Results of Proficiency Test
Pesticides in Textile
November 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, there are some Ecolabelling schemes imposing environmental requirements for textile products on a voluntary basis. Well-known programs are Milieukeur (the Netherlands) and Öko-Tex Standard 100 (Germany).
The Institute for Interlaboratory Studies organizes since 2004 a scheme of proficiency test for Pesticides in textile. As part of the annual proficiency test program 2010/2011, the Institute decided to continue this proficiency test on Pesticides in Textile.
In this interlaboratory study 17 laboratories in 9 different countries participated. See appendix 4 for a list of 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 this proficiency test. Sample preparation and analyses were subcontracted to an accredited laboratory.
It was decided to use three different textile samples in this PT, all positive on a number of pesticides. The participants were requested to report rounded and unrounded results. The unrounded results were preferably used for statistical evaluation.

2.1 QUALITY SYSTEM

The Institute for Interlaboratory Studies in Spijkenisse, the Netherlands, has implemented a quality system based on ISO guide 43, ILAC-G13:2007 and ISO 17043:2010. 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 'iis Interlaboratory Studies: Protocol for the Organisation, Statistics and Evaluation' of January 2010 (iis-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

Three different textile samples, all positive on a number of pesticides, were prepared by a third party. Sample #1096 was a blue cotton fabric fortified with Carbaryl and Parathion. Sample #1097 was an orange cotton fabric fortified with 4,4-DDD and Methoxychlor and sample #1100 was a white cotton fabric fortified with Esfenvalerate, Fenvalerate and Lambda Cyhalothrin. The three samples were each cut into pieces, well mixed and divided over 40 subsamples of 5 grams each. The samples were tested for homogeneity by an ISO17025 accredited laboratory by determination of a pesticide in accordance with an in house test method. See the following tables for the test results:

	Carbaryl in mg/kg
Sample #1096-1	0.798
Sample #1096-2	0.938
Sample #1096-3	0.896
Sample #1096-4	0.790

Table 1: homogeneity test results of sub samples #1096

	4,4-DDD in mg/kg	Methoxychlor in mg/kg
Sample #1097-1	3.95	8.53
Sample #1097-2	3.84	8.87
Sample #1097-3	3.99	8.69
Sample #1097-4	3.84	8.66
Sample #1097-5	3.84	8.96

Table 2: homogeneity test results of sub samples #1097

	Lambda Cyhalothrin in mg/kg
Sample #1100-1	12.55
Sample #1100-2	12.55
Sample #1100-3	12.80
Sample #1100-4	12.60

Table 2: homogeneity test results of sub samples #1100

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

	RSDr in %	RSDr in %	RSDr in %	RSDr in %
#1096	5.8	---	---	---
#1097	---	1.9	2.0	---
#1100	---	---	---	0.9

Table 3: repeatabilities of the sub samples #1096, #1097 and #1100

For the determination of the pesticides content an ‘in house’ test method was used. The calculated repeatabilities are all in good agreement with the respective repeatability of the laboratory that performed the homogeneity testing.
Therefore, homogeneity of subsamples #1096, #1097 and #1100 was assumed.
In total approx. 5 grams of each of the samples #1096, #1097 and #1100 were sent to the participating laboratories on November 3, 2010.

2.5 ANALYSES

The participants were asked to determine the concentrations of a limited number of prescribed pesticides, applying the analytical procedure that is routinely used in the laboratory.
To get comparable results a detailed report form, was sent together with the set of samples. On the report forms the requested pesticides, including the units and questions about the analytical details, were pre-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 per determination in appendix 1 of this report. The laboratories are presented by their code numbers.

Directly after the deadline, a reminder fax was sent to the laboratories that had not reported results at that moment. Shortly after the deadline, the available results were screened for suspect data. A result was called suspect in case the Huber Elimination Rule (a robust outlier test) found it to be an outlier. The laboratories that produced these suspect data were asked to check the results. Additional or corrected results are used for data analysis and original results are placed under 'Remarks' in the result tables in appendix 1.

3.1 STATISTICS

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.

First, the normality of the distribution of the various data sets per determination was checked by means of the Lilliefors-test. After removal of outliers, this check was repeated. Not all data sets proved to have a normal distribution, in which cases the statistical evaluation of the results should be used with due care.
In accordance to ISO 5725 (1986 and 1994) the original results per determination were submitted subsequently to Dixon and Grubbs outlier tests. Outliers are marked by D(0.01) for the Dixon test, by G(0.01) or DG(0.01) for the Grubbs test. Stragglers are marked by D(0.05) for the Dixon 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.
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).

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 5, nr.15-16).

3.3 Z-SCORES

To evaluate the performance of the participating laboratories the z-scores were calculated. As it was decided to evaluate the performance of the participants in this proficiency test (PT) against the literature requirements, the z-scores were calculated using a target standard deviation. This results in an evaluation independent of the spread of this interlaboratory study. The target standard deviation was calculated from the target reproducibility (preferable from a standard method) by division with 2.8.

The standard uncertainly (u_x) was calculated from the (target) standard deviation in accordance with ISO13528, paragraph 5.6:

$$u_x = 1.23 * (\text{st.dev (n)}) / \sqrt{n}$$

In ISO13528 is stated that if $u_x \geq 0.3$ * standard deviation for proficiency testing, the uncertainly of the assigned value is not negligible and need to be included in the interpretation of the results of the proficiency test. In the cases that the uncetainty is not neglictible (see appendix 1) the z'-scores were calculated in stead of the usual z-scores. The $z_{(target)}$ -scores were calculated in accordance with:

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

The $z'_{(target)}$ were calculated in accordance with ISO13528 paragraph 7.6:

$$z'_{(target)} = (\text{result – mean of PT}) / \sqrt{((\text{target standard deviation})^2 + (u_x)^2)}$$

Absolute values for z<2 are very common and absolute values for z>3 are very rare. The evaluation of $z'_{(target)}$ is not different as for common z-scores and both are evaluated 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.
Two participants did not report any test results. Three other participants reported results after the final reporting date. In total 15 of the 17 participants reported 108 numerical test results. Observed were 6 statistical outlying results, which is 5.6% of the numerical results. In proficiency studies, outlier percentages of 3 % - 7.5 % are quite normal.
Not all data sets proved to have a normal distribution. Not normal distributions were found for the following pesticides: 4,4-DDD and Parathion on #1096, Methoxychlor on #1097 and Lambda Cyhalothrin on #1100. In these cases, the results of the statistical evaluation should be used with care. One can see that this is justified from the Kernel Density Graphs.
Due to the lack of relevant standard test methods for the determination of pesticides with precision data, the calculated reproducibilities were compared with the reproducibilities calculated using Horwitz, see also paragraph 5.

