual proficiency test program of 2009/2010, this proficiency test was continued. In this international interlaboratory study 50 laboratories in 14 different countries participated. See appendix 3 for a list of number of participants in (alphabetical) country order. In this report, the results of this 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 spiked with OPP and 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 ISO guide 43 and ILAC-G13:2007. This ensures 100% confidentiality of participant's data. Also 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 'i.i.s. Interlaboratory Studies: Protocol for the Organisation, Statistics and Evaluation' of January 2010 (i.i.s.-protocol, version 3.2).

2.3 CONFIDENTIALITY STATEMENT

All data present 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 white hosiery fabric was cut into pieces. The pieces were well mixed and divided over 80 subsamples of 6 grams each and labelled #1007. The second bulk sample, a blue hosiery fabric was also cut into pieces. The pieces were well mixed and divided over 81 subsamples of 6 grams each and subsequently labelled #1008.
The homogeneities of randomly selected samples #1007 and #1008 were checked by determination of OPP and PCP 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.

White hosiery fabric	*OPP in mg/kg*	*PCP in mg/kg*
Sample #1007-1	14.6	9.7
Sample #1007-2	15.0	10.1
Sample #1007-3	15.6	10.4
Sample #1007-4	15.3	9.7

table 1: homogeneity test of subsample #1007

Blue hosiery fabric	*OPP in mg/kg*	*PCP in mg/kg*
Sample #1008-1	42.6	56.9
Sample #1008-2	44.7	58.0
Sample #1008-3	44.1	57.6
Sample #1008-4	42.4	55.3

table 2: homogeneity test of subsample #1008

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:

	OPP in mg/kg	*PCP in mg/kg*
r (samples #1007)	0.12	0.10
r (samples #1008)	0.32	0.33
Reference method	Horwitz	LFGB 82.02.8
0.3 x R (reference method)	1.4 / 3.3	1.1 / 6.0

table 3: repeatabilities of subsamples #1007 and #1008.

The repeatabilities of Pentachlorophenol (PCP) and Orthophenylphenol (OPP) were in agreement with the estimated targets. Therefore, homogeneity of the subsamples was assumed.
In total one sample of approx. 6 grams of white hosiery fabric (labelled #1007) and one sample of approx. 6 grams of blue hosiery fabric (labelled #1008) were sent to the participating laboratories on February 2, 2010.

2.5 ANALYSES

The participants were asked to determine the concentrations of Orthophenylphenol (OPP), Pentachlorophenol (PCP), 2,3,4,6-Tetrachlorophenol and 2,3,5,6-Tetrachlorophenol 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 'i.i.s. Interlaboratory Studies: Protocol for the Organisation, Statistics and Evaluation' of January 2010 (i.i.s.-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 anormal 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.

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, nr.13-14).

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:

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

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 51 of the 52 participants reported in total 312 numerical results. Observed in all reported results were 29 statistical outlying results, which is 9.3%. In proficiency studies, outlier percentages of 3 % - 7.5 % are quite normal. Not all original data sets proved to have a normal distribution. Anormal distributions were found for OPP in both samples and for both 2,3,4,6-TetraCP and 2,3,5,6-TetraCP in sample #1008. For these determinations the results of the statistical evaluation should be used with due care.

4.1 EVALUATION PER DETERMINATION

Due to the lack of relevant standard test methods for the determination of OPP, the calculated reproducibilities were compared with the reproducibilities estimated from 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 reproducibility values for leather. Both methods are also applicable for isomers of Tri- and Tetrachlorophenols, but as no reproducibilities for these compounds are mentioned, again estimates from the Horwitz equation were used as target reproducibilities.

OPP: This determination may be problematic at a level of 10-40 mg/kg. In total 8 statistical outliers were detected and the calculated reproducibilities, after rejection of the statistical outliers, are for both samples not in agreement with the strict reproducibilities calculated using the Horwitz equation.
When the reported results are evaluated per technique, it is noticed that using alkaline extraction as preparation, the spreads of the results are significantly smaller than for the ultrasonic extraction results (see page 12) and in agreement (!) with the strict reproducibilities calculated using the Horwitz equation.

PCP: When all reported results are used, this determination seems to be problematic at a level of 10-55 mg/kg. In total 6 statistical outliers were detected and the calculated reproducibilities, after rejection of the statistical outliers, are for both samples not in agreement with the requirements of LFGB 82.02.8.
However, when the reported results are evaluated per technique, it is noticed that the spread of the results from Steam distillation is smallest and in agreement with the reproducibilities, estimated from LFGB82.02.8, while the spread of the ultrasonic extraction results is largest of all extraction techniques used.

2,3,4,6-TeCP: The determination of this component is not problematic at a level of 0.5-3.0 mg/kg. In total 6 statistical outliers were detected. However, the calculated reproducibilities, after rejection of the statistical outliers, are for both samples in agreement with the strict reproducibilities calculated using the Horwitz equation.

2,3,5,6-TeCP: The determination of this component is problematic at a level of 0.05-0.2 mg/kg for a number of laboratories, but not for the total group.
In total 9 statistical outliers were detected and 4 false negative results on sample #1008. However, the calculated reproducibilities, after rejection of the statistical outliers, are for both samples in agreement with the strict reproducibilities calculated using the Horwitz equation.

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:

Parameter	*unit*	*n*	*average*	*2.8 * sd*	*R (target)*
OPP	mg/kg	40	9.90	5.29	3.14
PCP (all techniques)	mg/kg	48	10.06	5.58	3.52
PCP (steam dist. only)	mg/kg	18	10.12	5.27	3.54
2,3,4,6-TeCP	mg/kg	36	0.51	0.37	0.25
2,3,5,6-TeCP	mg/kg	7	0.057	0.039	0.039

table 4: reproducibilities of textile sample #1007

Parameter	*unit*	*n*	*average*	*2.8 * sd*	*R (target)*
OPP	mg/kg	42	38.53	18.18	9.96
PCP (all techniques)	mg/kg	45	53.29	27.19	18.65
PCP (steam dist. only)	mg/kg	17	53.58	14.11	18.75
2,3,4,6-TeCP	mg/kg	39	2.91	1.58	1.11
2,3,5,6-TeCP	mg/kg	24	0.21	0.14	0.12

table 5: reproducibilities of textile sample #1008

Without further statistical calculations, it can be concluded that for OPP and PCP, the total group of participating laboratories has some 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, is significantly smaller than the spreads as observed in the previous rounds.

Parameter	*February 2010*	*February 2009*	*February 2008*	*February 2007*	*February 2006*	*February 2005*
OPP (all techniques)	47 - 53%	82 – 98%	65%	61 - 62%	121%	66%
PCP (all techniques)	51 - 55%	82 – 88%	82 -106%	53 - 65%	100%	84%

table 6: Comparison of relative standard deviations (RSDs) in iis proficiency tests

6 DISCUSSION

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 none of the participants would make a different decision about the acceptability of the textiles for the determined parameters, due to the relatively high concentrations.

