Results of Proficiency Test
Disperse dyes in textile
March 2010

Organised by: Institute for Interlaboratory Studies
Spijkenisse, the Netherlands

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Report: iis10A04X

May 2010

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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 01/2008, 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 2010 interlaboratory study 54 laboratories in 12 different countries participated. See appendix 5 for the 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 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 #1021 (Violet fabric) and the textile sample #1022 (Brown fabric) were prepared from two different bulk materials by a third party laboratory. Each bulk sample, approximately 400 grams of material, was divided over 90 subsamples of 4 gram each. The samples were labelled and tested for homogeneity by a subcontracted laboratory. The homogeneity of the subsamples #1021 was checked by determination of Disperse Red 11 and Disperse Blue 3 and the homogeneity of the subsamples #1022 was checked by determination of Disperse Blue 26 in accordance with DIN54231:05 on 12-13 stratified random selected samples. See the following tables for the test results.

	Disperse Red 11 in mg/kg	Disperse Blue 3 in mg/kg
sample #1021-1	81.0	236.8
sample #1021-2	90.8	240.3
sample #1021-3	85.3	270.6
sample #1021-4	80.5	240.1
sample #1021-5	90.5	236.9
sample #1021-6	89.5	251.2
sample #1021-7	94.5	236.8
sample #1021-8	86.5	245.2
sample #1021-9	84.2	260.5
sample #1021-10	84.5	265.8
sample #1021-11	90.5	255.5
sample #1021-12	80.7	230.0

table 1: homogeneity test of subsamples #1021

	Disperse Blue 26 in mg/kg
sample #1022-1	100.5
sample #1022-2	94.5
sample #1022-3	105.6
sample #1022-4	100.1
sample #1022-5	99.6
sample #1022-6	99.8
sample #1022-7	94.9
sample #1022-8	99.5
sample #1022-9	109.7
sample #1022-10	105.8
sample #1022-11	100.9
sample #1022-12	101.1
sample #1022-13	95.5

table 2: homogeneity test of subsamples #1022

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 #1021 in mg/kg	Disp. Blue 3 #1021 in mg/kg	Disp. Blue 26 #1022 in mg/kg
r(calc)	12.9	36.6	12.4
Reference method	DIN54231:05	DIN54231:05	DIN54231:05
r(lit)	20.8	59.5	24.2

table 3: repeatabilities of subsamples #1022 and #1022

The repeatabilities of the results of homogeneity test for the determined allergenic dyestuffs were 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 #1021 and #1022 was sent to the participating laboratories on March 12, 2010.

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 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 ’i.i.s. 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 the results after the deadline and two participants did not report any test results.
Finally, 52 participants reported 150 numerical results. Observed were 10 outlying test results, which is 6.7% 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 anomal distribution was found for Disperse Blue 3 on sample #1021. In this case the statistical evaluation should be used with care. See also the discussion in chapter 5.

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 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 #1021: This material (violet fabric) was treated by a third party laboratory with allergenic dyestuffs in order to find the following banned disperse dyes: Disperse Blue 3 and Disperse Red 11. The results reported by the participants varied strongly (Disperse Blue 3 from 17.25 mg/kg – 427 mg/kg and Disperse Red 11 from 54.1 mg/kg – 7167 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. No other disperse dyes were reported to be present in sample #1021 (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 01/2008 of 50 mg/kg).

Textile #1022: This material (brown fabric) was treated by a third party laboratory with allergenic dyestuffs in order to find the banned disperse dye Disperse Blue 26. The results reported by the participants varied strongly from <20 mg/kg – 5174 mg/kg.
At least two laboratories (2265, 2266) would not have rejected this sample for containing too much Allergenic Dyestuffs (acc. to the limit of Öko-tex Std.100 edition 01/2008 of 50 mg/kg). All other laboratories would have rejected this sample. Several laboratories did not detect Disperse Blue 26, but reported ether the presence of Disperse Blue 35 (2 laboratories) or the presence of Disperse Brown 1 (2 laboratories), 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	46	51.6	73.1	41.4
Disperse Red 11	mg/kg	49	819.7	1180	656.8

table 4: reproducibilities of textile sample #1022

Parameter	unit	n	average	2.8 * sd	R (target)
Disperse Blue 26	mg/kg	41	630.4	958.4	505.2

table 5: reproducibility of textile sample #1022

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.

Parameter	March 2010	March 2009	March 2008	March 2007	April 2006
Disperse Blue 1	n.d.	n.d.	121%	n.d.	n.d.
Disperse Blue 3	142%	n.d.	n.e.	102%	n.d.
Disperse Blue 26	152%	150%	n.e.	133%	140%
Disperse Blue 35	n.d.	(235%)*	n.e.	n.d.	158%
Disperse Orange 3	n.d.	67%	98%	136%	150%
Disperse Red 1	n.d.	n.d.	176%	n.d.	n.d.
Disperse Red 11	144%	127%	n.e.	n.d.	157%
Disperse Yellow 9	n.d.	n.d.	86%	n.d.	n.d.
Disperse Yellow 49	n.d.	n.d.	n.e.	152%	n.d.

table 6: development of relative reproducibilities over the last five 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 #1021 and in sample #1022. 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 265 mg/kg, 763 mg/kg and 1277 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.

