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

Organised by: Institute for Interlaboratory Studies
Spijkenisse, the Netherlands

Author: ing. R.J. Starink
Corrector: dr. R.G. Visser & ing. N. Boelhouwer
Report: iis10A08

February 2011

CONTENTS

Appendices:

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 2010/2011, this proficiency test was continued. In this interlaboratory study 52 laboratories in 15 different countries participated. See appendix 3 for the number of participants per country. 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, ILAC-G13:2007 and ISO17043:2010. 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 black hosiery fabric was cut into pieces. The pieces were well mixed and divided over 70 subsamples of 6 grams each and labelled #1098. The second bulk sample, a cream hosiery fabric was also cut into pieces. The pieces were well mixed and divided over 70 subsamples of 6 grams each and subsequently labelled #1099.
The homogeneities of randomly selected samples #1098 and #1099 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.

Black hosiery fabric	*OPP in mg/kg*	*PCP in mg/kg*
Sample #1098-1	6.4	8.3
Sample #1098-2	6.6	8.7
Sample #1098-3	6.9	8.9
Sample #1098-4	6.6	8.7

table 1: homogeneity test of subsample #1098

Cream hosiery fabric	*OPP in mg/kg*	*PCP in mg/kg*
Sample #1099-1	425.4	823.1
Sample #1099-2	414.3	853.8
Sample #1099-3	410.6	851.0
Sample #1099-4	422.6	852.7
Sample #1099-5	429.3	857.2
Sample #1099-6	413.6	853.0
Sample #1099-7	408.4	832.1
Sample #1099-8	411.8	835.5

table 2: homogeneity test of subsample #1099

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 #1098)	0.6	0.7
Reference method	Horwitz	LFGB 82.02.8
0.3 x R (reference method)	0.7	22.6

table 3: repeatabilities of subsamples #1098.

	OPP in mg/kg	*PCP in mg/kg*
r (samples #1099)	21.5	35.4
Reference method	Horwitz	LFGB 82.02.8
0.3 x R (reference method)	22.6	88.7

table 4: repeatabilities of subsamples #1099

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 black hosiery fabric (labelled #1098) and one sample of approx. 6 grams of cream hosiery fabric (labelled #1099) were sent to the participating laboratories on November 3, 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 3, nr.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:

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

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 46 of the 52 participants reported 293 numerical results. Observed in all reported results were 40 statistical outlying results, which is 13.7%. 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 PCP, 2,3,4,6-TetraCP and 2,3,5,6-TetraCP in sample #1099. 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 only. 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: The determination of this component was problematic at high levels of 26-410 mg/kg. In total 10 statistical outliers were detected and the calculated reproducibilities, after rejection of the statistical outliers, are for both samples not at all in agreement with the strict reproducibilities calculated using the Horwitz equation.
When the reported results are evaluated per technique, it is noticed that for alkaline extraction the spreads of the results are significantly smaller than for ultrasonic and for steam distillation (see page 12) and in good agreement (!) with the strict reproducibilities calculated using the Horwitz equation.

PCP: The determination of this component was very problematic at a the high level of 540 mg/kg; 4 statistical outliers were detected and the calculated reproducibility, after rejection of the statistical outliers, is not at all in agreement with the requirements of LFGB 82.02.8. At the low level of 7.6 mg/kg, the determination was much less problematic. Although 5 statistical outliers were detected, the calculated reproducibility, after rejection of the statistical outliers, is almost in agreement with the requirements of LFGB 82.02.8.
When the results are evaluated per technique, it is noticed that none of evaluated techniques is superior to one of the other techniques, except for alkaline extraction (#1099), where the recovery is smallest and the spread of the results is largest compared with the other used techniques. Steam distillation is used by the majority of the reporting participants.

2,3,4,6-TeCP: The determination of this component was not problematic at a level of 0.5 mg/kg, but it was problematic at a level of 20 mg/kg. In total 15 statistical outliers were detected. The calculated reproducibility, after rejection of the statistical outliers, is in good agreement for sample #1098 with the reproducibility calculated using the Horwitz equation. However, the calculated reproducibility, after rejection of the statistical outliers, is not in agreement for sample #1099 with the target reproducibility.

2,3,5,6-TeCP: Sample #1098 did contain very little of this component (27 laboratories reported 'not detected').
The determination of this component in sample #1099 was problematic. On sample #1099 four statistical outliers and three false negative results were observed. After rejection of the statistical outliers, the calculated reproducibility is not at all in agreement with the strict reproducibility 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	37	26.34	23.28	7.21
PCP	mg/kg	41	7.62	3.13	2.67
2,3,4,6-TeCP	mg/kg	27	0.49	0.16	0.24
2,3,5,6-TeCP	mg/kg	6	0.061	0.081	(0.042)

table 5: reproducibilities of textile sample #1098

Parameter	*unit*	*n*	*average*	*2.8 * sd*	*R (target)*
OPP	mg/kg	37	408.1	191.4	74.0
PCP	mg/kg	42	537.1	355.5	188.0
2,3,4,6-TeCP	mg/kg	34	19.63	9.92	5.62
2,3,5,6-TeCP	mg/kg	28	1.65	1.42	0.69

table 6: reproducibilities of textile sample #1099

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.

Parameter	*December 2010*	*February 2010*	*February 2009*	*February 2008*	*February 2007*
OPP (all techniques)	88 - 47%	47 - 53%	82 – 98%	65%	61 - 62%
PCP (all techniques)	41 - 66%	51 - 55%	82 – 88%	82 -106%	53 - 65%

table 7: 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, except for 2,3,5,6-TeCP in both samples.

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 8: Ecolabelling Standards and Requirements for Textiles in EU

General

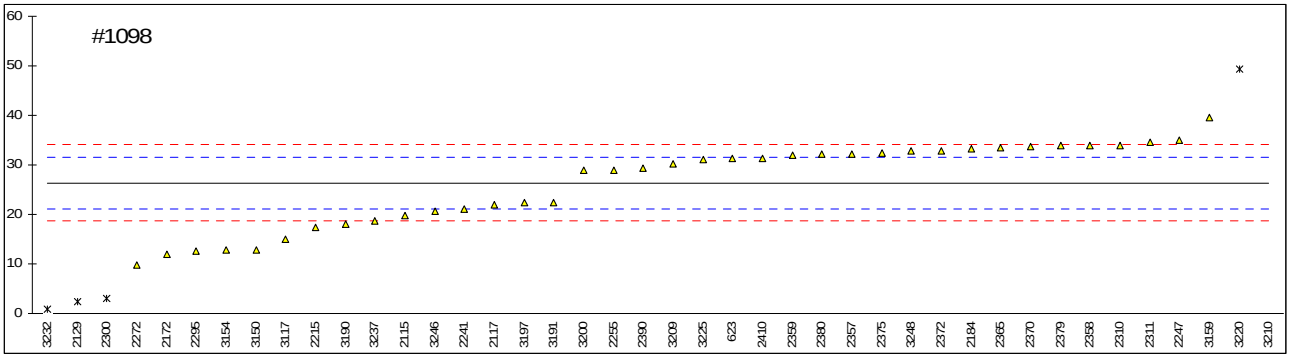
In this proficiency test for the determination of phenols in textile, it was noticed that all participants, except three, detected all phenols in both samples.

