Results of Proficiency Test
Phthalates in Leather
April 2018

Organised by: Institute for Interlaboratory Studies
Spijkenisse, the Netherlands

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CONTENTS

1 INTRODUCTION

The determination of Phthalates on 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 organised an interlaboratory study for the determination of Phthalates in leather in 2017. PT program. During the annual testing program of 2017/2018, it was decided to continue the proficiency test for the analysis of Phthalates in Leather.
In this interlaboratory study, 67 laboratories in 24 different countries registered. See appendix 4 for the number of participating laboratories per country.
In this report, the results of the 2018 proficiency test are presented and discussed. This report is also electronically available through the iis website www.iisnl.com.

2 SET UP

The Institute for Interlaboratory Studies (iis) in Spijkenisse, the Netherlands was the organiser of 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 (of 3 grams, labelled #18555) positive on Phthalates to each participant.
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 prepared. The bulk was grinded and subsequently homogenized. Out of this batch 83 subsamples of 3 grams each were packed in plastic bags and labelled #18555.
The homogeneity of the subsamples #18555 was checked by the determination of Benzylbutylphthalate (BBP) and Dicyclohexylphthalate (DCHP) on eight stratified randomly selected samples. The determination was performed in accordance with ISO/TS16181. See the following table for the test results.

	BBP in %M/M	DCHP in %M/M
Sample #18555-1	0.1554	0.1049
Sample #18555-2	0.1510	0.1057
Sample #18555-3	0.1610	0.1106
Sample #18555-4	0.1638	0.1104
Sample #18555-5	0.1692	0.1155
Sample #18555-6	0.1566	0.1087
Sample #18555-7	0.1621	0.1088
Sample #18555-8	0.1632	0.1110

Table 1: homogeneity test results of the subsamples #18555

From the above test results the repeatabilities were calculated and compared with the corresponding repeatability 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	DCHP in %M/M
r (observed)	0.016	0.009
ref. test method	ISO/TS16181:11	ISO/TS16181:11
r (ref. test method)	0.016	0.011

Table 2: evaluation of repeatabilities of the subsamples #18555

The calculated repeatabilities were in agreement with the corresponding repeatability of the reference method. Therefore, the homogeneity of subsamples #18555 was assumed.

To each of the participating laboratories, one sample of approx. 3 grams, labelled #18555 was sent on April 4, 2018.

2.5 ANALYSES

The participants were requested to determine on sample #18555, fourteen individual Phthalates and “other” Phthalates (when identified).

It was also requested to report if the laboratory was accredited for the requested determined components and some method details were the 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 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 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 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. In this PT, the criterion of ISO13528, paragraph 9.2.1 was met for all evaluated tests, therefore, the uncertainty of all assigned values may be negligible and need not be included in the PT report.

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, no problems were encountered with sample transport or reporting of the test results. A few participants reported the test results after the final reporting date and one other participant did not report at all.
Finally, 66 laboratories reported 123 numerical results. Observed were 2 statistically outlying test results, which is 1.6% of all results. In proficiency studies outlier percentages of 3% - 7.5% are quite normal.

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

4.1 EVALUATION PER COMPONENT

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

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 repeatability was multiplied with 3 to get an estimate of the target reproducibility.

BBP: The determination of BBP was problematic at the level of 0.15 %M/M. Two statistical outliers were observed. The calculated reproducibility after rejection of the statistical outliers is not in agreement with the estimated reproducibility of ISO/TS16181:2011.

DCHP: The determination of DCHP was problematic at the level of 0.10 %M/M. No statistical outliers were observed. However, the calculated reproducibility is not in agreement with the estimated reproducibility of ISO/TS16181:11.

For DEHP, DBP, DIDP, DINP, DNOP, DEP, DMP, DNHP, DIBP, 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 ISO/TS16181:2011 (R_{target}) in the next tables:

Parameter	unit	n	average	2.8 * sd	R (target)
BBP	%M/M	63	0.150	0.066	0.043
DCHP	%M/M	58	0.100	0.057	0.029

Table 3: reproducibilities of tests for sample #18555

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 COMPARISON OF THE PROFICIENCY TEST OF APRIL 2018 WITH PREVIOUS PTS

	April 2018	*April 2017*
Number of reporting labs	66	41
Number of results reported	123	127
Number of statistical outliers	2	9
Percentage outliers	1.6%	7.1%

Table 4: comparison with previous proficiency tests

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

	April 2018	*April 2017*	*ISO/TS 16181*
BBP	16%	13%	10%
DBP	n.e.	18%	10%
DIBP	n.e.	16%	10%
DCHP	21%	n.e.	10%

Table 5: development of relative uncertainties over the years

4.4 EVALUATION OF THE ANALYTICAL DETAILS

In this PT, it was asked to report, besides some analytical details, whether the laboratory was accredited for the determination of Phthalates in Leather. The majority (84%) 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.

