

Results of Proficiency Test
AZO dyes in leather
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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, 89 laboratories in 22 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 Spijkennisse was the organizer of this proficiency test. It was decided to use in this proficiency test 2 different leather samples (labelled #101L and #102L). One of the leather samples 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 Spijkennisse, the Netherlands, has implemented a quality system based on ISO guide 43 and ILAC-G13:2007. This ensures 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

Due to lack of suitable (positive) leather samples the 2009 PT had to be cancelled. And again during the planning of the 2010 PT only leather materials containing no banned AZO dyes could be purchased.

Fortunately iis was contacted by Clariant Chemicals (India) Limited with the offer to prepare a positive leather material for use in the 2010 PT. This offer was accepted with pleasure. The Corporate Product Safety Laboratory of Clariant Chemicals (India) Limited in Thane, India, did prepare 500 grams of leather fortified with an AZO dye that would give 2,4-Xylidene upon analysis. After cutting in 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.

	<i>2,4-Xylidine in mg/kg</i>
sample #101L-1	69.47
sample #101L-2	76.88
sample #101L-3	71.25
sample #101L-4	73.20
sample #101L-5	71.30
sample #101L-6	73.62
sample #101L-7	75.65
sample #101L-8	75.80

table 1: homogeneity test results of subsamples #102L

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:

	<i>2,4-Xylidine in mg/kg</i>
r (observed)	7.3
reference method	ISO17234:2010
r (reference method)	12.1

table 2: evaluation of the repeatability of subsamples #102L

The repeatability of the results of homogeneity test for 2,4-Xylidine was in agreement with 0.3 times the reproducibility mentioned in the reference method ISO17234:2010.

Therefore, homogeneity of the subsamples was assumed.

As second sample a leather containing no banned Azo dyes was used. Therefore no homogeneity was determined for sample #101L.

Approx. 4 grams of each of the samples #101L and #102L was sent to the participating laboratories on March 12, 2010.

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 set of samples. Furthermore, an extra report form for reporting of analysis details was enclosed. 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 'i.i.s. Interlaboratory Studies: Protocol for the Organization, Statistics and Evaluation' of January 2010 (i.i.s.-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.

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

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

The $z_{(\text{target})}$ -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 some reporting problems occurred. Seven participants reported test results after the deadline and 13 participants did not report any test results due to various reasons. Finally, 77 participants did report 99 numerical results. Observed were 5 outlying results, which is 6.6% of the numerical results on 2,4-Xylidine. In proficiency studies, outlier percentages of 3% - 7.5% are quite normal. The data set proved to have a normal distribution.

4.1 EVALUATION PER SAMPLE AND COMPONENT

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

Sample #101L:

Only 1 laboratory reported a high concentration of 4,4'-diaminodiphenyldisulfide and 12 other laboratories reported the presence of small amounts of aromatic amines in this sample, see appendix 2. The majority of the laboratories reported that no detectable amounts of aromatic amines were present. Therefore no significant conclusions were drawn.

Sample #102L:

2,4-Xylidine:

The determination of this aromatic amine at a concentration level of 90 mg/kg was not problematic. Only two laboratories reported test results lower than 30 mg/kg and another two laboratories reported "not detected", of which one laboratory probably had mixed up the samples because this laboratory reported 84 mg/kg 2,4-Xylidine for sample #101L. Several laboratories reported only the sum of 2,4- and 2,6-Xylidine. This gave no problems as 2,6-Xylidine was not present in sample #102L.

The test results reported by the participants vary from 6.967 – 132 mg/kg. The observed reproducibility (38.48 mg/kg, or 44% relative) is, after rejection of the five statistical outliers, in good agreement with the reproducibility requirement estimated from the reference standard test method ISO 17234-1:2010.

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 reproducibility 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 official test methods like ISO17234-1:2010 (equal to the reproducibility from LMBG 82.02.3:97) are in the next table.

Parameter	unit	n	Average	2.8 * sd	R(ISO17234)
2,4-Xylidine	mg/kg	72	88.12	38.48	48.25

table 3: reproducibility of aromatic amine in leather sample #102L

Without further statistical calculations, it can be concluded that for all 2,4-Xylidine the group of participating laboratories has no difficulties with the analysis at the concentration level of 90 mg/kg. See also the discussion in paragraphs 4.1 and 6.

5 COMPARISON WITH PREVIOUS INTERLABORATORY STUDIES

The spread in the results of 2,4-Xylidine is small in comparison with the spreads of the other aromatic amines as observed in previous PTs, see below table.