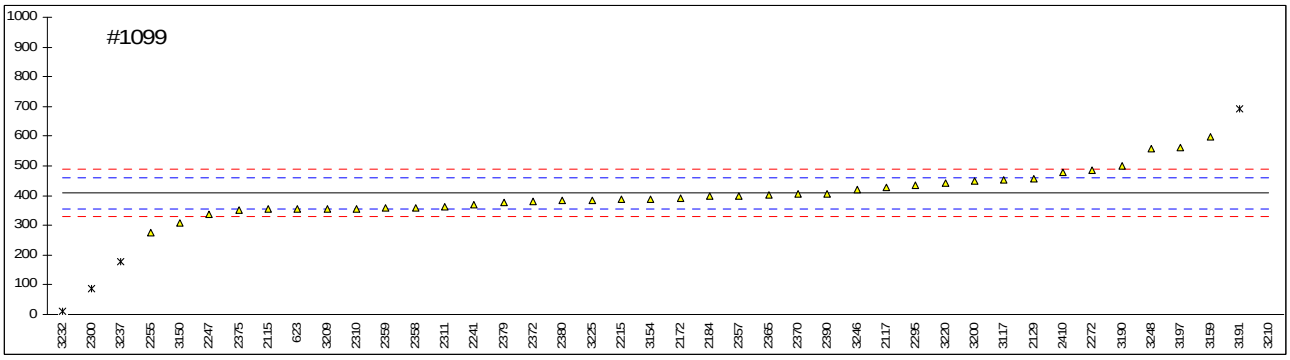
From this report can be concluded that the spreads observed in this interlaboratory study are mainly caused by the use of different release techniques. Many of the reported methods are in-house methods and the details of these methods vary widely (see appendix 2).
In the determination of Orthophenylphenol 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.

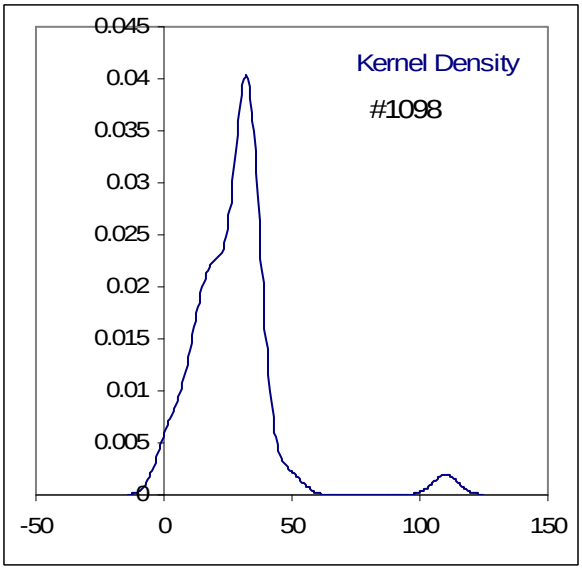
APPENDIX 1

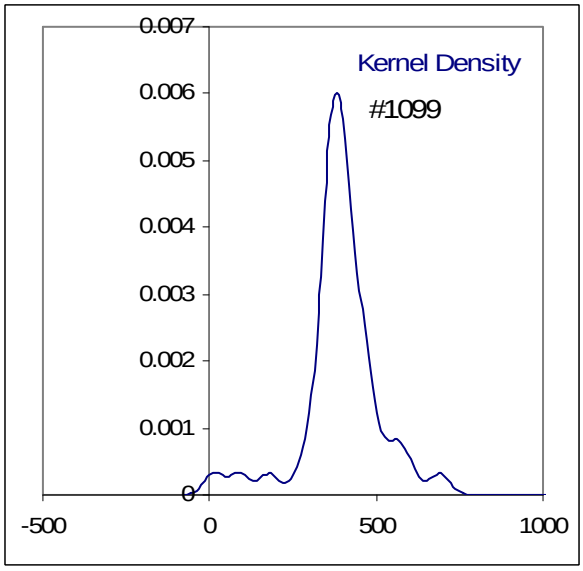
Determination of Orthophenylphenol (OPP) on samples #1098 and #1099; results in mg/kg

lab	method	#1098	mark	z(targ)	#1099	mark	z(targ)	Remarks
551		-----		-----	-----		-----	
623	In house	31.28		1.92	355.27		-2.00	
2115	OekoTex new draft	19.78		-2.55	355.06		-2.01	
2117	in house	22		-1.68	426		0.68	
2129	in house	2.4	G(0.05)	-9.29	455.3		1.79	
2172	in house	12.0		-5.57	390		-0.69	
2184	LFGB 82/02-8	33.16		2.65	397.32		-0.41	
2215	in house	17.50		-3.43	387.36		-0.79	
2241	inhouse (OPP)	21.1		-2.03	369.9		-1.45	
2247	LFGB 82/02-8	35.0		3.36	336.0		-2.73	
2255	in house	28.9		1.00	276.0		-5.00	
2272	XPG08015	9.836		-6.41	484.8		2.90	
2292		-----		-----	-----		-----	
2295	in house	12.59		-5.34	434.8		1.01	
2300	ISO17070:06	2.98	G(0.05)	-9.07	88.39	G(0.05)	-12.10	
2310	in house	33.9		2.94	356		-1.97	
2311	in house	34.5		3.17	362.0		-1.75	
2357	In house	32.2		2.28	399.0		-0.34	
2358	In house	33.87		2.92	358.27		-1.89	
2359	in house	31.964		2.18	358.2		-1.89	
2365	in house	33.567		2.81	402.651		-0.21	
2370	in house	33.7		2.86	404		-0.16	
2372	in house	32.87		2.54	381.6		-1.00	
2375	in house	32.325		2.32	351.247		-2.15	
2379	in house	33.849		2.92	377.903		-1.14	
2380	in house	32.069		2.23	383.09		-0.95	
2390	in house	29.412		1.19	407.564		-0.02	
2410	LFGB 82/02-8	31.364		1.95	476.85		2.60	
3104		-----		-----	-----		-----	
3117	LFGB 82/02-8	14.96		-4.42	453.96		1.74	
3150	in house	12.8		-5.26	307		-3.83	
3153	LFGB 82/02-8	-----		-----	-----		-----	
3154	in house	12.753		-5.27	388.09		-0.76	
3159	in house	39.62		5.16	597.7		7.18	
3170		-----		-----	-----		-----	
3172		-----		-----	-----		-----	
3185		-----		-----	-----		-----	
3190	LFGB 82/02-8	18.14		-3.18	498.28		3.41	
3191	GB/T18414.1-2006	22.5		-1.49	690.8	G(0.05)	10.70	
3197	LFGB B.82.0.08	22.4		-1.53	560		5.75	
3200	LFGB 82/02-8	28.84		0.97	450.0		1.59	
3209	ISO17070	30.32		1.55	355.71		-1.98	
3210	XPG08015	110	G(0.01)	32.48	3171	G(0.01)	104.58	
3220	LFGB 82/02-8	49.30	G(0.05)	8.92	441.72		1.27	
3225	in house	31.1		1.85	384.6		-0.89	
3232	ISO17070:07	0.78	G(0.05)	-9.92	11.35	G(0.05)	-15.02	
3233		-----		-----	-----		-----	
3237	LFBG 82/02-8	18.8		-2.93	178.5	G(0.05)	-8.69	
3243		n.d.		-----	n.d.		-----	
3246	in house	20.7		-2.19	420		0.45	
3248	in house	32.81		2.51	556.8		5.63	
8008		-----		-----	-----		-----	
	normality	not OK			not OK			
	n	37			37			
	outliers	5			5			
	mean (n)	26.34			408.11			
	st.dev. (n)	8.3146			68.351			
	R(calc.)	23.28			191.38			
	R(Horwitz)	7.21			73.98			


#1098
60
50
40
30
20
10
0
3232 2129 2300 2272 2172 2295 3154 3150 3117 2215 3190 3237 2115 3246 2241 2117 3197 3191 3200 2255 2390 3209 3225 623 2410 2359 2380 2357 2375 3248 2372 2184 2365 2370 2379 2358 2310 2311 2247 3159 3220 3210


#1099
1000
900
800
700
600
500
400
300
200
100
0
3232 2300 3237 2255 3150 2247 2375 2115 623 3209 2310 2359 2358 2311 2241 2379 2372 2380 3225 2215 3154 2172 2184 2357 2365 2370 2390 3246 2117 2295 3220 3200 3117 2129 2410 2272 3190 3248 3197 3159 3191 3210