The purity of the calibrants is without doubt one of the major problems in the analysis of disperse dyes. For example, one laboratory that reported first 1400 mg/kg disperse Blue 3 in sample #1021 using as calibrant C12972013 from Dr. Ehrenstorfer (batch 90209, 0.1 g, dye content 50%), retested the sample and found only 106 mg/kg when using as calibrant 215652-50G from Sigma-Aldrich (batch 48596TH, dye content 20%).
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. Regretfully only very few laboratories reported the necessary details of the calibrants (see appendix 3).
For Disperse Blue 3 at least ten laboratories used a calibrant with a purity of 20% (Dr. Ehrenstorfer or Sigma-Aldrich). Although the data distribution of these ten results does not show to be bimodal, the spread of the results is not any smaller than the spread of all results. Similar is observed for Disperse Red 11 and Disperse Blue 26. Possibly the presence of the small number of results with known calibrant purities is making it difficult to find any effect of the calibrants used.

The spreads observed in this interlaboratory study are clearly not caused by just one critical point in the analysis. Almost all participants used test method DIN54231. However, the detection technique and the purity of the various calibration standards that were used vary strongly (see also reference 12). And the problematic calibration and identification of the various components obviously are effecting the test results significantly.

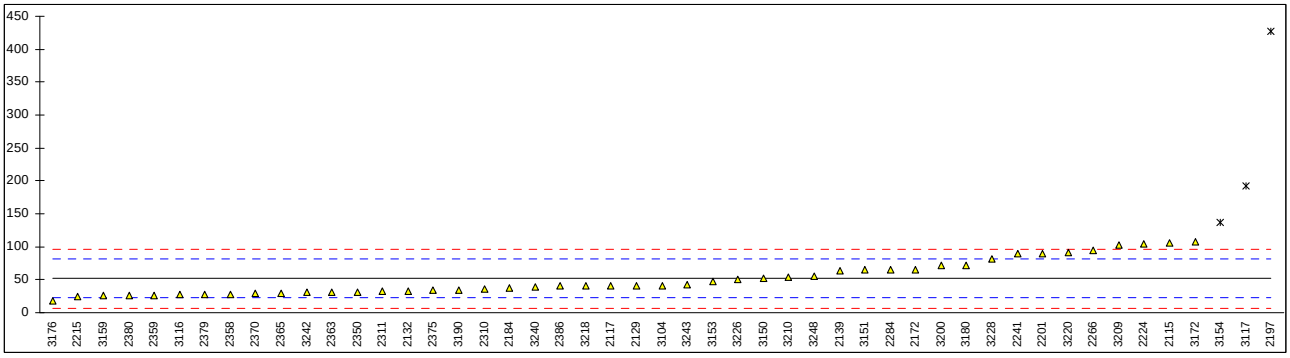
Each laboratory has to evaluate its performance in this study and make decisions about necessary corrective actions. Therefore, participation on a regular basis in this scheme could be helpful to improve the performance and the quality of the analytical results.

APPENDIX 1

Determination of Disperse Blue 3 (CASno. 2475-46-9) in sample #1021; results in mg/kg

lab	method	value	mark	z(targ)	remarks
2115	DIN54231	106.47	C	3.71	first reported 1400.73
2117	DIN54231	41		-0.72	
2121		-----		-----	
2129	DIN54231	41.25		-0.70	
2132	DIN54231	33		-1.26	
2139	DIN54231	63.4		0.80	
2172	DIN54231	65.3		0.93	
2184	DIN54231	37		-0.99	
2197	DIN54231	427	G(0.01)	25.41	
2201	DIN54231	90		2.60	
2215	in house	24.7		-1.82	
2224	in house	104		3.55	
2241	DIN54231	89		2.53	
2265	LFGB B 82.02-10	n.d.		-----	false negative?
2266	DIN54231	94.8		2.92	
2284	DIN54231	65.3	C	0.93	first reported 144.3
2310	DIN54231	36		-1.06	
2311	DIN54231	32.54		-1.29	
2350	DIN54231	31.1		-1.39	
2358	DIN54231	28		-1.60	
2359	DIN54231	26.8		-1.68	
2363	DIN54231	30.7		-1.42	
2365	DIN54231	30		-1.46	
2370	DIN54231	28.7		-1.55	
2375	DIN54231	34.3		-1.17	
2379	DIN54231	27.00		-1.67	
2380	DIN54231	25.545		-1.76	
2386	DIN54231	40		-0.79	
3104	DIN54231	41.31		-0.70	
3116	DIN54231	27	C	-1.67	first reported 21
3117	DIN54231	192	G(0.01)	9.50	
3150	DIN54231	52		0.03	
3151	DIN54231	65.25		0.92	
3153	DIN54231	47.2		-0.30	
3154	DIN54231	136.42	C,G(0.05)	5.74	first reported 123.20
3159	DIN54231	25.3		-1.78	
3172		107.1		3.76	
3174	DIN54231	<20		<-2.14	false negative?
3176		17.25	C	-2.33	first reported '---'
3180	DIN54231	72		1.38	
3185		-----		-----	
3190	DIN54231	35		-1.12	
3200	DIN54231	71.5		1.35	
3209	DIN54231	103		3.48	
3210	DIN54231	53.6		0.13	
3218	DIN54231	41		-0.72	
3220	DIN54231	91.3	C	2.69	first reported 'n.d.'
3226	DIN54231	50.32		-0.09	
3228	DIN54231	81		1.99	
3240	in house	39.9		-0.79	
3242	in house	30.4		-1.44	
3243	DIN54231	42		-0.65	
3248	DIN54231	55		0.23	
5012		-----		-----	

