Results of Proficiency Test
Pesticides in Textile
December 2016

Organised by: Institute for Interlaboratory Studies
Spijkenisse, the Netherlands

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CONTENTS

Appendices:

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), Öko-Tex Standard 100 (Germany) and Bluesign® (Switzerland), which has created a Bluesign® system substances list.

Since 2004, the Institute for Interlaboratory Studie organizes a proficiency testing (PT) scheme for Pesticides in Textile. During the annual proficiency testing program 2016-2017 it was decided to continue the PT for the analysis of pesticides.
In this interlaboratory study, 15 laboratories in 9 different countries registered for participation. In this report, the results of the 2016 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 this proficiency test. Sample analyses and fit-for-use and homogeneity testing were subcontracted to an ISO/IEC 17025 accredited laboratory. It was decided to send two different textile samples in this PT, both positive on a number of pesticides. 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 a regular basis by sending out questionnaires.

2.2 PROTOCOL

The protocol followed in the organisation of this proficiency test was the one as described for proficiency testing in the report 'iis Interlaboratory Studies: Protocol for the Organisation, Statistics and Evaluation' of April 2014 (iis-protocol, version 3.3). This protocol can be downloaded from 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 #16640 was a cotton fabric fortified with alpha- and beta-Endosulfan and Quinalphos. Sample #16641 was a cotton fabric positive on Carbaryl, alpha- and beta-Endosulfan, Parathion and Quinalphos. The two samples were each cut into pieces, well mixed and divided over 30 subsamples of 5 grams each.

The samples of batch #16640 were tested for homogeneity by determination of alpha-Endosulfan and Quinalphos in accordance with an in house test method on 8 stratified randomly selected samples.

	alpha-Endosulfan in mg/kg	Quinalphos in mg/kg
Sample #16640-1	47.2	47.2
Sample #16640-2	44.8	46.7
Sample #16640-3	39.9	42.4
Sample #16640-4	44.2	46.7
Sample #16640-5	39.5	38.7
Sample #16640-6	39.3	42.3
Sample #16640-7	47.9	47.4
Sample #16640-8	39.9	44.2

Table 1: homogeneity test results of sub samples #16640

From the above results, the relative standard deviations were calculated and compared with 0.3 times the corresponding average relative standard deviation of a previous PT in agreement with the procedure of ISO13528, Annex B2 in the next table:

	alpha-Endosulfan in mg/kg	Quinalphos in mg/kg
RSDr (observed)	8.4%	7.0%
Reference	PT 2011	PT 2011
0.3 * RSD (reference)	8.9%	9.6%

Table 2: relative standard deviations of subsamples #16640

The calculated relative standard deviations are in agreement with 0.3 times the relative standard deviation of the previous PT on these pesticides. Therefore, homogeneity of subsamples #16640 was assumed.

The samples of batch #16641 were tested for homogeneity by determination of Carbaryl in accordance with an in house test method on 8 stratified randomly selected samples.

	Carbaryl in mg/kg
Sample #16641-1	4.13
Sample #16641-2	4.08
Sample #16641-3	4.25
Sample #16641-4	4.22
Sample #16641-5	4.11
Sample #16641-6	4.21
Sample #16641-7	4.31
Sample #16641-8	4.09

Table 3: homogeneity test results of sub samples #16641

From the above results the repeatability was calculated and compared with 0.3 times the corresponding reproducibility of the target method and in agreement with the procedure of ISO13528, Annex B2 in the next table:

	Carbaryl in mg/kg
r (observed)	0.24
Reference	Horwitz
0.3 * R (reference)	0.45

Table 4: relative standard deviations of subsamples #16641

The calculated repeatability deviations is in agreement with 0.3 times the corresponding reproducibility of the target variation. Therefore, homogeneity of subsamples #16641 was assumed.

In total approx. 5 grams of each of the samples #16640 and #16641 were sent to the participating laboratories on November 16, 2016.

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 and a letter of instructions are prepared. 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 were 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.iisn.com.

3 RESULTS

During five weeks after sample dispatch, the 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 sample in the appendix 1 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 April 2014 (iis-protocol, version 3.3).

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.

In accordance to ISO 5725 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’s test, by G(0.01) or DG(0.01) for the Grubbs’ test and by R(0.01) for the Rosner’s. Stragglers are marked by D(0.05) for the Dixon’s test, by G(0.05) or DG(0.05) for the Grubbs’ test and by R(0.05) for the Rosner’s 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 significant 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.

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 analysis 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 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. 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, e.g. ISO reproducibilities, the z-scores were calculated using a target standard deviation. This results in an evaluation independent of the variation in this Interlaboratory Study.

The target standard deviation was calculated from the literature reproducibility by division with 2.8. In case no literature reproducibility was available, other target values were used, like Horwitz. 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 7.6:

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

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. Therefore the usual interpretation of z-scores is as follows:

|z| < 1 good
1 < |z| < 2 satisfactory
2 < |z| < 3 questionable
3 < |z| unsatisfactory

4 EVALUATION

During the execution of this proficiency test no serious problems occurred.
Two participants did not report any test results. In total 13 laboratories reported 109 numerical test results. Observed were 5 outlying results, which is 4.6% 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.

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.

Looking at the different pesticides, some are considered polar (like Carbaryl) and some non-polar (like Endosulfan, Parathion and Quinalphos). Only two participants used a polar extraction solvent for Carbaryl and a non-polar extraction solvent for the other pesticides, as expected.
Since the polarity of the pesticides is most important for the determination (see also paragraph 5 – Discussion), it was decided to exclude laboratories that used a polar solvent to extract the non-polar pesticides (for Endosulfan, Parathion and Quinalphos it concerns laboratories 339, 2532 and 3146). And to exclude laboratories that used a non-polar solvent to extract polar pesticides (for Carbaryl it concerns laboratories 2310, 2363, 2370 and 2492).

Furthermore, laboratory 2665 was excluded from all tests, since the test results for alpha- and beta-Endosulfan and Quinalphos were identical for both samples tested, which is highly unlikely to be.

