Results of Proficiency Test
Disperse dyes in textile
March 2011

Organised by: Institute for Interlaboratory Studies
                 Spijkenisse, the Netherlands

Author: dr. R.G. Visser
Correctors: ing. N. Boelhouwer & ing. R.J. Starink
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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 20 below listed dyes according to Öko-tex Standard 100 edition 01.01.2011 (see note 4 of appendix 4), of which 9 are mentioned in DIN54231:05:

- 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 iis09A04 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 2011 interlaboratory study 56 laboratories in 15 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 guide 43, ISO/IEC 17043:2010 and ILAC-G13:2007. This ensures 100% confidentiality of participant's data. Also 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 textile sample #11022 (Grey woven fabric) and the textile sample #11023 (Orange woven fabric) were prepared from two different bulk materials by a third party laboratory. Each bulk sample, approximately 500 grams of material, was divided over 90 subsamples of 4 gram each. The samples were labelled and subsequently tested for homogeneity by a subcontracted laboratory. The homogeneity of the subsamples #11022 was checked by determination of Disperse Blue 3 and Orange 1 and the homogeneity of the subsamples #11023 was checked by determination of Disperse Red 1 and Disperse Yellow 3 in accordance with DIN54231:05 on 15 stratified random selected samples. See the following tables for the test results.

	Disperse Blue 3 in mg/kg	Disperse Orange 1 in mg/kg
sample #11022-1	71.10	115.58
sample #11022-2	73.50	113.95
sample #11022-3	72.32	114.67
sample #11022-4	74.12	112.98
sample #11022-5	72.95	114.57
sample #11022-6	72.66	114.18
sample #11022-7	72.96	113.54
sample #11022-8	73.14	113.14
sample #11022-9	73.88	113.66
sample #11022-10	72.68	112.87
sample #11022-11	72.19	113.85
sample #11022-12	73.17	114.21
sample #11022-13	72.91	114.45
sample #11022-14	73.25	114.11
sample #11022-15	73.16	113.86

table 1: homogeneity test results of subsamples #11022

	Disperse Red 1 in mg/kg	Disperse Yellow 3 in mg/kg
sample #11023-1	210.75	146.40
sample #11023-2	208.60	145.80
sample #11023-3	209.70	143.50
sample #11023-4	210.30	144.60
sample #11023-5	208.69	145.30
sample #11023-6	211.20	144.80
sample #11023-7	209.30	146.20
sample #11023-8	207.86	144.20
sample #11023-9	208.66	145.80
sample #11023-10	208.55	143.50
sample #11023-11	209.75	145.70
sample #11023-12	210.60	143.60
sample #11023-13	208.90	145.60
sample #11023-14	211.10	144.80
sample #11023-15	210.90	144.20

table 2: homogeneity test results of subsamples #11023

From the results in table 1 and 2, the repeatabilities of the results were calculated and compared with 0.3 times the corresponding reproducibility of the target method in agreement with the procedure of ISO 13528, Annex B2 in the next table:

	Disp. Blue 3 #11022 in mg/kg	Disp. Orange 1 #11022 in mg/kg	Disp. Red 1 #11023 in mg/kg	Disp. Yellow 3 #11023 in mg/kg
r(calc.)	2.0	2.0	3.1	2.8
Reference method	DIN54231:05	DIN54231:05	DIN54231:05	DIN54231:05
0.3 x R(ref. method)	5.1	7.5	12.6	9.2

table 3: evaluation of repeatabilities of subsamples #11022 and #11023

The repeatabilities of the results of homogeneity test for the determined allergenic dyestuffs were in agreement with 0.3 times the respective reproducibilities mentioned in (or estimated from) the reference method DIN54231:05. Therefore homogeneity of the subsamples was assumed.

An amount of approx. 4 grams of each of the samples #11022 and #11023 was sent to the participating laboratories on March 9, 2011.

2.5 ANALYSES

The participants were asked to determine the concentrations of 20 forbidden disperse 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 details of the calibrants used was enclosed. Also a letter of instructions was sent along.

3 RESULTS

During four weeks after sample despatch 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 6.

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.

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.

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, 51 participants reported 198 numerical results. Observed were 18 outlying test results, which is 9.1% of the numerical results. In proficiency studies outlier percentages of 3% - 7.5% are quite normal.
All data sets 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 and all other reported test results of the disperse dyes present are summarised in appendix 2.
In DIN 54231:05 no reproducibilities are 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 #11022: This material (grey woven fabric) was treated by a third party laboratory with allergenic dyestuffs in order to find two banned disperse dyes: Disperse Blue 3 and Disperse Orange 1. The results reported by the participants varied strongly (Disperse Blue 3 from 10.7 mg/kg – 2388 mg/kg and Disperse Orange 1 from 52.4 mg/kg – 611 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 the case for Disperse Orange 1.
No other disperse dyes were reported to be present in sample #11022 (see appendix 2).
All laboratories would have rejected this sample for containing too much Allergenic Dyestuffs (acc. to the limit of Öko-tex Std.100 edition 01/2011 of 50 mg/kg).

