Results of Proficiency Test
Disperse dyes in textile
March 2015

Organised by: Institute for Interlaboratory Studies
Spijkenisse, the Netherlands

Author: ing. L. Dijkstra
Correctors: dr. R.G. Visser, ing. R.J. Starink & ing. C.M. Nijssen-Wester

Report: iis15A03

July 2015

CONTENTS

1 INTRODUCTION 3

2 SET UP 4

2.1 ACCREDITATION 4

2.2 PROTOCOL 4

2.3 CONFIDENTIALITY STATEMENT 4

2.4 SAMPLES 4

2.5 ANALYSES 6

3 RESULTS 6

3.1 STATISTICS 6

3.2 GRAPHICS 7

3.3 Z-SCORES 7

4 EVALUATION 8

4.1 EVALUATION PER SAMPLE 8

4.2 PERFORMANCE EVALUATION FOR THE GROUP OF LABORATORIES 9

5 DISCUSSION 10

Appendices:

1. Data and statistical results 11
2. Summary of all other reported disperse dyes 19
3. Summary of reported analytical details 20
4. Number of participants per country 22
5. Abbreviations and literature 23

1 INTRODUCTION

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

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

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

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

In this context and in response to requests from several laboratories, the Institute for Interlaboratory Studies (iis) organises a proficiency test for disperse dyes in textile in the annual proficiency test program since 2003.
In the 2015 interlaboratory study 85 laboratories in 23 different countries registered for participation. See appendix 4 for the number of participants per country. In this report the results of the 2015 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 textile samples, treated with banned disperse dyestuffs. The textile samples were prepared by two different third parties 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 ACCREDITATION

The Institute for Interlaboratory Studies in Spijkenisse, the Netherlands, is accredited in agreement with ISO/IEC 17043:2010 (R007), since January 2000, by the Dutch Accreditation Council (Raad voor Accreditatie). This PT falls under the accredited scope. This ensures strict adherence to protocols for sample preparation and statistical evaluation and 100% confidentially of participant's data. Feedback from the participants on the reported data is encouraged and customer's satisfaction is measured on regular basis by sending out questionnaires.

2.2 PROTOCOL

The protocol followed in the organisation was the one as described for proficiency testing in the report 'iis Interlaboratory Studies: Protocol for the Organisation, Statistics and Evaluation' of April 2014 (iis-protocol, version 3.3). This protocol can be downloaded via the FAQ page of the iis website http://www.iisnl.com.

2.3 CONFIDENTIALITY STATEMENT

All data presented in this report must be regarded as confidential and for use by the participating companies only. Disclosure of the information in this report is only allowed by means of the entire report. Use of the contents of this report for third parties is only allowed by written permission of the Institute for Interlaboratory Studies. Disclosure of the identity of one or more of the participating companies will be done only after receipt of a written agreement of the companies involved.

2.4 SAMPLES

Two different bulk materials, prepared by two different third parties, were used in this proficiency test. The first bulk sample, a polyester fabric dyed with two banned Allergenic dyes, was cut in small pieces and homogenized. From this batch, 100 subsamples were prepared of 3 gram each and labelled #15023.
The second bulk sample, a cotton fabric dyed with two other banned Allergenic dyes, was also cut in small pieces and homogenized. From this batch also 100 subsamples were prepared of 1.5 gram each.

The homogeneity of the subsamples #15023 was checked by determination of Disperse Red 17 in accordance with DIN54231:05 on 8 stratified randomly selected samples.
The homogeneity of the subsamples #15024 was checked by determination of Disperse Red 11 in accordance with DIN54231:05 on 8 stratified randomly selected samples.
See the following tables for the test results.

	Disperse Red 17 in mg/kg
sample #15023-1	98.3
sample #15023-2	96.1
sample #15023-3	93.2
sample #15023-4	101.4
sample #15023-5	103.1
sample #15023-6	107.5
sample #15023-7	105.1
sample #15023-8	108.2

table 1: homogeneity test of subsamples #15023

	Disperse Red 11 in mg/kg
sample #15024-1	26.7
sample #15024-2	28.7
sample #15024-3	29.7
sample #15024-4	26.6
sample #15024-5	26.7
sample #15024-6	30.1
sample #15024-7	29.8
sample #15024-8	27.1

table 2: homogeneity test of subsamples #15024

From the above test results, the repeatabilities were calculated and subsequently compared with the corresponding repeatabilities in agreement with the procedure of ISO 13528, Annex B2 in the next table:

	Disperse Red 17 #15023 in mg/kg	Disperse Red 11 #15024 in mg/kg
r(calc)	15.1	4.4
Reference method	DIN54231:05	DIN54231:05
r(reference)	27.1	7.5

table 3: repeatabilities of subsamples #15023 and #15024

The repeatabilities of the test results of the determined disperse dyes were both in good agreement with the repeatability that is mentioned in DIN54231:05. Therefore homogeneity of the subsamples was assumed.

To each of the participating laboratories, one sample #15023 and one sample #15024 were sent on March 4, 2015.

2.5 ANALYSES

The participants were asked to determine the concentrations of 20 forbidden allergenic dyes, 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 added.

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) 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 'iis Interlaboratory Studies: Protocol for the Organization, Statistics and Evaluation' of April 2014 (iis-protocol, version 3.3)
For the statistical evaluation the *unrounded* (when available) figures were used instead of the rounded results. Results reported as '<…' or '>…" were in general not used in the statistical evaluation.

First, the normality of the distribution of the various data sets per determination was checked by means of the Lilliefors-test a variant of the Kolmogorov-Smirnov test and by the calculation of skewness and kurtosis. Evaluation of the three normality indicators in combination with the visual evaluation of the graphic Kernel density plot, lead to judgement of the normality being either 'unknown', 'OK', 'suspect' or 'not OK'. After removal of outliers, this check was repeated. Not all data sets proved to have a normal distribution, in which cases the statistical evaluation of the results should be used with due care.

In accordance to ISO 5725 (1986 and 1994) the original results per determination were submitted subsequently to Dixon and Grubbs outlier tests. Outliers are marked by D(0.01) for the Dixon test, by G(0.01) or DG(0.01) for the Grubbs test and by R(0.01) for the Rosner General ESD test (see appendix 5, no.18). Stragglers are marked by D(0.05) for the Dixon test, by G(0.05) or DG(0.05) for the Grubbs test and by R(0.05) for the Rosner General ESD test. Both outliers and stragglers were not included in the calculations of the averages and the standard deviations.