4.1 EVALUATION PER SAMPLE AND PESTICIDE

All statistical results reported on the textile samples are summarised in appendix 1 and relevant method information is summarized in appendix 3 and all other positively reported pesticide test results are listed in appendix 2.

Textile #1096:

Carbaryl: The determination of this pesticide was very problematic at the level of 4.7 mg/kg. No statistical outliers were observed. However, the calculated reproducibility is not at all in agreement with the estimated target reproducibility (Horwitz'). One laboratory reported 'not detected' for this pesticide, while the other twelve laboratories reported more than 1 mg/kg.

4,4-DDD: The determination of this pesticide was very problematic at the low level of 0.28 mg/kg. No statistical outliers were observed. However, the calculated reproducibility is not at all in agreement with the target reproducibility (Horwitz'). Two laboratories reported test results above 0.5 mg/kg, while eleven laboratories reported test results below 0.5 mg/kg or 'not detected'.

Parathion: The determination of this pesticide was problematic at the level of 0.9 mg/kg. No statistical outliers were observed. However, the calculated reproducibility is not in agreement with the estimated target reproducibility (Horwitz'). One laboratory reported 'not detected' for this pesticide and two laboratories reported test results below 0.5 mg/kg, while the other eleven laboratories reported more than 0.5 mg/kg.

Textile #1097:

4,4-DDD: The determination of this pesticide was problematic at the level of 4.9 mg/kg. One statistical outlier was observed. The calculated reproducibility, after exclusion of the statistical outlier, is not in agreement with the estimated target reproducibility (Horwitz').
All fifteen laboratories reported a test result higher than 1 mg/kg.

Methoxychlor: The determination of this pesticide was very problematic at the level of 12.6 mg/kg. Two statistical outliers were observed. The calculated reproducibility, after exclusion of the statistical outliers, is not at all in agreement with the estimated target reproducibility (Horwitz).
All fifteen laboratories reported a test result higher than 1 mg/kg.

Textile #1100:

Esfenvalerate: The determination of this pesticide was problematic at the level of 0.68 mg/kg. One statistical outlier was observed. The calculated reproducibility, after exclusion of the statistical outlier, is not in agreement with the estimated target reproducibility (Horwitz).
One laboratory reported 'not detected' and one laboratory reported a result below 0.5 mg/kg, while 11 laboratories reported more than 0.5 mg/kg.

Fenvalerate: The determination of this pesticide was not problematic at the level of 1.0 mg/kg. One statistical outlier was observed. The calculated reproducibility, after exclusion of the statistical outlier, is in full agreement with the estimated target reproducibility (Horwitz).
Two laboratories reported 'not detected' for this pesticide, while the other nine laboratories reported more than 0.5 mg/kg.

Sum of Esfenvalerate and fenvalerate: In order to evaluate also the results of the two laboratories that reported the sum in stead of the separate components, the test results of the other laboratories were also summed.
The determination was problematic at the level of 1.6 mg/kg. Three statistical outliers were observed. The reproducibility, after exclusion of the statistical outliers, is not in agreement with the target reproducibility (Horwitz). One laboratory reported 'not detected', one laboratory reported a result below 1 mg/kg, while 13 laboratories reported more than 1 mg/kg.

Cyhalotrin-λ: The determination of this pesticide was problematic at the level of 11 mg/kg. One statistical outlier was observed. The calculated reproducibility, after exclusion of the statistical outlier, is not in agreement with the estimated target reproducibility (Horwitz'). One laboratory reported 'not detected', while 14 laboratories reported more than 1 mg/kg.

Sample #1100 was already used before, in PT iis08A01. When the data of both PTs are compared is it remarkable to notice that the consensus values for both rounds differ only very little, which implicates that both pesticides are fairly stable, see table 4.

	Sum Esfenvalerate + Fenvalerate		Lambda Cyhalotrin	
	iis08A01 (#0804)	iis10A07 (#1100)	iis08A01 (#0804)	iis10A07 (#1100)
number of results	21	11	24	13
mean	1.6	1.6	10.9	11.0
st.dev	0.5	0.4	3.8	4.5
reproducibility	1.5	1.1	10.8	12.6

table 4: Comparison of pesticides in samples #0804 and #1100

4.2 PERFORMANCE EVALUATION FOR THE GROUP OF LABORATORIES

A comparison has been made between the very strict reproducibilities as estimated by the Horwitz equation 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 (estimated via the Horwitz equation), are compared in the next 3 tables.

Parameter	*Unit*	*n*	*Average*	*2.8 * sd*	*R (target)*
Carbaryl	mg/kg	12	4.7	6.8	2.9
4,4-DDD	mg/kg	7	0.28	0.90	0.44
Parathion	mg/kg	13	0.89	1.82	0.74

table 5: reproducibilities of pesticides in sample #1096

Parameter	*Unit*	*n*	*average*	*2.8 * sd*	*R (target)*
4,4-DDD	mg/kg	14	4.9	5.2	2.4
Methoxychlor	mg/kg	12	12.6	9.9	3.9

table 6: reproducibilities of pesticides in sample #1097

Parameter	*Unit*	*n*	*average*	*2.8 * sd*	*R (target)*
Esfenvalerate	mg/kg	11	0.68	0.79	0.32
Fenvalerate	mg/kg	8	1.0	0.32	0.45
Sum Esf. + Fenvalerate	mg/kg	11	1.6	1.1	0.66
Lambda Cyhalotrin	mg/kg	13	11.0	12.6	5.5

table 7: reproducibilities of pesticides in sample #1100

Without further statistical calculations it can be concluded that for all determined pesticides, except fenvalerate, the group of participating laboratories has some difficulties with the analysis. See also the discussion in paragraphs 4.1 and 5.