Textile #11023: This material (orange woven fabric) was treated by a third party laboratory with allergenic dyestuffs in order to find two banned disperse dyes: Disperse Red 1 and Disperse Yellow 3. The results reported by the participants varied strongly (Disperse Red 1 from 25.4 mg/kg – 1645 mg/kg and Disperse Yellow 3 from 75.8 mg/kg – 2660 mg/kg). The spread of Disperse Red 1 is not in agreement with the estimated reproducibility of DIN54231:05. However, the spread of Disperse Yellow 3 is in full agreement with the estimated reproducibility of DIN54231:05.
All laboratories would have rejected this sample for containing too much Allergenic Dyestuffs (acc. to the limit of Öko-tex Std.100 edition 01/2011 of 50 mg/kg). One laboratory did not report Disperse Yellow 3, but reported the presence of Disperse Yellow 1 in stead, see appendix 2.

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	45	75.4	108.2	60.4
Disperse Orange 1	mg/kg	44	139.7	170.3	111.9

table 4: reproducibilities of dyes in textile sample #11022

Parameter	unit	n	average	2.8 * sd	R (target)
Disperse Red 1	mg/kg	48	216.6	216.8	173.6
Disperse Yellow 3	mg/kg	43	218.3	171.1	175.0

table 5: reproducibilities of dyes in textile sample #11023

Without further statistical calculations it can be concluded that for the detected disperse dyestuffs the group of participating laboratories may have some 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.

Parameter	March 2011	March 2010	March 2009	March 2008	March 2007
Disperse Blue 1	n.d.	n.d.	n.d.	121%	n.d.
Disperse Blue 3	143%	142%	n.d.	n.e.	102%
Disperse Blue 26	n.d.	152%	150%	n.e.	133%
Disperse Blue 35	n.d.	n.d.	(235%)*	n.e.	n.d.
Disperse Orange 1	122%	n.d.	n.d.	n.d.	n.d.
Disperse Orange 3	n.d.	n.d.	67%	98%	136%
Disperse Red 1	100%	n.d.	n.d.	176%	n.d.
Disperse Red 11	n.d.	144%	127%	n.e.	n.d.
Disperse Yellow 3	78%	n.d.	n.d.	n.d.	n.d.
Disperse Yellow 9	n.d.	n.d.	n.d.	86%	n.d.
Disperse Yellow 49	n.d.	n.d.	n.d.	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 quality improvement is present yet.

It was noticed that almost all participants found the spiked dyestuffs in sample #11022 and in sample #11023. However several false negative results were reported, while sometimes a different disperse dye was reported instead (see appendix 2).

One laboratory remarked that both samples were very heterogeneous. It found three very different test results in three determinations per sample.

From the findings in previous PTs it was concluded that the purity of the calibrants is without doubt one of the major problems in the analysis of disperse dyes. And the variety of used calibrants is large, see appendix 3. Also, it is remarkable to see that several laboratories reported a deviating purity in comparison with other laboratories for the identical calibrant.
Therefore it was investigated whether the spread of the results of laboratories that used the same calibrant would be smaller than the spread of all test results.
For Disperse Blue 3 at least 26 laboratories used a calibrant of Dr. Ehrenstorfer with a purity of 20%-24%; for Disperse Orange 1 at least 27 laboratories used a calibrant of Dr. Ehrenstorfer with a purity of 80%; for Disperse Red 1 at least 31 laboratories used a calibrant of Dr. Ehrenstorfer with a purity of 93.5-97.5% and for Disperse Yellow 3 at least 31 laboratories used a calibrant of Dr. Ehrenstorfer with a purity of 30%.
When the test results of the laboratories that used above calibrants, were evaluated separately, for two dyes significantly smaller spreads are observed (Disperse Red 1 and Disperse Yellow 3), while at the same time no effect on the average concentrations is present. This in contrast to Disperse Blue 3 and Disperse Orange 3, for which the spreads of the selected test results are not different from the spreads of all test results, but where both averages are higher than the averages of all test results.
As expected, the test results of laboratories that used identical calibrants, are better comparable and also will be in agreement with the reproducibility requirements of DIN54231:05 more easily 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 (see also reference 12).
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 #11022; results in mg/kg

