Results of Proficiency Test
Organotin in textile
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Organised by: Institute for Interlaboratory Studies (iis)
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Author: ing. A.S. Noordman-de Neef
Corrector: dr. R.G. Visser & ing. R.J. Starink

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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 (Germany).
On request of several laboratories, the Institute for Interlaboratory Studies decided to organize a proficiency test for Organotin components in textile in the annual proficiency test program of 2016/2017 for the first time. During the annual proficiency testing program of 2017/2018 it was decided to continue the round robin for the analysis of Organotin components in textile.
In this interlaboratory study 28 laboratories in 14 different countries registered for participation. See appendix 3 for the number of participants per country. In this report, the results of the 2017 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 (labelled #17650 and #17651, 3 grams each), both positive on Organotin. 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 IEC/ISO17043:2010. 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 March 2017 (iis-protocol, version 3.4). 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 batches of textile were enriched with different Organotin components. Each bulk material was cut into pieces and mixed well per batch. For sample #17650 in total 80 subsamples and for sample #17651 in total 78 subsamples were packed. All subsamples were packed of 3 grams each.
The homogeneity of sample #17650 was checked by the determination of Tributyltin (TBT) in accordance with an in-house test method on 7 stratified randomly selected subsamples. The homogeneity of sample #17651 was checked by the determination of Dimethyltin (DMT) on 7 stratified randomly selected subsamples. See the following table for the test results.

	TBT in mg/kg #17650	*DMT in mg/kg #17651*
Sample -1	3.50	5.70
Sample -2	4.36	5.77
Sample -3	4.04	5.23
Sample -4	4.66	5.79
Sample -5	4.22	5.88
Sample -6	3.80	5.30
Sample -7	3.96	5.21

Table 1: homogeneity test results of subsamples #17650 and subsamples #17651

From the above test results the repeatabilities were calculated and compared with 0.3 times the corresponding reproducibility of the target method, in agreement with the procedure of ISO 13528, Annex B2 in the next table:

	TBT in mg/kg #17650	*DMT in mg/kg #17651*
r (observed)	1.06	0.82
reference method	iis16A12	iis16A12
0.3 x R (reference method)	1.27	1.73

Table 2: repeatability of subsamples #17650 and subsamples #17651

The repeatabilities of Tributyltin (TBT) and Dimethyltin (DMT) were in agreement with 0.3 times the target requirements, based on the uncertainty observed in Organotin PT iis16A12. Therefore, homogeneities of the subsamples were assumed.
To each participating laboratory one sample, labelled #17650 and one sample, labelled #17651, was sent on November 15, 2017.

2.5 ANALYSES

The participants were requested to determine on samples #17650 and #17651 the concentrations of the following Organotin components: Monomethyltin (MMT), Dimethyltin (DMT), Trimethyltin (TMT), Tripropyltin (TPT), Monobutyltin (MBT), Dibutyltin (DBT), Tributyltin (TBT), Tetrabutyltin (TeBT), Monooctyltin (MOT), Dioctyltin (DOT), Trioctyltin (TOT), Diphenyltin (DPhT), Triphenyltin (TPhT) and Tricyclohexyltin (TCyHT) applying the analysis procedure that is routinely used in the laboratory. Also some analytical details were requested to be reported.

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 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 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 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 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 March 2017 (iis-protocol, version 3.4).

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 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. 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, 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 (preferably taken from a standardized test method) by division with 2.8. In case no literature reproducibility was available, other target values were used.

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 should be done in order to evaluate whether the reported test results are fit-for-use.

The z-scores were calculated according to:

$z_{(target)}$ = (test result - average of Proficiency Test) / target standard deviation

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

Absolute values for z<2 are very common and absolute values for z>3 are very rare.
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 problems occurred with the dispatch of the samples. One laboratory did not report any test results and none of the laboratories reported results after the final reporting date. Not all laboratories were able to report all analyses requested.
In total 27 participants reported 67 numerical test results. Observed were 6 outlying test results, which is 9.0% of the numerical test results. In proficiency studies, outlier percentages of 3% - 7.5% are quite normal.

4.1 EVALUATION PER TEST PER COMPONENT AND PER SAMPLE

In this section, the reported results are discussed per component and per sample. The test methods, which were used by the various laboratories were taken into account for explaining the observed differences when possible and applicable. These test methods are also in the tables in appendix 1 together with the original data. The abbreviations used in these tables are listed in appendix 4.