5 DISCUSSION

When the results of this interlaboratory study were compared to the Ecolabelling Standards and Requirements for Textiles in EU (see table 8), it could be noticed that all of the reporting laboratories would make the same decision about the acceptability of the textiles for the determined parameters. All participants would reject the textiles.

Ecolabel	EU-environmental criteria	Non skin contact	Direct skin contact	Baby clothes
Pesticides, total mg/kg	0.5	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 pesticides in textile, all the participants identified all spiked pesticides correctly. The spreads of the group regretfully could not be compared with the precision of a Standard Test Method because of the lack of a suitable test method with precision data.

Almost all participants used in-house methods. The details of the methods used, differ (see appendix 3) and consequently, the reproducibilities cannot be improved by only one change in the analysis.
When evaluating the given details of the test method, one may conclude that there is no clear relation between the details and the results reported by the participants.

The spreads that were found for the pesticides during the present proficiency test did not improve, compared with the spreads as observed in the previous rounds, except for Fenvalerate. This may be caused by the fact that now explicitly was asked to report both Fenvalerate and Esfenvalerate.
The low number of participating laboratories may (partly) explain for the relatively large spread of the other pesticides. Also in this PT four pesticides were evaluated that were not yet present in previous iis PTs.

	November 2010	*February 2010*	*February 2009*	*February 2008*	*February 2007*	*February 2006*	*February 2005*
Carbaryl	146	--	--	--	--	--	--
Cyhalothrin-lambda	114	--	--	99	--	--	--
Cypermetrin (=Σ)	--	41	--	--	77	--	--
4,4-DDD	106-327	--	--	--	--	--	--
Deltamethrin	--	--	--	104	--	--	--
Dimethoate	--	--	98	--	--	110-176	226
α/β-Endosulfan	--	41-55	58	--	59	--	154
Fenvalerate	32	--	66-103	90	--	52	138
Esfenvalerate	116	--	--	--	--	--	--
Malathion	--	--	--	--	--	206–214	--
Methoxychlor	78	--	--	40	--	--	--
Methylparathion	--	--	--	--	--	144-165	--
Monocrotophos	--	--	--	--	207	--	--
Parathion	204	--	--	--	--	--	--
Quinalfos	--	66	--	--	79-125	--	--

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

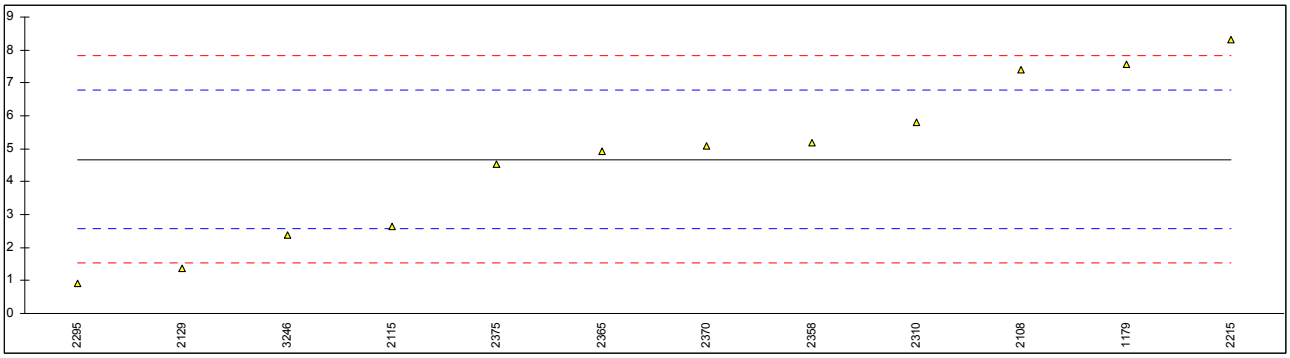
Finally, each laboratory has to evaluate its performance in this study and make decisions about necessary corrective actions. Therefore, participation on a regular basis in this scheme could be helpful to improve the performance and thus improve of the quality of the analytical results.

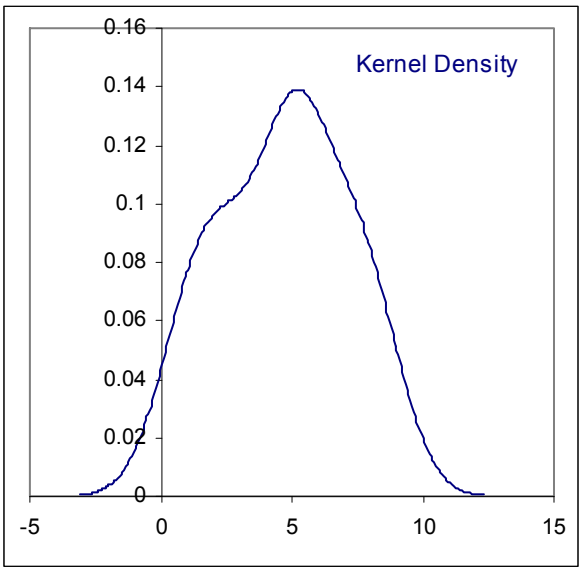
APPENDIX 1

Determination of Carbaryl on sample #1096; results in mg/kg

lab	method	value	mark	z'(targ)	remarks
1179	in house	7.57		2.76	
2108	in house	7.4		2.60	
2115	in house	2.63		-1.95	
2129	in house	1.36		-3.16	
2172		-----		-----	
2215	in house	8.30		3.46	
2295	in house	0.91		-3.59	
2310	in house	5.8		1.07	
2358	in house	5.17		0.47	
2365	in house	4.93		0.24	
2370	in house	5.10		0.41	
2375	in house	4.530		-0.14	
3117		-----		-----	
3170		-----		-----	
3172		-----		-----	
3220	in house	n.d.		-----	false negative?
3246	in house	2.38		-2.19	

normality	OK
n	12
outliers	0
mean (n)	4.673
st.dev. (n)	2.4372
R(calc.)	6.824
R(Horwitz)	1.660
U(mean)	0.865
R(Horwitz')	2.937

