Results of Proficiency Test
AZO dyes in leather
March 2013

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 proficiency test for banned AZO dyes in leather since 1997, with an exception in 2009.
In this 2013 interlaboratory study, 129 laboratories in 30 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 a sufficient amount 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 rounded and unrounded test results. These unrounded test results were 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, ILAC-G13:2007 and ISO/IEC 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 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

A suitable brown leather sample, positive on AZO dyes, was bought on the local market. After cutting it into small pieces of <0.1g, the material was mixed thoroughly. Five stratified randomly selected samples were tested using LFGB 82.02-3 to check the homogeneity of the batch. See the following table for the test results.

	Benzidine in mg/kg
sample #13022-1	64
sample #13022-2	65
sample #13022-3	56
sample #13022-4	56
sample #13022-5	61

table 1: homogeneity test results of subsamples #13022

From the above test results, the repeatability was calculated and compared with 0.3 times the corresponding reproducibility in agreement with the procedure of ISO13528, Annex B2, in the next table:

	Benzidine in mg/kg
r (observed)	12
reference method	ISO17234-1:2010
0.3 x R (reference method)	11

table 2: evaluation of the repeatability of subsamples #13022

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 #13022 was sent to each of the participating laboratories on February 27, 2013.

2.5 ANALYSES

The participants were requested 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 5.

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. Twenty seven participants reported test results after the deadline and four participants did not report any test results. Finally, 129 participants did report 166 numerical results. Observed were 6 outlying results, which is 4.7% of the numerical results. In proficiency studies, outlier percentages of 3% - 7.5% are quite normal.
Two aromatic amines present were detected by the majority of the participating laboratories. The data set of 2,4-Xylidene did proof to have a normal Gaussian distribution, the Benzidine data set shows a not normal distribution.
There is no reproducibility requirement for 2,4-Xylidene reported in ISO 17234-1:2010, therefore the target reproducibility was estimated from the reproducibilities of all aromatic amine compounds mentioned in ISO 17234-1:2010.

4.1 EVALUATION PER 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.

Benzidine: The determination of this aromatic amine at a concentration level of 100 mg/kg was problematic. Five statistical outliers were observed.
The test results reported by the participants vary from n.d. – 280 mg/kg.
The observed reproducibility after rejection of the statistical outliers is not in agreement with the reproducibility requirement estimated from the standard test method ISO 17234-1:2010.

2,4-Xylidene: The determination of this aromatic amine may be problematic, at a concentration level of 11 mg/kg. Only one statistical outlier was observed.
The test results reported by the participants vary from <5 – 94 mg/kg.
The observed reproducibility after rejection of the statistical outliers is not in agreement with the reproducibility requirement estimated from the standard test method ISO 17234-1:2010.

General: Twenty participants reported also the presence of other aromatic amines at different concentration levels.
Sixteen laboratories reported to have detected 4-Aminodiphenyl (between 3.0 – 14.1 mg/kg), eight laboratories 2,6-Xylidine (between 3.4 – 8.1 mg/kg), three laboratories 2-Napthylamine (between 1.5 – 10.1 mg/kg), 3,3-Methoxybenzidine (9.7 mg/kg), one laboratory 4-Amino-azobenzene (157.9 mg/kg) and one laboratory *o*-Toluidine (5.2 mg/kg), see appendix 2.

At least two laboratories would not have rejected this sample for containing too much banned Arylamines (according to OEKO-TEX Std 100 ed. 04/2013 of 20 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 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 test results, the average result, the calculated reproducibility (standard deviation*2.8) and the target reproducibility, derived from the official test method ISO17234-1:2010 (equal to the reproducibility from LMBG 82.02.3:97) are presented in the next table.

Parameter	unit	n	Average	2.8 * sd	R(target)
Benzidine	mg/kg	120	103.6	80.1	60.2
2,4-Xylidine	mg/kg	34	10.8	10.8	5.9

table 3: reproducibilities of aromatic amines in leather sample #13022

Without further statistical calculations, it can be concluded that the group of participating laboratories have 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 observed spread in the test results for the aromatic amines in the 2013 PT is large in comparison with the spread of the aromatic amine as observed in the previous PT, see below table.