4.1 EVALUATION PER SAMPLE AND PER PESTICIDE

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

Sample #16640

alpha-Endosulfan: The determination of this pesticide may be problematic at the level of 19.6 mg/kg. One statistical outlier was observed and four test results were excluded. The calculated reproducibility after rejection of the suspect data is not in agreement with the estimated target reproducibility (Horwitz').

beta-Endosulfan: The determination of this pesticide may be problematic at the level of 43.6 mg/kg. No statistical outliers were observed, but four test results were excluded. The calculated reproducibility after rejection of the suspect data is not in agreement with the estimated target reproducibility (Horwitz').

Quinalphos: The determination of this pesticide may be problematic at the level of 18.8 mg/kg. One statistical outlier was observed and four test results were excluded. The calculated reproducibility after rejection of the suspect data is not in agreement with the estimated target reproducibility (Horwitz').

Sample #16641

Carbaryl: The determination of this pesticide may be problematic at the level of 4.0 mg/kg. No statistical outliers were observed, but five test results were excluded. The calculated reproducibility after rejection of the suspect data is not in agreement with the estimated target reproducibility (Horwitz').

alpha-Endosulfan: The determination of this pesticide may be problematic at the level of 0.49 mg/kg. One statistical outlier was observed and four test results were excluded. The calculated reproducibility after rejection of the suspect data is not in agreement with the estimated target reproducibility (Horwitz').

beta-Endosulfan: The determination of this pesticide may be problematic at the level of 1.0 mg/kg. No statistical outliers were observed, but four test results were excluded. The calculated reproducibility after rejection of the suspect data is not in agreement with the estimated target reproducibility (Horwitz').

Parathion: The determination of this pesticide may be problematic at the level of 0.35 mg/kg. One statistical outlier was observed and three test results were excluded. The calculated reproducibility after rejection of the suspect data is not in agreement with the estimated target reproducibility (Horwitz').

Quinalphos: The determination of this pesticide may be problematic at the level of 0.54 mg/kg. One statistical outlier was observed and three test results were excluded. The calculated reproducibility after rejection of the suspect data is not in agreement with the estimated target reproducibility (Horwitz').

4.2 PERFORMANCE EVALUATION FOR THE GROUP OF LABORATORIES

A comparison has been made between the 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 two tables.

Parameter	*Unit*	*n*	*Average*	*2.8 * sd*	*R(target)*
alpha-Endosulfan	mg/kg	8	19.6	16.2	9.1
beta-Endosulfan	mg/kg	9	43.6	32.7	17.6
Quinalphos	mg/kg	7	18.8	16.9	9.7

Table 5: reproducibilities of pesticides in sample #16640

Parameter	*Unit*	*n*	*Average*	*2.8 * sd*	*R(target)*
Carbaryl	mg/kg	7	4.0	4.4	2.5
alpha-Endosulfan	mg/kg	8	0.49	0.56	0.35
beta-Endosulfan	mg/kg	9	1.0	1.4	0.7
Parathion	mg/kg	6	0.35	0.61	0.36
Quinalphos	mg/kg	7	0.54	0.78	0.46

Table 6: reproducibilities of pesticides in sample #16641

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.

4.3 COMPARISON OF THE PROFICIENCY TEST OF DECEMBER 2016 WITH PREVIOUS PTS

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

Table 7: 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 2016	*Nov 2014*	*Nov 2013*	*Nov 2012*	*Nov 2011*	*Nov 2010*	*Feb 2010*	*Feb 2009*	*Feb 2008*
Carbaryl	39	--	--	--	--	52	--	--	--
Cyhalothrin-lambda	--	--	--	45	--	41	--	--	35
Cypermethrin (=Σ)	--	--	26	28	--	--	15	--	--
4,4'-DDD	--	29	--	--	--	38	--	--	--
Deltamethrin	--	--	16	--	12	--	--	--	31
Dimethoate	--	54	--	--	--	--	--	35	--
α/β-Endosulfan	27-47	--	--	--	27-33	--	15-20	21	--
Fenvalerate	--	--	--	13-28	--	11	--	24-37	32
Esfenvalerate	--	--	--	22-41	--	42	--	--	--
Methoxychlor	--	35	--	--	22	28	--	--	14
Monocrotophos	--	--	--	38	--	--	--	--	--
Parathion	61	--	--	--	--	73	--	--	--
Quinalfos	32-52	--	--	--	24-39	--	24	--	--

Table 8: Comparison of uncertainties (in %) in iis proficiency tests on pesticides in textile

The precision that was found for the pesticides Carbaryl and Parathion during the present proficiency test did improve, while the precision for the other two pesticides was similar or slightly worse than before. The relative low number of participating laboratories may (partly) explain for the relatively large spreads.

5 DISCUSSION

Limits

When the results of this interlaboratory study were compared to the OEKO-TEX 100 Standard (see table 5), 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 9: 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.

Method

Most participants used an in-house method, therefore some method details were requested on the report form, while others were also requested to report some details during the evaluation of the data by e-mail. Other methods that were also used are: EN15662Mod (QuEChERS, for food/vegetable products), Oeko-Tex 201, EPA 8081B (for water samples) and DIN 38407-37 (for (waste) water samples).

Polarity of pesticides and choice of extraction solvent

Some pesticides are polar, others less polar or non-polar. When extracting the pesticide with a solvent, this will be an important factor. When a laboratory is using a multi residue determination, there is a possibility that the solvent chosen is not the optimal solvent for all the pesticides present and for some a single residue test should be done.
In this PT Endosulfan, Parathion and Quinalphos are non-polar, while Carbaryl is more polar. Two participants (2375 and 2358) used hexane/acetone for the non-polar pesticides and methanol for Carbaryl. Others used hexane/acetone or just acetone and one laboratory used acetone/ethyl acetate/hexane for all pesticides. As expected, the laboratories that used non-polar extraction solvents for Carbaryl, found a much smaller amount of Carbaryl than the group using a polar extraction solvent. Surprisingly, the group that used a polar solvent to extract the non-polar pesticides found higher (possibly false positive) test results.

