Results of Proficiency Test
Pesticides in Textile
December 2018

Organised by: Institute for Interlaboratory Studies
Spijkenisse, the Netherlands

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1 INTRODUCTION

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 leather, there are some Ecolabelling schemes imposing environmental requirements for textile & leather products on a voluntary basis. Well known organisations are for instance: Bluesign® (Switzerland), which has created a Bluesign® system substances list (BSSL) and Öko-Tex Standard 100 (Switzerland).
Since 2004, the Institute for Interlaboratory Studies (iis) organizes a proficiency scheme for Pesticides in textile, once per two years. During the annual proficiency testing program of 2018/2019, it was decided to continue the proficiency test for the analysis of Pesticides in textile.
In this interlaboratory study 19 laboratories in 12 different countries registered for participation. See appendix 4 for the number of participants per country. In this report, the results of the 2018 proficiency test are presented and discussed. This report is also electronically available through the iis website www.iisnl.com.

2 SET UP

The Institute for Interlaboratory Studies (iis) in Spijkenisse, the Netherlands was the organiser of the proficiency test (PT). Sample analyses for fit-for-use and homogeneity testing were subcontracted to an ISO/IEC 17025 accredited laboratory. It was decided to send two different textile samples of 3 grams each, both positive on pesticides and resp. labelled #18645 and #18646. The participants were requested to report rounded and unrounded test results. The unrounded test 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/IEC/17043:2010. This ensures strict adherence to protocols for sample preparation and statistical evaluation and 100% confidentiality 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 June 2018 (iis-protocol, version 3.5). This protocol is electronically available through the iis website www.iisnl.com, from the FAQ page.

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 pesticides, were prepared by a third party. Sample #18645 (dark blue cotton) and sample #18646 (beige cotton) were both positive on alpha- and beta-Endosulfan and Quinalphos. Per sample the batch was cut into pieces, well mixed and divided over 30 subsamples of 3 grams each.

The homogeneity of sample #18645 was checked by the determination of Quinalphos and the homogeneity of sample #18646 was checked by determination of beta-Endosulfan II in accordance with an inhouse test method on 4 stratified randomly selected subsamples for each sample.

	Quinalphos in mg/kg #18645	beta-Endosulfan II in mg/kg #18646
sample – 1	0.073	3.3
sample – 2	0.069	3.0
sample – 3	0.067	3.6
sample – 4	0.064	3.1

Table 1: homogeneity test results of subsamples #18645 and subsamples #18646

From the above test results the relative standard deviations were calculated and compared with 0.3 times the corresponding relative standard deviation of the target method, in agreement with the procedure of ISO13528, Annex B2 in the next table:

	Quinalphos in % #18645	beta-Endosulfan II in % #18646
RSD (observed)	5.6	8.1
reference method	iis16A10	iis16A10
0.3 x RSD (reference method)	10.3	8.1

Table 2: evaluation of the relative standard deviation of subsamples #18645 and subsamples #18646

The RSD% for Quinalphos (#18645) and beta-Endosulfan II (#18646) are in agreement with 0.3 times the relative standard deviation observed in previous PTs on pesticides. Therefore, homogeneity of the subsamples #18645 and #18646 was assumed.

To each of the participating laboratories 1 sample labelled #18645 and 1 sample labelled #18646 were sent on November 14, 2018.

2.5 ANALYSES

The participants were requested to determine on both samples the concentrations of a limited number of prescribed pesticides, applying the analytical procedure that is routinely used in the laboratory. It was also requested to report if the laboratory was accredited to determine the requested components and to report some analytical details of the test method used.

It was explicitly requested to treat the samples as if they were routine samples and to report the test results using the indicated units on the report form and not to round the results, but to report as much significant figures as possible. It was also requested not to report “less than’ results, which are above the detection limit, because such test results cannot be used for meaningful statistical evaluation.

To get comparable test results a detailed report form and a letter of instructions are prepared. On the report form the reporting units are given as well as the appropriate reference test methods (when applicable) that will be used during the evaluation. The detailed report form and the letter of instructions are both made available on the data entry portal www.kpmd.co.uk/sgs-iis-cts/. The participating laboratories are also requested to confirm the sample receipt on this data entry portal. The letter of instructions can also be downloaded from the iis website www.iisnl.com.

3 RESULTS

During five weeks after sample dispatch, the test results of the individual laboratories were gathered via the data entry portal www.kpmd.co.uk/sgs-iis-cts/. The reported test results are tabulated per determination in the appendix 1 and 2 of this report. The laboratories are represented by their code numbers.

Directly after the deadline, a reminder was sent to those laboratories that did not report test results at that moment. Shortly after the deadline, the available test results were screened for suspect data. A test 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 reported test results. Additional or corrected test results are used for the data analysis and the original results are placed under 'Remarks' in the result tables in appendix 1. Test results that came in after the deadline were not taken into account in this screening for suspect data and thus these participants were not requested for checks.

3.1 STATISTICS

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 June 2018 (iis-protocol, version 3.5).

For the statistical evaluation, the *unrounded* (when available) figures were used instead of the rounded test results. Test 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, a variant of the Kolmogorov-Smirnov test and by the calculation of skewness and kurtosis. Evaluation of the three normality indicators in combination with the visual evaluation of the graphic Kernel density plot, lead to judgement of the normality being either ‘unknown’, ‘OK’, ‘suspect’ or ‘not OK’.
After removal of outliers, this check was repeated. If a data set does not have a normal distribution, the (results of the) statistical evaluation should be used with due care.