Parameter	*March 2013*	*March 2012*	*March 2011*	*March 2010*	*March 2008*	*March 2007*	*April 2006*	*LMBG 82.02.3:97*
4-Aminodiphenyl	n.e	69%	n.e.	n.e.	n.e.	n.e.	127%	Unknown
Benzidine	77%	55%	n.e.	n.e.	105%	126%	133%	43 – 69%
3,3-Dimethylbenzidine	n.e	n.e.	n.e.	n.e.	n.d.	126%	n.e.	42 – 66%
o-Toluidine	n.e.	n.e.	n.e.	n.e.	140%	n.e.	n.e.	84– 103%
2,4-Xylidine	100%	n.e.	53%	44%	n.e.	n.e.	n.e.	n.e.

table 4: development of relative reproducibilities over the years

The average concentration of 2,4-Xylidene in the sample #13022 may be near or below the detection limit. This may explains the significant increase of the relative reproducibility. There is no detection limit mentioned in ISO17234-1:2010.

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.
Therefore, it can be concluded that the observed spread 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 Benzidine (CASno.92-87-5) in sample #13022; results in mg/kg

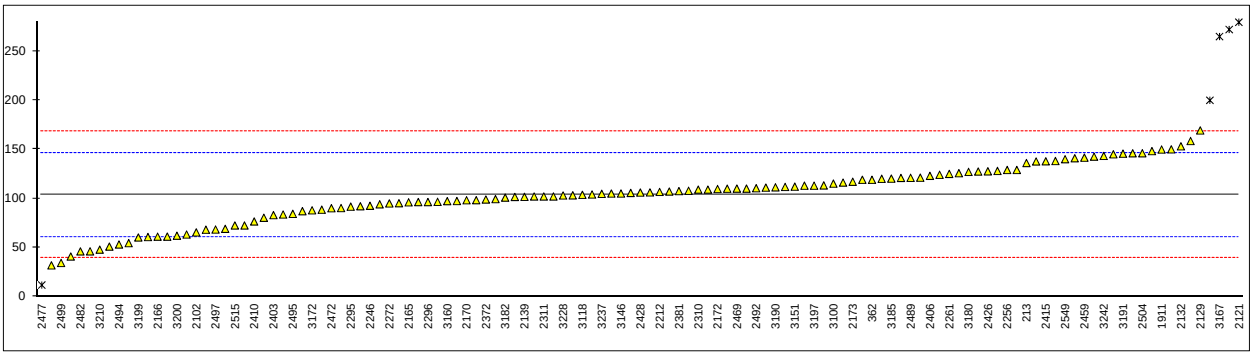
lab	method	value	mark	z(targ)	lab	method	value	mark	z(targ)
213	ISO17234-1	136.1		1.51	2429	ISO17234-1	113.27		0.45
348	ISO17234-1	97.36		-0.29	2432	in house	103.15		-0.02
362	ISO17234-1	119		0.71	2442	in house	99.32		-0.20
551	ISO17234-1	90.18		-0.63	2452	ISO17234-1	46.046		-2.68
840	ISO17234-1	107.8		0.19	2453		-----		-----
1911	ISO17234-1	149.8531		2.15	2459	ISO17234-1	141.550	C	1.76
2102	in house	65.38	C	-1.78	2469	ISO17234-1	110		0.30
2115	ISO17234-1	31.75		-3.34	2472	ISO17234-1	90		-0.63
2121	EN17234-1	279.6	G(0.01)	8.18	2476		-----		-----
2129	ISO17234-1	169.3		3.05	2477	DIN53316	11.65	G(0.01)	-4.28
2131	in house	72.45		-1.45	2479	ISO17234-1	128		1.13
2132	ISO17234-1	153.1		2.30	2482	ISO17234-1	45.98		-2.68
2139	ISO17234-1	101.6		-0.10	2489	ISO17234-1	121.0		0.81
2146	ISO17234-1	158.5		2.55	2492	in house	110.4		0.31
2165	EN14362-1	96		-0.36	2493		-----		-----
2166	ISO17234-1	61		-1.98	2494	ISO17234-1	53.05		-2.35
2170	ISO17234-1	98.10		-0.26	2495	ISO17234-1	84.3		-0.90
2172	ISO17234-1	109.6		0.28	2497	ISO17234-1	68.3	C	-1.64
2173	ISO17234-1	117		0.62	2499	ISO17234-1	34.222	C	-3.23
2184	ISO17234-1	102		-0.08	2504	ISO17234-1	146.05		1.97
2190	ISO17234-1	60.6		-2.00	2514	ISO17234-1	138.1		1.60
2201	ISO17234-1	120.9		0.80	2515	ISO17234-1	72.41		-1.45
2212	ISO17234-1	106.6		0.14	2526	ISO17234-1	104		0.02
2213	ISO17234-1	109		0.25	2534	ISO17234-1	n.d.		-----