Quantification ions used in MS

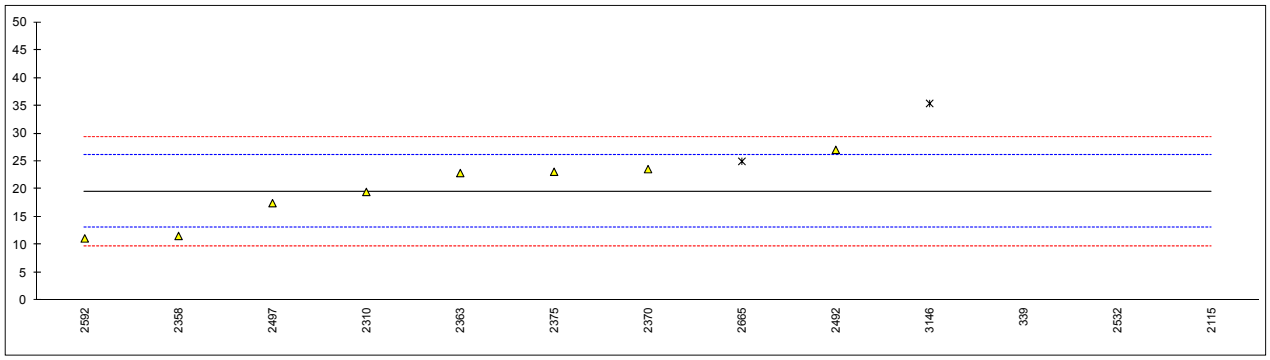
Not all laboratories used the same ions to quantify the different pesticides. But looking at the test results based on the different quantification ions, no correlation could be found.

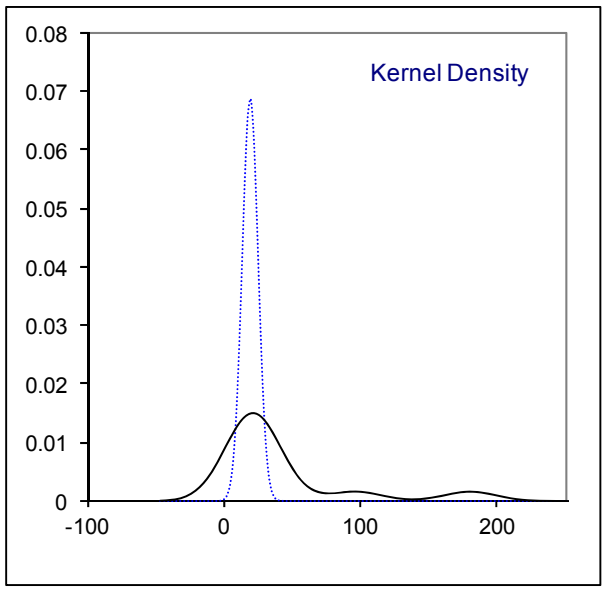
Finally, each laboratory has to evaluate its performance in this study and make decisions about necessary corrective actions. Therefore, participation on a regular basis in this scheme could be helpful to improve the performance and thus improve of the quality of the analytical results.

APPENDIX 1

Determination of alpha-Endosulfan (CAS No. 959-98-8) on sample #16640; results in mg/kg

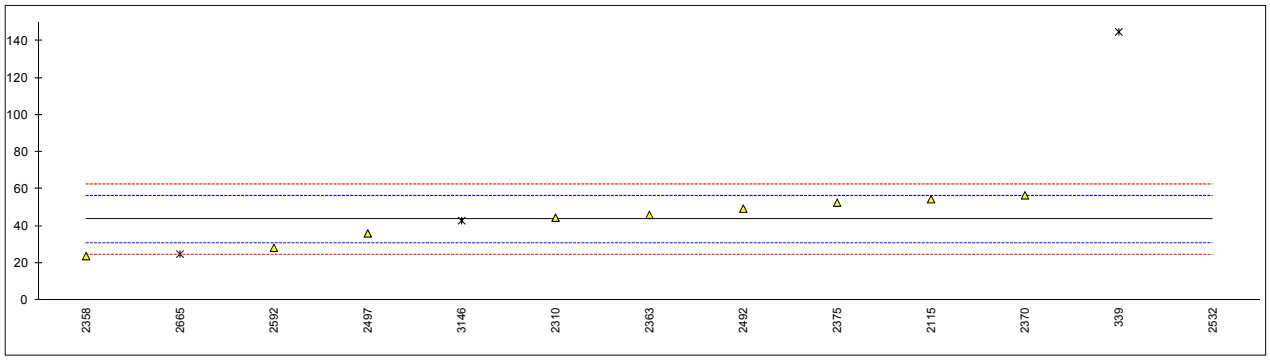
lab	method	value	mark	z'(targ)	remarks
339	EN15662Mod	96.6	ex	23.71	result excluded, see §4
2115	Oeko-Tex 201	440.29	D(0.01)	129.50	
2139		-----		-----	
2310	In house	19.5		-0.02	
2358	In house	11.5956		-2.45	
2363	INH-97	22.89		1.03	
2370	EPA 8081B	23.6		1.25	
2375	INH-210	23.1262		1.10	
2492	DIN 38407-37	27.07		2.31	
2497	In house	17.48		-0.64	
2532	In house	180.3	ex	49.48	result excluded, see §4
2592		11.15		-2.59	
2665	In house	25	ex	1.68	result excluded, see §4
3146	In house	35.4	ex	4.88	result excluded, see §4
3172		-----		-----	
	normality	OK			
	n	8			
	outliers	1 (+4ex)			
	mean (n)	19.551			
	st.dev. (n)	5.7943			
	R(calc.)	16.224			
	R(Horwitz')	9.097			

