Results of Proficiency Test
Phthalates in Leather
April 2017

Organised by: Institute for Interlaboratory Studies
Spijkenisse, the Netherlands

Author: ing. R.J. Starink
Corrector: dr. R.G. Visser & ing. A.S. Noordman-de Neef

Report: iis17A12

June 2017

CONTENTS

1 INTRODUCTION

The determination of phthalates in leather is known to give problems with the comparability of laboratory results. However, no appropriate leather reference materials are yet available.
As an alternative, participation in a proficiency test may enable laboratories to check and improve their performance. Therefore, on request of several participants, the Institute for Interlaboratory Studies decided to organise an interlaboratory study for the determination of Phthalates in leather in the 2016/2017 PT program.
In this first interlaboratory study, 41 laboratories in 19 different countries registered. See appendix 4 for the number of participating laboratories per country.
In this report the results of the 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 (PT). Sample analyses for fit-for-use and homogeneity testing were subcontracted to an ISO/IEC 17025 accredited laboratory. It was decided to send one leather sample (labelled #17547) positive on phthalates. The batch was especially prepared by a third party laboratory. 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 March 2017 (iis-protocol, version 3.4). This protocol can be downloaded via the FAQ page of the iis website www.iisnl.com.

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

A batch of leather doped to be positive with a number of Phthalates was obtained from a third party laboratory. The bulk was grinded and homogenized. Out of this batch 50 subsamples of 2 grams each were packed in aluminium foil and then put in a glass jar, labelled #17547.
The homogeneity of the subsamples #17547 was checked by the determination of Benzylbutylphthalate (BBP) and Diisobutylphthalate (DIBP) on six stratified randomly selected samples. The determination is performed in accordance with ISO/TS16181. See the following table for the test results.

	BBP in %M/M	DIBP in %M/M
Sample #17547-1	0.198	0.213
Sample #17547-2	0.190	0.203
Sample #17547-3	0.194	0.203
Sample #17547-4	0.200	0.207
Sample #17547-5	0.189	0.195
Sample #17547-6	0.185	0.196

Table 1: homogeneity test results of the subsamples #17547

From the above test results the repeatabilities were calculated and compared with the corresponding repeatabilities of the target method ISO/TS16181:11 and in agreement with the procedure of ISO 13528, Annex B2 in the next table;

	BBP in %M/M	DIBP in %M/M
r (observed) #17547	0.016	0.019
ref. test method	ISO/TS16181:11	ISO/TS16181:11
r (ref. test method)	0.019	0.020

Table 2: evaluation of repeatabilities of phthalate contents of the subsamples #17547

The calculated repeatabilities were in agreement with the respective target precision data. Therefore, the homogeneity of subsamples #17547 was assumed.

To each of the participating laboratories, one sample of approx. 2 grams, labelled #17547 was sent on March 22, 2017.

2.5 ANALYSIS

The participants were requested to determine on sample #17547, fourteen individual phthalates and “other” phthalates (when identified).
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 test results, but 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 can not be used for meaningful statistical calculations.

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 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 sample and determination in appendix 1 of this report. The laboratories are presented by the code numbers.

Directly after the deadline, a reminder was sent to those laboratories that had not reported 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 (no reanalyses). 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 wast 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.

According 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 test. 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 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 variation in this interlaboratory study.

The target standard deviation was calculated from the target reproducibility by division with 2.8. In case no literature reproducibility was available, other target values are 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-purpose.

The z-scores were calculated according to:

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

The $z_{(target)}$ scores are listed in the result tables of 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

In this proficiency test several problems were encountered with reporting of the test results. Therefore, it was decided to extend the final reporting date to provide the participants the opportunity to report their test results. A few participants reported the test results after the final reporting date.
Finally, 41 laboratories reported 127 numerical results. Observed were 9 statistically outlying test results, which is 7.1% of all results. In proficiency studies outlier percentages of 3% - 7.5% are quite normal.

All original data sets proved to have a normal Gaussian distribution.

In this PT was besides some analytical details also asked if the laboratory was accredited for the determination of Phthalates in leather. The majority (68%) of the participants reported to be ISO/IEC 17025 accredited for the determination of Phthalates in leather. As this is the majority of the group no separate statistical analysis has been performed.

4.1 EVALUATION PER COMPONENT

In this section the reported test results are discussed per component.

The majority of the group (44%) reported to have used ISO/TS16181 as test method. Also CPSC-CH-C1001-09.3 and ISO14389 were mentioned as test method by respectively 15% and 12% of the laboratories. Another 17% of the laboratories reported to have used an in house test method, probably based on one of the above mentioned official test methods.

It was decided to use the precision data from ISO/TS16181:2011, mentioned in Annex A.2. Regretfully, only repeatability data is mentioned in this test method. Therefore, the target reproducibility was estimated as follows: the target repeatability was multiplied with 3 to get an estimate of the target reproducibility.