For the determination of Organotin a number of the test methods with precision data are available (eg. ISO/TS 16179 and ISO 17353). Regretfully, none of the test methods describes the Organotin determination in textile only. In this proficiency test 10 participants used ISO 17353 as test method, which is applicable for water samples. And 10 participants used ISO/TS 16179 as test method, which is applicable for footwear materials.
The precision mentioned in both test methods did not been suitable. Therefore, the calculated reproducibility was compared against the reproducibility estimated from the Horwitz equation.

Not all original data sets proved to have a normal Gaussian distribution. These are referred to as “not OK” or “suspect”. The statistical evaluation should be used with due care, see also paragraph 3.1.

Sample #17650:

Dibutyltin (DBT): This determination may be problematic. Two statistical outliers were observed and one test result was excluded. The calculated reproducibility after rejection of the suspect data is not in agreement with the estimated reproducibility based on the Horwitz equation.

Tributyltin (TBT): This determination may be problematic. Two statistical outliers were observed. The calculated reproducibility after rejection of the statistical outliers is not in agreement with the estimated reproducibility based on the Horwitz equation.

Sample #17651:

Dimethyltin (DMT): This determination may be problematic. No statistical outliers were observed, but one test result was excluded. The calculated reproducibility after rejection of the suspect data is not in agreement with the estimated reproducibility based on the Horwitz equation.

Tributyltin (TBT): This determination may be problematic. Two statistical outliers were observed and one test result was excluded. The calculated reproducibility after rejection of the suspect data is not in agreement with the estimated reproducibility based on the Horwitz equation.

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 (standard deviation*2.8) and the target reproducibility are compared in the next table:

Components	*unit*	*n*	*Average*	*2.8 * sd*	*R (target)*
Dibutyltin (DBT)	mg/kg	13	0.079	0.077	0.052
Tributyltin (TBT)	mg/kg	20	3.22	2.64	1.21

Table 3: reproducibilities of Organotin components in sample #17650

Components	*unit*	*n*	*Average*	*2.8 * sd*	*R (target)*
Dimethyltin (DMT)	mg/kg	15	5.34	5.73	1.86
Tributyltin (TBT)	mg/kg	10	0.064	0.052	0.044

Table 4: reproducibilities of Organotin components in sample #17651

Without further statistical calculations, it can be concluded that for the observed Organotin components the group of participating laboratories may have difficulties with the analysis. See also the discussion in paragraph 5.

4.3 COMPARISON OF THE PROFICIENCY TEST OF DECEMBER 2017 WITH THE PREVIOUS PT

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

Components	*December 2017*	*December 2016*	*Horwitz (10-0.05 mg/kg)*
Dimethyltin (DMT)	38%	--	11-13%
Monobutyltin (MBT)	--	37%	11-13%
Dibutyltin (DBT)	35%	--	11-13%
Tributyltin (TBT)	29%	--	11-13%

Table 5: comparison of uncertainties in iis proficiency tests

The uncertainty observed in this PT is comparable to the uncertainty observed in previous PT of 2016. Tributyltin (TBT) seems easier to detect as the uncertainty is lower.
The uncertainty is still large in comparison with the requirements mentioned in the target.

4.4 EVALUATION ANALYTICAL DETAILS

For this PT some analysis details were requested (see appendix 2). From the answers given by 25 participants, the following can be summarized:
About 83% of the participants is accredited according to ISO/IEC 17025. About 64% used 1 gram of the samples and 24% used 0.5 gram or less (one participant). About 32% used a mixture or Methanol and Ethanol and about 28% used Acetone as extraction solvent. One participant used Hexane. Remarkedly, this participant did not detect one of the Organotins which was added to the textile.

The majority of the participants (76%) used ultrasonic bath for the extraction. Almost all participants used an extraction time of 60 minutes. About 56% of the participants reported to extract at 60°C and about 40% to extract at 40°C. About half of the group reported to observe a pH of 4.5 / 4.6 and 4 participants reported to observed a pH 5 / 5.6. About 50% adjust the pH. Some participants mentioned that measuring (and adjusting) the pH is not a part of the test method.
Unfortunately, no conclusions could be drawn of the effect of the analytical conditions used and the amount Organotin observed. Presumable this is also due to the small size of the group.

5 DISCUSSION

In this proficiency test for the determination of Organotin in textile, it was noticed that the majority of the participants was able to detect and quantify correctly Tributyltin (TBT) in sample #17650 and Dimethyltin (DMT) in sample #17651.