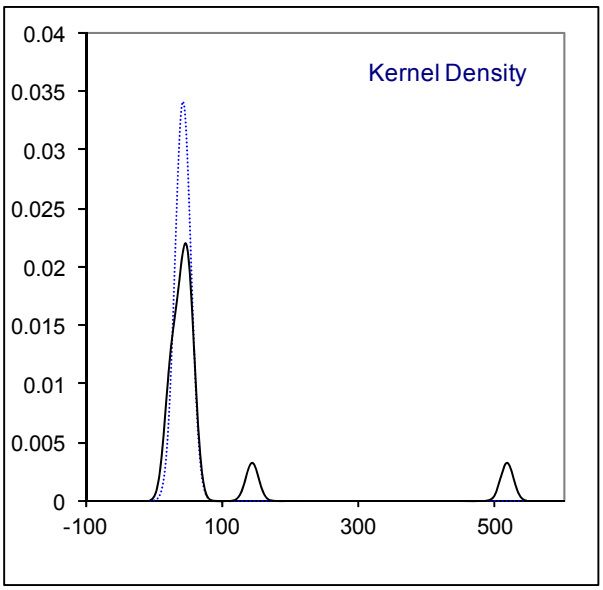




Determination of beta-Endosulfan (CAS No. 33213-65-9) on sample #16640; results in mg/kg

lab	method	value	mark	z'(targ)	remarks
339	EN15662Mod	144.8	ex	16.13	result excluded, see §4
2115	Oeko-Tex 201	54.58		1.75	
2139		-----		-----	
2310	In house	44.6		0.15	
2358	In house	23.9215		-3.14	
2363	INH-97	46.18		0.41	
2370	EPA 8081B	56.7		2.08	
2375	INH-210	52.7143		1.45	
2492	DIN 38407-37	49.49		0.93	
2497	In house	36.13		-1.20	
2532	In house	517.34	ex	75.53	result excluded, see §4
2592		28.40		-2.43	
2665	In house	25	ex	-2.97	result excluded, see §4
3146	In house	43	ex	-0.10	result excluded, see §4
3172		-----		-----	
	normality	OK			
	n	9			
	outliers	0 (+4ex)			
	mean (n)	43.635			
	st.dev. (n)	11.6815			
	R(calc.)	32.708			
	R(Horwitz')	17.560			

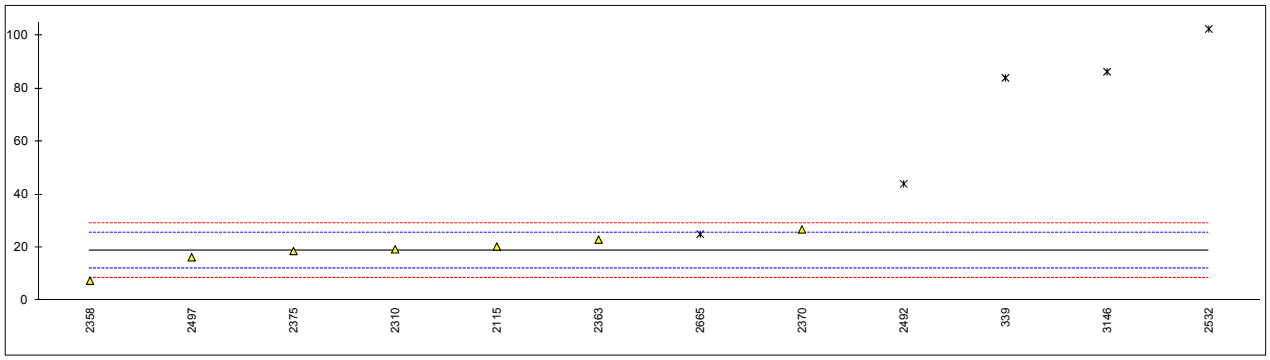


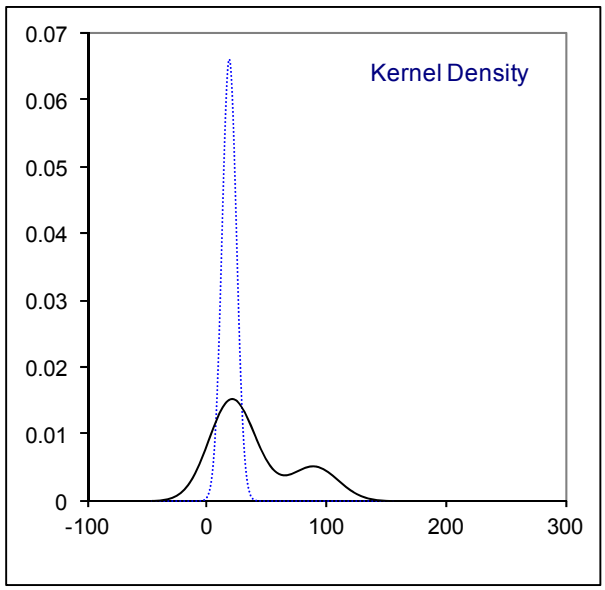


Determination of Quinalphos (CAS No. 13593-03-8) on sample #16640; results in mg/kg

lab	method	value	mark	z'(targ)	remarks
339	EN15662Mod	84.01	ex	18.88	result excluded, see §4
2115	Oeko-Tex 201	20.34		0.44	
2139		-----		-----	
2310	In house	19.3		0.14	
2358	In house	7.4119		-3.30	
2363	INH-97	22.95		1.19	
2370	EPA 8081B	26.8		2.31	
2375	INH-210	18.6537		-0.05	
2492	DIN 38407-37	44.01	D(0.05)	7.29	
2497	In house	16.31		-0.73	
2532	In house	102.44	ex	24.21	result excluded, see §4
2592		-----		-----	
2665	In house	25	ex	1.79	result excluded, see §4
3146	In house	86.3	ex	19.54	result excluded, see §4
3172		-----		-----	

normality	not OK
n	7
outliers	1 (+4ex)
mean (n)	18.824
st.dev. (n)	6.0519
R(calc.)	16.945
R(Horwitz')	9.669





