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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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 2013 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 2013 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/IEC 17043:2010 and ILAC-G13:2007. This ensures strict adherence to protocols for sample preparation and statistical evaluation and 100% confidentiality of the participant's data. Also the 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 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

The two textile samples were each prepared from two different bulk materials by a third party laboratory. Each bulk sample was dyed with a number of banned Allergenic Dyes. From the first bulk, 110 small pieces of fabric were cut and labelled #13023. The bulk material for sample #13024 was cut in small pieces and homogenised, the approximately 600 grams of material, was divided over 110 subsamples of 4 gram and labelled #13024. The samples were tested for homogeneity by a subcontracted laboratory. The homogeneity of the subsamples #13023 was checked by determination of Disperse Yellow 3. The homogeneity of the subsamples #13024 was checked by determination of Disperse Blue 3 and Disperse Orange 1 in accordance with DIN54231:05 on respective 8 and 15 stratified randomly selected samples.

See the following tables for the test results.

	Disperse Yellow 3 in mg/kg
sample #13023-1	100.5
sample #13023-2	104.3
sample #13023-3	111.1
sample #13023-4	111.2
sample #13023-5	107.5
sample #13023-6	106.8
sample #13023-7	101.5
sample #13023-8	103.0

table 1: homogeneity test of subsamples #13023

	Disperse Blue 3 in mg/kg	Disperse Orange 1 in mg/kg
sample #13024-1	71.10	115.58
sample #13024-2	73.50	113.95
sample #13024-3	72.32	114.67
sample #13024-4	74.12	112.98
sample #13024-5	72.95	114.57
sample #13024-6	72.66	114.18
sample #13024-7	72.96	113.54
sample #13024-8	73.14	113.14
sample #13024-9	73.88	113.66
sample #13024-10	72.68	112.87
sample #13024-11	72.19	113.85
sample #13024-12	73.17	114.21
sample #13024-13	72.91	114.45
sample #13024-14	73.25	114.11
sample #13024-15	73.16	113.86

table 2: homogeneity test of subsamples #13024

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:

	Disp. Yellow 3 #13023 in mg/kg	Disp. Blue 3 #13024 in mg/kg	Disp. Orange 1 #13024 in mg/kg
r(calc)	11.49	2.02	1.98
Reference method	DIN54231:05	DIN54231:05	DIN54231:05
0.3*R (reference)	25.41	17.53	27.40

table 3: repeatabilities of subsamples #13023 and #13024

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.

An amount of approx. 4 grams of each of the samples #13023 and #13024 was sent to the participating laboratories on March 6, 2013.

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 4.

3.1. STATISTICS

Statistical calculations were performed as described in the report 'iis Interlaboratory Studies: Protocol for the Organization, Statistics and Evaluation' of January 2010 (iis-protocol, version 3.2)

For the statistical evaluation the unrounded (when available) figures were used instead of the rounded results. Results reported as '<…' or '>…" were not used in the statistical evaluation.
Before further calculations, the normality of the distribution of the various data sets per determination was checked by means of the Lilliefors-test. In the case of an anormal distribution, the statistical evaluation should be used with care.

According to ISO 5725 (1986 and 1994, lit.7 and 8) the original results per determination were submitted subsequently to Dixon's and Grubbs' outlier tests. Outliers are marked by D(0.01) for the Dixon's test, by G(0.01) or DG(0.01) for the Grubbs' test. Stragglers are marked by D(0.05) for the Dixon's test, by G(0.05) or DG(0.05) for the Grubbs' test. Both outliers and stragglers were not included in the calculations of averages and standard deviations.

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.

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.
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.

The $z_{(target)}$-scores were calculated according to:

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

The $z_{(target)}$-scores are listed in the result tables in appendix 1.
Absolute values for $z<2$ are very common and absolute values for $z>3$ are very rare. The usual interpretation of z-scores is as follows:

| z | < 1 good
1 < | z | < 2 satisfactory
2 < | z | < 3 questionable
3 < | z | unsatisfactory

4 EVALUATION

During the execution of this proficiency test no problems occurred with the delivery of the samples. Seventeen participants reported test results after the deadline and two participants did not report any test results at all.
Finally, 83 participants reported 242 numerical results. Observed were 3 outlying test results, which is 1.2% of the numerical results. In proficiency studies outlier percentages of 3% - 7.5% are quite normal.
None of 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 #13023: This textile was dyed by a third party with the banned dye Disperse Yellow 3. The results reported by the participating laboratories vary strongly (from 16.5 mg/kg – 363.3 mg/kg). Only one statistical outlier was observed and the calculated reproducibility after rejection of the statistical outlier is in full agreement with the estimated reproducibility of DIN54231:05.
Only one laboratory reported also the presence of two other disperse dyes in sample #13023, see appendix 2.
Four laboratories (2127, 2475, 2497 and 2520) 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 #13024: This material was treated by a third party laboratory with the banned dyes Disperse Blue 3 and Disperse Orange 1. The results reported by the participating laboratories vary strongly (for Disperse Blue 3: from 10 – 279.9 mg/kg and for Disperse Orange 1: <1.0 – 475.5 mg/kg). For Disperse Blue 3 and Disperse Orange 1 as well, one statistical outlier was observed. The spread of Disperse Blue 3 after rejection of the statistical outlier is not at all in agreement with the estimated reproducibility of DIN54231:05.

