Institute for
Interlaboratory Studies

Results of Proficiency Test
Phthalates in Leather/Footwear
February 2023

Organized by: Institute for Interlaboratory Studies
Spijkenisse, the Netherlands

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1 INTRODUCTION

Phthalates is a restricted substance in a lot of applications. In the EU Phthalates are regulated in polymers by EC 1907/2006 (REACH). Furthermore, some Ecolabel organizations have mentioned limits for the use of Phthalates in consumer items like Textile and Leather. Well-known Ecolabelling organizations are OEKO-TEX® and BlueSign®.

Since 2017 the Institute for Interlaboratory Studies (iis) organizes a proficiency scheme for the determination of Phthalates in Leather/Footwear every year. During the annual proficiency testing program 2022/2023 it was decided to continue the proficiency test for the determination of Phthalates in Leather/Footwear.

In this interlaboratory study 37 laboratories in 17 countries registered for participation, see appendix 4 for the number of participants per country. In this report the results of the Phthalates in Leather/Footwear 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 organizer of this proficiency test (PT). Sample analyzes for fit-for-use and homogeneity testing were subcontracted to an ISO/IEC17025 accredited laboratory.
It was decided to send two different leather samples of 3 grams each labelled #23500 and #23501 respectively.
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/IEC17043:2010. 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 organization of this proficiency test was the one as described for proficiency testing in the report 'iis Interlaboratory Studies: Protocol for the Organisation, Statistics and Evaluation' of June 2018 (iis-protocol, version 3.5). This protocol is electronically available through the iis website www.iisnl.com, from the FAQ page.

2.3 CONFIDENTIALITY STATEMENT

All data presented in this report must be regarded as confidential and for use by the participating companies only. Disclosure of the information in this report is only allowed by means of the entire report. Use of the contents of this report for third parties is only allowed by written permission of the Institute for Interlaboratory Studies. Disclosure of the identity of one or more of the participating companies will be done only after receipt of a written agreement of the companies involved.

2.4 SAMPLES

For the first sample a batch of red grinded leather was selected to which a detectable level of Benzyl butyl phthalate (BBP) and Dibutyl phthalate (DBP) was added. After homogenization 50 small bags were filled with approximately 3 grams each and labelled #23500.
The homogeneity of the subsamples was checked by determination of BBP and DBP using an in house method on 10 stratified randomly selected subsamples.

	BBP in %M/M	DBP in %M/M
sample #23500-1	0.1553	0.1751
sample #23500-2	0.1542	0.1765
sample #23500-3	0.1530	0.1765
sample #23500-4	0.1810	0.1818
sample #23500-5	0.1660	0.1824
sample #23500-6	0.1589	0.1476
sample #23500-7	0.1506	0.1562
sample #23500-8	0.1480	0.1629
sample #23500-9	0.1558	0.1753
sample #23500-10	0.1498	0.1649

Table 1: homogeneity test results of subsamples #23500

From the above test results the repeatabilities are calculated and compared with 0.3 times the corresponding reproducibility of the reference method in agreement with the procedure of ISO13528, Annex B2 in the next table.

	BBP in %M/M	DBP in %M/M
r (observed)	0.0274	0.0323
reference method	iis memo 2201	iis memo 2201
0.3 x R (reference method)	0.0277	0.0300

Table 2: evaluation of the repeatabilities of subsamples #23500

The calculated repeatabilities are in agreement with 0.3 times the corresponding reproducibility of the reference method. Therefore, homogeneity of the subsamples was assumed.

For the second sample a batch of a grey grinded leather was selected to which a detectable level of Dicyclohexyl phthalate (DCHP) and Di-iso-nonyl phthalate (DINP) was added. After homogenization 50 small bags were filled with approximately 3 grams each and labelled #23501.
The homogeneity of the subsamples was checked by determination of DCHP and DINP using an in house method on 10 stratified randomly selected subsamples.

	DCHP in %M/M	DINP in %M/M
sample #23501-1	0.0454	0.0556
sample #23501-2	0.0446	0.0563
sample #23501-3	0.0385	0.0516
sample #23501-4	0.0446	0.0539
sample #23501-5	0.0404	0.0563
sample #23501-6	0.0406	0.0552
sample #23501-7	0.0375	0.0537
sample #23501-8	0.0410	0.0555
sample #23501-9	0.0414	0.0539
sample #23501-10	0.0392	0.0543

Table 3: homogeneity test results of subsamples #23501

From the above test results the repeatabilities were calculated and compared with 0.3 times the corresponding reproducibility of the reference method in agreement with the procedure of ISO13528, Annex B2 in the next table.

	DCHP in %M/M	DINP in %M/M
r (observed)	0.0076	0.0040
reference method	iis memo 2201	iis memo 2201
0.3 x R (reference method)	0.0073	0.0096

Table 4: evaluation of the repeatabilities of subsamples #23501

The calculated repeatabilities are in agreement with 0.3 times the corresponding reproducibility of the reference method. Therefore, homogeneity of the subsamples was assumed.

To each of the participating laboratories one leather sample labelled #23500 and one leather sample labelled #23501 was sent on January 25, 2023.

2.5 ANALYZES

The participants were requested to determine on samples #23500 and #23501, fourteen individual Phthalates and the total of other Phthalates:

BBP - Benzyl butyl phthalate	CAS No. 85-68-7
DEHP - Di-(2-ethylhexyl) phthalate	CAS No. 117-81-7
DBP - Dibutyl phthalate	CAS No. 84-74-2
DIDP - Di-iso-decyl phthalate	CAS No. 26761-40-0 & 68515-49-1
DINP - Di-iso-nonyl phthalate	CAS No. 28553-12-0 & 68515-48-0
DNOP - Di-n-octyl phthalate	CAS No. 117-84-0
DCHP - Dicyclohexyl phthalate	CAS No. 84-61-7
DEP - Diethyl phthalate	CAS No. 84-66-2
DMP - Dimethyl phthalate	CAS No. 131-11-3
DNHP - Di-n-hexyl phthalate	CAS No. 84-75-3
DIBP - Di-iso-butyl phthalate	CAS No. 84-69-5
DNPP - Di-n-pentyl phthalate	CAS No. 131-18-0
DPrP - Di-n-propyl phthalate	CAS No. 131-16-8
DMEP - Di-(2-methoxyethyl) phthalate	CAS No. 117-82-8

It was also requested to report if the laboratory was accredited for the determined components and to report some analytical details.
Furthermore, to ensure the homogeneity it was requested not to use less than 0.5 gram per determination. And not to dry or age the samples, nor determine volatile matter.