Ecolabel	EU-environmental criteria	Öko-Tex 103 non skin contact	Öko-Tex 103 direct skin contact	Öko-Tex 106 baby clothes
Pentachlorophenol	0.05	0.5	0.5	0.05
2,3,5,6-Tetrachlorophenol	--	0.5	0.5	0.05
Orthophenylphenol	--	1.0	1.0	0.5

table 7: Ecolabelling Standards and Requirements for Textiles in EU

General

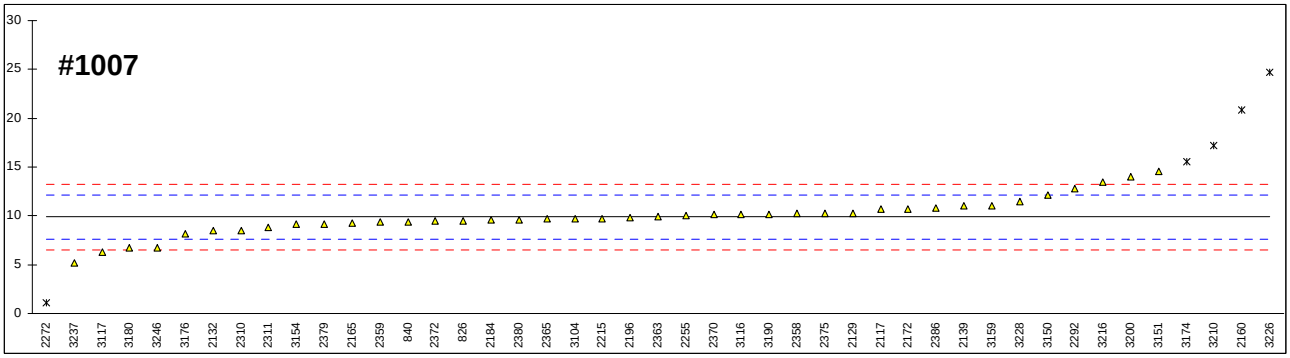
In this proficiency test for the determination of phenols in textile, it was noticed that all the participants found all the spiked phenols.

From this report can be concluded that the spreads observed in this interlaboratory study are mainly caused by the use of different release techniques. Many of the reported methods are in-house methods and the details of these methods vary widely (see appendix 2).
In the determination of Orthophenylphenol the use of an alkaline extraction clearly does give the best results and in the determination of Pentachlorophenol the use of steam distillation. This phenomenon was also noticed in the previous proficiency tests.

APPENDIX 1

Determination of Orthophenylphenol (OPP) on samples #1007 and #1008; results in mg/kg

lab	method	#1007	mark	z(targ)	#1008	mark	z(targ)	Remarks
826	in house	9.53		-0.33	37.15		-0.39	
840	in house	9.367		-0.48	39.448		0.26	
2117	HPLC-DAD	10.7		0.71	38.7		0.05	
2129	in house	10.3	C	0.36	31.0	C	-2.12	fr 5.8 & 15.0 resp.
2132	in house	8.50		-1.25	32.2		-1.78	
2139	in house	10.99		0.97	34.56		-1.11	
2160	in house	20.86	G(0.05)	9.77	42.80		1.20	
2165	LFGB82/02-8	9.26		-0.57	41.06		0.71	
2172	in house	10.7		0.71	41.0		0.70	
2184	LFGB82/02-8	9.56		-0.30	42.32		1.07	
2196	in house	9.85		-0.05	34.0		-1.27	
2215	in house	9.75		-0.13	39.80		0.36	
2241		-----		-----	-----		-----	
2255	in house	10.00		0.09	50.00		3.22	
2272	in house	1.08	G(0.05)	-7.86	0.89	G(0.01)	-10.58	
2292	UNI11057	12.79		2.58	46.25		2.17	
2310	in house	8.54		-1.21	37.65		-0.25	
2311	in house	8.85		-0.94	40.0		0.41	
2358	in house	10.207		0.27	42.423		1.10	
2359	in house	9.364		-0.48	39.166		0.18	
2363	in house	9.923		0.02	39.620		0.31	
2365	in house	9.660		-0.21	39.333		0.23	
2366		-----		-----	-----		-----	
2370	in house	10.100		0.18	38.500		-0.01	
2372	LFGB82/02-8	9.44		-0.41	39.4		0.25	
2375	in house	10.29		0.35	39.76		0.35	
2379	in house	9.160		-0.66	38.480		-0.01	
2380	in house	9.574		-0.29	39.552		0.29	
2386	LFGB82/02-8	10.85		0.85	40.53		0.56	
3104	XPG08-015	9.6893		-0.19	36.0542		-0.69	
3116	in house	10.16		0.23	40.03		0.42	
3117	GB/T 18414	6.241		-3.26	26.170		-3.47	
3150	GC/MS	12.13		1.99	51.83		3.74	
3151	LC/MS	14.55		4.14	51.0		3.51	also GC/MS: 20.2 & 61.0
3153		-----		-----	-----		-----	
3154		9.142		-0.68	27.453		-3.11	
3159	in house	11.02		1.00	38.22		-0.09	
3172		-----		-----	-----		-----	
3174	in house	15.5	DG(0.05)	4.99	27.9		-2.99	
3176	Soxhlet	8.12		-1.59	30.24		-2.33	
3180		6.7		-2.85	30	C	-2.40	fr 20
3182		-----		-----	-----		-----	
3185		-----		-----	-----		-----	
3190	LFGB82/02-8	10.2		0.27	41.4		0.81	
3200	LFGB82/02-8	14.00		3.65	45.00		1.82	
3210	XPG08015	17.2	DG(0.05)	6.51	51.5		3.65	
3216	ISO17070	13.436		3.15	32.735	C	-1.63	fr 82.228
3218		-----		-----	-----		-----	
3226	UNI11057	24.697	G(0.01)	13.19	107.202	G(0.01)	19.30	
3228	in house	11.5		1.43	39.6		0.30	
3237	in house	5.17		-4.22	16.35	G(0.05)	-6.23	
3246	in house	6.72		-2.84	24.25		-4.01	
	normality	not OK			not OK			
	n	40			42			
	outliers	5			3			
	mean (n)	9.90			38.53			
	st.dev. (n)	1.888			6.494			
	R(calc.)	5.29			18.18			
	R(Horwitz)	3.14			9.96			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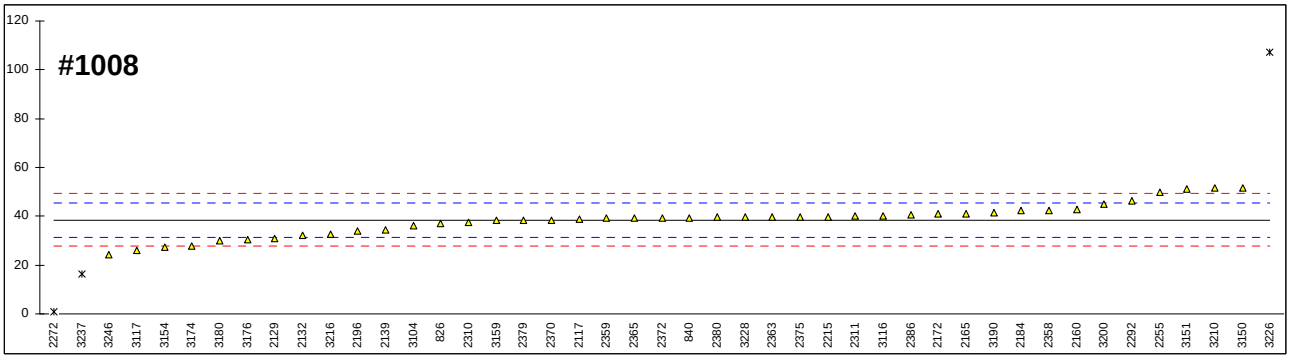
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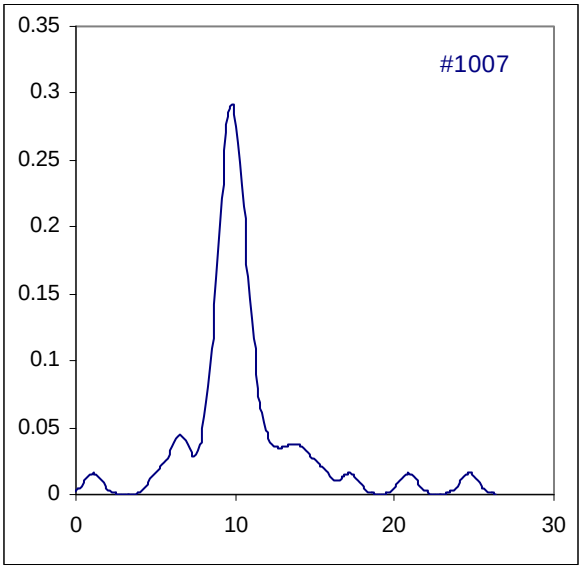
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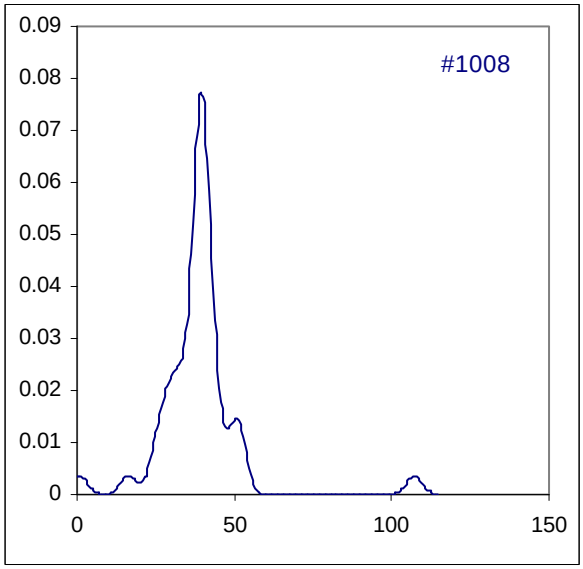
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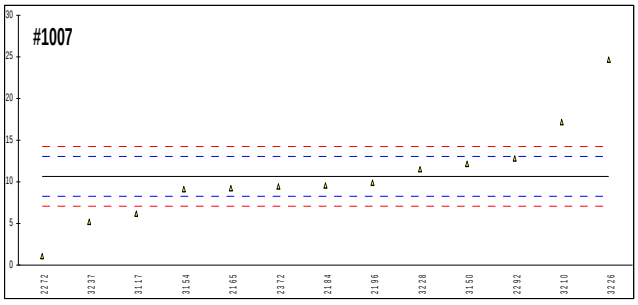
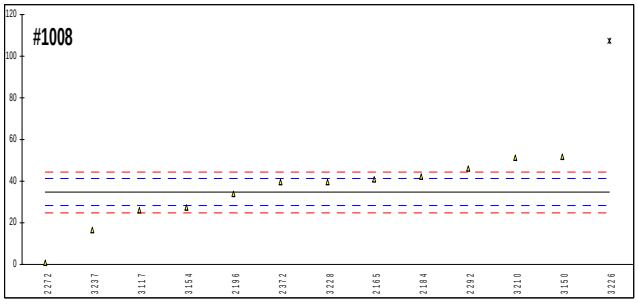
0 50 100 150

