Results of Proficiency Test
Pesticides in Textile
November 2011

Organised by: Institute for Interlaboratory Studies
Spijkenisse, the Netherlands

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Report: iis11A05

February 2012

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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 2011/2012, the institute decided to continue this proficiency test on Pesticides in Textile.
In this interlaboratory study 22 laboratories in 11 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 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 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 different textile samples, both positive on a number of pesticides, were prepared by a third party. Sample #11132 was a cotton fabric fortified with Deltametrin and Methoxychlor. Sample #11133 was a cotton fabric fortified with Endosulfan and Quinalfos. The two samples were each cut into pieces, well mixed and divided over 50 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:

	Deltametrin in mg/kg
Sample #11132-1	13.80
Sample #11132-2	15.00
Sample #11132-3	14.45
Sample #11132-4	14.55

Table 1: homogeneity test results of sub samples #11132

	Endosulfan in mg/kg
Sample #11133-1	265
Sample #11133-2	279
Sample #11133-3	280
Sample #11133-4	274

Table 2: homogeneity test results of sub samples #11133

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:

	Deltametrin in mg/kg	Endosulfan in mg/kg
r (observed)	1.39	19
reference method	Horwitz	Horwitz
0.3 x R (reference method)	1.30	16

Table 3: repeatabilities of the sub samples #11132 and #11133

The calculated repeatabilities are both somewhat larget than 0.3 x R (ref.), both are well in agreement with the repeatability of the in house test method used.
Therefore, homogeneity of subsamples #11132 and #11133 was assumed.

In total approx. 5 grams of each of the samples #11132 and #11133 were sent to the participating laboratories on November 19, 2011.

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, 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 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:

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

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

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

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. Four other participants reported the test results after the final reporting date. In total 18 of the 22 participants reported 161 numerical test results. Observed were 20 statistical outlying results, which is 12.4% 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: Endosulfan α, Methoxychlor on #11132 and Endosulfan β on sample#11133. 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 #11132:

Deltamethrin: The determination of this pesticide was not problematic at the level of 12 mg/kg. Two statistical outliers were observed. However, the calculated reproducibility after rejection of the statistical outliers is in full agreement with the estimated target reproducibility (Horwitz). One laboratory reported ‘not detected’ for this pesticide, while the other seventeen laboratories reported significantly more than 1 mg/kg.

Endosulfan, α: The determination of this pesticide was problematic at the low level of 0.37 mg/kg. One statistical outlier was observed. However, the calculated reproducibility after rejection of the statistical outlier is not in agreement

with the target reproducibility (Horwitz). Five laboratories reported test results above 0.5 mg/kg, while twelve laboratories reported test results below 0.5 mg/kg.

Endosulfan, β: The determination of this pesticide was very problematic at the low level of 0.45 mg/kg. One statistical outlier was observed. However, the calculated reproducibility after rejection of the statistical outlier is not at all in agreement with the target reproducibility (Horwitz). Ten laboratories reported test results below 0.5 mg/kg, while the other seven laboratories reported more than 0.5 mg/kg.

Methoxychlor: The determination of this pesticide was problematic at the level of 10 mg/kg. Four statistical outliers were observed. The calculated reproducibility after rejection of the statistical outliers is not in agreement with the target reproducibility (Horwitz). Seventeen laboratories reported a test result higher than 1 mg/kg. Only one laboratory reported a test result less than 1 mg/kg.

Quinalfos: The determination of this pesticide was problematic at the level of 1.1 mg/kg. One statistical outlier was observed. The calculated reproducibility after rejection of the statistical outlier is not in agreement with the target reproducibility (Horwitz). Ten laboratories reported a test result higher than 1 mg/kg, five laboratories reported test results less than 1 mg/kg and more than 0.5 mg/kg and two other laboratories reported less than 0.5 mg/kg.

Textile #11133:

Endosulfan, α: The determination of this pesticide was very problematic at the level of 50 mg/kg. Three statistical outliers were observed and the calculated reproducibility after rejection of the statistical outliers is not at all in agreement with the target reproducibility (Horwitz').

Endosulfan, β: The determination of this pesticide was very problematic at the level of 57 mg/kg. Four statistical outliers were observed and the calculated reproducibility after rejection of the statistical outliers is not at all in agreement with the target reproducibility (Horwitz').

Quinalfos: The determination of this pesticide was very problematic at the level of 49 mg/kg. Four statistical outliers were observed. The calculated reproducibility after rejection of the statistical outliers is not at all in agreement with the 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)*
Deltamethrin	mg/kg	15	11.68	3.80	3.61
Endosulfan, α	mg/kg	17	0.37	0.42	0.19
Endosulfan, β	mg/kg	17	0.45	0.63	0.23
Endosulfan, α + β	mg/kg	17	0.82	0.99	0.53
Methoxychlor	mg/kg	14	10.05	6.17	3.18
Quinalfos	mg/kg	16	1.14	1.25	0.50

Table 4: reproducibilities of pesticides in sample #11132

Parameter	*Unit*	*n*	*Average*	*2.8 * sd*	*R (target)*
Endosulfan, α	mg/kg	15	50.44	46.68	19.41
Endosulfan, β	mg/kg	13	56.72	42.28	19.61
Endosulfan, α + β	mg/kg	16	111.56	108.97	48.28
Quinalfos	mg/kg	13	49.26	32.82	16.61

Table 5: reproducibilities of pesticides in sample #11133

Without further statistical calculations it can be concluded that for all determined pesticides, except Deltamethrin, 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 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 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.

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 single change in the analysis.
When evaluating the given details of the test method, it was concluded that there is no clear relation between the details and the test results as reported by the participants.

The spreads that were found for the pesticides during the present proficiency test did not improve much, compared with the spreads as observed in the previous rounds, except for Deltamethrin and Methoxychlor. The lower concentration levels of these pesticides may be the reason for this. Also the relative low number of participating laboratories may (partly) explain for the relatively large spreads. Summarizing the test results for α and β Endosulfan for sample #11132 and #11133 as well did not improve the spreads.