2216		-----		-----	2538	in house	111.7		0.37
2235	ISO17234-1	116.18		0.58	2546	ISO17234-1	<30		-----
2238	ISO17234-1	102.0		-0.08	2549	ISO17234-1	140.0		1.69
2246	ISO17234-1	92.507		-0.52	2553	ISO17234-1	50.874		-2.45
2247	ISO17234-1	146.0		1.97	3100	ISO17234-1	115.1		0.53
2255	ISO17234-1	148.2		2.07	3104	ISO17234-1	105.60		0.09
2256	ISO17234-1	129		1.18	3116	ISO17234-1	113		0.44
2261	GB/T19942	125		0.99	3117	ISO17234-1	111		0.34
2271	ISO17234-1	96.3		-0.34	3118	ISO17234-1	103.66		0.00
2272	ISO17234-1	94.9		-0.41	3134	ISO17234-1	40.8		-2.92
2283	ISO17234-1	68.1		-1.65	3146	ISO17234-1	105		0.06
2284	ISO17234-1	63.2		-1.88	3150	ISO17234-1	88.5		-0.70
2286	ISO17234-1	120		0.76	3151	ISO17234-1	112		0.39
2287	ISO17234-1	87		-0.77	3153	ISO17234-1	145		1.92
2289	ISO17234-1	119		0.71	3154	DIN53316	140.95		1.74
2291	ISO17234-1	127.408		1.11	3160	ISO17234-1	97.21	C	-0.30
2295	ISO17234-1	91.6		-0.56	3167	ISO17234-1	265	G(0.01)	7.51
2296	ISO17234-1	96.3		-0.34	3172	ISO17234-1	87.9		-0.73
2297	ISO17234-1	69		-1.61	3176	ISO17234-1	124.1		0.95
2300	LFGB 82.02-3	83.58		-0.93	3180	ISO17234-1	127		1.09
2310	ISO17234-1	109		0.25	3182	EN14362-1	100.8		-0.13
2311	ISO17234-1	102		-0.08	3183	LFGB 852.02-3/9	137.69		1.58
2354	ISO17234-1	96.5		-0.33	3185	ISO17234-1	120.2		0.77
2359	ISO17234-1	98.2		-0.25	3190	ISO17234-1	111.3		0.36
2367	ISO17234-1	95.1		-0.40	3191	ISO17234-1	145.6		1.95
2368	ISO17234-1	92		-0.54	3192	LFGB 852.02-3	142.6		1.81
2370	LMBG82.02.3	107		0.16	3197	ISO17234-1	113		0.44
2372	ISO17234-1	98.9		-0.22	3199	ISO17234-1	60.2		-2.02
2373	ISO17234-1	94		-0.45	3200	ISO17234-1	62		-1.94
2375	ISO17234-1	109.9		0.29	3210	ISO17234-1	47.8		-2.60
2379	ISO17234-1	104.96	C	0.06	3214	ISO17234-1	121.17	C	0.82
2380	ISO17234-1	101.5		-0.10	3216	ISO17234-1	61.06		-1.98
2381	ISO17234-1	107.4		0.17	3218	ISO17234-1	110		0.30
2386	EN14362-1	129		1.18	3220	ISO17234-1	200.0	C, G(0.01)	4.48
2390	ISO17234-1	272.189	C, G(0.01)	7.84	3222	ISO17234-1	80.3		-1.09
2403	ISO17234-1	83		-0.96	3225	ISO17234-1	106.1		0.11
2406	ISO17234-1	123.02		0.90	3228	ISO17234-1	103		-0.03
2410	ISO17234-1	76.5		-1.26	3233	ISO17234-1	54.41		-2.29
2415	ISO17234-1	137.86		1.59	3237	ISO17234-1	104.70		0.05
2425	ISO17234-1	150.00		2.16	3242	ISO17234-1	143.3		1.84
2426	ISO17234-1	127.63		1.12	3248	ISO17234-1	125.7		1.03
2428	GB/T19942	106		0.11					