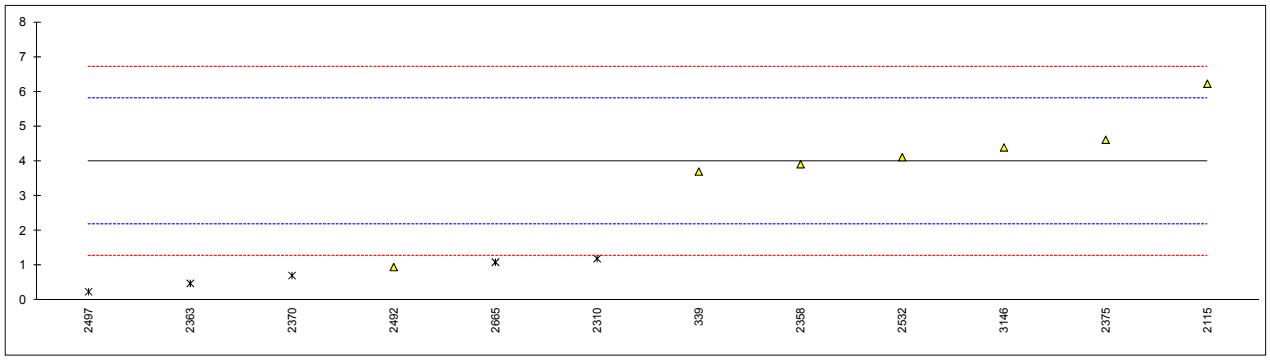
Determination of Carbaryl, Malathion, methyl-Parathion and Parathion on sample #16640; results in mg/kg

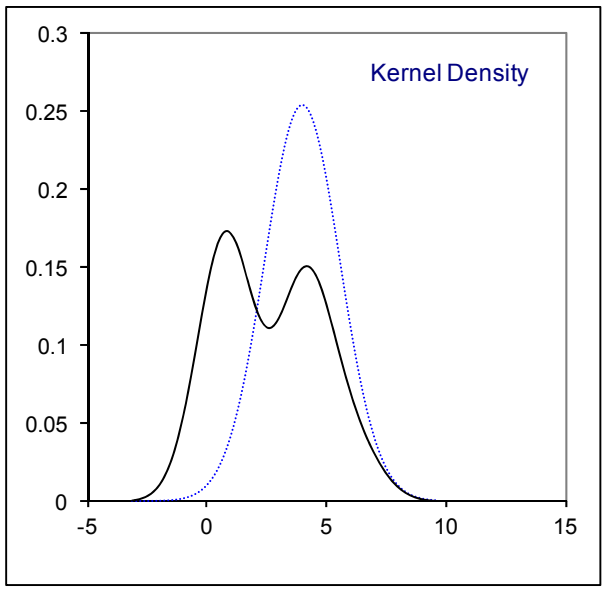
lab	method	Carbaryl	Malathion	methyl-Parathion	Parathion	remarks
339	EN15662Mod	<0.025	<0.010	<0.010	0.02921	
2115		-----	-----	-----	-----	
2139		-----	-----	-----	-----	
2310	In house	NOT DETECTED	NOT DETECTED	NOT DETECTED	NOT DETECTED	
2358	In house	n.d.	n.d.	n.d.	n.d.	
2363	INH-97	ND	ND	ND	ND	
2370	EPA 8081B	n.d.	n.d.	n.d.	n.d.	
2375		-----	-----	-----	-----	
2492		-----	-----	-----	-----	
2497	In house	0.0001	0.0001	0.0001	0.0049	
2532	In house	Not detected	Not detected	Not detected	Not detected	
2592		-----	-----	-----	-----	
2665	In house	0.03	0	0	<0.01	
3146	In house	<0,3	<0,3	<0,3	<0,3	
3172		-----	-----	-----	-----	
	n	4	4	4	4	
	mean (n)	<0.3	<0.3	<0.3	<0.3	

Determination of Carbaryl (CAS No. 63-25-2) on sample #16641; results in mg/kg

lab	method	value	mark	z'(targ)	remarks
339	EN15662Mod	3.706		-0.32	
2115	Oeko-Tex 201	6.23		2.47	
2139		-----		-----	
2310	In house	1.20	ex	-3.08	result excluded, see §4
2358	In house	3.9165		-0.08	
2363	INH-97	0.49	ex	-3.86	result excluded, see §4
2370	EPA 8081B	0.716	ex	-3.61	result excluded, see §4
2375	INH-210	4.6204		0.69	
2492	DIN 38407-37	0.96		-3.35	
2497	In house	0.251	ex	-4.13	result excluded, see §4
2532	In house	4.12		0.14	
2592		-----		-----	
2665	In house	1.1	ex	-3.19	result excluded, see §4
3146	In house	4.4		0.45	
3172		-----		-----	

normality	not OK
n	7
outliers	0 (+5ex)
mean (n)	3.993
st.dev. (n)	1.5741
R(calc.)	4.408
R(Horwitz')	2.539