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’ test results which are above the detection limit, because such test results cannot be used for meaningful statistical evaluations.

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 test results of the individual laboratories were gathered via the data entry portal www.kpmd.co.uk/sgs-iis-cts/. The reported test results are tabulated per sample and per determination in appendices 1 and 2 of this report. The laboratories are presented by their 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 reanalyzes). Additional or corrected test results are used for the data analysis and the original results are placed under 'Remarks' in the result tables in appendices 1 or 2.

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 organization of this proficiency test was the one as described for proficiency testing in the report 'iis Interlaboratory Studies: Protocol for the Organisation, Statistics and Evaluation' of June 2018 (iis-protocol, version 3.5).
For the statistical evaluation the *unrounded* (when available) figures were used instead of the rounded test results. Test results reported as '<...' or '>...' were not used in the statistical evaluation.

First, the normality of the distribution of the various data sets per determination was checked by means of the Lilliefors-test, a variant of the Kolmogorov-Smirnov test and by the calculation of skewness and kurtosis. Evaluation of the three normality indicators in combination with the visual evaluation of the graphic Kernel density plot, lead to judgement of the normality being either 'unknown', 'OK', 'suspect' or 'not OK'. After removal of outliers, this check was repeated. If a data set does not have a normal distribution, the (results of the) statistical evaluation should be used with due care.

The assigned value is determined by consensus based on the test results of the group of participants after rejection of the statistical outliers and/or suspect data.

According to ISO13528 all (original received or corrected) results per determination were submitted to outlier tests. In the iis procedure for proficiency tests, outliers are detected prior to calculation of the mean, standard deviation and reproducibility. For small data sets, Dixon (up to 20 test results) or Grubbs (up to 40 test results) outlier tests can be used. For larger data sets (above 20 test results) Rosner's outlier test can be used. 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 visualize the data against the reproducibilities from literature, Gauss plots were made, using the sorted data for one determination (see appendix 1). On the Y-axis the reported test results are plotted. The corresponding laboratory numbers are on the X-xis. 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 reference test method. Outliers and other data, which were excluded from the calculations, are represented as a cross. Accepted data are represented as a triangle.

Furthermore, Kernel Density Graphs were made. This 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 (dotted line) was projected over the Kernel Density Graph (smooth line) for reference. The Gauss curve is calculated from the consensus value and the corresponding standard deviation.

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 (derived from e.g. ISO or ASTM test methods), the z-scores were calculated using a target standard deviation. This results in an evaluation independent of the variation in this interlaboratory study.

The target standard deviation was calculated from the literature reproducibility by division with 2.8. In case no literature reproducibility was available, other target values were used, like Horwitz or an estimated reproducibility based on former iis proficiency tests.

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 in order to evaluate whether the reported test result is fit-for-use.

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 test result tables in appendix 1.

Absolute values for z<2 are very common and absolute values for z>3 are very rare. Therefore, the usual interpretation of z-scores is as follows:

	$\lvert z \rvert$	< 1	good
1 <	$\lvert z \rvert$	< 2	satisfactory
2 <	$\lvert z \rvert$	< 3	questionable
3 <	$\lvert z \rvert$		unsatisfactory

4 EVALUATION

In this proficiency test no problems were encountered with the dispatch of the samples. Six participants reported test results after the final reporting date and one participant did not report any test results. Not all laboratories were able to report all components requested.
In total 36 laboratories reported 160 numerical test results. Observed were 7 outlying test results, which is 4.4%. In proficiency studies outlier percentages of 3% - 7.5% are quite normal.

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

4.1 EVALUATION PER SAMPLE AND PER COMPONENT

In this section the reported test results are discussed per sample and per component. 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 together with the original data in appendix 1. The abbreviations, used in these tables, are explained in appendix 5.

Test method ISO16181 is considered to be the official test method for Phthalates in Leather/Footwear. Unfortunately, this test method provides a variety of unclear precision data. Therefore, the target reproducibility used for the evaluation of the test results of Phthalates in Polymers as prescribed in iis memo 1701 was also used for the evaluation of the quality of the test results of Phthalates in Leather/Footwear till 2021.
However, with the progress of the iis PTs of Phthalates in Leather/Footwear it was noticed that the relative standard deviations (RSD%) for Phthalates in iis PTs in Polymers is on average better than in iis PTs in Leather. Therefore, it was decided in 2022 PT not to use the target reproducibility based on Phthalates in Polymers any longer, but to develop a new target reproducibility based on the iis PTs for Phthalates in PTs in Leather/Footwear with the aim to estimate a more realistic target reproducibility for Phthalates in Leather/Footwear. An iis memo 2201 was made in which the development of the new precision data has been prescribed. The PT data for iis memo 2201 are obtained from 6 iis PTs and 26 different data sets for 12 different Phthalates. It is observed that the relative standard deviation of the subsequent PTs and the individual Phthalates is not dependent on the individual Phthalates and therefore one target reproducibility for all individual Phthalates has been developed. The target reproducibility based on iis memo 2201 was estimated as the relative standard deviation (21%) of the mean multiplied by 2.8. This target reproducibility was used for the evaluation of the quality of the test results in iis PTs since 2022.

sample #23500

BBP: This determination was not problematic. Two statistical outliers were observed. The calculated reproducibility after rejection of the statistical outliers is in agreement with the reproducibility derived from the iis memo 2201.

DBP: This determination was not problematic. Two statistical outliers were observed. The calculated reproducibility after rejection of the statistical outliers is in agreement with the reproducibility derived from the iis memo 2201.

The concentrations of the other reported Phthalates mentioned in paragraph 2.5 were near or below the detection limit. Therefore, for these components no z-scores were calculated. See appendix 2 for the reported test results.

sample #23501

DBP: This determination may be problematic. No statistical outliers were observed. However, the calculated reproducibility is not in agreement with the reproducibility derived from the iis memo 2201.

DINP: 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 reproducibility derived from the iis memo 2201.

DCHP: This determination may be problematic. One statistical outlier was observed. The calculated reproducibility after rejection of the statistical outlier is not in agreement with the reproducibility derived from the iis memo 2201.

The concentrations of the other reported Phthalates mentioned in paragraph 2.5 were near or below the detection limit. Therefore, for these components no z-scores were calculated. See appendix 2 for the reported test results.

4.2 PERFORMANCE EVALUATION FOR THE GROUP OF LABORATORIES

A comparison has been made between the reproducibility as declared by the reference test method and the reproducibility as found for the group of participating laboratories. The number of significant test results, the average, the calculated reproducibility (2.8 * standard deviation) and the target reproducibility derived from reference method are presented in the next tables.