General: All laboratories did identify all added banned phthalates correctly. Sample #17547 contained Benzylbutylphthalate (BBP), Dibutylphthalate (DBP) and Diisobutylphthalate (DiBP).

BBP: The determination of BBP was problematic at the level of 0.175 %M/M. Four statistical outliers were detected. The calculated reproducibility after rejection of the statistical outliers is not in agreement with the estimated reproducibility of ISO/TS16181:11.

DBP: The determination of DBP was problematic at the level of 0.153 %M/M. Three statistical outliers were detected. The calculated reproducibility after rejection of the statistical outliers is not in agreement with the estimated reproducibility of ISO/TS16181:11.

DIBP: The determination of DIBP was problematic at the level of 0.155 %M/M. Two statistical outliers were detected. The calculated reproducibility after rejection of the statistical outliers is not in agreement with the estimated reproducibility of ISO/TS16181:11.

For DEHP, DIDP, DINP, DNOP, DCHP, DEP, DMP, DNHP, DPHP, DNPP and DUP the group of participants agreed on a concentration below <0.05 %M/M. Therefore no significant conclusions were drawn for these phthalates.

4.2 PERFORMANCE EVALUATION FOR THE GROUP OF LABORATORIES

A comparison has been made between the reproducibilities as found for the group of participating laboratories and the estimated reproducibilities of ISO14389:2014 (R_{target}) in the next tables:

Parameter	unit	n	average	2.8 * sd	R (target)
BBP	%M/M	37	0.175	0.065	0.051
DBP	%M/M	38	0.153	0.077	0.044
DIBP	%M/M	39	0.155	0.071	0.045

Table 3: overview of results for sample #17547

Without further statistical calculations, it can be concluded that the total group of participating laboratories may have difficulties with the analysis of Phthalates in leather, see also the discussion in paragraphs 4.1 and 5.

4.3 EVALUATION OF THE PROFICIENCY TEST OF APRIL 2017

The performance of the proficiency test was compared expressed as uncertainty of the PT, see table below.

	April 2017	*ISO/TS 16181*
BBP	13%	10%
DBP	18%	10%
DIBP	16%	10%

Table 4: comparison of uncertainties (relative in %) of phthalates

5 DISCUSSION

In this proficiency test for the determination of phthalates in leather, it was noticed that the participants were able to detect all three phthalates in sample #17547. Regretfully, the observed reproducibilities were not in agreement with the target reproducibilities.

In this PT also some analytical details were asked (see appendix 3) to use for further analyses. It was observed that not all laboratories performed the same method for extracting the Phthalates from the leather. The majority of laboratories mentioned to have used ISO/TS16181 as test method, several others did use ISO14389 or CPSC-CH-C1001-09.3 as test method, a few participants mentioned to have used an in house test method or did not report any details.
Test method ISO/TS16181 describes the use of Hexane/Acetone as extraction/release solvent and ultrasonic extraction technique.
Test methods ISO14389 and CPSC-CH-C1001-09.3 describe a similar sample pathway to determine phthalates from leather: THF as release/extraction solvent and ultrasonic as release/extraction technique.
When the reported test results of the determined phthalates for ISO/TS16181 were evaluated separately, the calculated reproducibilities are small compared to the calculated reproducibilities of the whole group and (almost) in agreement with the requirements of the test method, except for DIBP (see appendix 1).

Furthermore, in ISO/TS 16181, ISO14389 and CPSC-CH-C1001-09.3 it is mentioned that prior to analysis the samples should be cut into small pieces with a dimension of respective <4, <5 and <2mm. As the majority of the group used one of the three test methods, it was remarkable to notice that a number of participants did not cut or grind the sample before analysis, but used it as received (approx. 8x8mm). The reported phthalate concentrations by these labs do not indicate an effect on the Phthalates determination for this sample.

6 CONCLUSION

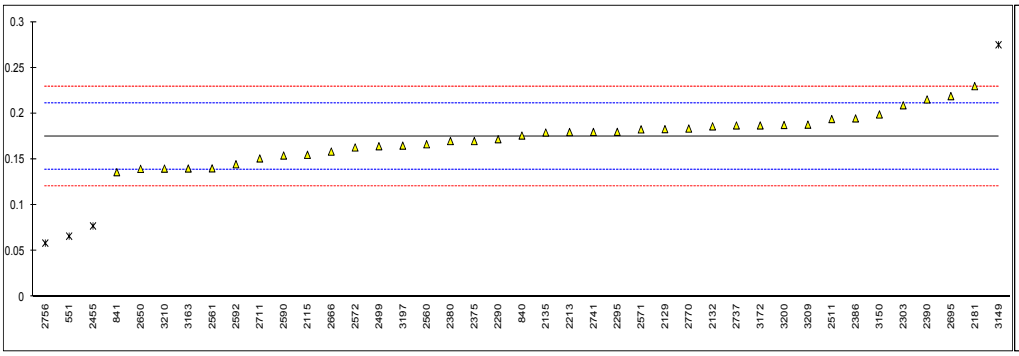
Although, it can be concluded that the majority of the participants have no problem with the determination on Phthalates in Leather of this PT, each participating laboratory will have to evaluate its performance in this study and decide about any corrective actions if necessary.