The spread of Disperse Orange 1 after rejection of the statistical outlier is not at all in agreement with the estimated reproducibility of DIN54231:05.
A number of laboratories reported also the presence of several other disperse dyes in sample #13024 (see appendix 2).
At least two laboratories (362 and 2127) 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 Yellow 3	mg/kg	82	102.8	82.3	82.4

table 4: reproducibility of textile sample #13023

Parameter	unit	n	average	2.8 * sd	R (target)
Disperse Blue 3	mg/kg	79	79.2	123.8	63.5
Disperse Orange 1	mg/kg	78	146.9	192.2	117.7

table 5: reproducibility of textile sample #13024

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 of Disperse Blue 3 and Disperse Orange 1. See also the discussion in paragraphs 4.1 and 5.

5 DISCUSSION

In this PT one of the samples from a previous PT (#110223 of iis11A02) was re-used as sample #13024. An overview of the differences in results is given in below table:

		#11022 in iis11A02			#13024 in iis13A02		
Parameter	unit	n	average	2.8 * sd	n	average	2.8 * sd
Disperse Blue 3	mg/kg	45	75.4	108.2	79	79.2	123.8
Disperse Orange 1	mg/kg	44	139.7	170.3	78	146.9	192.2

Table 6: comparison of results of identical samples in iis11A02 and iis13A02

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 spread may be explained by the increase of the number of participants (45 vs 79) and the difference in number of outliers. It is noticed that the textile treated with banned-dyes is stable for at least two years.

The relative spreads in the test results of the determined dyes in the iis13A02 PT are listed in the next table.

	March 2013	March 2012	March 2011	March 2010	March 2009	March 2008	est. DIN54231
Disperse Blue 1	n.e.	n.e.	n.e.	n.e.	n.e.	121%	80%
Disperse Blue 3	156%	117%	143%	142%	n.e.	n.e.	80%
Disperse Blue 26	n.e.	191%	n.e.	152%	150%	n.e.	80%
Disperse Blue 35	n.e.	n.e.	n.e.	n.e.	(235%)*	n.e.	80%
Disperse Orange 1	131%	n.e.	122%	n.e.	n.e.	n.e.	80%
Disperse Orange 3	n.e.	n.e.	n.e.	n.e.	67%	98%	80%
Disperse Red 1	n.e.	n.e.	100%	n.e.	n.e.	176%	80%
Disperse Red 11	n.e.	181%	n.e.	144%	127%	n.e.	80%
Disperse Yellow 3	80%	n.e.	78%	n.e.	n.e.	n.e.	80%
Disperse Yellow 9	n.e.	n.e.	n.e.	n.e.	n.e.	86%	80%

table 7: development of relative reproducibilities over the last years

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

From the above table it is clear that no quality improvement is present for the detected banned dyes.
It was noticed that almost all participants found the spiked dyestuffs in sample #13023 and in sample #13024.

Almost all participants used a calibrant from Sigma-Aldrich or Dr. Ehrerstorfer. Although, the concentrations of the various calibrants differ, it was noticed that this was not the cause of the large spread found for Disperse Blue 3 and Disperse Orange 1.
However, for all three disperse dyes it is noticed that the use of an Accustandard gives significantly higher results. For Disperse Blue 3 it is also noticed that the use of the Sigma-Aldrich powder standard of 7% gives significant lower results. For Disperse Orange 1, the use of the Sigma-Aldrich powder standard of 25% gives significant lower results.

The spreads observed in this interlaboratory study are clearly not caused by just one critical point in the analysis. Almost all participants reported to have used test method DIN54231. However, the detection technique and the purity of the various calibration standards that were used may vary strongly.
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.