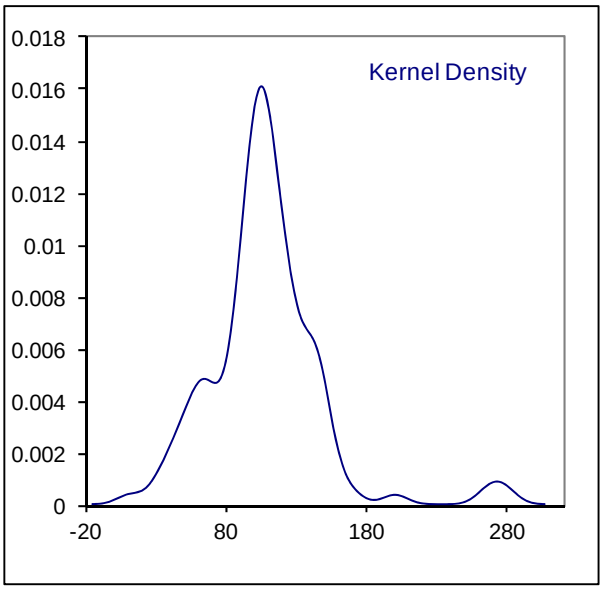
Normality not OK

n	120
outliers	5
mean (n)	103.64
st.dev. (n)	28.617
R(calc.)	80.128
R(ISO17234-1:2010)	60.199

compare R(Horwitz) = 23.092

Lab 2102 first reported: 130.75
Lab 2379 first reported: 9.57
Lab 2390 first reported: 215.468
Lab 2459 first reported: 197.250
Lab 2497 first reported 25.8
Lab 2499 first reported: 19.922
Lab 3160 first reported: 204.25
Lab 3214 first reported: 461.04
Lab 3220 first reported: 425