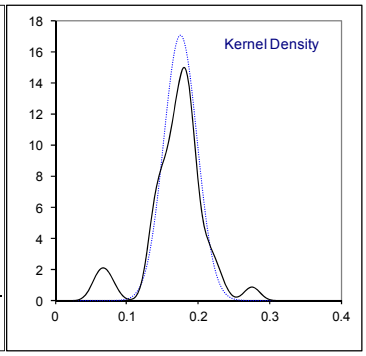
Therefore, participation on a regular basis in this scheme could be helpful to improve the performance and thus increase of the quality of the analytical results.

APPENDIX 1

Determination of BBP – Benzylbutylphthalate on sample #17547; results in %M/M

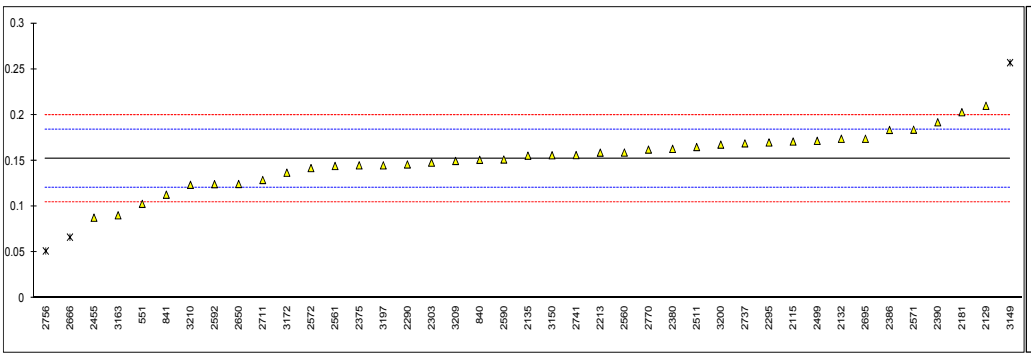
lab	method	value	mark	z(targ)	remarks
551	CPSC	0.06621	C,R(0.01)	-5.99	First reported 0.073912
840	ISO/TS 16181	0.176		0.06	
841		0.136		-2.14	
2115	ISO14389:2014	0.155		-1.10	
2129	ISO14389:2014Mod.	0.183		0.45	
2132	In house	0.1860		0.61	
2135		0.1793		0.24	
2181	ISO14389:2014	0.2299		3.03	
2213	ISO/TS 16181	0.1798		0.27	
2290	ISO/TS 16181	0.172		-0.16	
2295	In house	0.18		0.28	
2303		0.209		1.88	
2375	In house	0.170		-0.27	
2380	In house	0.170		-0.27	
2386	ISO/TS 16181	0.1947		1.09	
2390		0.2154	C	2.23	First reported 0.2961
2455	CPSC-CH-C1001-09.3	0.0773	C,R(0.01)	-5.38	First reported 0
2499	CPSC-CH-C1001-09.3	0.16433		-0.58	
2511	ISO/TS 16181	0.194		1.05	
2560	ISO14389	0.1665		-0.46	
2561	ISO14389:2014	0.1402		-1.91	
2571	CPSC-CH-C1001	0.18271		0.43	
2572	ISO/TS 16181	0.163		-0.65	
2590	CPSC-CH-C1001-09.3	0.1542		-1.14	
2592	CPSC-CH-C1001-09.3	0.1447		-1.66	
2650	ISO/TS 16181	0.1396		-1.94	
2666	ISO/TS 16181	0.1585		-0.90	
2695	ISO/TS 16181	0.219		2.43	
2711	ISO/TS 16181	0.151		-1.32	
2737	ISO/TS 16181	0.187		0.67	
2741	ISO/TS 16181	0.1799		0.28	
2756	ISO/TS 16181	0.05861	R(0.01)	-6.41	
2770	ISO/TS 16181	0.1836		0.48	
3149	In house	0.275	R(0.01)	5.52	
3150	DIN14389	0.199		1.33	
3163	In house	0.1400		-1.92	
3172	ISO/TS 16181	0.187		0.67	
3197	ISO/TS 16181	0.165		-0.54	
3200	ISO/TS 16181	0.1875		0.70	
3209	ISO/TS 16181	0.1879		0.72	
3210	In house	0.1399		-1.93	
					Only ISO/TS16181 data:
	normality	OK			OK
	n	37			15
	outliers	4			1
	mean (n)	0.17488			0.17671
	st.dev. (n)	0.023341			0.019672
	R(calc.)	0.06536			0.05508
	R(ISO/TS16181:11)	0.05083			0.05136