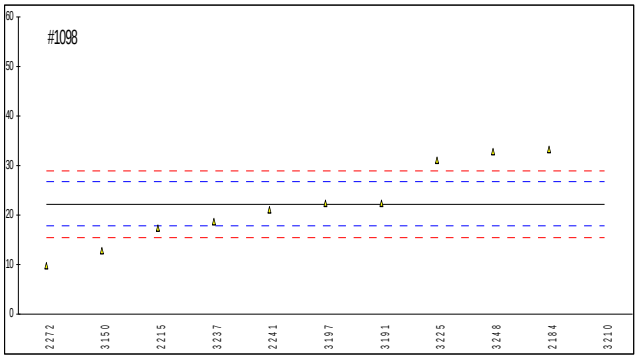

Kernel Density
#1098
0.045
0.04
0.035
0.03
0.025
0.02
0.015
0.01
0.005
0
-50 0 50 100 150

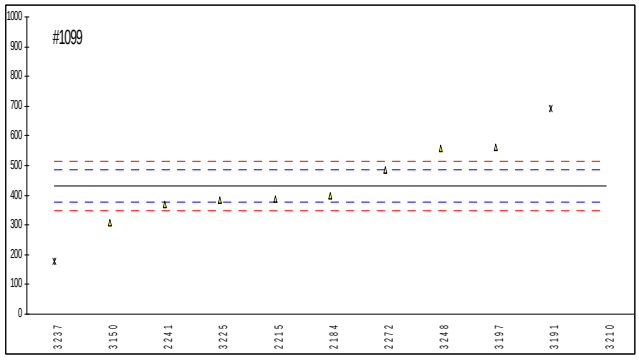

Kernel Density
#1099
0.007
0.006
0.005
0.004
0.003
0.002
0.001
0
-500 0 500 1000

Determination of Orthophenylphenol (OPP) on samples #1098 and #1099; results in mg/kg

Only ultrasonic extraction results (excl. alkaline)

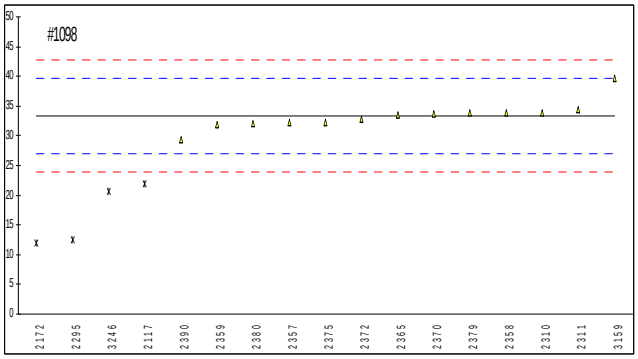
	#1098	#1099
normality	OK	OK
n	10	8
outliers	1	3
mean (n)	22.20	430.97
st.dev. (n)	8.084	92.321
R(calc.)	22.63	258.50
R(Horwitz)	6.24	77.48

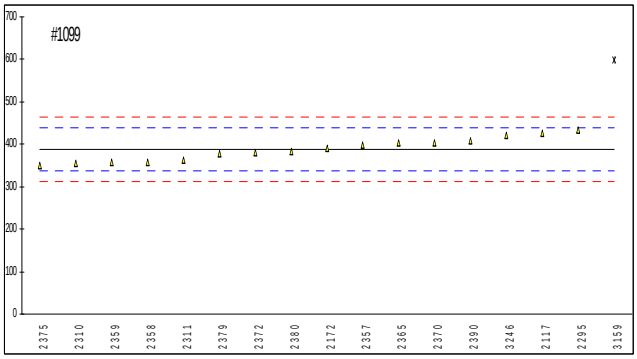




Only alkaline extraction results

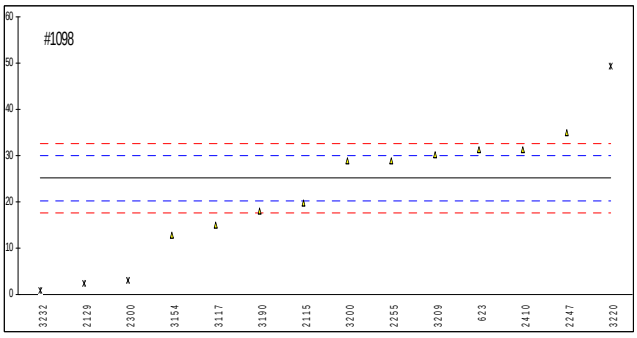
	#1098	#1099
normality	not OK	OK
n	13	16
outliers	4	1
mean (n)	33.37	388.27
st.dev. (n)	2.297	26.615
R(calc.)	6.43	74.52
R(Horwitz)	8.82	70.91

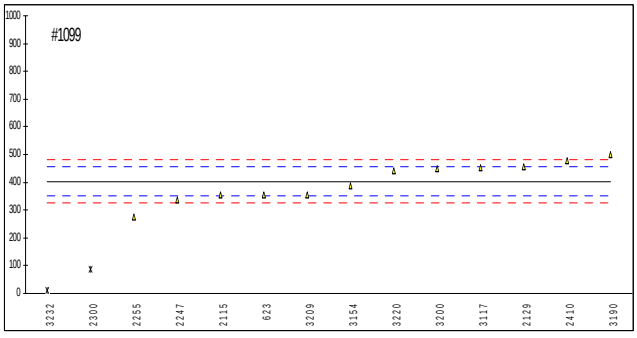




Only steam distillation/Soxhlet/ASE extraction results

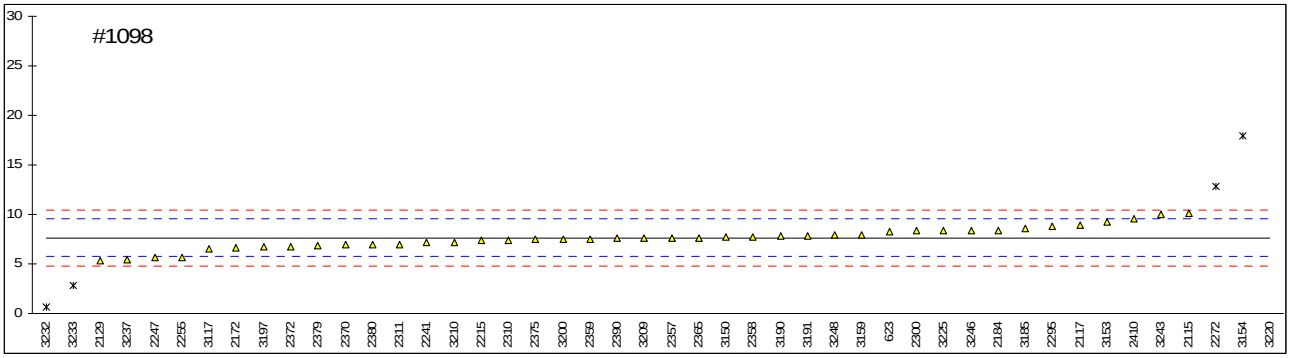
	#1098	#1099
normality	not OK	OK
n	10	12
outliers	4	2
mean (n)	25.13	403.52
st.dev. (n)	7.910	68.239
R(calc.)	22.15	191.07
R(Horwitz)	6.93	73.27