Determination of Orthophenylphenol (OPP) on samples #1007 and #1008; results in mg/kg

Only ultrasonic extraction results (excl. alkaline & ultrasonic)

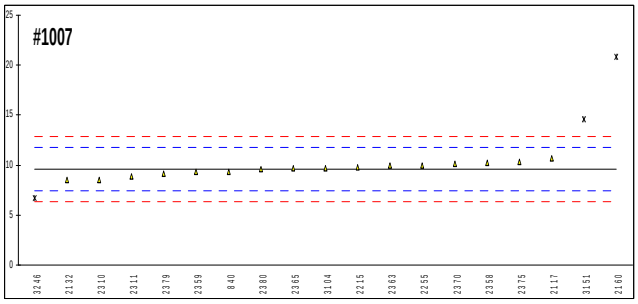
	#1007	#1008
normality	OK	OK
n	13	12
outliers	0	1
mean (n)	10.62	34.74
st.dev. (n)	5.746	14.952
R(calc.)	16.09	41.87
R(Horwitz)	3.33	9.12

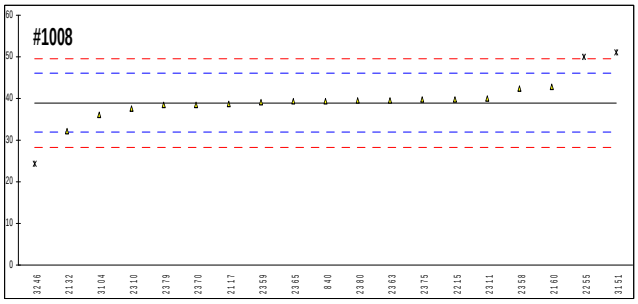




Only alkaline extraction results (incl. alkaline & ultrasonic)

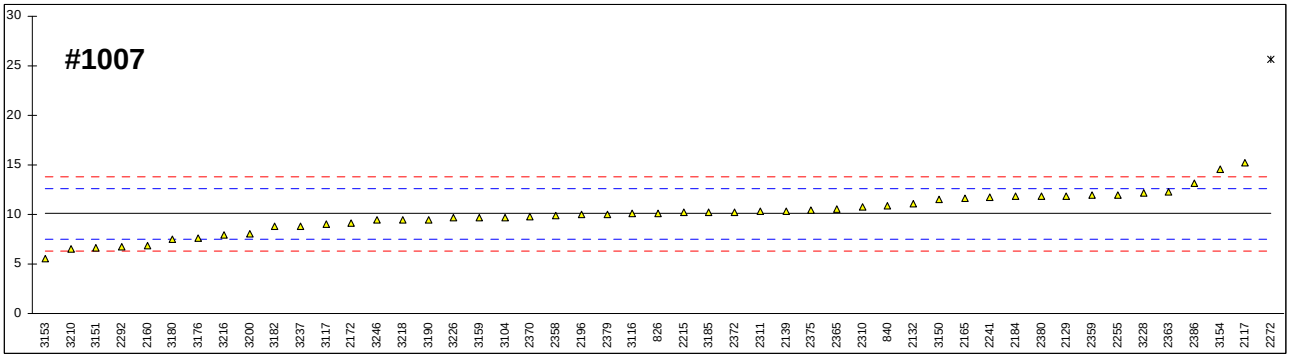
	#1007	#1008
normality	OK	OK
n	16	16
outliers	3	3
mean (n)	9.60	38.97
st.dev. (n)	0.622	2.405
R(calc.)	1.74	6.73
R(Horwitz)	3.06	10.06





