Results of Proficiency Test
AZO dyes in leather
March 2012

Organised by: Institute for Interlaboratory Studies
Spijkenisse, the Netherlands

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1 INTRODUCTION

The Institute for Interlaboratory Studies (iis) organizes every year a scheme of proficiency test for banned AZO dyes in leather since 1997, with an exception in 2009.
In this interlaboratory study, 92 laboratories in 26 different countries have participated (see appendix 4). In this report, the results of this proficiency test are presented and discussed.

2 SET UP

The Institute for Interlaboratory Studies in Spijkenisse was the organizer of this proficiency test. Due to lack of suitable materials it was decided to use in this proficiency test only one leather sample. This leather sample was prepared and tested for homogeneity by an accredited third party laboratory.
Participants were requested to report results with one extra figure. These results with an extra figure are preferably used for statistical evaluation. The participants were asked to report the analytical results using the indicated units on the report form.

2.1 QUALITY SYSTEM

The Institute for Interlaboratory Studies in Spijkenisse, the Netherlands, has implemented a quality system based on ISO guide 43 and EN/ISO 17043:2010. This ensures strict adherence to protocols for sample preparation and statistical evaluation and 100% confidentiality of participant's data. Also customer's satisfaction is measured on a regular basis by sending out questionnaires.

2.2 PROTOCOL

The protocol followed in the organization was the one as described for proficiency testing in the report 'iis Interlaboratory Studies: Protocol for the Organization, Statistics and Evaluation' of January 2010 (iis-protocol, version 3.2).

2.3 CONFIDENTIALITY STATEMENT

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

2.4 SAMPLES

A suitable sample, positive on two AZO dyes, was bought on the local market. After cutting it into pieces, the material was mixed thoroughly. Eight stratified randomly selected samples were tested using DIN 53316 to check the homogeneity of the batch. See the following table for the test results.

	Benzidine in mg/kg
sample #12032-1	410
sample #12032-2	415
sample #12032-3	402
sample #12032-4	409
sample #12032-5	408
sample #12032-6	420
sample #12032-7	419
sample #12032-8	406

table 1: homogeneity test results of subsamples #12032

From the above test results the repeatability was calculated and compared with 0.3 times the corresponding reproducibility of the target method in agreement with the procedure of ISO 13528, Annex B2 in the next table:

	Benzidine in mg/kg
r (observed)	22
reference method	ISO17234-1:2010
0.3 x R (reference method)	71

table 2: evaluation of the repeatability of subsamples #12032

The repeatability of the results of homogeneity test for Benzidine was in agreement with 0.3 times the reproducibility mentioned in the reference method ISO17234:2010.
Therefore, homogeneity of the subsamples was assumed.

Approx. 3 grams of sample #12032 was sent to the participating laboratories on March 7, 2012.

2.5 ANALYSES

The participants were asked to determine the concentrations of 23 forbidden aromatic amines and o-anisidine, applying the analysis procedure that is routinely used in the laboratory. To get comparable results reported a detailed report form, on which the requested amines and the units were pre-printed, was sent together with each sample. Also a letter of instructions was sent along.

3 RESULTS

During four weeks after sample despatch, the results of the individual laboratories were gathered. The original data are tabulated in the appendices of this report. The laboratories are presented by their code numbers.

Directly after the deadline, a reminder fax was sent to those laboratories that had not yet reported. Shortly after the deadline, the available results were screened for suspect data. A result was called suspect in case the Huber Elimination Rule (a robust outlier test, see lit.5) found it to be an outlier. The laboratories that produced these suspect data were asked to check the results. Additional or corrected data are placed under 'Remarks' in the result tables in appendix 1. A list of abbreviations used in the tables can be found in appendix 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.
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 some reporting problems occurred. Eighteen participants reported test results after the deadline and two participants did not report any test results. Finally, 90 participants did report 175 numerical results. Observed were 14 outlying results, which is 8.0% of the numerical results. In proficiency studies, outlier percentages of 3% - 7.5% are quite normal.
Both aromatic amines present were detected by the majority of the participating laboratories and both data sets did proof to have a normal Gaussian distribution.