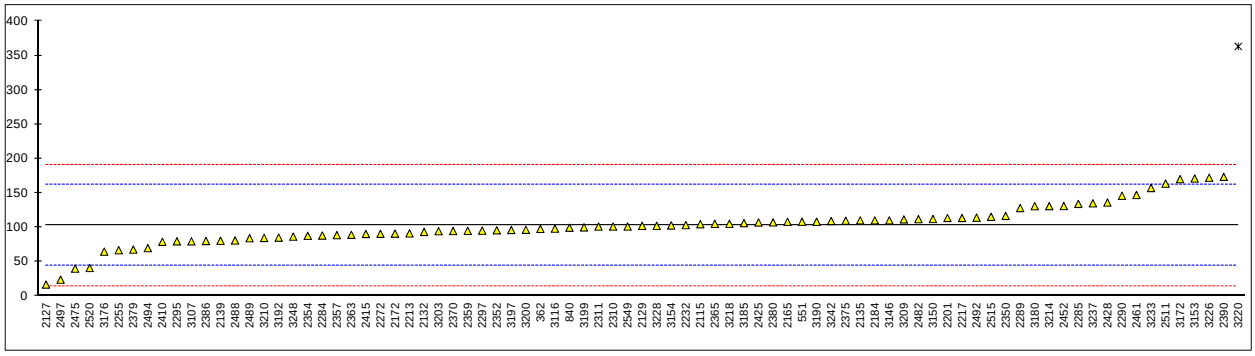
APPENDIX 1

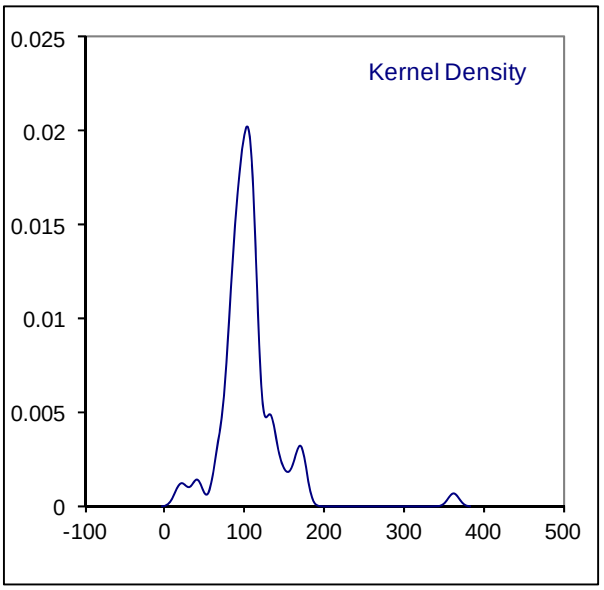
Determination of Disperse Yellow 3 (CASno. 2832-40-8) in sample #13023; results in mg/kg

lab	method	value	mark	z(targ)	Remarks
362	In house	97.6		-0.18	
551	DIN54231	108.00	C	0.18	First reported 379.70
840		99.3		-0.12	
2115	DIN54231	104.48		0.06	
2127	EN71-9	16.5		-2.93	
2129	DIN54231	102		-0.03	
2132	In house	93.2		-0.33	
2135	DIN54231	110		0.24	
2139	DIN54231	80.3		-0.76	
2165	DIN54231	108		0.18	
2172	DIN54231	90.7		-0.41	
2184	DIN54231	110		0.24	
2201	DIN54231	113.5		0.36	
2213	DIN54231	91		-0.40	
2217	In house	113.5		0.36	
2232	DIN54231	103.2		0.01	
2247		-----		-----	
2255	DIN54231	66.6		-1.23	
2272	DIN54231	90.4		-0.42	
2284	DIN54231	87.9		-0.51	
2285	GB/T 20383	134		1.06	
2289		128		0.86	
2290		145.8		1.46	
2295		79.5		-0.79	
2297	DIN54231	95		-0.27	
2310	DIN54231	101		-0.06	
2311	DIN54231	101		-0.06	
2350	DIN54231	116.5		0.47	
2352	DIN54231	95.52		-0.25	
2354		87.5		-0.52	
2357	DIN54231	88.5		-0.49	
2359	DIN54231	94.8		-0.27	
2363	DIN54231	89		-0.47	
2365	GB/T 20383	105.0		0.07	
2370	DIN54231	94.5		-0.28	
2375	DIN54231	109.5		0.23	
2379		67.52		-1.20	
2380	DIN54231	107.07		0.15	
2386	DIN54231	80.0		-0.77	
2390	DIN54231	173.376		2.40	
2410		78.8		-0.82	
2415	DIN54231	90.15		-0.43	
2425	DIN54231	107.025		0.14	
2428	GB/T 20383	136		1.13	
2447		-----		-----	
2452	DIN54231	130.838		0.95	
2461	GB/T 20383	147		1.50	
2475	DIN54231	39.73	C	-2.14	First reported 25.88
2482		111.8		0.31	
2488	DIN54231	80.7424		-0.75	
2489	DIN54231	84.0		-0.64	
2492	In house	114		0.38	
2494	DIN54231	69.54	C	-1.13	First reported 28.97
2497	DIN54231	23.61	C	-2.69	First reported 7.04
2511	DIN54231	163.5		2.06	
2515	DIN54231	115.2		0.42	
2520	DIN54231	40.665		-2.11	
2549	DIN54231	101.0		-0.06	
3107	DIN54231	79.5		-0.79	
3116	In house	98.0		-0.16	
3146	DIN54231	110		0.24	
3150	DIN54231	112		0.31	
3153	DIN54231	171		2.32	
3154		102.61		-0.01	
3172	In house	170.0		2.28	
3176		64.5		-1.30	
3180		130.7		0.95	
3185	DIN54231	106		0.11	
3190	DIN54231	108.0		0.18	
3192	DIN54231	84.9		-0.61	
3197		96		-0.23	
3199	In house	99.8		-0.10	
3200	DIN54231	96.3		-0.22	

3203	DIN54231	94.3	C	-0.29	First reported 225
3209		111.4		0.29	
3210	DIN54231	84.4		-0.63	
3214	DIN54231	130.72		0.95	
3218		105		0.07	
3220	DIN54231	363.3	G(0.01)	8.85	
3226	DIN54231	172.10		2.36	
3228		102		-0.03	
3233	DIN54231	157.14		1.85	
3237	In house	134.814		1.09	
3242	DIN54231	109.04		0.21	
3248	DIN54231	86.3		-0.56	

normality	not OK
n	82
outliers	1
mean (n)	102.797
st.dev. (n)	29.3893
R(calc.)	82.290
R(DIN54231:05)	82.378