For each assigned value, the uncertainty was determined in accordance with ISO13528. Subsequently the calculated uncertainty was evaluated against the respective requirement based on the target reproducibility in accordance with ISO13528. When the uncertainty passed the evaluation, no remarks are made in the report. However, when the uncertainty failed the evaluation it is mentioned in the report and it will have consequences for the evaluation of the test results.

Finally, the reproducibilities were calculated from the standard deviations by multiplying them with a factor of 2.8.

3.2 GRAPHICS

In order to visualise the data against the reproducibilities from literature, Gauss plots were made, using the sorted data for one determination (see appendix 1). On the Y-axis the reported analysis results are plotted. The corresponding laboratory numbers are on the X-axis. The straight horizontal line presents the consensus value (a trimmed mean). The four striped lines, parallel to the consensus value line, are the +3s, +2s, -2s and -3s target reproducibility limits of the selected 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 (see appendix 5; nos.16 and 17). Also a normal Gauss curve was projected over the Kernel Density Graph.

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.

When a laboratory did use a test method with a reproducibility that is significantly different from the reproducibility of the reference test method used in this report, it is strongly advised to recalculate the z-score, while using the reproducibility of the actual test method used, this in order to evaluate the fit-for-useness of the reported test result.

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, problems occurred with the delivery of the samples to the laboratories in Bangladesh, P.R. of China, Pakistan, Tunisia and Turkey. These laboratories received the samples late. Twenty-three participants reported test results after the deadline and two participants did not report any test results at all. Finally, 83 participants reported 275 numerical results. Observed were no less than 46 outlying test results, which is 16.7% (!) of the numerical results. In proficiency studies outlier percentages of 3% - 7.5% are quite normal.

Not all original data sets proved to have a normal Gaussian distribution. These are referred to as “not OK” or “suspect”. The statistical evaluation of these data sets should be used with due care, see also paragraph 3.1.

4.1 EVALUATION PER SAMPLE

In this section the results are discussed per sample. All test results reported on the textile samples are summarised in appendix 1. As in previous PTs almost all participants reported to have used DIN54231 as test method, only a small number of test details were requested to be reported (see appendix 3).
In DIN54231 no reproducibility is mentioned. Only the standard deviation for the repeatability is mentioned. Therefore, the target reproducibility was estimated as follows: the repeatability 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 #15023: This polyester was dyed by a third party with the banned dyes: Disperse Orange 1 and Disperse red 17. The results reported by the participating laboratories vary strongly (from 73.65 mg/kg – 1398 mg/kg for Disperse Orange 1 and from 35.8 mg/kg – 981 mg/kg for Disperse Red 17).
For Disperse Orange 1, nine statistical outliers were observed and the calculated reproducibility after rejection of the statistical outliers is not in agreement with the estimated reproducibility of DIN54231:05.
For Disperse Red 17, eleven statistical outliers were observed. The calculated reproducibility after rejection of the statistical outliers is not in 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 01/2015 of 50 mg/kg).

Textile #15024: This fabric was dyed by a third party with the banned dye: Disperse Blue 35 and Disperse Red 11. The results reported by the participating laboratories vary strongly (from 2.1 mg/kg – 129 mg/kg for Disperse Blue 35 and from 4.3 mg/kg – 437 mg/kg for Disperse Red 11).
For Disperse Blue 35, six statistical outliers were observed. The calculated reproducibility after rejection of the statistical outliers is not in agreement with the estimated reproducibility of DIN54231:05.
For Disperse Red 11, twenty statistical outliers were observed. The calculated reproducibility after rejection of the statistical outliers is not in agreement with the estimated reproducibility of DIN54231:05.
Laboratory 2386 reported the presence of Disperse Red 1 in sample #15024. Possibly the peak of Disperse Red 11 was misidentified by this laboratory (as laboratory 2272 did initially).
At least 29 laboratories would not have rejected this sample for containing too much Allergenic Dyestuffs (acc. to the limit of Öko-tex Std.100 edition 01/2012 of 50 mg/kg). All other laboratories would have rejected this sample.

4.2 PERFORMANCE EVALUATION FOR THE GROUP OF LABORATORIES

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

Parameter	unit	n	average	2.8 * sd	R (target)
Disperse Orange 1	mg/kg	71	226	266	181
Disperse Red 17	mg/kg	70	120	112	96

table 4: reproducibilities for sample #15023

Parameter	unit	n	average	2.8 * sd	R (target)
Disperse Blue 35	mg/kg	29	24	21	19
Disperse Red 11	mg/kg	59	29	33	23

table 5: reproducibilities for sample #15024

Without further statistical calculations it can be concluded that for the evaluated allergenic dyestuffs the group of participating laboratories may have difficulties with the analysis of Disperse Orange 1 and Disperse Red 11. See also the discussion in paragraphs 4.1 and 5.

5 DISCUSSION

The uncertainties in the test results of the evaluated Disperse dyes in the iis15A03 PT are listed in the next table and are comparable with previous proficiency tests.

	March 2015	March 2014	March 2013	March 2012	March 2011	2010 – 2006	target DIN54321
Disperse Blue 1	n.e.	n.e.	n.e.	n.e.	n.e.	43%	27%
Disperse Blue 3	n.e.	n.e.	56%	42%	51%	36 - 51%	27%
Disperse Blue 26	n.e.	n.e.	n.e.	68%	n.e.	47 - 56%	27%
Disperse Blue 35	31%	n.e.	n.e.	n.e.	n.e.	57 - 84%	27%
Disperse Blue 106	n.e.	28%	n.e.	n.e.	n.e.	n.e.	27%
Disperse Brown 1	n.e.	33%	n.e.	n.e.	n.e.	n.e.	27%
Disperse Orange 1	42%	n.e.	47%	n.e.	44%	n.e.	27%
Disperse Orange 3	n.e	31%	n.e.	n.e.	n.e.	24 – 54%	27%
Disperse Red 1	n.e.	n.e.	n.e.	n.e.	36%	63%	27%
Disperse Red 11	41%	n.e.	n.e.	65%	n.e.	45 - 56%	27%
Disperse Red 17	33%	n.e.	n.e.	n.e.	n.e.	n.e.	27%
Disperse Yellow 3	n.e.	n.e.	29%	n.e.	28%	n.e.	27%
Disperse Yellow 9	n.e.	n.e.	n.e.	n.e.	n.e.	31%	27%
Disperse Yellow 49	n.e.	n.e.	n.e.	n.e.	n.e.	54%	27%