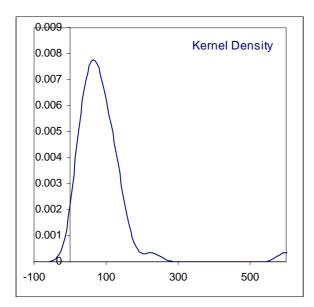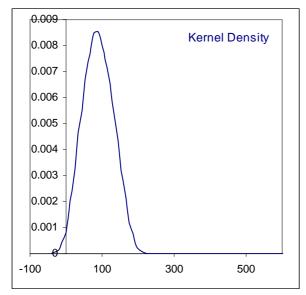| lab	method	value	mark	z(targ)	remarks
2115		138.432		2.92	
2120	in house (ASE)	1790	G(0.01)	79.44	
2121		-----		-----	
2129	DIN54231	81.8		0.30	
2135		600	G(0.01)	24.31	
2165	DIN54231	62		-0.62	
2172	DIN54231	109		1.56	
2184	DIN54231	68		-0.34	
2197		227	G(0.05)	7.02	
2201	DIN54231	124.0		2.25	
2215	in house	92.0		0.77	
2218	DIN54231	17.78		-2.67	
2241	DIN54231	71.0		-0.20	
2247	DIN54231	21.3		-2.51	
2255		-----		-----	
2261	GB/T 20383	42.0		-1.55	
2266	DIN54231	86.62		0.52	
2272		-----		-----	
2284	DIN54231	77		0.07	
2289		125		2.30	
2295	DIN54231	115		1.83	
2297	DIN54231	100		1.14	
2300	DIN54231	36.82		-1.79	
2410	DIN54231	120		2.07	
3107		-----		-----	
3116	DIN54231	68.0		-0.34	
3117		152	C	3.55	first reported 326
3146		54		-0.99	
3150	DIN54231	38.0		-1.73	
3151	DIN54231	28.5		-2.17	
3153	DIN54231	37.4		-1.76	
3154		-----		-----	
3159		-----		-----	
3170		61.37		-0.65	
3172	DIN54231	17.2		-2.70	
3174	DIN54231	121.96		2.16	
3176		10.7		-3.00	
3180		62.5		-0.60	
3185	DIN54231	40.1		-1.64	
3190	DIN54231	93.9		0.86	
3191	EN71-9	61		-0.67	
3192		100.8		1.18	
3197		73		-0.11	
3200	DIN54231	75.12		-0.01	
3209	DIN54231	89.5		0.65	
3210		160		3.92	
3214	DIN54231	120.18		2.07	
3218	DIN54231	35		-1.87	
3220	DIN54231	22.8		-2.44	
3225	DIN54231	69.47		-0.28	
3228	HPLC/DAD/MS	53		-1.04	
3237		-----		-----	
3240	GB/T 20383	129.98		2.53	
3243	DIN54231	2388	C,G(0.01)	107.15	first reported 1400
3246		48		-1.27	
3248		82.23		0.32	

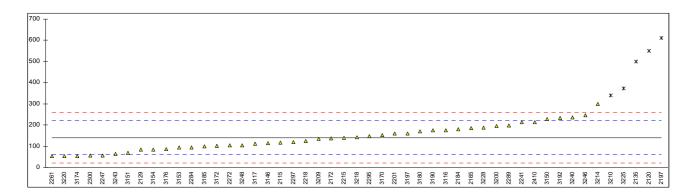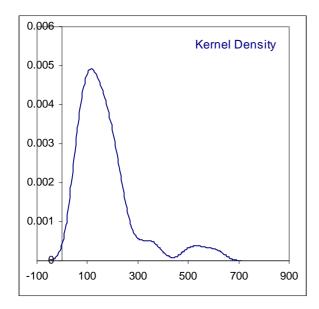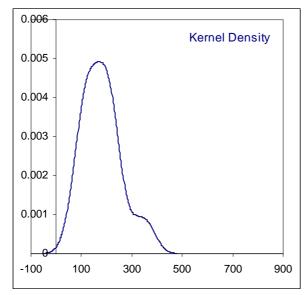|			Selected test results, see §5
normality	OK		OK
n	45		25
outliers	4		1
mean (n)	75.41		88.98
st.dev. (n)	38.637		37.234
R(calc.)	108.18		104.25
R(DIN54231:05)	60.43		71.30

Only 26 selected test results, see §5

Determination of Disperse Orange 1 (CASno. 2581-69-3) in sample #11022; results in mg/kg