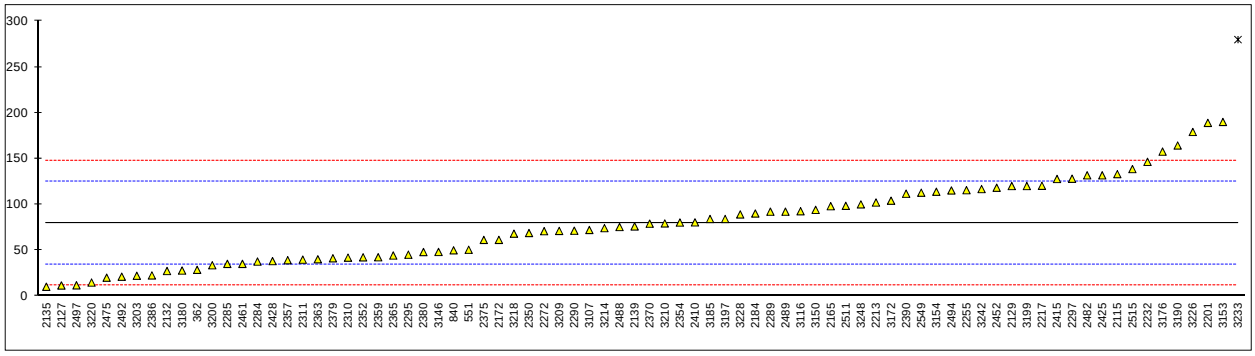


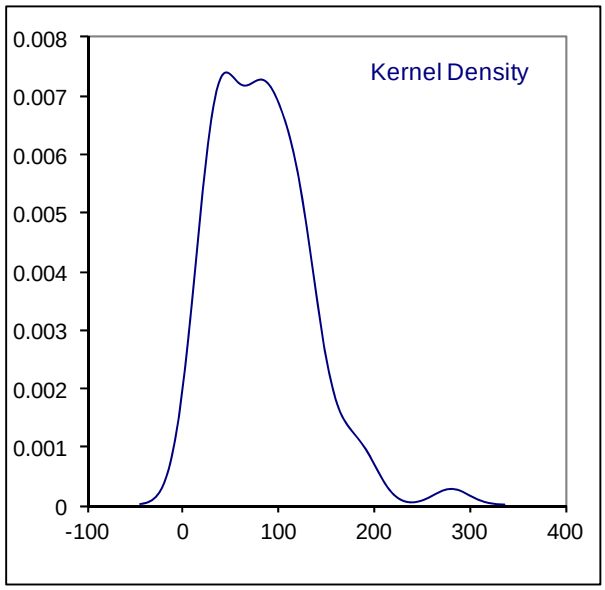
Determination of Disperse Blue 3 (CASno. 2475-46-9) in sample #13024; results in mg/kg

lab	method	value	mark	z(targ)	remarks
362	In house	28.5		-2.24	
551	DIN54231	50.4	C	-1.27	First reported 277.92
840		49.8		-1.30	
2115	DIN54231	133.01		2.38	
2127	EN71-9	11.4		-2.99	
2129	DIN54231	120		1.80	
2132	In house	27.2		-2.29	
2135	DIN54231	10		-3.05	
2139	DIN54231	75.9		-0.14	
2165	DIN54231	98		0.83	
2172	DIN54231	61.2		-0.79	
2184	DIN54231	90		0.48	
2201	DIN54231	189.0		4.85	
2213	DIN54231	102		1.01	
2217	In house	120.3		1.81	
2232	DIN54231	146.4		2.97	
2247		-----		-----	
2255	DIN54231	115.5		1.60	
2272	DIN54231	70.7		-0.37	
2284	DIN54231	37.5		-1.84	
2285	GB/T 20383	35	C	-1.95	First reported 109
2289		92		0.57	
2290		71.2		-0.35	
2295		45		-1.51	
2297	DIN54231	128		2.15	
2310	DIN54231	41.8		-1.65	
2311	DIN54231	39.6		-1.75	
2350	DIN54231	68.7		-0.46	
2352	DIN54231	42.15		-1.63	
2354		80.14		0.04	
2357	DIN54231	39		-1.77	
2359	DIN54231	42.2		-1.63	
2363	DIN54231	40		-1.73	
2365	GB/T 20383	44.12		-1.55	
2370	DIN54231	78.9		-0.01	
2375	DIN54231	61.16		-0.80	
2379		41.10		-1.68	
2380	DIN54231	47.94		-1.38	
2386	DIN54231	22.4		-2.51	
2390	DIN54231	111.634		1.43	
2410		80.3		0.05	
2415	DIN54231	127.73		2.14	
2425	DIN54231	131.71		2.32	
2428	GB/T 20383	38	C	-1.82	First reported 112
2447		-----		-----	
2452	DIN54231	118.134		1.72	
2461	GB/T 20383	35	C	-1.95	First reported 104
2475	DIN54231	19.92		-2.61	
2482		131.7		2.32	
2488	DIN54231	75.2686		-0.17	
2489	DIN54231	92.0		0.57	
2492	In house	21		-2.57	
2494	DIN54231	115.17		1.59	
2497	DIN54231	11.57		-2.98	
2511	DIN54231	98.4		0.85	
2515	DIN54231	138.5		2.62	
2520		-----		-----	
2549	DIN54231	112.72		1.48	
3107	DIN54231	72.0		-0.32	
3116	In house	92.5		0.59	
3146	DIN54231	48		-1.38	
3150	DIN54231	94		0.65	
3153	DIN54231	190		4.89	
3154		113.78		1.53	
3172	In house	104.0		1.10	
3176		157.6		3.46	
3180		27.7		-2.27	
3185	DIN54231	84	C	0.21	First reported 190
3190	DIN54231	164.3		3.76	
3192		-----		-----	
3197		84		0.21	
3199	In house	120		1.80	
3200	DIN54231	33.5		-2.02	