	November 2011	*November 2010*	*February 2010*	*February 2009*	*February 2008*	*February 2007*	*February 2006*
Carbaryl	--	146	--	--	--	--	--
Cyhalothrin-lambda	--	114	--	--	99	--	--
Cypermetrin (=Σ)	--	--	41	--	--	77	--
4,4-DDD	--	106-327	--	--	--	--	--
Deltamethrin	33	--	--	--	104	--	--
Dimethoate	--	--	--	98	--	--	110-176
α/β-Endosulfan	75-93	--	41-55	58	--	59	--
Fenvalerate	--	32	--	66-103	90	--	52
Esfenvalerate	--	116	--	--	--	--	--
Malathion	--	--	--	--	--	--	206–214
Methoxychlor	61	78	--	--	40	--	--
Methylparathion	--	--	--	--	--	--	144-165
Monocrotophos	--	--	--	--	--	207	--
Parathion	--	204	--	--	--	--	--
Quinalfos	67-110	--	66	--	--	79-125	--

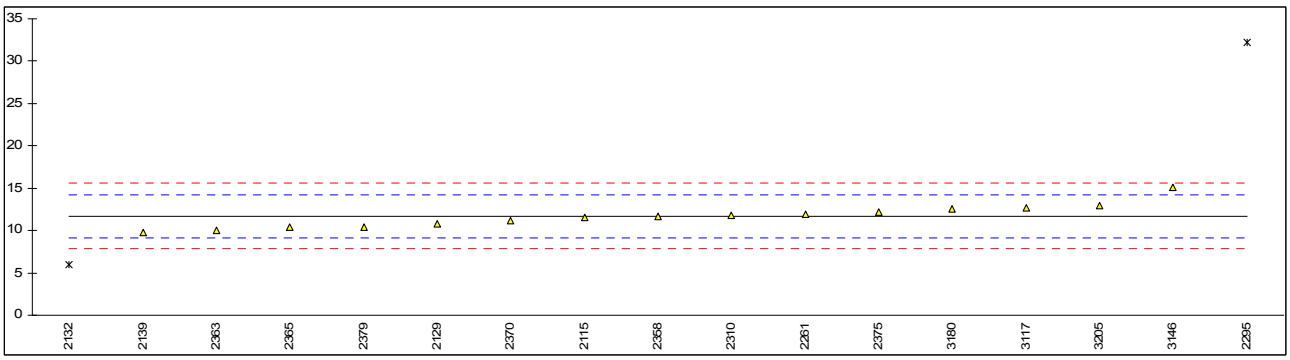
table 7: Comparison of relative standard deviations (RSDs in %) in iis proficiency tests

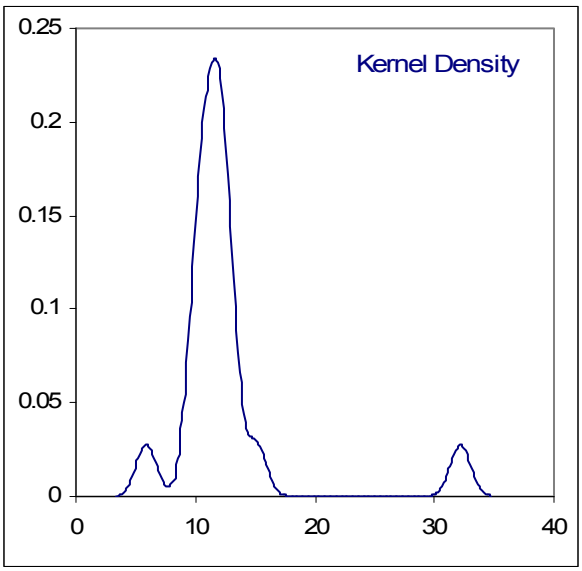
Finally, each laboratory has to evaluate its performance in this study and make decisions about necessary corrective actions. Therefore, participation on a regular basis in this scheme could be helpful to improve the performance and thus improve of the quality of the analytical results.

APPENDIX 1

Determination of Deltamethrin on sample #11132; results in mg/kg

lab	method	value	mark	z(targ)	remarks
1179		-----		-----	
2115	OEKO-TEX	11.57		-0.08	
2129	in house	10.8	C	-0.68	First reported 21.104
2132	in house	5.905	C,G(0.05)	-4.47	First reported 5.215
2139	in house/OEKO-TEX	9.8		-1.45	
2172		-----		-----	
2261	GB/T18412.1	11.91		0.18	
2295	in house	32.18	C,G(0.01)	15.89	First reported 3.218
2310	in house	11.78		0.08	
2358	in house	11.7		0.02	
2363	EPA8081B	10.05		-1.26	
2365	EPA8081B	10.44		-0.96	
2370	EPA8081B	11.1		-0.45	
2375	in house	12.21		0.41	
2379	EPA8081B/8270D	10.46		-0.94	
3117	GB/T18412.1&18412.4	12.74		0.82	
3146	DIN38407Mod.	15.1		2.65	
3163		-----		-----	
3172		-----		-----	
3180	in house	12.6		0.71	
3205	in house	12.9		0.95	
3220	in house	n.d.		-----	
	normality	OK			
	n	15			
	outliers	2			
	mean (n)	11.677			
	st.dev. (n)	1.3585			
	R(calc.)	3.804			
	R(Horwitz)	3.614			

