Results of Proficiency Test Pesticides 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, 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).
In response to requests from several laboratories, 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 2009/2010, the Institute decided to continue this proficiency test on Pesticides in Textile. In this, international interlaboratory study 23 laboratories in 11 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 this proficiency test. Sample preparation and analyses were subcontracted to an accredited laboratory.
It was decided to use in this round two different samples, both positive on 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 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 of Interlaboratory Studies. Disclosure of the identity of one or more of the participating companies will be done only after receipt of a written agreement of the companies involved**.**

2.4 SAMPLES

Two different textile samples both positive on pesticides were prepared by a third party laboratory. Sample #1005 is a Turquoise Blue cotton fabric and sample #1006 is an Ivory cotton fabric. Both samples were cut into pieces, well mixed and divided over 40 subsamples of 5 grams each. The samples were labelled and tested for homogeneity by an ISO17025 accredited laboratory. The homogeneities of random selected samples were checked by determination of a pesticide in accordance with an In house test method. See the following tables for the test results.
A third party laboratory prepared the samples and another (accredited) third party laboratory was subcontracted to perform the homogeneity tests.

Blue cotton fabric	Cypermethrin-1 in mg/kg
Sample #1005-1	2.3
Sample #1005-2	2.0
Sample #1005-3	2.8
Sample #1005-4	2.9

Table 1: homogeneity test of subsamples #1005

White cotton fabric	β-Endosulfan in mg/kg
Sample #1006-1	3.3
Sample #1006-2	3.0
Sample #1006-3	3.6
Sample #1006-4	3.1

Table 2: homogeneity test of subsamples #1006

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

	Cypermethrin-1 in mg/kg	β-Endosulfan in mg/kg
r (observed)	1.2	0.6

Table 3: repeatabilities of the subsamples #1005 and #1006

For the determination of the pesticides content an In house extraction method was used. The calculated repeatabilities are in good agreement with the usual repeatability of the laboratory that performed the homogeneity tests. Therefore, homogeneity of subsamples #1005 and #1006 was assumed.

In total approx. 5 grams of each of the samples #1005 and #1006 were sent to the participating laboratories on January 27, 2010.

2.5 ANALYSES

The participants were asked to determine the concentrations 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 ‘i.i.s. Interlaboratory Studies: Protocol for the Organisation, Statistics and Evaluation’ of January 2010 (i.i.s.-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 4, 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 z-scores were calculated in accordance with:

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

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

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

$\lvert z \rvert < 1$	good
$1 < \lvert z \rvert < 2$	satisfactory
$2 < \lvert z \rvert < 3$	questionable
$3 < \lvert z \rvert$	unsatisfactory

4 EVALUATION

During the execution of this proficiency test no serious problems occurred.
Two participants did not report any results. Two other participants reported results after the final reporting date. In total 21 of the 23 participants reported 85 numerical results.
Observed were 8 statistical outlying results, which is 9.4% of the numerical results. In proficiency studies, outlier percentages of 3 % - 7.5 % are quite normal.
All data sets proved to have a normal distribution.

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 2.

Textile #1005:

Cypermethrin (=Σ): This determination was not problematic at the level of 8.1 mg/kg. Two statistical outliers were observed. However, the calculated reproducibility is, after rejection of the statistical outliers, in good agreement with the estimated target reproducibility (Horwitz).

Monocrotophos: Regretfully, only five participants reported a numerical results, which were near or below the detection limit. Therefore no conclusions were drawn.

Textile #1006:

α-Endosulfan: This determination was problematic for two laboratories at the level of 2.3 mg/kg. Two statistical outliers were observed. However, the calculated reproducibility is, after rejection of the statistical outliers, in full agreement with the strict estimated target reproducibility (Horwitz).

β-Endosulfan: This determination was problematic at the level of 3.4 mg/kg. Two statistical outliers were observed. The calculated reproducibility is, after rejection of the statistical outliers, not in agreement with the strict estimated target reproducibility (Horwitz).

Quinalfos: This determination is problematic at the level of 3.0 mg/kg. Two statistical outliers were observed. The calculated reproducibility is, after rejection of the statistical outliers, not in agreement with the strict estimated target reproducibility (Horwitz).

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 2 tables.