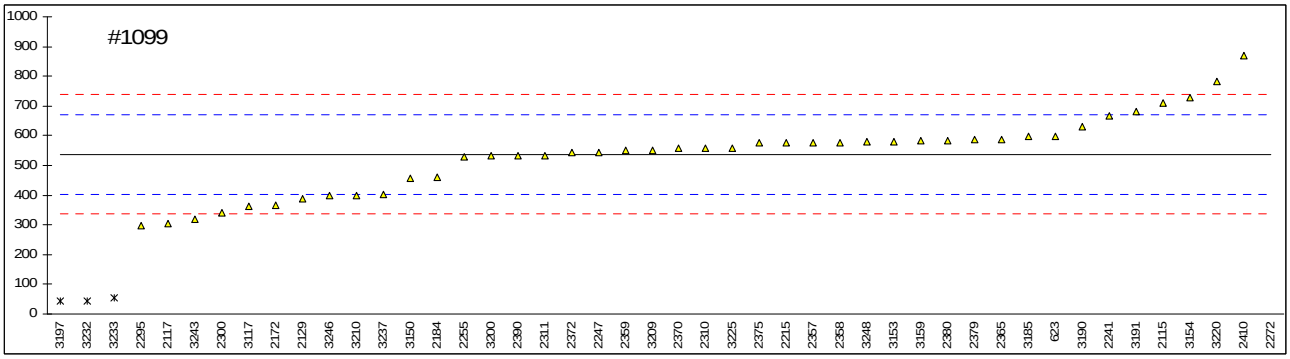


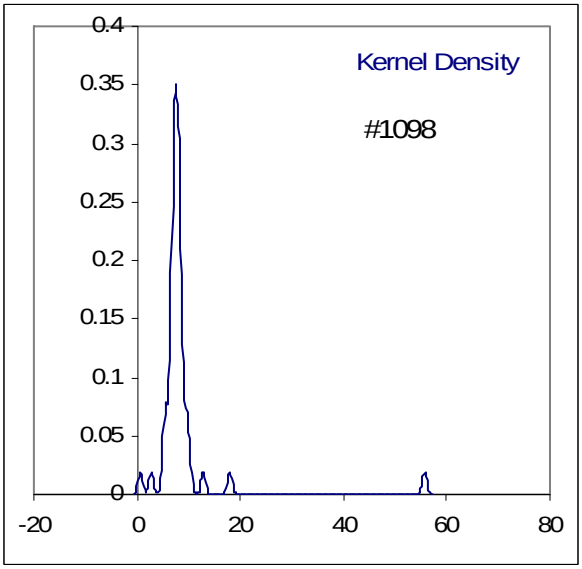


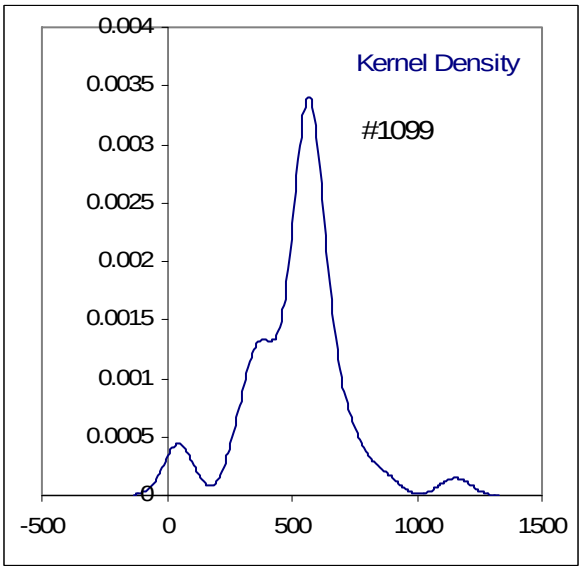
Determination of Pentachlorophenol (PCP) on samples #1098 and #1099; results in mg/kg

lab	method	#1098	mark	z(targ)	#1099	mark	z(targ)	Remarks
551		-----		-----	-----		-----	
623	LFGB82/02-8	8.24		0.65	598.86		0.92	
2115	OekoTex method	10.12		2.62	710.90		2.59	
2117	in house	8.9		1.34	303		-3.49	
2129	in house	5.3		-2.44	389.3		-2.20	
2172	in house	6.62		-1.05	367		-2.53	
2184	LFGB 82/02-8	8.42		0.84	461.83		-1.12	
2215	in house	7.38		-0.25	575.12		0.57	
2241	ISO17070	7.13		-0.51	666.3		1.92	
2247	LFGB 82/02-8	5.6		-2.12	542.6		0.08	
2255	LFGB 82/02-8	5.6		-2.12	529.0		-0.12	
2272	XPG08015	12.813	G(0.05)	5.45	1152	G(0.05)	9.16	
2292		-----		-----	-----		-----	
2295	in house	8.77		1.21	297.9		-3.56	
2300	ISO17070	8.34		0.76	339.7		-2.94	
2310	LFGB 82/02-8	7.44		-0.19	559		0.33	
2311	LFGB 82/02-8	6.99		-0.66	534.0		-0.05	
2357	LFGB 82/02-8	7.66		0.04	576.50		0.59	
2358	LFGB 82/02-8	7.76		0.15	577.17		0.60	
2359	LFGB 82/02-8	7.52		-0.10	550.3		0.20	
2365	LFGB 82/02-8	7.663		0.05	587.961		0.76	
2370	LFGB 82/02-8	6.96		-0.69	558		0.31	
2372	LFGB 82/02-8	6.736		-0.93	542.5		0.08	
2375	LFGB 82/02-8	7.470		-0.16	574.837		0.56	
2379	LFGB 82/02-8	6.902		-0.75	586.556		0.74	
2380	LFGB 82/02-8	6.960		-0.69	583.88		0.70	
2390	LFGB 82/02-8	7.624		0.00	533.35		-0.06	
2410	LFGB 82/02-8	9.573		2.05	870.26		4.96	
3104		-----		-----	-----		-----	
3117	LFGB 82/02-8	6.49		-1.19	362.97		-2.59	
3150	In house	7.70		0.08	458		-1.18	
3153	LFGB 82/02-8	9.25		1.71	579.6		0.63	
3154	LFGB 82//02-8	17.974	G(0.01)	10.87	727.31		2.83	
3159	In house	7.944		0.34	583.1		0.68	
3170		-----		-----	-----		-----	
3172		-----		-----	-----		-----	
3185	ISO17070	8.6		1.03	598		0.91	
3190	LFGB 82/02-8	7.78		0.17	631.99		1.41	
3191	GB/T18414.1-2006	7.8		0.19	681.8		2.15	
3197	LFGB 82/02-8	6.7		-0.97	42	DG(0.05)	-7.37	
3200	LFGB 82/02-8	7.52		-0.10	531.82		-0.08	
3209	ISO17070	7.64		0.02	551.88		0.22	
3210	XPG08015	7.18		-0.46	400		-2.04	
3220	LFGB 82/02-8	55.8	G(0.01)	50.58	782.3		3.65	
3225	in house	8.40		0.82	559.41		0.33	
3232	ISO17070	0.64	G(0.01)	-7.33	44.39	DG(0.05)	-7.34	
3233	in house	2.78	G(0.05)	-5.08	53.56	G(0.05)	-7.20	
3237	LFBG 82/02-8	5.4		-2.33	401.0		-2.03	
3243	LFBG 82/02-8	10		2.50	319		-3.25	
3246	in house	8.4		0.82	397		-2.09	
3248	in house	7.932		0.33	578.3		0.61	
8008		-----		-----	-----		-----	
	normality	OK			not OK			
	n	41			42			
	outliers	5			4			
	mean (n)	7.620			537.14			
	st.dev. (n)	1.1190			126.976			
	R(calc.)	3.133			355.53			
	R(LFBG82.02.8)	2.667			187.99			


#1098
30
25
20
15
10
5
0
3232 3233 2129 3237 2247 2255 3117 2172 3197 2372 2379 2370 2380 2311 2241 3210 2215 2310 2375 3200 2359 2390 3209 2357 2365 3150 2358 3190 3191 3248 3159 623 2300 3225 3246 2184 3185 2295 2117 3153 2410 3243 2115 2272 3154 3220


#1099
1000
900
800
700
600
500
400
300
200
100
0
3197 3232 3233 2295 2117 3243 2300 3117 2172 2129 3246 3210 3237 3150 2184 2255 3200 2390 2311 2372 2247 2359 3209 2370 2310 3225 2375 2215 2357 2358 3248 3153 3159 2380 2379 2365 3185 623 3190 2241 3191 2115 3154 3220 2410 2272