Component	unit	n	average	2.8 * sd	R(target)
BBP	%M/M	33	0.144	0.065	0.085
DBP	%M/M	34	0.110	0.039	0.065

Table 5: reproducibilities of tests on sample #23500

Component	unit	n	average	2.8 * sd	R(target)
DBP	%M/M	22	0.006	0.006	0.004
DINP	%M/M	33	0.086	0.058	0.050
DCHP	%M/M	31	0.061	0.041	0.036

Table 6: reproducibilities of tests on sample #23501

Without further statistical calculations it can be concluded that for the determination of BBP and DBP in sample #23500 there is a good compliance of the group of participants with the reference method.

4.3 COMPARISON OF THE PROFICIENCY TEST OF FEBRUARY 2023 WITH PREVIOUS PTS

	February 2023	February 2022	March 2021	May 2020	May 2019
Number of reporting laboratories	36	45	46	42	54
Number of test results	160	220	256	180	224
Number of statistical outliers	7	7	12	5	10
Percentage of statistical outliers	4.4%	3.2%	4.7%	2.8%	4.5%

Table 7: comparison with previous proficiency tests

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

The performance of the determinations, expressed as relative standard deviation (RSD), of this PTs was compared to uncertainties observed in PTs over the years, see below table.

Component	February 2023	February 2022	March 2021	May 2020	2017-2018	Target
BBP	16%	14%	17%	22%	13-16%	21%
DEHP	---	---	19%	25%	---	21%
DBP	13-33%	---	17-21%	---	18%	21%
DIDP	---	---	38%	---	---	21%
DINP	24%	20%	18%	---	---	21%
DNOP	---	22%	---	---	---	21%
DCHP	24%	---	---	16%	21%	21%
DEP	---	---	---	23-27%	---	21%
DMP	---	---	---	---	---	21%
DNHP	---	---	---	---	---	21%
DNPP	---	14%	---	---	---	21%
DIBP	---	16%	---	---	16%	21%

Table 8: development of uncertainties over the years

The uncertainty (RSD) of the determined Phthalates in this PT is comparable to the uncertainty observed in previous iis PTs.

4.4 EVALUATION OF THE ANALYTICAL DETAILS

The reported analytical details from the participants are listed in appendix 3. Based on the answers given by the participants the following can be summarized:

- About 85% of the reporting participants mentioned that they are accredited for the determination of Phthalates in Leather/Footwear.
- About 60% of the reporting participants used a test portion between 0.5 and 1 grams. About 35% used less sample material and about 5% used a sample intake of 2 – 3 grams.

- A vast majority (about 85%) of the reporting participants used an extraction time of 60 minutes.
- Almost all reporting participants used an extraction temperature of 50°C or 60°C.
- About 20% of the reporting particpants used Hexane/Acetone as solvent mixture to release the Phthalates. About 40% of the participants used Toluene and about 30% THF/Hexane as solvent.

Looking at the analytical details it may be remarkable that several participants used a sample intake of less than 0.5 grams. This deviates with the instruction in the letter of instructions “Please note, to ensure the homogeneity, do not use less than 0.5 gram per determination”. Furthermore, test method ISO16181-1 mentions a sample intake of 1.0 gram.

For BBP and DBP in sample #23500 the calculated reproducibility is in agreement with the target reproducibility. Therefore, no separate statistical analysis is performed.

5 DISCUSSION

In this proficiency test for the determination of Phthalates in Leather/Footwear it was noticed that almost all of the participants were able to detect the Phthalates present in samples #23500 and #23501.

When the results of this interlaboratory study were compared to the LEATHER STANDARD by OEKO-TEX® and with the similar BlueSign® systems substances list or RSL (see Table 9) it was noticed that not all participants would make identical decisions about the acceptability of the samples for the determined components.
One of the reporting participants would have accepted sample #23500 for all categories while all other participants would have rejected sample #23500 for all categories.
Three of the reporting participants would have accepted sample #23501 for all categories while all other participants would have rejected the sample #23501 for all categories.

Ecolabel	baby in %M/M	in direct skin contact in %M/M	no direct skin contact in %M/M
BlueSign® RSL	<0.05	<0.05	<0.05
OEKO-TEX® 100	<0.05	<0.05	<0.05

Table 9: BlueSign® RSL and LEATHER STANDARD by OEKO-TEX®

6 CONCLUSION

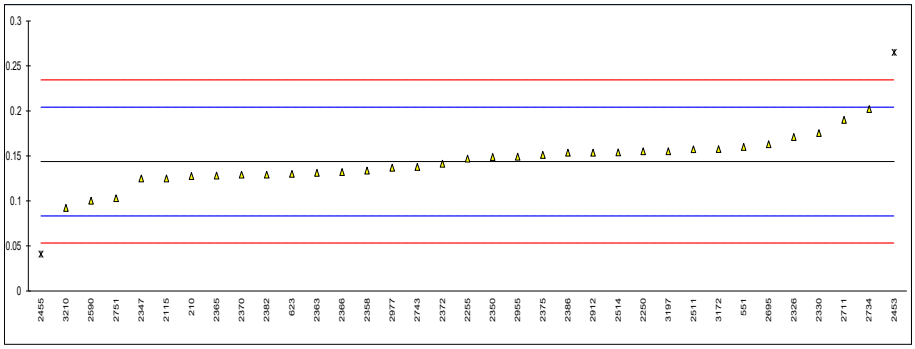
Although it can be concluded that most of the participants have no problem with the determination on Phthalates in Leather/Footwear in this PT, each participating laboratory will have to evaluate its performance in this study and decide about any corrective actions if necessary.
Therefore, participation on a regular basis in this scheme could be helpful to improve the performance and thus increase of the quality of the analytical results.