Parameter	*Unit*	*n*	*Average*	*2.8 * sd*	*R (target')*
Cypermethrin (=Σ)	mg/kg	18	8.061	3.327	3.730

table 4: reproducibilities of textile sample #1005

Parameter	*Unit*	*n*	*average*	*2.8 * sd*	*R (target)*
α-Endosulfan	mg/kg	18	2.300	0.934	0.909
β-Endosulfan	mg/kg	18	3.380	1.854	1.261
Quinalfos	mg/kg	18	3.035	1.998	1.150

table 5: reproducibilities of textile sample #1006

Without further statistical calculations it can be concluded that for all determined pesticides, 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 (table 6), 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 6: 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 a standard precision 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 2) 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 relation between the details and the results reported by the participants.

The majority of the group performed the extraction by ultrasonic extraction. This is an equilibrium extraction, which should be done at least two times on the same sample, each time with fresh solvent to release maximum components from the textile. It was not clear from the reported details if all participants have done this.

The spreads that were found for the pesticides during the present proficiency test have improved significantly, compared with the spreads as observed in the previous rounds.

Parameter	*February 2010*	*February 2009*	*February 2008*	*February 2007*	*February 2006*	*February 2005*
Cyhalothrin-lambda	--	--	99%	--	--	--
Cypermetrin (=Σ)	41%	--	--	77%	--	--
Deltamethrin	--	--	104%	--	--	--
Dimethoate	--	98%	--	--	110-176%	226%
α/β-Endosulfan	41-55%	58%	--	59%	--	154%
Fenvalerate	--	66-103%	90%	--	52%	138%
Malathion	--	--	--	--	206–214%	--
Methoxychlor	--	--	40%	--	--	--
Methylparathion	--	(204%)	--	--	144-165%	--
Monocrotophos	--	--	--	207%	--	--
Quinalfos	66%	--	--	79-125%	--	--

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

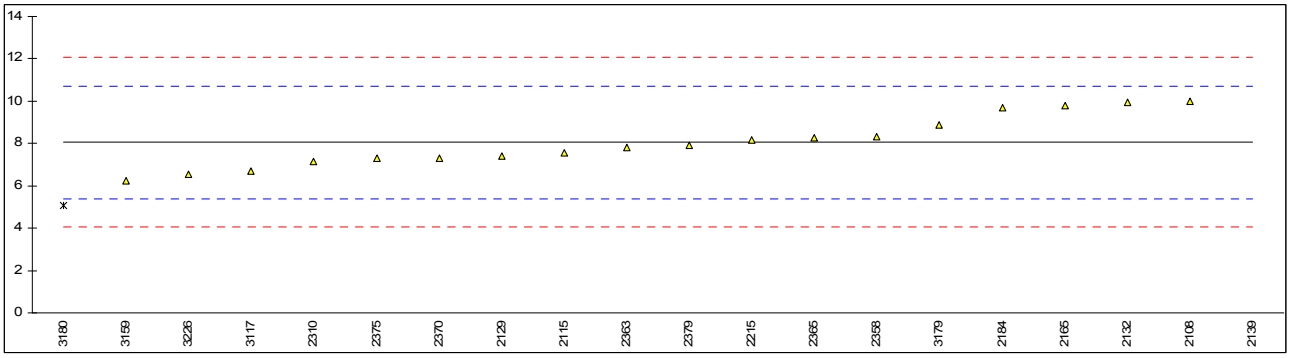
Result between brackets is near or below the limit of detection

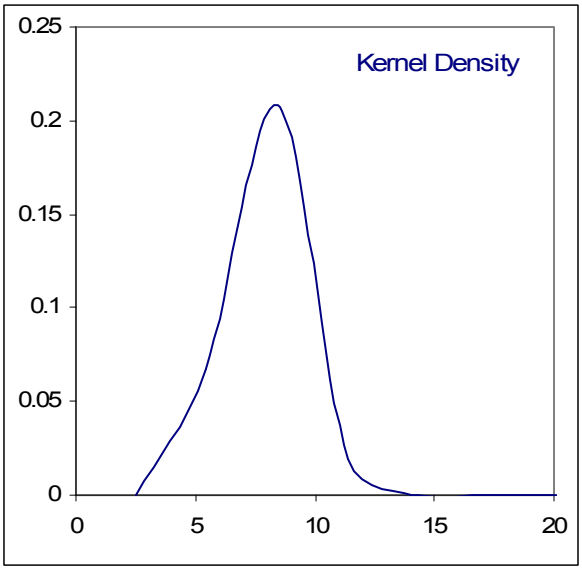
Finally, each laboratory has to evaluate its performance in this study and make decisions about necessary corrective actions. Therefore, participation on a regular basis in this scheme could be helpful to improve the performance and thus improve of the quality of the analytical results.