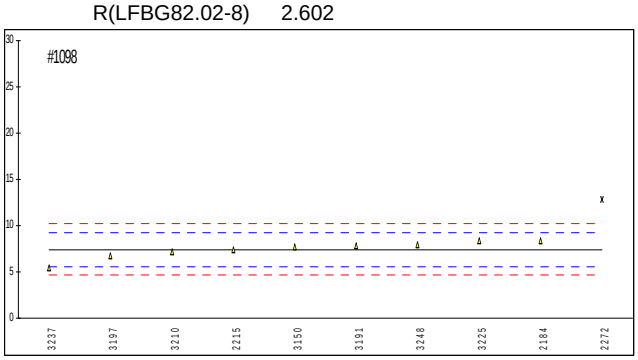

Kernel Density
#1098
0.4
0.35
0.3
0.25
0.2
0.15
0.1
0.05
0
-20 0 20 40 60 80

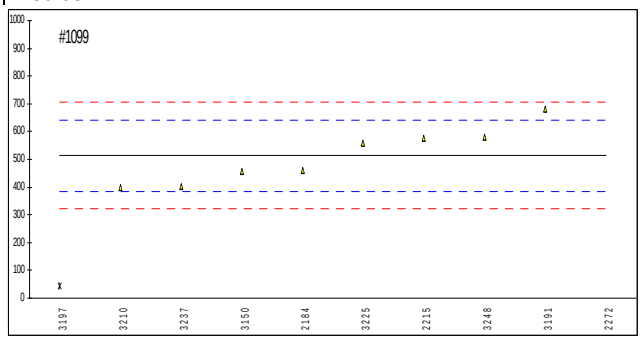

Kernel Density
#1099
0.004
0.0035
0.003
0.0025
0.002
0.0015
0.001
0.0005
0
-500 0 500 1000 1500

Determination of Pentachlorophenol (PCP) on samples #1098 and #1099; results in mg/kg

Only ultrasonic extraction results

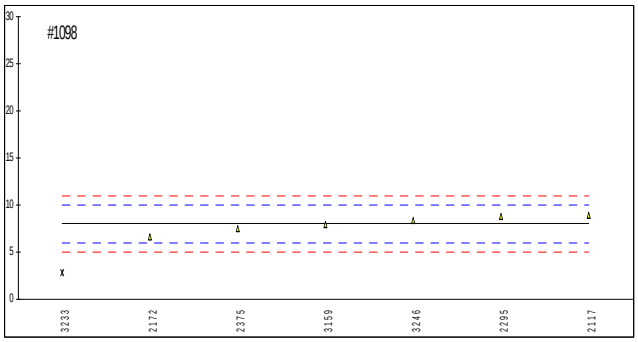
	#1098	#1099
normality	OK	OK
n	9	8
outliers	1	2
mean (n)	7.435	514.43
st.dev. (n)	0.9422	99.793
R(calc.)	2.638	279.42
R(LFBG82.02-8)	2.602	180.05

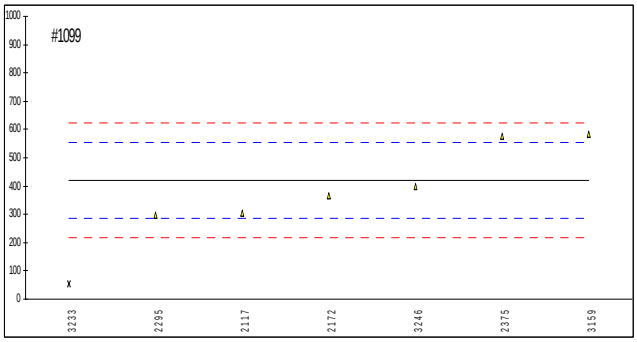




Only alkaline extraction results

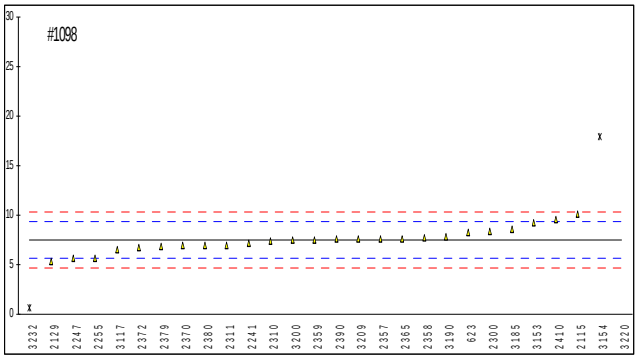
	#1098	#1099
normality	OK	OK
n	6	6
outliers	1	1
mean (n)	8.017	420.47
st.dev. (n)	0.8660	128.460
R(calc.)	2.425	359.69
R(LFBG82.02-8)	2.806	147.15

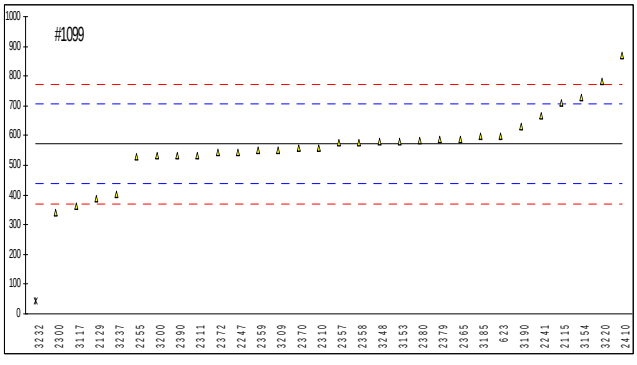




Only steam distillation/Soxhlet/ASE extraction results

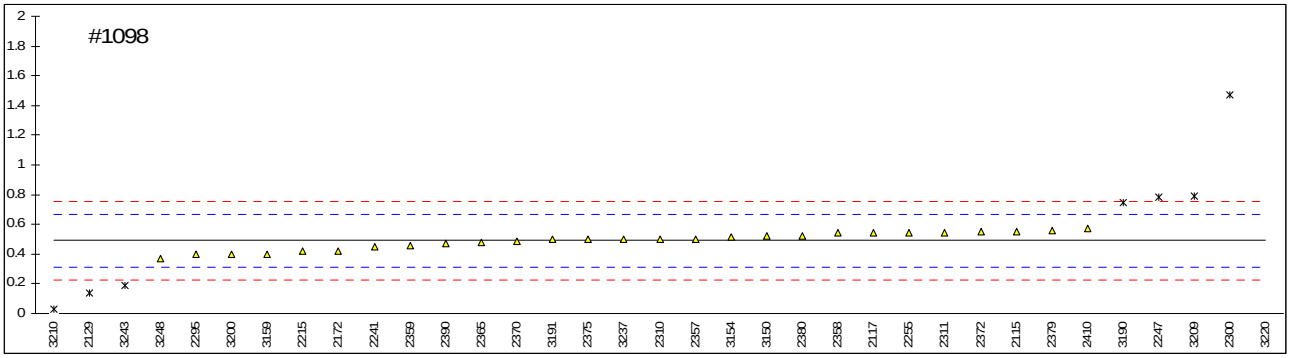
	#1098	#1099
normality	OK	not OK
n	25	29
outliers	3	1
mean (n)	7.496	571.77
st.dev. (n)	1.1534	113.530
R(calc.)	3.229	317.88
R(LFBG82.02-8)	2.624	200.12

