

**Results of Proficiency Test  
Allergenic dyestuffs in textile  
April 2006**

**Organised by: Institute for Interlaboratory Studies  
Spijkenisse, the Netherlands**

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## 1 INTRODUCTION

Coloured fabrics, when in contact with human skin, may cause Allergic Contact Dermatitis. The following twenty Dyestuffs are classified as allergenic.

• C.I. Disperse Blue 1	CASnr. 2475-45-8	C.I.nr	64 500
• C.I. Disperse Blue 3	CASnr. 2475-46-9	C.I.nr	61 505
• C.I. Disperse Blue 7	CASnr. 3179-90-6	C.I.nr	62 500
• C.I. Disperse Blue 26	CASnr. 3860-63-7	C.I.nr	63 305
• C.I. Disperse Blue 35	CASnr. 56524-77-7 / 56524-76-6		
• C.I. Disperse Blue 102	CASnr. 12222-97-8		
• C.I. Disperse Blue 106	CASnr. 12223-01-7		
• C.I. Disperse Blue 124	CASnr. 61951-51-7		
• C.I. Disperse Brown 1	CASnr. 23355-64-8		
• C.I. Disperse Orange 1	CASnr. 2581-69-3	C.I.nr	11 080
• C.I. Disperse Orange 3	CASnr. 730-40-5	C.I.nr	11 005
• C.I. Disperse Orange 37/76	CASnr. 13301-61-6	C.I.nr	11 132
• C.I. Disperse Red 1	CASnr. 2872-52-8	C.I.nr	11 110
• C.I. Disperse Red 11	CASnr. 2872-48-2	C.I.nr	62 015
• C.I. Disperse Red 17	CASnr. 3179-89-3	C.I.nr	11 210
• C.I. Disperse Yellow 1	CASnr. 119-15-3	C.I.nr	10 345
• C.I. Disperse Yellow 3	CASnr. 2832-40-8	C.I.nr	11 855
• C.I. Disperse Yellow 9	CASnr. 6373-73-5	C.I.nr	10 375
• C.I. Disperse Yellow 39	CASnr. 12236-29-2		
• C.I. Disperse Yellow 49	CASnr. 54824-37-2		

The German ban on azo dyes capable of releasing banned amines has become a widely publicised issue in the textile industry. Dyestuff manufacturers, processors and exporters in India are careful in selection of azo dyes. However, several Dyestuffs that are skin sensitizers are still being widely used in India for dyeing polyester and nylon. In this context and in response to requests from several laboratories, the Institute for Interlaboratory Studies (i.i.s.) decided to continue with organizing a proficiency test for Allergic Dyestuffs in textile in the annual proficiency test program of 2005/2006. In this international interlaboratory study 36 laboratories in 15 different countries participated. See appendix 4 for a list of number of participants in (alphabetical) country order. 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 send in this round robin 2 different with allergenic dyestuff treated textile samples. The textile samples were obtained from a participating 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 Spijkensisse, the Netherlands, has implemented a quality system based on ISO guide 43 and ILAC-G13:2000. 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 'i.i.s. Interlaboratory Studies: Protocol for the Organization, Statistics and Evaluation' of November 2003 (i.i.s.-protocol, version 3.0). The participants were asked to report the analytical results using the indicated units on the report form.

## 2.3 SAMPLES

The textile sample 0617 (Magenta coloured fabric) and the textile sample 0618 (Green coloured fabric) were prepared from two different bulk materials by a third party laboratory. Each bulk sample, approximately 400 grams of material, was cut into pieces and after mixing, divided over 50 subsamples of 4.0 gram each. The samples were labelled and tested for homogeneity. The homogeneity of the subsamples was checked by determination of an allergenic dyestuff in accordance with DIN54231:04 on 4 stratified random selected samples. See the following tables for the test results.

