Results of Proficiency Test Pesticides in Textile December 2012

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 2012/2013, the institute decided to continue this proficiency test on Pesticides in Textile.
In this 2012 interlaboratory study 22 laboratories in 10 different countries participated. See appendix 4 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 this proficiency test. Sample preparation and analyses were subcontracted to an accredited laboratory.
It was decided to use two different textile samples in this PT, both 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/IEC 17043:2010. This ensures strict adherence to protocols for sample preparation and statistical evaluation and 100% confidentially of participant's data. Feedback from the participants on the reported data is encouraged and customer's satisfaction is measured on regular basis by sending out questionnaires.

2.2 PROTOCOL

The protocol followed in the organisation of this proficiency test was the one as described for proficiency testing in the report 'iis Interlaboratory Studies: Protocol for the Organisation, Statistics and Evaluation' of January 2010 (iis-protocol, version 3.2).

2.3 CONFIDENTIALITY STATEMENT

All data presented in this report must be regarded as confidential and for use by the participating companies only. Disclosure of the information in this report is only allowed by means of the entire report. Use of the contents of this report for third parties is only allowed by written permission of the Institute for Interlaboratory Studies. Disclosure of the identity of one or more of the participating companies will be done only after receipt of a written agreement of the companies involved**.**

2.4 SAMPLES

Two different textile samples, both positive on a number of pesticides, were prepared by a third party. Sample #12160 was a cotton fabric fortified with Cypermethrin, Monocrotophos and Fenvalerate. Sample #12161 was a cotton fabric fortified with Fenvalerate and Cyhalothrin-lambda. The two samples were each cut into pieces, well mixed and divided over 35 subsamples of 5 grams each. The samples were tested for homogeneity by determination of a pesticide in accordance with an in house test method on 4 stratified randomly selected samples. See the following tables for the test results:

	Cypermethrin in mg/kg
Sample #12160-1	188.6
Sample #12160-2	193.8
Sample #12160-3	184.5
Sample #12160-4	190.2

Table 1: homogeneity test results of sub samples #12160

	Fenvalerate in mg/kg
Sample #12161-1	2.34
Sample #12161-2	2.32
Sample #12161-3	2.42
Sample #12161-4	2.29

Table 2: homogeneity test results of sub samples #12161

From the above results of the homogeneity tests, 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:

	Cypermethrin in mg/kg	Fenvalerate in mg/kg
r (observed)	10.8	0.16
reference method	Horwitz	Horwitz
0.3 x R (reference method)	11.6	0.28

Table 3: repeatabilities of the sub samples #12160 and #12161

The calculated repeatabilities were less than 0.3 times the estimated reproducibility calculated using the Horwitz equation. Therefore, homogeneity of subsamples #12160 and #12161 was assumed.
In total approx. 5 grams of each of the samples #12160 and #12161 were sent to the participating laboratories on November 7, 2012.

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.

For each assigned value the uncertainty was determined in accordance with ISO13528. Subsequently the calculated uncertainty was evaluated against the respective requirement based on the target reproducibility in accordance with ISO13528. When the uncertainty passed the evaluation no remarks are made in the report. However, when the uncertainty failed the evaluation it is mentioned in the report and it will have consequences for the evaluation of the test results.

Finally the reproducibilities were calculated from the standard deviations by multiplying them with a factor of 2.8.
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, nos.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 uncertainty (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 uncertainty is not negligible (see appendix 1) the z'-scores were calculated in stead of the usual z-scores.

The $z_{(target)}$ -scores were calculated in accordance with:

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

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

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

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

Absolute values for z<2 are very common and absolute values for z>3 are very rare. The 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.
Four participants did not report any test results. Three other participants reported the test results after the final reporting date. The 18 participants reported 106 numerical test results. Observed were 16 statistical outlying results, which is 15.1% 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 3 and all other positively reported pesticide test results are listed in appendix 2.

Textile #12160:

Cypermethrin: The determination of this pesticide was very problematic at the level of 323 mg/kg. Four statistical outliers were observed. The calculated reproducibility after rejection of the statistical outliers is not at all in agreement with the estimated target reproducibility (Horwitz').

Esfenvalarate: The determination of this pesticide may be problematic at the low level of 0.95 mg/kg. Two statistical outliers were observed. However, the calculated reproducibility after rejection of the statistical outliers is not in agreement with the estimated target reproducibility (Horwitz').

Fenvalerate: The determination of this pesticide may be very problematic at the low level of 1.63 mg/kg. Two statistical outliers were observed. The calculated reproducibility after rejection of the statistical outliers is not at all in agreement with the estimated target reproducibility (Horwitz').

Monocrotophos: The determination of this pesticide may be very problematic at the level of 5.76 mg/kg. Two statistical outliers were observed. The calculated reproducibility after rejection of the statistical outliers is not at all in agreement with the estimated target reproducibility (Horwitz').

Textile #12161:

Esfenvalarate: The determination of this pesticide may be problematic at the low level of 0.65 mg/kg. Two statistical outliers were observed. The calculated reproducibility after rejection of the statistical outliers is not in agreement with the estimated target reproducibility (Horwitz).

Fenvalerate: The determination of this pesticide may be problematic for a number of laboratories at the low level of 1.2 mg/kg. Three statistical outliers were observed. However, the calculated reproducibility after rejection of the statistical outliers is in full agreement with the estimated target reproducibility (Horwitz).