According to ISO5725 the original test results per determination were submitted subsequently to Dixon’s, Grubbs’ and/or Rosner’s 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 and by R(0.01) for the Rosner test. Stragglers are marked by D(0.05) for the Dixon test, by G(0.05) or DG(0.05) for the Grubbs test and by R(0.05) for the Rosner 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. In this PT, for one or more of the analytes the criterion of ISO13528, paragraph 9.2.1 was not met, therefore, the uncertainty of the assigned value for these analytes was not negligible. Subsequently, the uncertainty will be used to calculate z’-scores (see also paragraph 3.3).

Finally, the reproducibilities were calculated from the standard deviations by multiplying them with a factor of 2.8.

3.2 GRAPHICS

In order to visualise 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 test results are plotted. The corresponding laboratory numbers are on 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 reference test method. 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. The Kernel Density Graph is a method for producing a smooth density approximation to a set of data that avoids some problems associated with histograms. Also, a normal Gauss curve was projected over the Kernel Density Graph for reference.

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 variation of this interlaboratory study.

The target standard deviation was calculated from the target reproducibility (preferably taken from a standardized test method) by division with 2.8. In case no literature reproducibility was available, other target values were used. In some cases, a reproducibility based on former iis proficiency tests could be used.
The standard uncertainly (u_x) was calculated from the (target) standard deviation in accordance with ISO13528, paragraph 5.6:

$$u_x = 1.25 * (\text{st.dev}(n)) / \sqrt{n}$$

In ISO13528 is stated that if $u_x \geq 0.3$ * standard deviation for proficiency testing, the uncertainty of the assigned value is not negligible and needs to be included in the interpretation of the results of the proficiency test. Therefore, in this PT report, z'-scores were calculated instead of the usual z-scores. The z'(target)-scores were calculated in accordance with ISO13528 paragraph 9.5:

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

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.
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 with the dispatch of the samples.
Five participants did not report any test results. In total 14 laboratories reported 82 numerical test results. Observed were 15 outlying results, which is 19% of the numerical results. In proficiency studies, outlier percentages of 3% - 7.5% are quite normal.

Not all original data sets proved to have a normal Gaussian distribution. These are referred to as “not OK” and “suspect”. The statistical evaluation of these data should be used with due care.

4.1 EVALUATION PER SAMPLE AND PER COMPONENT

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 4.2 and 5.

The test results of the laboratories 339, 2115, 2131, 2795 and 3146 showed a significant number of statistical outliers. Because the test results are not independent, it was decided to exclude the other test results of this laboratory from statistical evaluation to determine the consensus value of each pesticide.

All statistical results reported on the textile samples are summarised in appendix 1 and 2 and relevant method information is summarized in appendix 3.

Sample #18645

alpha-Endosulfan I: The determination may be problematic at the level of 1.14 mg/kg. Two statistical outliers were observed and three other test results were excluded. The calculated reproducibility after rejection of the suspect data is not in agreement with the requirements estimated from the Horwitz equation and uncertainty (see §3.3).

beta-Endosulfan II: The determination was problematic for a number of laboratories at the level of 0.70 mg/kg. Two statistical outliers were observed and three other test results were excluded. However, the calculated reproducibility after rejection of the suspect data is in agreement with the requirements estimated from the Horwitz equation and uncertainty (see §3.3)

Quinalphos: The determination may be problematic at the level of 0.10 mg/kg. Three statistical outliers were observed and one other test result was excluded. The calculated reproducibility after rejection of the suspect data is in agreement with the requirements estimated from the Horwitz equation and uncertainty (see §3.3).

Sample #18646

alpha-Endosulfan I: The determination may be problematic at the level of 0.78 mg/kg. Three statistical outliers were observed and two other test results were excluded. The calculated reproducibility after rejection of the suspect data is not in agreement with the requirements estimated from the Horwitz equation and uncertainty (see §3.3).

beta-Endosulfan II: The determination may be problematic at the level of 1.34 mg/kg. Three statistical outliers were observed and two other test results were excluded. The calculated reproducibility after rejection of the suspect data is not in agreement with the requirements estimated from the Horwitz equation and uncertainty (see §3.3).

Quinalphos: The determination may be problematic at the level of 0.29 mg/kg. Two statistical outliers were observed and two other test results were excluded. The calculated reproducibility after rejection of the suspect data is not in agreement with the requirements estimated from the Horwitz equation and uncertainty (see §3.3).

4.2 PERFORMANCE EVALUATION FOR THE GROUP OF LABORATORIES

A comparison has been made between the estimated target reproducibility and the reproducibility as found for the group of participating laboratories. The number of significant results, the average test result, the calculated reproducibility (2.8 * standard deviation) and the target reproducibility are compared in the next tables:

Component	unit	n	average	2.8 * sd	R(target)
alpha-Endosulfan I	mg/kg	9	1.14	0.75	0.59
beta-Endosulfan II	mg/kg	9	0.70	0.35	0.36
Quinalphos	mg/kg	8	0.10	0.11	0.08

Table 3: reproducibilities of pesticides in sample #18645

Component	unit	n	average	2.8 * sd	R(target)
alpha-Endosulfan I	mg/kg	9	0.78	0.61	0.44
beta-Endosulfan II	mg/kg	9	1.34	1.27	0.78
Quinalphos	mg/kg	9	0.29	0.29	0.20

Table 4: reproducibilities of pesticides in sample #18646

Without further statistical calculations, it can be concluded that for the observed pesticides the group of participating laboratories may have difficulties with the analysis.