Textile	Disperse Red 11 concentration in mg/kg
sample 0617-1	133.5
sample 0617-2	137.7
sample 0617-3	130.6
sample 0617-4	132.4
sample 0617-5	134.4

Table 1: homogeneity test of subsamples 0617

Textile	Disperse Orange 3 concentration in mg/kg
sample 0618-1	285.9
sample 0618-2	288.9
sample 0618-3	286.1
sample 0618-4	291.2
sample 0618-5	289.4

Table 2: homogeneity test of subsamples 0618

From the results in table 1 and 2, the repeatabilities of the results were calculated. In the next table the calculated repeatabilities are compared with the requirements of DIN54231:04.

	r(calc) in mg/kg	r(lit) in mg/kg	Reference method
sample 0617	7.4	35.7	DIN54231:04
sample 0618	6.4	77.0	DIN54231:04

Table 3: repeatabilities of subsamples 0617 and 0618

The repeatabilities of the results of homogeneity test for the determined aromatic amines were in agreement with the repeatabilities mentioned in DIN54231:04. Therefore homogeneity of the subsamples was assumed.

One sample of approx. 4.0 grams of each of the samples 0617 and 0618 were sent to the participating laboratories on March 15, 2006.

## 2.4 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 of analysis details 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 5.

### 3.1 STATISTICS

Statistical calculations were performed as described in the report 'i.i.s. Interlaboratory Studies: Protocol for the Organization, Statistics and Evaluation' of November 2003 (i.i.s.-protocol, version 3.0)

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 results from a component in a sample are plotted. The corresponding laboratory numbers are under the X-axis. A continuous horizontal line presents the average of the reported data. The target reproducibility limits of the selected standard are presented by two dotted lines parallel to the average line at (average - target reproducibility) and at (average + target reproducibility). Outliers and other data, which were excluded from the calculations, are represented as a cross. All other 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 (see appendix 5; nr.13 and 14).

### 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:

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

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.

Six participants reported the results after the deadline and two participants did not report any results due to different reasons. Finally, 34 participants did send in 79 numerical results were reported. Observed were 7 outlying results, which is 8.1 % of the numerical results. In proficiency studies outlier percentages of 3 % - 7.5 % are quite normal.

Not all data sets proved to have a normal distribution. An anomalous distribution was found for Disperse Orange 3 of sample 0618. In this case the statistical evaluation should be used with care.

### 4.1 EVALUATION PER SAMPLE

In this section the results are discussed per sample. All statistical results reported on the textile samples are summarised in appendix 1 and all other reported results of the most relevant allergenic dyestuffs present are summarised in appendix 2.

**Textile 0617:** Sample 0617 (Magenta coloured fabric) was treated by the third party laboratory with allergenic dyestuff in order to find the following banned disperse dyes: Disperse Blue 35 and Disperse Red 11. The results reported by the participants varied strongly (Disperse Blue 35: 5.3 – 421.45 mg/kg; Disperse Red 11: 2.7 – 248.24 mg/kg). Twenty-two of the thirty laboratories, that reported results for sample 0617, would reject this textile sample for containing too much of a “potentially allergic dye” (approx. 60 mg/kg – detection limit).

Finally, the spreads were very large and not in agreement with the requirements of DIN54231:04. These large spreads may partly be explained by the observed differences in the detection and quantification of the Dyestuffs (see appendix 3). One participant reported the presence of Disperse Red 1 (see appendix 2).

**Textile 0618:** Sample 0618 (Green coloured fabric) was treated by the third party laboratory with allergenic dyestuff in order to find the following banned disperse dyes: Disperse Yellow 7 and Disperse Orange 3. Six of the 32 participants, that did analyze this sample, detected beside Disperse Orange

3, Disperse Blue 26, while only three participants reported a value for Disperse Yellow 7.

The results reported by the participants varied strongly (Disperse Orange 3: 29.6 – 1365 mg/kg; Disperse Blue 26: 88.2 – 790 mg/kg). All laboratories, except one (825) would reject this textile sample for containing too much of a “potentially allergic dye” (approx. 60 mg/kg – detection limit).