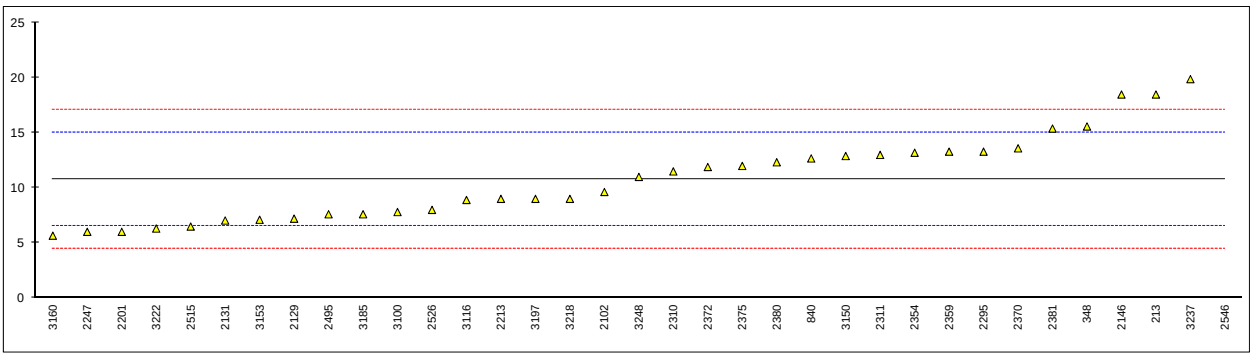


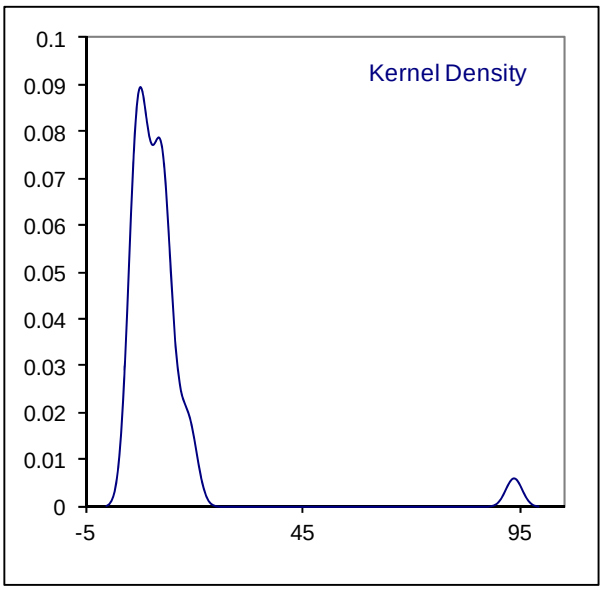
Determination of 2,4-Xylidene (CASno.95-68-1) in sample #13022; results in mg/kg

lab	method	value	mark	z(targ)	lab	method	value	mark	z(targ)
213	ISO17234-1	18.5		3.65	2429	ISO17234-1	n.d.		-----
348	ISO17234-1	15.59		2.27	2432		-----		-----
362	ISO17234-1	<5.0		-----	2442		-----		-----
551	ISO17234-1	n.d.		-----	2452		-----		-----
840	ISO17234-1	12.68		0.90	2453		-----		-----
1911		-----		-----	2459	ISO17234-1	n.d.		-----
2102	in house	9.63	C	-0.55	2469		-----		-----
2115		-----		-----	2472	ISO17234-1	<5		-----
2121		-----		-----	2476		-----		-----
2129	ISO17234-1	7.2		-1.70	2477	DIN53316	n.d.		-----
2131	in house	7.03		-1.78	2479	ISO17234-1	n.d.		-----
2132	ISO17234-1	<5		-----	2482		-----		-----
2139	ISO17234-1	<5		-----	2489	ISO17234-1	n.d.		-----
2146	ISO17234-1	18.5		3.65	2492		-----		-----
2165	EN14362-1	n.d.		-----	2493		-----		-----
2166	ISO17234-1	n.d.		-----	2494	ISO17234-1	n.d.		-----
2170		-----		-----	2495	ISO17234-1	7.6		-1.51
2172	ISO17234-1	n.d.		-----	2497		-----		-----
2173		-----		-----	2499		-----		-----
2184	ISO17234-1	<5		-----	2504		-----		-----
2190		-----		-----	2514		-----		-----
2201	ISO17234-1	6.0		-2.27	2515	ISO17234-1	6.48		-2.04
2212		-----		-----	2526	ISO17234-1	8		-1.32
2213	ISO17234-1/2	9		-0.85	2534	ISO17234-1	n.d.		-----
2216		-----		-----	2538		-----		-----
2235		-----		-----	2546	ISO17234-1	93.81	G(0.01)	39.34
2238	ISO17234-1	<5		-----	2549	ISO17234-1	n.d.		-----
2246	ISO17234-1	n.d.		-----	2553	ISO17234-1	<5		-----
2247	ISO17234-1	6.0		-2.27	3100	ISO17234-1	7.8		-1.42
2255		-----		-----	3104	ISO17234-1	<10		-----
2256	ISO17234-1	n.d.		-----	3116	ISO17234-1	8.9		-0.90
2261		-----		-----	3117		-----		-----
2271	ISO17234-1	<5.0		-----	3118		-----		-----
2272		-----		-----	3134		-----		-----
2283	ISO17234-1	n.d.		-----	3146	ISO17234-1	<10		-----
2284	ISO17234-1	<5.0		-----	3150	ISO17234-1	12.9		1.00
2286	ISO17234-1	<10		-----	3151		-----		-----
2287	ISO17234-1	<10		-----	3153	ISO17234-1	7.1		-1.75
2289		-----		-----	3154		-----		-----
2291	ISO17234-1	n.d.		-----	3160	ISO17234-1	5.65		-2.44
2295	ISO17234-1	13.3		1.19	3167	ISO17234-1	n.d.		-----
2296		-----		-----	3172		-----		-----
2297	ISO17234-1	<5		-----	3176		-----		-----
2300		-----		-----	3180		-----		-----
2310	ISO17234-1	11.5		0.34	3182		-----		-----
2311	ISO17234-1	13.0		1.05	3183		-----		-----
2354	ISO17234-1	13.2		1.14	3185	ISO17234-1	7.6		-1.51
2359	ISO17234-1	13.3		1.19	3190	ISO17234-1	<5		-----
2367	ISO17234-1	n.d.		-----	3191	ISO17234-1	<10		-----
2368	ISO17234-1	n.d.		-----	3192		-----		-----
2370	LMBG82.02.3	13.6		1.33	3197	ISO17234-1	9		-0.85
2372	ISO17234-1	11.9		0.53	3199	ISO17234-1	<10		-----
2373		-----		-----	3200	ISO17234-1	n.d.		-----
2375	ISO17234-1	12		0.57	3210		-----		-----
2379	ISO17234-1	n.d.		-----	3214	ISO17234-1	n.d.		-----
2380	ISO17234-1	12.33		0.73	3216		-----		-----
2381	ISO17234-1	15.4		2.18	3218	ISO17234-1	9		-0.85
2386	EN14362-1	<5		-----	3220	ISO17234-1	n.d.		-----
2390	ISO17234-1	n.d.		-----	3222	ISO17234-1	6.3		-2.13
2403	ISO17234-1	n.d.		-----	3225		-----		-----
2406	ISO17234-1	<8		-----	3228	ISO17234-1	n.d.		-----
2410		-----		-----	3233	ISO17234-1	n.d.		-----
2415		-----		-----	3237	ISO17234-1	19.90		4.32
2425		-----		-----	3242	ISO17234-1	n.d.		-----
2426	ISO17234-1	n.d.		-----	3248	ISO17234-1	11.0		0.10
2428	GB/T19942	n.d.		-----					