When the test results of this interlaboratory study were compared to the Öko-Tex Standard 100 (see table 6), it could be noted that some laboratories would make a different decision about the acceptability of the textile. One reporting laboratory would accept sample #17650 based on TBT for all classes (less than 0.5 mg/kg) and 22 of the reporting laboratories would have rejected sample #17650 based on TBT. The same was observed for sample #17651 based on the detection of DMT.

Öko-Tex Standard 100	Class 1 Baby clothes (mg/kg)	Class 2 Clothes direct skin contact (mg/kg)	Class 3 Clothes, no direct contact with skin (mg/kg)	Class 4 Decoration material (mg/kg)
TBT	0.5	1.0	1.0	1.0
DMT, MBT, DBT	1.0	2.0	2.0	2.0

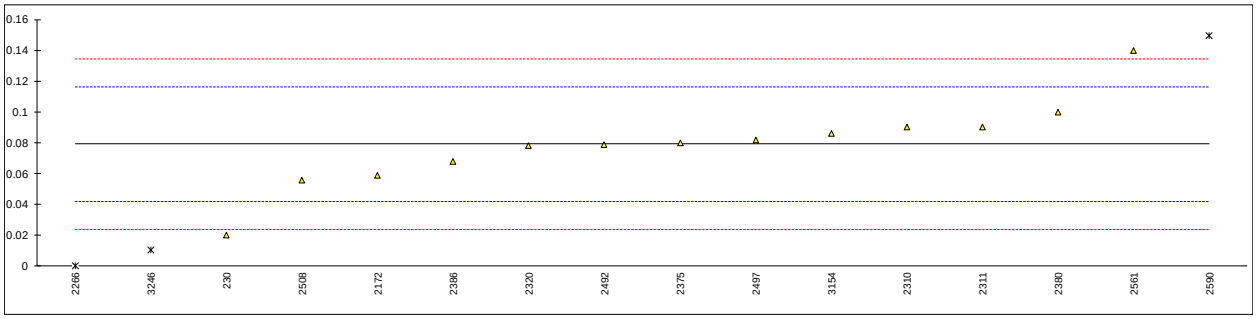
Table 6: Ecolabelling Standard and Requirements for Textiles in EU

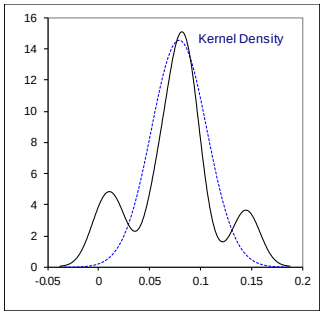
Although it is clear that not all laboratories followed the reported test method completely, it can be concluded that the observed variation in this interlaboratory study may not be caused by just one critical point in the analysis. Each participating laboratory will have to evaluate its performance in this study and decide about any corrective actions if necessary.

APPENDIX 1

Determination of Dibutyltin (DBT) on sample #17650; results in mg/kg

lab	method	value	mark	z(targ)	remarks
230	ISO17353	0.02		-3.19	
841		-----		-----	
2120	ISO TS 16179	< 0,30		-----	
2172	In house	0.05903		-1.08	
2266	ISO17353	0	ex	-4.27	excluded as 0 is not a real test result
2310	ISO17353	0.09		0.59	
2311	ISO17353	0.09		0.59	
2320	In house	0.0778		-0.06	
2375	ISO17353	0.08		0.05	
2380	ISO17353	0.0997		1.12	
2386	ISO17353	0.068		-0.59	
2390	ISO17353	n.d.		-----	
2492	In house	0.0785	C	-0.03	first reported: 0.785
2497	ISO TS 16179	0.082		0.16	
2508	ISO17353	0.056		-1.24	
2561	ISO TS 16179	0.14		3.29	
2590	ISO TS 16179	0.1497	DG(0.05)	3.82	
2666		-----		-----	
2730		-----		-----	
3146	ISO TS 16179	<0,1		-----	
3149		-----		-----	
3150		-----		-----	
3154	ISO TS 16179	0.086		0.38	
3176		-----		-----	
3210	In house	<0.5		-----	
3220	ISO TS 16179	n.d.		-----	
3237		-----		-----	
3246	ISO TS 16179	0.0103	DG(0.05)	-3.71	
	normality	not OK			
	n	13			
	outliers	2+1ex			
	mean (n)	0.07900			
	st.dev. (n)	0.027359	RSD=34.6%		
	R(calc.)	0.07660			
	st.dev.(Horwitz)	0.018522			
	R(Horwitz)	0.05186			