Lambda-cyhalothrin: The determination of this pesticide may be very problematic at the level of 9.17 mg/kg. Two statistical outliers were observed. The calculated reproducibility after rejection of the statistical outliers is not at all in agreement with the 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 or R' (target)*
Cypermethrin	mg/kg	14	323	253	103
Esfenvalerate	mg/kg	9	0.95	1.10	0.62
Fenvalerate	mg/kg	11	1.63	1.28	0.83
Monocrotophos	mg/kg	14	5.76	6.18	2.84

Table 4: reproducibilities of pesticides in sample #12160

Parameter	*Unit*	*n*	*Average*	*2.8 * sd*	*R or R' (target)*
Esfenvalerate	mg/kg	9	0.65	0.40	0.31
Fenvalerate	mg/kg	10	1.18	0.44	0.52
Lambda-cyhalothrin	mg/kg	15	9.17	11.43	4.67

Table 5: reproducibilities of pesticides in sample #12161

Without further statistical calculations it can be concluded that for all determined pesticides the group of participating laboratories has 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 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	Baby	Direct skin contact	With no direct skin contact	Decoration material
Pesticides, total mg/kg	0.5	1.0	1.0	1.0

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 the precision of a Standard Test Method because of the lack of a suitable test method with precision data.

The majority of the participants used in house methods and different standards to quantify the requested components (see appendix 3).
An explanation for the relative large spreads found may be the fact that the purity of available calibration standards may vary strongly. And it is to be expected that the test results of laboratories, that used identical calibrants, will be closer than the test results of laboratories that used a different calibrants. Significant different results for most components were found by two of the three participants that used a calibration standard from Accustandard.
During this proficiency test Fenvalerate was one of the positive components. One must keep in mind that Fenvalerate is a mixture of 4 isomers (R-R, S-S, S-R and R-S). One of the isomers is also known as Esfenvalerate (S-S isomer). So the concentration found for Esfenvalerate cannot be larger than the concentration found for Fenvalerate. Three laboratories reported a higher value for Esfenvalerate than for Fenvalerate which is in principle not possible.

The spreads that were found for the pesticides Monocrotophos, Esfenvalerate and Fenvalerate during the present proficiency test did improve, while the spreads of other pesticides did not improve in comparison with the spreads as observed in the previous rounds. The relative low number of participating laboratories may (partly) explain for the relatively large spreads.

	November 2012	*November 2011*	*November 2010*	*February 2010*	*February 2009*	*February 2008*	*February 2007*
Carbaryl	--	--	146	--	--	--	--
Cyhalothrin-lambda	125	--	114	--	--	99	--
Cypermetrin (=Σ)	78	--	--	41	--	--	77
4,4-DDD	--	--	106-327	--	--	--	--
Deltamethrin	--	33	--	--	--	104	--
Dimethoate	--	--	--	--	98	--	--
α/β-Endosulfan	--	75-93	--	41-55	58	--	59
Fenvalerate	37-78	--	32	--	66-103	90	--
Esfenvalerate	62-115	--	116	--	--	--	--
Malathion	--	--	--	--	--	--	--
Methoxychlor	--	61	78	--	--	40	--
Methylparathion	--	--	--	--	--	--	--
Monocrotophos	107	--	--	--	--	--	207
Parathion	--	--	204	--	--	--	--
Quinalfos	--	67-110	--	66	--	--	79-125

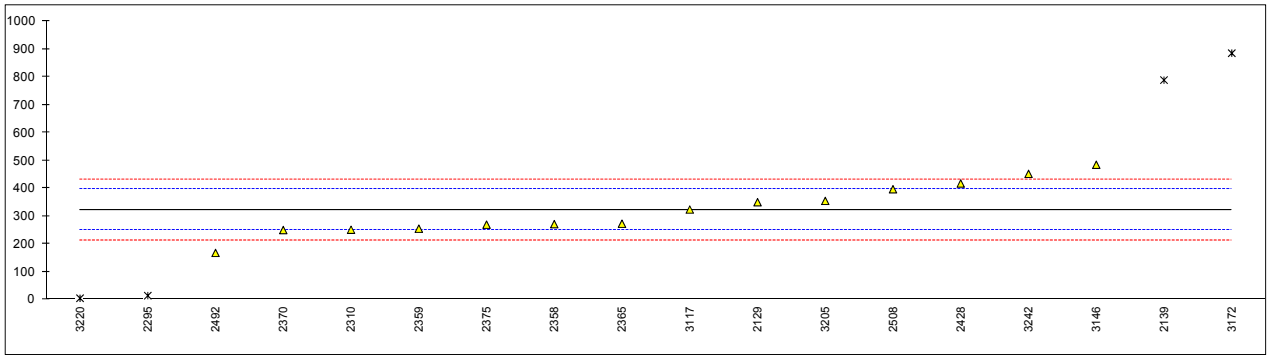
table 7: Comparison of relative standard deviations (RSDs in %) in iis proficiency tests