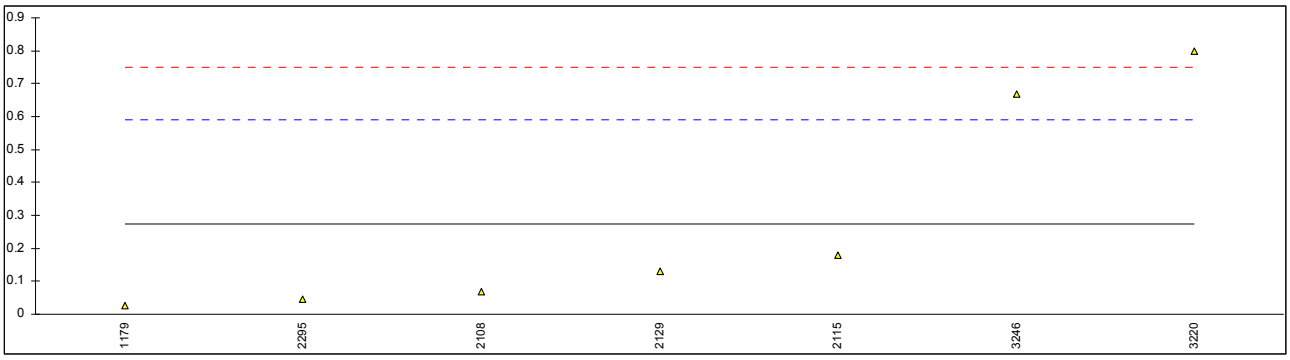




Determination of 4,4-DDD on sample #1096; results in mg/kg

lab	method	value	mark	z'(targ)	remarks
1179	in house	0.027		-1.56	
2108	in house	0.07		-1.29	
2115	in house	0.18		-0.60	
2129	in house	0.13		-0.91	
2172	in house	n.d.		-----	
2215	in house	n.d.		-----	
2295	in house	0.046		-1.44	
2310	in house	n.d.		-----	
2358		-----		-----	
2365	in house	<0.05		-----	
2370	in house	n.d.		-----	
2375	in house	n.d.		-----	
3117		-----		-----	
3170		-----		-----	
3172		-----		-----	
3220	in house	0.8		3.32	
3246	in house	0.67		2.50	

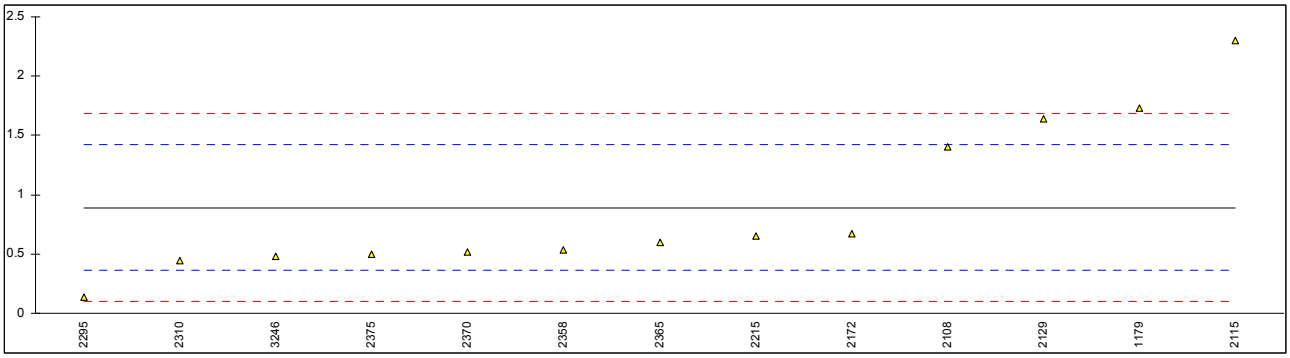
normality	not OK
n	7
outliers	0
mean (n)	0.275
st.dev. (n)	0.3209
R(calc.)	0.898
R(Horwitz)	0.149
U(mean)	0.149
R(Horwitz')	0.444

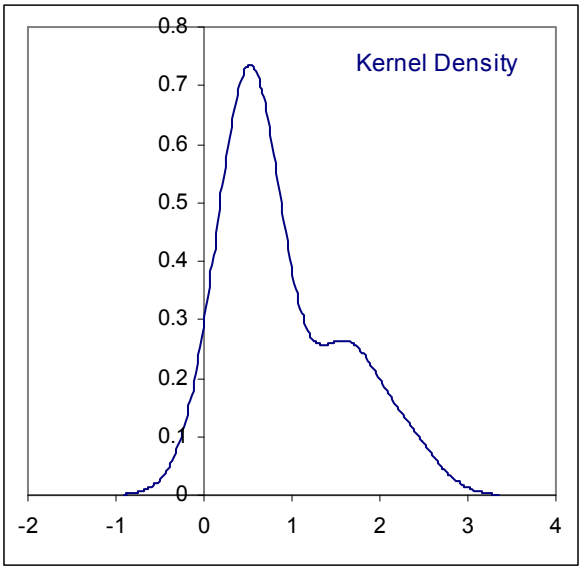


Determination of Parathion on sample #1096; results in mg/kg

lab	method	value	mark	z'(targ)	remarks
1179	in house	1.73		3.16	
2108	in house	1.4		1.92	
2115	in house	2.30		5.32	
2129	in house	1.64		2.82	
2172	in house	0.669		-0.84	
2215	in house	0.65		-0.91	
2295	in house	0.14		-2.84	
2310	in house	0.44		-1.71	
2358	in house	0.53		-1.37	
2365	in house	0.60		-1.10	
2370	in house	0.520		-1.40	
2375	in house	0.496		-1.49	
3117		-----		-----	
3170		-----		-----	
3172		-----		-----	
3220	in house	n.d.		-----	false negative?
3246	in house	0.48		-1.56	