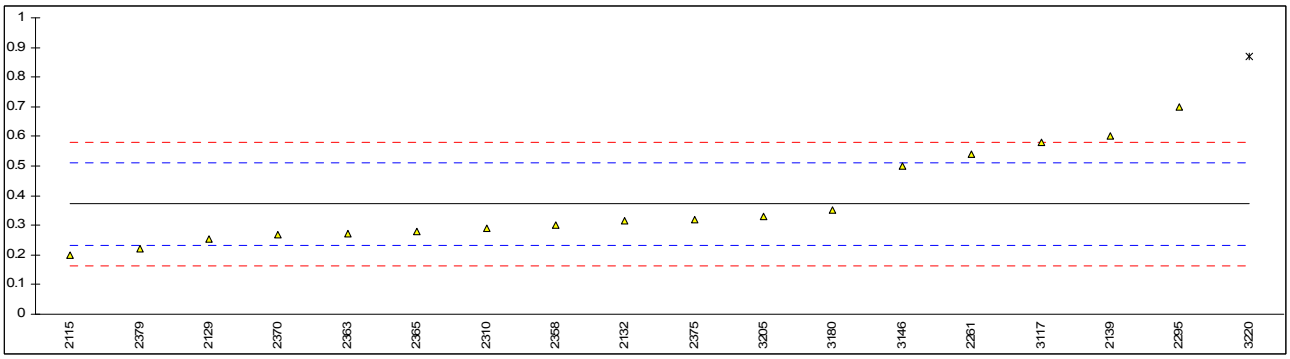


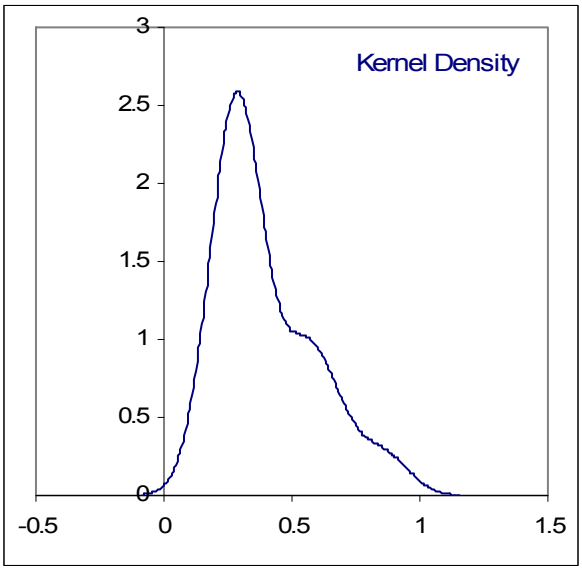


Determination of Endosulfan, α on sample #11132; results in mg/kg

lab	method	value	mark	z(targ)	remarks
1179		-----		-----	
2115	OEKO-TEX	0.20		-2.49	
2129	in house	0.253		-1.72	
2132	in house	0.315		-0.82	
2139	in house/OEKO-TEX	0.6		3.31	
2172		-----		-----	
2261	GB/T18412.1	0.54		2.44	
2295	in house	0.7	C	4.76	First reported 0.070
2310	in house	0.29		-1.18	
2358	in house	0.30		-1.04	
2363	EPA8081B	0.27		-1.47	
2365	EPA8081B	0.28		-1.33	
2370	EPA8081B	0.268		-1.50	
2375	in house	0.32		-0.75	
2379	EPA8081B/8270D	0.22		-2.20	
3117	GB/T18412.1&18412.4	0.58		3.02	
3146	DIN38407Mod.	0.50		1.86	
3163		-----		-----	
3172		-----		-----	
3180	in house	0.35		-0.31	
3205	in house	0.33		-0.60	
3220	in house	0.87	G(0.05)	7.22	

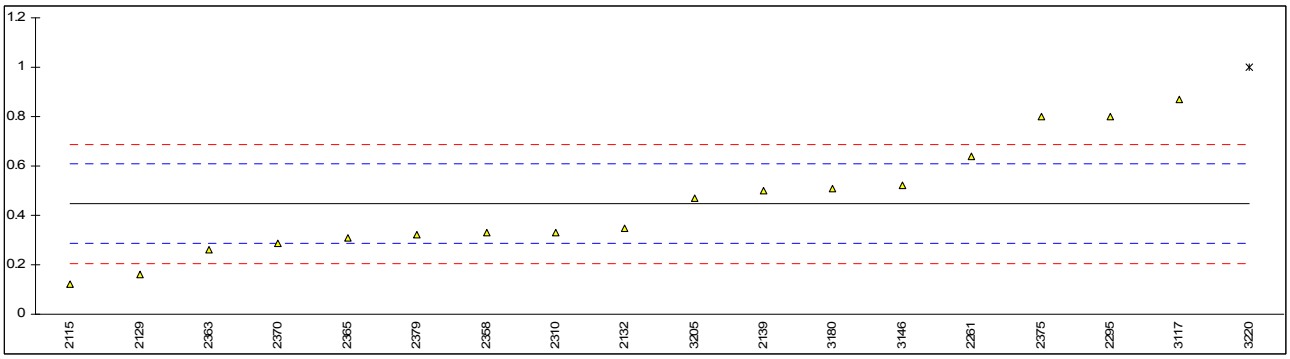
normality	not OK
n	17
outliers	1
mean (n)	0.372
st.dev. (n)	0.1508
R(calc.)	0.422
R(Horwitz)	0.193