table 6: development of uncertainties over the last years

From the above table it is clear that for all four Disperse dyes investigated in this PT, a quality improvement is observed. But all uncertainties are still above the target uncertainty of 27%, estimated from DIN 54231. All participants detected the added dyestuffs in both sample #15023 and sample #15024. However, a number of laboratories had difficulties to detect Disperse Blue 35, see also PT iis09A04.
From the details, it is clear that almost all participants used Methanol as extraction solvent. There is also little variation in temperature (except for two participants) and extraction time (except four participants) used: 70°C and 30 minutes. As intake 68 participants used 0.5 gram and 13 participants used 1.0 gram.
It is striking that all Kernel Density plots are quite similar. All plots show a heavy tail at the higher end. In these high end tails, 99% of all statistical outliers are present. A possible explanation for this phenomenon may be found in the calibration. DIN54231 prescribes a calibration at 6 concentrations, from 5 mg/l up to 50 mg/l methanol. When a laboratory prepares a stock solution of 500 mg/l for this purpose, it may encounter some difficulties with the dissolution of some of the dye(s) in methanol. Heating and sonication help to dissolve the dye(s). However, when the stock solution is kept at 4°C, something that a lab may do as standard procedure, part of the dye(s) may precipitate. This may be unnoticed due to the dark colour of the solution. The consequences of this may be lower actual concentrations of the calibration solutions and higher test results during the analysis of a sample. Skipping the cooling step at 4°C and direct dilution of the stock solution to the required calibration solution may prevent precipitation of the dyes and will result in reliable test results.

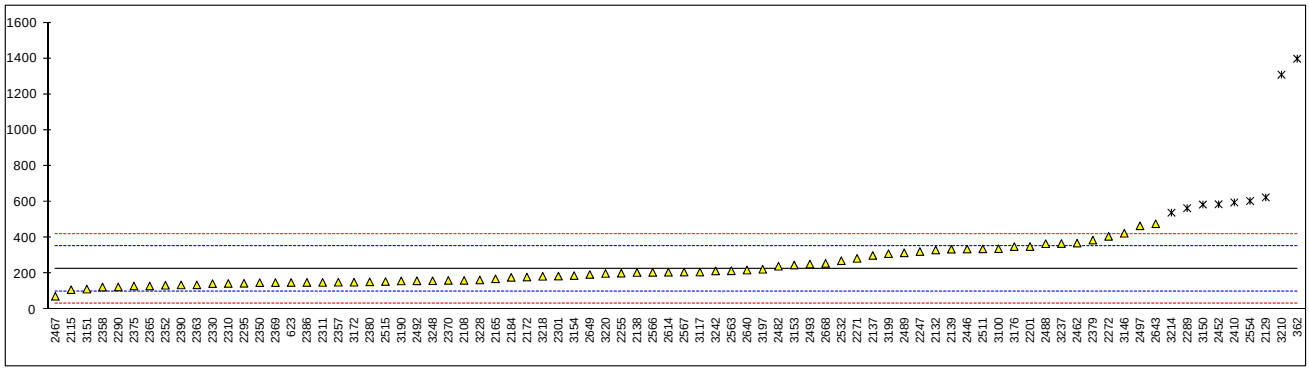
APPENDIX 1

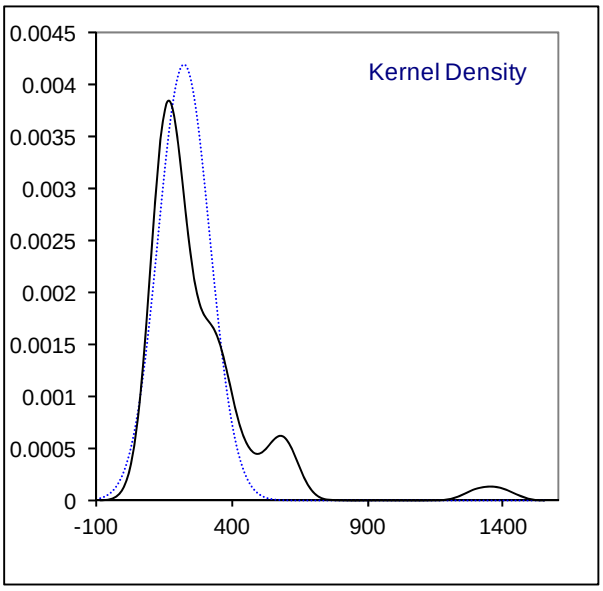
Determination of Disperse Orange 1 (CASno.2581-69-3) in sample #15023; results in mg/kg