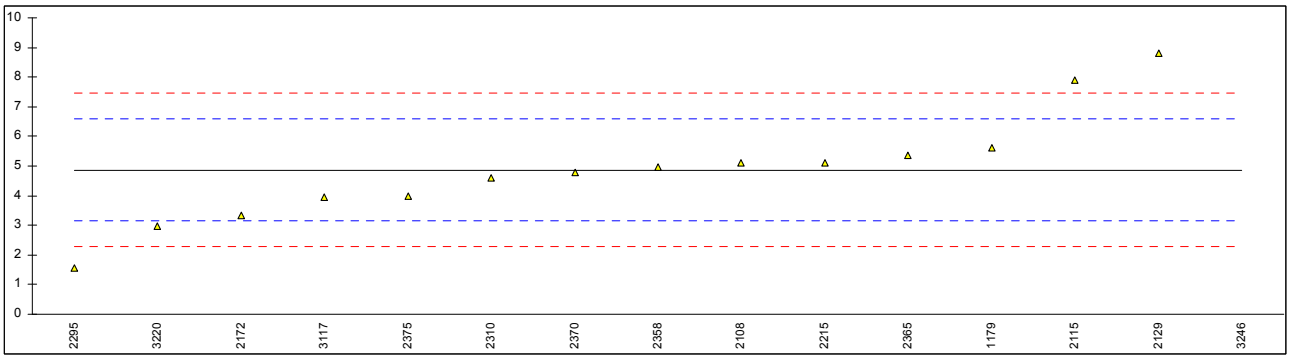
normality	not OK
n	13
outliers	0
mean (n)	0.892
st.dev. (n)	0.6495
R(calc.)	1.818
R(Horwitz)	0.407
U(mean)	0.222
R(Horwitz')	0.742

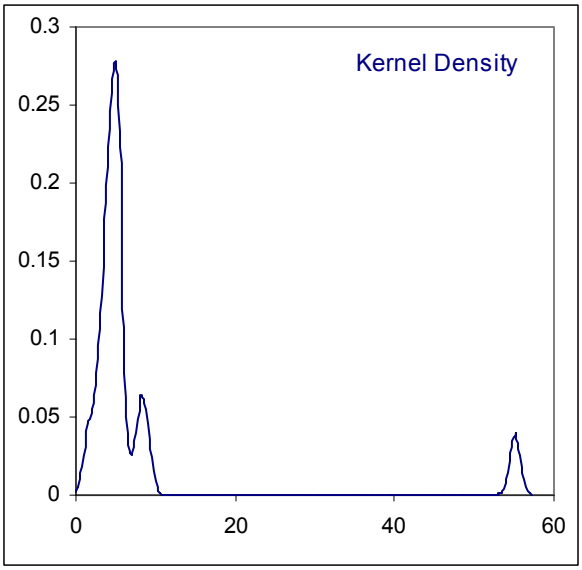




Determination of 4,4-DDD on sample #1097; results in mg/kg

lab	method	value	mark	z'(targ)	remarks
1179	in house	5.63		0.89	
2108	in house	5.1		0.28	
2115	in house	7.89		3.51	
2129	in house	8.79		4.56	
2172	in house	3.33		-1.78	
2215	in house	5.12		0.30	
2295	in house	1.54		-3.85	
2310	in house	4.6		-0.30	
2358	in house	4.97		0.13	
2365	in house	5.37		0.59	
2370	in house	4.80		-0.07	
2375	in house	4.000		-1.00	
3117	in house	3.94		-1.07	
3170		-----		-----	
3172		-----		-----	
3220	in house	2.97		-2.19	
3246	in house	55.16	G(0.01)	58.34	
	normality	OK			
	n	14			
	outliers	1			
	mean (n)	4.861			
	st.dev. (n)	1.8441			
	R(calc.)	5.163			
	R(Horwitz)	1.716			
	U(mean)	0.606			
	R(Horwitz')	2.414			

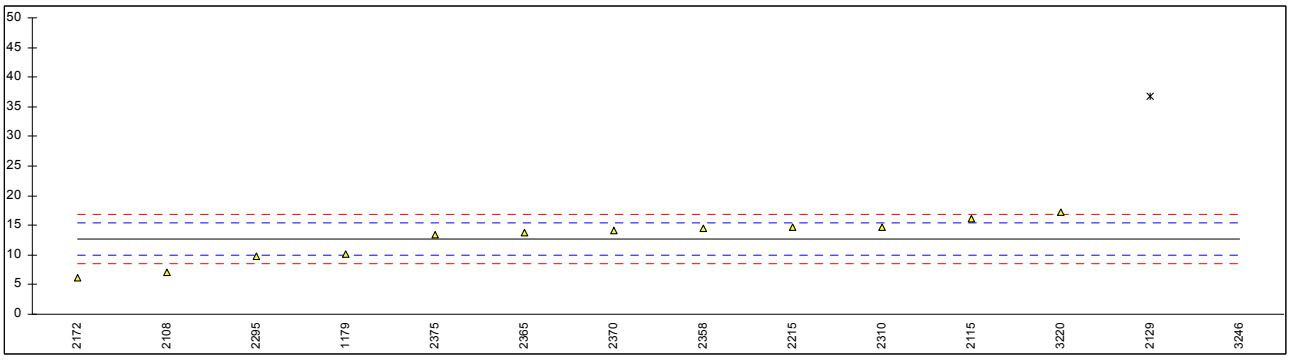


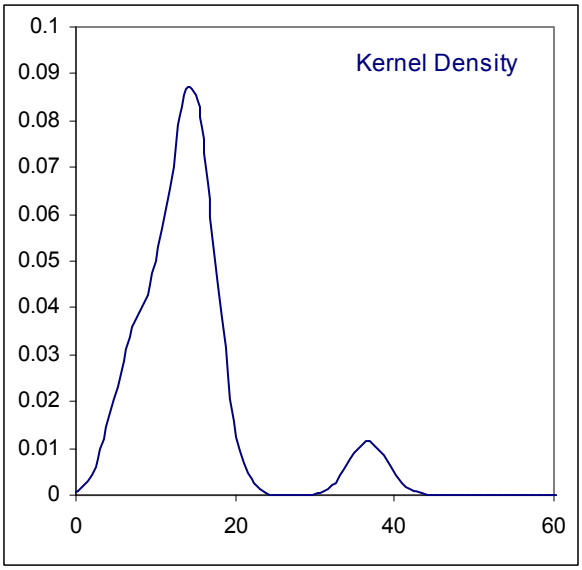


Determination of Methoxychlor on sample #1097; results in mg/kg

lab	method	value	mark	z(targ)	remarks
1179	in house	10.20		-1.77	
2108	in house	7.0		-4.09	
2115	in house	16.11		2.51	
2129	in house	36.7	G(0.01)	17.42	
2172	in house	6.16		-4.70	
2215	in house	14.6		1.41	
2295	in house	9.76		-2.09	
2310	in house	14.76		1.53	
2358	in house	14.5		1.34	
2365	in house	13.76		0.81	
2370	in house	14.2		1.12	
2375	in house	13.492		0.61	
3117		-----		-----	
3170		-----		-----	
3172		-----		-----	
3220	in house	17.22		3.31	
3246	in house	198.85	G(0.01)	134.82	

normality	not OK
n	12
outliers	2
mean (n)	12.647
st.dev. (n)	3.5326
R(calc.)	9.891
R(Horwitz)	3.867
U(mean)	1.254
R(Horwitz')	n.a.