normality	OK	
n	34	
outliers	1	
mean (n)	10.791	
st.dev. (n)	3.8702	
R(calc.)	10.837	
R(ISO17234-1:2010)	5.9089	compare R(Horwitz) = 3.3794

Lab 2102 first reported 19.27





APPENDIX 2

Summary of other reported aromatic amines

lab	aromatic amines
2129	4.6 mg/kg 4-Aminodiphenyl; 7.2 mg/kg 2,6-Xylidine
2190	5.2 mg/kg 4-Aminodiphenyl; 9.7 mg/kg 3,3-methoxybenzidine
2247	6 mg/kg 2,6-Xylidine
2295	6.5 mg/kg 4-Aminodiphenyl
2296	157.9 mg/kg 4-Amino-azobenzene
2300	3.4 mg/kg 2,6-xylidine; 3.23 mg/kg 4-Aminodiphenyl
2390	14.142 mg/kg 4-Aminodiphenyl
2428	4 mg/kg 4-Aminodiphenyl
2477	4 mg/kg 4-Amindiphenyl; 10.09 mg/kg 2-Napthylamine
2489	6.0 mg/kg 2,6-Xylidine 6 mg/kg
2495	3.0 mg/kg 4-Aminodiphenyl; 1.5 mg/kg 2-naphtylamine; 4.0 mg/kg 2,6-Xylidine
3117	6 mg/kg 4-Aminodiphenyl
3134	8.1mg/kg 2,6-Xylidene
3151	3.0 mg/kg 4-Aminodiphenyl
3154	2.38 mg/kg 4-Aminodiphenyl
3160	5.88 mg/kg 4-Aminodiphenyl; 3.41 mg/kg 2,6-Xylidine
3176	2.54 mg/kg 4-Aminodiphenyl
3214	7.79 mg/kg 4-Aminodiphenyl
3220	10.0 mg/kg 4-Aminodiphenyl; 7.0 mg/kg 2,6-Xylidine
3222	5.9 mg/kg 4-Aminodiphenyl; 4.7 mg/kg *o*-Toluidine; 5.2 mg 2-Napthylamine