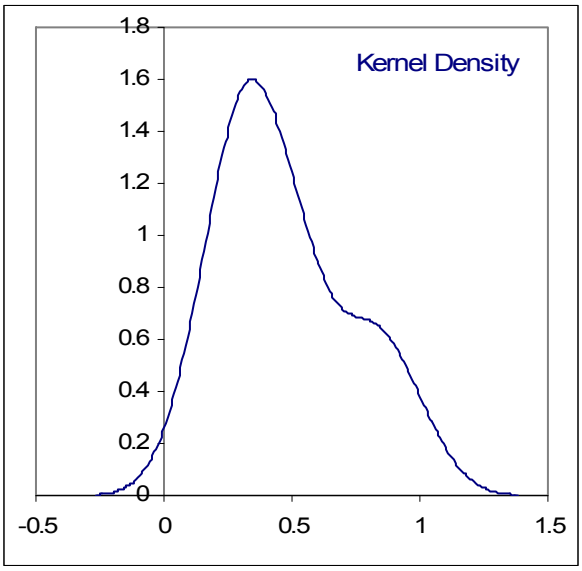




Determination of Endosulfan, β on sample #11132; results in mg/kg

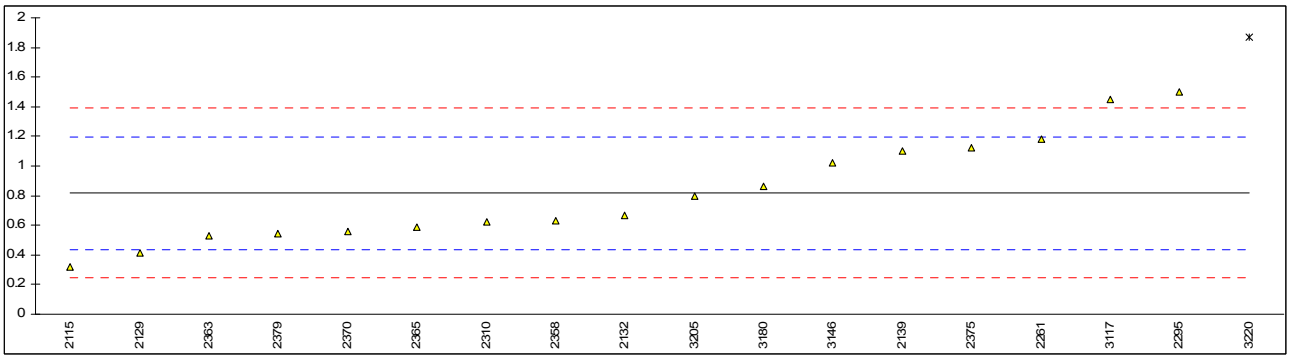
lab	method	value	mark	z(targ)	remarks
1179		-----		-----	
2115	OEKO-TEX	0.12		-4.05	
2129	in house	0.163		-3.51	
2132	in house	0.350		-1.19	
2139	in house/OEKO-TEX	0.5		0.67	
2172		-----		-----	
2261	GB/T18412.1	0.64		2.41	
2295	in house	0.8	C	4.39	First reported 0.08
2310	in house	0.33		-1.44	
2358	in house	0.33		-1.44	
2363	EPA8081B	0.26		-2.31	
2365	EPA8081B	0.31		-1.69	
2370	EPA8081B	0.289		-1.95	
2375	in house	0.80		4.39	
2379	EPA8081B/8270D	0.32		-1.56	
3117	GB/T18412.1&18412.4	0.87		5.26	
3146	DIN38407Mod.	0.52		0.92	
3163		-----		-----	
3172		-----		-----	
3180	in house	0.51		0.79	
3205	in house	0.47		0.30	
3220	in house	1.0	G(0.05)	6.88	
	normality	OK			
	n	17			
	outliers	1			
	mean (n)	0.446			
	st.dev. (n)	0.2232			
	R(calc.)	0.625			
	R(Horwitz)	0.226			

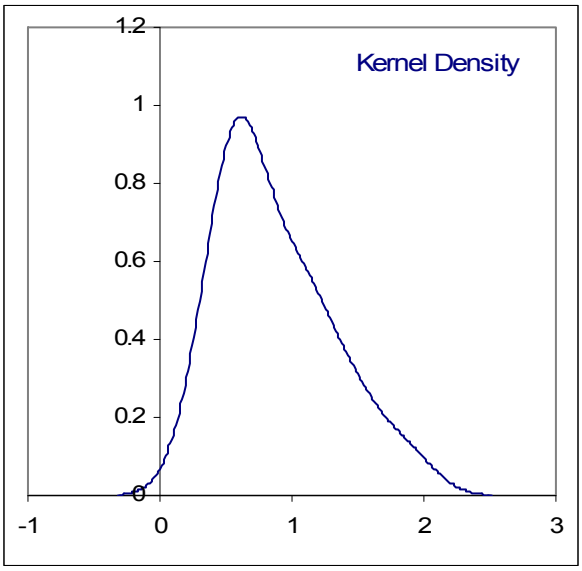




Determination of Endosulfan, α + β on sample #11132; results in mg/kg

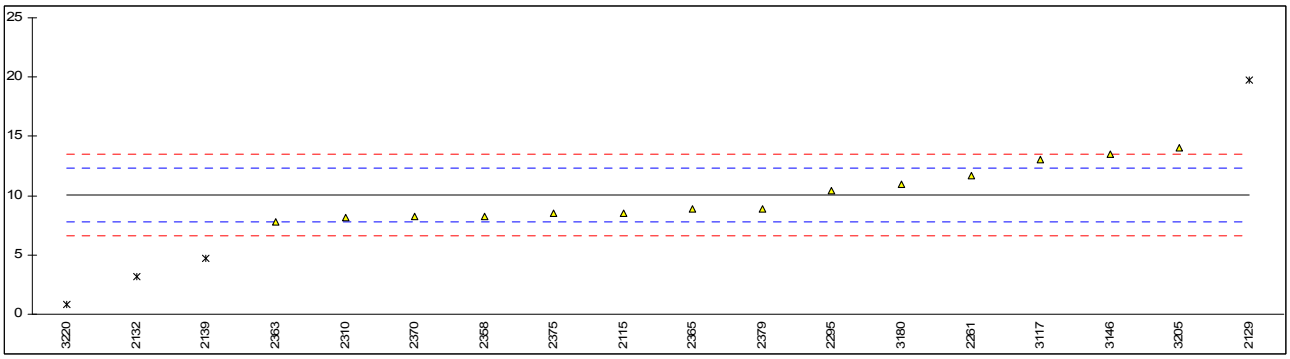
lab	method	value	mark	z(targ)	remarks
1179		-----		-----	
2115	OEKO-TEX	0.32		-2.61	
2129	in house	0.416		-2.11	
2132	in house	0.665		-0.80	
2139	in house/OEKO-TEX	1.1		1.48	
2172		-----		-----	
2261	GB/T18412.1	1.18		1.90	
2295	in house	1.5		3.58	
2310	in house	0.62		-1.04	
2358	in house	0.63		-0.98	
2363	EPA8081B	0.53		-1.51	
2365	EPA8081B	0.59		-1.19	
2370	EPA8081B	0.557		-1.37	
2375	in house	1.12		1.59	
2379	EPA8081B/8270D	0.54		-1.46	
3117	GB/T18412.1&18412.4	1.45		3.32	
3146	DIN38407Mod.	1.02		1.06	
3163		-----		-----	
3172		-----		-----	
3180	in house	0.86		0.22	
3205	in house	0.8		-0.09	
3220	in house	1.87	G(0.05)	5.52	
	normality	OK			
	n	17			
	outliers	1			
	mean (n)	0.818			
	st.dev. (n)	0.3533			
	R(calc.)	0.989			
	R(Horwitz)	0.534			