4.1 EVALUATION PER SAMPLE AND COMPONENT

In this section, the results are discussed per sample. All statistical results reported on the leather sample are summarised in appendix 1 and all other reported results of aromatic amines present are listed in appendix 2.

4-Aminodiphenyl: The determination of this aromatic amine at a concentration level of 24.6 mg/kg was problematic for a number of participants. Six statistical outliers were observed.
The test results reported by the participants vary from 0.54 – 821 mg/kg.
The observed reproducibility after rejection of the statistical outliers is in agreement with the estimated reproducibility requirement estimated from the standard test method ISO 17234-1:2010.

Benzidine: The determination of this aromatic amine at a concentration level of 422 mg/kg was problematic for a number of participants. Eight statistical outliers were observed.
The test results reported by the participants vary from 13.6 – 790 mg/kg.
The observed reproducibility after rejection of the statistical outliers is in full agreement with the reproducibility requirement estimated from the standard test method ISO 17234-1:2010.

General: Fifteen participants reported besides above aromatic amines also the presence of other aromatic amines at different concentration levels.
Ten participants reported to have detected 2-Naphtylamine (between 0.11 – 600 mg/kg) and six participants reported having detected 2.4-Diaminotoluene (between 8.9 – 33.3 mg/kg), see appendix 2.

4.2 PERFORMANCE EVALUATION FOR THE GROUP OF LABORATORIES

A comparison has been made between the reproducibility as declared by the relevant standard methods (references 1 - 4) and the reproducibilities as found for the group of participating laboratories.

The number of significant results, the average result, the calculated reproducibility (standard deviation*2.8) and the target reproducibility, derived from an official test method like ISO17234-1:2010 (equal to the reproducibility from LMBG 82.02.3:97) and Horwitz equation are in the next table.

Parameter	unit	n	Average	2.8 * sd	R(target)
4-Aminodiphenyl	mg/kg	80	24.59	16.85	15.82
Benzidine	mg/kg	81	421.6	230.1	244.8

table 3: reproducibility of aromatic amine in leather sample #12032

Without further statistical calculations, it can be concluded that the group of participating laboratories has on average no problems with the analysis of AZO dyes in leather.
See also the discussion in paragraphs 4.1 and 6.

5 COMPARISON WITH PREVIOUS INTERLABORATORY STUDIES

The spread in the results is small in comparison with the spreads of the other aromatic amines as observed in previous PTs, see below table.

Parameter	*March 2012*	*March 2011*	*March 2010*	*March 2008*	*March 2007*	*April 2006*	*LMBG 82.02.3:97*
4-Aminodiphenyl	69%	n.e.	n.e.	n.e.	n.e.	127%	Unknown
Benzidine	55%	n.e.	n.e.	105%	126%	133%	43 – 69%
3,3-Dimethylbenzidine	n.e.	n.e.	n.e.	n.d.	126%	n.e.	42 – 66%
o-Toluidine	n.e.	n.e.	n.e.	140%	n.e.	n.e.	84– 103%
2,4-Xylidine	n.e.	53%	44%	n.e.	n.e.	n.e.	n.e.

table 4: development of relative reproducibilities over the years

The observed spreads of the test results for both evaluated aromatic amines show a significant quality improvement since the previous PT in which they were evaluated.

6 DISCUSSION

From the reported test methods it appeared that most participants treated the leather samples according identical test methods: ISO17234-1 or LFBG 82.02.3.
Although almost all participants used the same test method, it can be concluded that the spread observed in this interlaboratory study is not caused by just one critical point in the analysis. Each participating laboratory will have to evaluate its performance in this study and decide about any corrective actions if necessary.