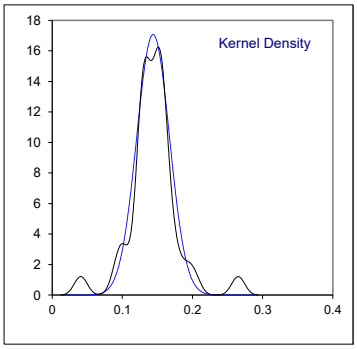
APPENDIX 1

Determination of BBP - Benzyl butyl phthalate on sample #23500; results in %M/M

lab	method	value	mark	z(targ)	remarks
210	CPSC-CH-C1001-09.4	0.127649		-0.53	
551	ISO16181-1	0.160		0.54	
623	In house	0.130		-0.46	
2115	ISO14389	0.125		-0.62	
2250	ISO14389	0.15517	C	0.38	first reported 1.5517
2255	ISO16181-1	0.147		0.11	
2265		-----		-----	
2326	ISO14389	0.171		0.90	
2330	ISO14389	0.1753		1.04	
2347	GB/T32440	0.125		-0.62	
2350	CPSC-CH-C1001-09.4	0.1486		0.16	
2358	ISO16181-1	0.1337		-0.33	
2363	ISO16181-1	0.131		-0.42	
2365	ISO16181-1	0.1281		-0.52	
2366	CPSC 09.4	0.1320		-0.39	
2370	CNS15138-1	0.129		-0.49	
2372	ISO14389	0.141235		-0.08	
2375	ISO16181-1	0.151		0.24	
2382	ISO16181-1	0.1291		-0.49	
2386	ISO16181-1	0.1536		0.32	
2453	ISO14389	0.265	R(0.01)	4.01	
2455	CPSC-CH-C1001-09.4	0.0408	R(0.01)	-3.41	
2511	ISO16181-1	0.1574		0.45	
2514	ISO16181-1	0.154		0.34	
2590	ISO16181-1	0.1002		-1.44	
2643		-----		-----	
2695	ISO16181-1	0.163		0.64	
2711	ISO16181-1	0.190		1.53	
2734	ISO16181	0.2019		1.92	
2743	ISO16181-1	0.1378		-0.20	
2751	ISO16181-1	0.1030		-1.35	
2912	ISO16181-1	0.1536		0.32	
2955	ISO16181-1	0.1490		0.17	
2977	ISO16181-1	0.13693		-0.23	
3172	ISO8124.6	0.1576		0.46	
3197	ISO16181-1	0.1552		0.38	
3210		0.0923		-1.71	

normality	OK
n	33
outliers	2
mean (n)	0.14380
st.dev. (n)	0.023364
RSD = 16 %	
R(calc.)	0.06542
st.dev.(iis memo 2201)	0.030198
R(iis memo 2201)	0.08455

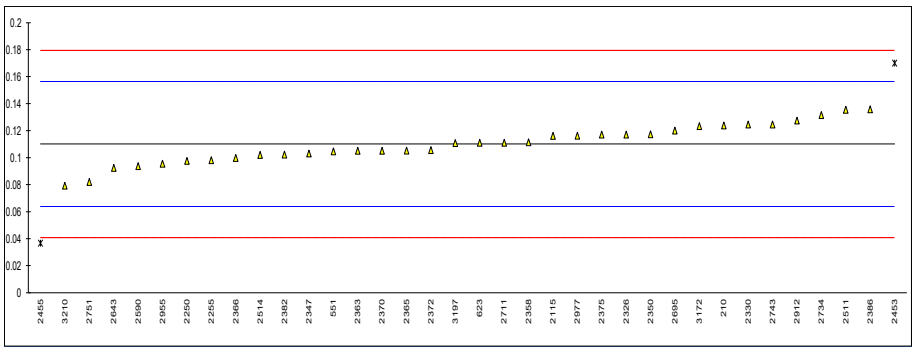


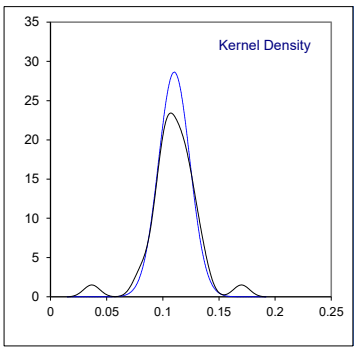


Determination of DBP - Dibutyl phthalate on sample #23500; results in %M/M

lab	method	value	mark	z(targ)	remarks
210	CPSC-CH-C1001-09.4	0.123796		0.59	
551	ISO16181-1	0.1045		-0.24	
623	In house	0.111		0.04	
2115	ISO14389	0.116		0.25	
2250	ISO14389	0.09753	C	-0.54	first reported 0.9753
2255	ISO16181-1	0.098		-0.52	
2265		-----		-----	
2326	ISO14389	0.117		0.30	
2330	ISO14389	0.1245		0.62	
2347	GB/T32440	0.103		-0.31	
2350	CPSC-CH-C1001-09.4	0.1173		0.31	
2358	ISO16181-1	0.1113		0.05	
2363	ISO16181-1	0.105		-0.22	
2365	ISO16181-1	0.1052		-0.21	
2366	CPSC 09.4	0.0997		-0.45	
2370	CNS15138-1	0.105		-0.22	
2372	ISO14389	0.105508		-0.20	
2375	ISO16181-1	0.117		0.30	
2382	ISO16181-1	0.1022		-0.34	
2386	ISO16181-1	0.1357		1.11	
2453	ISO14389	0.170	R(0.01)	2.59	
2455	CPSC-CH-C1001-09.4	0.0366	R(0.01)	-3.18	
2511	ISO16181-1	0.1354		1.09	
2514	ISO16181-1	0.102		-0.35	
2590	ISO16181-1	0.0937		-0.71	
2643	KS M1991	0.0924		-0.77	
2695	ISO16181-1	0.120		0.43	
2711	ISO16181-1	0.111		0.04	
2734	ISO16181	0.1315		0.92	
2743	ISO16181-1	0.1245		0.62	
2751	ISO16181-1	0.082		-1.22	
2912	ISO16181-1	0.1274		0.75	
2955	ISO16181-1	0.0955		-0.63	
2977	ISO16181-1	0.11613		0.26	
3172	ISO8124.6	0.1233		0.57	
3197	ISO16181-1	0.1107		0.03	
3210		0.0792		-1.34	

normality	OK
n	34
outliers	2
mean (n)	0.11012
st.dev. (n)	0.013935
RSD = 13 %	
R(calc.)	0.03902
st.dev.(iis memo 2201)	0.023124
R(iis memo 2201)	0.06475