3203	DIN54231	22		-2.52	
3209		71.0		-0.36	
3210	DIN54231	79.2		0.00	
3214	DIN54231	74.07		-0.23	
3218		68		-0.49	
3220	DIN54231	14.6		-2.85	
3226	DIN54231	179.06		4.41	
3228		89		0.43	
3233	DIN54231	279.93	C,G(0.01)	8.86	First reported 289.75
3237		-----		-----	
3242	DIN54231	116.72		1.66	
3248	DIN54231	100		0.92	

normality	not OK
n	79
outliers	1
mean (n)	79.177
st.dev. (n)	44.2185
R(calc.)	123.812
R(DIN54231:05)	63.450



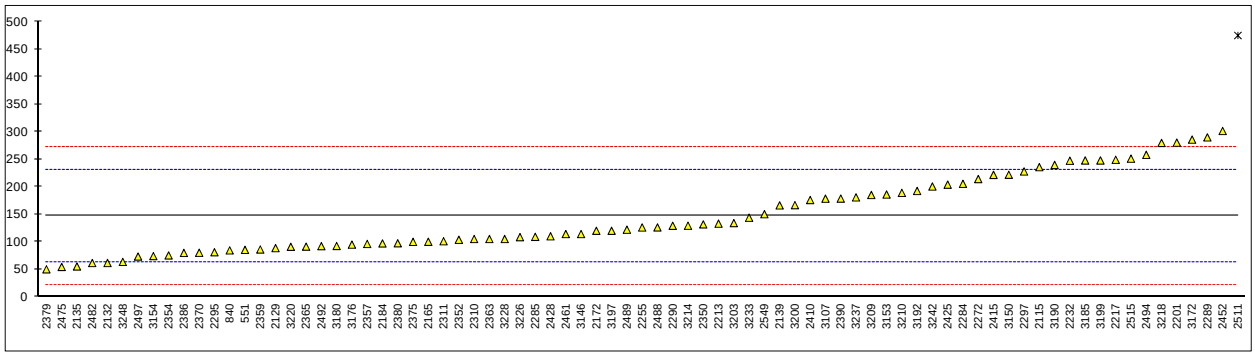


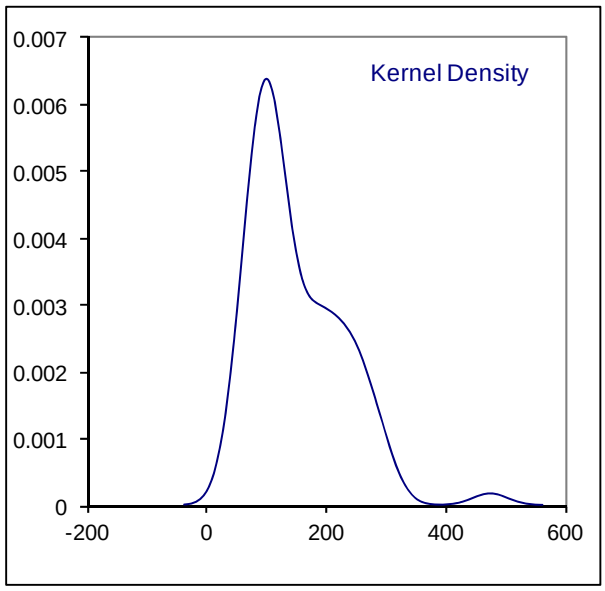
Determination of Disperse Orange 1 (CASno. 2581-69-3) in sample #13024; results in mg/kg