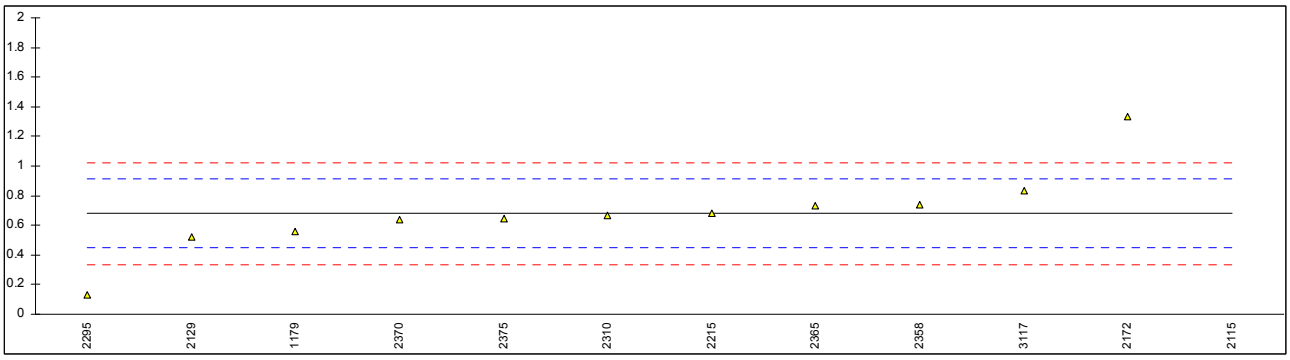


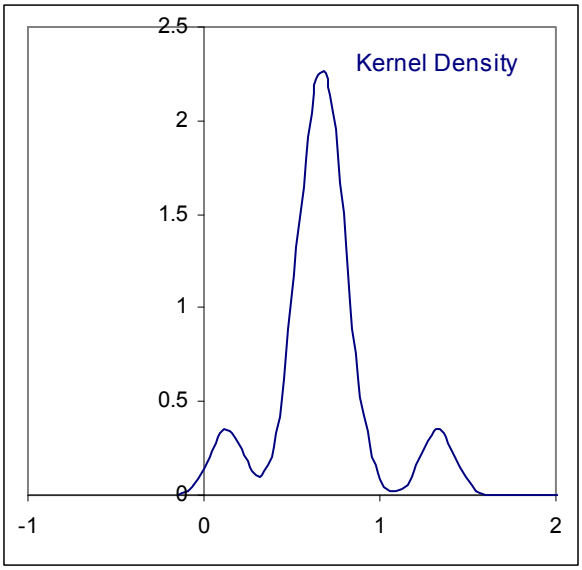


Determination of Esfenvalerate on sample #1100; results in mg/kg

lab	method	value	mark	z(targ)	remarks
1179	in house	0.559		-1.04	
2108	in house	-----		-----	reported the sum of esfenvalerate and fenvalerate 1.8 mg/kg
2115	in house	15.00	G(0.01)	124.31	
2129	in house	0.52		-1.38	
2172	in house	1.33		5.65	
2215	in house	0.68		0.01	
2295	in house	0.13		-4.77	
2310	in house	0.67		-0.08	
2358	in house	0.74		0.53	
2365	in house	0.73		0.44	
2370	in house	0.638		-0.36	
2375	in house	0.645		-0.30	
3117	in house	0.83		1.31	
3170		-----		-----	
3172		-----		-----	
3220	in house	n.d.		-----	false negative?
3246	in house	-----		-----	reported the sum of esfenvalerate and fenvalerate 23.43 mg/kg

normality	OK
n	11
outliers	1
mean (n)	0.679
st.dev. (n)	0.2823
R(calc.)	0.790
R(Horwitz)	0.323
U(mean)	0.105
R(Horwitz')	n.a.