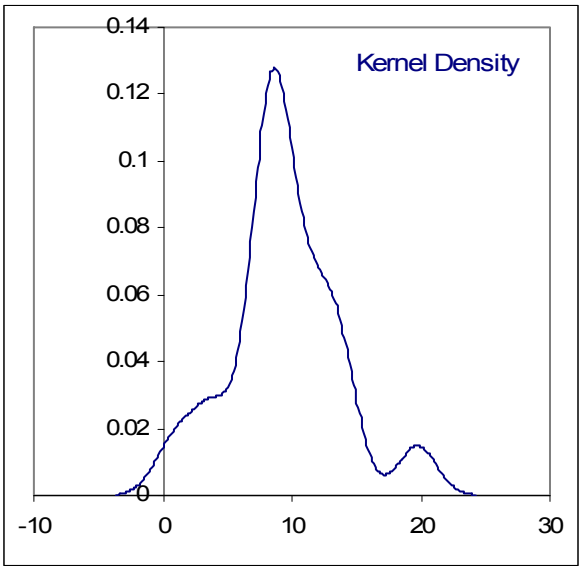




Determination of Methoxychlor on sample #11132; results in mg/kg

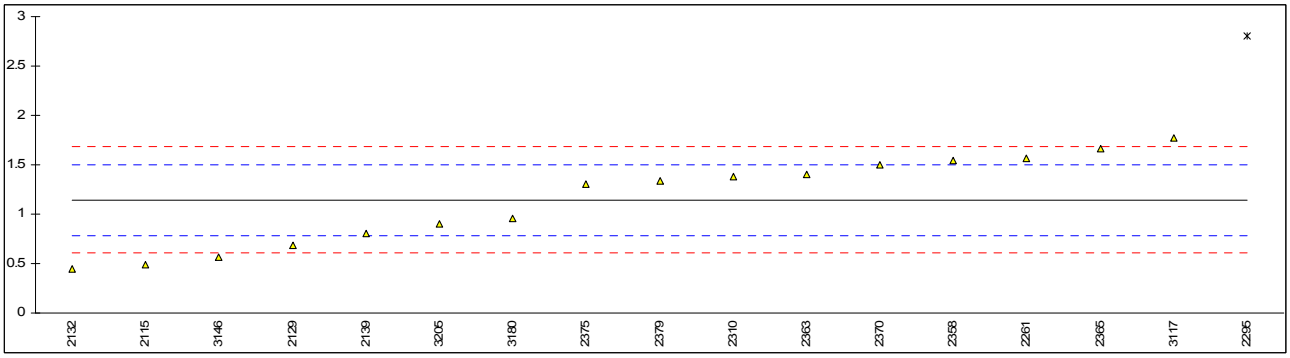
lab	method	value	mark	z(targ)	remarks
1179		-----		-----	
2115	OEKO-TEX	8.51		-1.36	
2129	in house	19.73	G(0.05)	8.51	
2132	in house	3.185	G(0.05)	-6.04	
2139	in house/OEKO-TEX	4.7	G(0.05)	-4.71	
2172		-----		-----	
2261	GB/T18412.1	11.70		1.45	
2295	in house	10.41	C	0.31	First reported 1.041
2310	in house	8.12		-1.70	
2358	in house	8.24		-1.60	
2363	EPA8081B	7.81		-1.97	
2365	EPA8081B	8.84		-1.07	
2370	EPA8081B	8.23		-1.61	
2375	in house	8.47		-1.39	
2379	EPA8081B/8270D	8.89		-1.02	
3117	GB/T18412.1&18412.4	13.04		2.63	
3146	DIN38407Mod.	13.5		3.03	
3163		-----		-----	
3172		-----		-----	
3180	in house	11.0		0.83	
3205	in house	14.0		3.47	
3220	in house	0.8	G(0.05)	-8.14	
	normality	not OK			
	n	14			
	outliers	4			
	mean (n)	10.054			
	st.dev. (n)	2.2050			
	R(calc.)	6.174			
	R(Horwitz)	3.182			

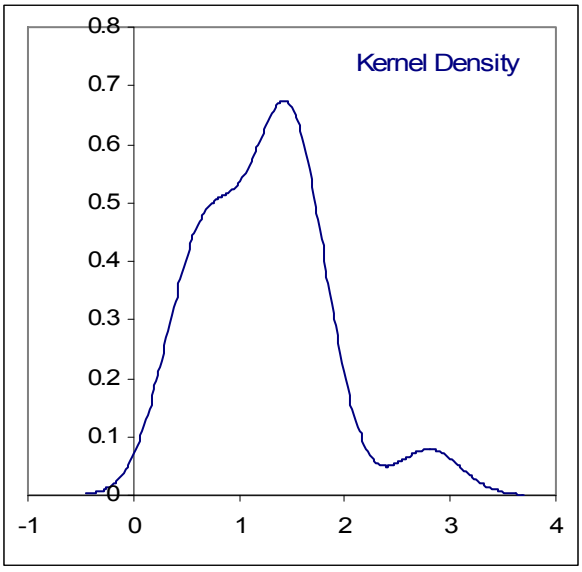




Determination of Quinalfos on sample #11132; results in mg/kg

lab	method	value	mark	z(targ)	remarks
1179		-----		-----	
2115	OEKO-TEX	0.49		-3.65	
2129	in house	0.690		-2.53	
2132	in house	0.450		-3.87	
2139	in house/OEKO-TEX	0.8		-1.92	
2172		-----		-----	
2261	GB/T18412.1	1.56		2.32	
2295	in house	2.8	C,G(0.05)	9.24	First reported 0.280
2310	in house	1.38		1.32	
2358	in house	1.54		2.21	
2363	EPA8081B	1.40		1.43	
2365	EPA8081B	1.66		2.88	
2370	EPA8081B	1.50		1.99	
2375	in house	1.30		0.87	
2379	EPA8081B/8270D	1.34		1.09	
3117	GB/T18412.1&18412.4	1.77		3.49	
3146	DIN38407Mod.	0.56		-3.26	
3163		-----		-----	
3172		-----		-----	
3180	in house	0.96		-1.02	
3205	in house	0.90		-1.36	
3220	in house	n.d.		-----	
	normality	OK			
	n	16			
	outliers	1			
	mean (n)	1.144			
	st.dev. (n)	0.4447			
	R(calc.)	1.245			
	R(Horwitz)	0.502			

