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

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CONTENTS

Appendices:

1 INTRODUCTION

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

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

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

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

In this context and in response to requests from several laboratories, the Institute for Interlaboratory Studies (iis) organises a proficiency test for disperse dyes in textile in the annual proficiency test program since 2003.
In the 2014 interlaboratory study 82 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 2014 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 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 organization was the one as described for proficiency testing in the report 'iis Interlaboratory Studies: Protocol for the Organization, Statistics and Evaluation' of April 2014 (iis-protocol, version 3.3).The participants were asked to report the analytical results using the indicated units on the report form.

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 third parties were used in this proficiency test. Each bulk sample was dyed with a number of banned Allergenic Dyes. The first bulk sample, a coloured polyester, was cut in small pieces and homogenized. From this batch 120 subsamples were prepared of 3 gram each and labelled #14023.
The second bulk sample, a coloured cotton, was also cut in small pieces and homogenized. From this batch 119 subsamples were prepared of 1.5 gram each.
The homogeneity of the subsamples #14023 was checked by determination of Disperse Blue 106. The homogeneity of the subsamples #14024 was checked by determination of

Disperse Orange 3 in accordance with DIN54231:05 on respective 7 and 5 stratified randomly selected samples.
See the following tables for the test results.

	Disperse Blue 106 in mg/kg
sample #14023-1	142.6
sample #14023-2	138.8
sample #14023-3	153.8
sample #14023-4	152.4
sample #14023-5	168.9
sample #14023-6	148.6
sample #14023-7	172.3

table 1: homogeneity test of subsamples #14023

	Disperse Orange 3 in mg/kg
sample #14024-1	285.9
sample #14024-2	288.9
sample #14024-3	286.1
sample #14024-4	291.2
sample #14024-5	289.4

table 2: homogeneity test of subsamples #14024

From the above test results, the repeatabilities were calculated and compared with 0.3 times the corresponding reproducibilities in agreement with the procedure of ISO 13528, Annex B2 in the next table:

	Disperse Blue 106 #14023 in mg/kg	Disperse Orange 3 #14024 in mg/kg
r(calc)	35.2	6.4
Reference method	DIN54231:05	DIN54231:05
0.3*R (reference)	37.0	69.3

table 3: repeatabilities of subsamples #14023 and #14024

The repeatabilities of the test results of the determined disperse dyestuffs were all in agreement with 0.3 times the estimated reproducibilities mentioned in DIN54231:05. Therefore homogeneity of the subsamples was assumed.

To each registered participant, one sample #14023 and one sample #14024 were sent on March 5, 2014.

2.5 ANALYSES

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

3 RESULTS

During four weeks after sample dispatch the results of the individual laboratories were gathered. The original data are tabulated in the appendices of this report. The laboratories are presented by their code numbers.
Directly after the deadline, a reminder fax was sent to those laboratories that had not yet reported. Shortly after the deadline the available results were screened for suspect data. A result was called suspect in case the Huber Elimination Rule (a robust outlier test, see lit.5) found it to be an outlier. The laboratories that produced these suspect data were asked to check the results. Additional or corrected data are placed under 'Remarks' in the result tables in appendix 1. A list of abbreviations used in the tables can be found in appendix 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.16). 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). 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 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 (see appendix 5; nos.14 and 15). 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 Pakistan. These laboratories received the samples late. Fourteen participants reported test results after the deadline and one participant did not report any test results at all.
Finally, 83 participants reported 234 numerical results. Observed were 7 outlying test results, which is 3.0% of the numerical results. In proficiency studies outlier percentages of 3% - 7.5% are quite normal.
All the data sets proved to have a normal distribution.

4.1 EVALUATION PER SAMPLE

In this section the results are discussed per sample. All test results reported on the textile samples are summarised in appendix 1. As almost all participants reported to have used DIN54231, this time it was requested to report only the details of the used calibrants.
In DIN54231 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 #14023: This textile was dyed by a third party with the banned dyes: Disperse Blue 106 and Disperse Brown 1. The results reported by the participating laboratories vary strongly (from <15 mg/kg – 554.17 mg/kg for Disperse Blue 106 and from <15 mg/kg – 2419.65 mg/kg for Disperse Brown 1).
For Disperse Blue 106, three statistical outliers were observed and the calculated reproducibility after rejection of the statistical outliers is in full agreement with the estimated reproducibility of DIN54231:05.
For Disperse Brown 1, two statistical outliers were observed. The calculated reproducibility after rejection of the statistical outliers is not in agreement with the estimated reproducibility of DIN54231:05.

Only one laboratory reported also the presence of small amounts of other disperse dyes in sample #14023, see appendix 2.
Only one laboratory would not have rejected this sample for containing too much Allergenic Dyestuffs (acc. to the limit of Öko-tex Std.100 edition 01/2012 of 50 mg/kg). All other laboratories would have rejected this sample.