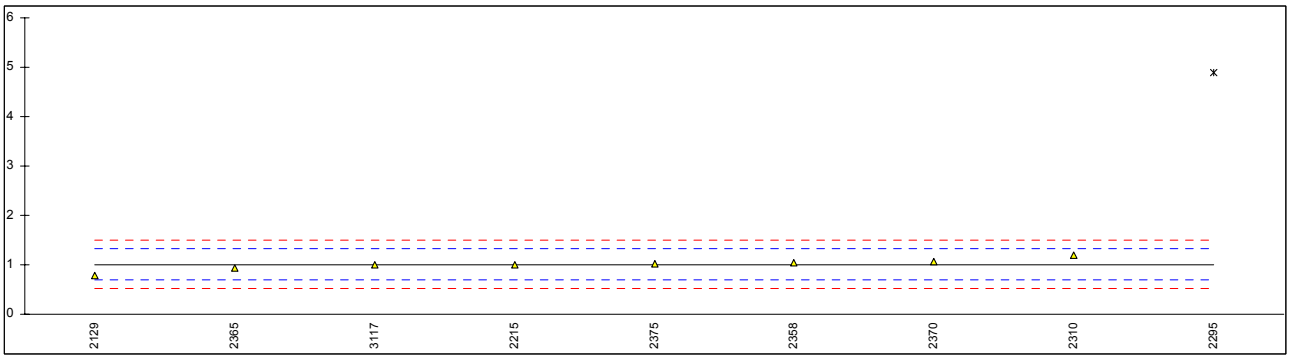


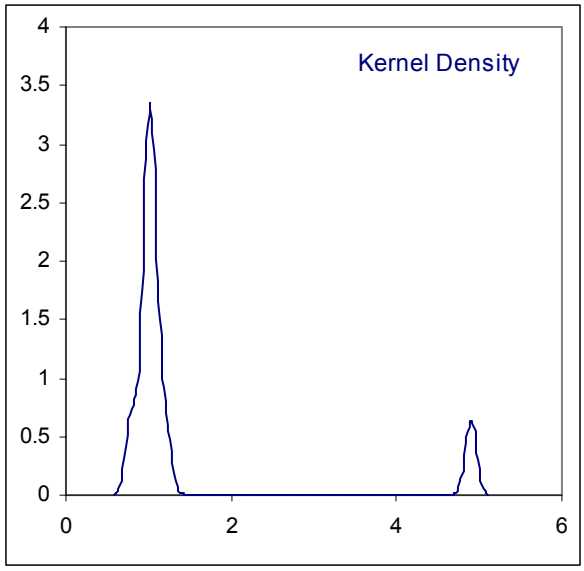


Determination of Fenvalerate on sample #1100; results in mg/kg

lab	method	value	mark	z(targ)	remarks
1179		-----		-----	
2108	in house	-----		-----	reported the sum of esfenvalerate and fenvalerate 1.8 mg/kg
2115		-----		-----	
2129	in house	0.79		-1.36	
2172	in house	n.d.		-----	false negative?
2215	in house	1.01		0.01	
2295	in house	4.90	G(0.01)	24.14	
2310	in house	1.2		1.19	
2358	in house	1.05		0.26	
2365	in house	0.94		-0.43	
2370	in house	1.06		0.32	
2375	in house	1.021		0.08	
3117	in house	1.00		-0.06	
3170		-----		-----	
3172		-----		-----	
3220	in house	n.d.		-----	false negative?
3246	in house	-----		-----	reported the sum of esfenvalerate and fenvalerate 23.43 mg/kg

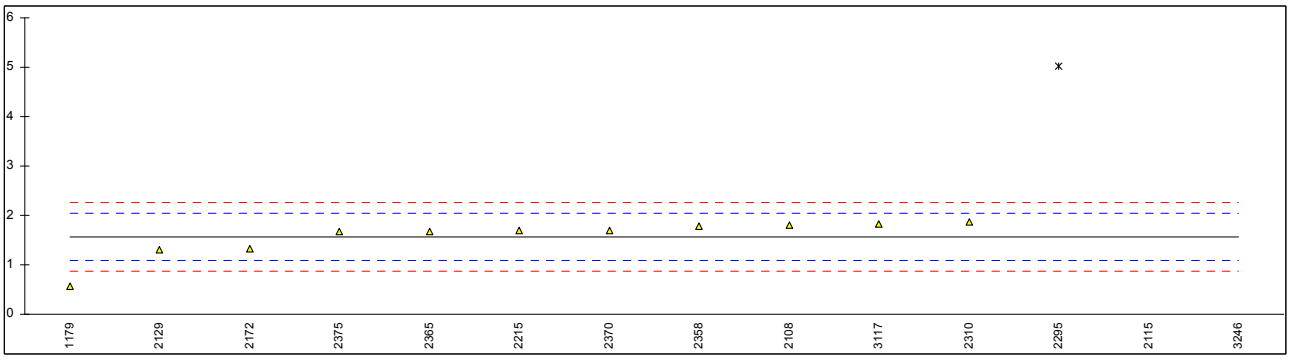
normality	OK
n	8
outliers	1
mean (n)	1.009
st.dev. (n)	0.1157
R(calc.)	0.324
R(Horwitz)	0.451
U(mean)	0.050
R(Horwitz')	n.a.

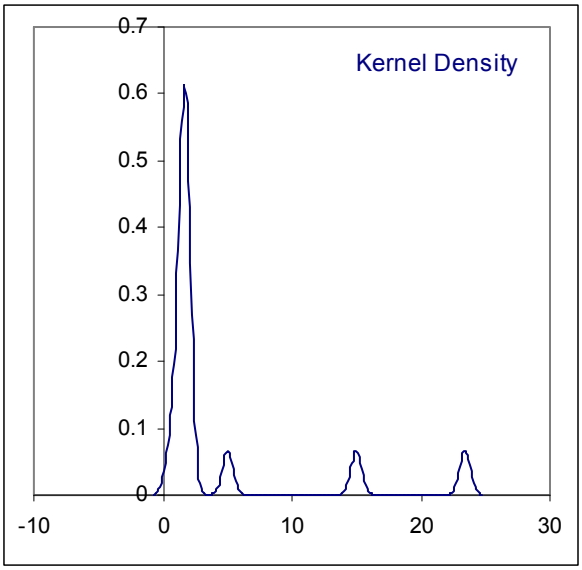




Determination of sum of Esfenvalerate and Fenvalerate on sample #1100; results in mg/kg

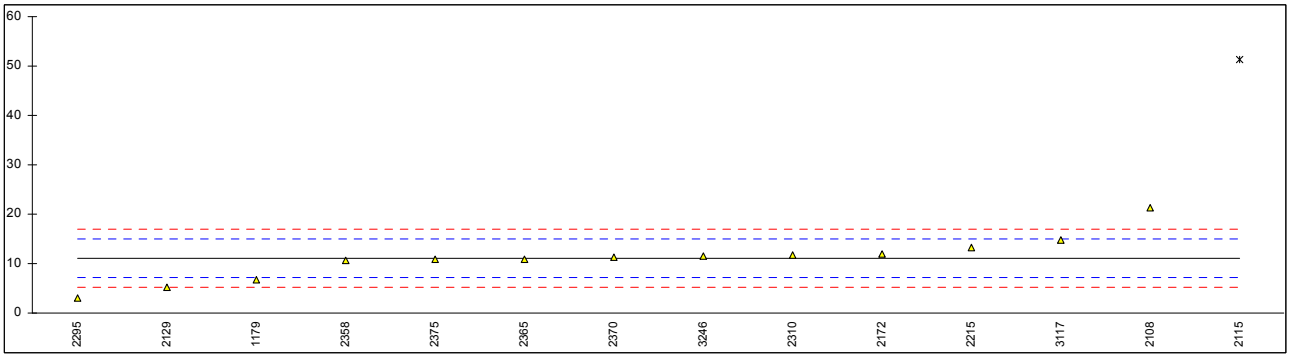
lab	method	value	mark	z(targ)	remarks
1179	in house	0.559		-4.30	
2108	in house	1.8		1.00	
2115	in house	15.00	G(0.01)	57.40	
2129	in house	1.31		-1.09	
2172	in house	1.33		-1.00	
2215	in house	1.69		0.53	
2295	in house	5.03	G(0.01)	14.81	
2310	in house	1.87		1.30	
2358	in house	1.79		0.96	
2365	in house	1.67		0.45	
2370	in house	1.698		0.57	
2375	in house	1.666		0.43	
3117	in house	1.83		1.13	
3170		-----		-----	
3172		-----		-----	
3220	in house	n.d.		-----	false negative?
3246	in house	23.43	G(0.01)	93.42	
	normality	not OK			
	n	11			
	outliers	3			
	mean (n)	1.565			
	st.dev. (n)	0.3816			
	R(calc.)	1.068			
	R(Horwitz)	0.655			
	U(mean)	0.142			
	R(Horwitz')	n.a.			