				Group 1:	Group 2:	Only Dr. Ehrenstorfer:
	normality	not OK		OK	OK	OK
	n	46		31	13	10
	outliers	3		0	0	0
	mean (n)	51.62		35.64	87.75	61.88
	st.dev. (n)	26.121		9.378	15.428	23.115
	R(calc.)	73.14		26.26	43.20	64.72
	R(DIN54231:05)	41.36		28.56	70.32	49.59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200
150
100
50
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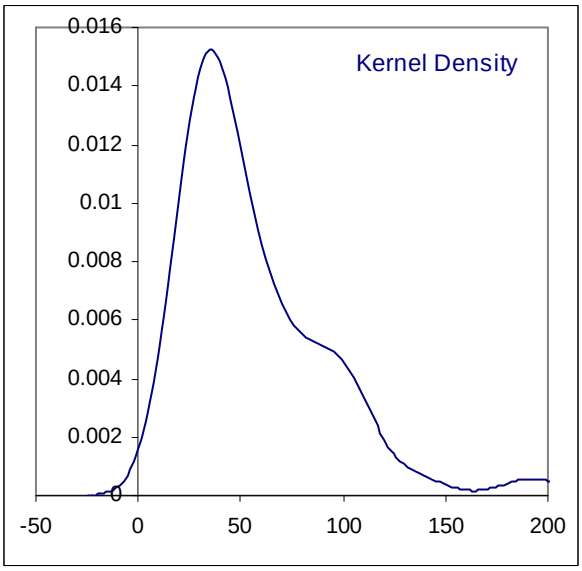
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0.014
0.012
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0.006
0.004
0.002
0
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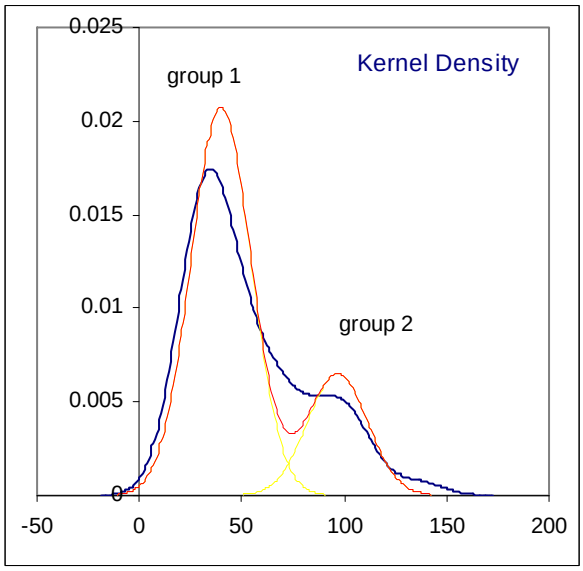
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group 2
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0.02
0.015
0.01
0.005
0
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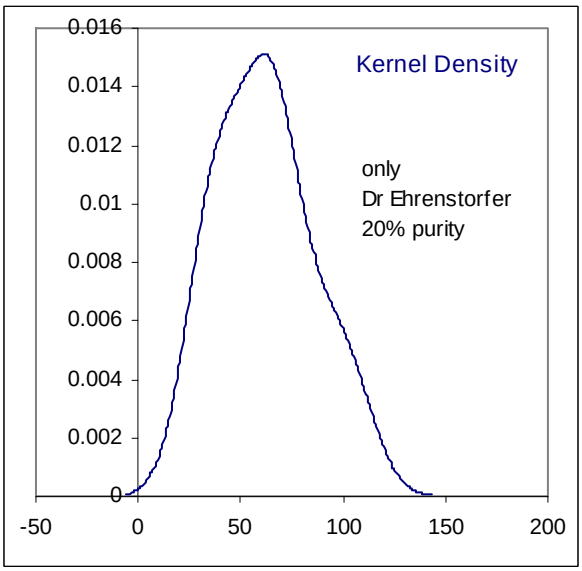
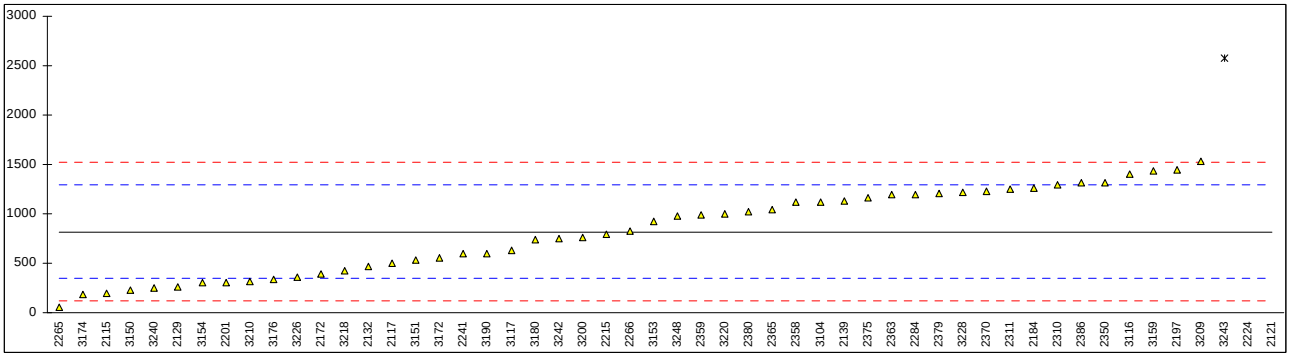
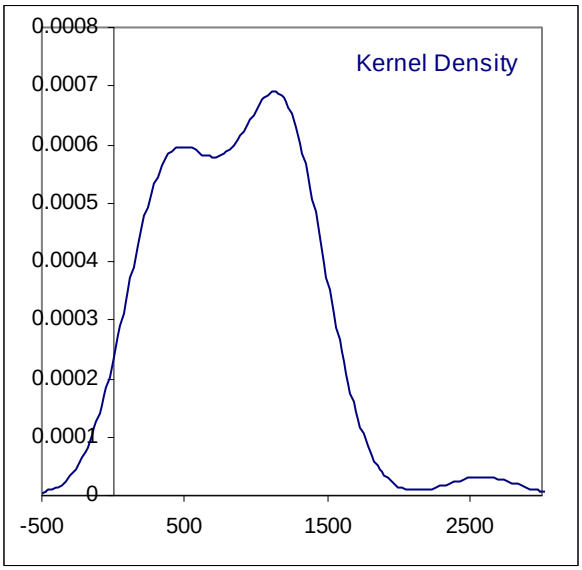