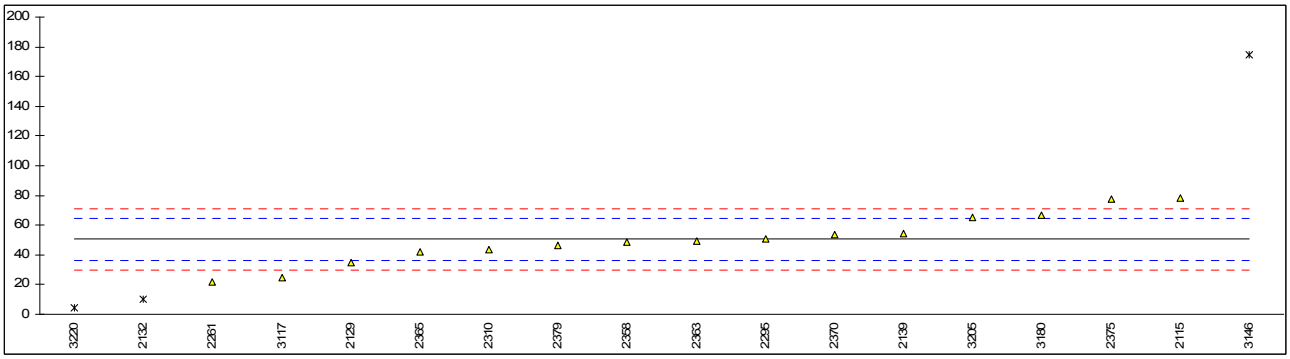


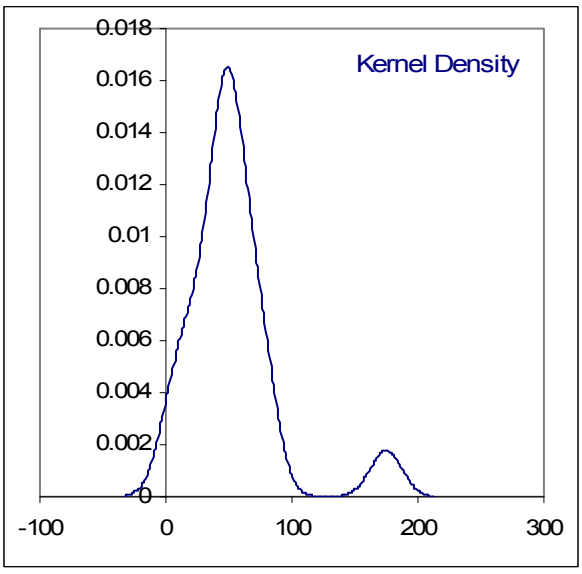


Determination of Endosulfan, α on sample #11133; results in mg/kg

lab	method	value	mark	z'(targ)	remarks
1179		-----		-----	
2115	OEKO-TEX	78.17		4.00	
2129	in house	35.131		-2.21	
2132	in house	9.865	G(0.05)	-5.85	
2139	in house/OEKO-TEX	54.1		0.53	
2172		-----		-----	
2261	GB/T18412.1	21.47		-4.18	
2295	in house	50.55	C	0.02	First reported 5.055
2310	in house	43.8		-0.96	
2358	in house	48.2		-0.32	
2363	EPA8081B	49.29		-0.17	
2365	EPA8081B	42.04		-1.21	
2370	EPA8081B	53.4		0.43	
2375	in house	77.35		3.88	
2379	EPA8081B/8270D	46.45		-0.58	
3117	GB/T18412.1&18412.4	24.50		-3.74	
3146	DIN38407Mod.	175	G(0.01)	17.97	
3163		-----		-----	
3172		-----		-----	
3180	in house	67.0		2.39	
3205	in house	65.2		2.13	
3220	in house	4.2	G(0.05)	-6.67	

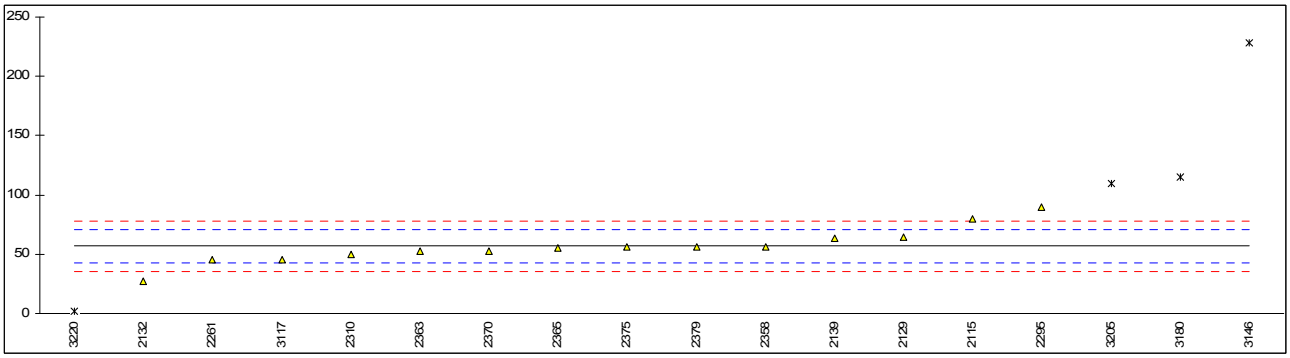
normality	OK
n	15
outliers	3
mean (n)	50.443
st.dev. (n)	16.6707
R(calc.)	46.678
R(Horwitz)	12.525
U(mean)	5.294
R(Horwitz')	19.407