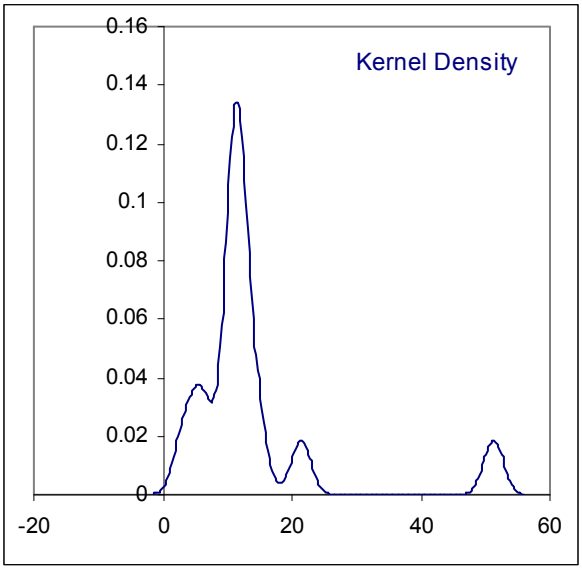




Determination of Lambda-cyhalothrin on sample #1100; results in mg/kg

lab	method	value	mark	z'(targ)	remarks
1179	in house	6.76		-2.17	
2108	in house	21.4		5.29	
2115	in house	51.25	G(0.01)	20.49	
2129	in house	5.29		-2.92	
2172	in house	12.0		0.50	
2215	in house	13.2		1.11	
2295	in house	3.13		-4.02	
2310	in house	11.71		0.35	
2358	in house	10.7		-0.16	
2365	in house	10.84		-0.09	
2370	in house	11.2		0.09	
2375	in house	10.764		-0.13	
3117	in house	14.78		1.92	
3170		-----		-----	
3172		-----		-----	
3220	in house	n.d.		-----	false negative?
3246	in house	11.47		0.23	
	normality	not OK			
	n	13			
	outliers	1			
	mean (n)	11.019			
	st.dev. (n)	4.4883			
	R(calc.)	12.567			
	R(Horwitz)	3.440			
	U(mean)	1.531			
	R(Horwitz')	5.497			





APPENDIX 2

Summary of all other reported pesticides in sample #1096; results in mg/kg

lab	method
1179	Methoxychlor: 0.019
2108	Methoxychlor: 0.03
2115	
2129	Methoxychlor: 0.15
2172	
2215	
2295	
2310	
2358	
2365	
2370	
2375	
3117	
3170	
3172	
3220	2,4-DDD: 3.14 and Fenvalerate 14.65
3246	

Summary of all other reported pesticides in sample #1097; results in mg/kg

lab	method
1179	2,4-DDD: 0.027 and Parathion: 0.025
2108	2,4-DDD: 0.05 and Parathion: 0.02
2115	2,4-DDD: traces
2129	2,4-DDD: 0.06 and Parathion: 0.12
2172	
2215	
2295	Carbaryl: 0.30 and 2,4-DDD: 0.028 and Parathion 0.004
2310	
2358	
2365	
2370	
2375	
3117	
3170	
3172	
3220	2,4-DDD: 0.84 and Fenvalerate: 7.77
3246	

Summary of all other reported pesticides in sample #1100; results in mg/kg

lab	method
1179	Methoxychlor: 0.026
2108	4,4-DDD: 0.01 and Methoxychlor: 0.08
2115	
2129	
2172	
2215	
2295	Carbaryl: 0.26
2310	
2358	
2365	
2370	
2375	
3117	
3170	
3172	
3220	
3246	

APPENDIX 3

Details of the methods used by the participants:

labnrs	method	technique/solvent	detection/quantification
1179			
2108	OEKOTEX method		GC/MS
2115	OEKOTEX method	acetone	GC/MS
2129	in house / EPA 8270C, 3545	ASE/acetone	MSD E1/NCI
2172	in house	ultrasonic/acetone-hexane	GC/MS
2215	in house	acetone-hexane	GC/MS
2295			
2310	in house / EPA 8081	ultrasonic/acetone-hexane	GC/MS & LC/MS
2358	in house / EPA 8081	ultrasonic/acetone-hexane	GC/MS & GC-ECD & HPLC-DAD
2365	in house / EPA 8081B	ultrasonic/acetone-hexane	GC-ECD & HPLC/MS (Carbaryl only)
2370	in house / EPA 8081B	ultrasonic/acetone-hexane	GC/MS & HPLC-DAD
2375	in house / EPA 8081B	acetone-hexane	GC/MS & GC-ECD & HPLC-DAD
3117	GB/T 18412.1-2006	ultrasonic/acetone-ethylacetate	MS
3170			
3172			
3220	in house	extraction	GC/MS
3246			

APPENDIX 4

Number of participants per country

1 lab in	THE NETHERLANDS
2 labs in	GERMANY
2 labs in	ITALY
4 labs in	P.R. of CHINA
2 labs in	TURKEY
3 labs in	INDIA
1 lab in	HONG KONG
1 lab in	TAIWAN R.O.C.
1 lab in	VIETNAM

APPENDIX 5

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
W = withdrawn on request of the participant
fr. = first reported

Literature:

1 iis Interlaboratory Studies, Protocol for the Organisation, Statistics & Evaluation, January 2010
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11 ISO13528: 05
12 ISO105 E4: 1994
13 ISO14184-1: 1994
14 M. Thompson and R. Wood, J. AOAC Int, 76, 926, (1993)
15 Analytical Methods Committee Technical brief, No4 January 2001.
16 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/).