Looking at the analytical details (see appendix 3), it may be remarkable that a number of participants used a sample intake of less than 0.5 grams in contradiction with the PT instructions ("Please note, to ensure the homogeneity, do not use less than 0.5 gram per determination"). Method ISO/TS16181:2011 describes of sample intake of 2 grams. However, test method CPSC-CH-C1001-09.3 mentions an intake of only 0.05 gram, but describes that for samples larger than 0.05 grams (which is the case here) 10 ml of THF can be added for every 0.1 gram of extra sample.

In total thirty-eight laboratories used a sample intake of 0.5 grams and higher, nineteen used a sample intake lower than 0.5 grams and 8 laboratories did not report the sample intake.
When only the test results of participants with a reported sample intake of 0.5 gram and higher are evaluated, the calculated reproducibility is smaller, but still not in agreement with the estimated reproducibility of ISO/TS16181:2011 (see page 11 for BBP and page 13 for DCHP). However, a sample intake of <0.5 grams appears to have a negative influence on the variation in the test results.

Some laboratories used room temperature instead of 50-60°C to extract the Phthalates, however this does not appear to be of influence in the test result. Also, the use of different solvent mixtures to release the Phthalates do not appear to be of significant influence.

5 DISCUSSION

In this proficiency test for the determination of Phthalates in leather, it was noticed that the majoritiy of the participants were able to detect the Phthalates present in sample #18555. Regretfully, the observed reproducibilities were not in agreement with the target reproducibilities.

It was found that a sample intake of ≥0.5 grams will give less variation in the test results. This was also mentioned in the PT instructions. One should be aware that when a sample batch of samples containing 3 grams of material is tested for homogeneity, this is based on the use of a significant amount of the sample. When only part of the sample is used (some participants used only 1/60 of the available sample), homogeneity of such a small sample might not meet the requirements and that will have an effect on the obtained and reported test result. It is strongly advised to use a sample size of at least 0.5 grams.

6 CONCLUSION

Participants are strongly advised to read the PT instructions carefully and to use a sample size that is at least 0.5 grams.

Although it can be concluded that most 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.

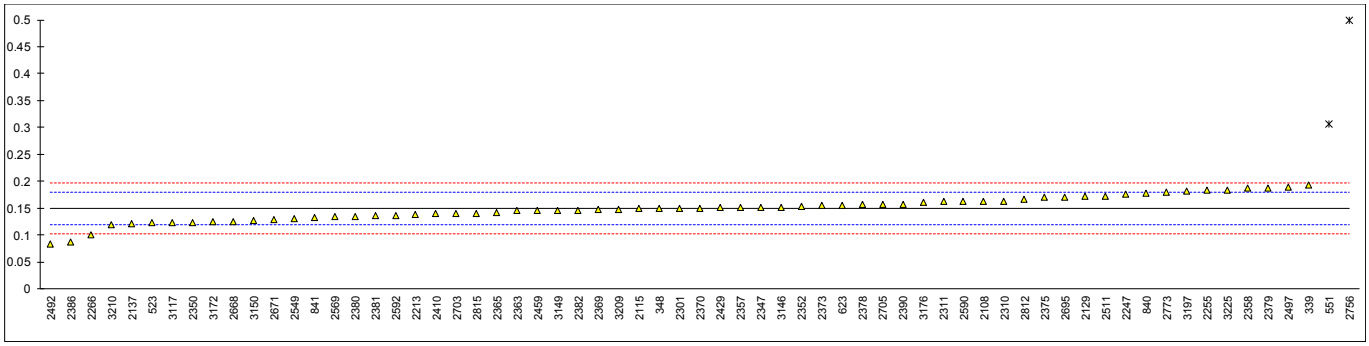
Therefore, participation on a regular basis in this scheme could be helpful to improve the performance and thus increase of the quality of the analytical results.