APPENDIX 1

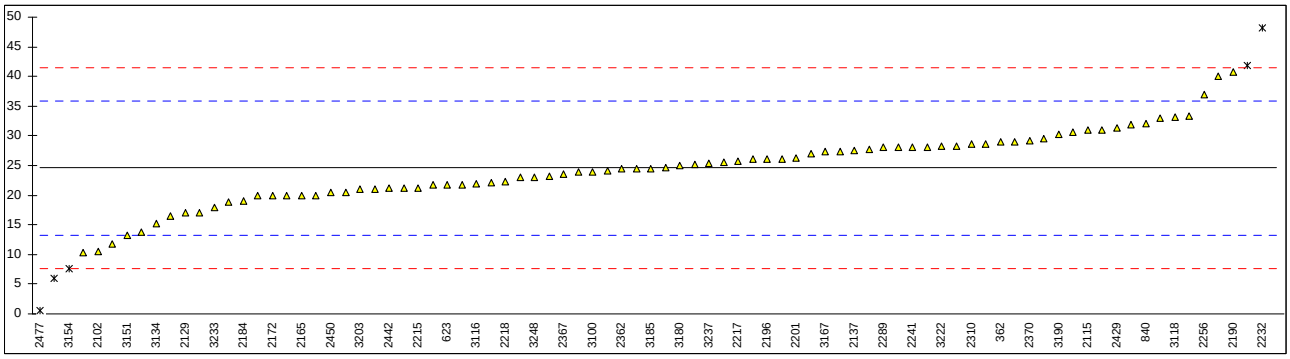
Determination of 4-Aminodiphenyl (CASno.92-67-1) in sample #12032; results in mg/kg

