Results of Proficiency Test
Disperse dyes in textile
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Organised by: Institute for Interlaboratory Studies
                  Spijkenisse, the Netherlands

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CONTENTS

Appendices:

1   INTRODUCTION

Coloured fabrics, when in contact with human skin, may cause Allergic Contact Dermatitis. The following twenty Dyestuffs are classified as allergenic. Textiles are not allowed to contain more than 50 mg/kg of the 20 below listed dyes according to Öko-tex Standard 100 edition 01/2012 (reference 13), of which 9 are mentioned in DIN54231:

- C.I. Disperse Blue 1   CASno 2475-45-8   C.I.no 64 500   (in DIN54231)
- C.I. Disperse Blue 3   CASno 2475-46-9   C.I.no 61 505   (in DIN54231)
- C.I. Disperse Blue 7   CASno 3179-90-6   C.I.no 62 500
- C.I. Disperse Blue 26   CASno 3860-63-7   C.I.no 63 305
- C.I. Disperse Blue 35   CASno 12222-75-2 (*)   (in DIN54231)
- C.I. Disperse Blue 102   CASno 12222-97-8
- C.I. Disperse Blue 106   CASno 12223-01-7   (in DIN54231)
- C.I. Disperse Blue 124   CASno 61951-51-7   (in DIN54231)
- C.I. Disperse Brown 1   CASno 23355-64-8
- C.I. Disperse Orange 1   CASno 2581-69-3   C.I.no 11 080
- C.I. Disperse Orange 3   CASno 730-40-5   C.I.no 11 005   (in DIN54231)
- C.I. Disperse Orange 37/76   CASno 13301-61-6   C.I.no 11 132   (in DIN54231)
- C.I. Disperse Red 1   CASno 2872-52-8   C.I.no 11 110   (in DIN54231)
- C.I. Disperse Red 11   CASno 2872-48-2   C.I.no 62 015
- C.I. Disperse Red 17   CASno 3179-89-3   C.I.no 11 210
- C.I. Disperse Yellow 1   CASno 119-15-3   C.I.no 10 345
- C.I. Disperse Yellow 3   CASno 2832-40-8   C.I.no 11 855   (in DIN54231)
- C.I. Disperse Yellow 9   CASno 6373-73-5   C.I.no 10 375
- C.I. Disperse Yellow 39   CASno 12236-29-2
- C.I. Disperse Yellow 49   CASno 54824-37-2

* Disperse Blue 35 consists of a mixture of components, of which the monomethylated 1,8-diamino-4,5-dihydroxyanthraquinone (CASno 56524-77-7) and the dimethylated 1,8-diamino-4,5-dihydroxyanthraquinone (CASno 56524-76-6) are responsible for the sensitizing potency of Disperse Blue 35, see also report iis09A04X of May 2009.

The German ban on the above disperse dyes has become a widely publicised issue in the textile industry. Dyestuff manufacturers, processors and exporters are careful in the selection of disperse dyes. However, several dyestuffs that are skin sensitizers may still be in use for dyeing polyester and nylon.

In this context and in response to requests from several laboratories, the Institute for Interlaboratory Studies (iis) organises a proficiency test for disperse dyes in textile in the annual proficiency test program since 2003.
In the 2012 interlaboratory study 79 laboratories in 19 different countries participated. See appendix 4 for the number of participants per country. In this report the results of this proficiency test are presented and discussed.

## 2	SET UP

The Institute for Interlaboratory Studies in Spijkenisse was the organizer of this proficiency test. It was decided to use in this proficiency test 2 different, with banned disperse dyestuffs treated, textile samples. The textile samples were prepared by a third party and tested for homogeneity by an accredited laboratory. The participants were asked to report the analytical results with one extra figure using the indicated units on the report form. These results with an extra figure are 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 and ILAC-G13:2007. This ensures strict adherence to protocols for sample preparation and statistical evaluation and 100% confidentiality of the participant's data. Also the customer's satisfaction is measured on a regular basis by sending out questionnaires.

### 2.2	PROTOCOL

The protocol followed in the organization was the one as described for proficiency testing in the report 'iis Interlaboratory Studies: Protocol for the Organization, Statistics and Evaluation' of January 2010 (iis-protocol, version 3.2).The participants were asked to report the analytical results using the indicated units on the report form.

### 2.3	CONFIDENTIALITY STATEMENT

All data present 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

The two textile samples were each prepared from two different bulk materials by a third party laboratory. Each bulk sample dyed with a number of banned Disperse Dyes. After cutting in small pieces and homogenisation, approximately 600 grams of each material, was divided over 120 subsamples of 4 gram each. The samples were labelled and tested for homogeneity by a subcontracted laboratory. The homogeneity of the subsamples #12033 was checked by determination of Disperse Red 11 and Disperse Blue 3 and the homogeneity of the subsamples #12034 was checked by determination of Disperse Blue 26 in accordance with DIN54231:05 on 15 stratified randomly selected samples.
See the following tables for the test results.