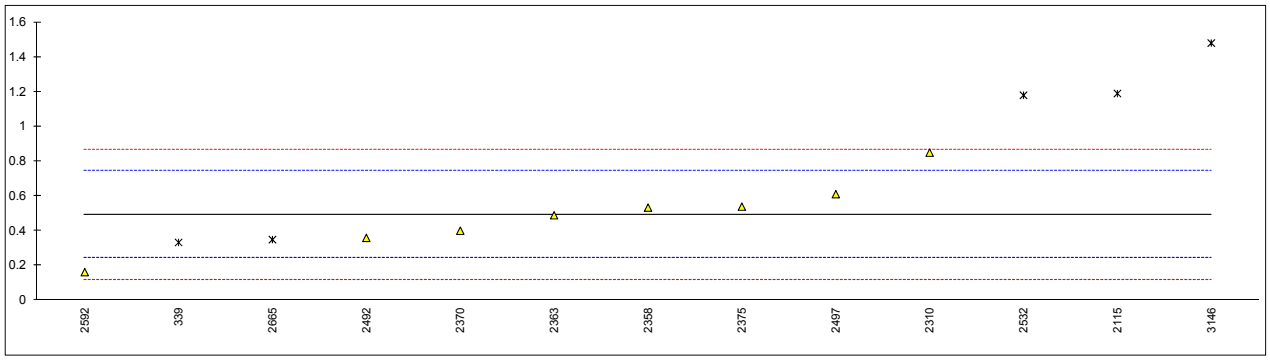


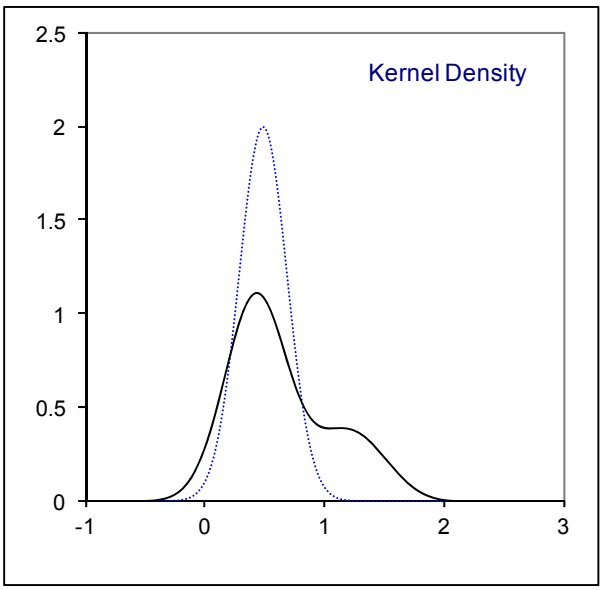


Determination of alpha-Endosulfan (CAS No. 959-98-8) on sample #16641; results in mg/kg

lab	method	value	mark	z'(targ)	remarks
339	EN15662Mod	0.3335	ex	-1.28	result excluded, see §4
2115	Oeko-Tex 201	1.19	D(0.05)	5.59	
2139		-----		-----	
2310	In house	0.85		2.86	
2358	In house	0.5338		0.32	
2363	INH-97	0.49		-0.03	
2370	EPA 8081B	0.401		-0.74	
2375	INH-210	0.5397		0.37	
2492	DIN 38407-37	0.36		-1.07	
2497	In house	0.611		0.94	
2532	In house	1.18	ex	5.51	result excluded, see §4
2592		0.163		-2.65	
2665	In house	0.35	ex	-1.15	result excluded, see §4
3146	In house	1.48	ex	7.91	result excluded, see §4
3172		-----		-----	

normality	suspect
n	8
outliers	1 (+4ex)
mean (n)	0.494
st.dev. (n)	0.2001
R(calc.)	0.560
R(Horwitz')	0.349

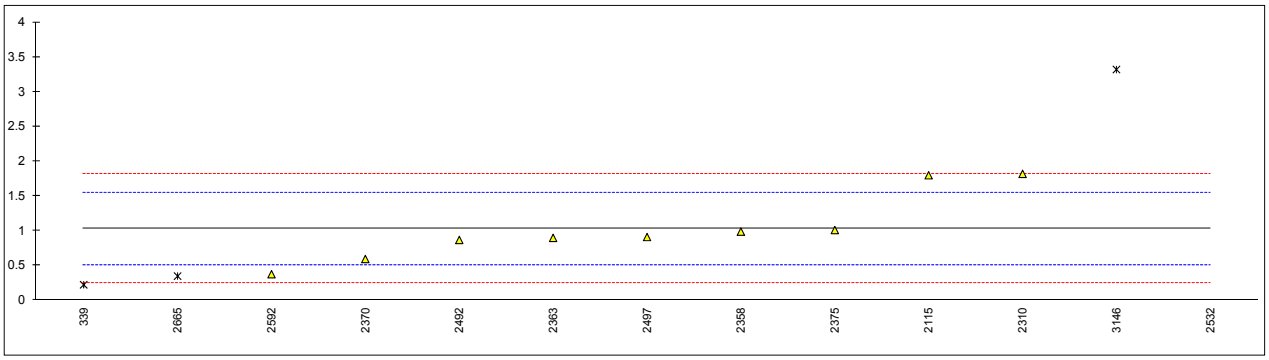


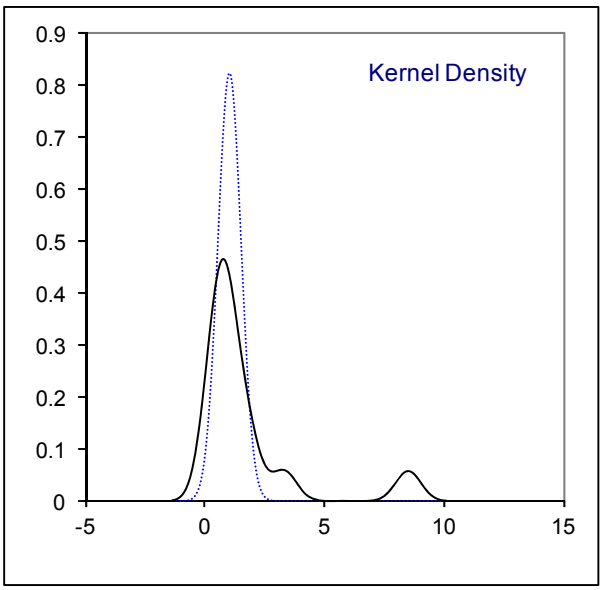


Determination of beta-Endosulfan (CAS No. 33213-65-9) on sample #16641; results in mg/kg

lab	method	value	mark	z'(targ)	remarks
339	EN15662Mod	0.2255	ex	-3.09	result excluded, see §4
2115	Oeko-Tex 201	1.80		2.95	
2139		-----		-----	
2310	In house	1.82		3.03	
2358	In house	0.9894		-0.16	
2363	INH-97	0.90		-0.50	
2370	EPA 8081B	0.596		-1.67	
2375	INH-210	1.0118		-0.07	
2492	DIN 38407-37	0.87		-0.62	
2497	In house	0.912		-0.46	
2532	In house	8.53	ex	28.77	result excluded, see §4
2592		0.377		-2.51	
2665	In house	0.35	ex	-2.61	result excluded, see §4
3146	In house	3.32	ex	8.78	result excluded, see §4
3172		-----		-----	

normality	OK
n	9
outliers	0 (+4ex)
mean (n)	1.031
st.dev. (n)	0.4861
R(calc.)	1.361
R(Horwitz')	0.730