lab	method	value	mark	z(targ)	remarks
2115		117.221		-0.56	
2120	in house (ASE)	550	G(0.01)	10.27	
2121		-----		-----	
2129	DIN54231	82.9		-1.42	
2135		500	G(0.01)	9.01	
2165	DIN54231	186		1.16	
2172	DIN54231	137		-0.07	
2184	DIN54231	180		1.01	
2197		611	G(0.01)	11.79	
2201	DIN54231	160.2		0.51	
2215	in house	139		-0.02	
2218	DIN54231	124.37		-0.38	
2241	DIN54231	212.3		1.82	
2247	DIN54231	56.0		-2.09	
2255		-----		-----	
2261	GB/T 20383	52.4		-2.18	
2266		-----		-----	
2272	DIN54231	103.8		-0.90	
2284	DIN54231	95		-1.12	
2289		198		1.46	
2295	DIN54231	148		0.21	
2297	DIN54231	120		-0.49	
2300	DIN54231	55.17		-2.11	
2410	DIN54231	213		1.83	
3107		-----		-----	
3116	DIN54231	174.0		0.86	
3117		111		-0.72	
3146		115		-0.62	
3150	DIN54231	228		2.21	
3151	DIN54231	69.0		-1.77	
3153	DIN54231	92.7		-1.17	
3154	DIN54231	84.43		-1.38	
3159		-----		-----	
3170		152.08		0.31	
3172	DIN54231	100.8		-0.97	
3174	DIN54231	54.41		-2.13	
3176		85.8		-1.35	
3180		170.8		0.78	
3185	DIN54231	99.2		-1.01	
3190	DIN54231	174.0		0.86	
3191		-----		-----	
3192		233.6		2.35	
3197		161		0.53	
3200	DIN54231	194.35		1.37	
3209	DIN54231	134.3		-0.13	
3210		340	DG(0.05)	5.01	
3214	DIN54231	299.52	C	4.00	first reported 578.53
3218	DIN54231	141		0.03	
3220	DIN54231	54.0		-2.14	
3225	DIN54231	372.27	DG(0.05)	5.82	
3228	HPLC/DAD/MS	187		1.18	
3237		-----		-----	
3240	GB/T 20383	235.76		2.40	
3243	DIN54231	63		-1.92	
3246		246		2.66	
3248		104.20		-0.89	

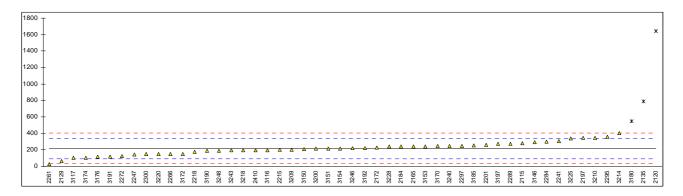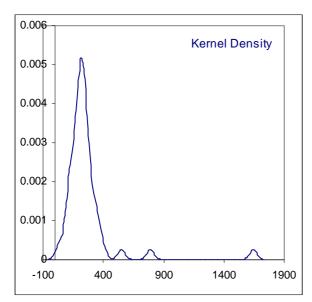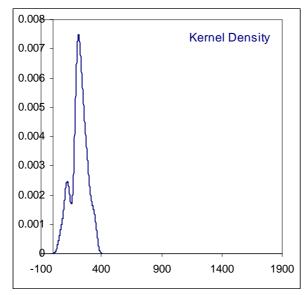|				Selected test results, see §5
	normality	OK		OK
	n	44		25
	outliers	5		2
	mean (n)	139.67		166.84
	st.dev. (n)	60.828		59.218
	R(calc.)	170.32		165.81
	R(DIN54231:05)	111.92		133.70

Only 27 selected test results, see §5

Determination of Disperse Red 1 (CASno. 2872-52-8) in sample #11023; results in mg/kg

lab	method	value	mark	z(targ)	remarks
2115		277.989		0.99	
2120	in house (ASE)	1645	G(0.01)	23.05	
2121		-----		-----	
2129	DIN54231	63.49		-2.47	
2135		790	G(0.01)	9.25	
2165	DIN54231	240		0.38	
2172	DIN54231	229		0.20	
2184	DIN54231	240		0.38	
2197		345		2.07	
2201	DIN54231	261.3		0.72	
2215	in house	201		-0.25	
2218	DIN54231	176.56		-0.65	
2241	DIN54231	304.3		1.42	
2247	DIN54231	146.0		-1.14	
2255		-----		-----	
2261	GB/T 20383	25.4		-3.08	
2266	DIN54231	149.10		-1.09	
2272	DIN54231	126		-1.46	
2284	DIN54231	297		1.30	
2289		275		0.94	
2295	DIN54231	358		2.28	
2297	DIN54231	251		0.56	
2300	DIN54231	147.50		-1.11	
2410	DIN54231	196		-0.33	
3107		-----		-----	
3116	DIN54231	197.0		-0.32	
3117		102		-1.85	
3146		294		1.25	
3150	DIN54231	211		-0.09	
3151	DIN54231	213.0		-0.06	
3153	DIN54231	243		0.43	
3154	DIN54231	213.05		-0.06	
3159		-----		-----	
3170		246.52		0.48	
3172	DIN54231	149.5		-1.08	
3174	DIN54231	107.02		-1.77	
3176		119.3		-1.57	
3180		550	C,G(0.01)	5.38	first reported 456.5
3185	DIN54231	253		0.59	
3190	DIN54231	186.7		-0.48	
3191	EN71-9	120		-1.56	
3192		222.6		0.10	
3197		273		0.91	
3200	DIN54231	212.25		-0.07	
3209	DIN54231	204.5		-0.19	
3210		345		2.07	
3214	DIN54231	402.00		2.99	
3218	DIN54231	195		-0.35	
3220	DIN54231	149.0		-1.09	
3225	DIN54231	335.94		1.93	
3228	HPLC/DAD/MS	239		0.36	
3237		-----		-----	
3240	GB/T 20383	247.33		0.50	
3243	DIN54231	194		-0.36	
3246		219		0.04	
3248		191.71		-0.40	