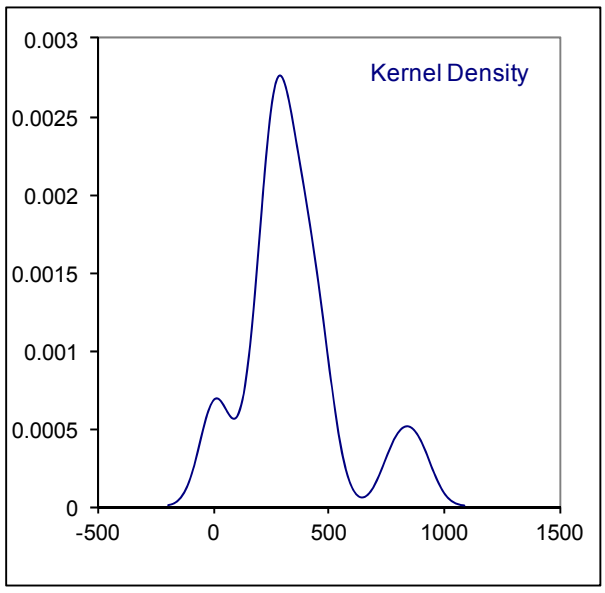
Finally, each laboratory has to evaluate its performance in this study and make decisions about necessary corrective actions. Therefore, participation on a regular basis in this scheme could be helpful to improve the performance and thus improve of the quality of the analytical results.

APPENDIX 1

Determination of Cypermethrin on sample #12160; results in mg/kg

lab	method	value	mark	z'(targ)	remarks
2115		-----		-----	
2129		350.218		0.75	
2139	in house	789.4	DG(0.05)	12.69	
2295	in house	14	DG(0.05)	-8.39	
2310	in house	251		-1.95	
2358	in house	271.4		-1.40	
2359	EPA8081B	255		-1.84	
2365	EPA8081B	272.8		-1.36	
2370	in house	250		-1.98	
2375	INH-210	269.36		-1.45	
2379		-----		-----	
2428	GB/T18412.1&3	417.50		2.58	
2492	OekoTex201	167.87		-4.21	
2493		-----		-----	
2508	DIN38407-2	396.94		2.02	
3117		324.0		0.03	
3146	INH-06	485		4.41	
3172	EPA8081A/GBT18412.1	886.399	DG(0.05)	15.32	
3205	in house	355		0.88	
3218		-----		-----	
3220	in house	4.6	DG(0.05)	-8.65	
3242	in house	452.30		3.52	
	normality	OK			
	n	14			
	outliers	4			
	mean (n)	322.74			
	st.dev. (n)	90.463			
	R(calc.)	253.30			
	R(Horwitz)	60.61			
	R(Horwitz')	102.99			
	U(mean)	29.74			