lab	method	value	mark	z(targ)	remarks
213		-----		-----	
362	in house	1398	R(0.01)	18.11	
551		-----		-----	
623	DIN54231	150.6		-1.17	
2108	DIN54231	162.3		-0.99	
2115	DIN54231	110.48	C	-1.79	first reported: 1723.0
2129	in house	624.95	C,R(0.01)	6.16	first reported: 848.34
2132	DIN54231	332.1		1.64	
2137	DIN54231	301.3		1.16	
2138	DIN54231	206.39		-0.30	
2139	DIN54231	336		1.70	
2165	DIN54231	171		-0.85	
2172	DIN54231	181		-0.70	
2184	DIN54231	179		-0.73	
2201	DIN54231	350.8		1.93	
2247	DIN54231	323		1.50	
2255	DIN54231	202.5		-0.36	
2271	DIN54231	285		0.91	
2272	DIN54231	407.9		2.81	
2289	DIN54231	564.8	R(0.01)	5.24	
2290	DIN54231	125.4		-1.56	
2295	DIN54231	146		-1.24	
2301	DIN54231	186.12		-0.62	
2310	DIN54231	145		-1.25	
2311	DIN54231	151		-1.16	
2330	DIN54231	144.18		-1.27	
2350	DIN54231	149.6		-1.18	
2352	DIN54231	135		-1.41	
2357	DIN54231	152.0		-1.14	
2358	DIN54231	125.00		-1.56	
2363	DIN54231	137		-1.38	
2365	DIN54231	131		-1.47	
2369	DIN54231	150		-1.18	
2370	DIN54231	162		-0.99	
2375	DIN54231	131		-1.47	
2379	DIN54231	386.7535		2.48	
2380	DIN54231	154.1		-1.11	
2386	DIN54231	150.9		-1.16	
2390	DIN54231	136.83		-1.38	
2410	DIN54231	597	R(0.01)	5.73	
2446	64B82.02.10	337.25		1.72	
2452	DIN54231	586.502	R(0.01)	5.57	
2462	DIN54231	370		2.22	
2467	DIN54231	73.6524		-2.36	
2482	DIN54231	241.278		0.23	
2488	DIN54231	367.10		2.18	
2489	DIN54231	316.0		1.39	
2492	in house	159.8		-1.02	
2493	DIN54231	253		0.42	
2497	ISO13373	466.35		3.71	
2511	DIN54231	337.8		1.73	
2515	DIN54231	155.79		-1.09	
2532	DIN54231	272		0.71	
2554	DIN54231	605	R(0.01)	5.86	
2563	DIN54231	216	C	-0.16	first reported: 21.6
2566	DIN54231	207		-0.29	
2567	DIN54231	208.50		-0.27	
2580		-----		-----	
2602		-----	W	-----	withdrawn, first reported: 685.3
2604		-----		-----	
2614	CPSD-AN-00048	208		-0.28	
2640	DIN54231	219.741		-0.10	
2643	DIN54231	478		3.89	
2649	DIN54231	195		-0.48	
2668	DIN54231	257.1		0.48	
3100	DIN54231	339		1.75	
3117	DIN54231	208.7		-0.27	
3146	DIN54231	425		3.07	
3150	DIN54231	585	R(0.01)	5.55	
3151	DIN54231	113.6		-1.74	
3153	DIN54231	248		0.34	
3154	DIN54231	188.98		-0.57	

3172	DIN54231	152		-1.14
3176	DIN54231	350.7		1.93
3190	DIN54231	159		-1.04
3197	DIN54231	224.2		-0.03
3199	in house	310.94		1.31
3210	DIN54231	1309	R(0.01)	16.74
3214	DIN54231	539.7	R(0.01)	4.85
3218	DIN54231	185		-0.63
3220	DIN54231	201.0		-0.39
3228	DIN54231	165		-0.94
3237	DIN54231	367.6694		2.19
3242	DIN54231	215		-0.17
3248	DIN54231	160		-1.02

normality	OK
n	71
outliers	9
mean (n)	226.076
st.dev. (n)	95.1023
R(calc.)	266.287
R(DIN54231:05)	181.168



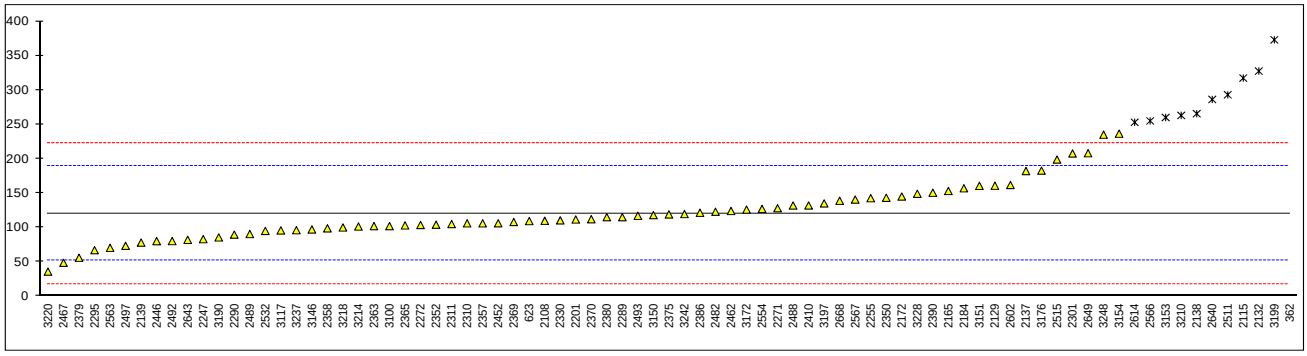


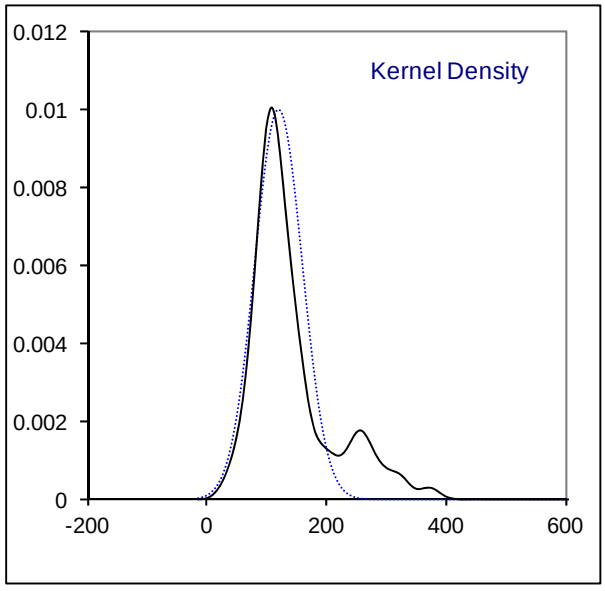
Determination of Disperse Red 17 (CASno.3179-89-3) in sample #15023; results in mg/kg