Textile #14024: This material was treated by a third party with the banned dye: Disperse Orange 3. The results reported by the participating laboratories vary strongly (from <15 – 719.20 mg/kg for Disperse Orange 3).
For Disperse Orange 3, two statistical outliers were observed. The calculated reproducibility after rejection of the statistical outliers is almost in agreement with the estimated reproducibility of DIN54231:05.
Four laboratories reported also the presence of several other disperse dyes in sample #14024 (see appendix 2).
At least two 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 Blue 106	mg/kg	76	216.8	170.2	173.7
Disperse Brown 1	mg/kg	74	273.2	251.8	218.9

table 4: reproducibilities of textile sample #14023

Parameter	unit	n	average	2.8 * sd	R (target)
Disperse Orange 3	mg/kg	77	132.7	117.4	106.3

table 5: reproducibility of textile sample #14024

Without further statistical calculations it can be concluded that for the detected allergenic dyestuffs the group of participating laboratories may have some difficulties with the analysis of Disperse Brown 1 and Disperse Orange 3. See also the discussion in paragraphs 4.1 and 5.

5 DISCUSSION

In this PT one of the samples from a previous PT (#0922 of iis09A04) was re-used as sample #14024. An overview of the differences in results is given in below table:

		#0922 in iis09A04			#14024 in iis14A02		
Parameter	unit	n	average	2.8 * sd	n	average	2.8 * sd
Disperse Orange 3	mg/kg	48	143.1	96.0	77	132.7	117.4

table 6: comparison of results of identical samples in iis09A04 and iis14A02

It is clear that the group performance in this year's PT did not improve since the previous PT in which the same sample was used. The difference in uncertainty (24% vs 32%) may be explained by the increase of the number of participants (48 vs 77) and the difference in number of outliers (5 vs 2). It is noticed that the textile treated with the banned dye Disperse Orange 3 is stable for at least five years.

The uncertainties in the test results of the determined Disperse dyes in the iis14A02 PT are listed in the next table and are comparable with previous proficiency tests.

	March 2014	March 2013	March 2012	March 2011	March 2010	March 2009	March 2008	est. DIN 54231
Disperse Blue 1	n.e.	n.e.	n.e.	n.e.	n.e.	n.e.	43%	29%
Disperse Blue 3	n.e.	56%	42%	51%	51%	n.e.	n.e.	29%
Disperse Blue 26	n.e.	n.e.	68%	n.e.	56%	54%	n.e.	29%
Disperse Blue 35	n.e.	n.e.	n.e.	n.e.	n.e.	(84%)*	n.e.	29%
Disperse Blue 106	28%	n.e.	n.e.	n.e.	n.e.	n.e.	n.e.	29%
Disperse Brown 1	33%	n.e.	n.e.	n.e.	n.e.	n.e.	n.e.	29%
Disperse Orange 1	n.e.	47%	n.e.	44%	n.e.	n.e.	n.e.	29%
Disperse Orange 3	31%	n.e.	n.e.	n.e.	n.e.	24%	35%	29%
Disperse Red 1	n.e.	n.e.	n.e.	36%	n.e.	n.e.	63%	29%
Disperse Red 11	n.e.	n.e.	65%	n.e.	51%	45%	n.e.	29%
Disperse Yellow 3	n.e.	29%	n.e.	28%	n.e.	n.e.	n.e.	29%
Disperse Yellow 9	n.e.	n.e.	n.e.	n.e.	n.e.	n.e.	31%	29%

table 7: development of uncertainties over the last years

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

From the above table it is clear that for Disperse Orange 3 no quality improvement may be observed. But all current uncertainties are close to or in agreement with the target uncertainty estimated from DIN 54231.
Also, it was noticed that almost all participants detected the spiked dyestuffs in both sample #14023 and sample #14024.

Almost all participants used a powder calibrant from Sigma-Aldrich, Dr. Ehrerstorfer or Fluka. Although, the concentrations of the various calibrants differ, it was noticed that this was not the cause of the large spread found for Disperse Brown 1 and Disperse Orange 3.

The spreads observed in this interlaboratory study are clearly not caused by just one critical point in the analysis. Almost all participants reported to have used test method DIN54231. However, the detection technique and the purity of the various calibration standards that were used may vary. Another important step in the procedure is the extraction. Extraction time, sample intake amount and extraction volume, deviating from the DIN54231 test method may lead to deviating test results.
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.