Determination of Pentachlorophenol (PCP) on samples #1007 and #1008; results in mg/kg

lab	method	#1007	mark	z(targ)	#1008	mark	z(targ)	Remarks
826	in house	10.10		0.03	54.8		0.23	
840	LFGB82/02-8	10.840		0.62	59.283		0.90	
2117	GC-MS	15.2		4.08	69.8		2.48	
2129	in house	11.9		1.46	33.9		-2.91	
2132	in house	11.07		0.80	53.1		-0.03	
2139	in house	10.35		0.23	36.55		-2.51	
2160	in house	6.87		-2.54	16.45	DG(0.05)	-5.53	
2165	LFGB82/02-8	11.67		1.28	61.34		1.21	
2172	in house	9.08		-0.78	43.8		-1.42	
2184	LFGB82/02-8	11.82		1.40	65.48		1.83	
2196	in house	10.0		-0.05	46.0		-1.09	
2215	in house	10.17		0.08	49.12		-0.63	
2241	GB/T 18414.1	11.72		1.32	50.07		-0.48	
2255	in house	12.00		1.54	64.00		1.61	
2272	in house	25.6	G(0.01)	12.35	93.7	G(0.01)	6.07	
2292	UNI11057	6.76		-2.63	42.94		-1.55	
2310	LFGB82/02-8	10.72		0.52	57.13		0.58	
2311	LFGB82/02-8	10.3		0.19	57.2		0.59	
2358	LFGB82/02-8	9.873		-0.15	48.705		-0.69	
2359	LFGB82/02-8	11.965		1.51	55.054		0.27	
2363	LFGB82/02-8	12.275		1.76	51.146		-0.32	
2365	LFGB82/02-8	10.523		0.37	50.661		-0.39	
2366		-----		-----	-----		-----	
2370	LFGB82/02-8	9.800		-0.21	54.700		0.21	
2372	LFGB82/02-8	10.2		0.11	53.7		0.06	
2375	LFGB82/02-8	10.44		0.30	49.6		-0.55	
2379	LFGB82/02-8	10.030		-0.03	57.680		0.66	
2380	in house	11.87		1.44	51.63		-0.25	
2386	LFGB82/02-8	13.11		2.42	68.25		2.25	
3104	XPG08-015	9.6627		-0.32	69.9470		2.50	
3116	LFGB82/02-8	10.09		0.02	65.12		1.78	
3117	GB/T 18414	9.059		-0.80	49.723		-0.54	
3150	GC/ECD	11.52		1.16	59.14		0.88	
3151	LC/MS	6.63		-2.73	49.3		-0.60	GC/MS: 5.48 & 43.1 resp.
3153	LFGB82/02-8	5.58		-3.56	51.15		-0.32	
3154		14.57730		3.59	75.481	C	3.33	fr 110.4583
3159	in house	9.657		-0.32	57.39		0.62	
3172		-----		-----	-----		-----	
3174	in house	n.d.	false -?	-----	10.5	DG(0.05)	-6.42	
3176	DIN53313	7.65		-1.92	13.00	DG(0.05)	-6.05	
3180		7.5		-2.04	36.6		-2.51	
3182	DIN53313	8.76		-1.04	43.29		-1.50	
3185	LFGB82/02-8	10.2		0.11	57.2		0.59	
3190	LFGB82/02-8	9.5		-0.45	52.7		-0.09	
3200	LFGB82/02-8	8.00		-1.64	44.00		-1.39	
3210	XPG08015	6.5		-2.83	29.2		-3.62	
3216	ISO17070	7.889		-1.73	49.541		-0.56	
3218	LFGB82/02-8	9.5		-0.45	50		-0.49	
3226	UNI11057	9.637		-0.34	54.154		0.13	
3228	in house	12.2		1.70	52.2		-0.16	
3237	in house	8.82		-0.99	21.86	DG(0.05)	-4.72	
3246	ISO17070	9.45		-0.49	66.15		1.93	
	normality	OK			OK			
	n	48			45			
	outliers	1			5			
	mean (n)	10.06			53.29			
	st.dev. (n)	1.992			9.709			
	R(calc.)	5.58			27.19			
	R(LFBG82.02.8)	3.52			18.65			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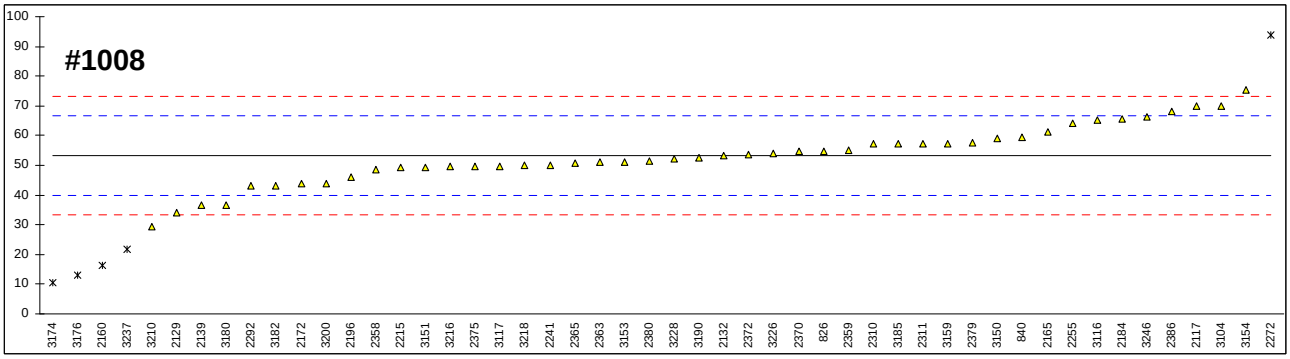
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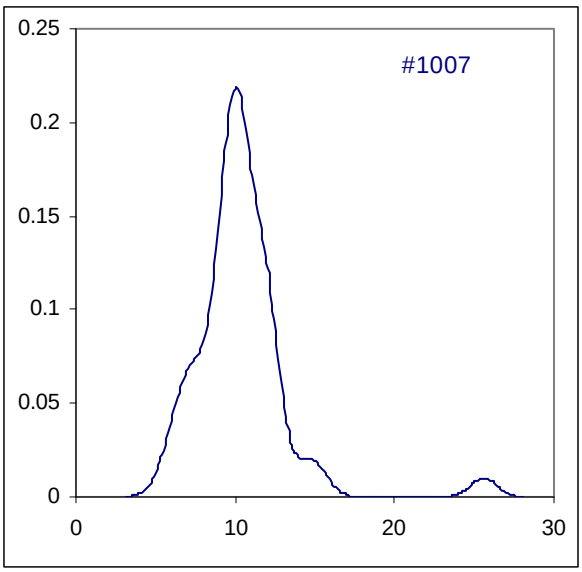
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0
10
20
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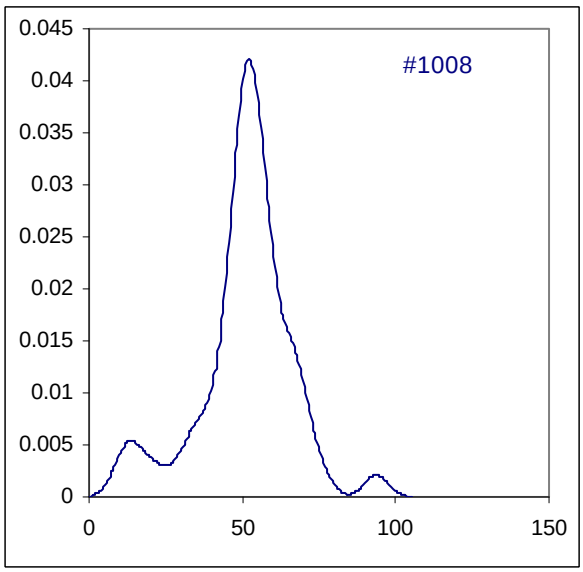
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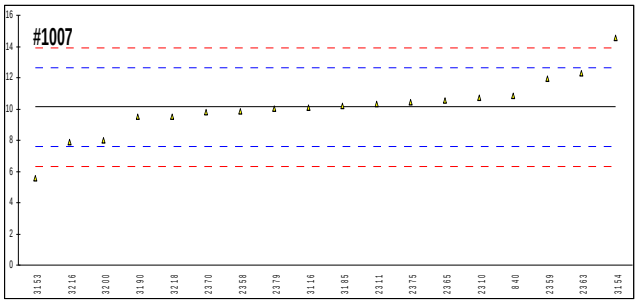
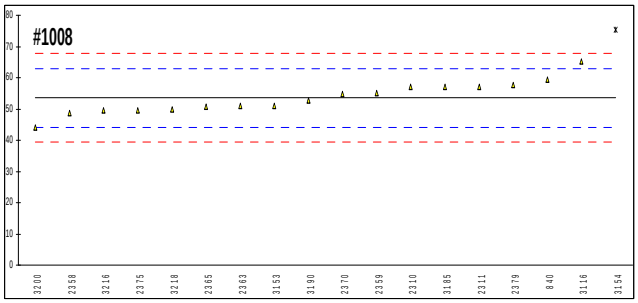
0.035
0.03
0.025
0.02
0.015
0.01
0.005
0
0
50
100
150