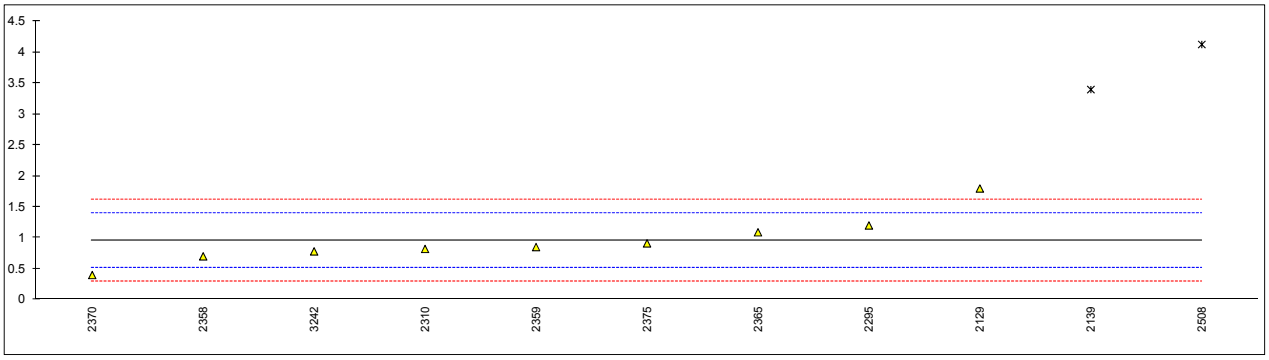


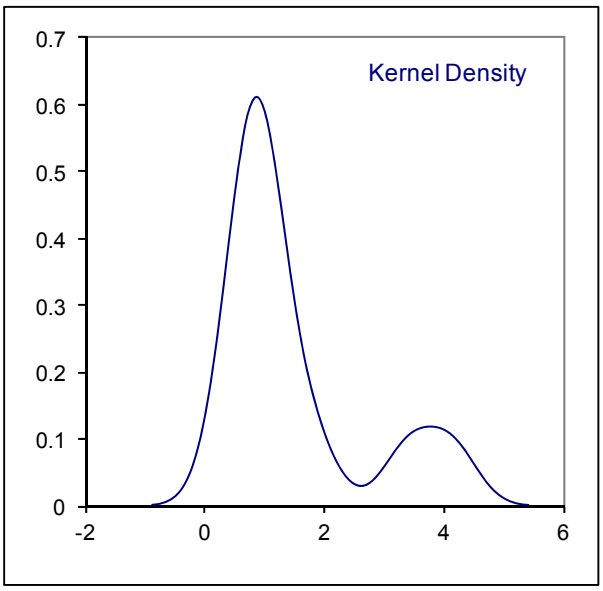


Determination of Esfenvalerate on sample #12160; results in mg/kg

lab	method	value	mark	z'(targ)	remarks
2115		-----		-----	
2129		1.798		3.82	
2139	in house	3.4	DG(0.01)	11.05	
2295	in house	1.2		1.13	
2310	in house	0.82		-0.58	
2358	in house	0.7		-1.13	
2359	EPA8081B	0.85		-0.45	
2365	EPA8081B	1.09		0.63	
2370	in house	0.398		-2.49	
2375	INH-210	0.91		-0.18	
2379		-----		-----	
2428	GB/T18412.1&3	n.d.		-----	
2492	OekoTex201	<1.0		-----	
2493		-----		-----	
2508	DIN38407-2	4.13	DG(0.01)	14.34	
3117		-----		-----	
3146		-----		-----	
3172		-----		-----	
3205	in house	<0.1		-----	
3218		-----		-----	
3220	in house	n.d.		-----	
3242	in house	0.78		-0.76	

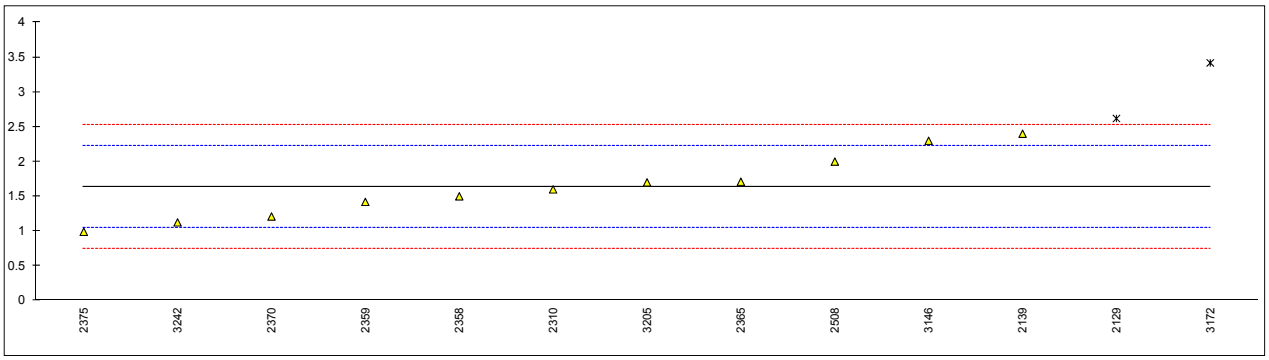
normality	OK
n	9
outliers	2
mean (n)	0.950
st.dev. (n)	0.3914
R(calc.)	1.096
R(Horwitz)	0.429
R(Horwitz')	0.621
U(mean)	0.160