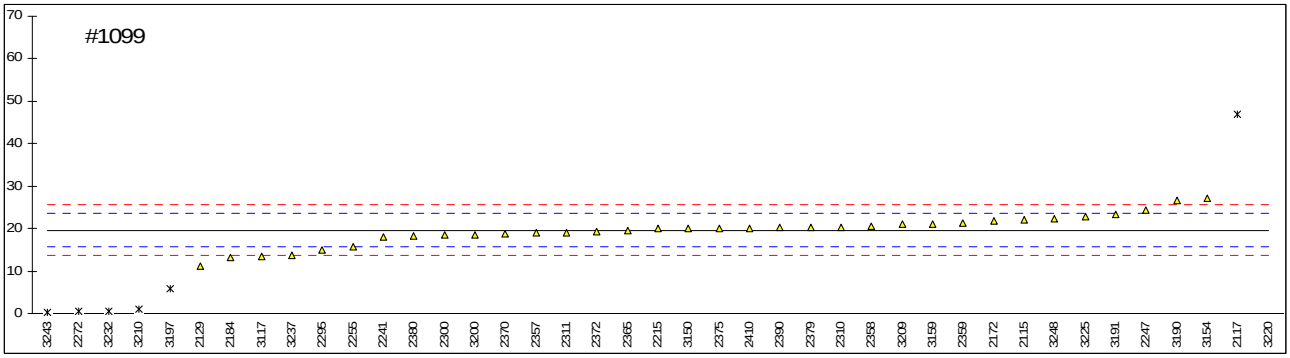


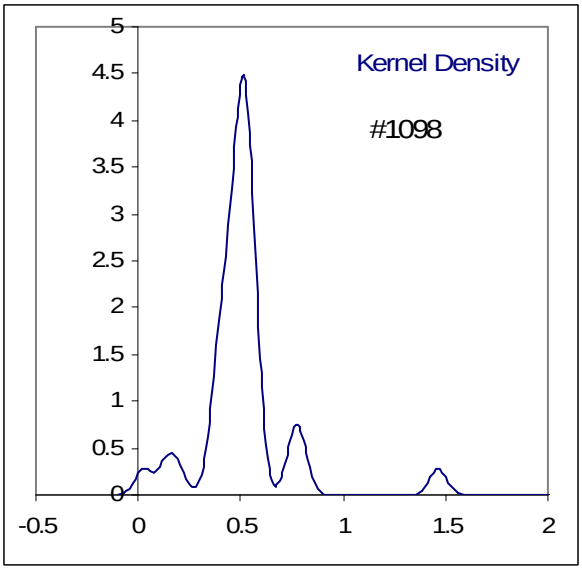


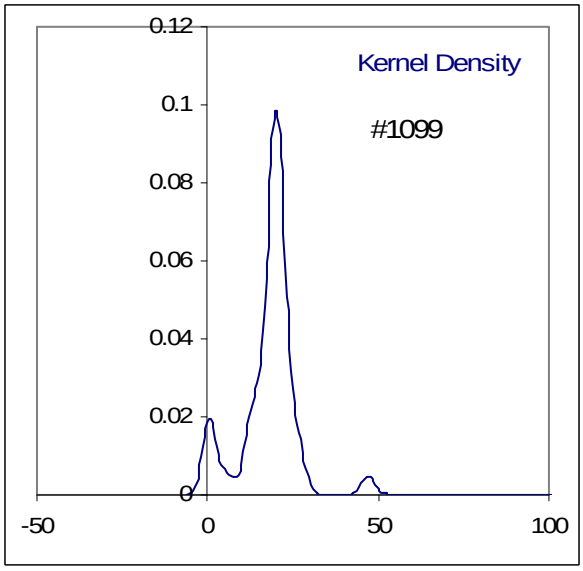
Determination of 2,3,4,6-Tetrachlorophenol on samples #1098 and #1099; results in mg/kg

lab	method	#1098	mark	z(targ)	#1099	mark	z(targ)	Remarks
551		-----		-----	-----		-----	
623	LFGB82/02-8	-----		-----	-----		-----	
2115	OekoTex method	0.55		0.70	22.16		1.26	
2117	in house	0.54		0.58	47	G(0.01)	13.64	
2129	in house	0.14	DG(0.05)	-4.01	11.2		-4.20	
2172	in house	0.422		-0.77	21.8		1.08	
2184	LFGB 82/02-8	-----		-----	13.24		-3.18	
2215	in house	0.42		-0.79	20.03		0.20	
2241	ISO17070	0.45		-0.45	18.1		-0.76	
2247	LFGB 82/02-8	0.78	DG(0.01)	3.34	24.41		2.38	
2255	LFGB 82/02-8	0.54		0.58	15.7		-1.96	
2272	XPG08015	n.d.		-----	0.526	DG(0.05)	-9.52	
2292		-----		-----	-----		-----	
2295	in house	0.40		-1.02	14.93		-2.34	
2300	ISO17070	0.47	G(0.01)	11.25	18.52		-0.55	
2310	LFGB 82/02-8	0.5		0.12	20.31		0.34	
2311	LFGB 82/02-8	0.54		0.58	19.1		-0.26	
2357	LFGB 82/02-8	0.50		0.12	19.01		-0.31	
2358	LFGB 82/02-8	0.54		0.58	20.64		0.50	
2359	LFGB 82/02-8	0.46		-0.34	21.3		0.83	
2365	LFGB 82/02-8	0.481		-0.09	19.408		-0.11	
2370	LFGB 82/02-8	0.487		-0.03	18.8		-0.41	
2372	LFGB 82/02-8	0.5491		0.69	19.23		-0.20	
2375	LFGB 82/02-8	0.500		0.12	20.100		0.23	
2379	LFGB 82/02-8	0.558		0.79	20.215		0.29	
2380	LFGB 82/02-8	0.522		0.38	18.319		-0.65	
2390	LFGB 82/02-8	0.473		-0.19	20.195		0.28	
2410	LFGB 82/02-8	0.573		0.96	20.118		0.24	
3104		-----		-----	-----		-----	
3117	LFGB 82/02-8	-----		-----	13.43		-3.09	
3150	In house	0.52		0.35	20.1		0.23	
3153	LFGB 82/02-8	-----		-----	-----		-----	
3154	LFGB 82//02-8	0.5150		0.30	27.176		3.76	
3159	In house	0.4015		-1.01	21.17		0.77	
3170		-----		-----	-----		-----	
3172		-----		-----	-----		-----	
3185	ISO17070	-----		-----	-----		-----	
3190	LFGB 82/02-8	0.75	G(0.01)	2.99	26.63		3.49	
3191	GB/T18414.1-08	0.5		0.12	23.3		1.83	
3197	LFGB 82/02-8	<0.5		-----	5.8	G(0.05)	-6.89	
3200	LFGB 82/02-8	0.40		-1.02	18.64		-0.49	
3209	ISO17070	0.79	DG(0.01)	3.45	21.17		0.77	
3210	XPG08015	0.03	G(0.05)	-5.27	1.14	G(0.01)	-9.21	
3220	LFGB 82/02-8	7.2	G(0.01)	76.98	197.75	G(0.01)	88.78	
3225	in house	<0.25		-----	22.88		1.62	
3232	ISO17070	<0.05		-----	0.61	G(0.01)	-9.48	
3233	in house	-----		-----	-----		-----	
3237	LFBG 82/02-8	0.5		0.12	13.6		-3.00	
3243	LFBG 82/02-8	0.19	DG(0.05)	-3.43	0.16	DG(0.05)	-9.70	
3246	in house	-----		-----	-----		-----	
3248	in house	0.3684		-1.39	22.44		1.40	
8008		-----		-----	-----		-----	
	normality	OK			not OK			
	n	27			34			
	outliers	8			7			
	mean (n)	0.489			19.629			
	st.dev. (n)	0.0565			3.5437			
	R(calc.)	0.158			9.922			
	R(Horwitz)	0.244			5.618			


#1098
2
1.8
1.6
1.4
1.2
1
0.8
0.6
0.4
0.2
0
3210 2129 3243 3248 2295 3200 3159 2215 2172 2241 2359 2390 2365 2370 3191 2375 3237 2310 2357 3154 3150 2380 2358 2117 2255 2311 2372 2115 2379 2410 3190 2247 3209 2300 3220