APPENDIX 1

Determination of Cypermethrin (=Σ) on sample #1005; results in mg/kg

lab	method	value	Mark	z(targ)	remarks
2108	OEKOTEX	9.98		1.44	
2115	OEKOTEX	7.57		-0.37	
2129	In house	7.4	C	-0.50	First reported 2.2
2132	In house	9.96		1.43	
2139	In house	754.10	G(0.01)	559.98	
2165	In house	9.8		1.31	
2184	In house	9.7		1.23	
2215	In house	8.18		0.09	
2310	In house	7.17		-0.67	
2358	In house	8.334		0.21	
2363	In house	7.828		-0.17	
2365	In house	8.275		0.16	
2370	In house	7.320		-0.56	
2372		-----		-----	
2375	EPA	7.3		-0.57	
2379	In house	7.901		-0.12	
3117	GB/T 18412.1	6.6884		-1.03	
3159	In house	6.24		-1.37	
3172		-----		-----	
3179	In house	8.9	C	0.63	First reported 2.7
3180		5.06	CG(0.05)	-2.25	Reported 3.56+1.50
3226	In house	6.548		-1.14	
	normality	OK			
	n	18			
	outliers	2			
	mean (n)	8.061			
	st.dev. (n)	1.1883			
	R(calc.)	3.327			
	R(Horwitz)	3.730			





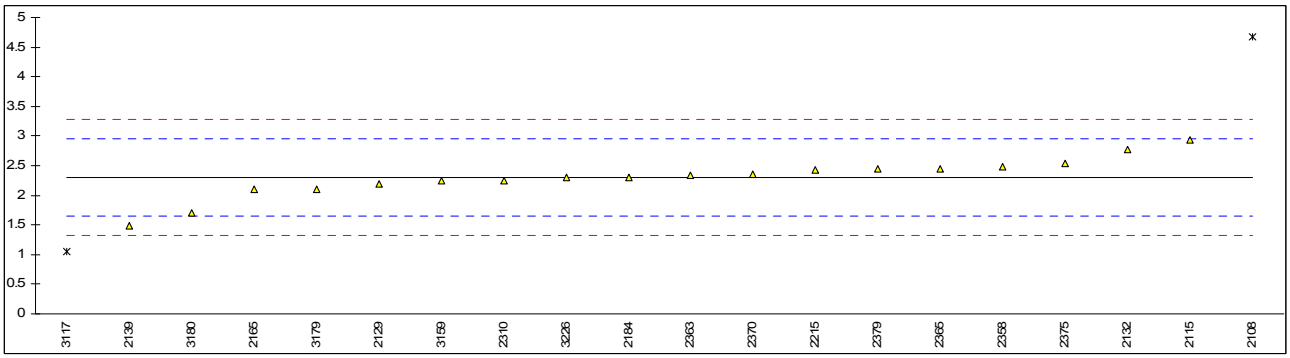
Determination of Monocrotophos on sample #1005; results in mg/kg