	Disperse Red 11 in mg/kg	Disperse Blue 3 in mg/kg
sample #12033-1	95.6	236.8
sample #12033-2	99.6	280.3
sample #12033-3	81.0	240.3
sample #12033-4	90.8	270.6
sample #12033-5	85.3	240.1
sample #12033-6	80.5	285.6
sample #12033-7	90.5	236.9
sample #12033-8	89.5	251.2
sample #12033-9	94.5	236.8
sample #12033-10	86.5	284.2
sample #12033-11	84.2	245.2
sample #12033-12	84.5	260.5
sample #12033-13	90.5	265.8
sample #12033-14	80.7	255.5
sample #12033-15	95.8	230.0

table 1: homogeneity test of subsamples #12033

	Disperse Blue 26 in mg/kg
sample #12034-1	100.5
sample #12034-2	94.5
sample #12034-3	105.6
sample #12034-4	111.0
sample #12034-5	100.1
sample #12034-6	99.6
sample #12034-7	99.8
sample #12034-8	94.9
sample #12034-9	99.5
sample #12034-10	109.7
sample #12034-11	105.8
sample #12034-12	100.9
sample #12034-13	89.9
sample #12034-14	101.1
sample #12034-15	95.5

table 2: homogeneity test of subsamples #12034

From the results in table 1 and 2, the repeatabilities of the results were calculated. In table 3 the calculated repeatabilities are compared with the requirements of DIN54231:05.

	Disp. Red 11 #12033 in mg/kg	Disp. Blue 3 #12033 in mg/kg	Disp. Blue 26 #12034 in mg/kg
r(calc)	16.9	52.8	16.0
Reference method	DIN54231:05	DIN54231:05	DIN54231:05
r(lit)	21.3	61.22	24.2

table 3: repeatabilities of subsamples #12033 and #12034

The repeatabilities of the test results of the determined disperse dyestuffs were all in agreement with the repeatabilities mentioned in DIN54231:05. Therefore homogeneity of the subsamples was assumed.

An amount of approx. 4 grams each of the samples #12033 and #12034 was sent to the participating laboratories on March 7, 2012.

2.5 ANALYSES

The participants were asked to determine the concentrations of 20 forbidden allergenic dyestuffs, applying the analysis procedure that is routinely used in the laboratory. To get comparable results a detailed report form, on which the requested dyestuffs and the units were pre-printed, was sent together with each set of samples. Furthermore an extra report form for reporting the analytical details was enclosed. Also a letter of instructions was sent along.

3 RESULTS

During four weeks after sample dispatch the results of the individual laboratories were gathered. The original data are tabulated in the appendices of this report. The laboratories are presented by their code numbers.
Directly after the deadline, a reminder fax was sent to those laboratories that had not yet reported. Shortly after the deadline the available results were screened for suspect data. A result was called suspect in case the Huber Elimination Rule (a robust outlier test, see lit.5) found it to be an outlier. The laboratories that produced these suspect data were asked to check the results. Additional or corrected data are placed under 'Remarks' in the result tables in appendix 1. A list of abbreviations used in the tables can be found in appendix 4.

3.1. STATISTICS

Statistical calculations were performed as described in the report 'iis Interlaboratory Studies: Protocol for the Organization, Statistics and Evaluation' of January 2010 (iis-protocol, version 3.2)

For the statistical evaluation the unrounded (when available) figures were used instead of the rounded results. Results reported as '<…' or '>…" were not used in the statistical evaluation.
Before further calculations, the normality of the distribution of the various data sets per determination was checked by means of the Lilliefors-test. In the case of an anormal distribution, the statistical evaluation should be used with care.

According to ISO 5725 (1986 and 1994, lit.7 and 8) the original results per determination were submitted subsequently to Dixon's and Grubbs' 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. Stragglers are marked by D(0.05) for the Dixon's test, by G(0.05) or DG(0.05) for the Grubbs' 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. When the uncertainty passed the evaluation, no remarks are made in the report. However, when the uncertainty failed the evaluation it is mentioned in the report and it will have consequences for the evaluation of the test results.

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 under 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. This is a method for producing a smooth density approximation to a set of data that avoids some problems associated with histograms.

3.3   Z-SCORES

To evaluate the performance of the individual participating laboratories the z-scores were calculated. In order to be able to have an objective evaluation of the performance of the individual participants, it was decided to evaluate this performance against the literature requirements. Therefore the z-scores were calculated using a target standard deviation. This target standard deviation was calculated from the literature reproducibility by division with 2.8.

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 the fit-for-useness of the reported test result.

The $z_{(target)}$-scores were calculated according to:

$z_{(target)}$ = (individual result - average of proficiency test) / target standard deviation

The $z_{(target)}$-scores are listed in the result tables in appendix 1.

Absolute values for z<2 are very common and absolute values for z>3 are very rare. 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

During the execution of this proficiency test no problems occurred with the delivery of the samples. All participants received the samples in time. Nine participants reported test results after the deadline and five participants did not report any test results at all.
Finally, 74 participants reported 224 numerical results. Observed were 12 outlying test results, which is 5.4% of the numerical results. In proficiency studies outlier percentages of 3% - 7.5% are quite normal.
Only the data set of Disperse Blue 3 proved to have a normal distribution.

4.1   EVALUATION PER SAMPLE

In this section the results are discussed per sample. All test results reported on the textile samples are summarised in appendix 1. As almost all participants reported to have used DIN54231, the additional analytical details were not summarized.
In DIN 54231 no reproducibility is mentioned. Only the standard deviation for the repeatability is mentioned. The target reproducibility is estimated as follows: the standard deviation was multiplied with 2.8 to get the target repeatability. And this was multiplied with 3 to get an estimate of the target reproducibility.