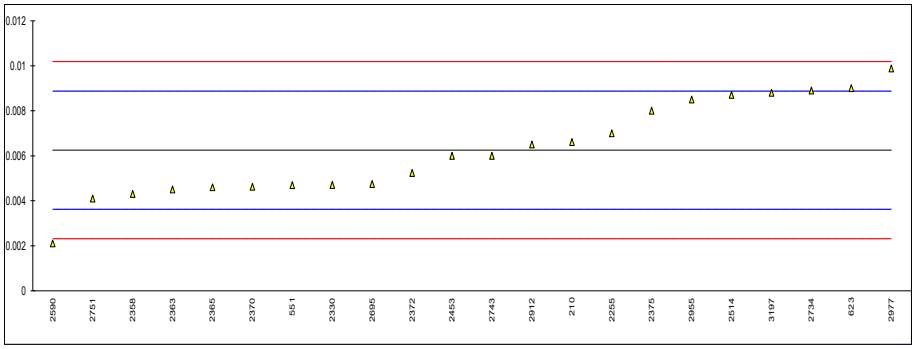


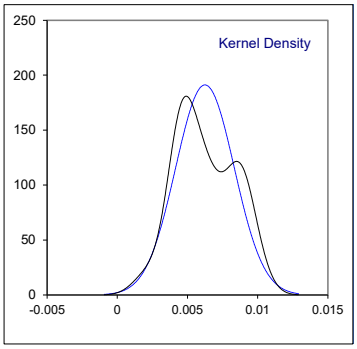


Determination of DBP - Dibutyl phthalate on sample #23501; results in %M/M

lab	method	value	mark	z(targ)	remarks
210	CPSC-CH-C1001-09.4	0.00661		0.27	
551	ISO16181-1	0.00469		-1.19	
623	In house	0.009		2.10	
2115		-----		-----	
2250	ISO14389	< 0.005		-----	
2255	ISO16181-1	0.007		0.57	
2265		-----		-----	
2326	ISO14389	ND		-----	
2330	ISO14389	0.0047		-1.18	
2347	GB/T32440	<0.005		-----	
2350	CPSC-CH-C1001-09.4	<0.015		-----	
2358	ISO16181-1	0.0043		-1.49	
2363	ISO16181-1	0.0045		-1.33	
2365	ISO16181-1	0.0046		-1.26	
2366	CPSC 09.4	<0.015		-----	
2370	CNS15138-1	0.00462		-1.24	
2372	ISO14389	0.0052358		-0.77	
2375	ISO16181-1	0.008		1.33	
2382	ISO16181-1	＜0.005		-----	
2386	ISO16181-1	<0.01		-----	
2453	ISO14389	0.006		-0.19	
2455		-----		-----	
2511		-----		-----	
2514	ISO16181-1	0.0087		1.87	
2590	ISO16181-1	0.002106		-3.16	
2643		-----		-----	
2695	ISO16181-1	0.00474		-1.15	
2711	ISO16181-1	< 0.05		-----	
2734	ISO16181	0.0089		2.02	
2743	ISO16181-1	0.0060		-0.19	
2751	ISO16181-1	0.0041		-1.64	
2912	ISO16181-1	0.0065		0.19	
2955	ISO16181-1	0.0085		1.72	
2977	ISO16181-1	0.00988		2.77	
3172	ISO8124.6	< 0.0005		<-4.38	possibly a false negative test result?
3197	ISO16181-1	0.0088		1.94	
3210		<0.002		<-3.24	possibly a false negative test result?

	normality	OK	
	n	22	
	outliers	0	
	mean (n)	0.00625	
	st.dev. (n)	0.002087	RSD = 33%
	R(calc.)	0.00584	
	st.dev.(iis memo 2201)	0.001312	
	R(iis memo 2201)	0.00367	



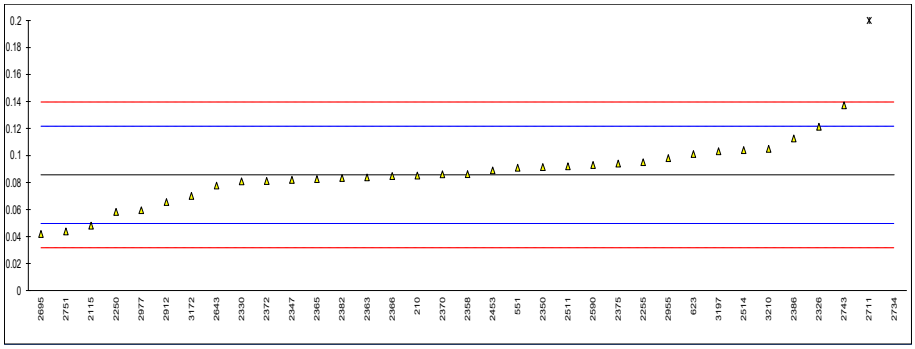


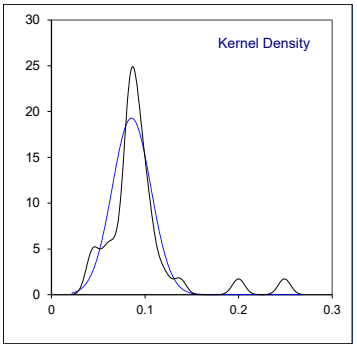
Determination of DINP - Di-iso-nonyl phthalate on sample #23501; results in %M/M

lab	method	value	mark	z(targ)	remarks
210	CPSC-CH-C1001-09.4	0.085034		-0.04	
551	ISO16181-1	0.0909		0.29	
623	In house	0.101	C	0.85	first reported “not detected”
2115	ISO14389	0.048		-2.09	
2250	ISO14389	0.0583	C	-1.52	first reported 0.583
2255	ISO16181-1	0.095		0.52	
2265		-----		-----	
2326	ISO14389	0.1212		1.97	
2330	ISO14389	0.0809	C	-0.27	first reported 0.1549
2347	GB/T32440	0.082		-0.20	
2350	CPSC-CH-C1001-09.4	0.0914		0.32	
2358	ISO16181-1	0.0862		0.03	
2363	ISO16181-1	0.0838		-0.10	
2365	ISO16181-1	0.0826		-0.17	
2366	CPSC 09.4	0.0847		-0.05	
2370	CNS15138-1	0.0860		0.02	
2372	ISO14389	0.0810653		-0.26	
2375	ISO16181-1	0.094		0.46	
2382	ISO16181-1	0.0833		-0.13	
2386	ISO16181-1	0.1127		1.50	
2453	ISO14389	0.089		0.18	
2455		-----		-----	
2511	ISO16181-1	0.0920		0.35	
2514	ISO16181-1	0.104		1.02	
2590	ISO16181-1	0.0929		0.40	
2643	KS M1991	0.0777		-0.44	
2695	ISO16181-1	0.0418		-2.44	
2711	ISO16181-1	0.20	C,R(0.01)	6.35	first reported 0.150
2734	ISO16181	0.2491	R(0.01)	9.08	
2743	ISO16181-1	0.1372		2.86	
2751	ISO16181-1	0.0437		-2.33	
2912	ISO16181-1	0.0655		-1.12	
2955	ISO16181-1	0.0980		0.68	
2977	ISO16181-1	0.05950		-1.46	
3172	ISO8124.6	0.0701		-0.87	
3197	ISO16181-1	0.1031		0.97	
3210		0.1049		1.07	

	normality	OK
	n	33
	outliers	2
	mean (n)	0.08568
	st.dev. (n)	0.020687
	R(calc.)	0.05792
	st.dev.(iis memo 2201)	0.017993
	R(iis memo 2201)	0.05038