Kernel Density
only
Dr Ehrenstorfer
20% purity
0.016
0.014
0.012
0.01
0.008
0.006
0.004
0.002
0
-50 0 50 100 150 200

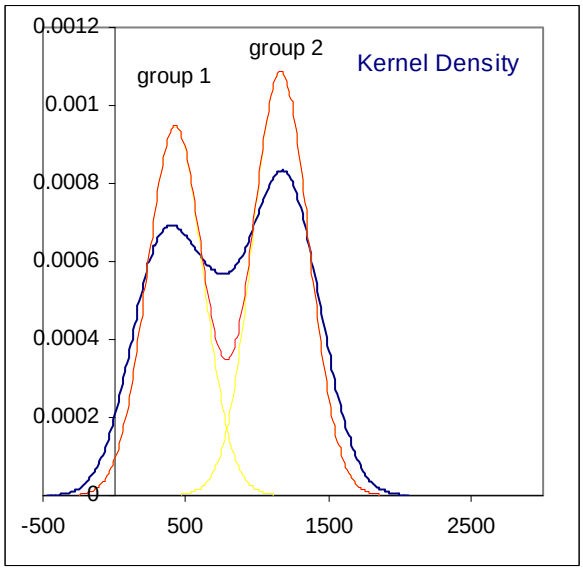
Determination of Disperse Red 11 (CASno. 2872-48-2) in sample #1021; results in mg/kg

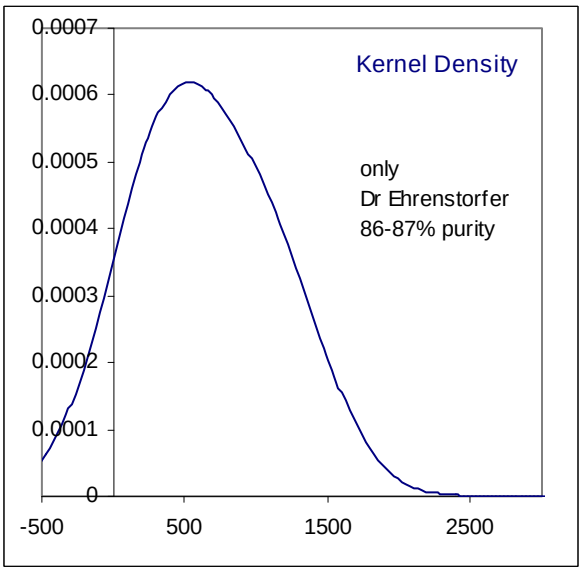
lab	method	value	mark	z(targ)	remarks
2115	DIN54231	191.74		-2.68	
2117	DIN54231	500		-1.36	
2121		7167	G(0.01)	27.06	
2129	DIN54231	259.88		-2.39	
2132	DIN54231	471		-1.49	
2139	DIN54231	1126.5		1.31	
2172	DIN54231	395		-1.81	
2184	DIN54231	1258		1.87	
2197	DIN54231	1445		2.67	
2201	DIN54231	306		-2.19	
2215	in house	795		-0.11	
2224	in house	5200	G(0.01)	18.67	
2241	DIN54231	593		-0.97	
2265	LFGB B 82.02-10	54.1		-3.26	
2266	DIN54231	823.5		0.02	
2284	DIN54231	1201.0		1.63	
2310	DIN54231	1294		2.02	
2311	DIN54231	1252		1.84	
2350	DIN54231	1320		2.13	
2358	DIN54231	1116		1.26	
2359	DIN54231	991.7		0.73	
2363	DIN54231	1194.8		1.60	
2365	DIN54231	1040		0.94	
2370	DIN54231	1230		1.75	
2375	DIN54231	1161		1.46	
2379	DIN54231	1206.64		1.65	
2380	DIN54231	1023.849		0.87	
2386	DIN54231	1320		2.13	
3104	DIN54231	1124		1.30	
3116	DIN54231	1400		2.47	
3117	DIN54231	630		-0.81	
3150	DIN54231	230		-2.51	
3151	DIN54231	537.4		-1.20	
3153	DIN54231	927		0.46	
3154	DIN54231	303.17		-2.20	
3159	DIN54231	1440		2.64	
3172		557.5		-1.12	
3174	DIN54231	188.22	C	-2.69	
3176		333.6		-2.07	
3180	DIN54231	736		-0.36	
3185		-----		-----	
3190	DIN54231	593		-0.97	
3200	DIN54231	764.7		-0.23	
3209	DIN54231	1533		3.04	
3210	DIN54231	310		-2.17	
3218	DIN54231	427		-1.67	
3220	DIN54231	998.69		0.76	
3226	DIN54231	360.78		-1.96	
3228	DIN54231	1216		1.69	
3240	in house	247.7		-2.44	
3242	in house	753.0		-0.28	
3243	DIN54231	2580	G(0.01)	7.50	
3248	DIN54231	983		0.70	
5012		-----		-----	