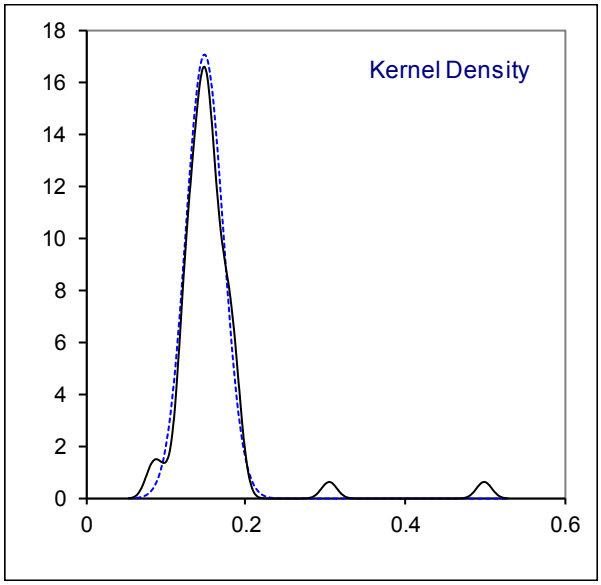
APPENDIX 1

Determination of BBP – Benzylbutylphthalate on sample #18555; results in %M/M

lab	method	value	mark	z(targ)	remarks
339	In house	0.1933		2.82	
348	CPSC-CH-C1001-09	0.150		0.03	
523	CPSC-CH-C1001-09.3	0.1227		-1.73	
551	In house	0.3058	C,R(0.01)	10.07	first reported: 3058.882
623	In house	0.156		0.42	
840	ISO/TS 16181	0.1779		1.83	
841	ISO/TS 16181	0.1333		-1.04	
2108	In house	0.163		0.87	
2115	ISO/TS 16181	0.149		-0.03	
2129	ISO/TS 16181	0.173		1.51	
2137	CPSC	0.1217		-1.79	
2213	ISO/TS 16181	0.138		-0.74	
2247	CPSC-CH-C1001-09.3	0.1766		1.75	
2255	ISO/TS 16181	0.183		2.16	
2266	ISO/TS 16181	0.1		-3.19	
2301	ISO/TS 16181	0.15		0.03	
2310	ISO/TS 16181	0.1634		0.90	
2311	ISO/TS 16181	0.162		0.80	
2330		-----		-----	
2347	ISO/TS 16181	0.1518		0.15	
2350		0.124		-1.64	
2352	ISO/TS 16181	0.1540		0.29	
2357	ISO/TS 16181	0.1512		0.11	
2358	ISO/TS 16181	0.1865		2.38	
2363	ISO/TS 16181	0.145		-0.29	
2365	ISO/TS 16181	0.14269		-0.44	
2369	ISO/TS 16181	0.1472	C	-0.15	reported: 1472 %M/M (probably a unit error)
2370	ISO/TS 16181	0.15034		0.05	
2373	In house	0.155		0.35	
2375	ISO/TS 16181	0.170		1.32	
2378	ISO/TS 16181	0.1571		0.49	
2379	CPSC-CH-C1001-09.3	0.188		2.48	
2380	CPSC-CH-C1001-09.3	0.13525		-0.92	
2381	CPSC-CH-C1001-09.3	0.13555		-0.90	
2382	In house	0.1467		-0.18	
2386	ISO/TS 16181	0.0872		-4.01	
2390	ISO14389	0.1577		0.53	
2410	CPSC-CH-C1001-09.3	0.14		-0.61	
2429	In house	0.1511		0.10	
2455	CPSC	nd		-----	false negative test result?
2459	ISO/TS 16181	0.145		-0.29	
2492	In house	0.0835		-4.25	
2497	ISO/TS 16181	0.1894		2.57	
2511	ISO/TS 16181	0.173		1.51	
2549	ISO/TS 16181	0.131		-1.19	
2569		0.134	C	-1.00	first reported: 1337
2590	ISO/TS 16181	0.16297		0.87	
2592		0.137		-0.81	
2668	In house	0.1252		-1.57	
2671		0.1293	C	-1.30	first reported: 293.9
2695	ISO/TS 16181	0.17045		1.35	
2703	In house	0.140		-0.61	
2705	In house	0.1574		0.51	
2756	ISO/TS 16181	0.5	C,R(0.01)	22.58	first reported: 0.0594
2773	ISO/TS 16181	0.18		1.96	
2812	ISO/TS 16181	0.167		1.13	
2815	ISO/TS 16181	0.14024		-0.60	
3117	ISO/TS 16181	0.123123		-1.70	
3146	In house	0.1524		0.19	
3149	In house	0.1462		-0.21	
3150	ISO/TS 16181	0.1278		-1.40	
3172		0.1241		-1.64	
3176	ISO/TS 16181	0.1607		0.72	
3197	ISO/TS 16181	0.1813		2.05	
3209	In house	0.1472		-0.15	
3210	In house	0.1185		-2.00	
3225	ISO/TS 16181	0.183		2.16	