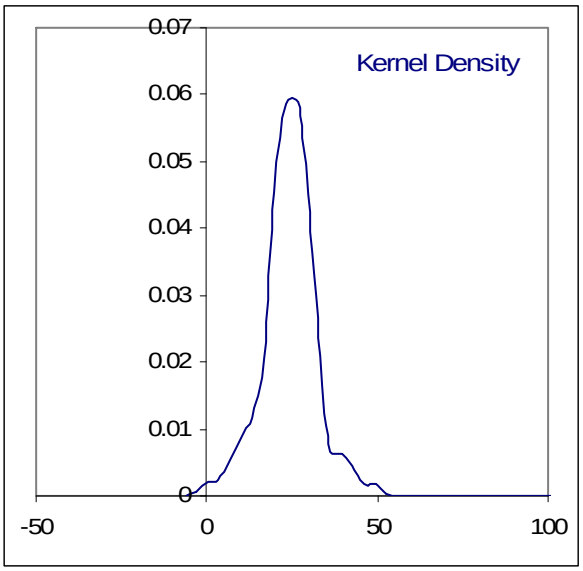
lab	method	value	mark	z(targ)	remarks
110	ISO17234-1	28.25		0.65	
362	ISO17234-1	28.92		0.77	
551	ISO17234-1	820.97	G(0.01)	140.93	
622	ISO17234-1	6.0037	C,G(0.05)	-3.29	First reported 4.3262
623	ISO17234-1	21.70		-0.51	
840	ISO17234-1	32		1.31	
2102	in house	10.51		-2.49	
2115	ISO17234-1	30.93		1.12	
2129	ISO17234-1	17		-1.34	
2131		-----		-----	
2132	ISO17234-1	27.3		0.48	
2137	ISO17234-1	27.5		0.52	
2139	ISO17234-1	11.7	C	-2.28	First reported 7.7
2146	ISO17234	32.9		1.47	
2165	GB/T 19942	20		-0.81	
2172	ISO17234-1	19.9		-0.83	
2184	ISO17234-1	19		-0.99	
2190	ISO17234-1	40.7		2.85	
2196	ISO17234-1	26		0.25	
2201	ISO17234-1	26.2		0.29	
2215	ISO17234	21.2		-0.60	
2217	ISO17234	25.7		0.20	
2218	ISO17234	22.2		-0.42	
2221	ISO17234-1	28		0.60	
2232	ISO17234-1	48.15	C,DG(0.05)	4.17	First reported 79.16
2236	ISO17234-1	<10		-----	
2238	ISO17234	28.7		0.73	
2241	ISO17234	28		0.60	
2247	ISO17234	30.7		1.08	
2252	ISO17234-1	25.2		0.11	
2255	ISO17234	29.52		0.87	
2256	ISO17234-1	37.0		2.20	
2261	GB/T 19942	20		-0.81	
2266	ISO17234-1	10.4		-2.51	
2272	ISO17234-1	17.1		-1.33	
2284	ISO17234-1	26		0.25	
2289	ISO17234	28		0.60	
2295	ISO17234-1	16.4		-1.45	
2310	ISO17234-1	28.7		0.73	
2311	ISO17234-1	21.2		-0.60	
2350	ISO17234	19.9		-0.83	
2359	ISO17234-1	25.5		0.16	
2362	ISO17234-1	24.4		-0.03	
2364	ISO17234-1	24		-0.10	
2366	ISO17234-1	22.1		-0.44	
2367	ISO17234-2	23.5		-0.19	
2368	ISO17234-1	26		0.25	
2370	ISO17234-1	29.2		0.82	
2372	LMBG 82.02-2	21.01		-0.63	
2375	ISO17234-1	24.08		-0.09	
2380	EN14362-1	23.00		-0.28	
2386	LFBG 82.02-3	33.4		1.56	
2390	ISO17234	13.68	C	-1.93	First reported 8.778
2403	ISO17234	29		0.78	
2413		-----		-----	
2429	ISO17234-1	31.33		1.19	
2432	in house	41.86	G(0.05)	3.06	
2442	in house	21.18		-0.60	
2450	ISO17234	20.5		-0.72	
2452		-----		-----	
2477	DIN53316	0.5395	DG(0.05)	-4.26	
3100	ISO17234-1	24		-0.10	
3104	ISO17234-1	21.79		-0.50	
3116	ISO17234	22		-0.46	
3117	ISO17234-1	31		1.13	
3118	ISO17234	33.18		1.52	
3134	ISO17234	15.2		-1.66	
3151	ISO17234-1	13.2		-2.02	
3153	ISO17234	24.6		0.00	
3154	DIN53316	7.66	G(0.05)	-3.00	
3160	ISO17234-1	31.91		1.30	
3163		-----		-----	
3167	ISO17234-1	27.3		0.48	

3172	ISO17234-1	18.8	-1.02
3180	ISO17234-1	25	0.07
3182	ISO17234-1	24.49	-0.02
3185	ISO17234-1	24.5	-0.02
3190	ISO17234	30.2	0.99
3191	ISO17234-1	28	0.60
3192	LFBG 82.02-3	27.7	0.55
3199	ISO17234-1	20.5	-0.72
3200	ISO17234-1	23.1	-0.26
3203	ISO17234	21	-0.63
3209	ISO17234-1	21.7	-0.51
3210		-----	-----
3218	ISO17234-1	27	0.43
3220	ISO17234	40.0	2.73
3222	ISO17234-1	28.2	0.64
3228	ISO17234-1	20	-0.81
3233	ISO17234-1	18.0	-1.17
3237	in house	25.342	0.13
3248	ISO17234	23	-0.28

normality	OK
n	80
outliers	6
mean (n)	24.588
st.dev. (n)	6.0185
R(calc.)	16.852
R(ISO17234-1:10)	15.822