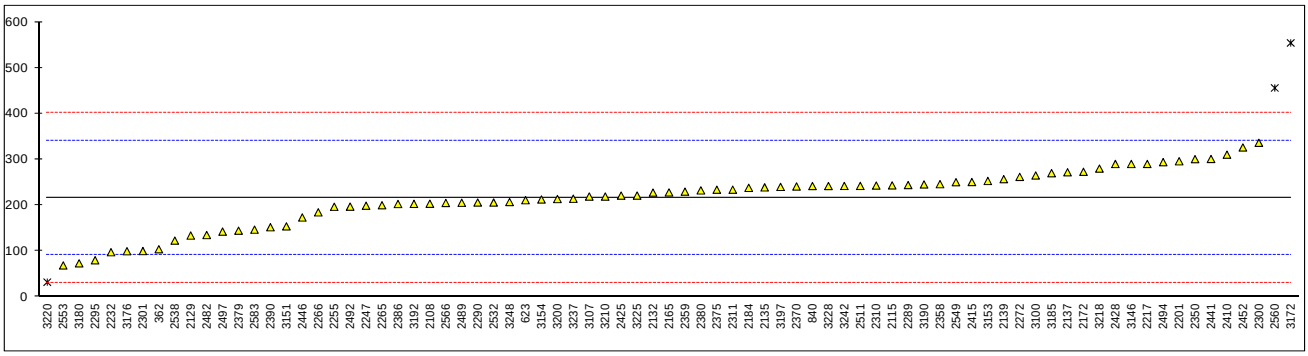
APPENDIX 1

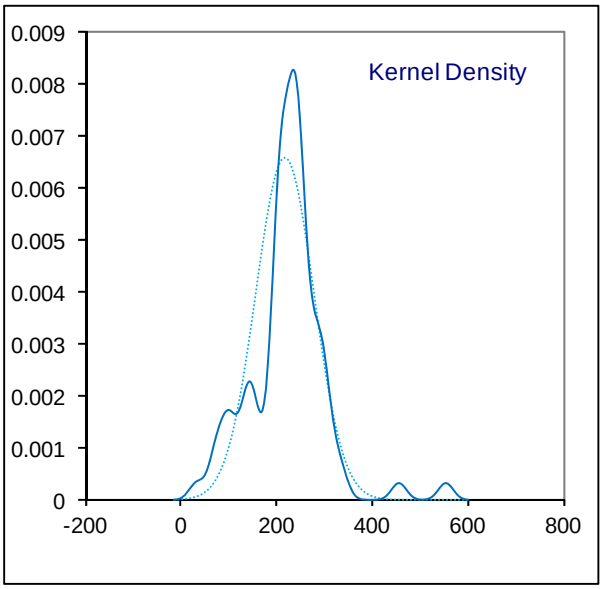
Determination of Disperse Blue 106 (CASno.12223-01-7) in sample #14023; results in mg/kg

lab	method	value	mark	z(targ)	remarks
362		104		-1.82	
551		-----		-----	
623	DIN54231	211.1		-0.09	
840	DIN54231	242		0.41	
2108		203.3		-0.22	
2115	DIN54231	243.38		0.43	
2129	INH-500	133.88	C	-1.34	First reported 80.4
2132	in house	227.6	C	0.17	First reported 79.9
2135	DIN54231	239		0.36	
2137	DIN54231	272		0.89	
2139	DIN54231	257		0.65	
2165	DIN54231	228		0.18	
2172	DIN54231	273		0.91	
2184	DIN54231	238		0.34	
2201	DIN54231	296		1.28	
2217	in house	290.2		1.18	
2232	DIN54231	97.50		-1.92	
2247	DIN54231	199.0		-0.29	
2255	DIN54231	196.7		-0.32	
2265	§64 LFGB B82.02-10	200.0		-0.27	
2266	DIN54231	184.5		-0.52	
2272	DIN54231	261.95		0.73	
2289	DIN54231	244		0.44	
2290		206		-0.17	
2295		80	C	-2.20	First reported 54.15
2300	DIN54231	336.23		1.92	
2301	DIN54231	99.974		-1.88	
2310	DIN54231	243		0.42	
2311	DIN54231	234		0.28	
2350		300.6		1.35	
2358	DIN54231	246		0.47	
2359		229.73		0.21	
2370	DIN54231	241		0.39	
2375	DIN54231	233.9		0.28	
2379		144.53		-1.16	
2380	DIN54231	232.45		0.25	
2386	DIN54231	202.7		-0.23	
2390	DIN54231	152.01		-1.04	
2410		310.4		1.51	
2415	DIN54231	250.7		0.55	
2425	DIN54231	221.06		0.07	
2428	GB/T20383	290		1.18	
2441		301		1.36	
2446	in house	173.33		-0.70	
2452	DIN54231	326.15		1.76	
2459		-----		-----	
2482	DIN54231	135		-1.32	
2489		205.43		-0.18	
2492		197		-0.32	
2494	DIN54231	294.11	C	1.25	First reported 495.21
2497	DIN54231	142.51		-1.20	
2511	DIN54231	242.13		0.41	
2532	DIN54231	206		-0.17	
2538	§64 LFGB B82.02-10	122.9		-1.51	
2549	DIN54231	250.3		0.54	
2553		68.7		-2.39	
2560	DIN54231	455.9	R(0.05)	3.85	
2566		205		-0.19	
2583	§64 LFGB 82.02-10	146.73		-1.13	
3100	DIN54231	265		0.78	
3107	DIN54231Mod.	219		0.04	
3146		290		1.18	
3151	CPSD-DE-AM	153.9	C	-1.01	First reported 76.5
3153	DIN54231	253		0.58	
3154	DIN54231	212.60		-0.07	
3172	DIN54231	554.17	R(0.01)	5.44	
3176	DIN54231	99.6	C	-1.89	First reported 75.74
3180	DIN54231	73.27		-2.31	
3185	DIN54231	270		0.86	
3190	in house	245.4		0.46	
3192		203		-0.22	
3197	DIN54231	240		0.37	
3199	CPSD-AN-00048-MTHD	<15		<-3.25	false negative?