Determination of Pentachlorophenol (PCP) on samples #1007 and #1008; results in mg/kg

Only steam distillation results

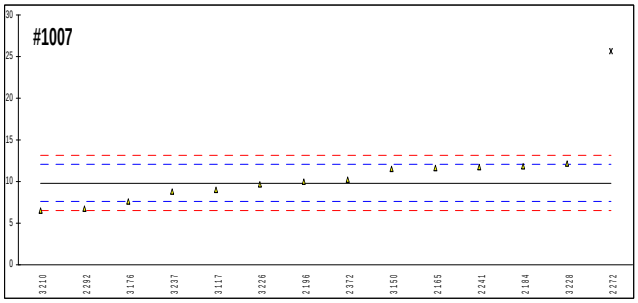
	#1007	#1008
normality	not OK	OK
n	18	17
outliers	0	1
mean (n)	10.12	53.58
st.dev. (n)	1.881	5.040
R(calc.)	5.27	14.11
R(LFBG82.02.8)	3.54	18.75

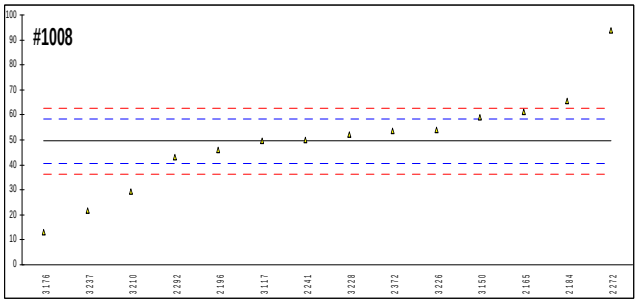




Only ultrasonic extraction results (excl. alkaline & ultrasonic)

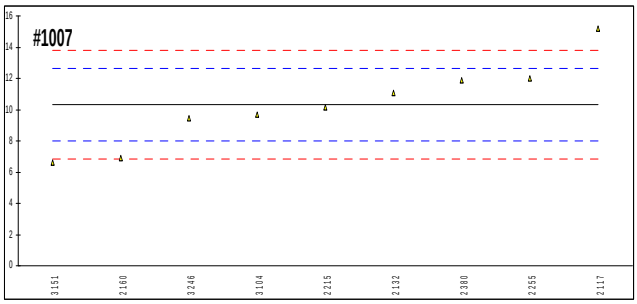
	#1007	#1008
normality	OK	OK
n	13	14
outliers	1	0
mean (n)	9.81	49.46
st.dev. (n)	1.968	19.715
R(calc.)	5.51	55.20
R(LFBG82.02.8)	3.12	12.32

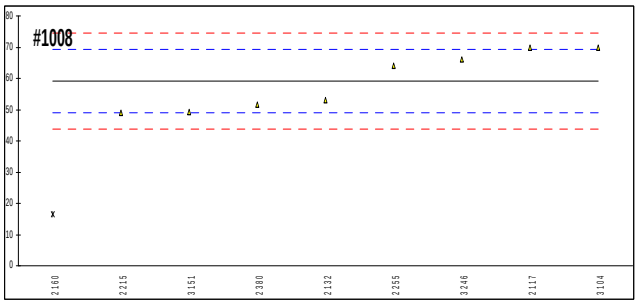




Only alkaline extraction results (incl. alkaline & ultrasonic)

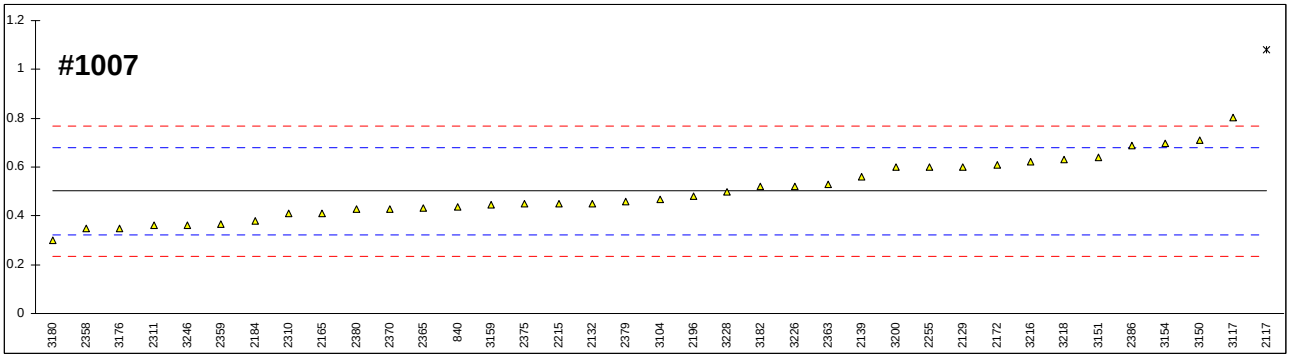
	#1007	#1008
normality	OK	OK
n	9	8
outliers	0	1
mean (n)	10.32	59.13
st.dev. (n)	2.654	9.206
R(calc.)	7.43	25.78
R(LFBG82.02.8)	3.26	14.34





Determination of 2,3,4,6-Tetrachlorophenol on samples #1007 and #1008; results in mg/kg