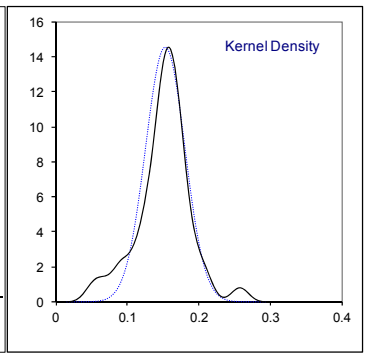




Determination of DBP – Dibutylphthalate on sample #17547; results in %M/M

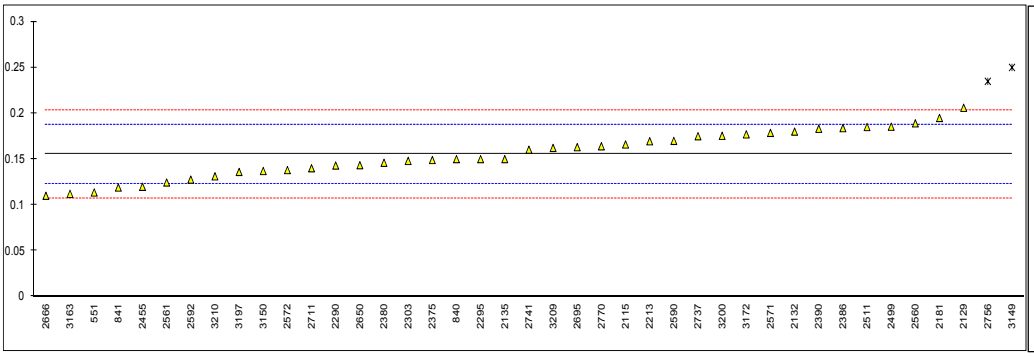
lab	method	value	mark	z(targ)	remarks
551	CPSC	0.102979		-3.14	
840	ISO/TS 16181	0.151		-0.11	
841		0.113		-2.50	
2115	ISO14389:2014	0.171		1.16	
2129	ISO14389:2014Mod.	0.210		3.62	
2132	In house	0.1740		1.35	
2135		0.1556		0.18	
2181	ISO14389:2014	0.2030		3.18	
2213	ISO/TS 16181	0.1589		0.39	
2290	ISO/TS 16181	0.146		-0.42	
2295	In house	0.17		1.09	
2303		0.148		-0.29	
2375	In house	0.145		-0.48	
2380	In house	0.163		0.65	
2386	ISO/TS 16181	0.1837		1.96	
2390		0.1920		2.48	
2455	CPSC-CH-C1001-09.3	0.0879	C	-4.09	First reported 0
2499	CPSC-CH-C1001-09.3	0.17174		1.20	
2511	ISO/TS 16181	0.165		0.78	
2560	ISO14389	0.159		0.40	
2561	ISO14389:2014	0.1443		-0.53	
2571	CPSC-CH-C1001	0.18388		1.97	
2572	ISO/TS 16181	0.142		-0.67	
2590	CPSC-CH-C1001-09.3	0.1514		-0.08	
2592	CPSC-CH-C1001-09.3	0.1245		-1.78	
2650	ISO/TS 16181	0.124625		-1.77	
2666	ISO/TS 16181	0.0666	DG(0.05)	-5.43	
2695	ISO/TS 16181	0.174		1.35	
2711	ISO/TS 16181	0.129		-1.49	
2737	ISO/TS 16181	0.169		1.03	
2741	ISO/TS 16181	0.1562		0.22	
2756	ISO/TS 16181	0.05158	DG(0.05)	-6.38	
2770	ISO/TS 16181	0.1622		0.60	
3149	In house	0.257	G(0.05)	6.58	
3150	DIN14389	0.156		0.21	
3163	In house	0.0905		-3.92	
3172	ISO/TS 16181	0.137		-0.99	
3197	ISO/TS 16181	0.145		-0.48	
3200	ISO/TS 16181	0.1676		0.94	
3209	ISO/TS 16181	0.1498		-0.18	
3210	In house	0.1238		-1.82	
					Only ISO/TS16181 data:
	normality	OK			OK
	n	38			13
	outliers	3			2
	mean (n)	0.15267			0.15425
	st.dev. (n)	0.027444			0.017003
	R(calc.)	0.07684			0.04761
	R(ISO/TS16181:2011)	0.04437			0.04483