Compare R(Horwitz) = 6.803





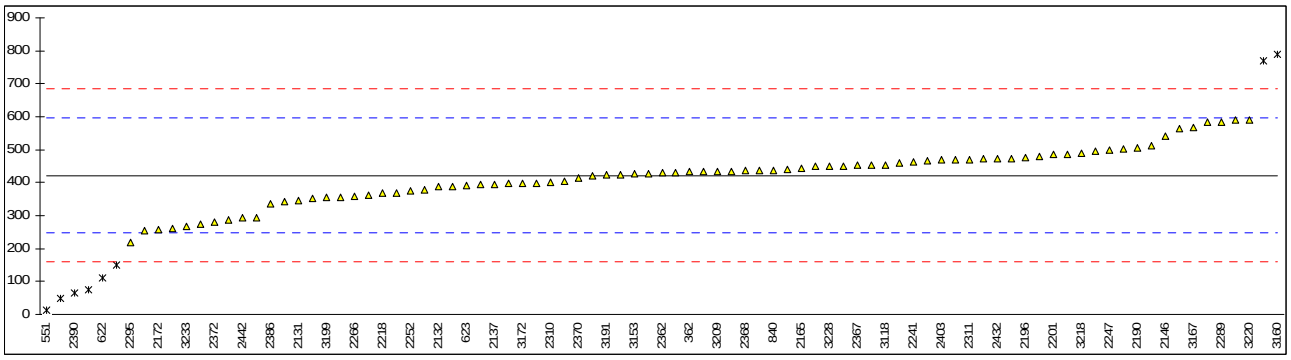
Determination of Benzidine (CASno.92-87-5) in sample #12032; results in mg/kg

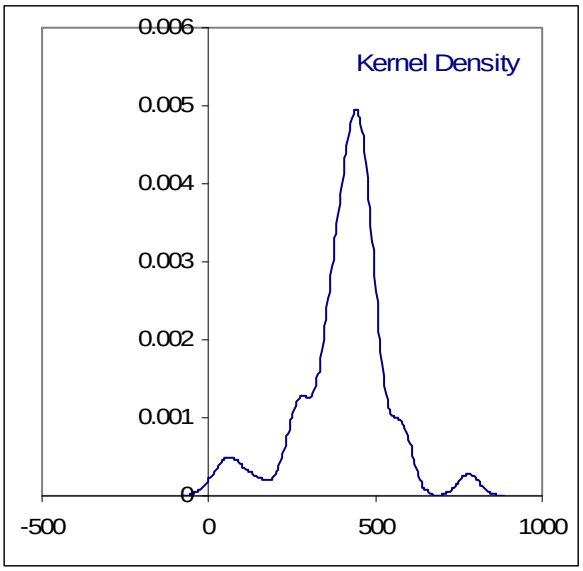
lab	method	value	mark	z(targ)	remarks
110	ISO17234-1	465.11		0.50	
362	ISO17234-1	432.6		0.13	
551	ISO17234-1	13.620	DG(0.05)	-4.67	
622	ISO17234-1	109.3013	C,DG(0.05)	-3.57	First reported 91.9990
623	ISO17234-1	390.28		-0.36	
840	ISO17234-1	438		0.19	
2102	in house	389.39		-0.37	
2115	ISO17234-1	771.00	DG(0.05)	4.00	
2129	ISO17234-1	362		-0.68	
2131	in house	347		-0.85	
2132	ISO17234-1	388.1		-0.38	
2137	ISO17234-1	395.9		-0.29	
2139	ISO17234-1	351		-0.81	
2146	ISO17234	542.7		1.39	
2165	GB/T 19942	443		0.24	
2172	ISO17234-1	257		-1.88	
2184	ISO17234-1	440		0.21	
2190	ISO17234-1	506.5		0.97	
2196	ISO17234-1	476		0.62	
2201	ISO17234-1	484.8		0.72	
2215	ISO17234	403		-0.21	
2217	ISO17234	501.5		0.91	
2218	ISO17234	369.9		-0.59	
2221	ISO17234-1	427		0.06	
2232	ISO17234-1	582.5	C	1.84	First reported 741.7
2236	ISO17234-1	431.1		0.11	
2238	ISO17234	460.0		0.44	
2241	ISO17234	464		0.49	
2247	ISO17234	498.0		0.87	
2252	ISO17234-1	375.6		-0.53	
2255	ISO17234	485.71		0.73	
2256	ISO17234-1	479.1		0.66	
2261	GB/T 19942	288		-1.53	
2266	ISO17234-1	359.0		-0.72	
2272	ISO17234-1	272.3		-1.71	
2284	ISO17234-1	512		1.03	
2289	ISO17234	583		1.85	
2295	ISO17234-1	218		-2.33	
2310	ISO17234-1	401		-0.24	
2311	ISO17234-1	471.0		0.57	
2350	ISO17234	370		-0.59	
2359	ISO17234-1	450.8		0.33	
2362	ISO17234-1	429.8		0.09	
2364	ISO17234-1	474		0.60	
2366	ISO17234-1	449.7		0.32	
2367	ISO17234-2	452		0.35	
2368	ISO17234-1	437		0.18	
2370	ISO17234-1	413		-0.10	
2372	LMBG 82.02-2	280.05		-1.62	
2375	ISO17234-1	589.78	C	1.92	First reported 733.27
2380	EN14362-1	453.00		0.36	
2386	LFBG 82.02-3	337		-0.97	
2390	ISO17234	64.30	C,DG(0.01)	-4.09	First reported 33.800
2403	ISO17234	468		0.53	
2413		-----		-----	
2429	ISO17234-1	424.35		0.03	
2432	in house	473.50		0.59	
2442	in house	292.75		-1.47	
2450	ISO17234	254		-1.92	
2452		-----		-----	
2477	DIN53316	74.4130	DG(0.01)	-3.97	
3100	ISO17234-1	399		-0.26	
3104	ISO17234-1	355.91		-0.75	
3116	ISO17234	398		-0.27	
3117	ISO17234-1	563		1.62	
3118	ISO17234	454.23		0.37	
3134	ISO17234	420.9		-0.01	
3151	ISO17234-1	261		-1.84	
3153	ISO17234	426		0.05	
3154	DIN53316	150.94	DG(0.05)	-3.10	
3160	ISO17234-1	789.55	DG(0.05)	4.21	
3163		-----		-----	
3167	ISO17234-1	568	C	1.67	First reported 695