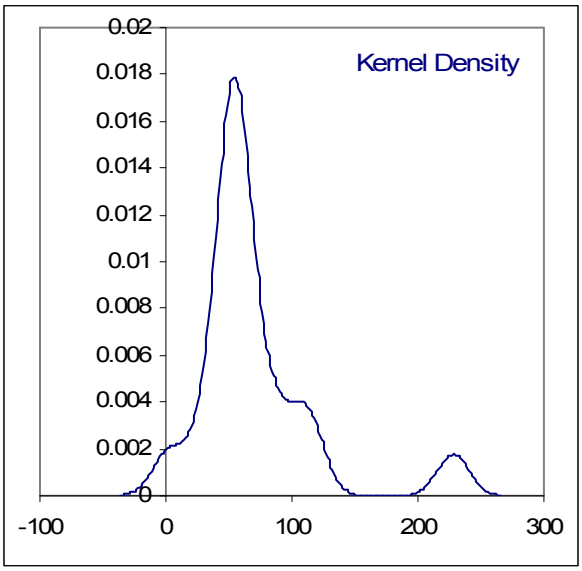




Determination of Endosulfan, β on sample #11133; results in mg/kg

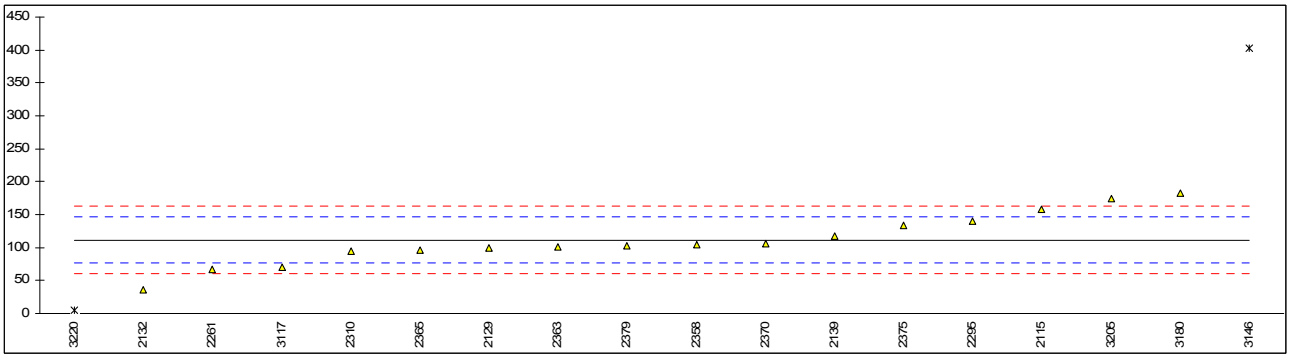
lab	method	value	mark	z'(targ)	remarks
1179		-----		-----	
2115	OEKO-TEX	80.08		3.34	
2129	in house	64.551		1.12	
2132	in house	26.740		-4.28	
2139	in house/OEKO-TEX	63.4		0.95	
2172		-----		-----	
2261	GB/T18412.1	45.19		-1.65	
2295	in house	89.48	C	4.68	First reported 8.948
2310	in house	50.2		-0.93	
2358	in house	56.4		-0.05	
2363	EPA8081B	52.52		-0.60	
2365	EPA8081B	54.93		-0.26	
2370	EPA8081B	52.6		-0.59	
2375	in house	56.13		-0.08	
2379	EPA8081B/8270D	56.38		-0.05	
3117	GB/T18412.1&18412.4	45.47		-1.61	
3146	DIN38407Mod.	228	G(0.01)	24.45	
3163		-----		-----	
3172		-----		-----	
3180	in house	115.0	DG(0.05)	8.32	
3205	in house	109.4	DG(0.05)	7.52	
3220	in house	1.4	G(0.01)	-7.90	
	normality	not OK			
	n	14			
	outliers	4			
	mean (n)	56.719			
	st.dev. (n)	15.0998			
	R(calc.)	42.279			
	R(Horwitz)	13.837			
	U(mean)	4.964			
	R(Horwitz')	19.612			

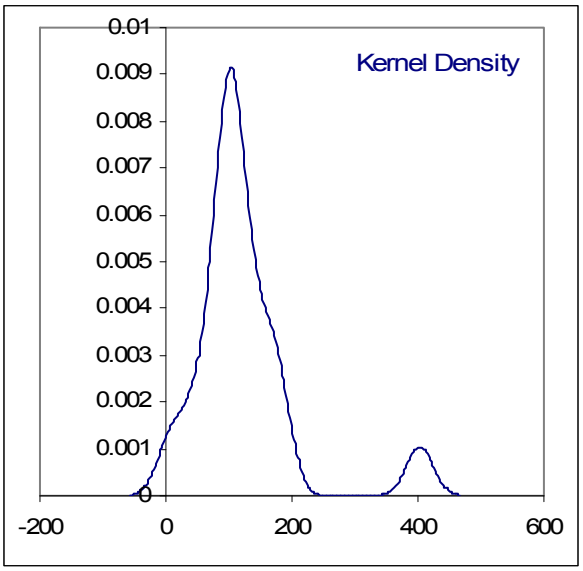




Determination of Endosulfan, α + β on sample #11133; results in mg/kg

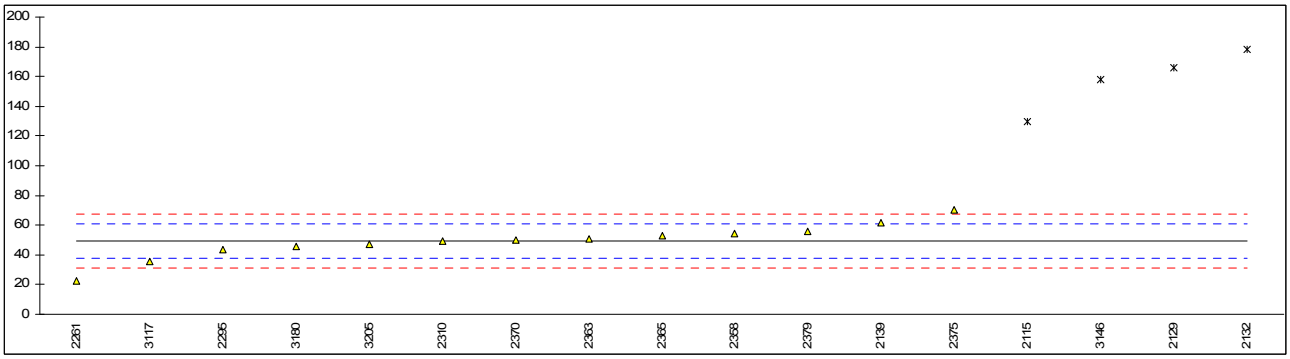
lab	method	value	mark	z'(targ)	remarks
1179		-----		-----	
2115	OEKO-TEX	158.25		2.71	
2129	in house	99.682		-0.69	
2132	in house	36.605		-4.35	
2139	in house/OEKO-TEX	117.5		0.34	
2172		-----		-----	
2261	GB/T18412.1	66.66		-2.60	
2295	in house	140.03		1.65	
2310	in house	94		-1.02	
2358	in house	104.6		-0.40	
2363	EPA8081B	101.81		-0.57	
2365	EPA8081B	96.97		-0.85	
2370	EPA8081B	106		-0.32	
2375	in house	133.48		1.27	
2379	EPA8081B/8270D	102.83		-0.51	
3117	GB/T18412.1&18412.4	69.97		-2.41	
3146	DIN38407Mod.	403	G(0.01)	16.90	
3163		-----		-----	
3172		-----		-----	
3180	in house	182		4.08	
3205	in house	174.6		3.66	
3220	in house	5.6	G(0.05)	-6.14	
	normality	OK			
	n	16			
	outliers	2			
	mean (n)	111.56			
	st.dev. (n)	38.918			
	R(calc.)	108.97			
	R(Horwitz)	34.76			
	U(mean)	11.97			
	R(Horwitz')	48.28			