Finally, the spreads found were very large and not in agreement with the requirement of DIN54231:04. Four participants reported also other Dyestuffs (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 methods 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 method DIN54231:04 are compared in the next tables.

Parameter	unit	n	average	2.8 * sd	R (target)
Disperse Blue 35	mg/kg	8	20.63	32.64	15.53
Disperse Red 11	mg/kg	29	76.33	119.97	61.17

Table 4: reproducibilities of sub sample 0617

Parameter	unit	n	average	2.8 * sd	R (target)
Disperse Blue 26	mg/kg	6	502.4	705.3	402.6
Disperse Orange 3	mg/kg	29	199.7	299.3	160.1

Table 5: reproducibilities of sub sample 0618

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

## 5 COMPARISON WITH PREVIOUS INTERLABORATORY STUDIES

In this proficiency test for the determination of allergenic dyestuffs in textile, it was noticed that almost all the participants found at least two of the four spiked dyestuffs.

Only 11 reported a result for Disperse Blue 35 and 3 (!) reported a result for Disperse Yellow 7. Six participants reported a high value for Disperse Blue 26.

In total five participants detected in the samples (0617 & 0618) the presence of other dyestuffs. However the majority of the participants did not report the presence of the other allergenic dyestuff..



Furthermore, the spreads of the group were large compared with derived precision data from E-DIN 54231:04. In E-DIN 54231 only the standard deviation for the repeatability is mentioned.

The reproducibility is calculated as follows: standard deviation multiplied with 2.8, to get the repeatability, multiplied with 3 to get the reproducibility.

Parameter	March 2006	March 2005
Disperse Blue 3	n.d.	136 %
Disperse Blue 26	140 %	243 %
Disperse Blue 35	158 %	n.d.
Disperse Orange 3	150 %	211 %
Disperse Red 11	157 %	n.d.
Disperse Yellow 49	n.d.	219 %

Table 6: relative reproducibilities

It is noticed that the RSD% for Disperse Blue 26 and Disperse Orange 3 as well have improved.

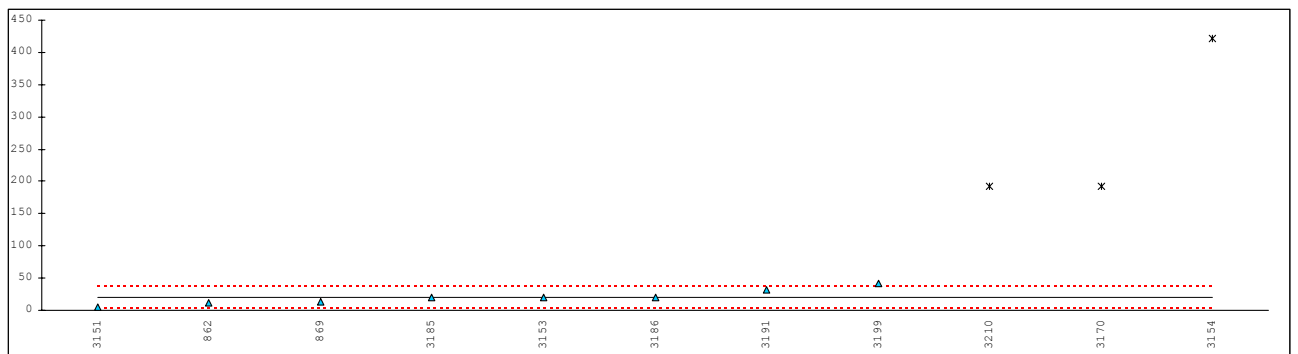
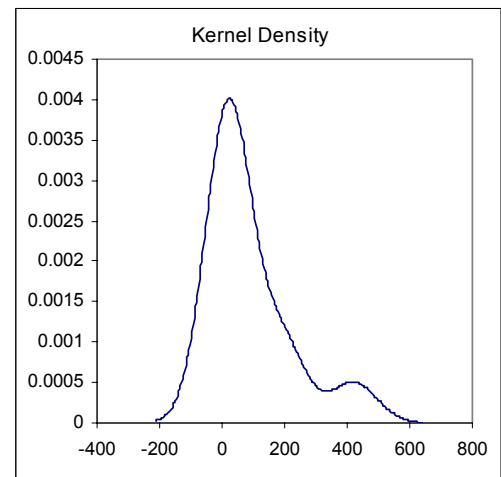
It appeared that four participants corrected for recovery, although this correction is not mentioned in the standardised method. The results of these 4 participants were not significantly higher than the other results as expected.