3200	DIN54231	213.6	C	-0.05	First reported 67.3
3210		219		0.04	
3218	DIN54231	280		1.02	
3220	DIN54231	32.13	C,R(0.05)	-2.98	First reported 241.0 mg/l
3225	DIN54231	221.1		0.07	
3228		242		0.41	
3237	in house	214.2525		-0.04	
3242	DIN54231	242.1		0.41	
3248	DIN54231	207.1		-0.16	

normality	OK
n	76
outliers	3
mean (n)	216.80
st.dev. (n)	60.783
R(calc.)	170.19
R(DIN54231:05)	173.73



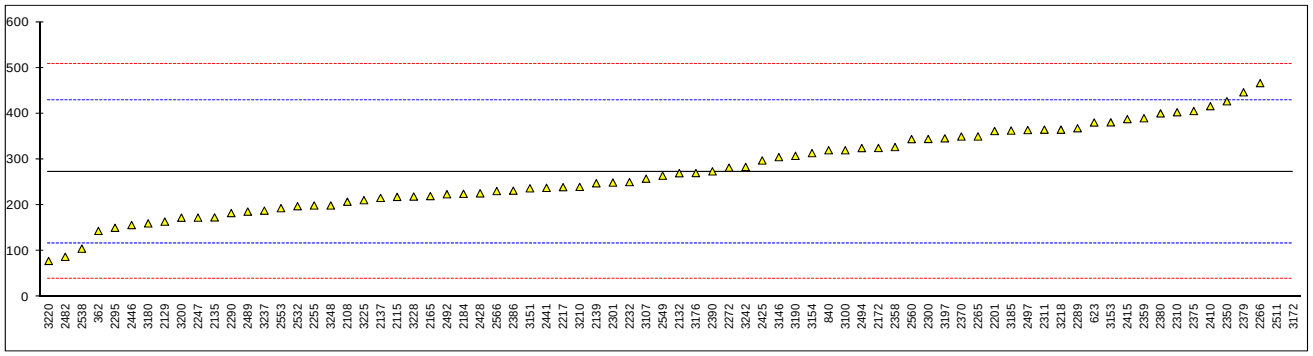


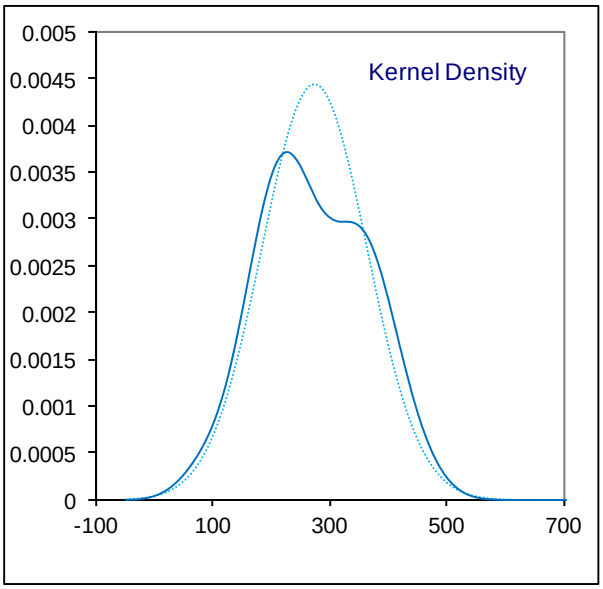
Determination of Brown 1 (CASno.23355-64-8) in sample #14023; results in mg/kg

lab	method	value	mark	z(targ)	remarks
362		144		-1.65	
551		-----		-----	
623	DIN54231	380.6		1.37	
840	DIN54231	320		0.60	
2108		207.7		-0.84	
2115	DIN54231	218.29		-0.70	
2129	INH-500	164.25		-1.39	
2132	in house	270.0		-0.04	
2135	DIN54231	173.5		-1.28	
2137	DIN54231	216		-0.73	
2139	DIN54231	248		-0.32	
2165	DIN54231	220		-0.68	
2172	DIN54231	325		0.66	
2184	DIN54231	225		-0.62	
2201	DIN54231	362		1.14	
2217	in house	239.47		-0.43	
2232	DIN54231	250.5		-0.29	
2247	DIN54231	173.0		-1.28	
2255	DIN54231	199.5		-0.94	
2265	§64 LFGB B82.02-10	350.1		0.98	
2266	DIN54231	466.5		2.47	
2272	DIN54231	282.1		0.11	
2289	DIN54231	368		1.21	
2290		183		-1.15	
2295		150.75		-1.57	
2300	DIN54231	344.63		0.91	
2301	DIN54231	249.571		-0.30	
2310	DIN54231	403		1.66	
2311	DIN54231	365		1.17	
2350		426.9		1.97	
2358	DIN54231	327		0.69	
2359		389.88		1.49	
2370	DIN54231	350		0.98	
2375	DIN54231	405.6		1.69	
2379		446.46		2.22	
2380	DIN54231	400.57		1.63	
2386	DIN54231	231.8		-0.53	
2390	DIN54231	273.95		0.01	
2410		416.2		1.83	
2415	DIN54231	387.90		1.47	
2425	DIN54231	297.75		0.31	
2428	GB/T20383	226		-0.60	
2441		238		-0.45	
2446	in house	156.79		-1.49	
2452		-----		-----	
2459		-----		-----	
2482	DIN54231	87.5		-2.38	
2489		186.19		-1.11	
2492		224		-0.63	
2494	DIN54231	324.85		0.66	
2497	DIN54231	364.14		1.16	
2511	DIN54231	1799.925	R(0.01)	19.52	
2532	DIN54231	198		-0.96	
2538	§64 LFGB B82.02-10	105.3		-2.15	
2549	DIN54231	264.5		-0.11	
2553		193.6		-1.02	
2560	DIN54231	344.4		0.91	
2566		231		-0.54	
2583		-----		-----	
3100	DIN54231	320		0.60	
3107	DIN54231Mod.	258		-0.19	
3146		305		0.41	
3151	CPSD-DE-AM	237.0		-0.46	
3153	DIN54231	381		1.38	
3154	DIN54231	313.77		0.52	
3172	DIN54231	2419.65	R(0.01)	27.45	
3176	DIN54231	270.20		-0.04	
3180	DIN54231	160.39		-1.44	
3185	DIN54231	363		1.15	
3190	in house	307.8		0.44	
3192		-----		-----	
3197	DIN54231	346		0.93	
3199	CPSD-AN-00048-MTHD	<15		<-3.30	False negative ?