3172	ISO17234-1	398.3		-0.27	
3180	ISO17234-1	437		0.18	
3182	ISO17234-1	471.64		0.57	
3185	ISO17234-1	435		0.15	
3190	ISO17234	496.0		0.85	
3191	ISO17234-1	424		0.03	
3192	LFBG 82.02-3	471		0.57	
3199	ISO17234-1	355.6		-0.75	
3200	ISO17234-1	395.1		-0.30	
3203	ISO17234	379		-0.49	
3209	ISO17234-1	434		0.14	
3210	ISO17234-1	47.5	C,DG(0.05)	-4.28	First reported 154
3218	ISO17234-1	488		0.76	
3220	ISO17234	591.0		1.94	
3222	ISO17234-1	342.7		-0.90	
3228	ISO17234-1	450		0.32	
3233	ISO17234-1	269		-1.75	
3237	in house	292.927		-1.47	
3248	ISO17234	433		0.13	

	normality	OK
	n	81
	outliers	8
	mean (n)	421.59
	st.dev. (n)	82.173
	R(calc.)	230.08
	R(ISO17234-1:2010)	244.81

Compare R(Horwitz) = 76.05





APPENDIX 2

Summary of all other reported AZO-dyes in sample #12032; results in mg/kg

lab	aromatic amines
362	28.41 mg/kg 2-Naphtylamine
2102	12.87 mg/kg 2-Naphtylamine; 23.87 mg/kg 3.3-Dimethoxybenzidine
2190	16.0 mg/kg 2-Naphtylamine
2251	11.2 mg/kg 3.3-Dimethoxybenzidine
2370	33.3 mg/kg 2.4-Diaminotoluene
2390	13.463 mg/kg 2.4-Diaminotoluene
2432	24.42 mg/kg 2-Naphtylamine
2442	9.99 mg/kg 2-Naphtylamine; 20.45 mg/kg 2.4-Diaminotoluene
2477	0.11 mg/kg 2-Naphtylamine; 0.21 mg/kg p-Chloraniline; 1.94 mg/kg 3.3-Dimethoxybenzidine; 2.58 mg/kg 3.3-Dimethylbenzidine;0.93 mg/kg 3.3-Dimethyl-4.4-diaminodiphenylmethane; 2.48 mg/kg 4.4-Diaminodiphenylether; 4.92 mg/kg 4.4-Diaminodiphenylsulfide; 0.90 mg/kg o-Toluidine
3118	16.39 mg/kg 2-Naphtylamine
3134	8.4 mg/kg 2-Naphtylamine; 12.9 mg/kg 2.4-Diaminotoluene
3163	600 mg/kg 2-Naphtylamine
3192	19.8 mg/kg 2-Naphtylamine
3203	8 mg/kg 2.4-Diaminotoluene
3222	14.4 mg/kg 2.4-Diaminotoluene

APPENDIX 3

Summary of analytical details

lab	Method used	Solvent for clean up	Detection (quantification)
110	ISO17234-1	Hexane	HPLC-DAD
362	ISO17234-1	--	GC/MS/MS
551	ISO17234-1	Hexane	GC/MS
622	ISO17234-1-2003	Hexane	GC/MS
623	ISO17234-1	Hexane	GC/MS