lab	method	value	mark	z(targ)	remarks
362	In house	<1.0		<-3.47	False negative?
551	DIN54231	85.2	C	-1.47	First reported 403.07
840		84.3		-1.49	
2115	DIN54231	235.81		2.12	
2127		-----		-----	
2129	DIN54231	88.5		-1.39	
2132	In house	61.3		-2.04	
2135	DIN54231	55		-2.19	
2139	DIN54231	166.2		0.46	
2165	DIN54231	100		-1.11	
2172	DIN54231	120		-0.64	
2184	DIN54231	97		-1.19	
2201	DIN54231	280.5		3.18	
2213	DIN54231	133		-0.33	
2217	In house	249.3		2.44	
2232	DIN54231	247.5		2.39	
2247		-----		-----	
2255	DIN54231	126.0		-0.50	
2272	DIN54231	214.2		1.60	
2284	DIN54231	205.5		1.40	
2285	GB/T 20383	109	C	-0.90	First reported 352
2289		290		3.41	
2290		129.1		-0.42	
2295		81		-1.57	
2297	DIN54231	228		1.93	
2310	DIN54231	105		-1.00	
2311	DIN54231	101		-1.09	
2350	DIN54231	131.7		-0.36	
2352	DIN54231	103.64		-1.03	
2354		75.18		-1.71	
2357	DIN54231	96		-1.21	
2359	DIN54231	86.0		-1.45	
2363	DIN54231	105		-1.00	
2365	GB/T 20383	91.13		-1.33	
2370	DIN54231	80.0		-1.59	
2375	DIN54231	99.8		-1.12	
2379		49.85		-2.31	
2380	DIN54231	97.26		-1.18	
2386	DIN54231	79.7		-1.60	
2390	DIN54231	178.647		0.76	
2410		176		0.69	
2415	DIN54231	221.79		1.78	
2425	DIN54231	204.01		1.36	
2428	GB/T 20383	110	C	-0.88	First reported 336
2447		-----		-----	
2452	DIN54231	301.748		3.68	
2461	GB/T 20383	114	C	-0.78	First reported 342
2475	DIN54231	54.14		-2.21	
2482		61.27		-2.04	
2488	DIN54231	126.1460		-0.49	
2489	DIN54231	122.0		-0.59	
2492	In house	92		-1.31	
2494	DIN54231	258.25		2.65	
2497	DIN54231	73.15	C	-1.75	First reported 19.97
2511	DIN54231	475.5	C,G(0.01)	7.82	First reported 355.2
2515	DIN54231	251.3		2.48	
2520		-----		-----	
2549	DIN54231	150.24		0.08	
3107	DIN54231	178.5		0.75	
3116	In house	<15		<-3.14	False negative
3146	DIN54231	114		-0.78	
3150	DIN54231	222		1.79	
3153	DIN54231	186		0.93	
3154		73.96		-1.73	
3172	DIN54231	286.0	C	3.31	First reported 474
3176		94.8		-1.24	
3180		92.3		-1.30	
3185	DIN54231	248		2.41	
3190	DIN54231	239.9		2.21	
3192	DIN54231	192.5		1.09	
3197		120		-0.64	
3199	In house	248		2.41	
3200	DIN54231	166.7		0.47	

3203	DIN54231	134	-0.31
3209		185.2	0.91
3210	DIN54231	189	1.00
3214	DIN54231	129.21	-0.42
3218		280	3.17
3220	DIN54231	90.9	-1.33
3226	DIN54231	108.45	-0.91
3228		105	-1.00
3233	DIN54231	143.78	-0.07
3237	In house	180.792	0.81
3242	DIN54231	200.65	1.28
3248	DIN54231	63.3	-1.99

normality	not OK
n	78
outliers	1
mean (n)	146.863
st.dev. (n)	68.6421
R(calc.)	192.198
R(DIN54231:05)	117.690





APPENDIX 2

Summary of all other reported Disperse dyes in samples #13023 and #13024; results in mg/kg

Lab	Other reported Disperse Dyes on #13023
2494	Disperse Blue 35 = 7.63, Disperse Orange 1 = 27.54

Lab	Other reported Disperse Dyes on #13024
2475	Disperse Red 11 = 32.65
2488	Disperse Orange 3 = 3.6995
2494	Disperse Orange 76 = 12
2497	Disperse Blue 1 = 61.74
2520	Disperse Blue 1 = 167.466, Disperse Yellow 3 = 1.5
3116	Disperse Yellow 3 = 101.5
3237	Disperse Red 11 = 9.6279, Disperse Yellow 3 = 6.8058