3200	DIN54231	172.9		-1.28	
3210		240		-0.42	
3218	DIN54231	365		1.17	
3220	DIN54231	78.46	C	-2.49	First reported 558.0 mg/l
3225	DIN54231	211.1		-0.79	
3228		219		-0.69	
3237	in house	188.2395		-1.09	
3242	DIN54231	283.67		0.13	
3248	DIN54231	199.5		-0.94	

normality	OK
n	74
outliers	2
mean (n)	273.21
st.dev. (n)	89.927
R(calc.)	251.80
R(DIN54231:05)	218.94



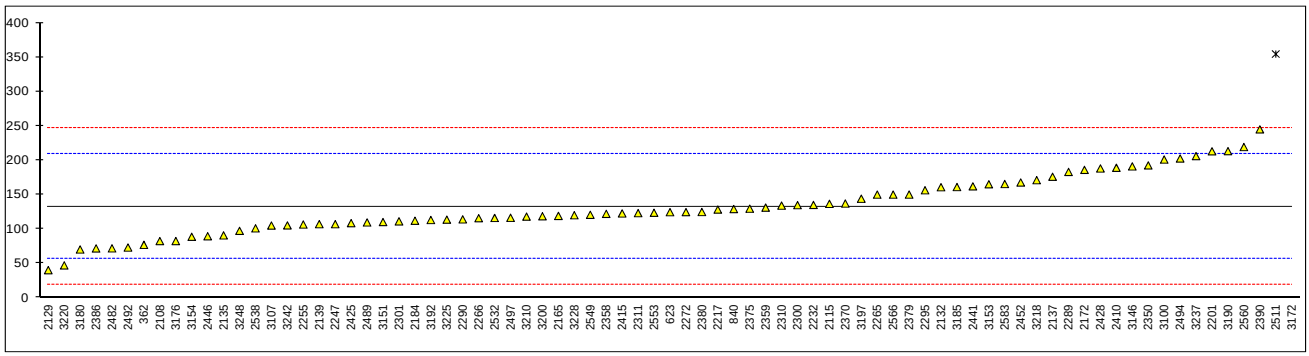


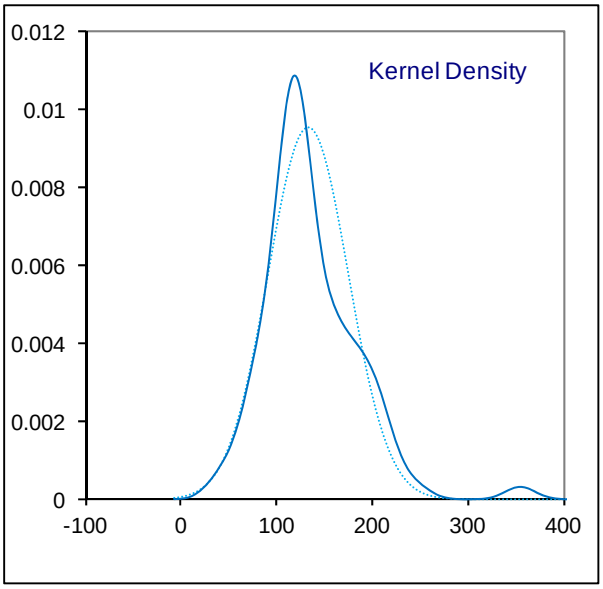
Determination of Disperse Orange 3 (CASno.730-40-5) in sample #14024; results in mg/kg