840	ISO17234-1	Hexane	GC/MS
2102	in house	Hexane	GC/MS
2115	ISO17234-1	MTBE	GC/MS
2129	ISO17234-1	MTBE	GC/MS
2131	in house	Hexane	GC/MS
2132	ISO17234-1	MTBE	LC/MS/MS
2137	ISO17234-1	MTBE	GC/MS
2139	ISO17234-1	Hexane	GC/MS
2146	ISO17234-2003	--	HPLC/DAD
2165	GB/T 19942	--	HPLC/DAD
2172	ISO17234-1	MTBE	GC/MS
2184	ISO17234-1	--	GC/MS
2190	ISO17234-1-2011	Hexane	GC/MS
2196	ISO17234-1	Hexane	GC/MS
2201	ISO17234-1	Hexane	HPLC/DAD
2215	ISO17234	MTBE	GC/MS
2217	ISO17234	Hexane	GC/MS
2218	ISO17234	MTBE	GC/MS
2221	ISO17234-1	Hexane	HPLC/DAD
2232	ISO17234-1	Hexane	GC/MS
2236	ISO17234-1	--	HPLC/DAD
2238	ISO17234	Hexane	HPLC/DAD
2241	ISO17234-2003	MTBE	GC/MS
2247	ISO17234	MTBE	HPLC/DAD
2252	ISO17234-1	Hexane	GC/MS
2255	ISO17234	--	GC/MS
2256	ISO17234-1	--	GC/MS
2261	GB/T 19942	MTBE	GC/MS
2266	ISO17234-1	Hexane	HPLC/UV
2272	ISO17234-1	Hexane	HPLC/UV
2284	ISO17234-1	Hexane	HPLC/UV
2289	ISO17234-2003	Hexane	HPLC/DAD
2295	ISO17234-1	Hexane	GC/MS
2310	ISO17234-1	Hexane	GC/MS
2311	ISO17234-1	Hexane	GC/MS
2350	ISO17234	MTBE	GC/MS
2359	ISO17234-1	Hexane	HPLC/DAD
2362	ISO17234-1	--	HPLC/DAD
2364	ISO17234-1-2010	MTBE	GC/MS
2366	ISO17234-1	MTBE	GC/MS
2367	ISO17234-2-2011	Hexylhydride	HPLC
2368	ISO17234-1	Hexane	GC/MS
2370	ISO17234-1	--	GC/MS
2372	LMBG 82.02-2	Hexane	GC/MS
2375	ISO17234-1	Hexane	GC/MS
2380	EN14362-1	Ethylacetate	GC/MS
2386	LFBG 82.02-3	MTBE	HPLC/UV
2390	ISO17234	Hexane	GC/MS
2403	ISO17234	MTBE	GC/MS
2413	--	--	--
2429	ISO17234-1	Hexane	GC/MS
2432	in house	Hexane	GC/MS
2442	in house	MTBE	GC/MS
2450	ISO17234	MTBE	GC/MS
2452	--	--	--
2477	DIN53316	Hexane	GC/MS
3100	ISO17234-1	--	GC/MS and HPLC/DAD
3104	ISO17234-1	--	GC/MS and HPLC/DAD
3116	ISO17234	--	GC/MS
3117	ISO17234-1	MTBE	HPLC/UV
3118	ISO17234	Hexane	GC/MS
3134	ISO17234	Hexane	GC/MS and GC/FID
3151	ISO17234-1	Hexane	GC/MS
3153	ISO17234	MTBE	HPLC/DAD
3154	DIN53316	MTBE	HPLC/DAD
3160	ISO17234-1	MTBE	HPLC/DAD