		only ISO/TS16181 data:	only ≥0.5 grams sample intake
normality	OK	suspect	OK
n	63	35	38
outliers	2	1	1
mean (n)	0.14951	0.15450	0.15465
st.dev. (n)	0.023422	0.023329	0.020581
R(calc.)	0.06558	0.06532	0.05763
st.dev.(ISO/TS16181:2011)	0.015519	0.016037	0.016053
R(ISO/TS16181:2011)	0.04345	0.04490	0.04495

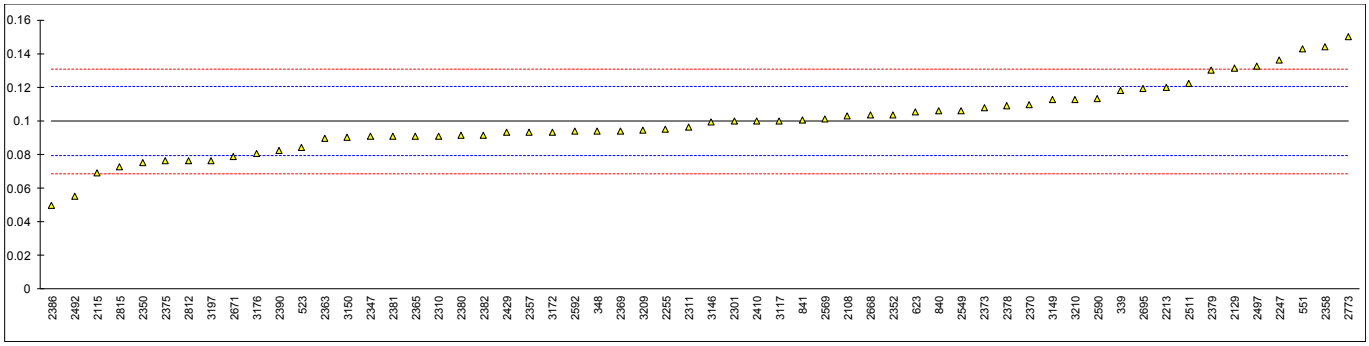


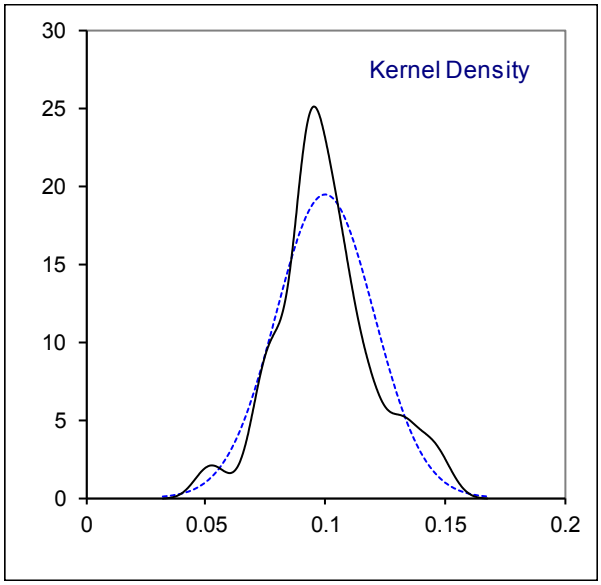


Determination of DCHP – Dicyclophexylphthalate on sample #18555; results in %M/M

lab	method	value	mark	z(targ)	remarks
339	In house	0.1180		1.76	
348	CPSC-CH-C1001-09	0.094		-0.56	
523	CPSC-CH-C1001-09.3	0.0840		-1.52	
551	In house	0.1428	C	4.16	first reported: 1428.796
623	In house	0.105		0.51	
840	ISO/TS 16181	0.1060		0.60	
841	ISO/TS 16181	0.1006		0.08	
2108	In house	0.103		0.31	
2115	ISO/TS 16181	0.069		-2.97	
2129	ISO/TS 16181	0.131		3.02	
2137		-----		-----	
2213	ISO/TS 16181	0.12		1.96	
2247	CPSC-CH-C1001-09.3	0.1364		3.54	
2255	ISO/TS 16181	0.095		-0.46	
2266		-----		-----	
2301	ISO/TS 16181	0.10		0.02	
2310	ISO/TS 16181	0.0910		-0.85	
2311	ISO/TS 16181	0.0964		-0.32	
2330		-----		-----	
2347	ISO/TS 16181	0.0907		-0.87	
2350		0.075		-2.39	
2352	ISO/TS 16181	0.1035		0.36	
2357	ISO/TS 16181	0.0933		-0.62	
2358	ISO/TS 16181	0.1439		4.26	
2363	ISO/TS 16181	0.0898		-0.96	
2365	ISO/TS 16181	0.09092		-0.85	
2369	ISO/TS 16181	0.0941	C	-0.55	reported: 941%M/M (probably a unit errro?)
2370	ISO/TS 16181	0.109323		0.92	
2373	In house	0.108		0.80	
2375	ISO/TS 16181	0.076		-2.29	
2378	ISO/TS 16181	0.1091		0.90	
2379	CPSC-CH-C1001-09.3	0.130		2.92	
2380	CPSC-CH-C1001-09.3	0.09125		-0.82	