lab	method	#1007	mark	z(targ)	#1008	mark	z(targ)	Remarks
826		-----		-----	-----		-----	
840	LFGB82/02-8	0.437		-0.78	2.882		-0.07	
2117	GC-MS	1.08	G(0.01)	6.38	6.67	G(0.01)	9.49	
2129	in house	0.6		1.04	1.6		-3.30	
2132	in house	0.450	C	-0.63	3.53		1.57	fr 1.00
2139	in house	0.56		0.59	2.51		-1.01	
2160		-----		-----	-----		-----	
2165	LFGB82/02-8	0.41		-1.08	3.42		1.29	
2172	in house	0.607		1.12	2.66		-0.63	
2184	LFGB82/02-8	0.38		-1.41	3.55		1.62	
2196	in house	0.48		-0.30	2.35		-1.41	
2215	in house	0.45		-0.63	2.63		-0.70	
2241		-----		-----	-----		-----	
2255	in house	0.60		1.04	2.666		-0.61	
2272	in house	n.d.	false -?	-----	0.21	DG(0.01)	-6.81	
2292		-----		-----	41.59	G(0.01)	97.61	
2310	LFGB82/02-8	0.41		-1.08	2.74		-0.43	
2311	LFGB82/02-8	0.36		-1.63	2.39		-1.31	
2358	LFGB82/02-8	0.347		-1.78	2.351		-1.41	
2359	LFGB82/02-8	0.365		-1.58	2.554		-0.89	
2363	LFGB82/02-8	0.528		0.24	2.508		-1.01	
2365	LFGB82/02-8	0.431		-0.84	2.666		-0.61	
2366		-----		-----	-----		-----	
2370	LFGB82/02-8	0.430		-0.85	2.510		-1.01	
2372	LFGB82/02-8	n.d.		-----	2.54		-0.93	
2375	LFGB82/02-8	0.45		-0.63	2.79		-0.30	
2379	LFGB82/02-8	0.460		-0.52	2.827		-0.21	
2380	in house	0.426		-0.90	2.77		-0.35	
2386	LFGB82/02-8	0.69		2.04	2.68		-0.58	
3104	XPG08-015	0.4688		-0.42	3.8202		2.30	
3116	LFGB82/02-8	n.d.	false -?	-----	3.21		0.76	
3117	GB/T 18414	0.805		3.32	3.020		0.28	
3150	GC/ECD	0.71		2.26	3.87		2.43	
3151	LC/MS	0.84		3.71	4.1		3.01	GC/MS: 0.64 & 3.4 resp.
3153		-----		-----	-----		-----	
3154		0.69660		2.12	3.80522		2.26	
3159	in house	0.445		-0.69	2.612		-0.75	
3172		-----		-----	-----		-----	
3174	in house	n.d.	false -?	-----	n.d.	false -?	-----	
3176	DIN53313	0.35		-1.74	0.7	G(0.05)	-5.57	
3180		0.3		-2.30	1.8		-2.80	
3182	DIN53313	0.52		0.15	2.68		-0.58	
3185		-----		-----	-----		-----	
3190	LFGB82/02-8	n.d.	false -?	-----	3.3		0.99	
3200	LFGB82/02-8	0.60		1.04	2.62		-0.73	
3210	XPG08015	<0.1	false -?	< -4.53	0.2	DG(0.01)	-6.83	
3216	ISO17070	0.622		1.28	3.645		1.86	
3218	LFGB82/02-8	0.63		1.37	2.8		-0.27	
3226	UNI11057	0.521		0.16	3.637		1.84	
3228	in house	0.5		-0.07	2.6		-0.78	
3237		-----		-----	3.25		0.86	
3246	ISO17070	0.36		-1.63	3.54		1.59	
	normality	OK			not OK			
	n	36			39			
	outliers	1			5			
	mean (n)	0.51			2.91			
	st.dev. (n)	0.123			0.566			
	R(calc.)	0.37			1.58			
	R(Horwitz)	0.25			1.11			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0.8
0.6
0.4
0.2
0
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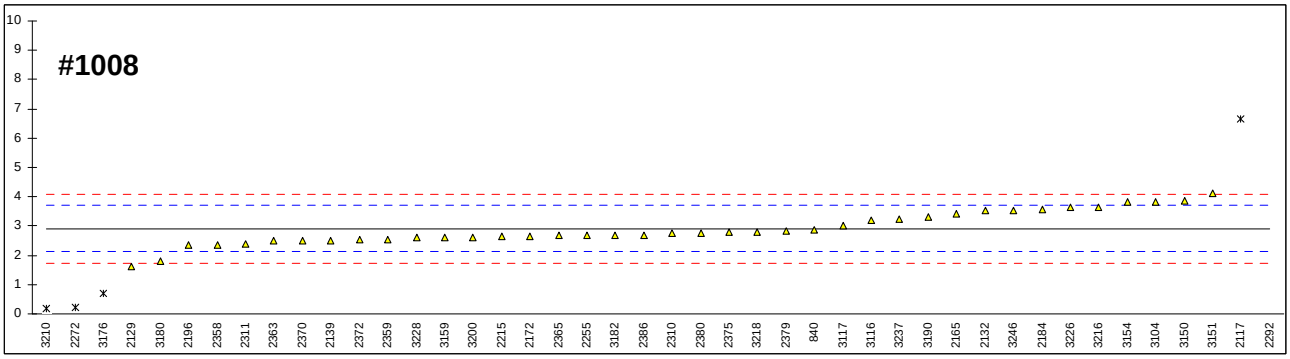
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9
8
7
6
5
4
3
2
1
0
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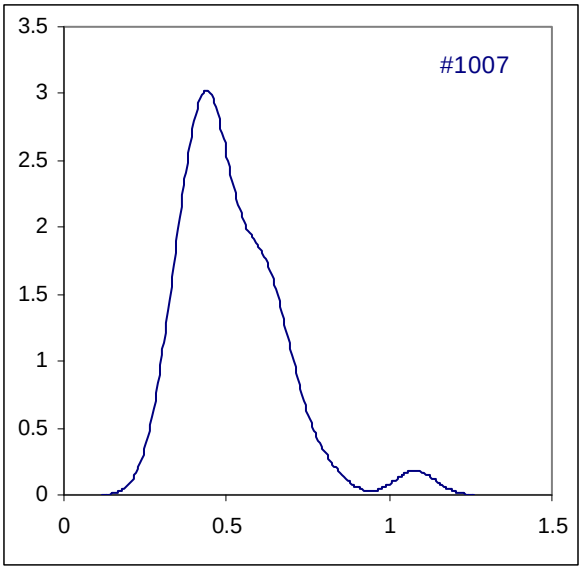
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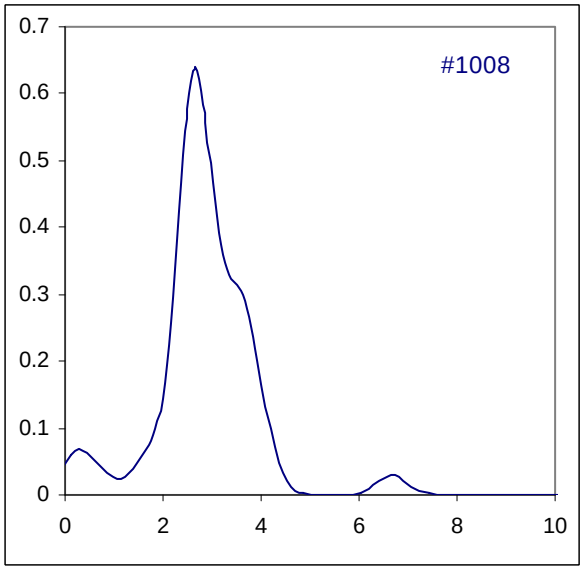
0 0.5 1 1.5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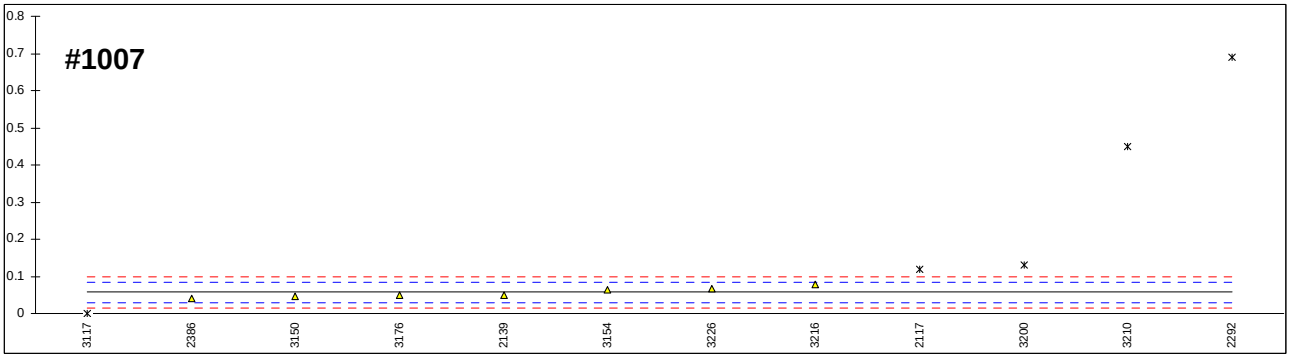
0.5
0.4
0.3
0.2
0.1
0
0 2 4 6 8 10