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
	DI Yellow 3			DI Blue 3			DI Orange 1		
362	Dr. Ehrerstorfer	100 mg/l	Solution	Dr. Ehrerstorfer	100 mg/l	Solution	Dr. Ehrerstorfer	100 mg/l	Solution
551	--	--	--	--	--	--	--	--	--
840	Sigma Aldrich	24%	Powder	Sigma Aldrich	7%	Powder	Sigma Aldrich	14%	Powder
2115	Dr. Ehrerstorfer	30%	Powder	Dr. Ehrerstorfer	24%	Powder	Dr. Ehrerstorfer	80%	Powder
2127	Dr. Ehrerstorfer	30%	Powder	Dr. Ehrerstorfer	24%	Powder	--	--	--
2129	Dr. Ehrerstorfer	30%	Powder	Dr. Ehrerstorfer	24%	Powder	Dr. Ehrerstorfer	80%	Powder
2132	Sigma Aldrich	30%	Powder	Sigma Aldrich	20%	Powder	Sigma Aldrich	25%	Powder
2135	Sigma Aldrich	30%	Powder	Sigma Aldrich	20%	Powder	Sigma Aldrich	25%	Powder
2139	Dr. Ehrerstorfer	30%	Powder	Dr. Ehrerstorfer	24%	Powder	Dr. Ehrerstorfer	80%	Powder
2165	Dr. Ehrerstorfer	30%	Powder	Accustd	100 mg/L	Solution	Dr. Ehrerstorfer	80%	Powder
2172	Sigma Aldrich	30%	Powder	Sigma Aldrich	20%	Powder	Sigma Aldrich	15%	Powder
2184	Dr. Ehrerstorfer	30%	Powder	Dr. Ehrerstorfer	24%	Powder	Dr. Ehrerstorfer	80%	Powder
2201	Dr. Ehrerstorfer	30%	Powder	Sigma Aldrich	20%	Powder	Dr. Ehrerstorfer	80%	Powder
2213	Dr. Ehrerstorfer	30%	Powder	Dr. Ehrerstorfer	24%	Powder	Dr. Ehrerstorfer	80%	Powder
2217	Dr. Ehrerstorfer	30%	Powder	Dr. Ehrerstorfer	24%	Powder	Dr. Ehrerstorfer	80%	Powder
2232	Sigma Aldrich	30%	Powder	Sigma Aldrich	20%	Powder	Sigma Aldrich	61.9%	Powder
2247	--	--	--	--	--	--	--	--	--
2255	Dr. Ehrerstorfer	30%	Powder	Dr. Ehrerstorfer	24%	Powder	Dr. Ehrerstorfer	80%	Powder
2272	Dr. Ehrerstorfer	30%	Powder	Dr. Ehrerstorfer	24%	Powder	Dr. Ehrerstorfer	80%	Powder
2284	Dr. Ehrerstorfer	30%	Powder	Sigma Aldrich	20%	Powder	Dr. Ehrerstorfer	80%	Powder
2285	Dr. Ehrerstorfer	30%	Powder	Dr. Ehrerstorfer	24%	Powder	Dr. Ehrerstorfer	80%	Powder
2289	Dr. Ehrerstorfer	30%	Powder	Dr. Ehrerstorfer	24%	Powder	Dr. Ehrerstorfer	80%	Powder
2290	Dr. Ehrerstorfer	30%	Powder	Sigma Aldrich	20%	Powder	Sigma Aldrich	15%	Powder
2295	Sigma Aldrich	30%	Powder	Sigma Aldrich	20%	Powder	Sigma Aldrich	15%	Powder
2297	Dr.Ehrerstorfer	--	--	--	--	--	--	--	--
2310	Sigma Aldrich	24%	Powder	Sigma Aldrich	7%	Powder	Sigma Aldrich	14%	Powder
2311	Sigma Aldrich	24%	Powder	Sigma Aldrich	7%	Powder	Sigma Aldrich	14%	Powder
2350	Sigma Aldrich	30%	Powder	Sigma Aldrich	20%	Powder	Sigma Aldrich	15%	Powder
2352	Sigma Aldrich	24%	Powder	Sigma Aldrich	7%	Powder	Sigma Aldrich	14%	Powder
2354	Sigma Aldrich	30%	Powder	Sigma Aldrich	20%	Powder	Sigma Aldrich	25%	Powder
2357	Sigma Aldrich	30%	Powder	Sigma Aldrich	20%	Powder	Sigma Aldrich	25%	Powder
2359	Sigma Aldrich	30%	Powder	Sigma Aldrich	20%	Powder	Sigma Aldrich	14%	Powder
2363	Sigma Aldrich	24%	Powder	Sigma Aldrich	7%	Powder	Sigma Aldrich	14%	Powder
2365	Sigma Aldrich	24%	Powder	Sigma Aldrich	7%	Powder	Sigma Aldrich	14%	Powder
2370	Sigma Aldrich	30%	Powder	Sigma Aldrich	20%	Powder	Sigma Aldrich	15%	Powder
2375	Sigma Aldrich	24%	Powder	Sigma Aldrich	7%	Powder	Sigma Aldrich	14%	Powder
2379	Sigma Aldrich	24%	Powder	Sigma Aldrich	7%	Powder	Sigma Aldrich	14%	Powder
2380	Sigma Aldrich	24%	Powder	Sigma Aldrich	7%	Powder	Sigma Aldrich	14%	Powder
2386	Sigma Aldrich	--	Powder	Sigma Aldrich	--	Powder	Sigma Aldrich	--	Powder
2390	Sigma Aldrich	23%	Powder	Sigma Aldrich	7%	Powder	Sigma Aldrich	15%	Powder
2410	Dr. Ehrerstorfer	30%	Powder	Dr. Ehrerstorfer	24%	Powder	Dr. Ehrerstorfer	80%	Powder
2415	Dr. Ehrerstorfer	30%	Powder	Dr. Ehrerstorfer	24%	Powder	Dr. Ehrerstorfer	80%	Powder
2425	Dr. Ehrerstorfer	30%	Powder	Sigma Aldrich	20%	Powder	Dr. Ehrerstorfer	80%	Powder
2428	Dr. Ehrerstorfer	30%	Powder	Dr. Ehrerstorfer	24%	Powder	Dr. Ehrerstorfer	80%	Powder
2447	--	--	--	--	--	--	--	--	--
2452	Sigma Aldrich	30%	Powder	Sigma Aldrich	20%	Powder	Dr. Ehrerstorfer	80%	Powder
2461	Dr. Ehrerstorfer	30%	Powder	Dr. Ehrerstorfer	24%	Powder	Dr. Ehrerstorfer	80%	Powder
2475	--			Dr. Ehrerstorfer	24%	Powder	Dr. Ehrerstorfer	80%	Powder
2482	Dr. Ehrerstorfer	30%	Powder	Sigma Aldrich	20%	Powder	MP Biomedicals	30%	Powder
2488	Dr. Ehrerstorfer	30%	Powder	Dr. Ehrerstorfer	24%	Powder	Dr. Ehrerstorfer	80%	Powder
2489	Dr. Ehrerstorfer	30%	Powder	Dr. Ehrerstorfer	24%	Powder	Dr. Ehrerstorfer	80%	Powder
2492	--	--	--	--	--	--	--	--	--
2494	Sigma Aldrich	30%	Powder	Dr. Ehrerstorfer	24%	Powder	Dr. Ehrerstorfer	--	Powder
2497	Dr. Ehrerstorfer	30%	Powder	Dr. Ehrerstorfer	24%	Powder	--	--	--
2511	Accustd	100 mg/l	Solution	Accustd	100 mg/l	Solution	Accustd	100 mg/l	Solution
2515	Sigma Aldrich	30%	Powder	Sigma Aldrich	20%	Powder	Sigma Aldrich	15%	Powder