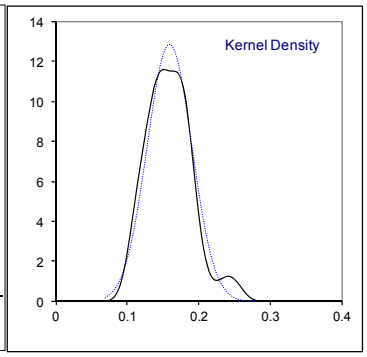




Determination of DIBP – Diisobutylphthalate on sample #17547; results in %M/M

lab	method	value	mark	z(targ)	remarks
551	CPSC	0.113589		-2.59	
840	ISO/TS 16181	0.150		-0.33	
841		0.119		-2.25	
2115	ISO14389:2014	0.166		0.66	
2129	ISO14389:2014Mod.	0.206		3.15	
2132	In house	0.1800		1.53	
2135		0.1500		-0.33	
2181	ISO14389:2014	0.1949		2.46	
2213	ISO/TS 16181	0.1695		0.88	
2290	ISO/TS 16181	0.143		-0.76	
2295	In house	0.15		-0.33	
2303		0.148		-0.45	
2375	In house	0.149		-0.39	
2380	In house	0.146		-0.58	
2386	ISO/TS 16181	0.1838		1.77	
2390		0.1831		1.73	
2455	CPSC-CH-C1001-09.3	0.1198	C	-2.20	First reported 0
2499	CPSC-CH-C1001-09.3	0.18539		1.87	
2511	ISO/TS 16181	0.185		1.84	
2560	ISO14389	0.189		2.09	
2561	ISO14389:2014	0.1245		-1.91	
2571	CPSC-CH-C1001	0.17861		1.45	
2572	ISO/TS 16181	0.138		-1.07	
2590	CPSC-CH-C1001-09.3	0.1699		0.91	
2592	CPSC-CH-C1001-09.3	0.1276		-1.72	
2650	ISO/TS 16181	0.143325		-0.74	
2666	ISO/TS 16181	0.1100		-2.81	
2695	ISO/TS 16181	0.163		0.48	
2711	ISO/TS 16181	0.140		-0.95	
2737	ISO/TS 16181	0.175		1.22	
2741	ISO/TS 16181	0.1603		0.31	
2756	ISO/TS 16181	0.23484	DG(0.05)	4.94	
2770	ISO/TS 16181	0.1640		0.54	
3149	In house	0.250	C,DG(0.05)	5.88	First reported 0.262
3150	DIN14389	0.137		-1.13	
3163	In house	0.1120		-2.69	
3172	ISO/TS 16181	0.177		1.35	
3197	ISO/TS 16181	0.136		-1.20	
3200	ISO/TS 16181	0.1754		1.25	
3209	ISO/TS 16181	0.1622		0.43	
3210	In house	0.1312		-1.49	
					Only ISO/TS16181 data:
	normality	OK			OK
	n	39			14
	outliers	2			1
	mean (n)	0.15528			0.15438
	st.dev. (n)	0.025205			0.020992
	R(calc.)	0.07057			0.05878
	R(ISO/TS16181:2011)	0.04513			0.04487





APPENDIX 2

Summary of other phthalates in sample #17547: results in %M/M

DEHP = Bis-2-ethylhexylphthalate
DIDP = Diisodecylphthalate
DINP = Diisononylphthalate
DNOP = Di-n-Octylphthalate
DCHP = Dicyclohexylphthalate
DEP = Diethylphthalate