<i>Parameter</i>	<i>March 2010</i>	<i>March 2008</i>	<i>March 2007</i>	<i>April 2006</i>	<i>April 2005</i>	<i>March 2004</i>	<i>LMBG 82.02.3:97</i>
4-Aminodiphenyl	n.a.	n.a.	n.a.	127%	n.a.	145%	Unknown
Benzidine	n.a.	105%	126%	133%	184%	162%	43 – 69%
3,3-Dimethylbenzidine	n.a.	n.d.	126%	n.a.	155%	n.a.	42 – 66%
o-Toluidine	n.a.	140%	n.a.	n.a.	175%	n.a.	84– 103%
2,4-Xylidine	44%	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.

table 4: development of relative reproducibilities over the years

The improvement over the years is clearly continuing. This is expected as from the details of the analyses provided by the participants it is clear that most of the participants adhered strictly to one and the same method.

6 DISCUSSION

In method LMBG 82.02-3:97 is stated (paragraph 3) that 'Die Quantifizierung der Amine erfolgt mittels HPLC/DAD' and in the valid method LMBG 82.02-3:97 (paragraph 10.1) that 'Für die Quantifizierung ist ausschließlich HPLC mit DAD einzusetzen'. However, in the last and valid 1998-version of LFGB 82.02-9 this restriction was deleted and GC/MS was allowed for quantification, while method LMBG 82.02-3:97 were not updated. Also in EN14362, ISO17234 and DIN 53316, HPLC is used for quantification and GC for qualification only. In 1998, a Dutch method was published as addendum to Dutch legislation. In this method (Stb. 339), quantification must be performed by HPLC/DAD. In the French official method XP G08-014 of 1997, no technique for quantification is prescribed.

In former rounds of this proficiency testing scheme it was clear that the HPLC/DAD method was superior over the GC/MS method for quantification. This is not confirmed in this PT as the spread of the GC/MS results now is smaller than the spread of the HPLC results. However, the low number of HPLC results may be the cause of the relatively large spread of the HPLC results.

<i>Parameter</i>	<i>unit</i>	<i>HPLC data</i>			<i>GC/MS data</i>		
		<i>n</i>	<i>average</i>	<i>2.8 * sd</i>	<i>n</i>	<i>average</i>	<i>2.8 * sd</i>
2,4-Xylidine	mg/kg	8	82.25	46.06	21	86.79	38.38

table 5: reproducibilities GC vs HPLC of the leather sample #102L

From the reported test methods it appeared that most participants treated the leather samples according identical test methods: ISO17234, EN14362 or LFGB 82.02.3. Regretfully too little information was received about the calibrants used by the participating laboratory to justify any significant conclusions on the effect of the calibrants used.

In total 6 participants corrected for recovery (usually via the internal standard method), although this correction is not mentioned in any of the standardised test methods. The results these 6 participants were not significantly different from the other test results.

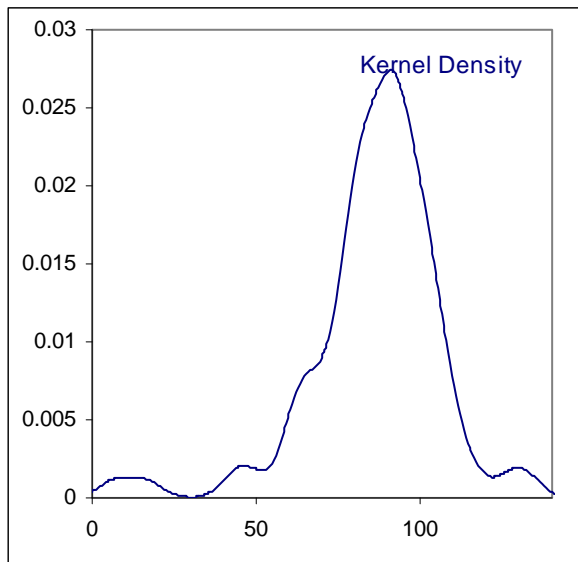
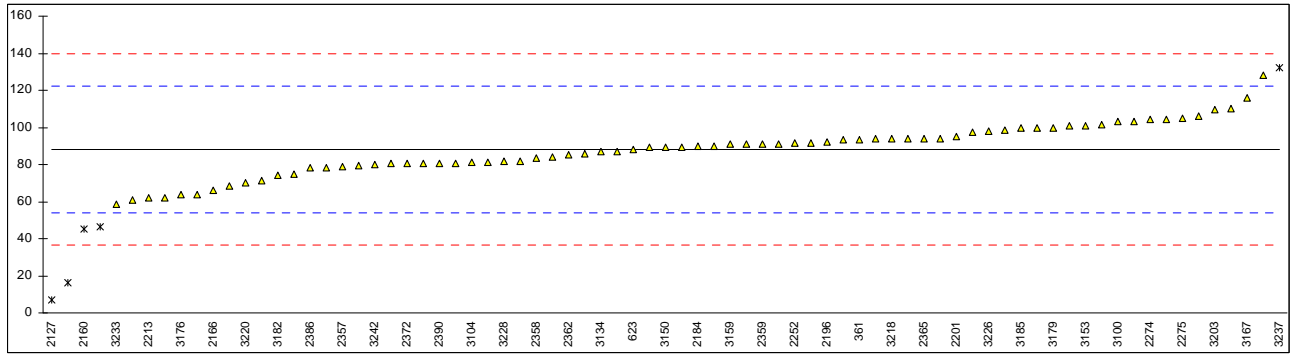
From the various above mentioned matters, it can be concluded that the spread observed in this interlaboratory study is not caused by just one critical point in the analysis. Each participating laboratory will have to evaluate its performance in this study and decide about any corrective actions if necessary.