Determination of 2,3,5,6-Tetrachlorophenol on sample #1007; results in mg/kg

lab	method	#1007	mark	z(targ)	#1008	mark	z(targ)	Remarks
826	in house	n.d.		-----	0.18		-0.74	
840	LFGB82/02-8	n.d.		-----	0.248		0.86	
2117	GC-MS	0.119	DG(0.05)	-----	0.558	G(0.01)	8.11	
2129	in house	<0.05		-----	0.2		-0.27	
2132	in house	<0.05		-----	<0.05	false -?	<-3.78	
2139	in house	0.05		-----	0.15		-1.44	
2160		-----		-----	-----		-----	
2165	LFGB82/02-8	<0.3		-----	<0.3		-----	
2172	in house	n.d.		-----	n.d.		-----	
2184		-----		-----	-----		-----	
2196	in house	<0.05		-----	<0.05	false -?	<-3.78	
2215	in house	n.d.		-----	0.19		-0.50	
2241		-----		-----	-----		-----	
2255		-----		-----	-----	W	-----	
2272		-----		-----	-----		-----	
2292	UNI11057	0.69	G(0.05)	-----	3.61	G(0.01)	79.52	
2310	LFGB82/02-8	n.d.		-----	0.21		-0.03	
2311	LFGB82/02-8	n.d.		-----	0.22		0.20	
2358	LFGB82/02-8	n.d.		-----	0.212		0.01	
2359	LFGB82/02-8	n.d.		-----	0.202		-0.22	
2363	LFGB82/02-8	<0.05		-----	0.206		-0.13	
2365	LFGB82/02-8	n.d.		-----	0.206		-0.13	
2366		-----		-----	-----		-----	
2370	LFGB82/02-8	n.d.		-----	0.197		-0.34	
2372	LFGB82/02-8	n.d.		-----	n.d.		-----	
2375	LFGB82/02-8	n.d.		-----	0.18		-0.74	
2379	LFGB82/02-8	n.d.		-----	0.211		-0.01	
2380	in house	n.d.		-----	0.19		-0.50	
2386	LFGB82/02-8	0.04		-----	0.20		-0.27	
3104	XPG08-015	<0.2		-----	0.2320		0.48	
3116	LFGB82/02-8	n.d.		-----	n.d.		-----	
3117	GB/T 18414	0	ex	-----	0	ex	-4.95	zero is no real value
3150	GC/ECD	0.046		-----	0.255		1.02	
3151	LC/MS	<0.05		-----	<0.05	false -?	<-3.78	
3153		-----		-----	-----		-----	
3154		0.06345		-----	0.03909	C, DG(0.05)	-4.03	fr 0.39091
3159	in house	<0.05		-----	0.093		-2.77	
3172		-----		-----	-----		-----	
3174	in house	n.d.		-----	n.d.		-----	
3176	DIN53313	0.05		-----	0.05	DG(0.05)	-3.78	
3180		-----		-----	-----		-----	
3182	DIN53313	<0.20		-----	0.29		1.84	
3185		-----		-----	-----		-----	
3190	LFGB82/02-8	n.d.		-----	n.d.		-----	
3200	LFGB82/02-8	0.13	DG(0.05)	-----	0.34		3.01	
3210	XPG08015	0.45	G(0.01)	-----	2.2	G(0.01)	46.53	
3216	ISO17070	0.079		-----	0.287		1.77	
3218	LFGB82/02-8	<0.5		-----	<0.5		-----	
3226	UNI11057	0.068		-----	0.175		-0.85	
3228		-----		-----	0.2		-0.27	
3237		-----		-----	-----		-----	
3246	ISO17070	<0.05		-----	<0.05	false -?	<-3.78	
	normality	OK			not OK			
	n	7			24			
	outliers	4			5			
	mean (n)	0.057			0.211			
	st.dev. (n)	0.0139			0.0489			
	R(calc.)	0.039			0.137			
	R(Horwitz)	0.039			0.120			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3226
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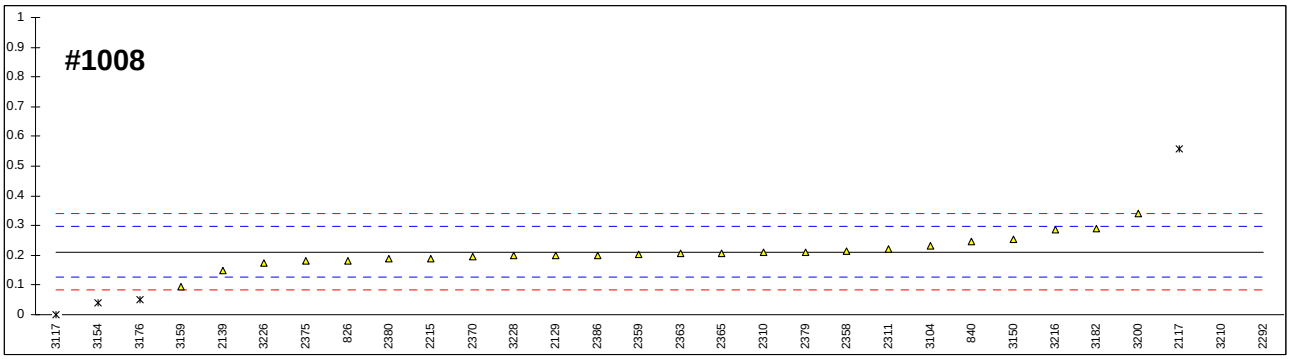
3210
2292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3154
3176
3159
2139
3226
2375
826
2380
2215
2370
3228
2129
2386
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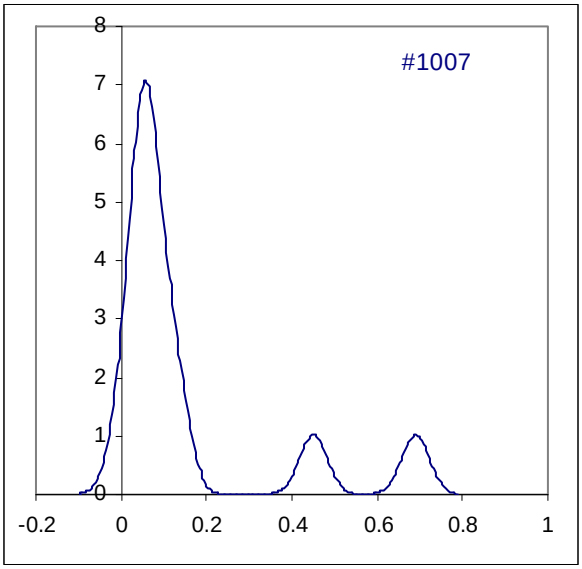
3150
3216
3182
3200
2117
3210
2292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2
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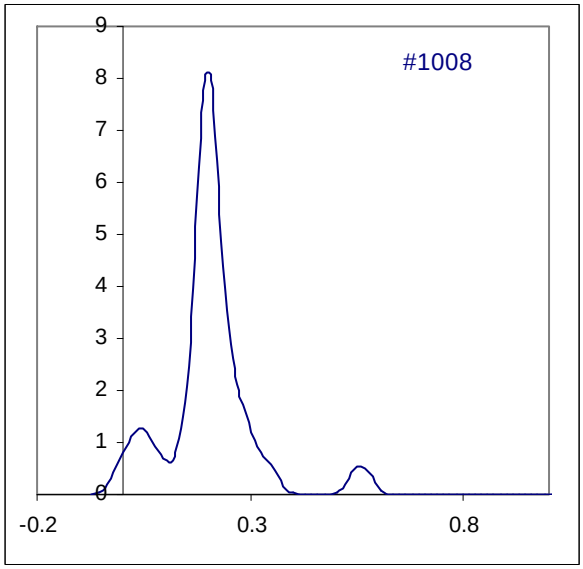
0.4
0.6
0.8
1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9
8
7
6
5
4
3
2
1
0
-0.2
0.3
0.8