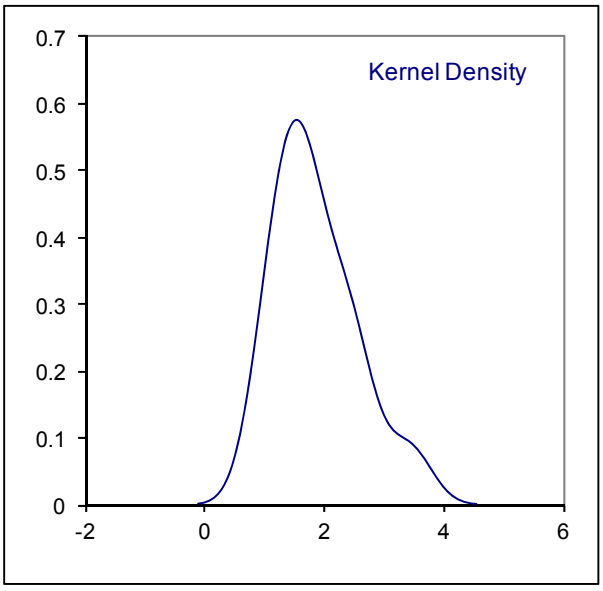




Determination of Fenvalerate on sample #12160; results in mg/kg

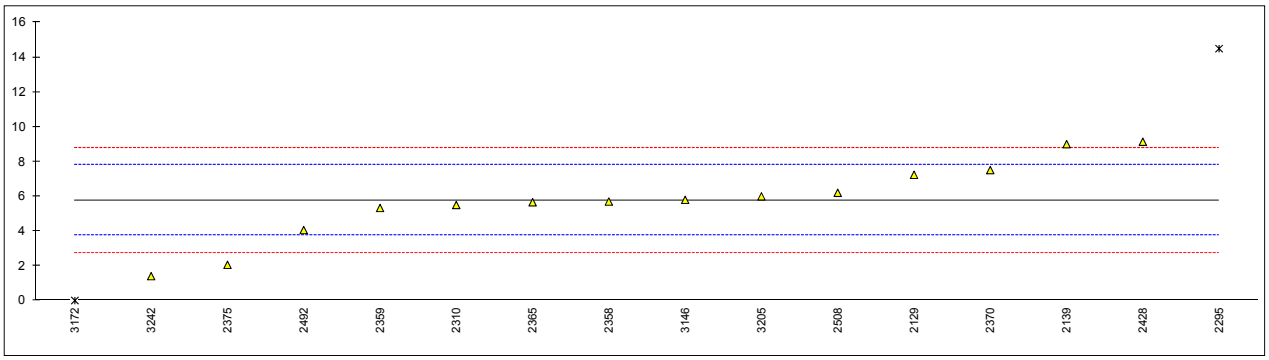
lab	method	value	mark	z'(targ)	remarks
2115		-----		-----	
2129		2.620	C,G(0.05)	3.34	First reported 3.391
2139	in house	2.4		2.59	
2295	in house	n.d.		-----	
2310	in house	1.60		-0.11	
2358	in house	1.5		-0.45	
2359	EPA8081B	1.42		-0.72	
2365	EPA8081B	1.71		0.26	
2370	in house	1.21		-1.43	
2375	INH-210	0.99		-2.17	
2379		-----		-----	
2428	GB/T18412.1&3	n.d.		-----	
2492	OekoTex201	<1.0		-----	
2493		-----		-----	
2508	DIN38407-2	2.0		1.24	
3117		-----		-----	
3146		2.3	C	2.26	Reported as sum esfenvalerate + fenvalerate
3172		3.420	C,G(0.05)	6.04	Reported as sum esfenvalerate + fenvalerate
3205	in house	1.7	C	0.23	First reported 3.4
3218		-----		-----	
3220	in house	n.d.		-----	
3242	in house	1.125		-1.71	
	normality	OK			
	n	11			
	outliers	2			
	mean (n)	1.632			
	st.dev. (n)	0.4575			
	R(calc.)	1.281			
	R(Horwitz)	0.679			
	R(Horwitz')	0.829			
	U(mean)	0.170			

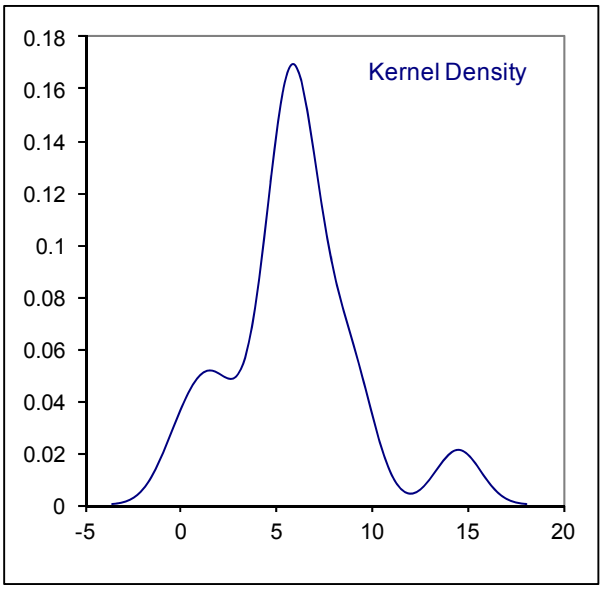




Determination of Monocrotophos on sample #12160; results in mg/kg

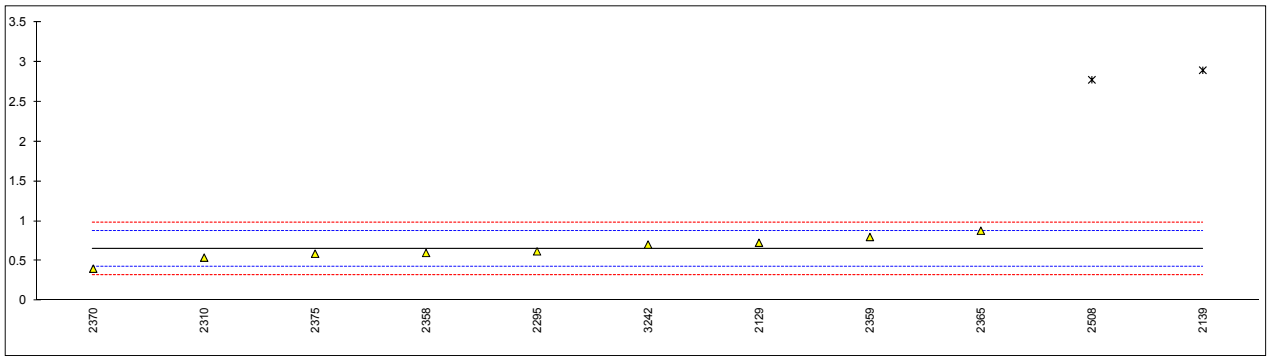
lab	method	value	mark	z'(targ)	remarks
2115		-----		-----	
2129		7.24		1.46	
2139	in house	9.0		3.20	
2295	in house	14.5	G(0.05)	8.63	
2310	in house	5.50		-0.25	
2358	in house	5.7		-0.06	
2359	EPA8081B	5.33		-0.42	
2365	EPA8081B	5.66		-0.10	
2370	in house	7.51		1.73	
2375	INH-210	2.06		-3.65	
2379		-----		-----	
2428	GB/T18412.1&3	9.14		3.34	
2492	OekoTex201	4.06		-1.68	
2493		-----		-----	
2508	DIN38407-2	6.20		0.44	
3117		-----		-----	
3146	INH-06	5.8		0.04	
3172	EPA8081A/GBT18412.1	0	ex	-5.68	Result excluded, zero is not a real result
3205	in house	6.0	C	0.24	First reported 14.6
3218		-----		-----	
3220	in house	n.d.		-----	
3242	in house	1.405		-4.30	
	normality	OK			
	n	14			
	outliers	2			
	mean (n)	5.758			
	st.dev. (n)	2.2056			
	R(calc.)	6.176			
	R(Horwitz)	1.982			
	R(Horwitz')	2.837			
	U(mean)	0.700			