Textile #12033: This material was dyed by a third party laboratory with both banned dyes Disperse Blue 3 and Disperse Red 11. The results reported by the participating laboratories vary strongly (Disperse Blue 3 from 3.26 mg/kg – 801.7 mg/kg and Disperse Red 11 from 25.7 mg/kg – 6406.7 mg/kg). The spread of Disperse Blue 3 is not at all in agreement with the estimated reproducibility of DIN54231:05. And the same is valid for the spread of Disperse Red 11.
A small number of laboratories reported also the presence of several other disperse dyes in sample #12033, see appendix 2.
At least two laboratories (551 and 3233) would not have rejected this sample for containing too much Allergenic Dyestuffs (acc. to the limit of Öko-tex Std.100 edition 01/2012 of 50 mg/kg). All other laboratories would have rejected this sample.

Textile #12034: This material was treated by a third party laboratory with the banned dye Disperse Blue 26. The results reported by the participating laboratories vary strongly from 'n.d.' – 21000 mg/kg. The spread of Disperse Blue 26 is not at all in agreement with the estimated reproducibility of DIN54231:05.
A number of laboratories reported also the presence of several other disperse dyes in sample #12034 (see appendix 2).
Several laboratories did not detect Disperse Blue 26, but reported either the presence of Disperse Blue 35 or the presence of Disperse Brown 1 or Disperse Yellow 49, see appendix 2.
At least four laboratories (2132, 2261, 2266 and 3233) would not have rejected this sample for containing too much Allergenic Dyestuffs (acc. to the limit of Öko-tex Std.100 edition 01/2012 of 50 mg/kg). All other laboratories would have rejected this sample.

4.2 PERFORMANCE EVALUATION FOR THE GROUP OF LABORATORIES

A comparison has been made between the reproducibilities as declared by the relevant standard method and the reproducibilities as found for the group of participating laboratories.
The number of significant results, the average results, the calculated reproducibilities (standard deviation*2.8) and the target reproducibilities, derived from the official test method DIN54231:05 are compared in the next tables.

Parameter	unit	n	average	2.8 * sd	R (target)
Disperse Blue 3	mg/kg	69	86.4	100.9	69.2
Disperse Red 11	mg/kg	70	634	1147	509

table 4: reproducibilities of textile sample #12033

Parameter	unit	n	average	2.8 * sd	R (target)
Disperse Blue 26	mg/kg	69	389	741	312

table 5: reproducibility of textile sample #12034

Without further statistical calculations it can be concluded that for the detected allergenic dyestuffs the group of participating laboratories may have some large difficulties with the analysis. See also the discussion in paragraphs 4.1 and 5.

5   DISCUSSION

The relative spreads in the results of the determined dyes are listed in the next table.

	March 2012	March 2011	March 2010	March 2009	March 2008	March 2007
Disperse Blue 1	n.e.	n.e.	n.e.	n.e.	121%	n.e.
Disperse Blue 3	117%	143%	142%	n.e.	n.e.	102%
Disperse Blue 26	191%	n.e.	152%	150%	n.e.	133%
Disperse Blue 35	n.e.	n.e.	n.e.	(235%)*	n.e.	n.e.
Disperse Orange 1	n.e.	122%	n.e.	n.e.	n.e.	n.e.
Disperse Orange 3	n.e.	n.e.	n.e.	67%	98%	136%
Disperse Red 1	n.e.	100%	n.e.	n.e.	176%	n.e.
Disperse Red 11	181%	n.e.	144%	127%	n.e.	n.e.
Disperse Yellow 3	n.e.	78%	n.e.	n.e.	n.e.	n.e.
Disperse Yellow 9	n.e.	n.e.	n.e.	n.e.	86%	n.e.
Disperse Yellow 49	n.e.	n.e.	n.e.	n.e.	n.e.	152%

table 6: development of relative reproducibilities over the last years

()* The cause of this large spread was investigated in the 2009 PT iis09A04

From the above table it is clear that no clear quality improvement is present.

It was noticed that almost all participants found the spiked dyestuffs in sample #12033 and in sample #12034. However several false negative results were reported, while sometimes a different disperse dye was reported instead.

During the investigation of the problems with Disperse Blue 35 during the 2009 PT, it was remarked that "*This procedure is comparable to that which should be followed for the detection of the allergenic disperse dye Disperse Blue 26: Disperse Blue 26 is N,N'-Dimethyl-1,5-Diamino-4,8-dihydroxyanthraquinone, which is the trans isomer of the dimethylated 1,8-diamino-4,5-dihydroxyanthraquinone in Disperse Blue 35! In D. Blue 26 only this dimethylated substance is regarded as the allergenic ingredient.*"
This dimethylated component of disperse blue 26 has CASno. 3860-63-7 as mentioned by Öko-tex.

In this PT, for Disperse Blue 26 three groups of results are observed (around 245 mg/kg, 765 mg/kg and 2500 mg/kg), which may be in accordance with the one component, the sum of two components and the sum of three components (the unmethylated component (CASno. 52365-48-7), the monomethylated and the dimethylated ones). However, this was not further investigated in this PT and therefore this conclusion is rather tentative. Another cause for the observed grouping may well be the use of calibrants with different purity.