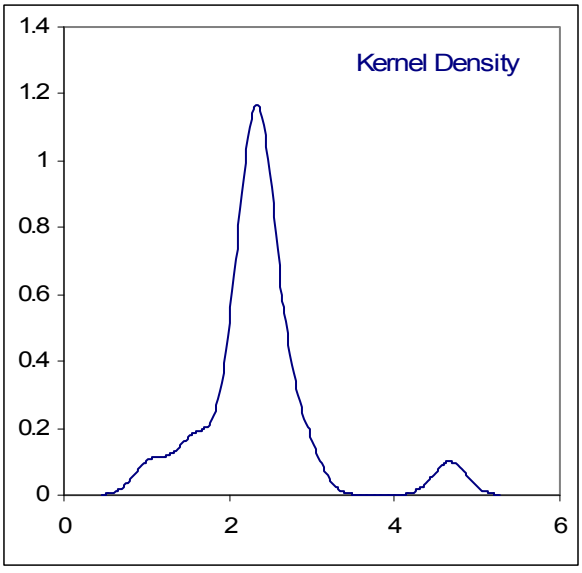
lab	method	value	mark	z(targ)	remarks
2108	OEKOTEX	0.354		-----	
2115	EPA8141B	n.d.		-----	
2129		-----		-----	
2132	In house	0.11		-----	
2139	In house	0.06		-----	
2165	In house	<0.5		-----	
2184	In house	<0.5		-----	
2215	In house	n.d.		-----	
2310	In house	n.d.		-----	
2358	In house	n.d.		-----	
2363	In house	n.d.		-----	
2365	In house	n.d.		-----	
2370	In house	n.d.		-----	
2372		-----		-----	
2375	EPA	n.d.		-----	
2379	In house	n.d.		-----	
3117	GB/T 18412.1	0.0219		-----	
3159	In house	<0.5		-----	
3172		-----		-----	
3179	In house	<0.1		-----	
3180		-----		-----	
3226	In house	0.4643		-----	
	normality	n.a.			
	n	5			
	outliers	0			
	mean (n)	0.202			
	st.dev. (n)	0.1956			
	R(calc.)	0.548			
	R(lit)	unknown			

Determination of α-Endosulfan on sample #1006; results in mg/kg

lab	method	value	mark	z(targ)	remarks
2108	OEKOTEX	4.67	G(0.01)	7.30	
2115	OEKOTEX	2.94		1.97	
2129	In house	2.2	C	-0.31	First reported 1.1
2132	In house	2.77	C	1.45	First reported 3.93
2139	In house	1.49		-2.50	
2165	In house	2.1		-0.62	
2184	In house	2.3		0.00	
2215	In house	2.42		0.37	
2310	In house	2.25		-0.15	
2358	In house	2.478		0.55	
2363	In house	2.343		0.13	
2365	In house	2.451		0.46	
2370	In house	2.350		0.15	
2372		-----		-----	
2375	EPA	2.53		0.71	
2379	In house	2.449		0.46	
3117	GB/T 18412.1	1.0511	G(0.05)	-3.85	
3159	In house	2.24		-0.19	
3172		-----		-----	
3179	In house	2.1	C	-0.62	First reported <0.1
3180		1.7		-1.85	
3226	In house	2.292		-0.03	

normality	OK
n	18
outliers	2
mean (n)	2.300
st.dev. (n)	0.3335
R(calc.)	0.934
R(Horwitz)	0.909