			Group 1:	Group 2:	Only Dr. Ehrenstorfer:
	normality	OK	OK	OK	OK
	n	49	23	26	8
	outliers	3	0	0	1
	mean (n)	819.66	423.60	1170.03	649.10
	st.dev. (n)	421.647	197.304	187.380	399.800
	R(calc.)	1180.61	552.45	524.66	1119.44
	R(DIN54231:05)	656.84	339.46	937.59	520.16


3000
2500
2000
1500
1000
500
0
2265 3174 2115 3150 3240 2129 3154 2201 3210 3176 3226 2172 3218 2132 2117 3151 3172 2241 3190 3117 3180 3242 3200 2215 2266 3153 3248 2359 3220 2380 2365 2358 3104 2139 2375 2363 2284 2379 3228 2370 2311 2184 2310 2386 2350 3116 3159 2197 3209 3243 2224 2121


Kernel Density
0.0008
0.0007
0.0006
0.0005
0.0004
0.0003
0.0002
0.0001
0
-500
500
1500
2500


group 2
group 1
Kernel Density
0.0012
0.001
0.0008
0.0006
0.0004
0.0002
0
-500
500
1500
2500

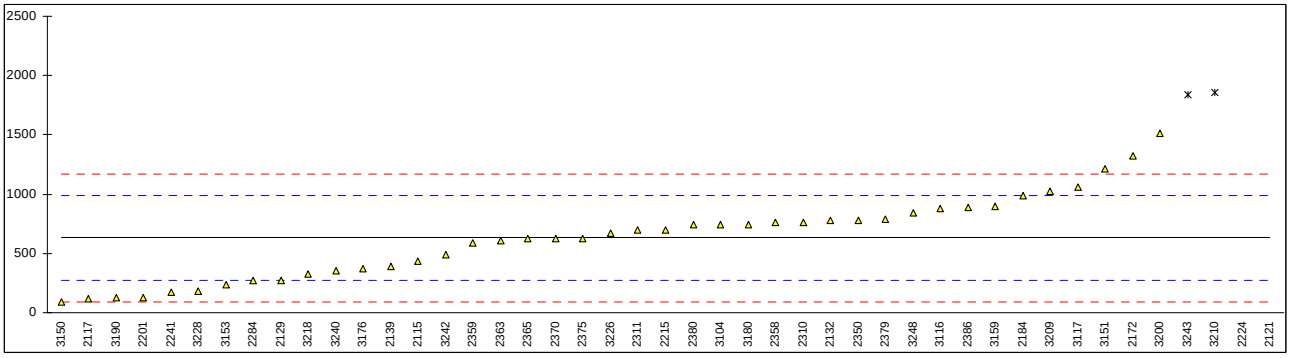

Kernel Density
only
Dr Ehrenstorfer
86-87% purity
0.0007
0.0006
0.0005
0.0004
0.0003
0.0002
0.0001
0
-500
500
1500
2500

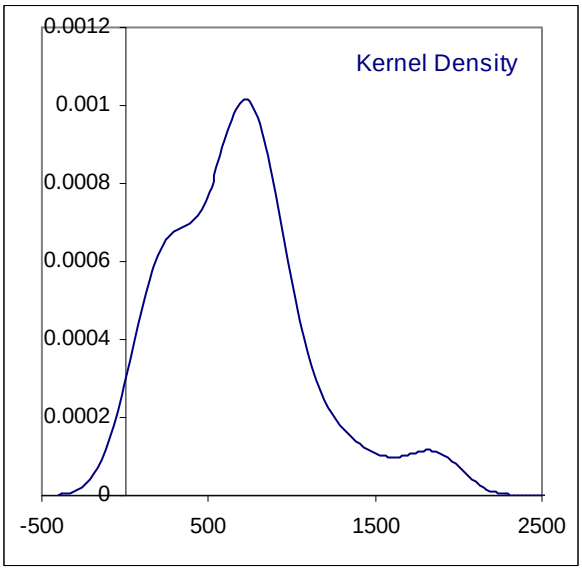
Determination of Disperse Blue 26 (CASno. 3860-63-7) in sample #1022; results in mg/kg