2520	Sigma Aldrich	30%	Powder	--	--	--	--	--	--
2549	Sigma Aldrich	30%	Powder	Dr. Ehrerstorfer	24%	Powder	Dr. Ehrerstorfer	80%	Powder
3107	Dr. Ehrerstorfer	30%	Powder	Dr. Ehrerstorfer	24%	Powder	Dr. Ehrerstorfer	80%	Powder
3116	Sigma Aldrich	30%	Powder	Sigma Aldrich	20%	Powder	Sigma Aldrich	15%	Powder
3146	Dr. Ehrerstorfer	30%	Powder	Sigma Aldrich	20%	Powder	Dr. Ehrerstorfer	80%	Powder
3150	Dr. Ehrerstorfer	30%	Powder	Dr. Ehrerstorfer	24%	Powder	Dr. Ehrerstorfer	80%	Powder
3153	Sigma Aldrich	30%	Powder	Sigma Aldrich	20%	Powder	Sigma Aldrich	15%	Powder
3154	Dr. Ehrerstorfer	30%	Powder	Dr. Ehrerstorfer	24%	Powder	Dr. Ehrerstorfer	80%	Powder
3172	Accustd	100 mg/l	Solution	Accustd	100 mg/l	Solution	Accustd	100 mg/l	Solution
3176	--	--	--	--	--	--	--	--	--
3180	Dr. Ehrerstorfer	30%	Powder	Dr. Ehrerstorfer	20%	Powder	Dr. Ehrerstorfer	80%	Powder
3185	Dr. Ehrerstorfer	30%	Powder	Dr. Ehrerstorfer	24%	Powder	Dr. Ehrerstorfer	80%	Powder
3190	Dr. Ehrerstorfer	30%	Powder	Dr. Ehrerstorfer	24%	Powder	Dr. Ehrerstorfer	80%	Powder
3192	Dr. Ehrerstorfer	30%	Powder	--	--	--	Dr. Ehrerstorfer	80%	Powder
3197	Dr. Ehrerstorfer	30%	Powder	Dr. Ehrerstorfer	24%	Powder	Dr. Ehrerstorfer	80%	Powder
3199	Sigma Aldrich	30%	Powder	Sigma Aldrich	20%	Powder	Dr. Ehrerstorfer	80%	Powder
3200	Dr. Ehrerstorfer	30%	Powder	Dr. Ehrerstorfer	24%	Powder	Dr. Ehrerstorfer	80%	Powder
3203	Dr. Ehrerstorfer	90%	Powder	Dr. Ehrerstorfer	20%	Powder	Dr. Ehrerstorfer	80%	Powder
3209	Dr. Ehrerstorfer	30%	Powder	Dr. Ehrerstorfer	24%	Powder	Dr. Ehrerstorfer	80%	Powder
3210	Dr. Ehrerstorfer	30%	Powder	Dr. Ehrerstorfer	24%	Powder	Dr. Ehrerstorfer	80%	Powder
3214	Sigma Aldrich	30%	Powder	Dr. Ehrerstorfer	11%	Powder	Dr. Ehrerstorfer	30%	Powder
3218	Dr. Ehrerstorfer	30%	Powder	Sigma Aldrich	20%	Powder	Dr. Ehrerstorfer	80%	Powder
3220	Dr. Ehrerstorfer	30%	Powder	Dr. Ehrerstorfer	24%	Powder	Dr. Ehrerstorfer	80%	Powder
3226	Fluka	96%	Powder	Sigma Aldrich	20%	Powder	Fluka	96%	Powder
3228	Dr. Ehrerstorfer	30%	Powder	Dr. Ehrerstorfer	50%	Powder	Dr. Ehrerstorfer	80%	Powder
3233	Sigma Aldrich	30%	Powder	Sigma Aldrich	20%	Powder	Sigma Aldrich	15%	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

3 labs in	BANGLADESH
1 lab in	BRAZIL
1 lab in	BULGARIA
1 lab in	EGYPT
3 labs in	FRANCE
9 labs in	GERMANY
7 labs in	HONG KONG
1 lab in	HUNGARY
8 labs in	INDIA
1 lab in	INDONESIA
4 labs in	ITALY
3 labs in	KOREA
23 labs in	P.R. of CHINA
1 lab in	PAKISTAN
1 lab in	SINGAPORE
1 lab in	SWITZERLAND
2 labs in	TAIWAN R.O.C.
1 lab in	THAILAND
2 labs in	TUNESIA
6 labs in	TURKEY
1 lab in	U.S.A.
1 lab in	UNITED KINGDOM
4 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
n.e. = not evaluated
n.d. = not detected

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