APPENDIX 3

Analytical details

lab	Method used	Solvent for clean up	Detection (quantification)
213	ISO17234-1	n-Hexane	
348	ISO17234-1	n-Hexane	
362	ISO17234-1	Hexane/MTBE	
551	ISO17234-1		
840	ISO17234-1		
1911	ISO17234-1/2	MTBE	HPLC/DAD
2102	in house		GC/MS
2115	ISO17234-1	n-Hexane	
2121	EN17234-1	n-Hexane	
2129	ISO17234-1	MTBE	
2131	in house	Hexane	
2132	ISO17234-1	MTBE	
2139	ISO17234-1	n-Hexane	
2146	ISO17234-1		
2165	EN14362-1	chlorobenzene	
2166	ISO17234-1	MTBE	
2170	ISO17234-1	MTBE	
2172	ISO17234-1	MTBE	
2173	ISO17234-1	Acetonitrile	
2184	ISO17234-1	n-Hexane	
2190	ISO17234-1	Hexane	
2201	ISO17234-1	n-Hexane	
2212	ISO17234-1	MTBE	
2213	ISO17234-1/2	MTBE	
2216			
2235	ISO17234-1	MTBE	
2238	ISO17234-1	n-Hexane	
2246	ISO17234-1	n-Hexane	
2247	ISO17234-1	MTBE	
2255	ISO17234-1		
2256	ISO17234-1	n-Hexane	
2261	GB/T19942	MTBE	
2271	ISO17234-1/2	MTBE	
2272	ISO17234-1	Methanol	
2283	ISO17234-1/2	n-Hexane	
2284	ISO17234-1/2	MTBE	
2286	ISO17234-1/2	MTBE	
2287	ISO17234-1/2	MTBE	
2289	ISO17234-1	Hexane	
2291	ISO17234-1	n-Hexane	
2295	ISO17234-1		
2296	ISO17234-1	MTBE	
2297	ISO17234-1	MTBE	
2300	LFGB 82.02-3		
2310	ISO17234-1	Hexane/MTBE	
2311	ISO17234-1	n-Hexane	
2354	ISO17234-1	MTBE/Methanol	
2359	ISO17234-1	Hexane	
2367	ISO17234-1	Hexyl hydride	
2368	ISO17234-1	n-Hexane	
2370	LMBG82.02.3		
2372	ISO17234-1	MTBE	
2373	ISO17234-1/2	n-Hexane	
2375	ISO17234-1		
2379	ISO17234-1	MTBE	
2380	ISO17234-1	n-Hexane	
2381	ISO17234-1	n-Hexane	
2386	EN14362-1	MTBE	
2390	ISO17234-1	n-Hexane	
2403	ISO17234-1	MTBE	
2406	ISO17234-1	n-Hexane	
2410	ISO17234-1	MTBE	
2415	ISO17234-1	n-Hexane	
2425	ISO17234-1/2	n-Hexane	
2426	ISO17234-1	n-Hexane	
2428	GB/T19942	n-Hexane	
2429	ISO17234-1/2		