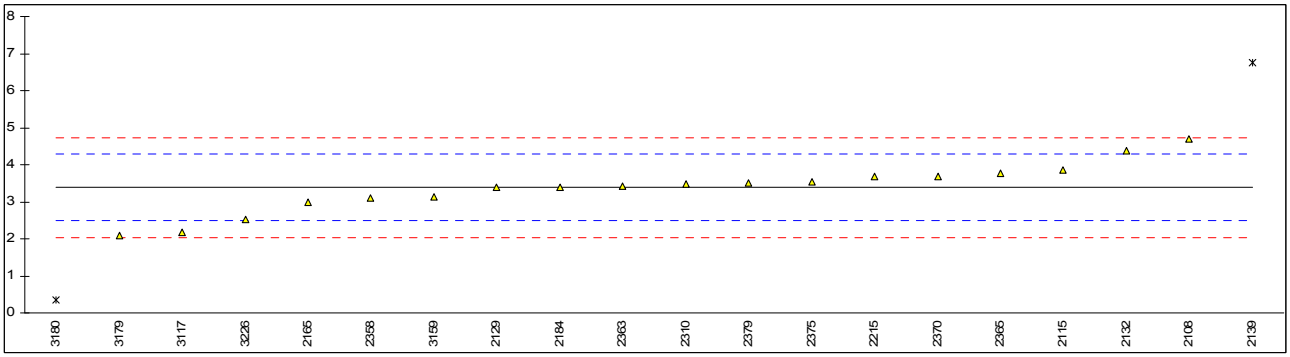


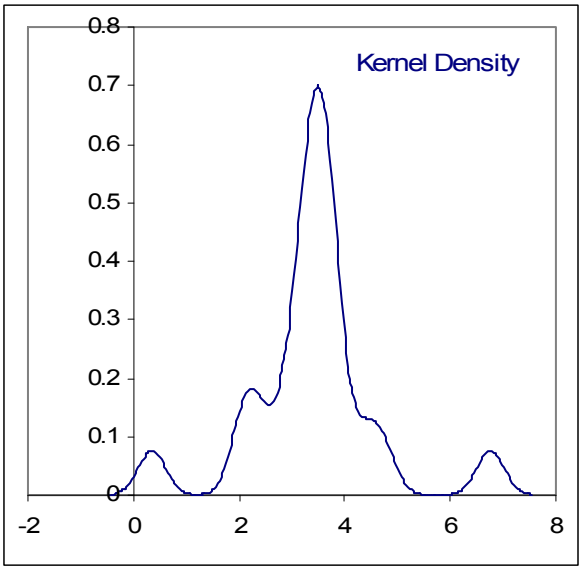


Determination of β-Endosulfan on sample #1006; results in mg/kg

lab	method	value	mark	z(targ)	remarks
2108	OEKOTEX	4.71		2.95	
2115	OEKOTEX	3.86		1.07	
2129	In house	3.4	C	0.04	First reported 1.1
2132	In house	4.37		2.20	
2139	In house	6.76	G(0.05)	7.51	
2165	In house	3.0		-0.84	
2184	In house	3.4		0.04	
2215	In house	3.68		0.67	
2310	In house	3.47		0.20	
2358	In house	3.112		-0.60	
2363	In house	3.418		0.08	
2365	In house	3.761		0.85	
2370	In house	3.690		0.69	
2372		-----		-----	
2375	EPA	3.53		0.33	
2379	In house	3.505		0.28	
3117	GB/T 18412.1	2.1739		-2.68	
3159	In house	3.13		-0.56	
3172		-----		-----	
3179	In house	2.1	C	-2.84	First reported <0.1
3180		0.35	G(0.01)	-6.73	
3226	In house	2.532		-1.88	

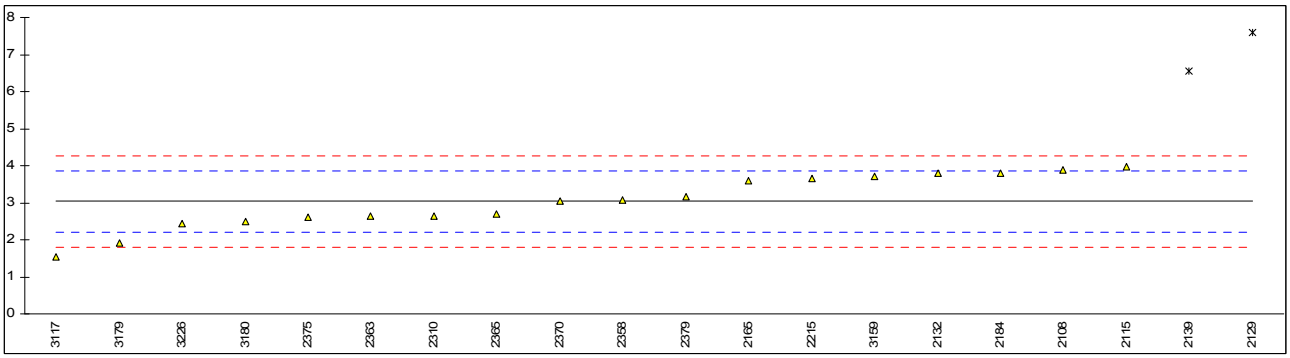
normality	OK
n	18
outliers	2
mean (n)	3.380
st.dev. (n)	0.6620
R(calc.)	1.854
R(Horwitz)	1.261