The spreads observed in this interlaboratory study are not caused by just one critical point in the analysis. Almost all participants used a method based on E-DIN54231 or E-DIN NMP 512. However, the detection technique differ strongly (see appendix 2). 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 thus rise of the quality of the analytical results.

**APPENDIX 1**

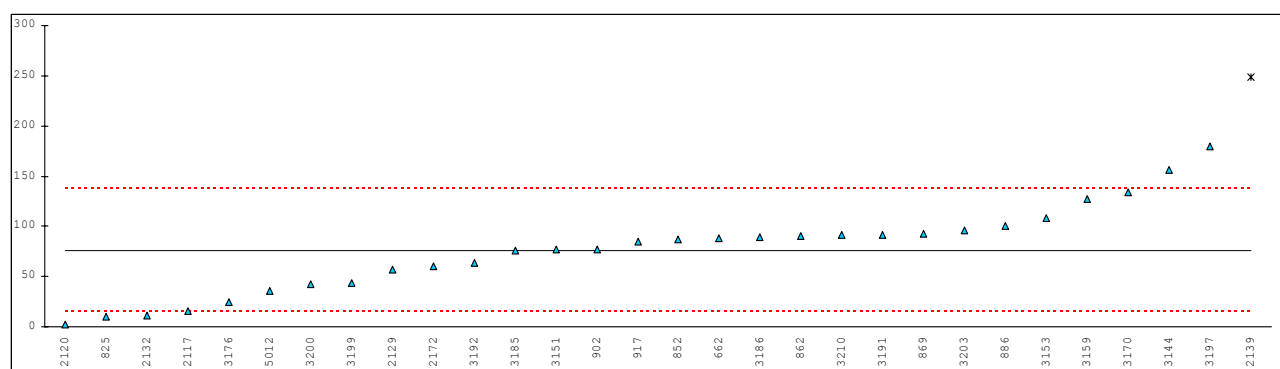
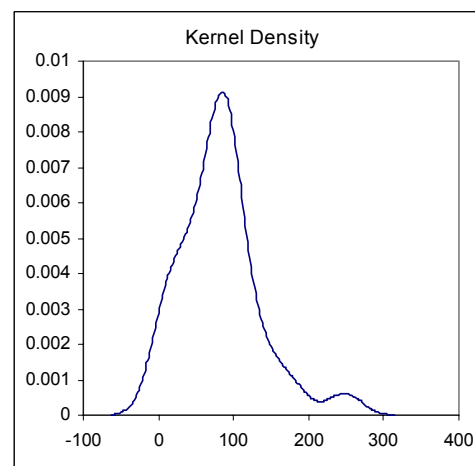
Determination of Disperse Blue 35 (CASno.12222-75-2) in textile sample #0617; Results in mg/kg