lab	method	value	mark	z(targ)	remarks
213		-----		-----	
362	in house	981	R(0.01)	25.04	
551		-----		-----	
623	DIN54231	109.3		-0.31	
2108	DIN54231	109.7		-0.30	
2115	DIN54231	317.4	R(0.05)	5.74	
2129	in house	160.74		1.18	
2132	DIN54231	327.5	R(0.05)	6.03	
2137	DIN54231	182.1		1.80	
2138	DIN54231	265.52	R(0.05)	4.23	
2139	DIN54231	78		-1.22	
2165	DIN54231	153		0.96	
2172	DIN54231	145		0.72	
2184	DIN54231	157		1.07	
2201	DIN54231	111.6		-0.25	
2247	DIN54231	83		-1.08	
2255	DIN54231	142.6		0.65	
2271	DIN54231	128		0.23	
2272	DIN54231	103.6		-0.48	
2289	DIN54231	115		-0.15	
2290	DIN54231	89.6		-0.89	
2295	DIN54231	67		-1.54	
2301	DIN54231	207.64		2.55	
2310	DIN54231	106		-0.41	
2311	DIN54231	105		-0.44	
2330	DIN54231	110.30		-0.29	
2350	DIN54231	143.2		0.67	
2352	DIN54231	104		-0.47	
2357	DIN54231	106.0		-0.41	
2358	DIN54231	98.74		-0.62	
2363	DIN54231	102		-0.53	
2365	DIN54231	103		-0.50	
2369	DIN54231	108		-0.35	
2370	DIN54231	112		-0.24	
2375	DIN54231	119		-0.03	
2379	DIN54231	55.9079		-1.87	
2380	DIN54231	115.0		-0.15	
2386	DIN54231	121.4		0.04	
2390	DIN54231	150.51		0.88	
2410	DIN54231	132		0.35	
2446	64B82.02.10	80.10		-1.16	
2452	DIN54231	106.123		-0.41	
2462	DIN54231	124		0.11	
2467	DIN54231	48.6378		-2.08	
2482	DIN54231	122.906		0.08	
2488	DIN54231	131.96		0.34	
2489	DIN54231	90.4		-0.86	
2492	in house	80.2		-1.16	
2493	DIN54231	117		-0.09	
2497	ISO13373	73.30		-1.36	
2511	DIN54231	293.0	R(0.05)	5.03	
2515	DIN54231	198.81		2.29	
2532	DIN54231	95		-0.73	
2554	DIN54231	127		0.20	
2563	DIN54231	70.35	C	-1.45	first reported:7.04
2566	DIN54231	255	R(0.05)	3.92	
2567	DIN54231	140.61		0.60	
2580		-----		-----	
2602	DIN54231	161.8		1.21	
2604		-----		-----	
2614	CPSD-AN-00048	253	R(0.05)	3.87	
2640	DIN54231	286.2505	R(0.05)	4.83	
2643	DIN54231	82		-1.11	
2649	DIN54231	208		2.56	
2668	DIN54231	138.8		0.54	
3100	DIN54231	102		-0.53	
3117	DIN54231	95.7		-0.71	
3146	DIN54231	97.1		-0.67	
3150	DIN54231	118		-0.06	
3151	DIN54231	160.5		1.18	
3153	DIN54231	260	R(0.05)	4.07	
3154	DIN54231	236.46		3.38	
3172	DIN54231	126		0.17	

3176	DIN54231	182.7		1.82
3190	DIN54231	85.5		-1.01
3197	DIN54231	135.0		0.43
3199	in house	373.025	R(0.05)	7.36
3210	DIN54231	263	R(0.05)	4.16
3214	DIN54231	101.4		-0.54
3218	DIN54231	100		-0.58
3220	DIN54231	35.8		-2.45
3228	DIN54231	149		0.84
3237	DIN54231	96.0025		-0.70
3242	DIN54231	119.5		-0.02
3248	DIN54231	235		3.34

normality	suspect
n	70
outliers	11
mean (n)	120.109
st.dev. (n)	39.8473
R(calc.)	111.572
R(DIN54231:05)	96.250



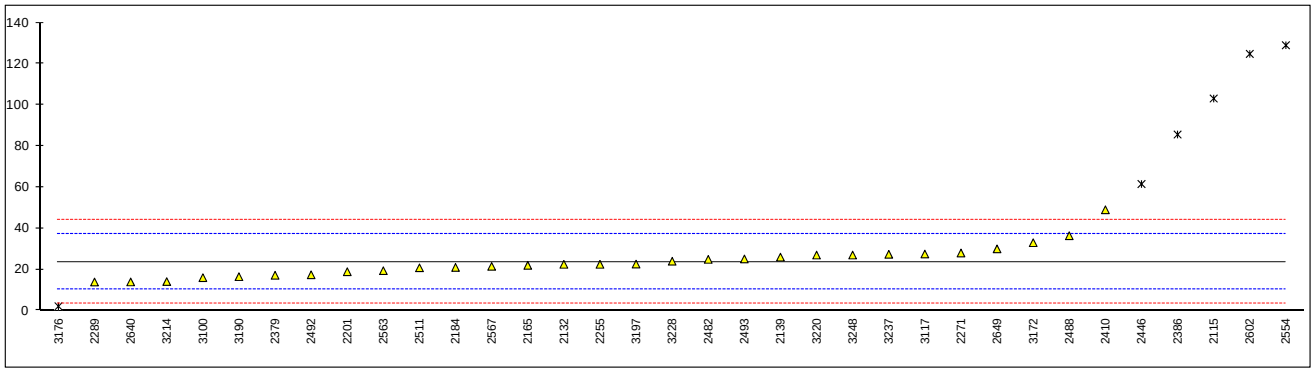


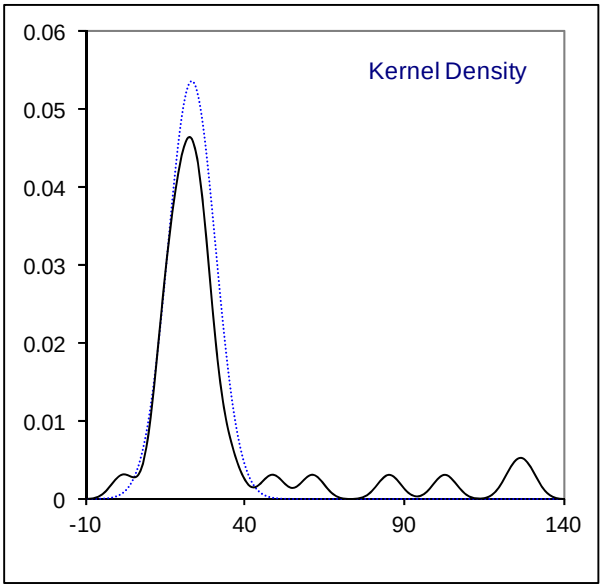
Determination of Disperse Blue 35 (CASno.12222-75-2) in sample #15024; results in mg/kg