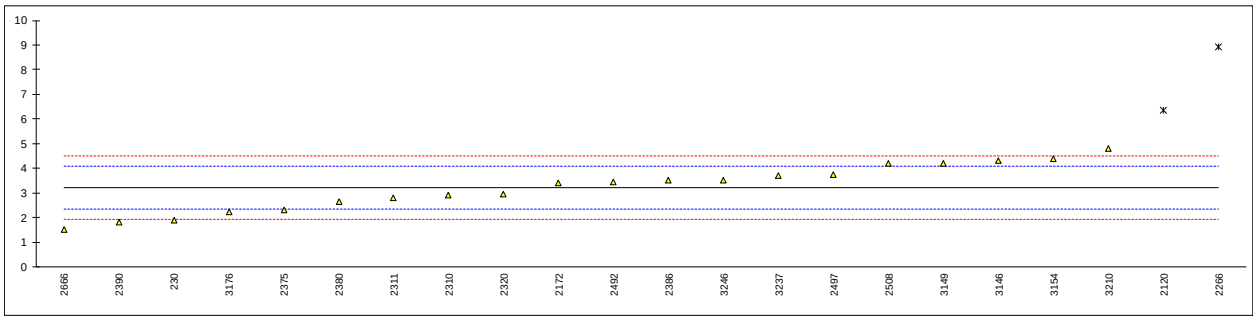


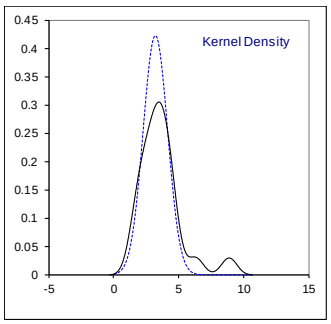


Determination of Tributyltin (TBT) on sample #17650; results in mg/kg

lab	method	value	mark	z(targ)	remarks
230	ISO17353	1.91		-3.03	
841		-----		-----	
2120	ISO TS 16179	6.34	R(0.05)	7.23	
2172	In house	3.423		0.48	
2266	ISO17353	8.93	R(0.01)	13.23	
2310	ISO17353	2.90		-0.73	
2311	ISO17353	2.8		-0.97	
2320	In house	2.953		-0.61	
2375	ISO17353	2.33		-2.05	
2380	ISO17353	2.6662		-1.28	
2386	ISO17353	3.504		0.66	
2390	ISO17353	1.812		-3.25	
2492	In house	3.4419		0.52	
2497	ISO TS 16179	3.751		1.24	
2508	ISO17353	4.202		2.28	
2561	ISO TS 16179	<0.05		<-7.34	possibly a false negative?
2590	ISO TS 16179	<L.O.Q.		-----	
2666	ISO TS 16179	1.500		-3.98	
2730		-----		-----	
3146	ISO TS 16179	4.329		2.58	
3149	ISO TS 16179	4.21		2.30	
3150		-----		-----	
3154	ISO TS 16179	4.380		2.69	
3176	ISO17353	2.22		-2.31	
3210	In house	4.797		3.66	
3220	ISO TS 16179	n.d.		-----	
3237	ISO TS 16179	3.697		1.11	
3246	ISO TS 16179	3.5152		0.69	

normality	OK	
n	20	
outliers	2	
mean (n)	3.21707	
st.dev. (n)	0.942568	RSD=29.3%
R(calc.)	2.63919	
st.dev.(Horwitz)	0.431717	
R(Horwitz)	1.20881	





Determination of other Organotin components on sample #17650; results in mg/kg

lab	MMT	DMT	TMT	TPT	MBT	TeBT
230	-----	-----	-----	-----	-----	-----
841	-----	-----	-----	-----	-----	-----
2120	< 0,30	< 0,30	< 0,30	< 0,30	< 0,30	< 0,30
2172	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
2266	0	0	0	0	0	0
2310	n.d.	0.06	n.d.	n.d.	n.d.	n.d.
2311	n.d.	0.071	n.d.	n.d.	n.d.	n.d.
2320	-----	0.1405	-----	-----	0.0331	-----
2375	-----	-----	-----	-----	-----	-----
2380	-----	0.0498	-----	-----	-----	-----
2386	-----	-----	-----	-----	-----	-----
2390	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
2492	-----	-----	-----	-----	-----	-----
2497	-----	-----	-----	-----	-----	-----
2508	-----	-----	-----	-----	-----	-----
2561	-----	-----	-----	-----	<0.05	<0.05
2590	<L.O.Q.	<L.O.Q.	<L.O.Q.	<L.O.Q.	<L.O.Q.	<L.O.Q.
2666	-----	-----	-----	-----	-----	-----
2730	-----	-----	-----	-----	-----	-----
3146	<0,1	<0,1	<0,1	not analyzed	<0,1	<0,1
3149	-----	-----	-----	-----	-----	-----
3150	-----	-----	-----	1.52	-----	-----
3154	-----	-----	-----	-----	-----	-----
3176	-----	-----	-----	-----	-----	-----
3210	-----	-----	-----	-----	<0.5	<0.5
3220	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
3237	-----	-----	-----	-----	-----	-----
3246	-----	-----	-----	-----	0.0385	n.d.