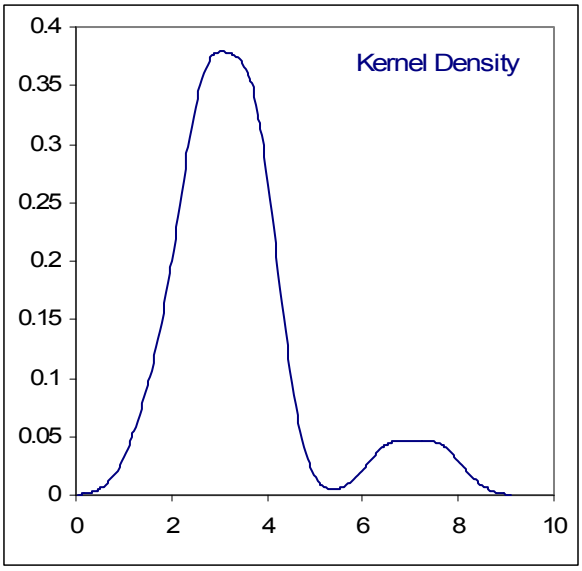




Determination of Quinalfos on sample #1006; results in mg/kg

lab	method	value	mark	z(targ)	remarks
2108	OEKOTEX	3.88		2.06	
2115	OEKOTEX	3.96		2.25	
2129	In house	7.6	CG(0.05)	11.11	First reported 3.4
2132	In house	3.79		1.84	
2139	In house	6.55	G(0.01)	8.56	
2165	In house	3.6	C	1.38	First reported 7.1
2184	In house	3.8	C	1.86	First reported 7.5
2215	In house	3.65		1.50	
2310	In house	2.65		-0.94	
2358	In house	3.059		0.06	
2363	In house	2.643		-0.95	
2365	In house	2.702		-0.81	
2370	In house	3.030		-0.01	
2372		-----		-----	
2375	EPA	2.6		-1.06	
2379	In house	3.161		0.31	
3117	GB/T 18412.1	1.5499		-3.61	
3159	In house	3.72	C	1.67	First reported 100.31
3172		-----		-----	
3179	In house	1.9	C	-2.76	First reported <0.1
3180		2.5		-1.30	
3226	In house	2.428		-1.48	
	normality	OK			
	n	18			
	outliers	2			
	mean (n)	3.035			
	st.dev. (n)	0.7137			
	R(calc.)	1.998			
	R(Horwitz)	1.150			





APPENDIX 2

Details of the methods used by the participants:

Lab	Method	Amount used (g)	Technique to release/extract	Solvent used	Ratio (g/mL)	Time (hrs)	Quantified with
2108	OEKOTEX	5	Soxhlet				
2115	OEKOTEX	2.5	ASE	acetone	1/20	0.25	GC/MS
2129	In house	4	ASE	acetone/Toluene	1/5	0.5	GC/MSD
2132	In house	1	Soxhlet	acetone	1/50	6	GC/ECD, LC/MS
2139	In house	1.5	ASE	hexane/acetone	1/100	0.5	GC/MS, GC/ECD, LC/DAD
2165	In house	1	ultrasonic	hexane	1/5	3	GC/MS
2184	In house	0.5	ultrasonic	hexane/acetone	1/10	2	GC/MS, LC/MS
2215	In house	2	ultrasonic	hexane/acetone	1/50	2*1	GC/MS
2310	In house	2	ultrasonic	hexane/acetone	1/10	1	GC/MS
2358	In house	1	ultrasonic	hexane/acetone	1/10	1	GC/ECD, GC/MS
2363	In house	0.5	ultrasonic	hexane/acetone	1/40	1	GC/ECD, GC/FPD
2365	In house	0.5	ultrasonic	hexane/acetone	1/10	1	GC/ECD. GC/MS
2370	In house	1	ultrasonic	hexane/acetone	1/2	1	GC/MS
2372							
2375	EPA	5		hexane/acetone	1/10	1	GC/MS
2379	In house	1	ultrasonic	hexane/acetone	1/50	1	GC/ECD, GC/FPD
3117	GB/T 18412.1	1	ultrasonic	hex/ethylacetate	1/50	0.5	GC
3159	In house	2.5	ultrasonic	hex/ace/dcm	1/50	1	GC/MS
3172							
3179	In house	0.5	ultrasonic	acetone	1/0.4	0.5	GC/MS
3180		1	ultrasonic	acetone	1/10	1.5	GC/MS
3226	In house	2	ultrasonic	hexane/acetone	1/50	2*0.5	GC/ECD

APPENDIX 3

List of participants on alphabetic country order:

3 laboratories in GERMANY

4 laboratories in HONG KONG

1 laboratory in INDIA

3 laboratories in ITALY

1 laboratory in KOREA

5 laboratories in P.R. of CHINA

1 laboratory in SWITZERLAND

2 laboratories in TAIWAN R.O.C.

1 laboratory in THAILAND

1 laboratory in TURKEY

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

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