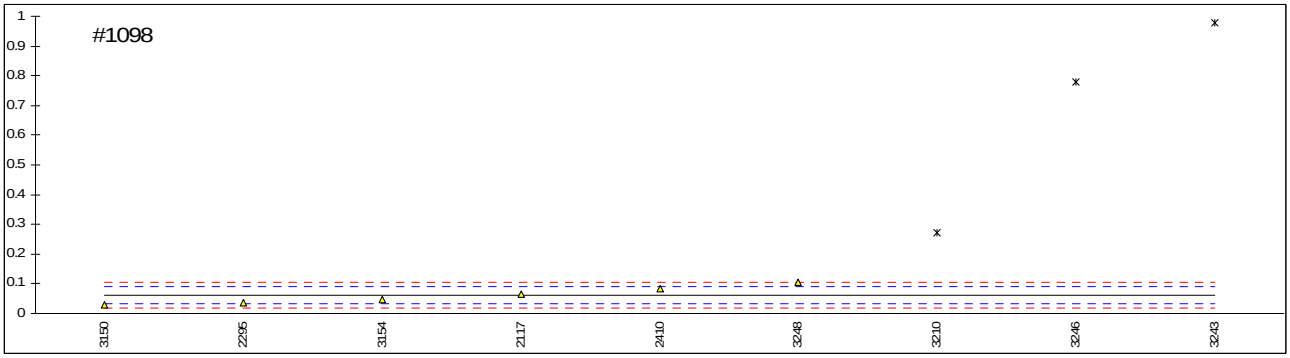

#1099
70
60
50
40
30
20
10
0
3243 2272 3232 3210 3197 2129 2184 3117 3237 2295 2255 2241 2380 2300 3200 2370 2357 2311 2372 2365 2215 3150 2375 2410 2390 2379 2310 2358 3209 3159 2359 2172 2115 3248 3225 3191 2247 3190 3154 2117 3220

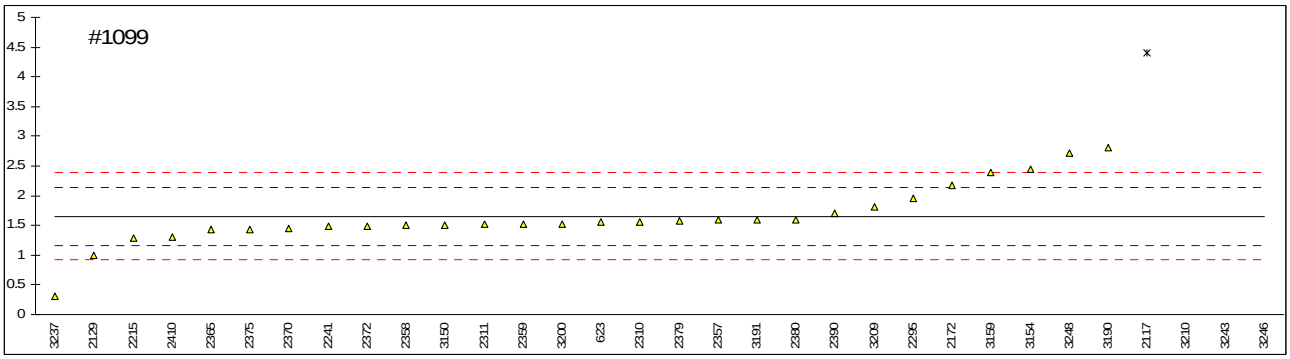

Kernel Density
#1098
5
4.5
4
3.5
3
2.5
2
1.5
1
0.5
0
-0.5 0 0.5 1 1.5 2

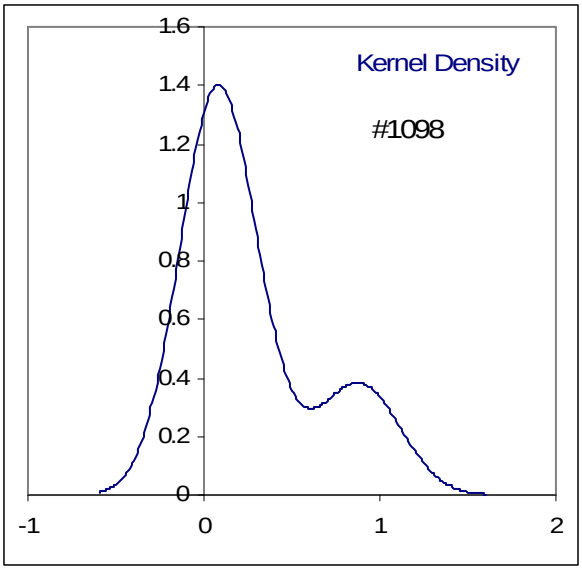

Kernel Density
#1099
0.12
0.1
0.08
0.06
0.04
0.02
0
-50 0 50 100

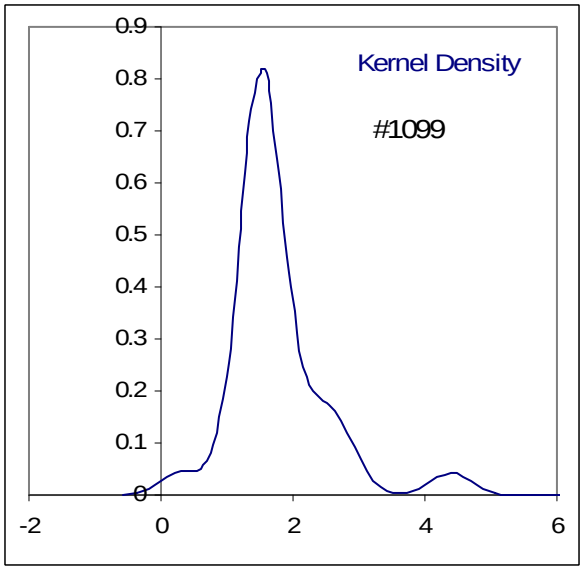
Determination of 2,3,5,6-Tetrachlorophenol on samples #1098 and #1099; results in mg/kg

lab	method	#1098	mark	z(targ)	#1099	mark	z(targ)	Remarks
551		-----		-----	-----		-----	
623	LFGB 82/02-8	n.d.		-----	1.55		-0.42	
2115		-----		-----	-----		-----	
2117	in house	0.066		-----	4.4	G(0.01)	11.20	
2129	in house	n.d.		-----	1.0		-2.66	
2172	in house	<0.05		-----	2.18		2.15	
2184		-----		-----	-----		-----	
2215	in house	n.d.		-----	1.29		-1.48	
2241	ISO17070	<0.1		-----	1.48		-0.71	
2247	LFGB/82.02.8	n.d.		-----	n.d.		-----	
2255		-----		-----	-----		-----	
2272		-----		-----	-----		-----	
2292		-----		-----	-----		-----	
2295	in house	0.035		-----	1.96		1.25	
2300	in house	-----		-----			-----	
2310	LFGB/82.02.8	n.d.		-----	1.56		-0.38	
2311	LFGB/82.02.8	n.d.		-----	1.52		-0.54	
2357	LFGB/82.02.8	n.d.		-----	1.59		-0.26	
2358	LFGB/82.02.8	n.d.		-----	1.51		-0.58	
2359	LFGB/82.02.2	n.d.		-----	1.52		-0.54	
2365	LFGB/82.02.8	<0.05		-----	1.426		-0.93	
2370	LFGB/82.02	n.d.		-----	1.45		-0.83	
2372	LFGB/82.02.8	n.d.		-----	1.481		-0.70	
2375	LFGB/82.02.8mod	n.d.		-----	1.440		-0.87	
2379	LFGB/82.02.8	n.d.		-----	1.580		-0.30	
2380	LFGB/82.02.8	n.d.		-----	1.60		-0.22	
2390	LFGB/82.02.2	n.d.		-----	1.71		0.23	
2410	LFGB/82.02.8	0.083		-----	1.301		-1.44	
3104		-----		-----	-----		-----	
3117		-----		-----	-----		-----	
3150	GC/ECD	0.03		-----	1.51		-0.58	
3153		-----		-----	-----		-----	
3154	LFGB/82.02.8	0.0478		-----	2.4545		3.27	
3159	in house	<0.050		-----	2.399		3.04	
3170		-----		-----	-----		-----	
3172		-----		-----	-----		-----	
3185		-----		-----	-----		-----	
3190	LFGB/82.02.8	n.d.		-----	2.81		4.72	
3191	GB/T18414.1	<0.1		-----	1.6		-0.22	
3197	KOH	<0.5		-----	<0.5		-----	False negative?
3200	LFGB/82.02.8	n.d.		-----	1.53		-0.50	
3209	ISO17070	n.d.		-----	1.82		0.68	
3210	XPG08015	0.27	ex	-----	12.3	G(0.01)	43.41	False positive?
3220	LFGB/82.02.8	n.d.		-----	n.d.		-----	
3225	in house	<0.25		-----	<0.25		-----	False negative?
3232	ISO17070	<0.05		-----	<0.05		-----	False negative?
3233		-----		-----	-----		-----	
3237		-----		-----	0.3		-5.52	
3243	B82.02-8	0.98	DG(0.01)	-----	29.7	G(0.01)	114.36	
3246	in house	0.78	DG(0.01)	-----	48.2	G(0.01)	189.80	
3248	in house	0.1041		-----	2.719		4.35	
8008		-----		-----	-----		-----	
	normality	OK			not OK			
	n	6			28			
	outliers	2			4			
	mean (n)	0.061			1.653			
	st.dev. (n)	0.0289			0.5060			
	R(calc.)	0.081			1.417			
	R(Horwitz)	(0.042)			0.687			