Lab	Method	DEHP	DIDP	DINP	DNOP	DCHP	DEP
551	CPSC	0.010384	ND	ND	ND	ND	ND
840	ISO/TS 16181	ND	ND	ND	ND	ND	ND
841		n.d	n.d	n.d	n.d	-----	n.d
2115	ISO14389:2014	-----	-----	-----	-----	-----	-----
2129	ISO14389:2014Mod.	<0,02	<0,02	<0,02	<0,02	<0,02	<0,02
2132	In house	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05
2135		-----	-----	-----	-----	-----	-----
2181	ISO14389:2014	-----	-----	-----	-----	-----	-----
2213	ISO/TS 16181	<0.005	<0.005	<0.005	<0.005	<0.005	<0.005
2290	ISO/TS 16181	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01
2295	In house	-----	-----	-----	-----	-----	-----
2303		<0.2	<0.2	<0.2	<0.2	<0.2	-----
2375	In house	-----	-----	-----	-----	-----	-----
2380	In house	-----	-----	-----	-----	-----	-----
2386	ISO/TS 16181	<0,01	<0,01	<0,01	<0,01	<0,01	<0,01
2390		ND	ND	ND	ND	ND	ND
2455	CPSC-CH-C1001-09.3	0	0	0	0	0	0
2499	CPSC-CH-C1001-09.3	-----	-----	-----	-----	-----	-----
2511	ISO/TS 16181	-----	-----	-----	-----	-----	-----
2560	ISO14389	ND	ND	ND	ND	ND	ND
2561	ISO14389:2014	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01
2571	CPSC-CH-C1001	<0.001	<0.01	<0.01	<0.001	<0.001	<0.001
2572	ISO/TS 16181	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01
2590	CPSC-CH-C1001-09.3	< L.O.Q	< L.O.Q	< L.O.Q	< L.O.Q	< L.O.Q	< L.O.Q
2592	CPSC-CH-C1001-09.3	-----	-----	-----	-----	-----	-----
2650	ISO/TS 16181	-----	-----	-----	-----	-----	-----
2666	ISO/TS 16181	-----	-----	-----	-----	-----	-----
2695	ISO/TS 16181	n.d	n.d	n.d	n.d	n.d	n.d
2711	ISO/TS 16181	-----	-----	-----	-----	-----	-----
2737	ISO/TS 16181	-----	-----	-----	-----	-----	-----
2741	ISO/TS 16181	<0.005	<0.005	<0.005	<0.005	<0.005	<0.005
2756	ISO/TS 16181	0.00132	-----	-----	-----	-----	-----
2770	ISO/TS 16181	ND	ND	ND	ND	ND	ND
3149	In house	-----	-----	-----	-----	-----	-----
3150	DIN14389	-----	-----	-----	-----	-----	-----
3163	In house	0.0035	-----	-----	-----	-----	-----
3172	ISO/TS 16181	< 0.005	< 0.005	< 0.005	< 0.005	< 0.005	< 0.005
3197	ISO/TS 16181	ND	ND	ND	ND	ND	ND
3200	ISO/TS 16181	<0.0100	<0.0100	<0.0100	<0.0100	<0.0100	<0.0100
3209	ISO/TS 16181	Not detected	Not detected	Not detected	Not detected	Not detected	Not detected
3210	In house	-----	-----	-----	-----	-----	-----
	normality	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.
	n	15	12	12	12	12	12
	outliers	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.
	mean (n)	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05
	st.dev. (n)	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.
	R(calc.)	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.
	R(ISO/TS16181:11)	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.

Summary of other phthalates in sample #17547: results in %M/M - continued

DMP = Dimethylphthalate
DNHP = Di-n-Hexylphthalate
DPHP = Di(2-propylheptyl)phthalate
DNPP = Di-n-Pentylphthalate
DUP = Diundecylphthalate

Lab	Method	DMP	DNHP	DPHP	DNPP	DUP	other
551	CPSC	ND	ND	ND	ND	ND	ND
840	ISO/TS 16181	ND	ND	-----	ND	ND	ND
841		n.d	n.d	-----	n.d	n.d	-----
2115	ISO14389:2014	-----	-----	-----	-----	-----	-----
2129	ISO14389:2014Mod.	<0,02	<0,02	<0,02	<0,02	<0,02	<0,02
2132	In house	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05
2135		-----	-----	-----	-----	-----	-----
2181	ISO14389:2014	-----	-----	-----	-----	-----	-----
2213	ISO/TS 16181	<0.005	<0.005	<0.005	<0.005	<0.005	<0.005
2290	ISO/TS 16181	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01
2295	In house	-----	-----	-----	-----	-----	-----
2303		-----	<0.2	-----	<0.2	-----	-----
2375	In house	-----	-----	-----	-----	-----	-----
2380	In house	-----	-----	-----	-----	-----	-----
2386	ISO/TS 16181	<0,01	<0,01	<0,01	<0,01	<0,01	<0,01
2390		ND	ND	ND	ND	ND	ND
2455	CPSC-CH-C1001-09.3	0	0	0	0	0	0
2499	CPSC-CH-C1001-09.3	-----	-----	-----	-----	-----	-----
2511	ISO/TS 16181	-----	-----	-----	-----	-----	-----
2560	ISO14389	ND	ND	ND	ND	ND	ND
2561	ISO14389:2014	<0.01	***0.0535 f+?***	-----	<0.01	-----	<0.01
2571	CPSC-CH-C1001	<0.001	<0.001	<0.001	<0.001	<0.01	<0.001
2572	ISO/TS 16181	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01
2590	CPSC-CH-C1001-09.3	< L.O.Q	< L.O.Q	< L.O.Q	< L.O.Q	< L.O.Q	< L.O.Q
2592	CPSC-CH-C1001-09.3	-----	-----	-----	-----	-----	-----
2650	ISO/TS 16181	-----	-----	-----	-----	-----	-----
2666	ISO/TS 16181	-----	NO	NO	-----	-----	-----
2695	ISO/TS 16181	n.d	n.d	n.d	n.d	n.d	n.d
2711	ISO/TS 16181	-----	-----	-----	-----	-----	-----
2737	ISO/TS 16181	-----	-----	-----	-----	-----	-----
2741	ISO/TS 16181	<0.005	<0.005	<0.005	<0.005	<0.005	-----
2756	ISO/TS 16181	-----	-----	-----	-----	-----	-----
2770	ISO/TS 16181	ND	ND	-----	ND	-----	-----
3149	In house	-----	-----	-----	-----	-----	-----
3150	DIN14389	-----	-----	-----	-----	-----	-----
3163	In house	-----	-----	-----	-----	-----	-----
3172	ISO/TS 16181	< 0.005	< 0.005	< 0.005	< 0.005	< 0.005	< 0.005
3197	ISO/TS 16181	ND	ND	ND	ND	ND	ND
3200	ISO/TS 16181	<0.0100	<0.0100	<0.0100	<0.0100	<0.0100	<0.0100
3209	ISO/TS 16181	Not detected	Not detected	Not detected	Not detected	Not detected	Not detected
3210	In house	-----	-----	-----	-----	-----	-----
	normality	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.
	n	12	11	11	12	11	11
	outliers	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.
	mean (n)	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05
	st.dev. (n)	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.
	R(calc.)	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.
	R(ISO/TS16181:11)	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.