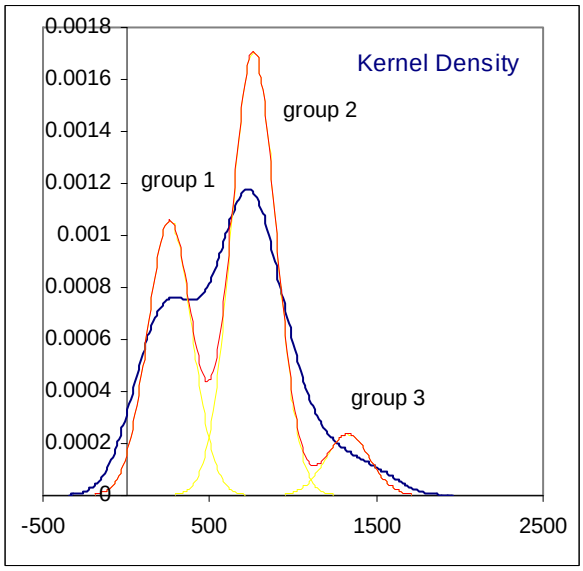
lab	method	value	mark	z(targ)	remarks
2115	DIN54231	436.49		-1.07	
2117	DIN54231	121		-2.82	
2121		5174	G(0.01)	25.18	
2129	DIN54231	275.7		-1.97	
2132	DIN54231	778		0.82	
2139	DIN54231	393.9		-1.31	
2172	DIN54231	1320		3.82	
2184	DIN54231	985		1.97	
2197		-----		-----	
2201	DIN54231	128		-2.78	
2215	in house	699		0.38	
2224	in house	4400	G(0.01)	20.89	
2241	DIN54231	172		-2.54	
2265		-----		-----	
2266	DIN54231	n.d.		-----	false negative?
2284	DIN54231	269.7		-2.00	
2310	DIN54231	764		0.74	
2311	DIN54231	698.40		0.38	
2350	DIN54231	780		0.83	
2358	DIN54231	758		0.71	
2359	DIN54231	590.8		-0.22	
2363	DIN54231	610.2		-0.11	
2365	DIN54231	621		-0.05	
2370	DIN54231	626		-0.02	
2375	DIN54231	628.2		-0.01	
2379	DIN54231	787.32		0.87	
2380	DIN54231	741.172		0.61	
2386	DIN54231	890		1.44	
3104	DIN54231	744		0.63	
3116	DIN54231	880		1.38	
3117	DIN54231	1057		2.36	
3150	DIN54231	95		-2.97	
3151	DIN54231	1214		3.23	
3153	DIN54231	239		-2.17	
3154	DIN54231	n.d.		-----	false negative?
3159	DIN54231	897		1.48	
3172		-----		-----	
3174	DIN54231	<20	C	<-3.38	false negative?
3176		373.35		-1.42	
3180	DIN54231	746		0.64	
3185		-----		-----	
3190	DIN54231	125		-2.80	
3200	DIN54231	1517.2		4.92	
3209	DIN54231	1020		2.16	
3210	DIN54231	1861	DG(0.05)	6.82	
3218	DIN54231	322		-1.71	
3220	DIN54231	n.d.		-----	false negative?
3226	DIN54231	669.86		0.22	
3228	DIN54231	183		-2.48	
3240	in house	355.4		-1.52	
3242	in house	490.5		-0.78	
3243	DIN54231	1840	DG(0.05)	6.70	
3248	DIN54231	844		1.18	
5012		-----		-----	

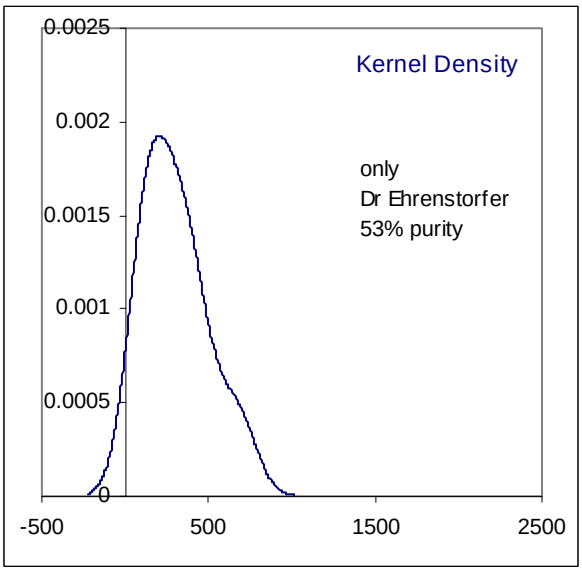
		Group 1:	Group 2:	Group 3:
normality	OK	OK	OK	n.a.
n	41	15	24	4
outliers	4	0	0	0
mean (n)	630.39	265.34	762.73	1277.05
st.dev. (n)	342.279	126.554	141.370	193.144
R(calc.)	958.38	354.35	395.84	540.80
R(DIN54231:05)	505.17	212.63	611.22	1023.34

	Only Dr. Ehrenstorfer calibrant (53% purity):
normality	OK
n	8
outliers	1
mean (n)	302.46
st.dev. (n)	191.965
R(calc.)	537.50
R(DIN54231:05)	242.38


2500
2000
1500
1000
500
0
3150 2117 3190 2201 2241 3228 3153 2284 2129 3218 3240 3176 2139 2115 3242 2359 2363 2365 2370 2375 3226 2311 2215 2380 3104 3180 2358 2310 2132 2350 2379 3248 3116 2386 3159 2184 3209 3117 3151 2172 3200 3243 3210 2224 2121


Kernel Density
0.0012
0.001
0.0008
0.0006
0.0004
0.0002
0
-500
500
1500
2500


Kernel Density
group 1
group 2
group 3
0.0018
0.0016
0.0014
0.0012
0.001
0.0008
0.0006
0.0004
0.0002
0
-500
500
1500
2500


Kernel Density
only
Dr Ehrenstorfer
53% purity
0.0025
0.002
0.0015
0.001
0.0005
0
-500
500
1500
2500

APPENDIX 2

Summary of all other reported Disperse dyes in samples #1022 and #1022; results in mg/kg