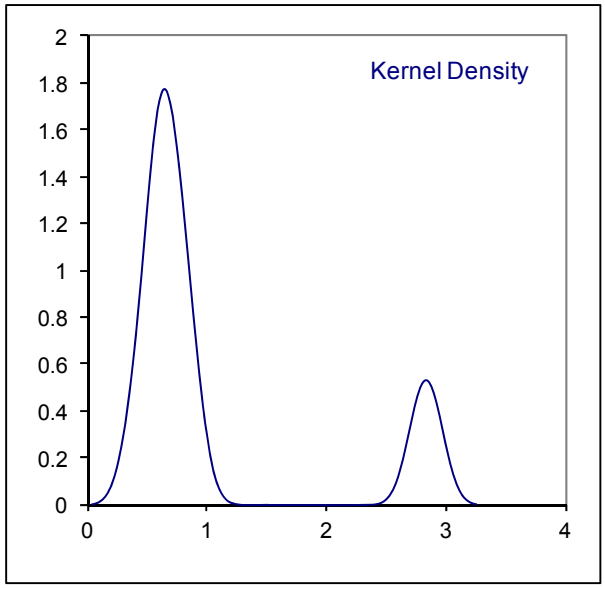




Determination of Esfenvalerate on sample #12161; results in mg/kg

lab	method	value	mark	z(targ)	remarks
2115		-----		-----	
2129		0.728		0.69	
2139	in house	2.9	DG(0.01)	20.22	
2295	in house	0.62		-0.28	
2310	in house	0.54		-1.00	
2358	in house	0.6		-0.46	
2359	EPA8081B	0.80		1.34	
2365	EPA8081B	0.88		2.05	
2370	in house	0.401		-2.25	
2375	INH-210	0.59		-0.55	
2379		-----		-----	
2428	GB/T18412.1&3	n.d.		-----	
2492	OekoTex201	<1.0		-----	
2493		-----		-----	
2508	DIN38407-2	2.78	DG(0.01)	19.14	
3117		-----		-----	
3146		-----		-----	
3172		-----		-----	
3205	in house	<0.1		<-4.97	False negative?
3218		-----		-----	
3220	in house	n.d.		-----	
3242	in house	0.705		0.48	
	normality	OK			
	n	9			
	outliers	2			
	mean (n)	0.652			
	st.dev. (n)	0.1439			
	R(calc.)	0.403			
	R(Horwitz)	0.311			