MMT = Monomethyltin
DMT = Dimethyltin
TMT = Trimethyltin
TPT = Tripropyltin
MBT = Monobutyltin
TeBT = Tetrabutyltin

Determination of other Organotin components on sample #17650; results in mg/kg == continued

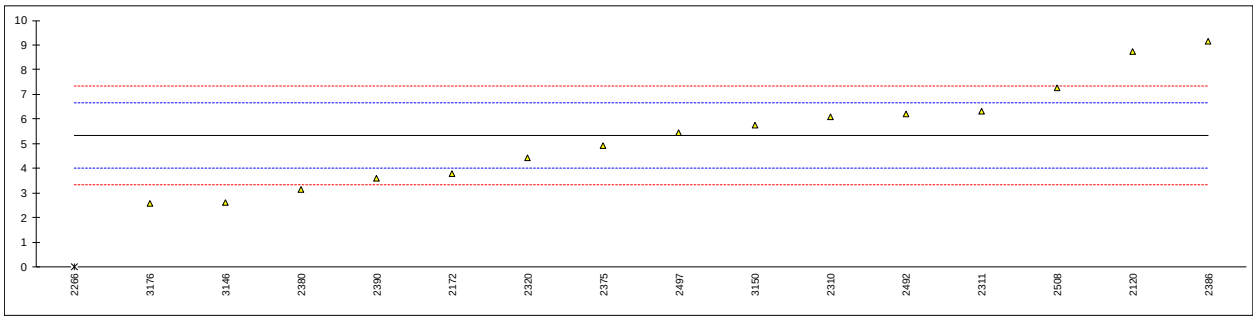
lab	MOT	DOT	TOT	DPhT	TPhT	TCyHT
230	-----	-----	-----	-----	-----	-----
841	-----	-----	-----	-----	-----	-----
2120	< 0,30	< 0,30	< 0,30	< 0,30	< 0,30	< 0,30
2172	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
2266	0	0	0	0	0	0
2310	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
2311	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
2320	-----	-----	-----	-----	-----	-----
2375	-----	-----	-----	-----	-----	-----
2380	-----	-----	-----	-----	-----	-----
2386	-----	-----	-----	-----	-----	-----
2390	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
2492	-----	-----	-----	-----	-----	-----
2497	-----	-----	-----	-----	-----	-----
2508	-----	-----	-----	-----	-----	-----
2561	<0.05	<0.05	-----	<0.05	<0.05	<0.05
2590	<L.O.Q.	<L.O.Q.	<L.O.Q.	<L.O.Q.	<L.O.Q.	<L.O.Q.
2666	-----	-----	-----	-----	-----	-----
2730	-----	-----	-----	-----	-----	-----
3146	<0,1	<0,1	<0,1	<0,1	<0,1	<0,1
3149	-----	-----	-----	-----	-----	-----
3150	-----	-----	-----	-----	-----	-----
3154	-----	-----	-----	-----	-----	-----
3176	-----	-----	-----	-----	-----	-----
3210	<0.5	<0.5	-----	-----	<0.5	<0.5
3220	2.23	n.d.	-----	n.d.	n.d.	n.d.
3237	-----	-----	-----	-----	-----	-----
3246	n.d.	n.d.	-----	-----	n.d.	n.d.

