**Institute for
Interlaboratory Studies**

Results of Proficiency Test
Aniline in Textile
June 2024

Organized by: **Institute for Interlaboratory Studies**
                     Spijkenisse, The Netherlands

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1　INTRODUCTION

Aniline is a chemical compound that is used as raw material for the synthesis of modern synthetic dyes. Firmly bound in the crystal structure of the synthetic dye it is not suspected to be harmful. However, free Aniline is classified as carcinogenic and mutagenic. In 2021 the European Union issued Commision Directive EU 2021/903 with limit values for Aniline in textile for the use in toys. Next to this, both OEKOTEX® and Bluesign® mention limits for the presence of Aniline in textile.

On request of a number of participants the Institute for Interlaboratory Studies (iis) decided to organize a proficiency scheme for the determination of Aniline in Textile in 2023. During the annual proficiency testing program of 2024 it was decided to continue the proficiency test for the determination of Aniline in Textile.

In this interlaboratory study 19 laboratories in 9 countries registered for participation, see appendix 3 for the number of participants per country. In this report the results of the Aniline in Textile proficiency test 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 #24600 and #24601 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 beige cotton which was made positive on Aniline by a third party was selected. The batch was cut into small pieces. After homogenization 50 small plastic bags were filled with approximately 3 grams each and labelled #24600.
The homogeneity of the subsamples was checked by determination of Aniline in accordance with ISO14362-1 on 8 stratified randomly selected subsamples.

	Aniline in mg/kg
sample #24600-1	30.49
sample #24600-2	31.46
sample #24600-3	29.77
sample #24600-4	29.87
sample #24600-5	27.78
sample #24600-6	27.54
sample #24600-7	30.05
sample #24600-8	28.90

Table 1: homogeneity test results of subsamples #24600

From the above test results the repeatability was calculated and compared with 0.3 times the target reproducibility as derived from iis memo 2202 in agreement with the procedure of ISO13528, Annex B2 in the next table.

	Aniline in mg/kg
r (observed)	3.74
reference method	iis memo 2202
0.3 x R (reference method)	5.20

Table 2: evaluation of the repeatability of subsamples #24600

The calculated repeatability is in agreement with 0.3 times the target reproducibility as derived from iis memo 2202. Therefore, homogeneity of the subsamples was assumed.

For the second sample a batch of green cotton which was made positive on Aniline by a third party was selected. The batch was cut into small pieces. After homogenization 50 small plastic bags were filled with approximately 3 grams each and labelled #24601.

The homogeneity of the subsamples was checked by determination of Aniline in accordance with ISO14362-1 on 8 stratified randomly selected subsamples.

	Aniline in mg/kg
sample #24601-1	77.56
sample #24601-2	72.42
sample #24601-3	68.88
sample #24601-4	73.44
sample #24601-5	73.64
sample #24601-6	76.38
sample #24601-7	71.80
sample #24601-8	74.91

Table 3: homogeneity test results of subsamples #24601

From the above test results the repeatability was calculated and compared with 0.3 times the target reproducibility as derived from iis memo 2202 in agreement with the procedure of ISO13528, Annex B2 in the next table.

	Aniline in mg/kg
r (observed)	7.64
reference method	iis memo 2202
0.3 x R (reference method)	13.0

Table 4: evaluation of the repeatability of subsamples #24600

The calculated repeatability is in agreement with 0.3 times the target reproducibility as derived from iis memo 2202. Therefore, homogeneity of the subsamples was assumed.

To each of the participating laboratories two textile samples labelled #24600 and #24601 respectively were sent on May 15, 2024.

2.5   ANALYZES

The participants were requested to determine the Aniline content.
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 component 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 appendix 1 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 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 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:

$$
\begin{aligned}
|z| &< 1 \quad &&\text{good} \\
1 < |z| &< 2 \quad &&\text{satisfactory} \\
2 < |z| &< 3 \quad &&\text{questionable} \\
3 < |z| & \quad &&\text{unsatisfactory}
\end{aligned}
$$

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