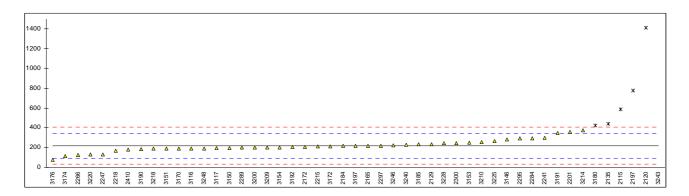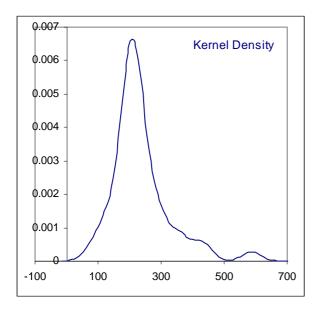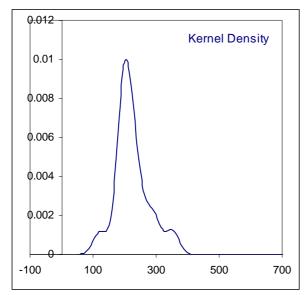|			Selected test results, see §5
normality	OK		OK
n	48		31
outliers	3		0
mean (n)	216.56		215.54
st.dev. (n)	77.436		66.897
R(calc.)	216.82		187.31
R(DIN54231:05)	173.55		172.73

Only 31 selected test results, see §5

Determination of Disperse Yellow 3 (CASno. 2832-40-8) in sample #11023; results in mg/kg

lab	method	value	mark	z(targ)	remarks
2115		586.792	G(0.01)	5.90	
2120	in house (ASE)	1415	G(0.01)	19.15	
2121		-----		-----	
2129	DIN54231	232.1		0.22	
2135		440	DG(0.05)	3.55	
2165	DIN54231	220		0.03	
2172	DIN54231	207		-0.18	
2184	DIN54231	215		-0.05	
2197		776	G(0.01)	8.93	
2201	DIN54231	356.4		2.21	
2215	in house	213		-0.09	
2218	DIN54231	166.88	C	-0.82	first reported 540.43
2241	DIN54231	301.4		1.33	
2247	DIN54231	131.4		-1.39	
2255		-----		-----	
2261		-----		-----	
2266	DIN54231	123.15		-1.52	
2272		-----		-----	
2284	DIN54231	296		1.24	
2289		199		-0.31	
2295	DIN54231	293		1.20	
2297	DIN54231	220		0.03	
2300	DIN54231	242.39		0.39	
2410	DIN54231	180		-0.61	
3107		-----		-----	
3116	DIN54231	190.4		-0.45	
3117		195		-0.37	
3146		284		1.05	
3150	DIN54231	197		-0.34	
3151	DIN54231	189.0		-0.47	
3153	DIN54231	249		0.49	
3154	DIN54231	201.37		-0.27	
3159		-----		-----	
3170		190.13		-0.45	
3172	DIN54231	214.3		-0.06	
3174	DIN54231	114.37		-1.66	
3176		75.8		-2.28	
3180		426	DG(0.05)	3.32	
3185	DIN54231	232		0.22	
3190	DIN54231	183.6		-0.56	
3191	EN71-9	346		2.04	
3192		206.1		-0.20	
3197		220		0.03	
3200	DIN54231	200.60		-0.28	
3209	DIN54231	201.2		-0.27	
3210		255		0.59	
3214	DIN54231	375.00		2.51	
3218	DIN54231	188		-0.49	
3220	DIN54231	128.0		-1.45	
3225	DIN54231	265.24		0.75	
3228	HPLC/DAD/MS	242		0.38	
3237		-----		-----	
3240	GB/T 20383	230.45		0.19	
3243	DIN54231	2660	C,G(0.01)	39.08	first reported 2000
3246		225		0.11	
3248		192.42		-0.41	

					Selected test results, see §5
	normality	OK			not OK
	n	43			30
	outliers	6			1
	mean (n)	218.32			223.37
	st.dev. (n)	61.097			53.327
	R(calc.)	171.07			149.32
	R(DIN54231:05)	174.95			179.00

Only 31 selected test results, see §5

APPENDIX 2

Summary of all other reported Disperse dyes in samples #11022 and #11023; results in mg/kg