APPENDIX 1

Determination of 2,4-Xylidine (CASno.95-68-1) in sample #102L; results in mg/kg

lab	method	value	mark	z(targ)	remarks
361	ISO/TS17234	93.6104		0.32	
622	ISO/TS17234	80.54		-0.44	
623	in house	88.03		-0.01	
840	ISO/TS17234	100.58		0.72	
1051	ISO/TS17234	86.9		-0.07	
2102		-----		-----	
2115	ISO/TS17234	91.83		0.22	
2117	LFGB 82.02-3	110		1.27	
2121		75		-0.76	
2127	EN14362	6.967	G(0.01)	-4.71	
2129	ISO/TS17234	61		-1.57	
2132	ISO/TS17234	104.5		0.95	
2146	ISO/TS17234	-----		-----	did not test for 2,4- and 2,6-Xylidine
2156		-----		-----	
2160	B 82.02-3	45.5	DG(0.05)	-2.47	reported 45.5 mg/kg as sum of 2,4- and 2,6-Xylidine
2166	ISO/TS17234	66.0		-1.28	
2170	ISO/TS17234	16.48	G(0.01)	-4.16	
2172	ISO/TS17234	80.8		-0.42	
2173	ISO/TS17234	105.97		1.04	
2184	ISO/TS17234	90		0.11	
2196	ISO/TS17234	92		0.23	
2201	ISO/TS17234	95		0.40	
2213	ISO/TS17234	62	C	-1.52	first reported 42 mg/kg
2215	ISO/TS17234	89		0.05	
2221	ISO/TS17234	64		-1.40	
2227		-----		-----	
2235	ISO/TS17234	46.5	CDG(0.05)	-2.42	first reported 31.2 mg/kg
2239	ISO/TS17234	n.d.		-----	reported 7 mg/kg 2,6-Xylidine (22 mg/L)
2252	ISO/TS17234	91.5		0.20	
2256	ISO/TS17234	n.d.		-----	samples mixed-up? reported 84 mg/kg 2,4-Xylidine in #101L
2261	in house	62		-1.52	
2272	ISO/TS17234	n.d.		-----	
2274	ISO/TS17234	104.3		0.94	
2275	ISO/TS17234	105		0.98	
2284	ISO/TS17234	80.3		-0.45	
2289	ISO/TS17234	100		0.69	
2291	ISO/TS17234	103		0.86	
2310	ISO/TS17234	98.8		0.62	
2311	ISO/TS17234	91		0.17	
2350	ISO/TS17234	93.4		0.31	
2357	ISO/TS17234	79		-0.53	
2358	ISO/TS17234	83.5		-0.27	
2359	ISO/TS17234	91		0.17	
2362	ISO/TS17234	85		-0.18	
2364	ISO/TS17234	84		-0.24	
2365	ISO/TS17234	94		0.34	
2366	ISO/TS17234	91		0.17	
2367	ISO/TS17234	78		-0.59	
2368	ISO/TS17234	82		-0.36	
2370	ISO/TS17234	93.7		0.32	
2372	ISO/TS17234	80.4		-0.45	
2375	ISO/TS17234	81		-0.41	
2379	ISO/TS17234	97.55		0.55	
2380	ISO/TS17234	101.474		0.77	
2386	LFGB 82.02-3+9	78		-0.59	
2390	ISO/TS17234	80.741		-0.43	
3100	ISO/TS17234	103		0.86	
3104	ISO/TS17234	81		-0.41	
3116	ISO/TS17234	89		0.05	
3117	ISO/TS17234	94		0.34	
3134	ISO/TS17234	86.9		-0.07	
3149		-----		-----	
3150	LFGB 82.02-4	89		0.05	
3153	ISO/TS17234	101		0.75	
3154	DIN53316	68.18	C	-1.16	first reported 48.81 mg/kg
3159	ISO/TS17234	91.0		0.17	
3167	ISO/TS17234	116	C	1.62	first reported 116 mg/kg 2,6-Xylidine
3170		-----		-----	
3172		-----		-----	
3174		-----		-----	