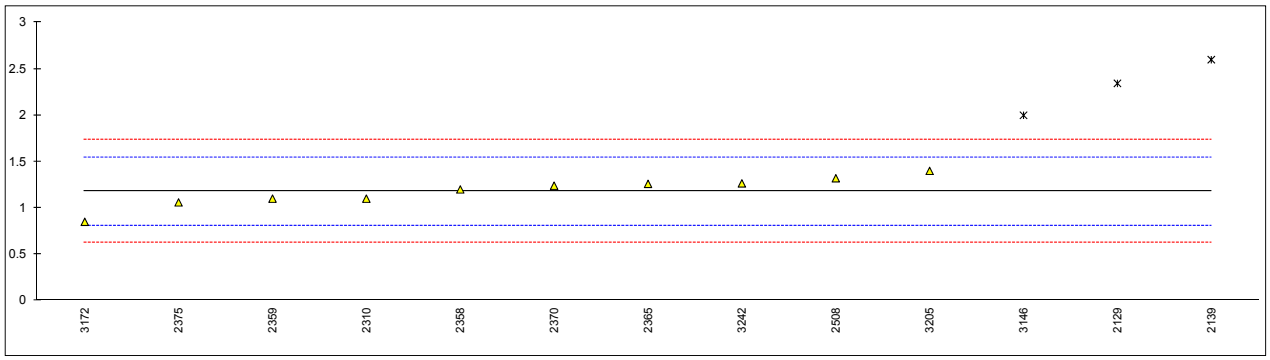


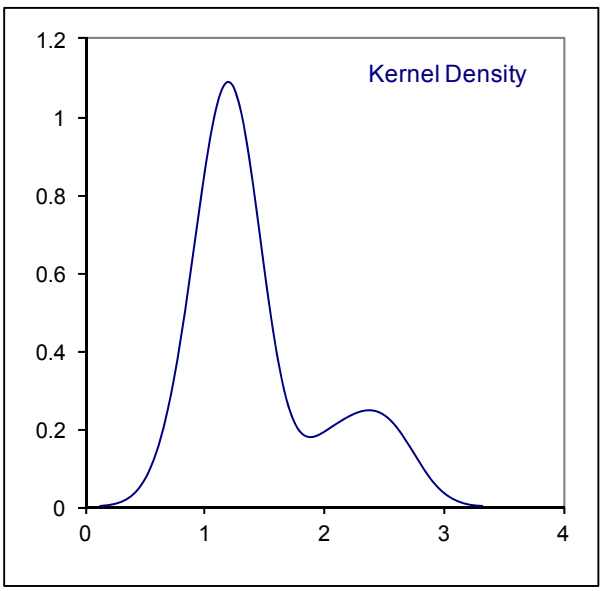


Determination of Fenvalerate on sample #12161; results in mg/kg

lab	method	value	mark	z(targ)	remarks
2115		-----		-----	
2129		2.344	C,DG(0.01)	6.33	First reported 2.163
2139	in house	2.6	DG(0.01)	7.72	
2295	in house	n.d.		-----	
2310	in house	1.10		-0.43	
2358	in house	1.2		0.11	
2359	EPA8081B	1.10		-0.43	
2365	EPA8081B	1.26		0.44	
2370	in house	1.24		0.33	
2375	INH-210	1.06		-0.65	
2379		-----		-----	
2428	GB/T18412.1&3	n.d.		-----	
2492	OekoTex201	<1.0		-----	
2493		-----		-----	
2508	DIN38407-2	1.32		0.76	
3117		-----		-----	
3146		2	C,G(0.01)	4.46	Reported as sum esfenvalerate + fenvalerate
3172		0.85	C	-1.79	Reported as sum esfenvalerate + fenvalerate
3205	in house	1.4	C	1.20	First reported 3.6
3218		-----		-----	
3220	in house	n.d.		-----	
3242	in house	1.265		0.46	

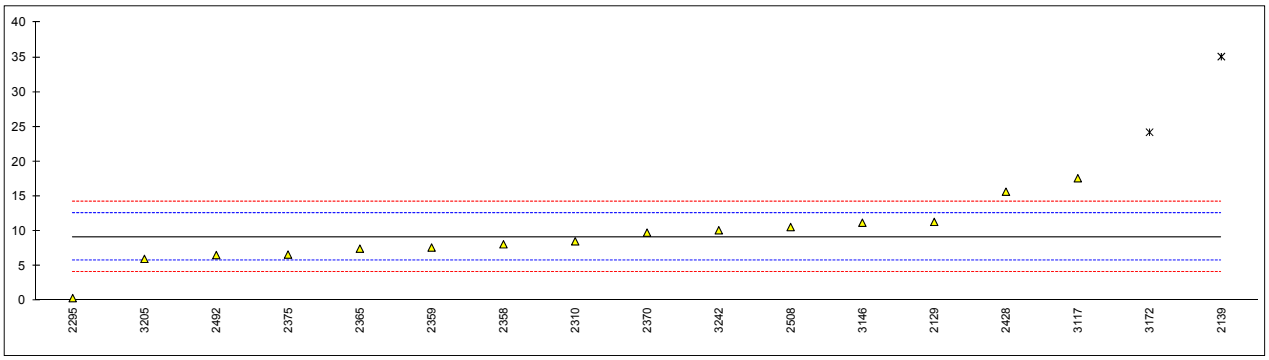
normality	OK
n	10
outliers	3
mean (n)	1.179
st.dev. (n)	0.1570
R(calc.)	0.439
R(Horwitz)	0.515

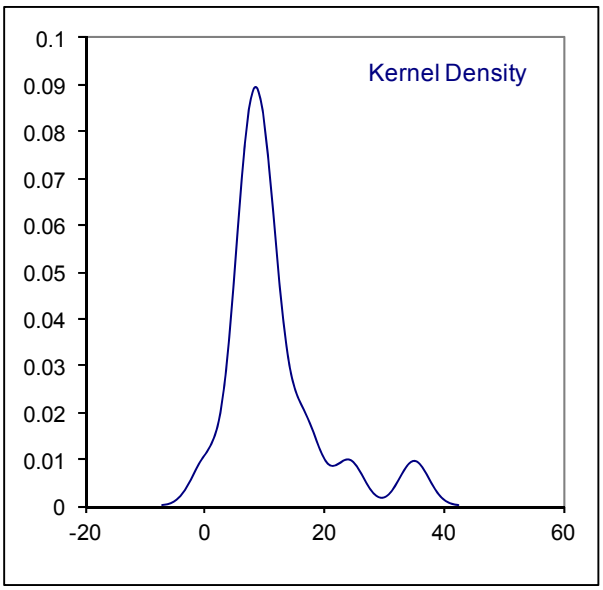




Determination of Lambda-cyhalothrin on sample #12161; results in mg/kg

lab	method	value	mark	z'(targ)	remarks
2115		-----		-----	
2129		11.32		1.29	
2139	in house	35.1	G(0.01)	15.54	
2295	in house	0.35		-5.28	
2310	in house	8.52		-0.39	
2358	in house	8.1		-0.64	
2359	EPA8081B	7.63		-0.92	
2365	EPA8081B	7.47		-1.02	
2370	in house	9.77		0.36	
2375	INH-210	6.61		-1.53	
2379		-----		-----	
2428	GB/T18412.1&3	15.66		3.89	
2492	OekoTex201	6.55		-1.57	
2493		-----		-----	
2508	DIN38407-2	10.58		0.85	
3117		17.6		5.06	
3146	INH-06	11.2		1.22	
3172	EPA8081A/GBT18412.1	24.220	G(0.05)	9.02	
3205	in house	6.0	C	-1.90	First reported 23.6
3218		-----		-----	
3220	in house	n.d.		-----	
3242	in house	10.12		0.57	
	normality	OK			
	n	15			
	outliers	2			
	mean (n)	9.165			
	st.dev. (n)	4.0819			
	R(calc.)	11.429			
	R(Horwitz)	2.942			
	R(Horwitz')	4.672			
	U(mean)	1.296			