APPENDIX 3

Method information as reported by the participating laboratories

lab	1. ISO/IEC17025 accredited for phthalates?	2. sample grinded or cut prior to analysis or used as received?	3. Sample intake (in grams)?	4. Technique used to release/extract the phthalate(s)?	4a. internal standard added?	4b. solvent (mixture) used to release the analyte(s)?
551	Yes	Cut		Ultrasonic	Yes	THF
840	No	Cut	0.5	Ultrasonic	Yes	
841	Yes	---		---	---	
2115	Yes	Cut	0.3 g	Ultrasonic	Yes	THF + N-Hexane
2129	Yes	Cut	0,5 g	Ultrasonic	Yes	THF
2132	Yes	Used as received	0.05 g	Ultrasonic	Yes	THF, hexane
2135	No	Cut	0.3	Ultrasonic	No	THF / Acetonitrile
2181	Yes	Cut	0,5	Ultrasonic	Yes	THF/hexane
2213	Yes	Cut	2	Ultrasonic	Yes	n-hexane and acetone
2290	---	---		---	---	
2295	Yes	Cut		Ultrasonic	Yes	THF
2303	Yes	Cut	0.5	Ultrasonic	Yes	THF/Hexane
2375	Yes	Cut	0.1	Ultrasonic	Yes	THF-Hexane
2380	Yes	Used as received	0.1095 g	Ultrasonic	Yes	THF
2386	Yes	Used as received	8*8mm	Ultrasonic	Yes	n-Hexan/Aceton
2390	Yes	Cut	0.1036 g	Ultrasonic	Yes	THF + n-Hexane
2455	No	Grinded	~0.5 g	Ultrasonic	No	THF/hexane
2499	Yes	Used as received	0,5	Ultrasonic	Yes	THF/Hexane
2511	No	Used as received	0.100 g	Ultrasonic	Yes	
2560	Yes	Cut	0.502 g	Ultrasonic	Yes	THF then n-hexane
2561	Yes	Cut	0.5	Ultrasonic	Yes	10ml THF , 20ml Hexane.
2571	No	Grinded		Soxhlet	No	Ethoxyethane
2572	---	---		---	---	
2590	Yes	Cut	0,300 g	Ultrasonic	Yes	THF
2592	No	Used as received	0,2 to 1 g	Ultrasonic	Yes	THF
2650	Yes	Cut	0.5 grams	Ultrasonic	Yes	20% acetone and 80% hexane
2666	Yes	Cut	2,0048	Ultrasonic	Yes	hexane/acetone
2695	No	Cut	2 g	Ultrasonic	No	Acetone/Hexane
2711	No	Used as received	2	Ultrasonic	Yes	n-hexane/acetone 80/20 vol.
2737	Yes	Used as received	0.3 grams	Ultrasonic	Yes	Tetrahydrofuran/hexane=1:2
2741	No	Cut	0.5	Ultrasonic	Yes	n-hexane/acetone
2756	No	Cut	2.0gm	Ultrasonic	Yes	Hexane:Acetone
2770	Yes	Cut	0.5g	Ultrasonic	Yes	n-hexane/acetone
3149	Yes	---	1 g	Ultrasonic	Yes	toluene
3150	Yes	Cut	0,1	Ultrasonic	Yes	THF
3163	No	Cut	0.2g	Other	No	Toluene
3172	Yes	Cut	5 x 5mm	Ultrasonic	No	THF-ACN
3197	Yes	Cut	0,5 g	Ultrasonic	Yes	Acetone/Hexane
3200	Yes	Used as received	2.0g	Ultrasonic	Yes	n-hexane/acetone
3209	Yes	Cut	2 X 2mm	Ultrasonic	Yes	THF+n-Hexane
3210	Yes	Used as received	1g	Ultrasonic	Yes	Hexane/acetone (80/20)