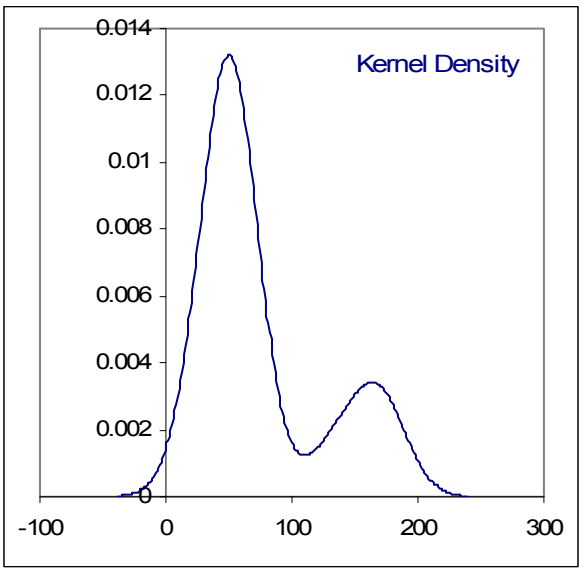




Determination of Quinalfos on sample #11133; results in mg/kg

lab	method	value	mark	z'(targ)	remarks
1179		-----		-----	
2115	OEKO-TEX	129.40	G(0.05)	13.51	
2129	in house	166.265	DG(0.05)	19.72	
2132	in house	178	C,DG(0.05)	21.70	First reported 208.0
2139	in house/OEKO-TEX	61.7		2.10	
2172		-----		-----	
2261	GB/T18412.1	22.52		-4.51	
2295	in house	43.7	C	-0.94	First reported 4.37
2310	in house	49.4		0.02	
2358	in house	54.3		0.85	
2363	EPA8081B	50.93		0.28	
2365	EPA8081B	52.95		0.62	
2370	EPA8081B	50.3		0.18	
2375	in house	70.43		3.57	
2379	EPA8081B/8270D	55.96		1.13	
3117	GB/T18412.1&18412.4	35.32		-2.35	
3146	DIN38407Mod.	158	G(0.01)	18.33	
3163		-----		-----	
3172		-----		-----	
3180	in house	45.5		-0.63	
3205	in house	47.3		-0.33	
3220	in house	n.d		-----	
	normality	OK			
	n	13			
	outliers	4			
	mean (n)	49.255			
	st.dev. (n)	11.7224			
	R(calc.)	32.823			
	R(Horwitz)	12.274			
	U(mean)	3.999			
	R(Horwitz')	16.614			





APPENDIX 2

Summary of all other reported pesticides in sample #11132; results in mg/kg

lab	method
1179	
2115	4,4-DDD = 0.098;
2129	Esfenvalerate = 0.010; Fenvalerate = 0.022;
2132	
2139	
2172	
2261	
2295	Esfenvalerate = 0.50; Fenvalerate = 0.24; Lambda-cyhalotrin = 0.10;
2310	
2358	
2363	
2365	
2370	
2375	
2379	
3117	
3146	
3163	
3172	
3180	
3205	
3220	2,4-DDD = 1.28; 4,4-DDD = 1.3; Esfenvalerate = 2.2; Fenvalerate = 3.7;

Summary of all other reported pesticides in sample #11133; results in mg/kg

lab	Method
1179	
2115	
2129	Fenvalerate = 0.017;
2132	Esfenvalerate = 0.415;
2139	
2172	
2261	
2295	Esfenvalerate = 0.30; lambda-cyhalotrin = 0.07;
2310	
2358	
2363	
2365	
2370	
2375	
2379	
3117	
3146	
3163	
3172	
3180	
3205	
3220	2,4-DDD = 1.3; 4,4-DDD = 1.3; Esfenvalerate = 3.0; Fenvalerate = 3.2; Methoxychlor = 0.9;

APPENDIX 3

Details of the methods used by the participants:

Lab	Method	Technique/solvent	dectection
1179			
2115	OEKO-TEX	ACE/Acetone	GC/MS-MS
2129	in house	Acetone:Acetic Acid (v:v/1000:1)	GC/MSD EI+NCi
2132	in house	ultrasonic/Cyclohexane(GC) & Methanol(LC)	GC/ECD & GC/MS & LC/MS/MS
2139	in house & OEKO-TEX	ultrasonic/Acetone-Hexane	GC/MS & LC/MS/MS
2172			
2261	GB/T 18412.1-2006	Hexane-Ethylacetate (1/1)	MS
2295	in house	ultrasonic/Cyclohexanol	GC/ECD & GC/MS
2310	in house with ref to EPA 8081B	ultrasonic/Acetone-Hexane	GC/MS
2358	in house	ultrasonic/Acetone-Hexane (1:1 v:v)	GC/ECD & GC/MSD
2363	EPA3620C/3630C/8081B	ultrasonic/Acetone-Hexane (1:1 v:v)	ECD & MS
2365	EPA8081B:2007	ultrasonic/Acetone-Hexane (1:1)	GC/ECD & MS (ext.std)
2370	EPA8081B	ultrasonic/Acetone-Hexane (1:1)	GC/MSD
2375	in house/ pest. Ref EPA8081B	Acetone/Hexane (1/1:v/v)	GC/MS & GC/ECD
2379	EPA8081B/8270D	ultrasonic/Acetone-Hexane	ECD & MS
3117	GB/T 18412.1 & 18412.4	ultrasonic/Acetone-Hexane(1:4) & Hexane/Acetate ester(1:1)	GC/MSD
3146	DIN38407 F2 Mod.	ACE/Acetone-Hexane (1:1)	GC/MS
3163			
3172			
3180	in house		GC/MS/MS
3205	in house	ultrasonic/Acetone	GC/ECD & GC/NPD
3220	in house	Hexane	GC/MS

APPENDIX 4

Number of participants per country

3 labs in	GERMANY
2 labs in	HONG KONG
2 labs in	INDIA
2 labs in	ITALY
1 lab in	KOREA
5 labs in	P.R. of CHINA
1 lab in	SWITZERLAND
1 lab in	TAIWAN R.O.C.
1 lab in	THAILAND
2 labs in	THE NETHERLANDS
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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3 Öko-Tex Standard 100; February 2008
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6 Horwitz, Journal of AOAC International Vol. 79 No.3, 1996
7 P.L. Davies, Fr Z. Anal. Chem, 351, 513, (1988)
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9 ISO 5725, (1986)
10 ISO 5725, parts 1-6, (1994)
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 February 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/).