Lab	Other reported Disperse Dyes on #11022	Other reported Disperse Dyes on #11023
2115	-	-
2120	-	-
2121	-	-
2129	-	-
2135	-	-
2165	-	-
2172	-	-
2184	-	-
2197	-	-
2201	-	-
2215	-	-
2218	-	-
2241	-	-
2247	-	-
2255	-	-
2261	-	-
2266	-	-
2272	-	112.1 mg/kg Disperse Yellow 1
2284	-	-
2289	-	-
2295	-	-
2297	3.95 mg/kg Disperse Yellow 3	-
2300	-	-
2410	-	-
3107	-	-
3116	-	-
3117	-	277 mg/kg Disperse Orange 76=37
3146	-	-
3150	-	-
3151	-	-
3153	-	-
3154	-	-
3159	-	-
3170	-	-
3172	-	-
3174	-	-
3176	-	-
3180	-	-
3185	-	-
3190	-	-
3191	-	-
3192	-	-
3197	-	-
3200	-	-
3209	-	-
3210	-	-
3214	-	-
3218	-	-
3220	-	-
3225	150.72 mg/kg Disperse Blue 1	-
3228	-	-
3237	-	-
3240	-	-
3243	-	-
3246	-	-
3248	-	-

APPENDIX 3

Details of the calibrants used

Lab	calibrants used for Disperse Blue 3			
	Brand	Batch/Lotno	Concentration	State of matter
2115	Dr. Ehrenstorfer	90608	24%	solid
2120	Dr. Ehrenstorfer	90608	24%	solid
2121				
2129	Dr. Ehrenstorfer	C12972013	24%	solid
2135	Sigma-Aldrich	21564-3	20%	solid
2165	Dr. Ehrenstorfer	50620	20%	solid
2172	Dr. Ehrenstorfer	90608	24%	solid
2184	AccuStandard	DYE-004S	100mg/L	solution
2197				solid
2201	Sigma-Aldrich	86197KJ	20%	solid
2215	Dr. Ehrenstorfer	C12972013	24%	solid
2218	AccuStandard	DYE-004S	100mg/L	solution
2241	Dr. Ehrenstorfer	50620	20%	solid
2247	Dr. Ehrenstorfer	C12972013	24%	solid
2255	Dr. Ehrenstorfer	C12972013	20%	solid
2261				solid
2266	Sigma-Aldrich	21565-1	20%	solid
2272				
2284	Sigma-Aldrich	48596TH	9%	solid
2289	Dr. Ehrenstorfer	C12972013	24%	solid
2295				
2297	Dr. Ehrenstorfer	90608	24%	solid
2300	Dr. Ehrenstorfer	50620	20%	solid
2410	Dr. Ehrenstorfer	90608	24%	solid
3107				
3116	Sigma-Aldrich	215651	20%	solid
3117	Dr. Ehrenstorfer	C12972013	24%	solid
3146	Sigma-Aldrich	10302DF	various	solution
3150	Dr. Ehrenstorfer	C12972013	20%	solid
3151	Sigma-Aldrich	21565-1	20%	solid
3153	Sigma-Aldrich	03430JR	20%	solid
3154				
3159				
3170	Sigma-Aldrich	02413AD	20%	solid
3172	AccuStandard	DYE-004S	100mg/L	solution
3174	Dr. Ehrenstorfer	90608	24%	solid
3176	Dr. Franke GmbH	0343052	20%	solid
3180	BASF	020745	20%	solid
3185	Dr. Ehrenstorfer	90608	24%	solid
3190	Dr. Ehrenstorfer	90608	24%	solid
3191	Dr. Ehrenstorfer	C12972013	24%	solid
3192	Dr. Ehrenstorfer	C12972013	20%	solid
3197	Dr. Ehrenstorfer	90409	50% (?)	solid
3200	Dr. Ehrenstorfer	C12972013	20%	solid
3209	Dr. Ehrenstorfer	90409	20%	solid
3210	Dr. Ehrenstorfer	C12972013	20%	solid
3214	Sigma-Aldrich	21565-1	20%	solid
3218	Dr. Ehrenstorfer	90409	50% (?)	solid
3220	Dr. Ehrenstorfer		60%	solid
3225	Dr. Ehrenstorfer	50620	20%	solid
3228	Dr. Ehrenstorfer	50620	20%	solid
3237				
3240	Dr. Ehrenstorfer	C12972013	20%	solid
3243	Sigma-Aldrich	21565-1	20%	solid
3246	Sigma-Aldrich		20%	solid
3248	Dr. Ehrenstorfer	C12972013	24%	solid