Another explanation for the bi- and trimodal data distributions may be the fact that the purity of avialable calibration standards may vary strongly (see reference 12).
And it is to be expected that the test results of laboratories, that used identical calibrants, will be more close together than the test results of laboratories, that used different calibrants.

The spreads observed in this interlaboratory study are clearly not caused by just one critical point in the analysis. Almost all participants reported to have used test method DIN54231. However, the detection technique and the purity of the various calibration standards that were used may vary strongly.
Each laboratory has to evaluate its performance in this study and make decisions about necessary corrective actions. Therefore, participation on a regular basis in this scheme could be helpful to improve the performance and the quality of the analytical results.

APPENDIX 1

Determination of Disperse Blue 3 (CASno. 2475-46-9) in sample #12033; results in mg/kg

lab	method	value	mark	z(targ)	remarks
551	DIN54231	3.26		-3.36	
623	DIN54231	89.63		0.13	
840	DIN54231	73.5		-0.52	
2115		-----		-----	
2129	DIN54231	147		2.45	
2132	DIN54231	55.6		-1.25	
2137	DIN54231	93.3		0.28	
2139	DIN54231	129.2		1.73	
2165	DIN54231	167		3.26	
2172	DIN54231	55.5		-1.25	
2184	DIN54231	81		-0.22	
2197		-----		-----	
2201	DIN54231	50		-1.47	
2217	DIN54231	126		1.60	
2218	DIN54231	50.01		-1.47	
2241	DIN54231	129		1.72	
2246	DIN54231	105.5		0.77	
2247	DIN54231	109		0.91	
2252	DIN54231	n.d.		-----	
2255	DIN54231	127.5		1.66	
2261		-----		-----	
2265		-----		-----	
2266	DIN54231	10.8		-3.06	
2272	DIN54231	19.4		-2.71	
2284	DIN54231	93.2		0.27	
2289	DIN54231	164		3.14	
2290	DIN54231	71.7		-0.59	
2295	DIN54231	81		-0.22	
2300	DIN54231	47		-1.59	
2310	DIN54231	79.5		-0.28	
2311	DIN54231	76.2		-0.41	
2350	DIN54231	53.4		-1.33	
2352	DIN54231	65		-0.87	
2358	DIN54231	75.75		-0.43	
2359	DIN54231	79.5		-0.28	
2363	DIN54231	78		-0.34	
2365	DIN54231	99		0.51	
2370	DIN54231	84.6		-0.07	
2375	DIN54231	102.36		0.65	
2379	DIN54231	89.40		0.12	
2380	DIN54231	75.05		-0.46	
2386	DIN54231	66.3		-0.81	
2390	DIN54231	146.85		2.44	
2410	DIN54231	120	C	1.36	First reported 280
2425	DIN54231	117.00		1.24	
2427	DIN54231	233.9	G(0.01)	5.96	
2446	DIN54231	102.35		0.65	
2452		-----		-----	
2462	DIN54231	76		-0.42	
2481		-----		-----	
2492	OEKO-Tex	801.7	G(0.01)	28.93	
3104	DIN54231	78.7		-0.31	
3116	DIN54231	106		0.79	
3117	DIN54231	305.8	C,G(0.01)	8.87	First reported 537.4
3146	DIN54231	81		-0.22	
3150	DIN54231	170		3.38	
3151	DIN54231	49.5		-1.49	
3153	DIN54231	38.1		-1.95	
3154	DIN54231	107.91		0.87	
3172	in house	95.1		0.35	
3176	DIN54231	92.4		0.24	
3180	DIN54231	51.4		-1.42	
3185	DIN54231	81		-0.22	
3190	DIN54231	81.7		-0.19	
3192	DIN54231	90.9		0.18	
3197	DIN54231	115		1.16	
3199	DIN54231	88.964		0.10	
3200	DIN54231	52.4		-1.37	
3209	DIN54231	68.4		-0.73	
3210	DIN54231	33		-2.16	
3214	DIN54231	92.07	C	0.23	First reported 209.26
3218	DIN54231	52		-1.39	
3220	DIN54231	96.0		0.39	

3225	DIN54231	85.2	-0.05
3228	DIN54231	160	2.98
3233	in house	18.5	-2.75
3242	DIN54231	115	1.16
3246	DIN54231	76	-0.42
3248	DIN54231	120	1.36

| normality	OK
n	69
outliers	3
mean (n)	86.40
st.dev. (n)	36.032
R(calc.)	100.89
R(DIN54231:05)	69.24