2381	CPSC-CH-C1001-09.3	0.09085		-0.86	
2382	In house	0.0914		-0.81	
2386	ISO/TS 16181	0.0494		-4.86	
2390	ISO14389	0.0826		-1.66	
2410	CPSC-CH-C1001-09.3	0.10		0.02	
2429	In house	0.0931		-0.64	
2455	CPSC	nd		-----	false negative test result?
2459	ISO/TS 16181	ND		-----	false negative test result?
2492	In house	0.0550		-4.32	
2497	ISO/TS 16181	0.1322		3.13	
2511	ISO/TS 16181	0.122		2.15	
2549	ISO/TS 16181	0.106		0.60	
2569		0.101	C	0.12	first reported: 1009
2590	ISO/TS 16181	0.11305		1.28	
2592		0.0937		-0.58	
2668	In house	0.1032		0.33	
2671		0.0787	C	-2.03	first reported: 787.3
2695	ISO/TS 16181	0.11911		1.87	
2703		-----		-----	
2705		-----		-----	
2756		-----		-----	
2773	ISO/TS 16181	0.15		4.85	
2812	ISO/TS 16181	0.076		-2.29	
2815	ISO/TS 16181	0.07256		-2.63	
3117	ISO/TS 16181	0.100049		0.03	
3146	In house	0.0991		-0.06	
3149	In house	0.1124		1.22	
3150	ISO/TS 16181	0.09032		-0.91	
3172		0.0933		-0.62	
3176	ISO/TS 16181	0.0807		-1.84	
3197	ISO/TS 16181	0.0764		-2.26	
3209	In house	0.0942		-0.54	
3210	In house	0.1124		1.22	
3225		-----		-----	

		only ISO/TS16181 data:	only ≥0.5 grams sample intake
normality	OK	OK	OK
n	58	32	35
outliers	0	0	0
mean (n)	0.09976	0.09992	0.09941
st.dev. (n)	0.020483	0.022012	0.017504
R(calc.)	0.05735	0.06163	0.04901
st.dev.(ISO/TS16181:2011)	0.010355	0.010372	0.010318
R(ISO/TS16181:2011)	0.02899	0.02904	0.02889





APPENDIX 2

Summary of other Phthalates in sample #18555: results in %M/M

DEHP = Bis-2-ethylhexylphthalate
DBP = Dibutylphthalate
DIDP = Diisodecylphthalate
DINP = Diisononylphthalate
DNOP = Di-n-Octylphthalate
DEP = Diethylphthalate
DMP = Dimethylphthalate