RSD = 24%

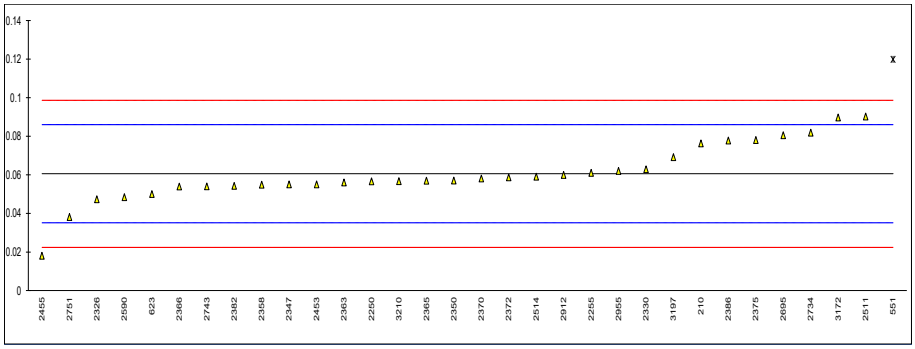


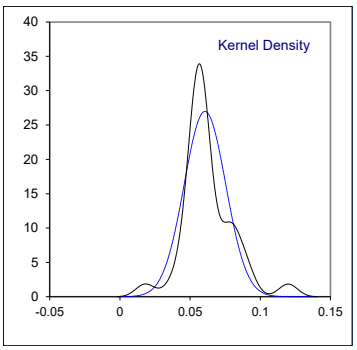


Determination of DCHP - Dicyclohexyl phthalate on sample #23501; results in %M/M

lab	method	value	mark	z(targ)	remarks
210	CPSC-CH-C1001-09.4	0.076222		1.23	
551	ISO16181-1	0.1198	R(0.05)	4.66	
623	In house	0.050		-0.83	
2115		-----		-----	
2250	ISO14389	0.0566	C	-0.31	first reported 0.566
2255	ISO16181-1	0.061		0.04	
2265		-----		-----	
2326	ISO14389	0.0473		-1.04	
2330	ISO14389	0.0629	C	0.19	first reported 0.1060
2347	ISO16181-1	0.055		-0.44	
2350	CPSC-CH-C1001-09.4	0.0570		-0.28	
2358	ISO16181-1	0.0548		-0.45	
2363	ISO16181-1	0.0560		-0.36	
2365	ISO16181-1	0.0569		-0.29	
2366	CPSC 09.4	0.0539		-0.52	
2370	CNC15138-1	0.0580		-0.20	
2372		0.0586526		-0.15	
2375	ISO16181-1	0.078		1.37	
2382	ISO16181-1	0.0542		-0.50	
2386	ISO16181-1	0.0778		1.36	
2453	ISO14389	0.055		-0.44	
2455	CPSC-CH-C1001-09.4	0.0180		-3.35	
2511	ISO16181-1	0.0902		2.33	
2514	ISO16181-1	0.059		-0.12	
2590	ISO16181-1	0.0484		-0.95	
2643		-----		-----	
2695	ISO16181-1	0.0805		1.57	
2711	ISO16181-1	<0.05		-----	
2734	ISO16181	0.0818		1.67	
2743	ISO16181-1	0.0540		-0.51	
2751	ISO16181-1	0.0381		-1.76	
2912	ISO16181-1	0.0599		-0.05	
2955	ISO16181-1	0.0620		0.12	
2977	ISO16181-1	not determined		-----	
3172	ISO8124-6	0.0897		2.29	
3197	ISO16181-1	0.0691		0.67	
3210		0.0567		-0.30	

normality	suspect	
n	31	
outliers	1	
mean (n)	0.06054	
st.dev. (n)	0.014797	RSD = 24%
R(calc.)	0.04143	
st.dev.(iis memo 2201)	0.012713	
R(iis memo 2201)	0.03560	





APPENDIX 2

Summary of other reported Phthalates in sample #23500: results in %M/M

DEHP = Di-(2-ethylhexyl) phthalate
DIDP = Di-iso-decyl phthalate
DINP = Di-iso-nonyl phthalate
DNOP = Di-n-octyl phthalate
DCHP = Dicyclohexyl phthalate
DEP = Diethyl phthalate
DMP = Dimethyl phthalate

Lab	DEHP	DIDP	DINP	DNOP	DCHP	DEP	DMP
210	-----	-----	-----	-----	-----	-----	-----
551	-----	-----	-----	-----	-----	-----	-----
623	0.001	Not Detected	Not Detected	Not Detected	Not Detected	Not Detected	Not Detected
2115	-----	-----	-----	-----	-----	-----	-----
2250	< 0.005	< 0.005	< 0.005	< 0.005	< 0.005	< 0.005	< 0.005
2255	Not Detected	Not Detected	Not Detected	Not Detected	Not Detected	Not Detected	Not Detected
2265	-----	-----	-----	-----	-----	-----	-----
2326	ND	ND	ND	ND	ND	ND	ND
2330	Not Detected	Not Detected	Not Detected	Not Detected	Not Detected	Not Detected	Not Detected
2347	<0.005	<0.010	<0.010	<0.005	<0.005	<0.005	<0.005
2350	<0.015	<0.015	<0.015	<0.015	<0.015	<0.015	<0.015
2358	not detected	not detected	not detected	not detected	not detected	not detected	not detected
2363	<0.003	<0.003	<0.003	<0.003	<0.003	<0.003	<0.003
2365	＜0.003	＜0.010	＜0.010	＜0.003	＜0.003	＜0.003	＜0.003
2366	<0.015	<0.015	<0.015	<0.015	<0.015	<0.015	<0.015
2370	<0.00300	<0.00300	<0.00300	<0.00300	<0.00300	<0.00300	<0.00300
2372	not detected	not detected	not detected	not detected	not detected	not detected	not detected
2375	-----	-----	-----	-----	-----	-----	-----
2382	＜0.005	＜0.005	＜0.005	＜0.005	＜0.005	＜0.005	＜0.005
2386	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01
2453	-----	-----	-----	-----	-----	-----	-----
2455	-----	-----	-----	-----	-----	-----	-----
2511	-----	-----	-----	-----	-----	-----	-----
2514	-----	-----	-----	-----	-----	-----	-----
2590	-----	-----	-----	-----	-----	-----	-----
2643	-----	-----	-----	-----	-----	-----	-----
2695	<0.002	<0.002	<0.002	<0.002	<0.002	<0.002	<0.002
2711	< 0.05	< 0.05	< 0.05	< 0.05	< 0.05	-----	-----
2734	not detected	not detected	not detected	not detected	not detected	not detected	not detected
2743	Not detected	Not detected	Not detected	Not detected	Not detected	Not detected	Not detected
2751	-----	-----	-----	-----	-----	-----	-----
2912	-----	-----	-----	-----	<0.001	<0.001	-----
2955	not detected	not detected	not detected	not detected	not detected	not detected	not detected
2977	<0,010	<0,010	<0,002	<0,001	not determined	not determined	not determined
3172	< 0.0005	< 0.0005	< 0.0005	< 0.0005	< 0.0005	< 0.0005	< 0.0005
3197	ND	ND	ND	ND	ND	ND	ND
3210	<0.002	<0.002	<0.002	<0.002	<0.002	<0.002	<0.002