lab	method	value	mark	z(targ)	remarks
213		-----		-----	
362	in house	<15.0		-----	
551		-----		-----	
623	DIN54231	n.d.		-----	
2108	DIN54231	n.d.		-----	
2115	DIN54231	103.1	R(0.01)	11.75	
2129		-----		-----	
2132	DIN54231	22.5		-0.17	
2137	DIN54231	<5		<-2.75	false negative test result?
2138		-----		-----	
2139	DIN54231	26		0.35	
2165	DIN54231	22		-0.24	
2172	DIN54231	n.d.		-----	
2184	DIN54231	21		-0.39	
2201	DIN54231	18.9		-0.70	
2247	DIN54231	n.d.		-----	
2255	DIN54231	22.5		-0.17	
2271	DIN54231	28		0.64	
2272		-----		-----	
2289	DIN54231	13.9		-1.44	
2290	DIN54231	<15		-----	
2295		-----		-----	
2301		-----		-----	
2310	DIN54231	n.d.		-----	
2311	DIN54231	n.d.		-----	
2330	DIN54231	n.d.		-----	
2350		-----		-----	
2352	DIN54231	n.d.		-----	
2357	DIN54231	n.d.		-----	
2358	DIN54231	n.d.		-----	
2363	DIN54231	<15		-----	
2365	DIN54231	<15		-----	
2369	DIN54231	n.d.		-----	
2370	DIN54231	n.d.		-----	
2375		-----		-----	
2379	DIN54231	17.1760		-0.96	
2380	DIN54231	n.d.		-----	
2386	DIN54231	85.6	R(0.01)	9.16	
2390		-----		-----	
2410	DIN54231	49		3.75	
2446	64B82.02.10	61.53	R(0.01)	5.60	
2452		-----		-----	
2462	DIN54231	n.d.		-----	
2467	DIN54231	n.d.		-----	
2482	DIN54231	24.904		0.19	
2488	DIN54231	36.41		1.89	
2489		-----		-----	
2492	in house	17.4		-0.92	
2493	DIN54231	25.1		0.22	
2497		-----		-----	
2511	DIN54231	20.8		-0.42	
2515	DIN54231	<15		-----	
2532	DIN54231	n.d.		-----	
2554	DIN54231	129	R(0.01)	15.57	
2563	DIN54231	19.39	C	-0.63	first reported: 1.94
2566	DIN54231	n.d.		-----	
2567	DIN54231	21.5		-0.32	
2580		-----		-----	
2602	DIN54231	124.8	R(0.01)	14.95	
2604	64LFGB82.02.10	n.d.		-----	
2614		-----		-----	
2640	DIN54231	13.9433		-1.43	
2643	DIN54231	n.d.		-----	
2649	DIN54231	30		0.94	
2668	DIN54231	n.d.		-----	
3100	DIN54231	16		-1.13	
3117	DIN54231	27.5		0.57	
3146	DIN54231	<20	C	-----	first reported: n.d
3150		-----		-----	
3151		-----		-----	
3153	DIN54231	<20		-----	
3154		-----		-----	
3172	DIN54231	33		1.38	

3176	DIN54231	2.1	R(0.05)	-3.18
3190	DIN54231	16.5		-1.06
3197	DIN54231	22.6		-0.15
3199	in house	<15		-----
3210		-----		-----
3214	DIN54231	14.1		-1.41
3218		-----		-----
3220	DIN54231	27.0		0.50
3228	DIN54231	24		0.05
3237	DIN54231	27.3596		0.55
3242	DIN54231	n.d.		-----
3248	DIN54231	27		0.50

normality	OK
n	29
outliers	6
mean (n)	23.637
st.dev. (n)	7.4414
R(calc.)	20.836
R(DIN54231:05)	18.942



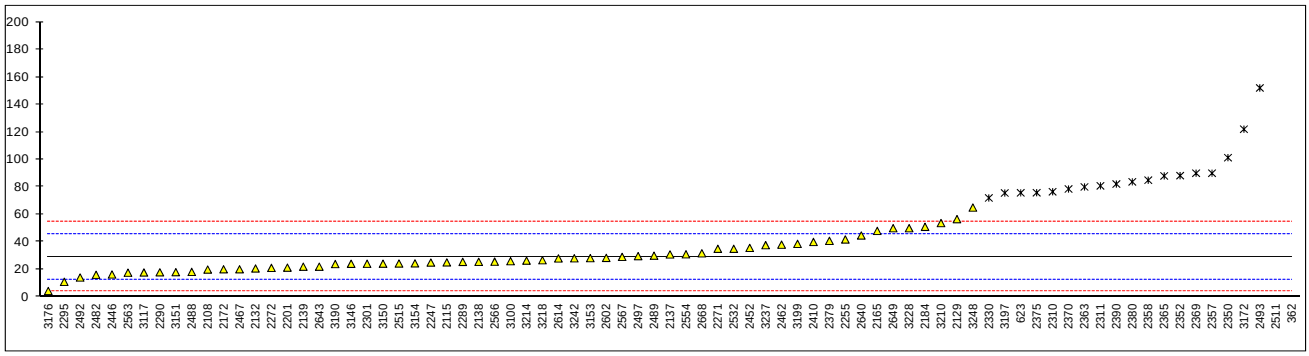


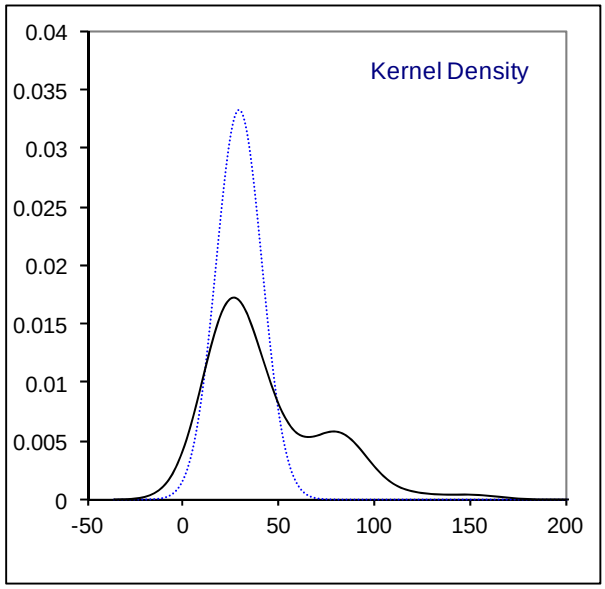
Determination of Disperse Red 11 (CASno.2872-48-2) in sample #15024; results in mg/kg