Lab	DEHP	DBP	DIDP	DINP	DNOP	DEP	DMP
339	<0.001	<0.001	<0.010	<0.010	<0.002	<0.001	<0.001
348	<0.005	<0.005	<0.005	0.014	<0.005	<0.005	<0.005
523	<0.0150	<0.0150	<0.0150	<0.0150	<0.0150	-----	-----
551	-----	-----	-----	-----	-----	-----	-----
623	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
840	not detected	not detected	not detected	0.0060	not detected	not detected	not detected
841	-----	n.d	n.d	0.00688	n.d	n.d	n.d
2108	-----	-----	-----	-----	-----	-----	-----
2115	-----	-----	-----	0.0084	-----	-----	-----
2129	-----	-----	-----	0.00936	-----	-----	-----
2137	-----	-----	-----	-----	-----	-----	-----
2213	<0.005	<0.005	<0.005	0.006	<0.005	<0.005	<0.005
2247	ND	ND	ND	ND	ND	ND	ND
2255	ND	ND	ND	0.010	ND	ND	ND
2266	-----	-----	-----	-----	-----	-----	-----
2301	ND	ND	ND	ND	ND	ND	ND
2310	Not Detected	Not Detected	Not Detected	0.0076	Not Detected	Not Detected	Not Detected
2311	Not Detected	Not Detected	Not Detected	0.0067	Not Detected	Not Detected	Not Detected
2330	-----	-----	-----	-----	-----	-----	-----
2347	<0.005	<0.005	<0.005	<0.005	<0.005	<0.005	<0.005
2350	-----	-----	-----	0.012	-----	-----	-----
2352	-----	-----	-----	-----	-----	-----	-----
2357	ND	ND	ND	ND	ND	-----	-----
2358	n.d.	n.d.	n.d.	0.0183	n.d.	n.d.	n.d.
2363	ND	ND	ND	ND	ND	ND	ND
2365	<0.003	<0.003	<0.010	<0.010	<0.003	<0.003	<0.003
2369	<50	<50	<50	<50	<50	<50	<50
2370	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
2373	ND	ND	ND	ND	ND	ND	ND
2375	-----	-----	-----	0.009	-----	-----	-----
2378	-----	-----	-----	-----	-----	-----	-----
2379	0.002	0.001	Not detected	0.011	Not detected	Not detected	Not detected
2380	-----	-----	-----	0.00768	-----	-----	-----
2381	-----	-----	-----	0.00775	-----	-----	-----
2382	-----	-----	-----	-----	-----	-----	-----
2386	<0,003	<0,003	<0,003	0.004	<0,003	<0,003	<0,003
2390	N.D	N.D	N.D	N.D	N.D	N.D	N.D
2410	-----	-----	-----	-----	-----	-----	-----
2429	ND	ND	ND	ND	ND	ND	ND
2455	nd	nd	nd	nd	nd	nd	nd
2459	ND	ND	ND	ND	ND	ND	ND
2492	-----	-----	-----	-----	-----	-----	-----
2497	0.0059	0.0003	-----	0.00327	-----	-----	-----
2511	-----	-----	-----	-----	-----	-----	-----
2549	ND	ND	ND	ND	ND	ND	ND
2569	-----	-----	-----	-----	-----	-----	-----
2590	-----	-----	-----	-----	-----	-----	-----
2592	-----	-----	-----	0.0118	-----	-----	-----
2668	Not Detected	Not Detected	Not Detected	Not Detected	Not Detected	Not Detected	Not Detected
2671	-----	-----	-----	-----	-----	-----	-----
2695	-----	-----	-----	0.01401	-----	-----	-----
2703	-----	-----	-----	-----	-----	-----	-----
2705	0	0.00072	0	0.00915	0	0	0
2756	0.03	0.003	-----	-----	ND	-----	-----
2773	ND	ND	ND	0.006	ND	ND	ND
2812	-----	-----	-----	-----	-----	-----	-----
2815	0.00071	0.00023	0.00184	0.00784	0.00015	-----	-----
3117	0.001532	0	0	0	0	0	0
3146	<0,005	<0,005	<0,005	0.0066	<0,005	n.a.	<0,005
3149	-----	0.00049	-----	0.0052	-----	-----	-----
3150	-----	-----	-----	0.00454	-----	-----	-----
3172	< 0.005	< 0.005	< 0.005	< 0.005	< 0.005	< 0.005	< 0.005
3176	-----	-----	-----	0.0175	-----	-----	-----
3197	ND	ND	ND	0.0112	ND	ND	ND
3209	-----	-----	-----	-----	-----	-----	-----
3210	<0.0020	<0.0020	<0.0050	0.0091	<0.0020	<0.0020	<0.0020
3225	ND	ND	ND	ND	ND	-----	-----

Summary of other Phthalates in sample #18555: results in %M/M - continued

DNHP = Di-n-Hexylphthalate
DIBP = Diisobutylphthalate
DPHP = Di(2-propylheptyl)phthalate
DNPP = Di-n-Pentylphthalate
DUP = Diundecylphthalate
Other = Total other Phthalates