Lab	Other reported Dyes on #1022	Other reported Dyes on #1022
2115	-	-
2117	-	-
2121	-	-
2129	-	-
2132	-	-
2139	-	-
2172	-	-
2184	-	-
2197	-	70 mg/kg disperse blue 35
2201	-	-
2215	-	-
2224	-	-
2241	-	-
2265	-	23.7 mg/kg disperse brown 1
2266	-	-
2284	-	-
2310	-	-
2311	-	-
2350	-	-
2358	-	-
2359	-	-
2363	-	-
2365	-	-
2370	-	-
2375	-	-
2379	-	-
2380	-	-
2386	-	-
3104	-	-
3116	-	-
3117	-	-
3150	-	-
3151	-	-
3153	-	-
3154	-	318.73 mg/kg disperse blue 35
3159	-	-
3172	-	-
3174	-	-
3176	-	-
3180	-	-
3185	-	-
3190	-	-
3200	-	-
3209	-	-
3210	-	-
3218	-	-
3220	-	118.69 mg/kg disperse brown 1
3226	-	-
3228	-	-
3240	-	-
3242	-	-
3243	-	-
3248	-	-
5012	-	-

APPENDIX 3

Details of the calibration used

lab	calibrants used	int/ext.	corr. rec.
2115	Dr. Ehrenstorfer; purities: disp. red 11: 87%, disp. blue 3: 50%, disp. blue 26: 53%	ext	no
2117	Dr. Ehrenstorfer; purities: disp. red 11: 50%, disp. blue 3: 20%, disp. blue 26: 53%	ext	no
2121			
2129	Dr. Ehrenstorfer mixed standard 1, 5, 10 mg/L	ext	no
2132	Sigma-Aldrich; purities: disp. red 11: 30%, disp. blue 3: 20%, disp. blue 26: 33.3%	ext	no
2139	Dr. Ehrenstorfer; purities: disp. red 11: 86%, disp. blue 3: 20%, disp. blue 26: 53%	ext	no
2172	1, 3, 5 mg/L	ext	no
2184	---	ext	no
2197	10, 20, 30, 40, 50 mg/L	ext	no
2201	Dr. Ehrenstorfer; purities: disp. red 11: 87%, disp. blue 26: 53% & Aldrich; disp. blue 3: 20%	ext	no
2215	1, 3, 5 ppm	ext	yes
2224	Dr. Ehrenstorfer; purities: disp. red 11: 86%, disp. blue 3: 20%, disp. blue 26: 53%	ext	no
2241	0.3, 0.5, 1.0, 1.5, 2.0 mg/L	ext	no
2265	Dr. Ehrenstorfer & Sigma-Aldrich	ext	no
2266	n/a	ext	no
2284	purities: disp. red 11: 87%, disp. blue 3: 20%, disp. blue 26: 53%	ext	no
2310	0.1, 0.2, 0.5, 1.2 mg/L	ext	no
2311	0.4 mg/L – 10.0 mg/L	ext	no
2350	0.4, 0.5, 0.8, 1.0 mg/L	ext	yes
2358	0.4 - 1.0 mg/L	ext	no
2359	0.4, 0.5, 0.8, 1.0 mg/L	ext	no
2363	0.3, 0.5, 1.0, 1.5, 2.0 mg/L	ext	no
2365	0.4, 0.6, 0.8, 1.0, 1.5 mg/L	ext	no
2370	1, 3, 5, 7, 10 ug/ml	ext	no
2375	0.4 - 1 mg/L	ext	no
2379	1, 3, 5, 10, 20, 50 mg/L	ext	no
2380	external standard	ext	no
2386	---	ext	no
3104	Dr. Ehrenstorfer, Sigma-Aldrich & Aakash: 100, 200, 400, 600, 800 ug/L	ext	no
3116	---		
3117		ext	no
3150	in house, 10 + 100 mg/L	ext	no
3151	Sigma-Aldrich; purities: disp. red 11: 30%, disp. blue 3: 20% & Ludewig; disp. blue 26: 100%	ext	no
3153	0.8 - 70 ppm	ext	no
3154	Accustandard solutions DYE-009S, DYE-004S & DYE-018S	ext	no
3159	Dr. Ehrenstorfer: 1, 3, 5 mg/L	ext	no
3172			
3174	5 – 30 ug/ml	ext	no
3176			
3180	---	ext	no
3185			
3190	Dr. Ehrenstorfer; purities: disp. red 11: 86%, disp. blue 3: 20%, disp. blue 26: 53%	ext	no
3200	purities: disp. red 11: 87%, disp. blue 3: 20%, disp. blue 26: 53%	ext	no
3209	20ppm	ext	no
3210	---	ext	no
3218	0.1, 0.2, 0.4 ppm	ext	no
3220	Dr. Ehrenstorfer	ext	no
3226	Dr. Ehrenstorfer; purities: disp. red 11: 87%, disp. blue 3: 20%, disp. blue 26: 53.6%	int	no
3228	1.0, 2.0, 3.0 ug/ml	ext	no
3240	1, 2, 5, 7, 10 ppm; 5, 10, 20, 30, 50 ppm	ext	no
3242	5, 10, 15, 20, 25 ppm	ext	yes
3243	Accustandard solutions, 10 – 100 pm	std add	no
3248	Dr. Ehrenstorfer	ext	yes
5012			