APPENDIX 3, continued

Details of the calibrants used

Lab	Brand	Batch/Lotno	Concentration	State of matter
	calibrants used for Disperse Orange 1			
2115	Sigma-Aldrich	1273753	96.2%	solid
2120	Sigma-Aldrich	03806AV	25%	solid
2121				
2129	Dr. Ehrenstorfer	C12972101	80%	solid
2135	Sigma-Aldrich	21228-8	25%	solid
2165	Dr. Ehrenstorfer	50620	80%	solid
2172	Dr. Ehrenstorfer	50620	80%	solid
2184	AccuStandard	DYE-005S	100mg/L	solution
2197	LGC Standards			solid
2201	Sigma-Aldrich	17497HJ	15%	solid
2215	Dr. Ehrenstorfer	C12972101	80%	solid
2218	AccuStandard	DYE-005S	100mg/L	solution
2241	Dr. Ehrenstorfer	50620	80%	solid
2247	Dr. Ehrenstorfer	C12972101	80%	solid
2255	Dr. Ehrenstorfer	C12972101	80%	solid
2261				solid
2266				
2272	Dr. Ehrenstorfer	50620	80%	solid
2284	Dr. Ehrenstorfer	50620	22% (?)	solid
2289	Dr. Ehrenstorfer	C12972101	80%	solid
2295				
2297	Dr. Ehrenstorfer	50620	80%	solid
2300	Fluka	1275753	96%	solid
2410	Dr. Ehrenstorfer	50620	80%	solid
3107				
3116	Dr. Ehrenstorfer	C12972101	80%	solid
3117	Dr. Ehrenstorfer	C12972101	80%	solid
3146	Sigma-Aldrich	FW31834	various	solution
3150	Dr. Ehrenstorfer	C12972101	80%	solid
3151	Sigma-Aldrich	21228-8	25%	solid
3153	Sigma-Aldrich	03806AV	25%	solid
3154	Sigma-Aldrich		25%	solid
3159				
3170	Sigma-Aldrich	04217ED	25%	solid
3172	AccuStandard	DYE-005S	100mg/L	solution
3174	Fluka	1275753	91%	solid
3176	Bruno Ludewig	00641	30%	solid
3180	Sigma-Aldrich	03806AV	25%	solid
3185	Dr. Ehrenstorfer	91106	80%	solid
3190	Dr. Ehrenstorfer	50620	80%	solid
3191				
3192	Dr. Ehrenstorfer	C12972101	80%	solid
3197	Dr. Ehrenstorfer	50620	80%	solid
3200	Dr. Ehrenstorfer	C12972101	80%	solid
3209	Dr. Ehrenstorfer	50620	80%	solid
3210	Dr. Ehrenstorfer	C12972101	80%	solid
3214	Dr. Ehrenstorfer	50620	80%	solid
3218	Dr. Ehrenstorfer	50620	80%	solid
3220				
3225	Dr. Ehrenstorfer	50620	80%	solid
3228	Dr. Ehrenstorfer	50620	80%	solid
3237				
3240	Dr. Ehrenstorfer	C12972101	80%	solid
3243	Sigma-Aldrich	29173	96%	solid
3246	Dr. Ehrenstorfer		80%	solid
3248	Dr. Ehrenstorfer	C12972101	80%	solid

APPENDIX 3, continued

Details of the calibrants used

	calibrants used for Disperse Red 1			
Lab	Brand	Batch/Lotno	Concentration	State of matter
2115	Dr. Ehrenstorfer	71016	96%	solid
2120	Sigma-Aldrich	13624BC	95%	solid
2121				
2129	Dr. Ehrenstorfer	C12972210	94%	solid
2135	Sigma-Aldrich	34420-6	95%	solid
2165	Dr. Ehrenstorfer	71016	94%	solid
2172	Dr. Ehrenstorfer	71016	94%	solid
2184	AccuStandard	DYE-007S	100mg/L	solution
2197				solid
2201	Sigma-Aldrich	B624BC	95%	solid
2215	Dr. Ehrenstorfer	C12972210	94%	solid
2218	AccuStandard	DYE-007S	100mg/L	solution
2241	Dr. Ehrenstorfer	71016	94%	solid
2247	Dr. Ehrenstorfer	C12972210	94%	solid
2255	Dr. Ehrenstorfer	C12972210	94%	solid
2261				solid
2266	Sigma-Aldrich	34420-6	95%	solid
2272	Dr. Ehrenstorfer	71016	94%	solid
2284	Dr. Ehrenstorfer	71016	94%	solid
2289	Dr. Ehrenstorfer	C12972210	94%	solid
2295				
2297	Dr. Ehrenstorfer	71016	94%	solid
2300	Fluka	1258722	96%	solid
2410	Dr. Ehrenstorfer	71016	94%	solid
3107				
3116	Dr. Ehrenstorfer	C12972210	94%	solid
3117	Dr. Ehrenstorfer	C12972210	94%	solid
3146	Sigma-Aldrich	03301EQ	various	solution
3150	Dr. Ehrenstorfer	C12972210	94%	solid
3151	Sigma-Aldrich	34420-6	95%	solid
3153	Sigma-Aldrich	05917TF	95%	solid
3154	Dr. Ehrenstorfer	C12972210	94%	solid
3159				
3170	Sigma-Aldrich	02113KX	50%	solid
3172	AccuStandard	DYE-007S	100mg/L	solution
3174	Dr. Ehrenstorfer	71016	94%	solid
3176	Bruno Ludewig	05958	30%	solid
3180	Sigma-Aldrich	02113KX	50%	solid
3185	Dr. Ehrenstorfer	71016	94%	solid
3190	Dr. Ehrenstorfer	71016	94%	solid
3191	Dr. Ehrenstorfer	C12972210	94%	solid
3192	Dr. Ehrenstorfer	C12972210	94%	solid
3197	Dr. Ehrenstorfer	71016	94%	solid
3200	Dr. Ehrenstorfer	C12972210	94%	solid
3209	Dr. Ehrenstorfer	71016	94%	solid
3210	Dr. Ehrenstorfer	C12972210	94%	solid
3214	Sigma-Aldrich	34420-6	95%	solid
3218	Dr. Ehrenstorfer	70427	93.5%	solid
3220	Dr. Ehrenstorfer		86%	solid
3225	Dr. Ehrenstorfer	71031	97.5%	solid
3228	Dr. Ehrenstorfer	71016	94%	solid
3237				
3240	Dr. Ehrenstorfer	C12972210	94%	solid
3243	Sigma-Aldrich	34420-6	50%	solid
3246	Dr. Ehrenstorfer		94%	solid
3248	Dr. Ehrenstorfer	C12972210	94%	solid