Lab	DNHP	DIBP	DPHP	DNPP	DUP	other
339	<0.001	<0.001	-----	<0.001	-----	-----
348	<0.005	<0.005	-----	<0.005	-----	-----
523	<0.0150	<0.0150	-----	<0.0150	-----	<0.0150
551	-----	-----	-----	-----	-----	-----
623	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
840	not detected	not detected	not detected	not detected	not detected	-----
841	n.d	n.d	n.d	n.d	n.d	n.d
2108	-----	-----	-----	-----	-----	-----
2115	-----	-----	-----	-----	-----	-----
2129	-----	-----	-----	-----	-----	-----
2137	-----	-----	-----	-----	-----	-----
2213	<0.005	<0.005	<0.005	<0.005	<0.005	<0.005
2247	ND	ND	ND	ND	ND	ND
2255	ND	ND	ND	ND	ND	ND
2266	-----	-----	-----	-----	-----	-----
2301	ND	ND	ND	ND	ND	-----
2310	Not Detected	Not Detected	Not Detected	Not Detected	Not Detected	-----
2311	Not Detected	Not Detected	Not Detected	Not Detected	Not Detected	-----
2330	-----	-----	-----	-----	-----	-----
2347	<0.005	<0.005	<0.005	<0.005	<0.005	<0.005
2350	-----	-----	-----	-----	-----	-----
2352	-----	-----	-----	-----	-----	-----
2357	-----	ND	-----	-----	-----	-----
2358	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
2363	ND	ND	ND	ND	ND	ND
2365	<0.003	<0.003	<0.003	<0.003	<0.003	<0.003
2369	<50	<50	<50	<50	<50	-----
2370	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
2373	ND	ND	ND	ND	ND	ND
2375	-----	-----	-----	-----	-----	-----
2378	-----	-----	-----	-----	-----	-----
2379	Not detected	Not detected	Not detected	Not detected	Not detected	Not tested
2380	-----	-----	-----	-----	-----	-----
2381	-----	-----	-----	-----	-----	-----
2382	-----	-----	-----	-----	-----	-----
2386	<0,003	<0,003	<0,003	<0,003	<0,003	<0,003
2390	N.D	N.D	N.D	N.D	N.D	N.D
2410	-----	-----	-----	-----	-----	-----
2429	ND	ND	ND	ND	ND	ND
2455	nd	nd	nd	nd	-----	-----
2459	ND	ND	ND	ND	ND	0.145
2492	-----	-----	-----	-----	-----	-----
2497	-----	-----	-----	-----	-----	-----
2511	-----	-----	-----	-----	-----	-----
2549	ND	ND	ND	ND	ND	ND
2569	-----	-----	-----	-----	-----	-----
2590	-----	-----	-----	-----	-----	-----
2592	-----	-----	-----	-----	-----	-----
2668	Not Detected	Not Detected	Not Detected	Not Detected	Not Detected	Not Detected
2671	-----	-----	-----	-----	-----	-----
2695	-----	-----	-----	-----	-----	-----
2703	-----	-----	-----	-----	-----	-----
2705	-----	-----	-----	-----	-----	-----
2756	-----	0.004	-----	-----	-----	-----
2773	ND	ND	ND	ND	ND	-----
2812	-----	-----	-----	-----	-----	-----
2815	0	0	-----	0	-----	-----
3117	0	0	0	0	0	0
3146	<0,005	<0,005	n.a.	<0,005	n.a.	0.2581
3149	-----	-----	-----	-----	-----	-----
3150	-----	-----	-----	-----	-----	-----
3172	< 0.005	< 0.005	< 0.005	< 0.005	< 0.005	< 0.005
3176	-----	-----	-----	-----	-----	-----
3197	ND	ND	ND	ND	ND	ND
3209	-----	-----	-----	-----	-----	-----
3210	<0.0020	<0.0020	-----	<0.0020	<0.0020	-----
3225	-----	ND	-----	-----	-----	-----