lab	5. extraction time (minutes) and temperature (°C)?	6. analysis technique used to quantify the phthalate(s)?	7. If an MS-technique was used, which ions were used for quantification?
551	60ºC for 1 hour	CG-MS	149-206-167-223-104
840			
841			
2115	1 h, 60°C	GC-MS	206; 149; 223; 205 ; 91
2129	60 min / 60 °C	GC/MS	nn
2132	60 min, room temperature	GCMS	206 for BBP, 223 for DIBP, DBP
2135	60 °C , 60min	GC/MS	149
2181	1 hour, 60°C	GC-MS	223 for DIBP, DBP; 149 for BBP
2213	60 minute and 50 degree centigrade	GC MS	depends upon analyte of intertest (But in general is 149 mass)
2290			
2295	120 min and 25C	GC-MS Analysis	205,223,206,91,149 and 104
2303	150 minutes / room temperature	GC-MS	149
2375	60	GCMS	
2380	60 Min & 60 (°C)	GC-MS	DBP=223, BBP=91 & DIBP=149
2386	60min 50°C	GC-MS	
2390	60 minutes at 60 C	GCMS	DBP= (223,149, 167 , 205) , BBP = (206, 149, 91) , DIBP = (149, 223, 104)
2455	~4 hours	GC-MS	
2499	120 minutes and 25 °C	GC-MS	149, 205, 206, 223
2511		GC-MSMS	223/205/206/91/149
2560	60°C, 1 hour	GCMS	DIBP-149, DBP-149, BBP-149
2561	60 mins 60 oC	GC-MS	
2571	6 hours; 150	GC/MS	
2572			
2590	60 min - 60°C	GC-MS	
2592	1 h, rt	GC-MS	149
2650	60 minutes / 50ºC	GC-MS	149 / 293 / 307
2666	60 min 50°C	GC-MS	ALL 149 EXCEPTED DMP (163), DINP (293), DIDP (307)
2695	60 min., at 50°C	GC-MS	223, 223, 206
2711	60 min, Init 30°C, final temp 40°C	GC-MS	BBP: 149/206/238; DIBP; DBP: 149/223/205 (Analyte: target/Q1/Q2)
2737	60minutes	GC-MSD	BBP F149,91,206 DBP F149,223 DIBP F149,223
2741	1 h at 50 °C	GC-MS	206 (BBP), 223 (DBP,DIBP)
2756	1 hr at 50 degree centigrade	Chromatogram	
2770	60min,50°C	GC-MS	DIBP:149£¬223£¬205;DBP:149£¬223.205;BBP149£¬206£¬238
3149	15 min	GC-MS, ext. Std	
3150	1h 60°C	external Standard	149, 163, 59
3163	60min – 60°C	GCMS	149
3172	1h - 35°C	LC-MS	--
3197	60 minutes and 50C	GC-MS	149, 223, 167, 105, 205, 279
3200	60min	GC-MSD	149
3209	60 minutes at 40°C.	Mass Spectrometry	BBP:206, DBP:223, DIBP:149
3210	60 min at 50°C	GC/MS	149

APPENDIX 4

Number of participating laboratories per country

2 labs in BANGLADESH
1 lab in BRAZIL
1 lab in ETHIOPIA
1 lab in FRANCE
5 labs in GERMANY
1 lab in HONG KONG
1 lab in INDIA
8 labs in ITALY
4 labs in P.R. of CHINA
1 lab in PAKISTAN
1 lab in POLAND
1 lab in SPAIN
1 lab in TAIWAN R.O.C.
1 lab in THE NETHERLANDS
1 lab in TUNISIA
3 labs in TURKEY
1 lab in U.S.A.
2 labs in UNITED KINGDOM
5 labs 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 evaluation
n.a.	= not applicable
n.e.	= not evaluated
n.d.	= not detected
f+	= false positive test result?

Literature:

1 iis, Interlaboratory Studies: Protocol for the Organisation, Statistics and Evaluation, March 2017
2 ISO/TS16181:11
3 P.L. Davies, Fr Z. Anal. Chem, 351, 513, (1988)
4 W.J. Conover, Practical; Nonparametric Statistics, J. Wiley&Sons, NY, p.302, (1971)
5 ISO 5725, (1986)
6 ISO 5725, parts 1-6, (1994)
7 ISO 13528:05
8 M. Thompson and R. Wood, J. AOAC Int, 76, 926, (1993)
9 W.J. Youden and E.H. Steiner, Statistical Manual of the AOAC, (1975)
10 G. Rohm, J. Bohnen & H. Kruessmann, GIT Labor-Fachzeitschrift, p 1080, 11, (1997)
11 Bernard Rosner, Percentage Points for a Generalized ESD Many-Outlier Procedure, T*echnometrics*, 25(2), 165-172, (1983)
12 Analytical Methods Committee Technical brief, No 4.January 2001
13 P.J. Lowthian and M. Thompson, The Royal Society of Chemistry, Analyst, 127, 1359-1364, (2002)
14 Horwitz, W and Albert, R, J. AOAC Int, 79, 3, 589, (1996)