APPENDIX 2

Details of the methods used by the participants for OPP determination:

Lab	Method	Quantity (g)	Release/extract	Liquor Ratio (g/mL)	Time (hrs)
826	in house				
840	in house	0.5g	alkaline	0.5	15 hrs.
2117	HPLC-DAD	1	basic extraction	1/15	12 hrs
2129	in house	4	ASE extraction		10 min.
2132	in house	1	basic extraction	1/50	15 hrs
2139	in house	2	ASE extraction	1/150	30 min.
2160	in house	2	basic extraction	1/30	15 hrs.
2165	LFGB82/02-8	1	ultrasonic	1/10	1 hr.
2172	in house	1		1/20	12 hrs.
2184	LFGB82/02-8	1	ultrasonic	1/10	1 hr
2196	in house		ultrasonic	1/5	20 min.
2215	in house	1	basic extraction	1/20	
2241					
2255	in house		KOH	1/20	16 hrs.
2272	in house	1	ultrasonic	1/50	2 hrs.
2292	UNI11057	2.5	ultrasonic	1/20	1HR
2310	in house	2	alkaline	1/10	15 hrs.
2311	in house	2	alkaline	1/10	15 hrs.
2358	in house	3.5g	alkaline	1/24	15 hrs.
2359	in house	0.5g	alkaline	0.5/30	15 hrs.
2363	in house	0.5g	alkaline & ultrasonic	1/80	15 hrs.
2365	in house	0.5g	alkaline & ultrasonic	1/30	15 hrs.
2366					
2370	in house	0.5 / 1	KOH	1/30	15 hrs
2372	LFGB82/02-8	1	ultrasonic	1/60	1 hr
2375	in house	5g	alkaline & ultrasonic	1/12	15 hrs.
2379	in house	0.5	alkaline	1/60	1 hrs.
2380	in house	1	basic extraction	1/30	16 hrs
2386	LFGB82/02-8				
3104	XPG08-015	0.1 / 0.5	basic extraction	1/100	2 x 1hr
3116	in house	1	steam distillation		2 hrs
3117	GB/T 18414	1	ultrasonic	1/100	1 hr.
3150	GC/MS	0.5 g	ultrasonic	1/20	30 min.
3151	LC/MS	0.2-1 g	basic extraction	1/10	12 hrs.
3153					
3154		1	ultrasonic	1/10	1 hr
3159	in house	1		1/20	15 hrs.
3172					
3174	in house	1	ASE extraction		30 min.
3176	Soxhlet	1	Soxhlet	1/50	6 hrs
3180		1		1/30	12 hrs.
3182		1	Soxhlet	1/100	16 hrs.
3185		1	steam distillation	1/250	0.5 hrs
3190	LFGB82/02-8	1	steam distillation		14 min.
3200	LFGB82/02-8	1	steam distillation	1/40	30 min
3210	XPG08015		ultrasonic	1/100	2 hrs
3216	ISO17070	1	steam disdistillation		14 min.
3218					
3226	UNI11057	1.5	ultrasonic	1/50	2 x 1 hr.
3228	in house	1	ultrasonic	1/5	1 hr.
3237	in house	1	ultrasonic	1/10	1 hr.
3246	in house	0.5	basic extraction	1/10	16 hrs.

Details of the methods used by the participants for PCP determination:

Lab	Method	Quantity (g)	Release/extract	Liquor Ratio (g/mL)	Time (hrs)
826	in house				
840	LFGB82/02-8	1g	steam	1/500	
2117	GC-MS	1	basic extraction	1/15	12 hrs
2129	in house	4	ASE extraction		10 min.
2132	in house	1	basic extraction	1/50	15 hrs
2139	in house	2	ASE extraction	1/150	30 min.
2160	in house	2	basic extraction	1/30	15 hrs.
2165	LFGB82/02-8	1	ultrasonic	1/10	1 hr.
2172	in house	1		1/20	12 hrs.
2184	LFGB82/02-8	1	ultrasonic	1/10	1 hr
2196	in house		ultrasonic	1/5	20 min.
2215	in house	1	basic extraction	1/20	
2241	GB/T 18414.1	1	ultrasonic	1/80	25 min.
2255	in house		KOH	1/20	16 hrs.
2272	in house	1	ultrasonic	1/50	2 hrs.
2292	UNI11057	2.5	ultrasonic	1/20	1hr
2310	LFGB82/02-8	2	steam distillation	1/10	
2311	LFGB82/02-8	2	steam distillation	1/10	
2358	LFGB82/02-8	2.5g	steam distillation		
2359	LFGB82/02-8	3.5g	steam distillation	3-3.5/500	
2363	LFGB82/02-8	1g	steam distillation	1/500	
2365	LFGB82/02-8	1g	steam distillation	1/500	
2366					
2370	LFGB82/02-8	0.5 / 1	steam distillation	1/500	
2372	LFGB82/02-8	1	ultrasonic	1/60	1 hr
2375	LFGB82/02-8	2g	steam distillation	1/30	
2379	LFGB82/02-8	0.5	steam distillation	OPP 1/60	
2380	in house	1	basic extraction	1/30	16 hrs
2386	LFGB82/02-8				
3104	XPG08-015	0.1 / 0.5	basic extraction	1/100	2 x 1hr
3116	LFGB82/02-8	1	steam distillation		
3117	GB/T 18414	1	ultrasonic	1/100	1 hr.
3150	GC/ECD	0.5 g	ultrasonic	1/20	30 min.
3151	LC/MS	0.2-1 g	basic extraction	1/10	12 hrs.
3153	LFGB82/02-8	0.5	steam distillation		
3154		1	steam distillation		
3159	in house	1		1/20	15 hrs.
3172					
3174	in house	1	ASE extraction		30 min.
3176	DIN53313	1	ultrasonic	1/50	30 min.
3180		1		1/30	12 hrs.
3182	DIN53313	1	Soxhlet	1/100	16 hrs.
3185	LFGB82/02-8	1	steam distillation	1/250	
3190	LFGB82/02-8	1	steam distillation		
3200	LFGB82/02-8	1	steam distillation	1/40	
3210	XPG08015		ultrasonic	1/100	2 hrs
3216	ISO17070	1	steam disdistillation		
3218	LFGB82/02-8	1	steam disdistillation		
3226	UNI11057	1.5	ultrasonic	1/50	2 x 1 hr.
3228	in house	1	ultrasonic	1/5	1 hr.
3237	in house	1	ultrasonic	1/10	1 hr.
3246	ISO17070	0.5	basic extraction	1/10	16 hrs.

APPENDIX 3

List of number of participants on alphabetic country order

2 labs in BANGLADESH
1 lab in FRANCE
6 labs in GERMANY
7 labs in HONG KONG
2 labs in INDIA
3 labs in ITALY
2 labs in KOREA
16 labs in P.R. of CHINA
1 lab in SPAIN
1 lab in SWITZERLAND
2 labs in TAIWAN R.O.C.
3 labs in THAILAND
4 labs in TURKEY
2 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
W	= test result withdrawn by participant

Literature:

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11 ISO14184-1:1994
12 M. Thompson and R. Wood, J. AOAC Int, 76, 926, (1993)
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15 ISO 13528:2005, Statistical methods for use in proficiency testing by interlaboratory comparisons