lab	method	value	mark	Z(targ)	remarks
662	DIN54231	ND		----	
825	DIN54231	ND		----	
852	DIN54231	ND		----	
862	DIN54231	12.3		-1.41	
869	DIN NMP512	13.2		-1.26	
886	DIN NMP512	ND		----	
902	DIN54231	ND		----	
917		----		----	
2117		----		----	
2120		----		----	
2129	DIN54231	<37.5		----	
2131	INHOUSE	POSITIVE		----	
2132	DIN54231	<5		----	False negative result
2139	DIN54231	ND		----	
2152		----		----	
2172	DIN54231	<15		----	
3144		----		----	
3150		----		----	
3151	DIN54231	5.3		-2.60	
3153	DIN54231	20		-0.11	
3154	DIN54231	421.45	G(0.05)	67.88	
3159	DIN54231	<75		----	
3170	DIN54231	192.2	DG(0.01)	29.06	
3172		----		----	
3176		----		----	
3185	DIN54231	20		-0.11	
3186	INHOUSE	20.63		0.00	
3191	DIN54231	31		1.76	
3192		----		----	
3197		----		----	
3199	DIN54231	42.62		3.72	
3200		----		----	
3203		----		----	
3210	DIN54231	192	DG(0.01)	29.02	
3211		----		----	
5012		----		----	
	normality	OK			
	n	8			
	outliers	3			
	mean (n)	20.63			
	st.dev. (n)	11.659			
	R(calc.)	32.64			
	R(DIN54231:04)	16.53			



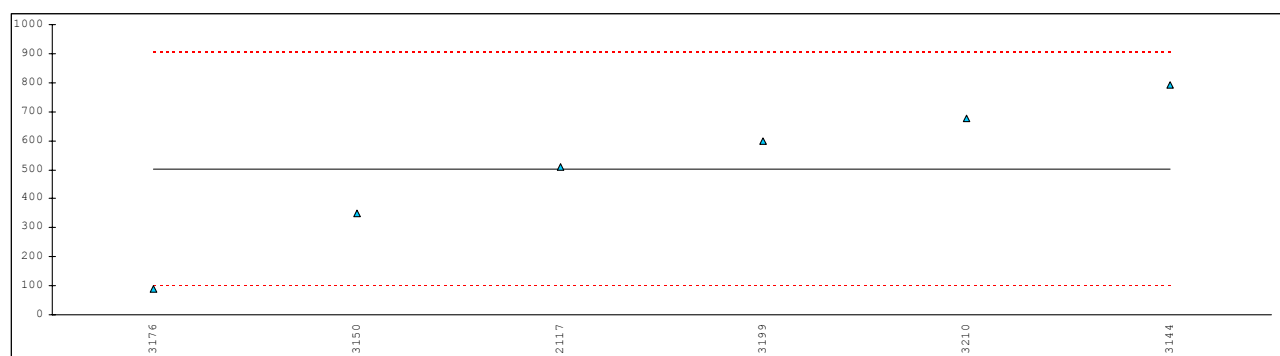
Determination of Disperse Red 11 (CASno. 2872-52-8) in textile sample #0617; Result in mg/kg

lab	method	value	mark	Z(targ)	remarks
662	DIN54231	88.6		0.56	
825	DIN54231	10.2		-3.03	
852	DIN54231	87		0.49	
862	DIN54231	90.3		0.64	
869	DINNMP512	92.2		0.73	
886	DINNMP512	100.2		1.09	
902	DIN54231	77		0.03	
917	DIN54231	85.3		0.41	
2117	INHOUSE	16		-2.76	
2120	DIN54231	2.7		-3.37	With ASE technique 128 mg/kg
2129	DIN54231	57		-0.88	
2131	INHOUSE	POSITIVE		----	
2132	DIN54231	11.2		-2.98	
2139	DIN54231	248.24	G(0.05)	7.87	With ASE technique 413.61 mg/kg
2152		----		----	
2172	DIN54231	59.8		-0.76	
3144	DIN54231	156		3.65	
3150		----		----	
3151	DIN54231	77		0.03	
3153	DIN54231	108		1.45	
3154	DIN54231	ND		----	
3159	DIN54231	127		2.32	
3170	DIN54231	133.7		2.63	
3172		----		----	
3176	INHOUSE	24.45		-2.37	
3185	DIN54231	76		-0.02	
3186	INHOUSE	88.95		0.58	
3191	DIN54231	92		0.72	
3192	DIN54231	63.3		-0.60	
3197	INHOUSE	180		4.75	
3199	DIN54231	43.06		-1.52	
3200	DIN54231	42.7		-1.54	
3203	INHOUSE	96		0.90	
3210	DIN54231	91.9		0.71	
3211		----		----	
5012	DIN54231	36		-1.85	
	normality	OK			
	n	29			
	outliers	1			
	mean (n)	76.33			
	st.dev. (n)	42.846			
	R(calc.)	119.97			
	R(DIN54231:04)	61.17			