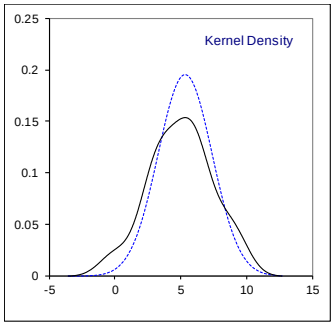
MOT = Monooctyltin
DOT = Dioctyltin
TOT = Trioctyltin
DPhT = Diphenyltin
TPhT = Triphenyltin
TCyHT = Tricyclohexyltin

Determination of Dimethyltin (DMT) on sample #17651; results in mg/kg

lab	method	value	mark	z(targ)	remarks
230		-----		-----	
841		-----		-----	
2120	ISO TS 16179	8.74		5.13	
2172	In house	3.783		-2.34	
2266	ISO17353	0	ex	-8.04	excluded as 0 is not a real test result; possibly a false negative?
2310	ISO17353	6.10		1.15	
2311	ISO17353	6.325		1.49	
2320	In house	4.4399		-1.35	
2375	ISO17353	4.91		-0.64	
2380	ISO17353	3.1343		-3.32	
2386	In house	9.155		5.75	
2390	ISO17353	3.607		-2.61	
2492	In house	6.1912		1.29	
2497	ISO TS 16179	5.442		0.16	
2508	ISO17353	7.267		2.91	
2561		-----		-----	
2590		-----		-----	
2666		-----		-----	
2730		-----		-----	
3146	ISO TS 16179	2.617		-4.10	
3149		-----		-----	
3150	ISO TS 16179	5.76		0.64	
3154		-----		-----	
3176	ISO17353	2.58		-4.15	
3210		-----		-----	
3220	ISO TS 16179	n.d.		-----	possibly a false negative?
3237		-----		-----	
3246		-----		-----	

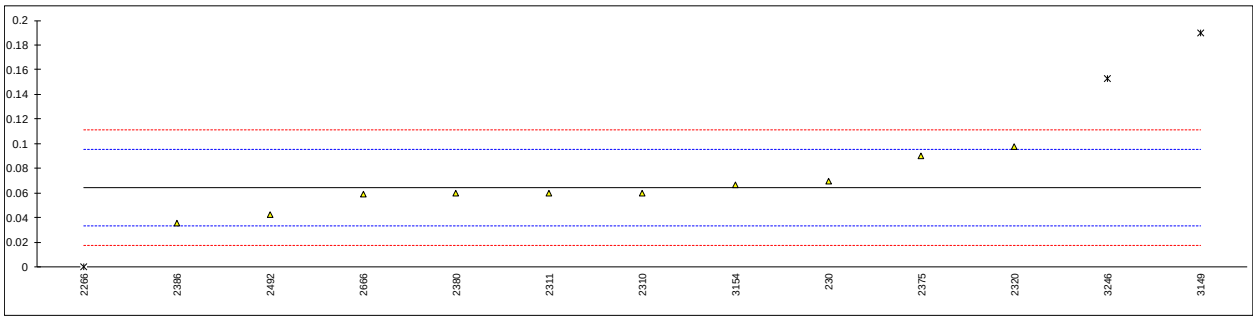
normality	OK	
n	15	
outliers	0+1ex	
mean (n)	5.33676	
st.dev. (n)	2.046017	RSD=38.3%
R(calc.)	5.72885	
st.dev.(Horwitz)	0.663638	
R(Horwitz)	1.85819	

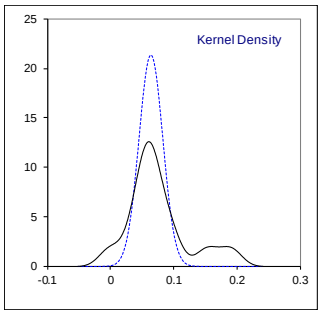




Determination of Tributyltin (TBT) on sample #17651; results in mg/kg

lab	method	value	mark	z(targ)	remarks
230	ISO17353	0.07		0.37	
841		-----		-----	
2120	ISO TS 16179	< 0,30		-----	
2172	In house	n.d.		-----	
2266	ISO17353	0	ex	-4.13	excluded as 0 is not a real test result
2310	ISO17353	0.06		-0.27	
2311	ISO17353	0.06		-0.27	
2320	In house	0.0976		2.15	
2375	ISO17353	0.09		1.66	
2380	ISO17353	0.0597		-0.29	
2386	In house	0.036		-1.82	
2390	ISO17353	n.d.		-----	
2492	In house	0.0428		-1.38	
2497		-----		-----	
2508		-----		-----	
2561	ISO TS 16179	<0.05		-----	
2590		-----		-----	
2666	ISO TS 16179	0.05936		-0.31	
2730		-----		-----	
3146	ISO TS 16179	<0,1		-----	
3149	ISO TS 16179	0.190	DG(0.05)	8.09	
3150		-----		-----	
3154	ISO TS 16179	0.067		0.18	
3176		-----		-----	
3210	In house	<0.5		-----	
3220	ISO TS 16179	n.d.		-----	
3237		-----		-----	
3246	ISO TS 16179	0.1529	DG(0.05)	5.71	
	normality	OK			
	n	10			
	outliers	2+1ex			
	mean (n)	0.06425			
	st.dev. (n)	0.018723	RSD=29.1%		
	R(calc.)	0.05242			
	st.dev.(Horwitz)	0.015538			
	R(Horwitz)	0.04351			