Kernel Density
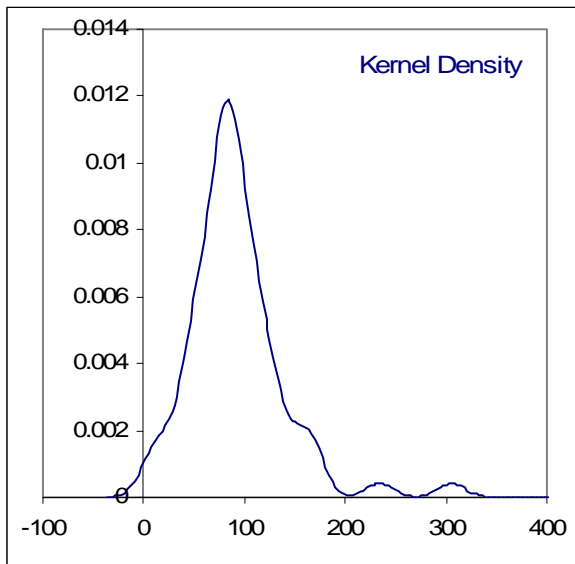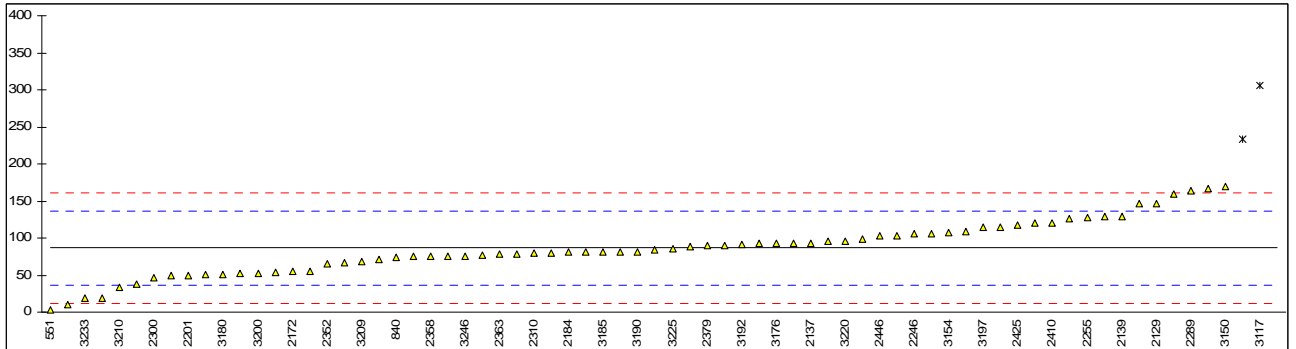
Determination of Disperse Red 11 (CASno. 2872-48-2) in sample #12033; results in mg/kg

lab	method	value	mark	z(targ)	remarks
551	DIN54231	34.14		-3.31	
623	DIN54231	1024.62		2.15	
840	DIN54231	1198		3.10	
2115		-----		-----	
2129	DIN54231	210		-2.34	
2132	DIN54231	539.5		-0.52	
2137	DIN54231	252.5		-2.10	
2139	DIN54231	609.2		-0.14	
2165	DIN54231	480		-0.85	
2172	DIN54231	500		-0.74	
2184	DIN54231	1109		2.61	
2197		-----		-----	
2201	DIN54231	492		-0.79	
2217	DIN54231	613		-0.12	
2218	DIN54231	2694.52	G(0.05)	11.34	
2241	DIN54231	360		-1.51	
2246	DIN54231	1270.6	C	3.50	First reported 2359.3
2247	DIN54231	288		-1.91	
2252	DIN54231	256.2		-2.08	
2255	DIN54231	240.93		-2.17	
2261	GB/T 20383	85.48		-3.02	
2265		-----		-----	
2266	DIN54231	75.0		-3.08	
2272	DIN54231	526.7		-0.59	
2284	DIN54231	345.0		-1.59	
2289	DIN54231	480		-0.85	
2290	DIN54231	775.1		0.77	
2295	DIN54231	326		-1.70	
2300	DIN54231	205		-2.37	
2310	DIN54231	1060		2.34	
2311	DIN54231	1105.2		2.59	
2350	DIN54231	1610		5.37	
2352	DIN54231	1144		2.80	
2358	DIN54231	1320		3.77	
2359	DIN54231	1296		3.64	
2363	DIN54231	1145		2.81	
2365	DIN54231	1532		4.94	
2370	DIN54231	1050		2.29	
2375	DIN54231	1487		4.69	
2379	DIN54231	1016.97		2.10	
2380	DIN54231	1357.18		3.98	
2386	DIN54231	1040		2.23	
2390	DIN54231	1960.331	C,G(0.05)	7.30	First reported 3307.37
2410	DIN54231	540		-0.52	
2425	DIN54231	366.00		-1.48	
2427	DIN54231	543.6		-0.50	
2446	DIN54231	223.66		-2.26	
2452		-----		-----	
2462	DIN54231	645		0.06	
2481	in house	1830	G(0.05)	6.58	
2492	OEKO-Tex	6406.7	C,G(0.01)	31.77	First reported 7580.8
3104	DIN54231	728		0.51	
3116	DIN54231	422		-1.17	
3117	DIN54231	1499.7		4.76	
3146	DIN54231	524		-0.61	
3150	DIN54231	767		0.73	
3151	DIN54231	382.5		-1.39	
3153	DIN54231	725		0.50	
3154	DIN54231	166.63		-2.58	
3172	in house	2375.2	G(0.05)	9.58	
3176	DIN54231	256.2		-2.08	
3180	DIN54231	549.2		-0.47	
3185	DIN54231	534		-0.55	
3190	DIN54231	203.6		-2.37	
3192	DIN54231	204.5		-2.37	
3197	DIN54231	253		-2.10	
3199	DIN54231	348.240		-1.58	
3200	DIN54231	393.2		-1.33	
3209	DIN54231	630.4		-0.02	
3210	DIN54231	816		1.00	
3214	DIN54231	464.69		-0.94	
3218	DIN54231	564		-0.39	
3220	DIN54231	299.0		-1.85	