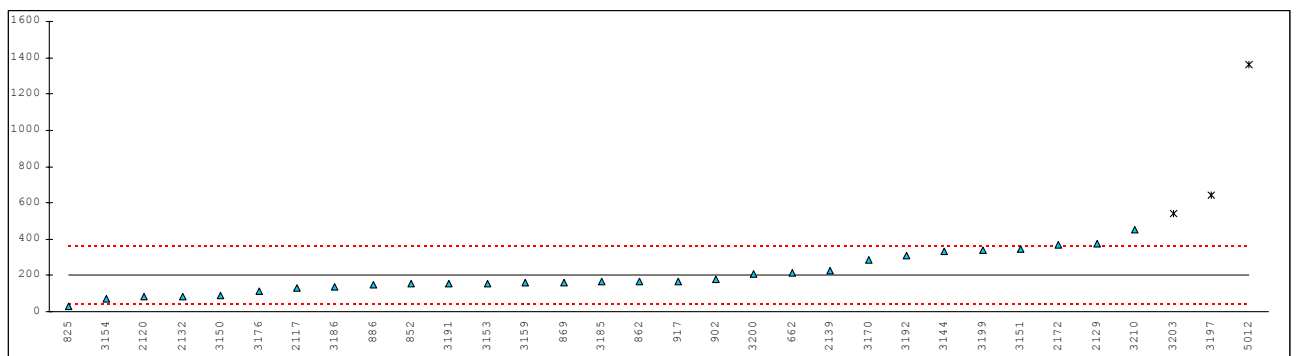
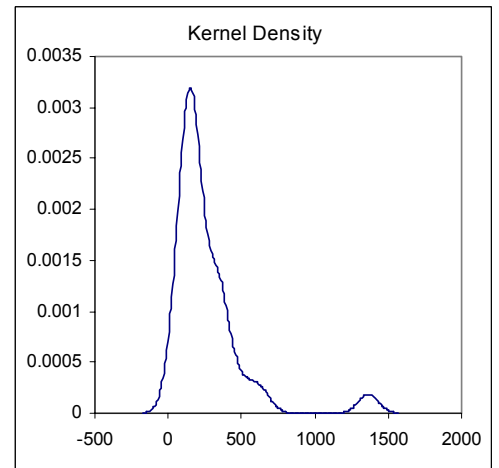
Determination of Disperse Blue 26 (CI no. 63 305) in textile sample #0618; Results in mg/kg

lab	method	value	mark	Z(targ)	remarks
662	DIN54231	ND		----	
825	DIN54231	ND		----	
852	DIN54231	ND		----	
862	DIN54231	ND		----	
869	DINNMP512	ND		----	
886	DINNMP512	ND		----	
902	DIN54231	ND		----	
917		----		----	
2117	INHOUSE	510		0.05	
2120		----		----	
2129	DIN54231	<37.5		----	
2131		----		----	
2132	DIN54231	<5		----	
2139	INHOUSE	ND		----	
2152		----		----	
2172	DIN54231	<15		----	
3144	DIN54231	790		2.00	
3150	DIN54231	350		-1.06	
3151		----		----	
3153	DIN54231	ND		----	
3154	DIN54231	ND		----	
3159	DIN54231	<75		----	
3170		----		----	
3172		----		----	
3176	INHOUSE	88.2		-2.88	
3185	DIN54231	<20		----	
3186		----		----	
3191		----		----	
3192		----		----	
3197		----		----	
3199	DIN54231	600.1		0.68	
3200		----		----	
3203		----		----	
3210	DIN54231	676		1.21	
3211		----		----	
5012		----		----	
	normality	OK			
	n	6			
	outliers	0			
	mean (n)	502.4			
	st.dev. (n)	251.89			
	R(calc.)	705.3			
	R(DIN54231:04)	402.6			