APPENDIX 3

Method information as reported by the participating laboratories

lab	ISO/IEC17025 accredited for Phthalates	Sample intake (in grams)	Solvent (mixture) used to release the analytes	Extraction time (in minutes)	Extraction tem-perature (in °C)
339	No	0.5	THF	60	60
348	No	0.5	THF	60	60
523	Yes	0.4	THF	120	35
551	Yes				
623	Yes	0.1	THF/Hexane	60	60
840	Yes	1x1mm	hexan : acetone (4:1)	60	50
841	---				
2108	Yes	1.1	THF/Hexan	60	60
2115	Yes	0.5	Acetone/Hexane	60	50
2129	Yes	0.5	THF	60	60
2137	Yes				
2213	Yes	1	80:20 (N-Hexane:Acetone)	60	50
2247	Yes	0.0596	Tetrahydorfuran (THF)	30	25
2255	Yes	0.501	n-Hexane/Acetone (80/20)	60	50
2266	No	2.02	acétone/hexane	60	50
2301	Yes	0.5	Hexane:Acetone	60	50
2310	Yes	0.5	Acetone & hexane	60	50
2311	Yes	0.5	Acetone/Hexane (2:8)	60	50
2330	---				
2347	Yes	2	hexane	60	50
2350	Yes	0.1	THF/Hexane	60	60
2352	Yes	2	HEXANE:ACETONE=8:2	60	50
2357	Yes	2.0	n-Hexane;Acetone=8;2	60	50
2358	Yes	2	Hexane:Acetone 8:2	60	50
2363	Yes	1	Hexane:Acetone=8:2	60	50
2365	Yes	0.5	N-hexane:Aceton=4:1	60	50
2369	---	0.5	n-Hexane/acetone	60	50
2370	Yes	0.5	n-hexane/acetone,80%/20%	60	50
2373	Yes	0.1	HEXANE,TETRAHYDROFURAN	60	60
2375	Yes	0.5	Hexane:Acetone	60	50
2378	Yes	2	Hexane:Acetone=8:2	60	50
2379	Yes	0.1	Tetrahydrofuran : Hexane	30	room temp.
2380	Yes	0.1041	Tetrahydrofuran	60	60
2381	Yes	0.1	n-Hexane, THF	60	60
2382	No	0.1035	Hexane, Tetrahydrofuran	60	60
2386	Yes	0.3	n-Hexan:Aceton (80:20)	60	60
2390	Yes	0.5	THF: n-Hexane	60	60
2410	Yes		THF	60	40
2429	Yes	0.3	Hex:TFH=2:1	60	60
2455	Yes	0.25	cyclohexane/THF	1 day	room temp
2459	---				
2492	Yes	0.3	Tetrahydrofuran (THF)	60	60
2497	Yes	2	hexane	60	50

lab	ISO/IEC17025 accredited for Phthalates	Sample intake (in grams)	Solvent (mixture) used to release the analytes	Extraction time (in minutes)	Extraction tem-perature (in °C)
2511	Yes	0.1	THF/ACN	60	AMBIENT
2549	Yes	0.3	THF:CAN	60	60
2569	Yes	1	n-Hexane/Acetone	60	50
2590	Yes	1	acetone/Hexane 80/20 mixture	60	50
2592	No	0.2	THF	60	30
2668	Yes	0.3	THF:Hexane	60	60
2671	---				
2695	No	2	acetone/ exane 20/80	60	50
2703	Yes	0.101	thf with 3mg/l dehp-d4	150	60
2705	No	2	Diethylether	360	50
2756	No	1	HEXANE:ACETONE(80:20)	60	50
2773	Yes		n-hexane /acetone	60	50
2812	No	2	hexane %80 asetone %20	60	50
2815	Yes	2	hexane:acetone 80:20	60	50
3117	Yes	0.506		60	50
3146	Yes	0.5	Tetrahydrofuran & Acetonitrile	60	70
3149	Yes	1	Toluene	60	60
3150	No	1	n-hexane/acetone 80/20	60	50
3172	Yes	0.5	THF-ACN 1:2	60	25
3176	Yes	0.5	n-hexane/acetone	60	50
3197	Yes	2	Acetone/Hexane	60	50
3209	Yes	0.05	THF& ACN	60	40
3210	Yes	1.000	80% Hexane / 20% Acetone	60	50
3225	Yes	0.5	Hexane:Acetone	60	50

APPENDIX 4

Number of participating laboratories per country

3 labs in	BANGLADESH
1 lab in	BRAZIL
1 lab in	CAMBODIA
1 lab in	ETHIOPIA
3 labs in	FRANCE
6 labs in	GERMANY
3 labs in	HONG KONG
9 labs in	INDIA
2 labs in	INDONESIA
6 labs in	ITALY
3 labs in	KOREA
1 lab in	LUXEMBOURG
1 lab in	MEXICO
12 labs in	P.R. of CHINA
2 labs in	PAKISTAN
1 lab in	SPAIN
1 lab in	SWITZERLAND
1 lab in	TAIWAN R.O.C.
1 lab in	THAILAND
1 lab in	TUNISIA
4 labs in	TURKEY
1 lab in	U.S.A.
1 lab in	UNITED KINGDOM
2 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:

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