Determination of other Organotin components on sample #17651; results in mg/kg

lab	MMT	TMT	TPT	MBT	DBT	TeBT
230	-----	-----	-----	-----	-----	-----
841	-----	-----	-----	-----	-----	-----
2120	< 0,30	< 0,30	< 0,30	< 0,30	< 0,30	< 0,30
2172	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
2266	0	0	0	0	0	0
2310	0.06	n.d.	n.d.	n.d.	n.d.	n.d.
2311	0.061	n.d.	n.d.	n.d.	n.d.	n.d.
2320	-----	-----	-----	-----	-----	-----
2375	-----	-----	-----	-----	-----	-----
2380	-----	-----	-----	-----	-----	-----
2386	0.094	0.093	-----	-----	-----	-----
2390	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
2492	0.0564	0.0802	-----	-----	-----	-----
2497	0.0472	0.0283	-----	-----	-----	-----
2508	-----	-----	-----	-----	-----	-----
2561	-----	-----	-----	<0.05	<0.05	<0.05
2590	-----	-----	-----	-----	-----	-----
2666	-----	-----	-----	-----	-----	-----
2730	-----	-----	-----	-----	-----	-----
3146	<0,1	<0,1	not analyzed	<0,1	<0,1	<0,1
3149	-----	-----	-----	-----	-----	-----
3150	-----	-----	-----	-----	-----	-----
3154	-----	-----	-----	-----	-----	-----
3176	-----	3.48	-----	-----	-----	-----
3210	-----	-----	-----	<0.5	<0.5	-----
3220	n.d.	n.d.	n.d.	0.042	n.d.	n.d.
3237	-----	-----	-----	-----	-----	-----
3246	-----	-----	-----	n.d.	n.d.	n.d.

MMT = Monomethyltin
TMT = Trimethyltin
TPT = Tripropyltin
MBT = Monobutyltin
DBT = Dibutyltin
TeBT = Tetrabutyltin

Determination of other Organotin components on sample #17651; results in mg/kg == continued

lab	MOT	DOT	TOT	DPhT	TPhT	TCyHT
230	-----	-----	-----	-----	-----	-----
841	-----	-----	-----	-----	-----	-----
2120	< 0,30	< 0,30	< 0,30	< 0,30	< 0,30	< 0,30
2172	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
2266	0	0	0	0	0	0
2310	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
2311	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
2320	-----	-----	-----	-----	-----	-----
2375	-----	-----	-----	-----	-----	-----
2380	-----	-----	-----	-----	-----	-----
2386	-----	-----	-----	-----	-----	-----
2390	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
2492	-----	-----	-----	-----	-----	-----
2497	-----	-----	-----	-----	-----	-----
2508	-----	-----	-----	-----	-----	-----
2561	<0.05	<0.05	-----	<0.05	<0.05	<0.05
2590	-----	-----	-----	-----	-----	-----
2666	-----	-----	-----	-----	-----	-----
2730	-----	-----	-----	-----	-----	-----
3146	<0,1	<0,1	<0,1	<0,1	<0,1	<0,1
3149	-----	-----	-----	-----	-----	-----
3150	-----	-----	-----	-----	-----	-----
3154	-----	-----	-----	-----	-----	-----
3176	-----	-----	-----	-----	-----	-----
3210	<0.5	<0.5	-----	-----	<0.5	<0.5
3220	n.d.	n.d.	-----	n.d.	n.d.	n.d.
3237	-----	-----	-----	-----	-----	-----
3246	n.d.	n.d.	-----	-----	n.d.	n.d.