3163	--	--	GC/MS
3167	ISO17234-1	MTBE	HPLC/DAD
3172	ISO17234-1	Hexane	LC/UV/MS
3180	ISO17234-1	Hexane	GC/MS
3182	ISO17234-1	MTBE	HPLC/UV
3185	ISO17234-1	--	GC/MS and HPLC/DAD
3190	ISO17234	Hexane	HPLC/DAD
3191	ISO17234-1	Hexane	GC/MS and HPLC/DAD
3192	LFBG 82.02-3	MTBE	CE/DAD
3199	ISO17234-1	MTBE	GC/MS
3200	ISO17234-1	Hexane	GC/MS
3203	ISO17234-2010	Hexane	HPLC/UV
3209	ISO17234-1-2010	--	GC/MS and HPLC/DAD
3210	ISO17234-1	Methanol	HPLC/UV
3218	ISO17234-1	MTBE	GC/MS and HPLC/DAD
3220	ISO17234	Hexane	GC/MS and HPLC/DAD
3222	ISO17234-1	Methanol	GC/MS
3228	ISO17234-1	Hexane	GC/MS
3233	ISO17234-1	Hexane	LC/MS
3237	in house	Hexane	GC/MS
3248	ISO17234	--	GC/MS

APPENDIX 4

Number of participants per country

3 labs in	BANGLADESH
1 lab in	BRAZIL
1 lab in	BULGARIA
1 lab in	FINLAND
4 labs in	FRANCE
5 labs in	GERMANY
1 lab in	GREECE
9 labs in	HONG KONG
1 lab in	HUNGARY
4 labs in	INDIA
3 labs in	INDONESIA
3 labs in	ITALY
3 labs in	KOREA
1 lab in	MEXICO
33 labs in	P.R. of CHINA
1 lab in	PAKISTAN
1 lab in	SINGAPORE
1 lab in	SPAIN
2 labs in	SWITZERLAND
2 labs in	TAIWAN R.O.C.
1 lab in	THAILAND
2 labs in	THE NETHERLANDS
1 lab in	TUNESIA
3 labs in	TURKEY
4 labs in	U.S.A.
1 lab 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

Literature:

1 DIN 53316
2 ISO 17234:2010
3 LMBG 82.02-3:97
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10 W.J. Conover, Practical; Nonparametric Statistics, J. Wiley&Sons, NY, p.302, (1971)
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