3225	DIN54231	674.1	0.22
3228	DIN54231	452	-1.01
3233	in house	25.7	-3.35
3242	DIN54231	620	-0.08
3246	DIN54231	774	0.77
3248	DIN54231	376	-1.42

|		Group 1:	Group 2:	Group 3:
normality	not OK	OK	OK	unknown
n	70	52	19	3
outliers	5	0	0	1
mean (n)	634.72	426.25	1268.17	2343.35
st.dev. (n)	409.559	205.367	231.878	368.129
R(calc.)	1146.77	575.03	649.26	1030.76
R(DIN54231:05)	508.64	341.58	1016.26	1877.87
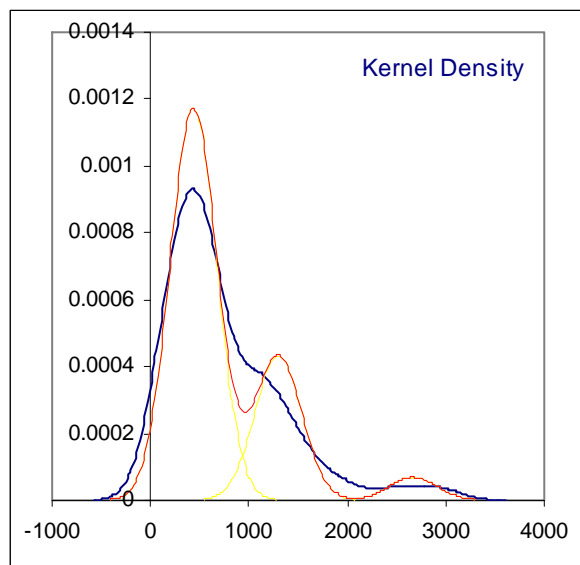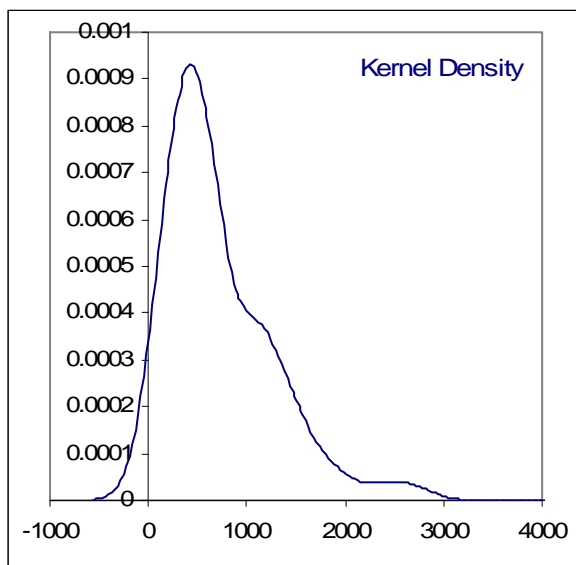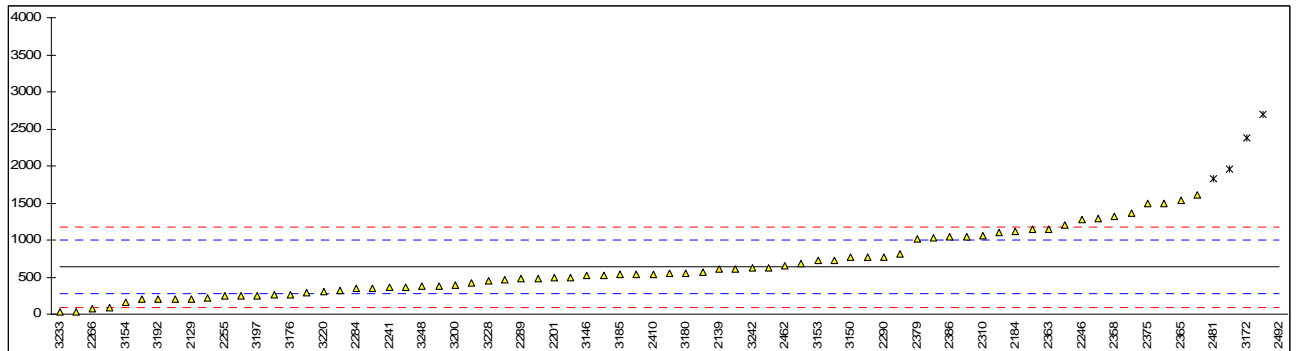
Determination of Disperse Blue 26 (CASno. 3860-63-7) in sample #12034; results in mg/kg