4.3 COMPARISON OF THE PROFICIENCY TEST OF DECEMBER 2018 WITH PREVIOUS PTS

	December 2018	December 2016	November 2014	November 2013	November 2012
Number of reporting labs	14	13	21	22	18
Number of test results reported	81	109	53	56	106
Number of statistical outliers	15	5	3	6	16
Percentage outliers	19%	4.6%	5.7%	10.7%	15.1%

Table 5: comparison with previous proficiency tests

In proficiency tests, outlier percentages of 3% - 7.5% are quite normal.

The performance of the determinations of the proficiency test was compared, expressed as relative standard deviation (RSD) or uncertainty of the PTs, see below table.

	Dec 2018	Dec 2016	Nov 2014	Nov 2013	Nov 2012	Nov 2008 - 2011
Carbaryl	--	39	--	--	--	52
Cyhalothrin-lambda	--	--	--	--	45	35 – 41
Cypermethrin (=Σ)	--	--	--	26	28	15
4,4'-DDD	--	--	29	--	--	38
Deltamethrin	--	--	--	16	--	12 - 31
Dimethoate	--	--	54	--	--	35
α/β-Endosulfan	18-34	27-47	--	--	--	15 - 33
Fenvalerate	--	--	--	--	13-28	11 - 37
Esfenvalerate	--	--	--	--	22-41	42
Methoxychlor	--	--	35	--	--	14 – 28
Parathion	--	61	--	--	--	73
Quinalphos	35-38	32-52	--	--	--	24 - 39
Monocrotophos	--	--	--	--	38%	--

Table 6: comparison of uncertainties (in %) in iis proficiency tests on pesticides in textile

The precision that was found for the pesticides during the present proficiency test did improve. The relative low number of participating laboratories may (partly) explain for the relatively large variations.

4.4 EVALUATION OF ANALYTICAL DETAILS

For this PT, some analysis details were requested (see appendix 3). From the answers given the following can be summarized:
Seven of the fourteen reporting laboratories mentioned to be accredited according to ISO/IEC17025 for the determination of pesticides in textile.
Six participants used for intake 1 gram. Five other participants used 0.5-0.6 gram and three participants used 2 grams for intake.
Nine participants mentioned to have used Ultrasonic for extraction at 50°C for 60 minutes.
Seven participants used a Hexane/Acetone mixture as extraction solvent. All other reporting participants used a different extraction solvent.

5 DISCUSSION

When the results of this interlaboratory study were compared to the OEKO-TEX 100 Standard (see table 7), it could be noticed that a number of the reporting laboratories would make a different decision about the acceptability of the textiles for the determined parameters.

OEKO-TEX 100	Baby	Direct skin contact	With no direct skin contact	Decoration material
pesticides, total mg/kg	0.5	1.0	1.0	1.0

Table 7: OEKO-TEX 100

Furthermore, the Ecolabelling Standards and Requirements for Textiles in EU only allow 0.5 mg/kg of total pesticides in raw cotton.

Most participants used an in-house method, therefore some method details were requested on the report form.

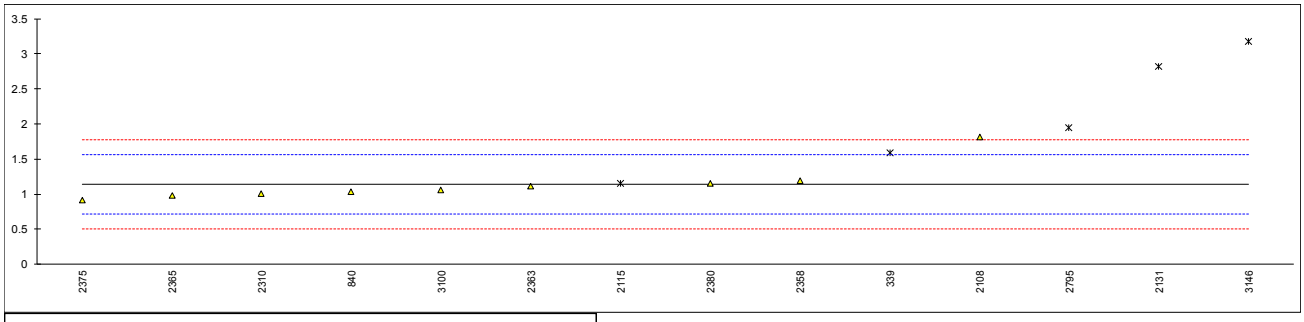
Finally, each laboratory has to evaluate its performance in this study and make decisions about necessary corrective actions. Therefore, participation on a regular basis in this scheme could be helpful to improve the performance and thus improve of the quality of the analytical results.

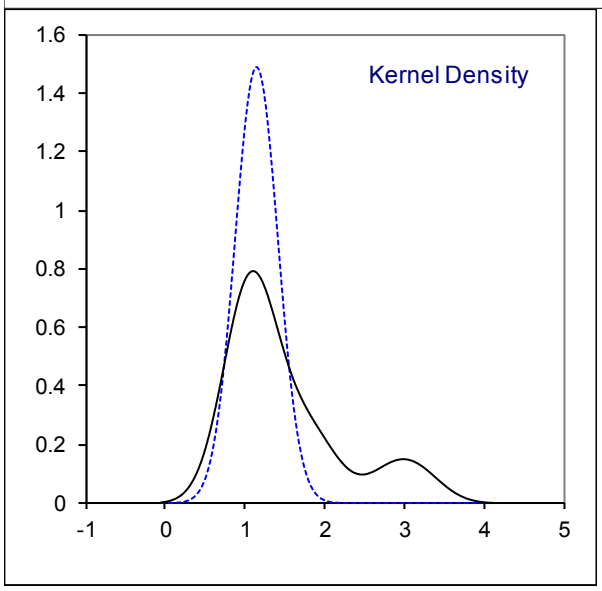
APPENDIX 1

Determination of alpha-Endosulfan I (CAS No. 959-98-8) on sample #18645; results in mg/kg