Summary of other reported Phthalates in sample #23500: results in %M/M - continued

DNHP = Di-n hexyl phthalate
DIBP = Di-iso-butyl phthalate
DNPP = Di-n-pentyl phthalate
DPrP = Di-n-propyl phthalate
DMEP = Di-(2-methoxyethyl) phthalate
Other = Total Other Phthalates

Lab	DNHP	DIBP	DNPP	DPrP	DMEP	Other
210	-----	-----	-----	-----	-----	-----
551	-----	-----	-----	-----	-----	-----
623	Not Detected	Not Detected	Not Detected	Not Detected	Not Detected	Not Detected
2115	-----	-----	-----	-----	-----	-----
2250	< 0.005	< 0.005	< 0.005	< 0.005	< 0.005	< 0.005
2255	Not Detected	Not Detected	Not Detected	Not Detected	Not Detected	Not Detected
2265	-----	-----	-----	-----	-----	-----
2326	ND	ND	ND	ND	ND	ND
2330	Not Detected	Not Detected	Not Detected	Not Detected	Not Detected	Not Analyzed
2347	<0.005	<0.005	<0.005	<0.005	<0.005	-----
2350	<0.015	<0.015	<0.015	<0.015	<0.015	<0.015
2358	not detected	not detected	not detected	not detected	not detected	not applicable
2363	<0.003	<0.003	<0.003	<0.003	<0.003	<0.003
2365	＜0.003	＜0.003	＜0.003	＜0.003	＜0.003	-----
2366	<0.015	<0.015	<0.015	<0.015	<0.015	<0.015
2370	<0.00300	<0.00300	<0.00300	<0.00300	<0.00300	<0.00300
2372	not detected	not detected	not detected	not detected	not detected	not detected
2375	-----	-----	-----	-----	-----	-----
2382	＜0.005	＜0.005	＜0.005	＜0.005	＜0.005	＜0.005
2386	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01
2453	-----	-----	-----	-----	-----	-----
2455	-----	-----	-----	-----	-----	-----
2511	-----	-----	-----	-----	-----	-----
2514	-----	-----	-----	-----	-----	-----
2590	-----	-----	-----	-----	-----	-----
2643	-----	-----	-----	-----	-----	-----
2695	<0.002	<0.002	<0.002	<0.002	<0.002	<0.002
2711	-----	< 0.05	-----	-----	-----	-----
2734	not detected	not detected	not detected	not detected	not detected	not detected
2743	Not detected	Not detected	Not detected	Not detected	Not detected	Not detected
2751	-----	-----	-----	-----	-----	-----
2912	-----	-----	-----	-----	-----	-----
2955	not detected	not detected	not detected	not detected	not detected	not detected
2977	<0,001	<0,001	<0,001	not determined	<0,001	not determined
3172	< 0.0005	< 0.0005	< 0.0005	< 0.0005	< 0.0005	-----
3197	ND	ND	ND	ND	ND	-----
3210	<0.002	<0.002	<0.002	<0.002	<0.002	<0.002

Summary of other reported Phthalates in sample #23501: results in %M/M

BBP = Benzyl butyl phthalate
DEHP = Di-(2-ethylhexyl) phthalate
DIDP = Di-iso-decyl phthalate
DNOP = Di-n-octyl phthalate
DEP = Diethyl phthalate
DMP = Dimethyl phthalate

Lab	BBP	DEHP	DIDP	DNOP	DEP	DMP
210	-----	-----	-----	-----	-----	-----
551	-----	-----	-----	-----	-----	-----
623	0.003	0.001	Not Detected	Not Detected	Not Detected	Not Detected
2115	-----	-----	0.01	-----	-----	-----
2250	< 0.005	< 0.005	< 0.005	< 0.005	< 0.005	< 0.005
2255	Not Detected	Not Detected	Not Detected	Not Detected	Not Detected	Not Detected
2265	-----	-----	-----	-----	-----	-----
2326	ND	ND	0.0354	ND	ND	ND
2330	Not Detected	Not Detected	0.0287	Not Detected	Not Detected	Not Detected
2347	<0.005	<0.005	<0.010	<0.005	<0.005	<0.005
2350	<0.015	<0.015	<0.015	<0.015	<0.015	<0.015
2358	not detected	not detected	0.0126	not detected	not detected	not detected
2363	<0.003	<0.003	<0.003	<0.003	<0.003	<0.003
2365	＜0.003	＜0.003	＜0.010	＜0.003	＜0.003	＜0.003
2366	<0.015	<0.015	<0.015	<0.015	<0.015	<0.015
2370	<0.00300	<0.00300	<0.00300	<0.00300	<0.00300	<0.00300
2372	not detected	not detected	not detected	not detected	not detected	not detected
2375	-----	-----	0.019	-----	-----	-----
2382	＜0.005	＜0.005	＜0.005	＜0.005	＜0.005	＜0.005
2386	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01
2453	-----	-----	-----	-----	-----	-----
2455	-----	-----	-----	-----	-----	-----
2511	-----	-----	-----	-----	-----	-----
2514	-----	-----	-----	-----	-----	-----
2590	-----	-----	0.0130	-----	-----	-----
2643	-----	-----	-----	-----	-----	-----
2695	<0.002	<0.002	<0.002	<0.002	<0.002	<0.002
2711	< 0.05	< 0.05	0.0363	< 0.05	-----	-----
2734	not detected	not detected	0.0400	not detected	not detected	not detected
2743	Not detected	Not detected	Not detected	Not detected	Not detected	Not detected
2751	-----	-----	0.0076	-----	-----	-----
2912	<0.001	-----	0.0119	-----	-----	-----
2955	not detected	not detected	not detected	not detected	not detected	not detected
2977	<0,001	<0,001	<0,010	<0,001	not determined	not determined
3172	< 0.0005	< 0.0005	< 0.0005	< 0.0005	< 0.0005	< 0.0005
3197	ND	ND	ND	ND	ND	ND
3210	<0.002	<0.002	0.0280	<0.002	<0.002	<0.002

