Institute for
Interlaboratory Studies

Results of Proficiency Test
Phthalates in Textile
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Organized by: Institute for Interlaboratory Studies
Spijkenisse, The Netherlands

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1 INTRODUCTION

Phthalates are commonly used as plasticizers to increase softness of plastic, especially in PVC. In the clothing industry, they can be found in synthetic textile, synthetic leather, buttons, coated fabric, plastisol and dye printing.

Since 2019 the Institute for Interlaboratory Studies (iis) organizes a proficiency scheme for the determination of Phthalates in Textile every year. During the annual proficiency testing program of 2024 it was decided to continue the proficiency test for the determination of Phthalates in Textile.

In this interlaboratory study 71 laboratories in 27 countries registered for participation, see appendix 4 for the number of participants per country. In this report the results of the proficiency test on Phthalates in Textile are presented and discussed.

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 a laboratory that has performed the tests in accordance with for ISO/IEC17043 relevant requirements of ISO/IEC17025.
It was decided to send two different textile samples of 3 grams each labelled #24570 and #24571 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 black viscose was selected with a detectable level of Di-butyl phthalate (DBP) and Di-iso-decyl phthalate (DIDP). The batch was cut into small pieces and after homogenization 90 small plastic bags were filled with approximately 3 grams each and labelled #24570.
The homogeneity of the subsamples was checked by determination of DBP and DIDP according to ISO14389 on 6 stratified randomly selected subsamples.

	DBP in %M/M	DIDP %M/M
sample #24570-1	0.1199	0.0624
sample #24570-2	0.1235	0.0620
sample #24570-3	0.1140	0.0592
sample #24570-4	0.1200	0.0592
sample #24570-5	0.1193	0.0609
sample #24570-6	0.1246	0.0594

Table 1: homogeneity test results of subsamples #24570

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

	DBP in %M/M	DIDP %M/M
r (observed)	0.0105	0.0040
reference method	iis memo 1701	iis memo 1701
0.3 x R (reference method)	0.0162	0.0081

Table 2: evaluation of the repeatabilities of subsamples #24570

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

For the second sample a batch of purple polyester was selected with a detectable level of Diethyl phthalate (DEP). The batch was cut into small pieces and after homogenization 90 small plastic bags were filled with approximately 3 grams each and labelled #24571.
The homogeneity of the subsamples was checked by determination of DEP according to ISO14389 on 7 stratified randomly selected subsamples.

	DEP %M/M
sample #24571-1	0.0691
sample #24571-2	0.0673
sample #24571-3	0.0664
sample #24571-4	0.0735
sample #24571-5	0.0685
sample #24571-6	0.0733
sample #24571-7	0.0703

Table 3: homogeneity test results of subsamples #24571

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

	DEP %M/M
r (observed)	0.0077
reference method	iis memo 1701
0.3 x R (reference method)	0.0094

Table 4: evaluation of the repeatabilities of subsamples #24571

The calculated repeatability is in agreement with 0.3 times the estimated reproducibility of the reference method. Therefore, homogeneity of the subsamples was assumed.

To each of the participating laboratories two textile samples labelled #24570 and #24571 respectively were sent on April 10, 2024.

2.5 ANALYZES

The participants were requested to determine on samples #24570 and #24571 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

To ensure homogeneity it was requested not to use less than 0.5 gram per determination. It was also requested to report if the laboratory was accredited for the determined components and to report some analytical details.

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 method (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 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 data analysis and original test results are placed under 'Remarks' in the result tables in appendices 1 and 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 dataset 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-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 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 of 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:

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

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