Determination of Disperse Orange 3 (CASno. 730-40-5) in textile sample #0618; Results in mg/kg

lab	method	value	mark	Z(targ)	remarks
662	DIN54231	213.7		0.24	
825	DIN54231	29.6		-2.98	
852	DIN54231	155		-0.78	
862	DIN54231	165		-0.61	
869	DINNMP512	160.2		-0.69	
886	DINNMP512	145.95		-0.94	
902	DIN54231	176		-0.42	
917	DIN54231	166.7		-0.58	
2117	INHOUSE	132		-1.18	
2120	DIN54231	81		-2.08	With ASE technique 425 mg/kg
2129	DIN54231	375		3.07	
2131	INHOUSE	POSITIVE		----	
2132	DIN54231	81.4		-2.07	
2139	DIN54231	225.41		0.45	With ASE technique 461.18 mg/kg
2152		----		----	
2172	DIN54231	370		2.98	
3144	DIN54231	334		2.35	
3150	DIN54231	92		-1.88	
3151	DIN54231	345		2.54	
3153	DIN54231	157		-0.75	
3154	DIN54231	71		-2.25	
3159	DIN54231	158		-0.73	
3170	DIN54231	288.3		1.55	
3172		----		----	
3176	INHOUSE	110.7		-1.56	
3185	DIN54231	164		-0.63	
3186	INHOUSE	135		-1.13	
3191	DIN54231	155		-0.78	
3192	DIN54231	307.3		1.88	
3197	INHOUSE	640	DG(0.05)	7.70	
3199	DIN54231	341.2	C	2.47	First reported 493.6
3200	DIN54231	206.7		0.12	
3203	INHOUSE	544	DG(0.05)	6.02	
3210	DIN54231	450		4.38	
3211		----		----	
5012	DIN54231	1365	G(0.01)	20.39	
	normality	not OK			
	n	29			
	outliers	3			
	mean (n)	199.7			
	st.dev. (n)	106.89			
	R(calc.)	299.3			
	R(DIN54231:04)	160.1			



**APPENDIX 2**

Summary of all other reported Disperse-dyes in textile sample #0617; results in mg/kg

Lab	Others reported Dyes
662	
825	
852	
862	
869	
886	
902	
917	
2117	
2120	
2129	
2131	
2132	
2139	
2152	
2172	
3144	
3150	Disperse Red 1 = 18
3151	
3153	
3154	
3159	
3170	
3172	
3176	
3185	
3186	
3191	
3192	
3197	
3199	
3200	
3203	
3210	
3211	
5012	

## Summary of all other reported Dyestuffs textile sample #0618; results in mg/kg

lab	Other reported dyes
662	
825	
852	
862	
869	
886	Disperse Yellow 7 = 67.65
902	
917	
2117	
2120	
2129	
2131	
2132	
2139	
2152	
2172	
3144	
3150	
3151	
3153	
3154	
3159	Disperse Yellow 7 = 112
3170	
3172	
3176	
3185	
3186	Disperse Orange 11 = 5.94
3191	
3192	
3197	Disperse Blue 124 = 293
3199	Disperse Blue 35 = 5.418
3200	
3203	
3210	Disperse Blue 35 = 35.0
3211	
5012	