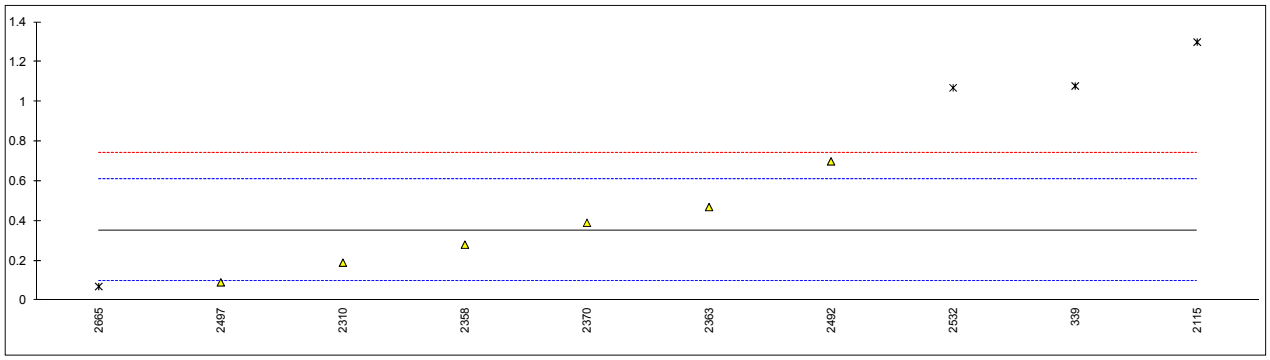


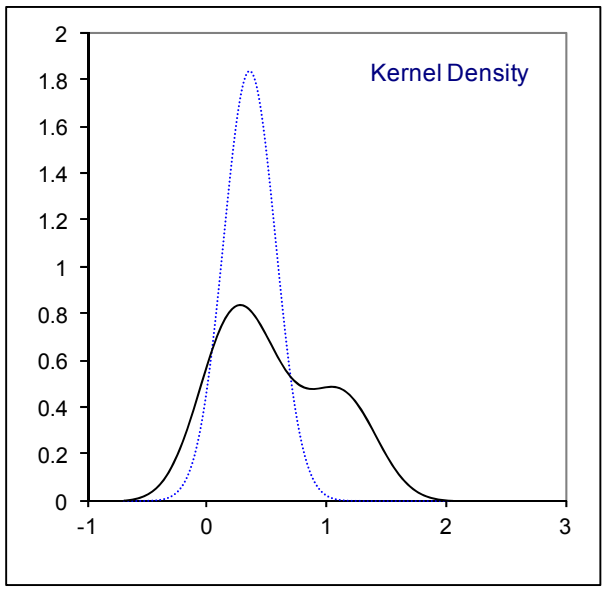


Determination of Parathion (CAS No. 56-38-2) on sample #16641; results in mg/kg

lab	method	value	mark	z'(targ)	remarks
339	EN15662Mod	1.079	ex	5.62	result excluded, see §4
2115	Oeko-Tex 201	1.30	D(0.05)	7.33	
2139		-----		-----	
2310	In house	0.19		-1.27	
2358	In house	0.2808		-0.57	
2363	INH-97	0.47		0.90	
2370	EPA 8081B	0.391		0.29	
2375	INH-210	-----		-----	
2492	DIN 38407-37	0.70		2.68	
2497	In house	0.091		-2.04	
2532	In house	1.07	ex	5.55	result excluded, see §4
2592		-----		-----	
2665	In house	0.07	ex	-2.20	result excluded, see §4
3146	In house	<0,3		-----	
3172		-----		-----	

normality	OK
n	6
outliers	1 (+3ex)
mean (n)	0.354
st.dev. (n)	0.2172
R(calc.)	0.608
R(Horwitz')	0.362

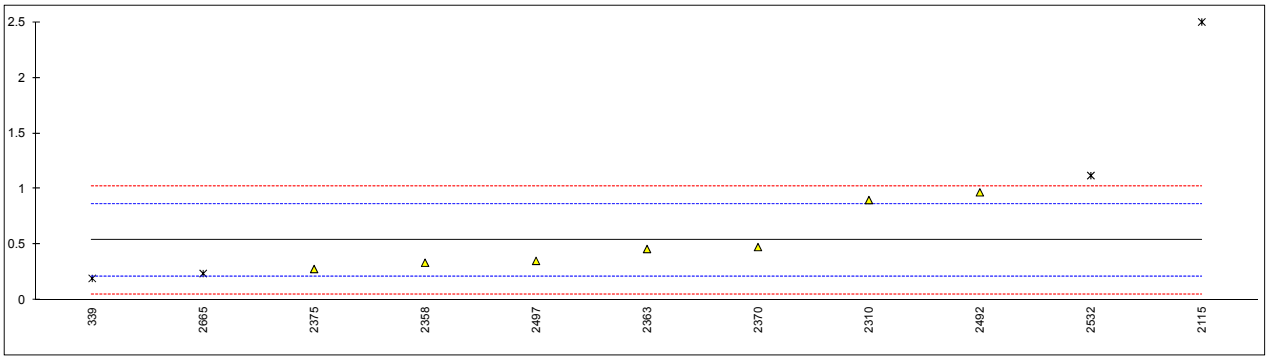


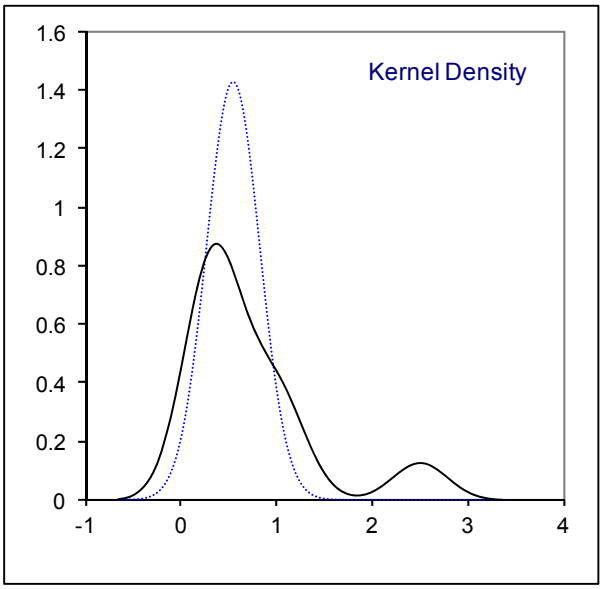


Determination of Quinalphos (CAS No. 13593-03-8) on sample #16641; results in mg/kg