Summary of other reported Phthalates in sample #23501: results in %M/M - continued

DNHP = Di-n-hexyl phthalate
DIBP = Di-iso-butyl phthalate
DNPP = Di-n-pentyl phthalate
DPrP = Di-n-propyl phthalate
DMEP = Di-(2-methoxyethyl) phthalate
Other = Total Other Phthalates

Lab	DNHP	DIBP	DNPP	DPrP	DMEP	Other
210	-----	-----	-----	-----	-----	-----
551	-----	-----	-----	-----	-----	-----
623	Not Detected	Not Detected	Not Detected	Not Detected	Not Detected	Not Detected
2115	-----	-----	-----	-----	-----	-----
2250	< 0.005	< 0.005	< 0.005	< 0.005	< 0.005	< 0.005
2255	Not Detected	Not Detected	Not Detected	Not Detected	Not Detected	Not Detected
2265	-----	-----	-----	-----	-----	-----
2326	ND	ND	ND	ND	ND	ND
2330	Not Detected	Not Detected	Not Detected	Not Detected	Not Detected	Not Analyzed
2347	<0.005	<0.005	<0.005	<0.005	<0.005	-----
2350	<0.015	<0.015	<0.015	<0.015	<0.015	<0.015
2358	not detected	not detected	not detected	not detected	not detected	not applicable
2363	<0.003	<0.003	<0.003	<0.003	<0.003	<0.003
2365	＜0.003	＜0.003	＜0.003	＜0.003	＜0.003	-----
2366	<0.015	<0.015	<0.015	<0.015	<0.015	<0.015
2370	<0.00300	<0.00300	<0.00300	<0.00300	<0.00300	<0.00300
2372	not detected	not detected	not detected	not detected	not detected	not detected
2375	-----	-----	-----	-----	-----	-----
2382	＜0.005	＜0.005	＜0.005	＜0.005	＜0.005	＜0.005
2386	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01
2453	-----	-----	-----	-----	-----	-----
2455	-----	-----	-----	-----	-----	-----
2511	-----	-----	-----	-----	-----	-----
2514	-----	-----	-----	-----	-----	-----
2590	-----	-----	-----	-----	-----	-----
2643	-----	-----	-----	-----	-----	-----
2695	<0.002	<0.002	<0.002	<0.002	<0.002	<0.002
2711	-----	< 0.05	-----	-----	-----	-----
2734	not detected	not detected	not detected	not detected	not detected	not detected
2743	Not detected	Not detected	Not detected	Not detected	Not detected	Not detected
2751	-----	-----	-----	-----	-----	-----
2912	-----	-----	-----	-----	-----	-----
2955	not detected	not detected	not detected	not detected	not detected	not detected
2977	<0,001	<0,001	<0,001	not determined	<0,001	not determined
3172	< 0.0005	< 0.0005	< 0.0005	< 0.0005	< 0.0005	-----
3197	ND	ND	ND	ND	ND	-----
3210	<0.002	<0.002	<0.002	<0.002	<0.002	<0.002

APPENDIX 3 Analytical details

lab	ISO/IEC17025 accredited	Sample intake (in grams)	Solvent (mixture) used to release the analytes	Extraction time (in minutes)	Extraction temp. (in °C)
210	Yes				
551	Yes	0.5000 g	Toluene	60 min	60.0 °C
623	Yes	0.1	THF : Hexane	60	60
2115	Yes	0.3 g	THF and Hexane	60 min	60°C
2250	Yes	0.3	Tetrahydrofuran / Acetonitrile (1:2)	60	60
2255	Yes	0.3	nHexane +Acetone (80/20)	60	50
2265	---				
2326	Yes	0.1 G	THF/ HEXANE	60 MINUTES	60 C
2330	Yes	0.3 g	THF and Hexane	60 min	60 C
2347	---				
2350	Yes	0.5g	THF + ACN	2h 30min	60 ℃
2358	Yes	1g	Toluene	60	60
2363	Yes	2.5	toluene	60	60
2365	Yes	0.5g	Toluene	60min	60℃
2366	Yes				
2370	Yes	0.5g	THF：Hexane=10：20mL	30 min	room temperature
2372	No	0.3g	THF	60 min	60°C
2375	No	1 gram	Toluene	60 min	60 C
2382	Yes	1.0g	Toluene	60min	60℃
2386	Yes	0.5 g	n-Hexane/ Aceton 80/20 VV	60 min	50°C
2453	No	±100 mg			
2455	Yes	Approximately 0.5 grams each determination	THF/n-Hexane	~180 minutes	~60 °C
2511	Yes				
2514	Yes	23500=0.5215 23501=0.4804	n-hexane:acetone=80:20		50
2590	Yes	1	toluene	60	60°C
2643	Yes	0.3 g	THF + HEXANE	60 min	70
2695	Yes	SAMPLE #23500 1.0154 grams SAMPLE #23501 0.9998 grams	TOLUENE	60	60
2711	No	1	80 Hexane/25 Acetone	60	50
2734	Yes	2 g	Hexane / Acetone	1h	40°C
2743	Yes	1	Not applicable	30 min	60°C
2751	Yes	0,5 gram	Toluen	60 min	50 °C
2912	---			60 minute	
2955	Yes	0.5gm	n-Hexane & Acetone (80:20)	50	
2977	No	0,3g	THF:HEXANE 1:2	60 minutes	60°C
3172	Yes			60 min	
3197	Yes	0,5g	Toluen		60
3210	---	1	Toluène	60	60

APPENDIX 4

Number of participants per country

3 labs in BANGLADESH
1 lab in BRAZIL
1 lab in CAMBODIA
1 lab in FRANCE
3 labs in GERMANY
1 lab in HONG KONG
1 lab in INDONESIA
9 labs in ITALY
2 labs in KOREA, Republic of
1 lab in MOROCCO
5 labs in P.R. of CHINA
1 lab in PAKISTAN
1 lab in PORTUGAL
2 labs in TAIWAN
1 lab in TUNISIA
3 labs in TURKEY
1 lab in U.S.A.

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
fr.	= first reported
f+?	= possibly a false positive test result?
f-?	= possibly a false negative test result?

Literature

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