Lab	method	value	mark	z'(targ)	remarks
339	In house	1.59	ex	2.12	Test result excluded see §4.1
840	In house	1.03	C	-0.53	First reported 2.19
2108	In house	1.82		3.21	
2115	In house	1.152	ex	0.05	Test result excluded see §4.1
2131	In house	2.81375	DG(0.01)	7.92	
2310	In house	1.012		-0.62	
2358	In house	1.1953		0.25	
2363	In house	1.11		-0.15	
2365	In house	0.982		-0.76	
2375	In house	0.92		-1.05	
2380	EPA8081B	1.1523		0.05	
2386		-----		-----	
2390		-----		-----	
2795		1.950	ex	3.83	Test result excluded see §4.1
3100	GB/T18412.1	1.0587		-0.40	
3146	In house	3.17	DG(0.01)	9.61	
3154		-----		-----	
3163		-----		-----	
3220		-----		-----	

normality	not OK	
n	9	
outliers	2 (+3excl)	
mean (n)	1.1423	
st.dev. (n)	0.26808	RSD% = 23%
R(calc.)	0.7506	
st.dev.(Horwitz')	0.21111	
R(Horwitz')	0.5911	

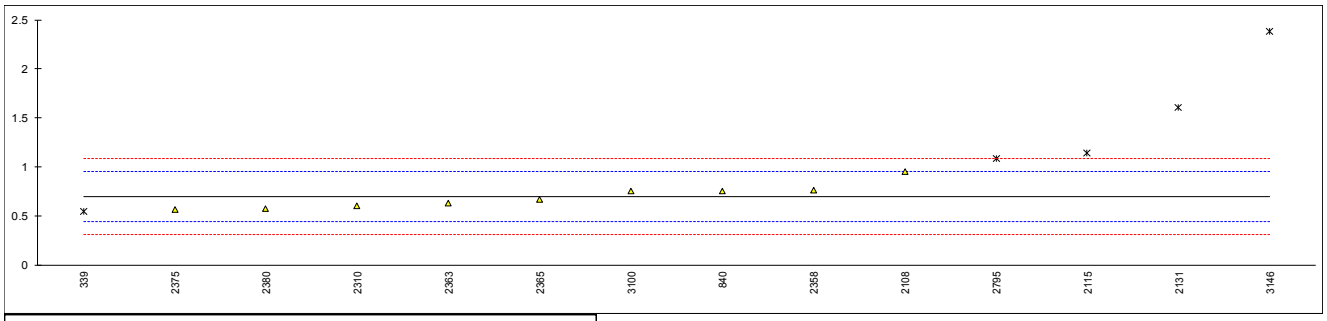


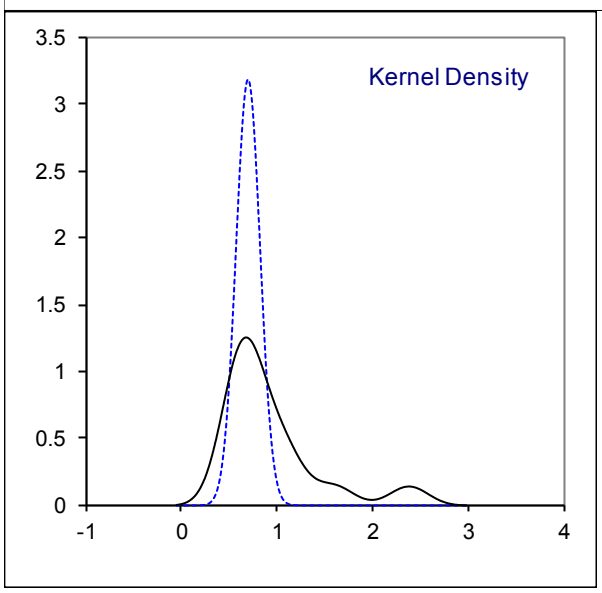


Determination of beta-Endosulfan II (CAS No. 33213-65-9) on sample #18645; results in mg/kg

lab	method	value	mark	z'(targ)	remarks
339	In house	0.553	ex	-1.14	Test result excluded see §4.1
840	In house	0.8	C	0.46	First reported 2.5
2108	In house	0.96		2.00	
2115	In house	1.143	ex	3.42	Test result excluded see §4.1
2131	In house	1.6028	G(0.05)	6.98	
2310	In house	0.604		-0.75	
2358	In house	0.7714		0.55	
2363	In house	0.63		-0.55	
2365	In house	0.677		-0.18	
2375	In house	0.57		-1.01	
2380	EPA8081B	0.5803		-0.93	
2386		-----		-----	
2390		-----		-----	
2795		1.089	ex	3.00	Test result excluded see §4.1
3100	GB/T18412.1	0.7555		0.42	
3146	In house	2.38	G(0.01)	12.99	
3154		-----		-----	
3163		-----		-----	
3220		-----		-----	

normality	not OK	
n	9	
outliers	2 (+3excl)	
mean (n)	0.7009	
st.dev. (n)	0.12512	RSD% = 18%
R(calc.)	0.3503	
st.dev.(Horwitz')	0.12929	
R(Horwitz')	0.3620	