lab	method	value	mark	z(targ)	remarks
362		76.9		-1.47	
551		-----		-----	
623	DIN54231	124.4		-0.22	
840	DIN54231	129		-0.10	
2108		82.4		-1.32	
2115	DIN54231	136.53		0.10	
2129	INH-500	40.05		-2.44	
2132	in house	160.7		0.74	
2135	DIN54231	90.7		-1.11	
2137	DIN54231	176		1.14	
2139	DIN54231	107		-0.68	
2165	DIN54231	119		-0.36	
2172	DIN54231	186		1.40	
2184	DIN54231	112		-0.54	
2201	DIN54231	213		2.11	
2217	in house	128.23		-0.12	
2232	DIN54231	135		0.06	
2247	DIN54231	107.0		-0.68	
2255	DIN54231	106.5		-0.69	
2265	§64 LFGB B82.02-10	150.0		0.46	
2266	DIN54231	115.7		-0.45	
2272	DIN54231	124.5		-0.22	
2289	DIN54231	183	C	1.32	First reported 236
2290		114		-0.49	
2295		156.3		0.62	
2300	DIN54231	134.7		0.05	
2301	DIN54231	111.075		-0.57	
2310	DIN54231	134		0.03	
2311	DIN54231	123		-0.26	
2350		192.5		1.57	
2358	DIN54231	122		-0.28	
2359		131.09		-0.04	
2370	DIN54231	137		0.11	
2375	DIN54231	129.5		-0.08	
2379		150.03	C	0.46	First reported 236.60
2380	DIN54231	124.68		-0.21	
2386	DIN54231	71.7		-1.61	
2390	DIN54231	244.89		2.95	
2410		189	C	1.48	First reported 263.1
2415	DIN54231	122.6		-0.27	
2425	DIN54231	108.50		-0.64	
2428	GB/T20383	188		1.46	
2441		162		0.77	
2446	in house	89.41		-1.14	
2452	DIN54231	167.64		0.92	
2459		-----		-----	
2482	DIN54231	71.8		-1.60	
2489		109.48		-0.61	
2492		73		-1.57	
2494	DIN54231	202.49		1.84	
2497	DIN54231	116.25		-0.43	
2511	DIN54231	354.48	R(0.01)	5.84	
2532	DIN54231	116		-0.44	
2538	§64 LFGB B82.02-10	100.9		-0.84	
2549	DIN54231	120.6		-0.32	
2553		123.6		-0.24	
2560	DIN54231	219.2		2.28	
2566		150		0.46	
2583	§64 LFGB 82.02-10	165.43		0.86	
3100	DIN54231	201		1.80	
3107	DIN54231Mod.	105		-0.73	
3146		191		1.54	
3151	CPSD-DE-AM	110.1		-0.59	
3153	DIN54231	165		0.85	
3154	DIN54231	88.69		-1.16	
3172	DIN54231	719.20	R(0.01)	15.44	
3176	DIN54231	82.44		-1.32	
3180	DIN54231	70.15		-1.65	
3185	DIN54231	161	C	0.75	First reported 237
3190	in house	213.2		2.12	
3192		113		-0.52	
3197	DIN54231	144		0.30	
3199	CPSD-AN-00048-MTHD	<15		<-3.10	False negative?

3200	DIN54231	118.5		-0.37	
3210		118		-0.39	
3218	DIN54231	171	C	1.01	First reported 240
3220	DIN54231	47.03	C	-2.26	First reported 353 mg/l
3225	DIN54231	113.6		-0.50	
3228		120		-0.33	
3237	in house	206.025		1.93	
3242	DIN54231	105.20		-0.72	
3248	DIN54231	97.3		-0.93	

normality	OK
n	77
outliers	2
mean (n)	132.69
st.dev. (n)	41.932
R(calc.)	117.41
R(DIN54231:05)	106.33





APPENDIX 2

Summary of all other reported Disperse dyes in samples #14023 and #14024; results in mg/kg

Lab	Other reported Disperse Dyes on #14023
2497	Disperse Blue 124 = 26.34; Disperse Orange 76 = 6.58; Disperse Yellow 3 = 0.87

Lab	Other reported Disperse Dyes on #14024
2300	Disperse Blue 35 = 17.88
3155	Disperse Yellow 7 = 46.2
3199	Disperse Yellow 7 = 109.98
3210	Disperse Blue 26 = 1668

APPENDIX 3

Details of the calibrants used by the participants:

Lab	Brand name	composition	Powder/ solution	Brand name	composition	Powder/ solution	Brand name	composition	Powder/ solution
	Disperse Blue 106			**Disperse Brown 1**			**Disperse Orange 3**		
362	Fluka	--	powder	Dr. Ehrerstorfer	50.30%	powder	Dr. Ehrerstorfer	96%	powder
551	--	--	--	--	--	--	--	--	--
623	Fluka	--	powder	Dr. Ehrerstorfer	50.30%	powder	Aldrich	90%	powder
840	Fluka	100%	powder	Accustd	44%	powder	Sigma Aldrich	90%	powder
2108	Dr. Ehrerstorfer	100%	powder	Dr. Ehrerstorfer	50.30%	powder	Dr. Ehrerstorfer	96%	powder
2115	Dr. Ehrerstorfer	100%	powder	Dr. Ehrerstorfer	50.30%	powder	Dr. Ehrerstorfer	85%	powder
2129	Dr. Ehrerstorfer	30%	powder	Dr. Ehrerstorfer	30%	powder	Dr. Ehrerstorfer	30%	powder
2132	Sigma Aldrich	95%	powder	Dr. Ehrerstorfer	50%	powder	Sigma Aldrich	30%	powder
2135	CIBA	100%	powder	Dr. Ehrerstorfer	50.30%	powder	Sigma Aldrich	90%	powder
2137	Dr. Ehrerstorfer	100%	powder	Dr. Ehrerstorfer	50.30%	powder	Dr. Ehrerstorfer	92%	powder
2139	Dr. Ehrerstorfer	100%	powder	Dr. Ehrerstorfer	50.30%	powder	Dr. Ehrerstorfer	90%	powder
2165	Dr. Ehrerstorfer	100%	powder	Dr. Ehrerstorfer	50.30%	powder	Dr. Ehrerstorfer	90.50%	powder
2172	Yorkshire	50%	powder	Ludewig	29%	powder	Sigma Aldrich	90%	powder
2184	Dr. Ehrerstorfer	100%	powder	Dr. Ehrerstorfer	50.30%	powder	Dr. Ehrerstorfer	90%	powder
2201	Fluka	100%	powder	Ludewig	50%	powder	Sigma Aldrich	92.40%	powder
2217	Dr. Ehrerstorfer	100%	powder	Dr. Ehrerstorfer	50.30%	powder	Dr. Ehrerstorfer	96%	powder
2232	Yorkshire	50%	powder	Ludewig	29%	powder	Sigma Aldrich	90%	powder
2247	Dr. Ehrerstorfer	100%	powder	Dr. Ehrerstorfer	50.30%	powder	Dr. Ehrerstorfer	90.50%	powder
2255	Dr. Ehrerstorfer	100%	powder	Dr. Ehrerstorfer	50.30%	powder	Dr. Ehrerstorfer	85%	powder
2265	Dr. Ehrerstorfer	100%	powder	Dr. Ehrerstorfer	50.30%	powder	Dr. Ehrerstorfer	96%	powder
2266	Fluka	--	powder	Sigma-Aldrich	--	powder	Sigma Aldrich	90%	powder
2272	Dr. Ehrerstorfer	100%	powder	Dr. Ehrerstorfer	50.30%	powder	Dr. Ehrerstorfer	78.0%	powder
2289	Dr. Ehrerstorfer	100%	powder	Dr. Ehrerstorfer	50%	powder	Dr. Ehrerstorfer	85%	powder
2290	Dr. Ehrerstorfer	100%	powder	Dr. Ehrerstorfer	50.3%	powder	Dr. Ehrerstorfer	90%	powder
2295	Sigma Aldrich	35%	powder	Dr. Ehrerstorfer	50.30%	powder	Sigma Aldrich	90%	powder
2300	Dr. Ehrerstorfer	--	powder	Dr. Ehrerstorfer	--	powder	Dr. Ehrerstorfer	--	powder
2301	Yorkshire	29%	powder	Ludewig	29%	powder	Sigma Aldrich	90%	powder
2310	--	100%	powder	Sigma-Aldrich	44%	powder	Sigma Aldrich	90%	powder
2311	Fluka	100%	powder	--	--	powder	Sigma Aldrich	90%	powder
2350	Fluka	100%	powder	Accustd	44%	powder	Sigma Aldrich	90%	powder
2358	Fluka	100%	powder	Accustd	100%	powder	Sigma Aldrich	90%	powder
2359	Fluka	100%	powder	Accustd	44%	powder	Sigma Aldrich	86%	powder
2370	Fluka	100%	powder	Accustd	44%	powder	Sigma Aldrich	90%	powder
2375	Fluka	100%	powder	Accustd	44%	powder	Sigma Aldrich	90%	powder
2379	Fluka	100%	powder	Dr. Ehrerstorfer	50.30%	powder	Sigma Aldrich	90%	powder
2380	Fluka	100%	powder	Accustd	44%	powder	Sigma Aldrich	90%	powder
2386	Fluka	--	powder	Accustd	--	powder	Sigma Aldrich	--	powder
2390	Fluka	100%	powder	Accustd	44%	powder	Sigma Aldrich	90%	powder
2410	Dr. Ehrerstorfer	100%	powder	Dr. Ehrerstorfer	83%	powder	Dr. Ehrerstorfer	96%	powder
2415	Dr. Ehrerstorfer	100%	powder	Dr. Ehrerstorfer	50.30%	powder	Dr. Ehrerstorfer	90%	powder
2425	Dr. Ehrerstorfer	100%	powder	Dr. Ehrerstorfer	50.30%	powder	Dr. Ehrerstorfer	90%	powder
2428	Dr. Ehrerstorfer	100%	powder	Dr. Ehrerstorfer	50.30%	powder	Dr. Ehrerstorfer	85%	powder
2441	Dr. Ehrerstorfer	100%	powder	Dr. Ehrerstorfer	50.30%	powder	Dr. Ehrerstorfer	90%	powder
2446	Dr. Ehrerstorfer	100%	powder	Dr. Ehrerstorfer	50.30%	powder	Dr. Ehrerstorfer	85%	powder
2452	Dr. Ehrerstorfer	--	powder	--	--	--	Dr. Ehrerstorfer	--	powder
2459	--	--	--	--	--	--	--	--	--
2482	Neochema	100µg/ml	solution	Neochema	100µg/ml	solution	Neochema	100µg/ml	solution
2489	Dr. Ehrerstorfer	100%	powder	Dr. Ehrerstorfer	50.30%	powder	Dr. Ehrerstorfer	90%	powder
2492	Dr. Ehrerstorfer	100%	powder	Dr. Ehrerstorfer	100%	powder	Dr. Ehrerstorfer	50.30%	powder
2494	Sigma Aldrich	100%	powder	Dr. Ehrerstorfer	100%	powder	--	--	--
2497	Dr. Ehrerstorfer	100%	powder	Dr. Ehrerstorfer	50.30%	powder	Dr. Ehrerstorfer	90%	powder
2511	Dr. Ehrerstorfer	100%	powder	Accustd	101.2µg/ml	solution	Accustd	100.4µg/ml	solution
2532	Dr. Ehrerstorfer	100%	powder	Dr. Ehrerstorfer	50.30%	powder	Dr. Ehrerstorfer	96%	powder
2538	Dr. Ehrerstorfer	87%	powder	Dr. Ehrerstorfer	50.30%	powder	Dr. Ehrerstorfer	90.50%	powder
2549	Dr. Ehrerstorfer	100%	powder	Dr. Ehrerstorfer	50.30%	powder	Dr. Ehrerstorfer	90%	powder
2553	Yorkshire	50%	powder	Ludewig	29%	powder	Sigma Aldrich	90%	powder
2560	Dr. Ehrerstorfer	100%	powder	Dr. Ehrerstorfer	50.30%	powder	Dr. Ehrerstorfer	90%	powder