lab	method	value	mark	z(targ)	remarks
213		-----		-----	
362	in house	437	R(0.01)	48.70	
551		-----		-----	
623	DIN54231	75.7	R(0.01)	5.55	
2108	DIN54231	19.9		-1.12	
2115	DIN54231	25.1		-0.50	
2129	in house	56.59		3.26	
2132	DIN54231	20.7	C	-1.02	first reported: 258.4
2137	DIN54231	30.9		0.20	
2138	DIN54231	25.52		-0.45	
2139	DIN54231	22		-0.87	
2165	DIN54231	48		2.24	
2172	DIN54231	20.1		-1.09	
2184	DIN54231	51		2.60	
2201	DIN54231	21.3		-0.95	
2247	DIN54231	25		-0.51	
2255	DIN54231	41.8		1.50	
2271	DIN54231	35		0.69	
2272	DIN54231	21.1	C	-0.97	first reported under disperse red 1
2289	DIN54231	25.5		-0.45	
2290	DIN54231	17.9		-1.36	
2295	DIN54231	11		-2.18	
2301	DIN54231	24.13		-0.61	
2310	DIN54231	76.5	R(0.01)	5.64	
2311	DIN54231	80.8	R(0.01)	6.16	
2330	DIN54231	72.00	R(0.01)	5.11	
2350	DIN54231	101.3	R(0.01)	8.60	
2352	DIN54231	88.2	R(0.01)	7.04	
2357	DIN54231	90.0	R(0.01)	7.26	
2358	DIN54231	84.92	R(0.01)	6.65	
2363	DIN54231	80	R(0.01)	6.06	
2365	DIN54231	88	R(0.01)	7.02	
2369	DIN54231	90	R(0.01)	7.26	
2370	DIN54231	78.5	R(0.01)	5.88	
2375	DIN54231	75.8	R(0.01)	5.56	
2379	DIN54231	40.7968		1.38	
2380	DIN54231	83.7	R(0.01)	6.50	
2386	DIN54231	<15		-----	
2390	DIN54231	82.10	R(0.01)	6.31	
2410	DIN54231	40		1.28	
2446	64B82.02.10	16.31		-1.55	
2452	DIN54231	35.646		0.76	
2462	DIN54231	38		1.04	
2467	DIN54231	20.1193		-1.09	
2482	DIN54231	16.079		-1.57	
2488	DIN54231	18.19		-1.32	
2489	DIN54231	30.0		0.09	
2492	in house	14.1		-1.81	
2493	DIN54231	152	R(0.01)	14.66	
2497	ISO13373	29.68		0.05	
2511	DIN54231	277.7	R(0.01)	29.67	
2515	DIN54231	24.29		-0.59	
2532	DIN54231	35		0.69	
2554	DIN54231	31		0.21	
2563	DIN54231	17.61	C	-1.39	first reported: 1.76
2566	DIN54231	25.65		-0.43	
2567	DIN54231	29.12		-0.02	
2580		-----		-----	
2602	DIN54231	28.4		-0.10	
2604		-----		-----	
2614	CPSD-AN-00048	28		-0.15	
2640	DIN54231	44.699		1.84	
2643	DIN54231	22		-0.87	
2649	DIN54231	50		2.48	
2668	DIN54231	31.72		0.29	
3100	DIN54231	26		-0.39	
3117	DIN54231	17.8		-1.37	
3146	DIN54231	24.1		-0.62	
3150	DIN54231	24.2	C	-0.60	first reported:242
3151	DIN54231	18.0		-1.34	
3153	DIN54231	28.2		-0.13	
3154	DIN54231	24.43		-0.58	
3172	DIN54231	122	R(0.01)	11.08	

3176	DIN54231	4.3		-2.98
3190	DIN54231	23.9		-0.64
3197	DIN54231	75.6	R(0.01)	5.54
3199	in house	38.5973		1.12
3210	DIN54231	53.7		2.92
3214	DIN54231	26.4		-0.34
3218	DIN54231	26.7		-0.31
3220	DIN54231	n.d.		-----
3228	DIN54231	50		2.48
3237	DIN54231	37.6504		1.00
3242	DIN54231	28.1		-0.14
3248	DIN54231	65		4.27

	normality	OK
	n	59
	outliers	20
	mean (n)	29.255
	st.dev. (n)	11.9639
	R(calc.)	33.499
	R(DIN54231:05)	23.444





APPENDIX 2

Summary of all other reported Disperse dyes in samples #15023; results in mg/kg

Lab	Other reported Disperse Dyes on #15024
---	none

Summary of all other reported Disperse dyes in samples #15024; results in mg/kg

Lab	Other reported Disperse Dyes on #15024
2386	Disperse Red 1 = 28.3 mg/kg; possibly misidentified the Disperse Red 11 peak; when 28.3 m/kg Disperse Red 11 z = -0.11