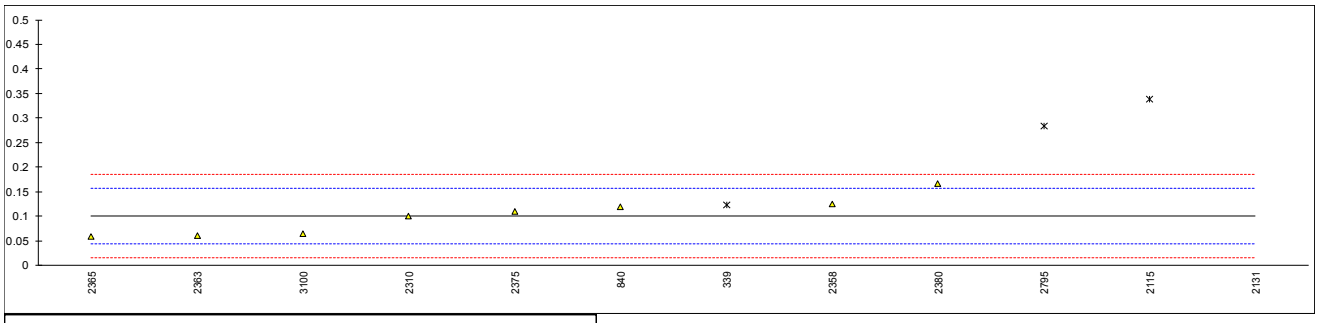


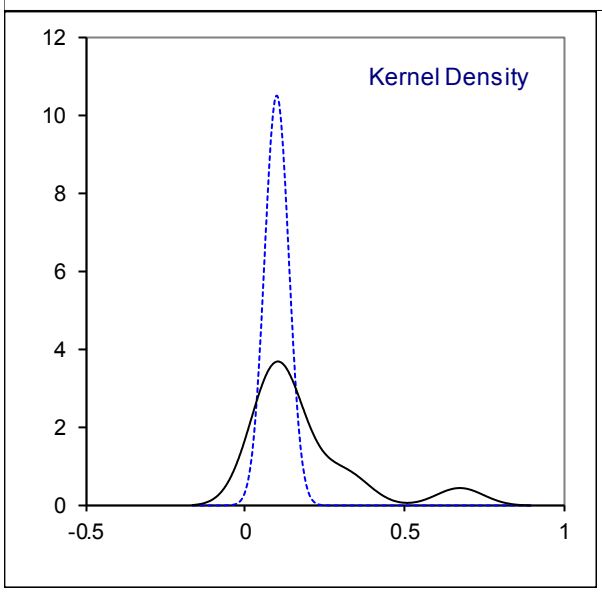


Determination of Quinalphos (CAS No. 13593-03-8) on sample #18645; results in mg/kg

lab	method	value	mark	z'(targ)	remarks
339	In house	0.123	ex	0.79	Test result excluded see §4.1
840	In house	0.12	C	0.69	First reported 0.42
2108		-----		-----	
2115	In house	0.338	DG(0.01)	8.40	
2131	In house	0.6743	G(0.01)	20.30	
2310	In house	0.101		0.01	
2358	In house	0.1253		0.87	
2363	In house	0.06		-1.44	
2365	In house	0.058		-1.51	
2375	In house	0.11		0.33	
2380	EPA8081B	0.1658		2.31	
2386		-----		-----	
2390		-----		-----	
2795		0.284	DG(0.01)	6.49	
3100	GB/T18412.1	0.0649		-1.26	
3146		-----		-----	
3154		-----		-----	
3163		-----		-----	
3220		-----		-----	

normality	OK	
n	8	
outliers	3 (+1excl)	
mean (n)	0.10063	
st.dev. (n)	0.037916	RSD% = 38%
R(calc.)	0.10617	
st.dev.(Horwitz')	0.028254	
R(Horwitz')	0.07911	