3176		63.6		-1.42	reported 63.6 mg/kg as sum of 2,4- and 2,6-Xylydine
3179	ISO/TS17234	100		0.69	
3182	ISO/TS17234	74.473		-0.79	
3185	ISO/TS17234	100		0.69	
3190	ISO/TS17234	90		0.11	
3203	ISO/TS17234	109.81		1.26	
3204		-----		-----	
3210	ISO/TS17234	79.3		-0.51	
3218	ISO/TS17234	94		0.34	
3220	ISO/TS17234	70	C	-1.05	first reported 41 mg/kg
3226	ISO/TS17234	97.74		0.56	
3228	EN14362	82		-0.36	
3232	DIN53316	71.58		-0.96	
3233	ISO/TS17234	58.8		-1.70	
3237	in house	132	G(0.05)	2.55	
3242	in house	80.0		-0.47	
3246	EN14362	128		2.31	
3247	ISO/TS17234	86		-0.12	
3248	ISO/TS17234	94		0.34	
normality		OK			
n		72			
outliers		5			
mean (n)		88.122			
st.dev. (n)		13.7426			
R(calc.)		38.479			
R(ISO17234-1)		48.254			



APPENDIX 2

Summary of all other reported AZO-dyes in sample #101L; results in mg/kg

lab	aromatic amines
622	0.73 mg/kg p-Chloraniline & 6.44 mg/kg 4,4'-diaminodiphenylsulfide
1051	20.9 mg/kg 4,4'-diaminodiphenylsulfide & 16.9 mg/kg 2,4-diaminotoluene
2102	1 mg/kg p-Chloraniline
2115	0.65 mg/kg 4-Aminoazotoluene
2127	2.128 mg/kg 4-Aminodiphenyl
2129	2.0 mg/kg p-Chloraniline & 2.0 mg/kg o-toluidine
2132	5.7 mg/kg Benzidine & 11.6 mg/kg 4,4'-diaminodiphenylsulfide
2160	4.6 mg/kg Benzidine & 3.8 mg/kg p-Chloraniline
2170	6.44 mg/kg 4,4'-diaminodiphenylsulfide
2252	4.6 mg/kg Benzidine & 6.5 mg/kg 4,4'-diaminodiphenylsulfide
3172	9.3 mg/kg Benzidine & 10.8 mg/kg 3,3'-dimethyl-4,4'-diaminodiphenylmethane
3226	54.00 mg/kg 4,4'-diaminodiphenylsulfide
3237	1.45 mg/kg Benzidine & 1.85 mg/kg p-Chloraniline

Summary of all other reported AZO-dyes in sample #102L; results in mg/kg

lab	aromatic amines
622	100.98 mg/kg 2,6-Xylidine
2102	5 mg/kg 3,3'-dimethylbenzidine
3210	116.1 mg/kg 2,6-Xylidine