APPENDIX 3

Summary of reported analytical details

Lab	Mass in g.	Extraction solvent	Temp of ultrasonic bath in °C	Extraction time in min	Remarks
213					
362	1.0	15 ml, methanol	70 °C	30	
551					
623	1	15 ml, methanol	70 °C	30	
2108	0.5	7.5 ml, methanol	70 °C	30	
2115	0.5	7.5 ml, methanol	70 °C	10	
2129	0.5	7.5 ml, methanol	70 °C	30.0	
2132	0.5	7.5 ml, methanol	70 °C	30	
2137	0.1-0.5	5-10 ml, methanol	70 °C	30	
2138	0.5000	7.5 ml, methanol	70 °C	30	
2139	0.5	10 ml, methanol	70 °C	30	
2165	0.5	7.5 ml, methanol	70 °C	30	
2172	0.5	7.5 ml, methanol	70 °C	30	
2184	0.5	7.5 ml, methanol	70 °C	30	
2201	0.5	7.5 ml, methanol	70 °C	30	
2247	0.5039/0.3692	7.5 ml, methanol	70 °C	30	
2255	0.5	7.5 ml, methanol	70 °C	30	
2271	0.5	7.5 ml, methanol	70 °C	30	
2272	0.5	7.5 ml, methanol	70 °C	30	
2289	0.5	7.5 ml, methanol	70 °C	30	
2290	0.5	7.5 ml, methanol	70 °C	30	
2295	0.5	7.5 ml, methanol	70 °C	30	
2301	0.5005	7.5 ml, methanol	70 °C	30	
2310	1	15 ml, methanol	70 °C	30	
2311	1.0	15 ml, methanol	70 °C	30	
2330	0.5	7.5 ml, methanol	70 °C	30	
2350	1.0	15 ml, methanol	70 °C	30	
2352	1	15 ml, methanol	70 °C	30	
2357	0.5	7.5 ml, methanol	70 °C	30	
2358	1.0	15 ml, methanol	70 °C	30	
2363	1	15 ml, methanol	70 °C	30	
2365	0.5	7.5 ml, methanol	70 °C	30	
2369	1.0	15 ml, methanol	70 °C	30	
2370	0.5	7.5 ml, methanol	70 °C	30	
2375	0.3	5 ml, methanol	70 °C	30	
2379	1	15 ml, methanol	70 °C	30	
2380	1.0	15 ml, methanol	70 °C	30	
2386	0.5	15 ml, methanol	70 °C	30	
2390	1	15 ml, methanol	70 °C	30	
2410	0.5	7.5 ml, methanol	70 °C	30	
2446	0.5	7.5 ml, methanol	70 °C	30	
2452	0.5	7.5 ml, methanol	70 °C	30	
2462	0.5	7.5 ml, methanol	70 °C	30	
2467	0.5022/0.5009	7.5 ml, methanol	70 °C	30	
2482	0.5	7.5 ml, methanol	70 °C	30	
2488	0.5	7.5 ml, methanol	70 °C	30	
2489	0.5001	7.5 ml, methanol	70 °C	30	

Lab	Mass in g.	Extraction solvent	Temp of ultrasonic bath in °C	Extraction time in min	Remarks
2492	0.5	7.5 ml, methanol	70 °C	30	
2493	0.1	3 ml, methanol	70 °C	30	
2497	0.5	pyridine/water 1:1	100 °C	35	
2511	0.5	7.5 ml, methanol	70 °C	30	
2515					
2532	0.5	7.5 ml, methanol	70 °C	30	
2554	0.5	7.5 ml, methanol	70 ± °C	30	
2563	0.5	7.5 ml, methanol	70 °C	30	
2566	0.5	7.5 ml, methanol	70 °C	30	
2567	0.5	7.5 ml, methanol	70 °C	30	
2580	1/0.5	20 ml, 100% ethanol	25 °C	15	
2602	0.5	7.5 ml, methanol	70 °C	30	
2604	0.5	7.5 ml, methanol	70 °C	30	
2614	0.5015	7.5 ml, methanol	70 °C	30	
2640	0.5	7.5 ml, methanol	70 °C	30	
2643	0.5	7.5 ml, methanol	70 °C	30	
2649	0.5045	7.5 ml, methanol	70 °C	30	
2668	0.5	7.5 ml, methanol	70 °C	30	
3100	0.5000	7.5 ml, methanol	70 °C	30	
3117	0.5	7.5 ml, methanol	70 °C	30	
3146	0.5	7.5 ml, methanol	70 °C	30	
3150	0.5	7.5 ml, methanol	70 °C	30	
3151	0.5	7.5 ml, methanol	70 °C	30	
3153	0.5	7.5 ml, methanol	70 °C	30	
3154	0.4	7.5 ml, methanol	70 °C	30	
3172					
3176	0.5	7.5 ml, methanol	70 °C	30	
3190	0.5	7.5 ml, methanol	70 °C	30	
3197	0.5	7.5 ml, methanol	70 °C	30	
3199	0.5023/0.5027	7.5 ml, methanol	70 °C	30	
3210	0.500	7.5 ml, methanol	70 °C	2	
3214	0.3	4.5 ml, methanol	70 °C	30	
3218	0.5	7.5 ml, methanol	70 °C	30	
3220	0.5	7.5 ml, methanol	70 °C	30	
3228	0.5	7.5 ml, methanol	70 °C	30	
3237	1.00	15 ml, methanol	70 °C	30	
3242	0.5	7.5 ml, methanol	70 °C	30	
3248	0.5003	7.5 ml, methanol	70 °C	30	

APPENDIX 4

Number of participants per country

3 labs in	BANGLADESH
1 lab in	BRAZIL
1 lab in	BULGARIA
2 labs in	CAMBODIA
1 lab in	FRANCE
13 labs in	GERMANY
6 labs in	HONG KONG
1 lab in	HUNGARY
10 labs in	INDIA
2 labs in	INDONESIA
3 labs in	ITALY
6 labs in	KOREA
1 lab in	MOROCCO
18 labs in	P.R. of CHINA
1 lab in	PAKISTAN
1 lab in	ROMANIA
2 labs in	TAIWAN R.O.C.
1 lab in	THAILAND
2 labs in	TUNISIA
6 labs in	TURKEY
1 lab in	U.S.A.
1 lab in	UNITED KINGDOM
2 labs 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
R(0.01) = outlier in Rosner's outlier test
R(0.05) = straggler in Rosner's outlier test
n.e. = not evaluated
n.d. = not detected

Literature:

1 DIN 54231:2004
2 DIN 54231:2005
3 iis Interlaboratory Studies: Protocol for the Organisation, Statistics and Evaluation, April 2014
4 XP G 08-014:97
5 P.L. Davies, Fr Z. Anal. Chem, 351, 513, (1988)
6 W.J. Conover, Practical; Nonparametric Statistics, J. Wiley&Sons, NY, p.302, (1971)
7 ISO 5725, (1986)
8 ISO 5725, parts 1-6, (1994)
9 M. Thompson and R. Wood, J. AOAC Int, 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
13 Öko-tex Std.100 edition 01/2012, available via http://www.oeko-tex.com/
14 M. Thompson and R. Wood, J. AOAC Int, 76, 926, (1993)
15 G. Rohm, J. Bohnen & H. Kruessmann, GIT Labor-Fachzeitschrift, p 1080, 11, (1997)
16 Analytical Methods Committee Technical Brief, No4 January 2001
17 The Royal Society of Chemistry 2002, Analyst 2002, 127 page1359-1364, P.J. Lowthian and M. Thompson. (see www.rsc.org/suppdata/an/b2/b205600n/)
18 Bernard Rosner, Percentage Points for a Generalized ESD Many-Outlier Procedure, T*echnometrics*, 25(2), pp. 165-172, (1983)