MOT = Monooctyltin
DOT = Dioctyltin
TOT = Trioctyltin
DPhT = Diphenyltin
TPhT = Triphenyltin
TCyHT = Tricyclohexyltin

APPENDIX 2

Analytical details

lab	method	ISO/IEC 17025 acc. for comp(s) of this PT	Sample material used (in g)	Extraction by:	Solvent used to extract/release	Extraction time (in minutes)/ temperature (in °C)	pH after adding the buffer to the extraction solvent	Extraction solution acidified until pH 4.5
230	ISO17353	---	---	---	---	---	---	---
841		---	---	---	---	---	---	---
2120	ISO TS 16179	No	0.5	Ultrasonic bath	10 ml MeOH/EtOH 80:20 + 0,5 ml Tropolone	60/60	n.a.	No
2172	In house	Yes	1	Ultrasonic bath	Methanol/Ethanol	60/60	4.5	Yes
2266	ISO17353	Yes	1	Aqeous	Diethyldithiocarbamate Sodium	60/40	---	No
2310	ISO17353	Yes	1	Solvent Extr.	Acetone	60/40	4.5 - 5.0	Yes
2311	ISO17353	Yes	1	Ultrasonic bath	Acetone	60/40	5.4	Yes
2320	In house	Yes	1.5038	Liquid - Liquid	Acetone	60/40	4.5	No
2375	ISO17353	Yes	1	Ultrasonic bath	Acetone	60/40	4.5	---
2380	ISO17353	Yes	1.005	Solvent Extr.	Acetone	60/40	4.5±0.3	4.5±0.3
2386	ISO17353	Yes	1.0/0.5	Ultrasonic bath	Acetone	60/40	4.5	4.5
2390	ISO17353	Yes	1.5	Ultrasonic bath	Acetone	60/40	4.5	Yes; pH 4.6
2492	In house	Yes	0.3	Ultrasonic bath	Ethanol and Acetic Acid	60/40	n.a.	n.a.
2497	ISO TS 16179	Yes	1	Liquid - Liquid	MeOH/EtOH, than buffer solution, than Iso-Octane	60/60	4.6	Yes
2508	ISO17353	---	0.5	Ultrasonic bath	95% Ethanol and 5% Acetic acid	60/40	---	---
2561	ISO TS 16179	Yes	1	Ultrasonic bath	MeOH/EtOH 80:20 v/v	60/60	n.a.	No
2590	ISO TS 16179	Yes	1	Ultrasonic bath	MeOH/EtOH 80:20 v/v	60/60	4.5	No
2666	ISO TS 16179	Yes	1	Ultrasonic bath	Methanol/Ethanol	60/60	5.6	No
2730	In house	No	1	Ultrasonic bath	n-Hexane	60/60	---	---
3146	ISO TS 16179	Yes	0.5	Ultrasonic bath	MeOH/EtOH 80:20 v/v	60/60	5	No
3149	ISO TS 16179	No	1	Ultrasonic bath	MeOH/EtOH 80:20 + Tropolone	60/60	---	---
3150	ISO TS 16179	Yes	0.5	Ultrasonic bath	MeOH/EtOH 80:20 v/v	60/60	4.5	No
3154	ISO TS 16179	---	---	---	---	---	---	---
3176	ISO17353	Yes	1	Ultrasonic bath	MeOH	30/25	4.5	Yes
3210	In house	No	1	Ultrasonic bath	Methanol/Ethanol	60/60	---	No
3220	ISO TS 16179	Yes	1	Ultrasonic bath	MeOH/EtOH 80:20 v/v	60/60	4.5	Yes
3237	ISO TS 16179	Yes	0.5	Liquid - Liquid	Methanol and Tropolone	60/60	4.5	Yes
3246	ISO TS 16179	Yes	0.5	Ultrasonic bath	MeOH/EtOH 80:20 v/v +Tropolone	60/60	4.5	No

APPENDIX 3

Number of participants per country

1 lab in BANGLADESH
3 labs in FRANCE
6 labs in GERMANY
1 lab in HONG KONG
3 labs in INDIA
3 labs in ITALY
1 lab in MAURITIUS
1 lab in P.R. of CHINA
1 lab in PAKISTAN
1 lab in PORTUGAL
1 lab in SRI LANKA
3 labs in TURKEY
1 lab in UNITED KINGDOM
2 labs in VIETNAM

APPENDIX 4

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
E	= probably an error in calculations
U	= test result probably reported in a different unit
W	= test result withdrawn on request of participant
ex	= test result excluded from statistical evaluation
n.a.	= not applicable
n.e.	= not evaluated
n.d.	= not detected
fr.	= first reported

Literature:

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9 ISO 5725:1986
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11 ISO105 E4:1994
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