APPENDIX 3

Details of the analysis methods used by the participants

Lab	solvents	detection methods	Calibration standards	Corr. Rec.
361	Methanol, n-Hexane	GC/MS	Mix A, B and C, 1,5,10,15,20,30 mg/L with IS mix(10 mg/L)	No
622		GC/MS	Ext Std for Quantitation with range 12-68 mg/kg	
623		GC/MS & HPLC/UV-DAD	Cal.curve, 1,5,10,15,20,30 mg/L	No
840			Cal curve ranges (5,10,15,20,30 ppm)	No
1051	MTBE	GCMS & HPLC/DAD	Sigma, Chem Service	No
2102	n-hexane	GC/MS	p-chloraniline MERCK, 3,3-dimethylbenzidine Sigma	No
2115	MTBE	GC/MS	Dr. Ehrenstorfer techn. purity 98.5% salt	No
2117	n-Hexane, MTBE	GC/MS & HPLC/UV	Azo Dyes mix 9, Dr. Ehrenstorfer 100mg/ul	No
2121				
2127	MTBE	HPLC-MS	in house Std's	No
2129	MTBE	GC/MS & LC-TOF	p-Chloranilin, o-toluidin(Riedel,2,4-Xylidine(Fluka)	No
2132	MTBE	GC/MS & HPLC/DAD		No
2146		HPLC-DAD		No
2156				
2160	MTBE	GC-MS	Dr.Ehrenstorfer,cal with 5 points (10,20,30,40,50 ppm)	Yes
2166	MTBE	HPLC/UV (DAD)		No
2170	Methanol	GC/MS	2,4,10,15 ppm	No
2172	MTBE	GC/MS & HPLC/DAD	Component method 5,15,30 mg/L Int.Std 10mg/L	No
2173	Hexane	GC/MS & LC/MS	Dr.Ehrenstorfer Azo dyes-mix6, 50mg/L	No
2184		GC/MS	Naphthalene-d8	No
2196	MTBE	GC/MS & HPLC/DAD	IS1&IS2, 10mg of each IS/ml of the IS solvent	No
2201	n-Hexane	GC/MS & HPLC/DAD	2,4-Xylidine, Dr.Ehrenstorfer 98.5%	No
2213	Methanol	GC/MS & HPLC	Dr.Ehrenstorfer, 5,15,30,ppm	No
2215	MTBE	GC/MS & HPLC/DAD	5,15,30 ppm	Yes
2221	n-hexane	GC/MS & HPLC/DAD	2,4-Xylidine(99.3%purity), 4,10,20,80 mg/kg	No
2227				
2235	n-Hexane, MTBE	TLC & HPLC/DAD & GC/MS	2,6-Xylidine, 23.9 µg/ml in MeOH	No
2239		GC/MS		No
2252	MTBE	GC/MS HPLC/DAD		No
2256	n-Hexane, MTBE	GC/MS & HPLC	Conc.	Yes
2261	MTBE	GC/MS & HPLC/DAD	2,4-Xylidine single std 16.625,33.25,66.5 ppm	Yes
2272	Hexane	GC/MS & HPLC/DAD	Dr.Ehrenstorfer Std, 5-50 mg/kg	No
2274	MTBE	GC/MS & HPLC/DAD	zie report form	No
2275	MTBE	GC/MS & HPLC/DAD	Multi point Cal curve 0.6, 3.0,15 ppm	No
2284	Sillica Gel, MTBE	GC/MS	Cert. mixed std sol. / cal curve 1-5 µg/ml	No
2289	n-Hexane, MTBE	GC/MS & HPLC	Multi point lin cal, 0.6, 1.5, 3.0, 10 mg/L	No
2291	MTBE	GC/MS & HPLC	2,4-Xylidine, 10,20,50,80,100 µg/ml	No
2310	Hexane	GC/MS & HPLC/DAD	5,10,20 ppm	No
2311	n-Hexane	HPLC/DAD & GC/MS	2,5,10,15,20,30 mg/L	No
2350	MTBE	GC/MS & HPLC/DAD	Neat and 5,10,20,30,50 mg/L	No
2357	MTBE	HPLC/DAD & GC/MS	D10:10mg/kg	No
2358	MTBE	GC/MS & HPLC/DAD	2.5,5,10,15,20,30 mg/L	No
2359	MTBE	GC/MS	1,2,5,5,10,20,30 µg/ml	No
2362		GC/MS	1-30 mg/L	No
2364	MTBE	GC/MS & HPLC/DAD	95-68-1:5,10,15,20,30 mg/L	No
2365	MTBE	GC/MSD & HPLC/DAD	2,4-Xylidine, 2.5,5.0,10.0,15.0,30.0 mg/L	No
2366	MTBE	GC/MS & HPLC/DAD	Mixed Std, 2.5,5.0,10,20,30 mg/L	No
2367	MTBE	GC/MS & HPLC/DAD	95-68-1, 55,10,15,20,30mg/L	No
2368	MTBE	GC/MS	concentration	No
2370	MTBE	GC/MS	3,5,10,20,30,40,50 µg/L	No
2372	No	GC/MS	4,8,16,24,32,40 µg/mL	No
2375	Hexane	GC/MS & HPLC/DAD	range 1-30 mg/L	No
2379	MTBE	GC/MS & HPLC/DAD	3,5,10,20,30,50,100 mg/L	No

