Institute for
Interlaboratory Studies

Results of Proficiency Test
Colorants (Banned Dyes) in Textile
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Organized by: Institute for Interlaboratory Studies
Spijkenisse, the Netherlands

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1 INTRODUCTION

Colored fabrics, when in contact with human skin, may cause Allergic Contact Dermatitis. Several dyestuffs are therefore classified as allergenic, potential carcinogenic or banned for other reasons. The OEKOTEX® Standard 100 and the BlueSign® RSL list many allergenic, carcinogenic and other banned dyestuffs.

Since 2005 the Institute for Interlaboratory Studies (iis) organizes a proficiency scheme for the determination of Colorants (Banned Dyes only) in Textile every year. In 2016 the scope was extended with carcinogenic and other banned dyes. During the annual proficiency testing program of 2024 it was decided to continue the proficiency test for the determination of Colorants (Banned Dyes) in Textile.

In this interlaboratory study 62 laboratories in 24 countries registered for participation, see appendix 4 for the number of participants per country. In this report the results of the Colorants (Banned Dyes) 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 approximately 3 grams each labelled #24605 and #24606 respectively.
The participants were requested to report rounded and unrounded test results. The unrounded test results were preferably used for statistical evaluation.

2.1 ACCREDITATION

The Institute for Interlaboratory Studies in Spijkenisse, the Netherlands, is accredited in agreement with ISO/IEC17043:2010 (R007), since January 2000, by the Dutch Accreditation Council (Raad voor Accreditatie). This PT falls under the accredited scope. 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 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 orange polyester was selected, positive on Disperse Brown 1 and Disperse Red 1. This batch was cut into small pieces. After homogenization 100 small plastic bags were filled with approximately 3 grams each and labelled #24605.
The homogeneity of the subsamples was checked by determination of Disperse Brown 1 and Disperse Red 1 according to an in-house test method on 8 stratified randomly selected subsamples.

	Disperse Brown 1 in mg/kg	Disperse Red 1 in mg/kg
sample #24605-1	335	249
sample #24605-2	369	267
sample #24605-3	364	275
sample #24605-4	347	253
sample #24605-5	337	238
sample #24605-6	325	239
sample #24605-7	324	231
sample #24605-8	336	239

Table 1: homogeneity test results of subsamples #24605

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

	Disperse Brown 1 in mg/kg	Disperse Red 1 in mg/kg
r (observed)	46.9	43.1
reference test method	DIN54231:22	DIN54231:22
0.3 x R (reference test method)	80.8	57.5

Table 2: evaluation of the repeatabilities of subsamples #24605

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

For the second sample a batch of blue cotton was selected, positive on Direct Black 38. This batch was cut into small pieces. After homogenization 100 small plastic bags were filled with approximately 3 grams each and labelled #24606.
The homogeneity of the subsamples was checked by determination of Direct Black 38 according to DIN54231 test method on 8 stratified randomly selected subsamples.

	Direct Black 38 in mg/kg
sample #24606-1	52.2
sample #24606-2	53.7
sample #24606-3	49.5
sample #24606-4	59.1
sample #24606-5	56.3
sample #24606-6	55.6
sample #24606-7	57.2
sample #24606-8	49.4

Table 3: homogeneity test results of subsamples #24606

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

	Direct Black 38 in mg/kg
r (observed)	10.0
reference test method	DIN54231:22
0.3 x R (reference test method)	13.0

Table 4: evaluation of the repeatability of subsamples #24606

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

To each of the participating laboratories one polyester sample labelled #24605 and one cotton sample labelled #24606 respectively were sent on May 15, 2024.

2.5 ANALYZES

The participants were requested to determine the concentrations of 37 banned allergenic dyes, applying the analysis procedure that is routinely used in the laboratory. See the list of colorants in appendix 2.
To ensure homogeneity, it was requested not to use less than 0.5 grams per determination.
It was 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 the 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 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-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 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:

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

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