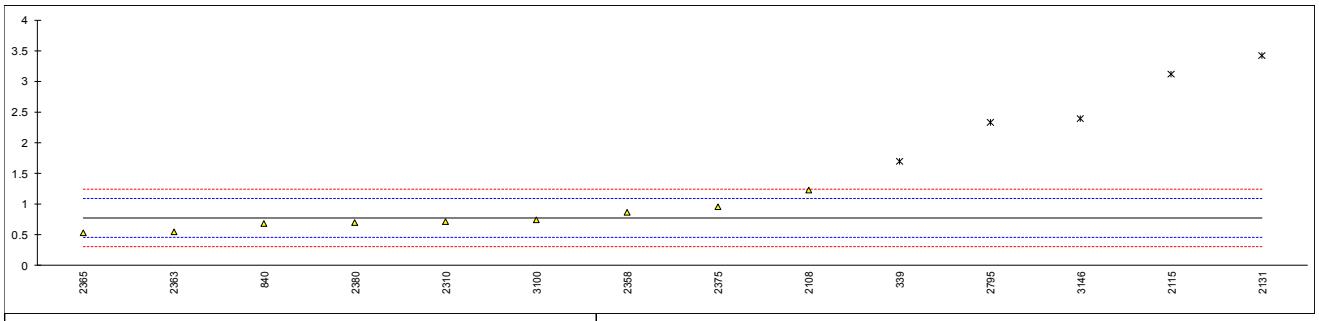


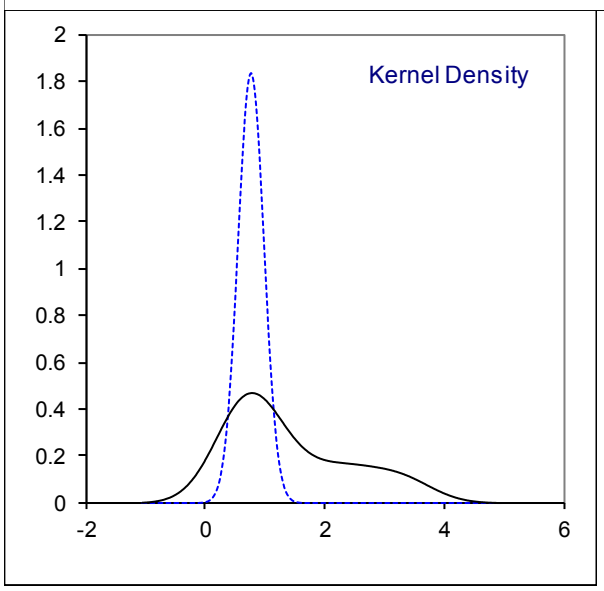


Determination of alpha-Endosulfan I (CAS No. 959-98-8) on sample #18646; results in mg/kg

lab	method	value	mark	z'(targ)	remarks
339	In house	1.7	ex	5.87	Test result excluded see §4.1
840	In house	0.69		-0.54	
2108	In house	1.23		2.89	
2115	In house	3.116	DG(0.05)	14.86	
2131	In house	3.4133	DG(0.05)	16.74	
2310	In house	0.7196		-0.35	
2358	In house	0.8606		0.54	
2363	In house	0.54		-1.49	
2365	In house	0.535		-1.53	
2375	In house	0.96		1.17	
2380	EPA8081B	0.7049		-0.45	
2386		-----		-----	
2390		-----		-----	
2795		2.325	G(0.05)	9.84	
3100	GB/T18412.1	0.7388		-0.23	
3146	In house	2.39	ex	10.25	Test result excluded see §4.1
3154		-----		-----	
3163		-----		-----	
3220		-----		-----	

normality	not OK	
n	9	
outliers	3 (+2excl)	
mean (n)	0.7754	
st.dev. (n)	0.21735	RSD% = 28%
R(calc.)	0.6086	
st.dev.(Horwitz')	0.15754	
R(Horwitz')	0.4411	

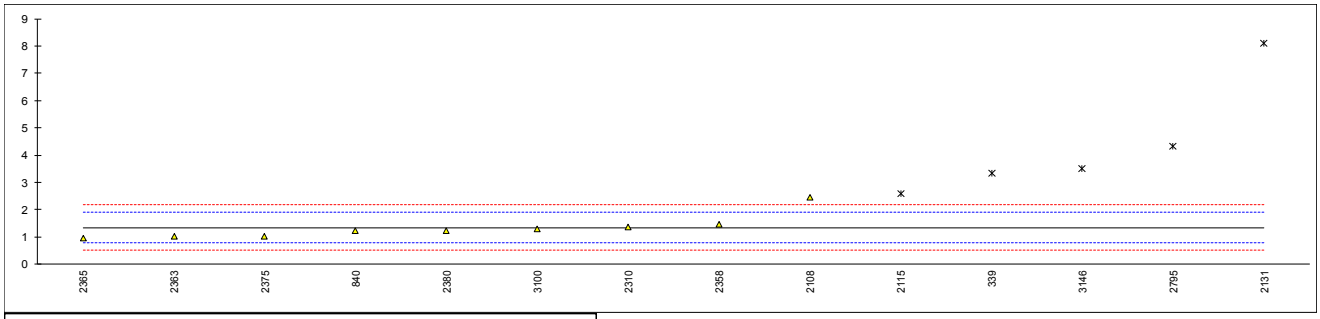


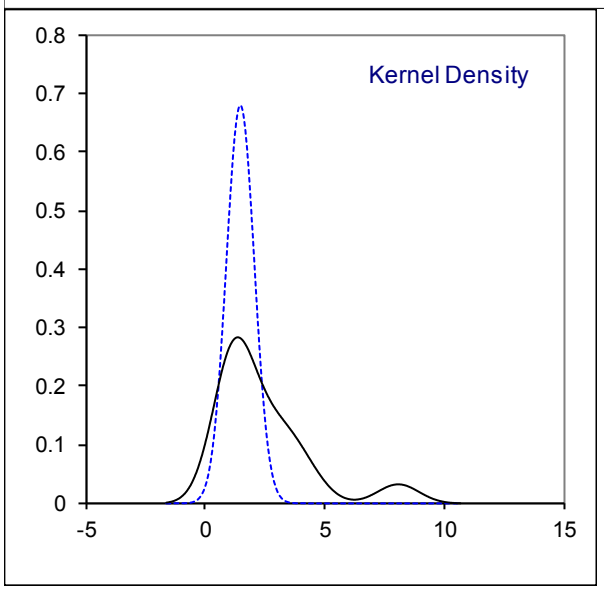


Determination of beta-Endosulfan II (CAS No. 33213-65-9) on sample #18646; results in mg/kg