2566	Dr. Ehrerstorfer	100%	powder	Dr. Ehrerstorfer	50.30%	powder	Sigma Aldrich	90%	powder
2583	Yorkshire	25-50%	powder	--	--	--	Sigma Aldrich	35%	powder
3100	Dr. Ehrerstorfer	100%	powder	Ludewig	50%	powder	Dr. Ehrerstorfer	90%	powder
3107	Dr. Ehrerstorfer	100%	powder	Ludewig	50%	powder	--	--	--
3146	Dr. Ehrerstorfer	100%	powder	Dr. Ehrerstorfer	50.30%	powder	Dr. Ehrerstorfer	90%	powder
3151	Yorkshire	50%	powder	Ludewig	50.50%	powder	Sigma Aldrich	90%	powder
3153	Dr. Ehrerstorfer	87%	powder	Ludewig	50%	powder	Dr. Ehrerstorfer	90.50%	powder
3154	Dr. Ehrerstorfer	100%	powder	Sigma-Aldrich	--	powder	Dr. Ehrerstorfer	90.50%	powder
3172	Dr. Ehrerstorfer	--	powder	Accustd	100µg/ml	solution	Accustd	100µg/ml	solution
3176	Dr. Ehrerstorfer	100%	powder	Dr. Ehrerstorfer	50.30%	powder	Dr. Ehrerstorfer	85%	powder
3180	Dr. Ehrerstorfer	100%	powder	Dr. Ehrerstorfer	50.30%	powder	Dr. Ehrerstorfer	90.50%	powder
3185	Dr. Ehrerstorfer	100%	powder	Dr. Ehrerstorfer	50.30%	powder	Dr. Ehrerstorfer	96%	powder
3190	Dr. Ehrerstorfer	100%	powder	Ludewig	50%	powder	Dr. Ehrerstorfer	90%	powder
3192	Dr. Ehrerstorfer	100%	powder	--	--	--	Dr. Ehrerstorfer	90%	powder
3197	Dr. Ehrerstorfer	100%	powder	Ludewig	50%	powder	Dr. Ehrerstorfer	90%	powder
3199	Yorkshire	50%	powder	Ludewig	29%	powder	Sigma Aldrich	90%	powder
3200	Fluka	30%	powder	Dr. Ehrerstorfer	50.30%	powder	Dr. Ehrerstorfer	85%	powder
3210	Dr. Ehrerstorfer	100%	powder	Dr. Ehrerstorfer	50.30%	powder	Dr. Ehrerstorfer	90%	powder
3218	Dr. Ehrerstorfer	100%	powder	Ludewig	50.30%	powder	Dr. Ehrerstorfer	90%	powder
3220	Dr. Ehrerstorfer	100%	powder	Dr. Ehrerstorfer	50.30%	powder	Dr. Ehrerstorfer	80%	powder
3225	Dr. Ehrerstorfer	100%	powder	Dr. Ehrerstorfer	50.30%	powder	Dr. Ehrerstorfer	90%	powder
3228	Dr. Ehrerstorfer	100%	powder	Dr. Ehrerstorfer	50.30%	powder	Dr. Ehrerstorfer	85%	powder
3237	Dr. Ehrerstorfer	100%	powder	Dr. Ehrerstorfer	--	powder	Dr. Ehrerstorfer	85%	powder
3242	Fluke	100%	powder	Sigma-Aldrich	100%	powder	Dr. Ehrerstorfer	85%	powder
3248	Dr. Ehrerstorfer	100%	powder	Dr. Ehrerstorfer	50.30%	powder	Dr. Ehrerstorfer	90%	powder
3237	Dr. Ehrerstorfer	30%	Powder	Dr. Ehrerstorfer	24%	Powder	Dr. Ehrerstorfer	80%	Powder
3242	Sigma Aldrich	30%	Powder	Dr. Ehrerstorfer	24%	Powder	Dr. Ehrerstorfer	80%	Powder
3248	Dr. Ehrerstorfer	30%	Powder	Dr. Ehrerstorfer	24%	Powder	Dr. Ehrerstorfer	80%	Powder

APPENDIX 4

Number of participants per country

4 labs in	BANGLADESH
1 lab in	BRAZIL
1 lab in	BULGARIA
2 labs in	FRANCE
13 labs in	GERMANY
7 labs in	HONG KONG
1 lab in	HUNGARY
10 labs in	INDIA
3 labs in	INDONESIA
3 labs in	ITALY
4 labs in	KOREA
14 labs in	P.R. of CHINA
2 labs in	PAKISTAN
1 lab in	SINGAPORE
1 lab in	SRI LANKA
1 lab in	SWITZERLAND
1 lab in	TAIWAN R.O.C.
1 lab in	THAILAND
2 labs in	TUNESIA
5 labs in	TURKEY
1 lab in	U.S.A.
1 lab in	UNITED KINGDOM
3 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

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