APPENDIX 2

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

	#12160				
lab	Deltametrin	Cyhalotrin	λ-cyhalotrin	Parathion	Quinalphos
2115					
2129	<0.1		<0.1	<0.1	0.427
2139					0.2
2295					0.17
2310					
2358					
2359					
2365	<0.05		<0.2	<0.2	<0.2
2370					
2375					
2379					
2428					
2492	<1.0		<1.0	<1.0	<1.0
2493					
2508	0.0	0.0	0.0	0.0	0.0
3117					
3146	<0.5	<0.5	<0.5	<0.5	<0.5
3172		0.130			
3205	<0.1	<0.1	<0.1	<0.05	0.21
3218					
3220					
3242					0.22

	#12161					
lab	Cypermetrin	Deltametrin	Cyhalotrin	Monocroptos	Parathion	Quinalphos
2115						
2129	<0.1	<0.1		<0.1	<0.1	<0.1
2139						0.1
2295						
2310						
2358						
2359						
2365	<0.05	<0.05		<0.2	<0.2	<0.2
2370						
2375						
2379						
2428						
2492	<1.0	<1.0		<1.0	<1.0	<1.0
2493						
2508	0.0	0.0	0.0	0.0	0.0	0.0
3117						
3146	<0.5	<0.5	1.0	<0.5	<0.5	<0.5
3172			0.857			
3205	<0.1	<0.1	<0.1	<0.1	<0.05	0.05
3218						
3220						
3242						

APPENDIX 3

Details of the methods used by the participants:

Lab	component	Brand name	composition	Batch
2115				
2129	Fenvalerate	Dr. Ehrensdorfer	single	00308
	Esfenvalerate	Dr. Ehrensdorfer	single	80429
	Lambda-cyhalothrin	Fluka	single	STE8038X
	Monocrotophos	Dr. Ehrensdorfer	single	10912
	Cypermethrin	Inst.of org. Ind. Chem	mixture	No/ 1F/10
2139	Fenvalerate	Accustd	Single	Lot 212111148
	Esfenvalerate	Accustd	Single	Lot 212081215
	Lambda-cyhalothrin	Accustd	Single	Lot 212061350-01
	Monocrotophos	Accustd	Single	Lot 211041054-05
	Cypermethrin	Accustd	Single	Lot 212071028-01
2295				
2310	Fenvalerate	Accustd	Single	
	Lambda-cyhalothrin	Accustd	Single	
	Monocrotophos	Accustd	Single	
	Cypermethrin	Accustd	Single	
2358	Fenvalerate	Chem service		PS1032
	Lambda-cyhalothrin	Chem service		PS2018
	Monocrotophos	Chem service		PS609
	Cypermethrin	Chem service		PS1068
2359	Fenvalerate	Chem service	Mixture	446-15A
	Lambda-cyhalothrin	Chem service	single	446-94A
	Monocrotophos	Chem service	single	450-149A
	Cypermethrin	Chem service	Mixture	440-85A
2365	Esfenvalerate	Dr. Ehrensdorfer	single	80917
	Fenvalerate	Dr. Ehrensdorfer	Mixture	00308
	Lambda-cyhalothrin	Dr. Ehrensdorfer	single	90506
	Monocrotophos	Dr. Ehrensdorfer	single	10912
	Cypermethrin	Chem service	Mixture	440-85A
2370	Esfenvalerate	Fluka	Mixture	SZB8234XV
	Fenvalerate	Fluka	Mixture	SZB8308XV
	Lambda-cyhalothrin	Fluka	mixture	SZBA200X
2375	Cypermethrin	Dr. Ehrensdorfer		70417
	Esfenvalerate	Dr. Ehrensdorfer	Single	80429
2379				
2428	Pytrethroid	Dr. Ehrensdorfer	Mix of 12	20326CY
	Organophosphorus	Dr. Ehrensdorfer	Mix of 30	10118TO
2492				
2493				
2508	Pest mix 15 + 34	Neochema	mixture	
3117				
3146		Dr. Ehrensdorfer	mixture	All in one, selfmade
3172	Cypermethrin	Accustd	Single	Lot 212021183-01
	Lambda-cyhalothrin	Accustd	Single	Lot 212041156-01
	Fenvalerate			
3205	Monocrotophos	Dr. Ehrensdorfer	single	00914IO
	Mix 192	Dr. Ehrensdorfer	Mixture	10420IO
	Mix 195	Dr. Ehrensdorfer	Mixture	01011IO
3218				
3220		Dr. Ehrensdorfer		
3242				

APPENDIX 4

Number of participants per country

4 labs in	GERMANY
2 labs in	HONG KONG
1 lab in	HUNGARY
3 labs in	INDIA
2 labs in	ITALY
1 lab in	KOREA
5 labs in	P.R. of CHINA
1 lab in	TAIWAN R.O.C.
1 lab in	THAILAND
2 labs in	TURKEY

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:

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9 ISO 5725, (1986)
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