lab	method	value	mark	z'(targ)	remarks
339	In house	3.33	DG(0.05)	7.15	
840	In house	1.24		-0.35	
2108	In house	2.46		4.03	
2115	In house	2.606	ex	4.55	Test result excluded see §4.1
2131	In house	8.0905	G(0.01)	24.24	
2310	In house	1.357		0.07	
2358	In house	1.4596		0.44	
2363	In house	1.01		-1.18	
2365	In house	0.973		-1.31	
2375	In house	1.01		-1.18	
2380	EPA8081B	1.2439		-0.34	
2386		-----		-----	
2390		-----		-----	
2795		4.315	DG(0.05)	10.69	
3100	GB/T18412.1	1.2833		-0.19	
3146	In house	3.52	ex	7.83	Test result excluded see §4.1
3154		-----		-----	
3163		-----		-----	
3220		-----		-----	

normality	not OK	
n	9	
outliers	3 (+2excl)	
mean (n)	1.3374	
st.dev. (n)	0.45330	RSD% = 34%
R(calc.)	1.2692	
st.dev.(Horwitz')	0.27862	
R(Horwitz')	0.7801	

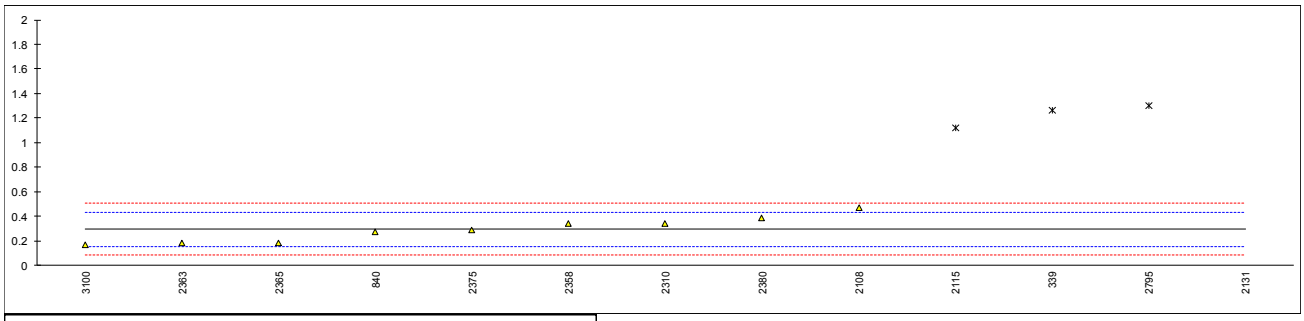


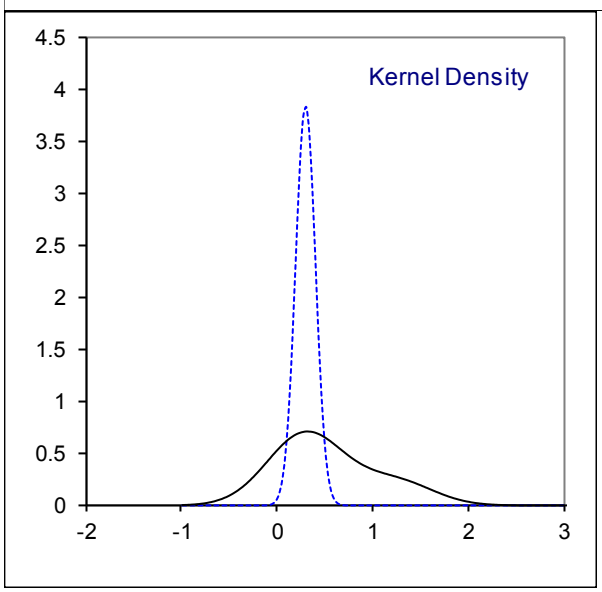


Determination of Quinalphos (CAS No. 13593-03-8) on sample #18646; results in mg/kg

lab	method	value	mark	z'(targ)	remarks
339	In house	1.26	G(0.01)	13.61	
840	In house	0.27	C	-0.32	First reported 840
2108	In house	0.47		2.49	
2115	In house	1.120	C,ex	11.64	First reported 1.784. Test result excluded see §4.1
2131	In house	5.8984	G(0.01)	78.87	
2310	In house	0.344		0.72	
2358	In house	0.3408		0.68	
2363	In house	0.18		-1.59	
2365	In house	0.185		-1.52	
2375	In house	0.29		-0.04	
2380	EPA8081B	0.3888		1.35	
2386		-----		-----	
2390		-----		-----	
2795		1.302	ex	14.20	Test result excluded see §4.1
3100	GB/T18412.1	0.1664		-1.78	
3146		-----		-----	
3154		-----		-----	
3163		-----		-----	
3220		-----		-----	

normality	OK	
n	9	
outliers	2 (+2excl)	
mean (n)	0.29278	
st.dev. (n)	0.103917	RSD% = 35%
R(calc.)	0.29097	
st.dev.(Horwitz')	0.071070	
R(Horwitz')	0.19900	





APPENDIX 2

Determination of Carbaryl, Malathion, methyl-Parathion and Parathion on sample #18645; results in mg/kg

lab	method	Carbaryl	Malathion	methyl-Parathion	Parathion	remarks
339	In house	<0.1	<0.02	<0.01	<0.01	
840	In house	not detected	not detected	not detected	not detected	
2108		-----	-----	-----	-----	
2115		-----	-----	-----	-----	
2131	In house	0	0	0	0	
2310	In house	NOT DETECTED	NOT DETECTED	NOT DETECTED	NOT DETECTED	
2358	In house	n.d.	n.d.	n.d.	n.d.	
2363	In house	ND	ND	ND	ND	
2365	In house	<0.2	<0.05	<0.05	<0.05	
2375		-----	-----	-----	-----	
2380		-----	-----	-----	-----	
2386		-----	-----	-----	-----	
2390		-----	-----	-----	-----	
2795		-----	-----	-----	-----	
3100	GB/T18412.1	<0.20	<0.10	<0.10	<0.05	
3146		-----	-----	-----	-----	
3154		-----	-----	-----	-----	
3163		-----	-----	-----	-----	
3220		-----	-----	-----	-----	