lab	method	value	mark	z(targ)	remarks
551	DIN54231	n.d.		-----	
623	DIN54231	684.02		2.65	
840	DIN54231	413		0.22	
2115		-----		-----	
2129	DIN54231	369		-0.18	
2132	DIN54231	34.3	C	-3.19	First reported n.d.
2137	DIN54231	97.1		-2.62	
2139	DIN54231	159.6		-2.06	
2165	DIN54231	322		-0.60	
2172	DIN54231	209		-1.62	
2184	DIN54231	744		3.19	
2197		-----		-----	
2201	DIN54231	328		-0.55	
2217	DIN54231	465		0.68	
2218	DIN54231	177.56		-1.90	
2241	DIN54231	790		3.60	
2246	DIN54231	889.6		4.50	
2247	DIN54231	192		-1.77	
2252	DIN54231	178.4		-1.89	
2255	DIN54231	205.13		-1.65	
2261	GB/T 20383	12.97		-3.38	
2265		-----		-----	
2266	DIN54231	25.8		-3.26	
2272	DIN54231	1121.2	G(0.05)	6.58	
2284	DIN54231	160.0		-2.06	
2289	DIN54231	295		-0.84	
2290	DIN54231	232.4		-1.41	
2295	DIN54231	235		-1.38	
2300	DIN54231	75		-2.82	
2310	DIN54231	528		1.25	
2311	DIN54231	464.8		0.68	
2350	DIN54231	732		3.08	
2352	DIN54231	643		2.28	
2358	DIN54231	711		2.89	
2359	DIN54231	703		2.82	
2363	DIN54231	730		3.07	
2365	DIN54231	852		4.16	
2370	DIN54231	336		-0.47	
2375	DIN54231	578.8	C	1.71	First reported 1033
2379	DIN54231	255.39		-1.20	
2380	DIN54231	966.79		5.19	
2386	DIN54231	768		3.41	
2390	DIN54231	82.31		-2.75	
2410	DIN54231	260		-1.16	
2425	DIN54231	167.18		-1.99	
2427	DIN54231	283.6		-0.95	
2446	DIN54231	197.07		-1.72	
2452		-----		-----	
2462	DIN54231	427		0.34	
2481	in house	21000	C,G(0.01)	185.20	First reported 8700
2492	OEKO-Tex	4821.0	C,G(0.01)	39.82	First reported 1687.8
3104	DIN54231	182		-1.86	
3116	DIN54231	232		-1.41	
3117	DIN54231	734.2		3.10	
3146	DIN54231	176		-1.91	
3150	DIN54231	793		3.63	
3151	DIN54231	351		-0.34	
3153	DIN54231	166		-2.00	
3154	DIN54231	n.d.		-----	
3172	in house	859.9		4.23	
3176	DIN54231	1549.5	G(0.01)	10.43	
3180	DIN54231	741.5		3.17	
3185	DIN54231	470		0.73	
3190	DIN54231	181.4		-1.86	
3192	DIN54231	198.2		-1.71	
3197	DIN54231	180		-1.88	
3199	DIN54231	515.393		1.14	
3200	DIN54231	256.5		-1.19	
3209	DIN54231	686.3		2.67	
3210	DIN54231	963		5.16	
3214	DIN54231	209.86		-1.61	
3218	DIN54231	326		-0.56	
3220	DIN54231	118.0		-2.43	

3225	DIN54231	342.9	-0.41
3228	DIN54231	305	-0.75
3233	in house	11.3	-3.39
3242	DIN54231	375	-0.12
3246	DIN54231	352	-0.33
3248	DIN54231	125	-2.37

			Group 1:	Group 2:	Group 3:
normality	not OK		OK	OK	unknown
n	69		50	19	3
outliers	4		0	0	1
mean (n)	388.86		245.22	766.85	2497.23
st.dev. (n)	264.807		130.576	101.844	2023.803
R(calc.)	741.46		365.61	285.16	5666.65
R(DIN54231:05)	311.62		196.51	614.52	2001.18
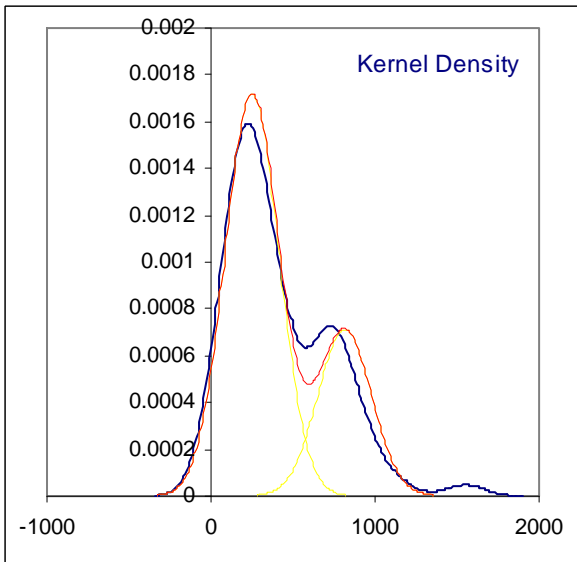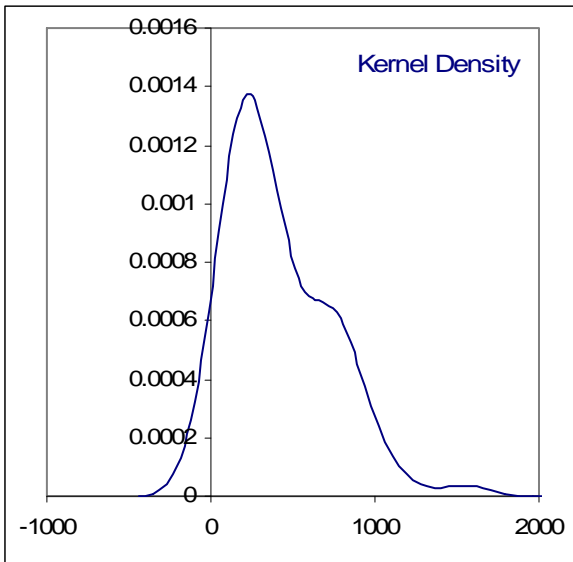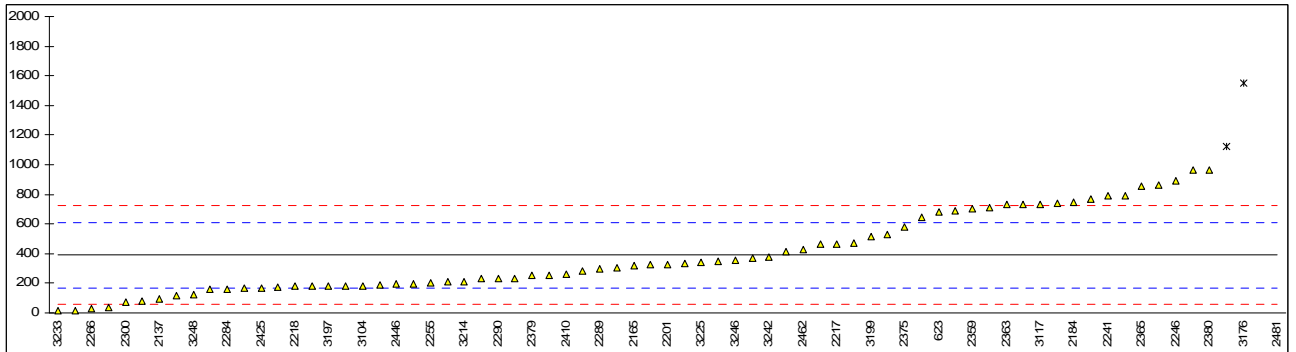
APPENDIX 2