#1098
1
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0
3150
2295
3154
2117
2410
3248
3210
3246
3243


#1099
5
4.5
4
3.5
3
2.5
2
1.5
1
0.5
0
3237
2129
2215
2410
2365
2375
2370
2241
2372
2358
3150
2311
2359
3200
623
2310
2379
2357
3191
2380
2390
3209
2295
2172
3159
3154
3248
3190
2117
3210
3243
3246


Kernel Density
#1098
1.6
1.4
1.2
1
0.8
0.6
0.4
0.2
0
-1
0
1
2


Kernel Density
#1099
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0
-2
0
2
4
6

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)
551					
623	In house	5	Steam distillation		
2115	OekoTex new draft	5	Soxhlet/ASE extraction		
2117	in house	1.2	Basic extraction	1/30	12h
2129	in house	1	Soxhlet / ASE extraction		
2172	in house	0.5	incubate in oven	1/20	12h
2184	LFGB 82/02-8	1	Ultrasonic	1/10	1h
2215	in house	1.0035	Ultrasonic	1/20	4h
2241	inhouse (OPP)	1.0	Ultrasonic	1/ 50	1h
2247	LFGB 82/02-8	1	Steam distillation		
2255	in house		Steam distillation	1/20	
2272	XPG08015	1	Ultrasonic	1/100	2
2292					
2295	in house	1	Basic extraction	1/30	12
2300	ISO17070:06	1 & 0.5	Soxhlet extraction		
2310	in house	2	Alkaline extraction	1/10	15
2311	in house	1	Alkaline extraction	1/60	
2357	In house	0.5	Alkaline extraction	1/20	15
2358	In house	0.5	Alkaline/Basic extraction	1/120	15
2359	in house	0.5	Alkaline digestion	0.5/60	15
2365	in house	0.5	Alkaline digestion	1/60	15
2370	in house	0.5	Alkaline/basic extraction	1/30	16
2372	in house	0.5	Alkaline digestion	1/60	16
2375	in house	1	Basic extraction	1/60	15
2379	in house	0.5	Basic extraction	1/10	
2380	in house	2	Alkaline/basic extraction	1/60	16
2390	in house	0.5	Alkaline digestion	1/60	16
2410	LFGB 82/02-8	1	steam distillation		1.5
3104					
3117	LFGB 82/02-8	1.00	steam distillation		7
3150	in house	0.5	Ultrasonic	1/20	0.5
3153					
3154	in house	2.0	Steam distillation		16 min
3159	in house		Basic extraction	1/20	12
3170					
3172					
3185					
3190	LFGB 82/02-8	1.0	steam distillation		
3191	GB/T18414.1-2006	1	Ultrasonic	1/110	25min
3197	LFGB B.82.0.08	1	Ultrasonic	1/5	1
3200	LFGB 82/02-8	1	steam distillation	1/40	0.5 (2x)
3209	ISO17070	1.0	steam distillation		
3210	XPG08015	1	Ultrasonic	1/50	
3220	LFGB 82/02-8	1	steam distillation		0.33
3225	in house	0.2	Ultrasonic	1/30	1
3232	ISO17070:07	1	steam distillation		
3233					
3237	LFBG 82/02-8	1	Ultrasonic	1/10	0.5
3243					
3246	in house	0.5	Basic extraction	1/20	16
3248	in house	1	Ultrasonic		1
8008					

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

Lab	Method	Quantity (g)	Release/extract	Liquor Ratio (g/mL)	Time (hrs)
551					
623	LFGB82/02-8	5	Steam distillation		
2115	OekoTex method	5	Soxhlet/ASE extraction		
2117	in house	1.2	Basic extraction	1/30	12h
2129	in house	1	Soxhlet / ASE extraction		
2172	in house	0.5	incubate in oven	1/20	12h
2184	LFGB 82/02-8	1	Ultrasonic	1/10	1h
2215	in house	1.0035	Ultrasonic	1/20	4h
2241	ISO17070	1.0	Steam distillation	1/250	3h
2247	LFGB 82/02-8	1	Steam distillation		
2255	LFGB 82/02-8	1	Steam distillation		
2272	XPG08015	1	Ultrasonic	1/100	2h
2292					
2295	in house	1	Basic extraction	1/30	12h
2300	ISO17070	1 & 0.19	Soxhlet extraction		1h
2310	LFGB 82/02-8	2	Steam distillation		3 to 4h
2311	LFGB 82/02-8	1	Steam distillation		
2357	LFGB 82/02-8	0.5	Steam distillation	1/10 & 1/100	2h
2358	LFGB 82/02-8	2.5	Steam distillation	1/120	15h
2359	LFGB 82/02-8	2.0	Steam distillation	2/500	
2365	LFGB 82/02-8	0.5	Steam distillation	1/500	3h
2370	LFGB 82/02-8	1	Steam distillation		4h
2372	LFGB 82/02-8	1	Steam distillation		1h
2375	LFGB 82/02-8	1	Basic extraction	1/60	15h
2379	LFGB 82/02-8	0.5	Steam distillation		
2380	LFGB 82/02-8	2	Steam distillation		16h
2390	LFGB 82/02-8	1	Steam distillation		2.5h
2410	LFGB 82/02-8	1	steam distillation		1.5 h
3104					
3117	LFGB 82/02-8	1.00	steam distillation		7h
3150	In house	0.5	Ultrasonic	1/20	30min
3153	LFGB 82/02-8	1	Steam distillation		
3154	LFGB 82//02-8	2.0	Steam distillation		16min
3159	In house		Basic extraction	1/20	12h
3170					
3172					
3185	ISO17070	1.0	Steam distillation		1.5h
3190	LFGB 82/02-8	1.0	steam distillation		
3191	GB/T18414.1-2006	1	Ultrasonic	1/110	25min
3197	LFGB 82/02-8	1	Ultrasonic	1/5	1h
3200	LFGB 82/02-8	1	steam distillation	1/40	2 x 30min
3209	ISO17070	1.0	steam distillation		
3210	XPG08015	1	Ultrasonic	1/50	
3220	LFGB 82/02-8	1	steam distillation		20 min
3225	in house	0.2	Ultrasonic	1/30	1h
3232	ISO17070	1	steam distillation		
3233	in house	1	Basic extraction	1/20	12-15 h
3237	LFBG 82/02-8	1	Ultrasonic	1/10	30min
3243	LFBG 82/02-8				
3246	in house	0.5	basic extraction	1/20	16h
3248	in house	1g	Ultrasonic		1h
8008					

APPENDIX 3

Number of participants per country

2 labs in	BANGLADESH
1 lab in	BRASIL
2 labs in	FRANCE
5 labs in	GERMANY
8 labs in	HONG KONG
7 labs in	INDIA
1 lab in	INDONESIA
3 labs in	ITALY
1 lab in	KOREA
13 labs in	P.R. of CHINA
1 lab in	PAKISTAN
2 labs in	TAIWAN R.O.C.
1 lab in	THAILAND
4 labs in	TURKEY
1 lab 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; January 2007
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 January 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