APPENDIX 4

Details of the analysis used by the participants

lab	Intake	Extraction	procedure /other pre-treatment	detection/quantification
2115	0.5 g	7.5 ml methanol	ultrasonic 70°C 30 min , 0.45um PTFE filter	LC/MS
2117				HPLC-DAD/ LC-MS
2121				
2129	0.5 g	7.5 ml methanol	ultrasonic 70°C 30 min , 0.45um PTFE filter	LC/MS
2132	0.5 g	7.5 ml methanol	70°C 30 min , utrasonic	HPLC-DAD
2139	0.5 g	methanol	syringe filter	HPLC-UV
2172	0.5 g	methanol		HPLC-DAD/MS
2184				LC-DAD/MS
2197	0.5 g	7.5 ml methanol	ultrasonic 70°C 30 min, filtration	HPLC-MS
2201	0.5 g	7.5 ml methanol	70°C , 30 min ultrasonic , 0.45um PTFE membrane filter	HPLC-MS/MS
2215	0.5 g	7.5 ml methanol	30 min ultrasonic	HPLC-DAD/MS
2224	1.0 g	methanol	70°C ultrasonic	HPLC-DAD
2241	1.0 g	15 ml methanol	70/72°C , 30 min ultrasonic , 0.45um PTFE syringe filter	HPLC-MS
2265	1.0 g	10 ml methanol	ultrasonic	HPLC-DAD
2266		methanol		HPLC-DAD/LC-MS
2284	0.5 g	7.5 ml methanol	ultrasonic 70°C 30 min	HPLC/MS/UV
2310	1.0 g	15 ml methanol	70°C 30 min , ultrasonic	HPLC-DAD/MS
2311	1.0 g	15 ml methanol		LC-MS
2350	1.0 g	methanol	70°C 30 min ultrasonic 0.2 um PTFE syringe filter	LC/MS & HPLC/DAD/MS
2358	1.0 g			HPLC/DAD/MS
2359	1.0 g	methanol		LC/MS
2363	1.0 g	15 ml methanol	70-72°C 30 min ultrasonic , 0.45um PTFE syringe filter	HPLC-/MS
2365	1.0 g	15 ml methanol	30 min ultrasonic	HPLC/DAD/MS
2370	0.5 g	methanol	70°C 30 min ultrasonic	HPLC-/MS
2375	1.0 g	15 ml methanol	ultrasonic	HPLC/DAD
2379	0.5 g	methanol		HPLC-/MS & HPLC/UV
2380	1 g	15 ml	sonication , PTFE syringe filter	HPLC/DAD/MS
2386	1 g	15ml methanol		LC/MS
3104	0.5 g		ultrasonic	LC/MS/MS
3116				UPLC/DAD/MS
3117	0.5 g	7.5ml methanol	30 min ultrasonic , 0.45um PTFE membrane filter	HPLC-/MS
3150	0.5 g	7.5ml methanol	70°C 30 min , ultrasonic	LC/MS
3151	0.5 g	7.5ml methanol	70°C 30 min ultrasonic , 0.45um PTFE syringe filter	HPLC/UV/MS
3153	1 g	methanol	70°C 30 min ultrasonic	LC/MS/MS & HPLC/DAD
3154	1 g	methanol		HPLC/DAD/MS
3159	0.5 g	7.5ml methanol	70°C 30 min	UPLC/PDA/SQD
3172				
3174	0.5 g	5ml methanol	30 min sonicated , 0.45um PTFE syringe filter	LC/MS/MS
3176				
3180	0.5 g	7.5ml methanol		HPLC/DAD/MS
3185				
3190	0.5 g	7.5ml methanol	70/72°C , 30 min ultrasonic , 0.45um PTFE membrane filter	HPLC-/MS
3200	0.5 g	7.5ml methanol	70/72°C , 30 min ultrasonic , 0.45um PTFE membrane filter	HPLC/DAD
3209	0.5 g	7.5ml methanol	70°C , 30 min ultrasonic	LC/MS , HPLC/DAD
3210				HPLC/DAD
3218	0.5 g	methanol		LC/MS
3220	0.5 g	7.5ml methanol	30 min ultrasonic	LC/MS
3226	0.5 g	10ml methanol	70°C , 30 min ultrasonic , 0.45um PTFE filter	HPLC/DAD
3228	0.5 g	7.5ml methanol	70/72°C , 30 min ultrasonic ,	HPLC/DAD/MS
3240	1.0 g	10ml methanol	70°C , 30 min ultrasonic , 0.45um filter	HPLC/UV
3242	1 g	methanol		LC-MS/HPLC DAD
3243	0.5 g	7.5ml methanol		HPLC/DAD
3248	0.5 g	7.5ml methanol	ultrasonic	HPLC/UV/MS
5012				

APPENDIX 5

Number of participants in alphabetical country order

1 lab in	BANGLADESH
3 labs in	FRANCE
9 labs in	GERMANY
8 labs in	HONG KONG
4 labs in	INDIA
3 labs in	ITALY
2 labs in	KOREA
17 labs in	P.R. of CHINA
1 lab in	SWITZERLAND
1 lab in	TAIWAN R.O.C.
2 labs in	THAILAND
1 lab in	THE NETHERLANDS

APPENDIX 6

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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2 DIN 54231:2005
3 iis Interlaboratory Studies: Protocol for the Organisation, Statistics and Evaluation, January 2010
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9 M. Thompson and R. Wood, J. AOAC Int, 76, 926, (1993)
10 G. Rohm, J. Bohnen & H. Kruessmann, GIT Labor-Fachzeitschrift, p 1080, 11, (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