Summary of all other reported Disperse dyes in samples #12033 and #12034; results in mg/kg

Lab	Other reported Disperse Dyes on #12033
2265	Disperse Red 17 = 27.17
2386	Disperse Blue 26 = 62.1
2390	Disperse Blue 35 = 3.95, Disperse Brown 1 = 7.70, Disperse Orange 76 = 115.16
3176	Disperse blue 1 = 15.0

Lab	Other reported Disperse Dyes on #12034
551	Disperse Blue 35 = 11.48
2132	Disperse Blue 35 = 36.4
2246	Disperse Blue 35 = 378.9
2252	Disperse Blue 35 = 20.3
2265	Disperse Brown 1 = 47.1, Disperse Yellow 49 = 51.39
2272	Disperse Brown 1 = 119.5
2295	Disperse Blue 35 = 78
2390	Disperse Blue 35 = 7356.16, Disperse Brown 1 = 21.28, Disperse Orange 1 = 34.69, Disperse Orange 76 = 142.62
2481	Disperse Brown 1 = 1190
3117	Disperse Blue 35 = 78.6
3172	Disperse Blue 35 = 408.1
3214	Disperse Blue 35 = 514.98

APPENDIX 3

Number of participants per country

  3 labs in BANGLADESH

  1 lab in BRAZIL

  4 labs in FRANCE

10 labs in GERMANY

12 labs in HONG KONG

  1 lab in HUNGARY

  6 labs in INDIA

  1 lab in INDONESIA

  2 labs in ITALY

  4 labs in KOREA

21 labs in P.R. of CHINA

  1 lab in PAKISTAN

  1 lab in SWITZERLAND

  2 labs in TAIWAN R.O.C.

  1 lab in THAILAND

  1 lab in TUNESIA

  4 labs in TURKEY

  1 lab in U.S.A.

  3 labs in VIETNAM

APPENDIX 4

Abbreviations:

C   = final result after checking of first reported suspect 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
n.e.   = not evaluated
n.d.   = not detected

Literature:

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2   DIN 54231:2005
3   iis Interlaboratory Studies: Protocol for the Organisation, Statistics and Evaluation, January 2010
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5   P.L. Davies, Fr Z. Anal. Chem, <u>351</u>, 513, (1988)
6   W.J. Conover, Practical; Nonparametric Statistics, J. Wiley&Sons, NY, p.302, (1971)
7   ISO 5725, (1986)
8   ISO 5725, parts 1-6, (1994)
9   M. Thompson and R. Wood, J. AOAC Int, <u>76</u>, 926, (1993)
10   G. Rohm, J. Bohnen & H. Kruessmann, GIT Labor-Fachzeitschrift, p 1080, <u>11</u>, (1997)
11   Kazumi Sasaki, Mari Sakai, Kazuma Matusita, Yoko Masuda and Koremaro Sato, Chemical Structure Analysis for Azo Type Disperse Dyes by Mass Spectroscopy and Detection of Dyestuff in Textile Products Causing Allergic Contact Dermatitis, BUNSEKI KAGAKU, Vol. 57 (2008) , No. 10 pp.833-850
12   D. Balasubramanian and K.J. Janakiraman, Asian Textile Journal, p 51-57, March 2004
13   Öko-tex Std.100 edition 01/2012, available via http://www.oeko-tex.com/