lab	method	value	mark	z'(targ)	remarks
339	EN15662Mod	0.1962	ex	-2.12	result excluded, see §4
2115	Oeko-Tex 201	2.50	C,D(0.05)	12.07	first reported: 250
2139		-----		-----	
2310	In house	0.90		2.22	
2358	In house	0.3373		-1.25	
2363	INH-97	0.46		-0.49	
2370	EPA 8081B	0.478		-0.38	
2375	INH-210	0.2806		-1.60	
2492	DIN 38407-37	0.97		2.65	
2497	In house	0.354		-1.14	
2532	In house	1.12	ex	3.57	result excluded, see §4
2592		-----		-----	
2665	In house	0.24	ex	-1.85	result excluded, see §4
3146	In house	<0,3		-----	
3172		-----		-----	

normality	OK
n	7
outliers	1 (+3ex)
mean (n)	0.540
st.dev. (n)	0.2792
R(calc.)	0.782
R(Horwitz')	0.455





Determination of Malathion and methyl-Parathion on sample #16641; results in mg/kg

lab	method	Malathion	methyl-Parathion	remarks
339	EN15662Mod	<0.010	<0.010	
2115		-----	-----	
2139		-----	-----	
2310	In house	NOT DETECTED	NOT DETECTED	
2358	In house	n.d.	n.d.	
2363	INH-97	ND	ND	
2370	EPA 8081B	n.d.	n.d.	
2375		-----	-----	
2492		-----	-----	
2497	In house	0.0001	0.0001	
2532	In house	Not detected	Not detected	
2592		-----	-----	
2665	In house	0	0	
3146	In house	<0,3	<0,3	
3172		-----	-----	
	n	4	4	
	mean (n)	<0.3	<0.3	

APPENDIX 2

Details of the methods used by the participants:

Lab	ISO17025 accredited?	Release/ extraction	Extraction solution	Time and temperature	Clean up step?	Analysis technique
339	No	Solid/liquid Quechers	Water/Acetonitrile	1 min at RT	hexane/Acetone (70:30)	GC/MS-MS
2115	Yes	ASE	Acetone	20 min at 120°C	n-hexane	GC/MS-MS
2139	---					
2310	Yes	solvent extraction	Hexane/Acetone (1:1)	1 hr at 50°C	Hexane/Acetone (1:1)	GCMS + GCECD
2358	Yes	Ultrasonic extraction	Hexane/Acetone (1:1)/Methanol	60 min at 50°C	Hexane/Acetone (1:1)	GC/MS, GC/ECD and 1 LC/DAD
2363	No	Ultrasonic	Hexane/Acetone (1:1)	1 hr	Hexane/Acetone (1:1), carbaryl: acetonitrile	GC/MS, carbaryl met LC/MS
2370	Yes	Ultrasonicate	Hexane/Acetone (1:1)	1 hr at 60°C	No	GC/MS
2375	Yes	GC and LC: Ultrasonic	GC: Hexane-Acetone (1:1) - LC: Methanol	GC and LC: 1hr at 50°C		GC: - LC:
2492	Yes	Soxhlet	Acetone	3 hrs	Methanol	GC/MS-MS
2497	No	Solid/liquid extraction	Acetone/Ethyl acetate/Hexane	60 min at 40°C		GC: - LC:
2532	No	Ultra sonication	step 1 Methanol, step 2 Acetone/Hexane	30 min methanol and 30 min acetone/hexane	Toluene	GC/MS
2592	No					
2665	Yes	SPE	Acetonitrile	30 min at RT	-	GC/MS-MS and LC/MS-MS
3146	Yes	ultrasonic	step 1 Methanol, step 2 Acetone/Hexane	2 x2 30 min at RT		
3172	---					

Quantification ions used in MS

Lab	Carbaryl	alpha-Endosulfan	beta-Endosulfan	Parathion	Quinalphos
339	144 >155.1	241 > 206	206.9 > 172	291 > 109	146 > 118
2115	144>115	195>159	195>159	179>109	146>118
2139					
2310	144	277	277	291	146
2358				291	146
2363	202	339	195	291	146
2370	144	241	195	109	146
2375					
2492	115-89 & 144-115	195-159 & 241-206	195-159 & 241-206	291-109	146-118 & 298-156
2497					
2532	144 (115,116)	195 (241,170)	195 (241,170)	109 (291, 97, 139)	146 (157, 118)
2592					
2665	GC 144 > 115.1 LC 202 > 145	240.9 > 205.9	195 > 125	291 > 109	GC 146 > 118 LC 299 > 163
3146					
3172					

APPENDIX 3

Number of participants per country

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

APPENDIX 4

Abbreviations:

C = final 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
n.a. = not applicable
n.d. = not detected
ex = test result excluded from calculations

Literature:

1 iis Interlaboratory Studies, Protocol for the Organisation, Statistics & Evaluation, April 2014
2 Öko-Tex Standard 100; January 2014
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9 ISO 5725. parts 1-6. (1994)
10 ISO105 E4: 1994
11 ISO14184-1: 1994
12 ISO13528-05
13 M. Thompson and R. Wood. J. AOAC Int. 76. 926. (1993)
14 Analytical Methods Committee Technical brief, No4 January 2001.
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19 Blue Sign label BSSL v6.0, July 2016