APPENDIX 3, continued

Details of the calibrants used

Lab	Brand	Batch/Lotno	Concentration	State of matter
	calibrants used for Disperse Yellow 3			
2115	Sigma-Aldrich	1274181	98.1% (?)	solid
2120	Dr. Ehrenstorfer	51118	30%	solid
2121				
2129	Dr. Ehrenstorfer	C12972310	30%	solid
2135	Sigma-Aldrich	21568-6	30%	solid
2165	Dr. Ehrenstorfer	51118	30%	solid
2172	Dr. Ehrenstorfer	51118	30%	solid
2184	AccuStandard	DYE-003S	100mg/L	solution
2197	Fluka	403636/1		solid
2201	Dr. Ehrenstorfer	51118	30%	solid
2215	Dr. Ehrenstorfer	C12972310	30%	solid
2218	AccuStandard	DYE-003S	100mg/L	solid
2241	Dr. Ehrenstorfer	51118	30%	solid
2247	Dr. Ehrenstorfer	C12972310	30%	solid
2255				
2261				solid
2266	Sigma-Aldrich	21568-6	30%	solid
2272				
2284	Dr. Ehrenstorfer	51118	30%	solid
2289	Dr. Ehrenstorfer	C12972310	30%	solid
2295				
2297	Dr. Ehrenstorfer	51118	30%	solid
2300	Fluka	1274181	96%	solid
2410	Dr. Ehrenstorfer	51118	30%	solid
3107				
3116	Dr. Ehrenstorfer	C12972310	30%	solid
3117	Dr. Ehrenstorfer	C12972310	30%	solid
3146	Dr. Ehrenstorfer	51118	various	solution
3150	Dr. Ehrenstorfer	C12972310	30%	solid
3151	Sigma-Aldrich	21568-6	30%	solid
3153	Sigma-Aldrich	01409LM	30%	solid
3154	Dr. Ehrenstorfer	C12972310	30%	solid
3159				
3170	Sigma-Aldrich	10010AD	30%	solid
3172	AccuStandard	DYE-003S	100mg/L	solid
3174	Dr. Ehrenstorfer	51118	30%	solid
3176	Dr. Franke GmbH	04409BK	30%	solid
3180	Sigma-Aldrich	01409LM	30%	solid
3185	Dr. Ehrenstorfer	51118	30%	solid
3190	Dr. Ehrenstorfer	51118	30%	solid
3191	Dr. Ehrenstorfer	C12972310	30%	solid
3192	Dr. Ehrenstorfer	C12972310	30%	solid
3197	Dr. Ehrenstorfer	51118	30%	solid
3200	Dr. Ehrenstorfer	C12972310	30%	solid
3209	Dr. Ehrenstorfer	51118	30%	solid
3210	Dr. Ehrenstorfer	C12972310	30%	solid
3214	Sigma-Aldrich	21568-6	30%	solid
3218	Dr. Ehrenstorfer	51118	30%	solid
3220	Dr. Ehrenstorfer		81% (?)	solid
3225	Dr. Ehrenstorfer	00507	30%	solid
3228	Dr. Ehrenstorfer	51118	30%	solid
3237				
3240	Dr. Ehrenstorfer	C12972310	30%	solid
3243	AccuStandard	DYE-003N	30%	solid
3246	Fluka		unknown	solid
3248	Dr. Ehrenstorfer	C12972310	30%	solid

APPENDIX 4

Number of participants per country

   1 lab in BANGLADESH

  3 labs in FRANCE

  9 labs in GERMANY

  7 labs in HONG KONG

  4 labs in INDIA

  2 labs in ITALY

   1 lab in KOREA

19 labs in P.R. of CHINA

   1 lab in PORTUGAL

   1 lab in SWITZERLAND

   1 lab in TAIWAN R.O.C.

   1 lab in THAILAND

  4 labs in TURKEY

   1 lab in UNITED KINGDOM

   1 lab in VIETNAM

APPENDIX 5

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.a.	= not applicable
n.d.	= not detected
fr.	= first reported

Literature:

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