## APPENDIX 3

## Details of the analysis methods used by the participants:

lab	Method	Deviations	Quantified	Confirmation	INT/EXT used	Rec. corr.
662	DIN54231	--	HPLC/DAD/MS	--	Ext. std.	Yes
825	DIN54231	--	LC/MS	HPLC/DAD	Ext. std.	--
852	DIN54231	--	HPLC/MS	HPLC/DAD/MS	Ext. std.	No
862	DIN54231	--	HPLC/MSD	HPLC/DAD/MSD	Ext. std.	No
869	DIN NMP 512	--	HPLC/MS	HPLC/DAD/MS	Ext. std.	No
886	DIN NMP 512 / DIN54231	--	HPLC/MSD	TLC	Ext. std.	No
902	DIN54231	--	HPLC/MS	HPLC/MS	Ext. std.	Yes
917	DIN54231	--	HPLC/DAD/MS	LC/MS	Ext. std.	No
2117	In house	1g/10ml MeoH	HPLC/DAD	TLC	Ext. std.	No
2120	DIN54231	--	HPLC/DAD	TLC	Ext. std.	No
2129	DIN54231	--	LC/MSD/DAD	--	Ext. std.	No
2131	In house	--	LC/DAD	LC/MS	Ext. std.	No
2132	DIN54231	--	HPLC/DAD	HPLC/DAD	Ext. std.	No
2139	In house	--	HPLC/UV, HPLC/MS	MS spectrum	Ext. std.	No
2152	--	--	--	--	--	--
2172	DIN54231	--	HPLC/DAD/MS	DAD Spectrum	Ext. std.	No
3144	DIN54231	--	HPLC/UV	LC/MS	Ext. std.	No
3150	DIN54231	--	TLC, HPLC/DAD	TLC	Ext. std.	No
3151	DIN54231	Extraction at 80°C	LC/MS	LC/MS	Ext. std.	No
3153	DIN54231	--	LC/MS	HPLC/DAD	Ext. std.	No
3154	DIN54231	0.2-0.4 g with 10 mL MeoH	LC/MS	HPLC/DAD	Ext. std.	No
3159	DIN54231	--	HPLC/PDA/MS	HPLC.PDA/MS	Ext. std.	Yes
3170	--	--	--	--	--	--
3172	--	--	--	--	--	--
3176	--	--	--	--	--	--
3185	DIN54231	--	LC/MS	--	Ext. std.	Yes
3186	DIN54231	--	LC/MS	HPLC/DAD	Ext. std.	No
3191	Din54231	--	Hplc/dad	Spectra	Ext. std.	No
3192	DIN54231	--	HPLC/MS-MS DAD	HPLC/MS-MS	Ext. std.	No
3197	DIN54231	--	HPLC/DAD	TLC	Ext. std.	No
3199	DIN54231	--	LC/MS	HPLC	Ext. std.	No
3200	DIN54231	--	HPLC/UV	TLC/UV	Ext. std.	No
3203	In house	3 times extracted /10 mL	HPLC/DAD	--	Ext. std.	No
3210	DIN54231	--	HPLC/UV	HPLC/UV	Ext. std.	No
3211	In house	--	HPLC/UV	--	Ext. std.	No
5012	DIN54231	--	LC/MS	standards	Ext. std.	No



**APPENDIX 4****List of participants on alphabetical country order**

<b>Number of laboratories</b>	<b>Country</b>
1 laboratory in	FRANCE
8 laboratories in	GERMANY
5 laboratories in	HONG KONG
3 laboratories in	INDIA
1 laboratory in	ITALY
2 laboratories in	KOREA
7 laboratories in	P.R. of CHINA
1 laboratory in	PORTUGAL
1 laboratory in	SWITZERLAND
1 laboratory in	TAIWAN R.O.C.
1 laboratory in	THAILAND
1 laboratory in	THE NETHERLANDS
3 laboratories in	TURKEY
1 laboratory in	U.S.A.

## 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

### Literature:

- 1 DIN 53316
- 2 LMBG 82.02-2:98
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- 9 P.L. Davies, Fr Z. Anal. Chem, 351, 513, (1988)
- 10 W.J. Conover, Practical; Nonparametric Statistics, J. Wiley&Sons, NY, p.302, (1971)
- 11 ISO 5725, (1986)
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- 14 G. Rohm, J. Bohnen & H. Kruessmann, GIT Labor-Fachzeitschrift, p 1080, 11, (1997)