Determination of Carbaryl, Malathion, methyl-Parathion and Parathion on sample #18646; results in mg/kg

lab	method	Carbaryl	Malathion	methyl-Parathion	Parathion	remarks
339	In house	<0.035	<0.02	<0.01	<0.01	
840	In house	not detected	not detected	not detected	not detected	
2108		-----	-----	-----	-----	
2115		-----	-----	-----	-----	
2131	In house	0	0	0	0	
2310	In house	NOT DETECTED	NOT DETECTED	NOT DETECTED	NOT DETECTED	
2358	In house	n.d.	n.d.	n.d.	n.d.	
2363	In house	ND	ND	ND	ND	
2365	In house	<0.2	<0.05	<0.05	<0.05	
2375		-----	-----	-----	-----	
2380		-----	-----	-----	-----	
2386		-----	-----	-----	-----	
2390		-----	-----	-----	-----	
2795		-----	-----	-----	-----	
3100	GB/T18412.1	<0.20	<0.10	<0.10	<0.05	
3146		-----	-----	-----	-----	
3154		-----	-----	-----	-----	
3163		-----	-----	-----	-----	
3220		-----	-----	-----	-----	

APPENDIX 3

Details of the methods used by the participants:

Lab	ISO17025 accredited	Intake sample amount	Extraction type	Extraction solvent	Extraction time	Extraction temp.
339	No	1g	QUECHERS	After water addition, extraction with Acetonitrile	1 hr	Room temperature
840	No	2g	Ultrasonic extraction	hexan/acetone (1/1)	60 mins	50
2108	Yes	1 g	---	---	---	---
2115	Yes	0.5 g	Soxhlet / AES extraction	Acetone	20 min	120 °C
2131	No	1.26 g	QUECHERS	Water/Acetonitril	30 min	Room temperature
2310	Yes	2 gram	Ultrasonic extraction	Acetone:Hexane(1:1)	1 hour	50°C
2358	No	28	Ultrasonic extraction	Hexane & Acetone 1:1	60 mins	50 °C
2363	No	1g	Ultrasonic extraction	Hexane&Acetone	60min	50 °C
2365	Yes	0.5g	Ultrasonic extraction	Hexane/acetone(1/1:v/v) or methanol	60min	50 °C
2375	Yes	0.5	Ultrasonic extraction	Hexane / Acetone 1:1	60 min.	50
2380	No	0.60 g	Ultrasonic extraction	Hexane/Acetone (1/1:V/V)	60 min	50 °C
2386	---	---	---	---	---	---
2390	---	---	---	---	---	---
2795	No	1 g	Other	Acetonitril	20 min	Room temperature
3100	Yes	1.0g	Ultrasonic extraction	n-Hexane / Ethylacetate	25	Room temperature
3146	Yes	0,5	Ultrasonic extraction	MeOH	60	Room temperature
3154	---	---	---	---	---	---
3163	---	---	---	---	---	---
3220	---	---	---	---	---	---

APPENDIX 4

Number of participants per country

1 lab in BANGLADESH
1 lab in FRANCE
5 labs in GERMANY
1 lab in HONG KONG
2 labs in INDIA
1 lab in ITALY
3 labs in P.R. of CHINA
1 lab in PAKISTAN
1 lab in SWITZERLAND
1 lab in THE NETHERLANDS
1 lab in TURKEY
1 lab in VIETNAM

APPENDIX 5

Abbreviations:

C	= final test result after checking of first reported suspect test 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
R(0.01)	= outlier in Rosner's outlier test
R(0.05)	= straggler in Rosner's outlier test
W	= test result withdrawn on request of participant
ex	= test result excluded from statistical evaluations
n.a.	= not applicable
n.e.	= not evaluated
n.d.	= not detected
fr.	= first reported

Literature:

1 iis Interlaboratory Studies, Protocol for the Organisation, Statistics & Evaluation, June 2018
2 OEKO-Tex Standard 100; January 2017
3 Blue Sign (BSSL) version 6.0. July 01, 2016
4 Impacts of Environmental Standards and requirements in EU Countries. Aug 99
5 Horwitz. Journal of AOAC International Vol. 79 No.3. 1996
6 P.L. Davies. Fr. Z. Anal. Chem. 351. 513. (1988)
7 W.J. Conover. Practical; Nonparametric Statistics. J. Wiley&Sons. NY., 302, (1971)
8 ISO 5725:86
9 ISO 5725. parts 1-6. (1994)
10 ISO105 E4:94
11 ISO14184-1:94
12 ISO13528:05
13 M. Thompson and R. Wood. J. AOAC Int. 76. 926. (1993)
14 Analytical Methods Committee Technical brief, No 4 January 2001.
15 P.J. Lowthian and M. Thompson, The Royal Society of Chemistry, Analyst, 127, 1359-1364, (2002)
16 Official Journal of the European Communities L133/29: May 2002
17 E DIN 54233-3:10 (entwurf)
18 Bernard Rosner, Percentage Points for a Generalized ESD Many-Outlier Procedure, *Technometrics*, 25(2), 165-172, (1983)