2432	in house	n-Hexane	
2442	in house	n-Hexane	
2452	ISO17234-1	n-Hexane	
2453			
2459	ISO17234-1	n-Hexane	
2469	ISO17234-1	Hexane	
2472	ISO17234-1/2	n-Hexane	
2476			
2477	DIN53316		
2479	ISO17234-1	Acetonitrile	
2482	ISO17234-1	MTBE	
2489	ISO17234-1	MTBE	
2492	in house	n-Hexane	
2493			
2494	ISO17234-1	Hexane	
2495	ISO17234-1	MTBE	
2497	ISO17234-1	MTBE	
2499	ISO17234-1	MTBE/ethyl acetate	
2504	ISO17234-1	MTBE	
2514	ISO17234-1		
2515	ISO17234-1	n-Hexane/MTBE	
2526	ISO17234-1	MTBE	
2534	ISO17234-1	n-Hexane	
2538	In house		
2546	ISO17234-1	Hexane/MTBE	
2549	ISO17234-1	MTBE	
2553	ISO17234-1	n-Hexane	
3100	ISO17234-1	n-Hexane	
3104	ISO17234-1		GC/MS, UPLC/DAD
3116	ISO17234-1		
3117	ISO17234-1	MTBE	GC/MS, HPLC/DAD
3118	ISO17234-1	MTBE	
3134	ISO17234-1	n-Hexane	
3146	ISO17234-1	n-Hexane	
3150	ISO17234-1	Hexane	
3151	ISO17234-1	n-Hexane	GC/MS
3153	ISO17234-1	MTBE	
3154	DIN53316	MTBE	
3160	ISO17234-1	MTBE	
3167	ISO17234-1	Hexane	
3172	ISO17234-1		
3176			
3180	ISO17234-1		
3182	EN14362-1		
3183	LFGB 852.02-3/9	Hexane/MTBE	
3185	ISO17234-1	MTBE	
3190	ISO17234-1	n-Hexane	
3191	ISO17234-1	n-Hexane	
3192	LFGB 852.02-3	MTBE	
3197	ISO17234-1	n-Hexane	
3199	ISO17234-1	MTBE	
3200	ISO17234-1		
3210	ISO17234-1		
3214	ISO17234-1	MTBE	
3216	ISO17234-1	n-Hexane	
3218	ISO17234-1	MTBE	
3220	ISO17234-1	Hexane	
3222	ISO17234-1	Acetonitrile	
3225	ISO17234-1	MTBE	
3228	ISO17234-1	Hexane	
3233	ISO17234-1	n-Hexane	
3237	ISO17234-1		
3242	ISO17234-1	MTBE	
3248	ISO17234-1	n-Hexane	

APPENDIX 4

Number of participants per country

6 labs in	BANGLADESH
1 lab in	BRAZIL
1 lab in	BULGARIA
1 lab in	EGYPT
1 lab in	FINLAND
4 labs in	FRANCE
11 labs in	GERMANY
1 lab in	GREECE
13 labs in	HONG KONG
1 lab in	HUNGARY
10 labs in	INDIA
2 labs in	INDONESIA
10 labs in	ITALY
2 labs in	JAPAN
2 labs in	KOREA
1 lab in	MEXICO
1 lab in	MOROCCO
32 labs in	P.R. of CHINA
3 labs in	PAKISTAN
1 lab in	SINGAPORE
3 labs in	SPAIN
1 lab	SRI LANKA
2 labs in	SWITZERLAND
3 labs in	TAIWAN R.O.C.
3 labs in	THAILAND
1 lab in	THE NETHERLANDS
1 lab in	TUNESIA
5 labs in	TURKEY
2 labs in	U.S.A.
1 lab	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
n.e. = not evaluated
n.d. = not detected

Literature:

1 DIN 53316
2 ISO 17234:2010
3 LMBG 82.02-3:97
4 LMBG 82.04-2:98
5 EN14362-1/2, March 2002
6 Staatsblad van het Koninkrijk der Nederlanden 339, bijlage II, 23 april 1998
7 iis-Interlaboratory Studies: Protocol for the Organisation, Statistics and Evaluation, January 2010
8 XP G 08-014:97
9 P.L. Davies, Fr Z. Anal. Chem, 351, 513, (1988)
10 W.J. Conover, Practical; Nonparametric Statistics, J. Wiley&Sons, NY, p.302, (1971)
11 ISO 5725, (1986)
12 ISO 5725, parts 1-6, (1994)
13 M. Thompson and R. Wood, J. AOAC Int, 76, 926, (1993)
14 G. Rohm, J. Bohnen & H. Kruessmann, GIT Labor-Fachzeitschrift, p 1080, 11, (1997)
15 OEKO-TEX Std 100, p19, (ed. 04/2013)