2380	Ethylacetate	GC/MSD & HPLC/DAD	Internal Cal. Std's, conc. 10 mg/L	No
2386	MTBE	HPLC/UV	5,10,20,30,40,50 µg/kg	Yes
2390	MTBE	GC/MS	1,5,10,15,20,30,ppm	Yes
3100	MTBE	GC/MS & HPLC/UV	Linear, 3,15,30 ppm	No
3104	n-Hexane	GC/MS & HPLC	Chem service, 5,10,20,30 mg/L	No
3116		GC/MS & HPLC/DAD		
3117	None	HPLC/DAD & GC/MS	2,4-Xylidine 63.504 mg/L	No
3134	MTBE	GC/MS & GC/FID	External Std's, based on analyte conc.	No
3149				
3150	no clean up	GC/MS	InHouse, 3, 7.5, 15, 30 mg/L	No
3153	MTBE	GC/MSD & HPLC/DAD	0.6, 3, 10, 20 ppm	No
3154	MTBE	HPLC/DAD	2,4-Xylidine(Sigma/Aldrich) single std 10µg/ml	No
3159	Nil	GC/MS & HPLC/UV	5,15,30 mg/L Chem Service	No
3167	MTBE	HPLC/DAD & GC/MS	30 mg/kg amine mixture std's	No
3170				
3172	n-Hexane	HPLC/UV	single component 20 mg/l	No
3174				
3176				
3179	MTBE	GC/MS&HPLC	weighed in acetonitrile, dilution in MTBE, 0.3-9µg/ml	No
3182	MTBE	HPLC/UV	Calibration conc. 1,3,10 ppm	No
3185	MTBE	HPLC/DAD	Standard Solutions 0.6,3,15 ppm	No
3190	n-Hexane	GC/MS & HPLC/UV	Linear, 0.1,1,3,5,10,50 ppm	No
3203	MTBE	HPLC/UV	Three Levels, 2.0,4.0,8.0 mg/L Std's in MeOH	No
3204				
3210		HPLC/DAD		No
3218	MTBE	GC/MS & HPLC/UV	3 ppm standards	No
3220	Hexane	GC/MS & HPLC	Dr.Ehrenstorfer	No
3226	MTBE	GC/MS	Std of AA 100 µg/ml (ready to use)	No
3228	None	GC/MS	Dr.Ehrenstorfer(Zie report form)	No
3232	n-Hexane	GC/MS	CRM;s from Dr.Ehrenstorfer&3 point cal 10,30,60 ppm	No
3233	n-Hexane	GC/MS	solutions 5 – 50 mg/L	No
3237	MTBE	GC/MS	10, 20, 30 Dr Ehrenstorfer	No
3242	MTBE	GC/MS & HPLC/DAD	5,10,15,20,50ppm	No
3246		GC/MS	Individual amine reference material	No
3247	MTBE	GC/MS	Isotec, Dr.Ehrenstorfer,Supelco,Fluka,Aldrich,1-50ppm	No
3248	Methanol	GC/MS & HPLC/UV	Dr.Ehrenstorfer, 5,10,20 ppm	No

APPENDIX 4

List of participants on alphabetical country order

1 lab in BANGLADESH
1 lab in BULGARIA
1 lab in CYPRUS
1 lab in FINLAND
3 labs in FRANCE
10 labs in GERMANY
1 lab in GREECE
11 labs in HONG KONG
7 labs in INDIA
2 labs in INDONESIA
4 labs in ITALY
1 lab in KOREA
1 lab in MALAYSIA
30 labs in P.R. of CHINA
1 lab in PAKISTAN
1 lab in SINGAPORE
2 labs in TAIWAN R.O.C.
2 labs in THAILAND
1 lab in THE NETHERLANDS
4 labs in TURKEY
1 lab in U.S.A.
2 labs in VIETNAM

APPENDIX 5

Abbreviations:

C	= final result after checking of first reported suspect result
D(0.01)	= outlier in Dixon's outlier test
D(0.05)	= straggler in Dixon's outlier test
G(0.01)	= outlier in Grubbs' outlier test
G(0.05)	= straggler in Grubbs' outlier test
DG(0.01)	= outlier in Double Grubbs' outlier test
DG(0.05)	= straggler in Double Grubbs' outlier test
n.a.	= not applicable
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)