Results of Proficiency Test
AZO dyes in leather
March 2014

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. During the annual proficiency testing program 2013/2014, it was decided to continue the round robin for the analysis of banned AZO dyes in leather. In this interlaboratory study, 132 laboratories in 29 different countries have participated (see appendix 4). In this report, the results of the 2014 proficiency test are presented and discussed. This report is also electronically available through the iis internet site www.iisnl.com.

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 purchased on the local market. Sample analyses for fit-for-use and homogeneity testing were subcontracted to 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 ACCREDITATION

The Institute for Interlaboratory Studies in Spijkenisse, the Netherlands, is accredited in agreement with ISO/IEC 17043:2010 (R007), since January 2000, by the Dutch Accreditation Council (Raad voor Accreditatie). This ensures strict adherence to protocols for sample preparation and statistical evaluation and 100% confidentially of participant's data. Feedback from the participants on the reported data is encouraged and customer's satisfaction is measured on regular basis by sending out questionnaires

2.2 PROTOCOL

The protocol followed in the organization was the one as described for proficiency testing in the report 'iis Interlaboratory Studies: Protocol for the Organization, Statistics and Evaluation' of April 2014 (iis-protocol, version 3.3).

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. In total 140 sub samples were prepared with 2.5 gram leather and labelled #14022. Eight stratified randomly selected samples were tested using ISO17234-1 to check the homogeneity of the batch. See the following table for the test results.

	Benzidine in mg/kg
sample #14022-1	106.8
sample #14022-2	116.6
sample #14022-3	109.8
sample #14022-4	108.6
sample #14022-5	107.2
sample #14022-6	105.1
sample #14022-7	106.9
sample #14022-8	114.7

Table 1: homogeneity test results of subsamples #14022

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)	11.5
reference method	ISO17234-1:2010
0.3 x R (reference method)	19.1

Table 2: evaluation of the repeatability of subsamples #14022

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.

One sample with approx. 2.5 grams (labelled #14022) testing material was sent to each of the participating laboratories on March 5, 2014.

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 April 2014 (iis-protocol, version 3.3)
For the statistical evaluation the *unrounded* (when available) figures were used instead of the rounded results. Results reported as ‘<…’ or ‘>…” were in general not used in the statistical evaluation.

First, the normality of the distribution of the various data sets per determination was checked by means of the Lilliefors-test a variant of the Kolmogorov-Smirnov test and by the calculation of skewness and kurtosis. Evaluation of the three normality indicators in combination with the visual evaluation of the graphic Kernel density plot, lead to judgement of the normality being either ‘unknown’, ‘OK’, ‘suspect’ or ‘not OK’. After removal of outliers, this check was repeated. Not all data sets proved to have a normal distribution, in which cases the statistical evaluation of the results should be used with due care.

In accordance to ISO 5725 (1986 and 1994) the original results per determination were submitted subsequently to Dixon and Grubbs outlier tests. Outliers are marked by D(0.01) for the Dixon test, by G(0.01) or DG(0.01) for the Grubbs test and by R(0.01) for the Rosner General ESD test (see appendix 5, no.15). Stragglers are marked by D(0.05) for the Dixon test, by G(0.05) or DG(0.05) for the Grubbs test and by R(0.05). Both outliers and stragglers were not included in the calculations of the averages and the standard deviations.

For each assigned value, the uncertainty was determined in accordance with ISO13528. Subsequently the calculated uncertainty was evaluated against the respective requirement based on the target reproducibility in accordance with ISO13528. When the uncertainty passed the evaluation, no remarks are made in the report. However, when the uncertainty failed the evaluation it is mentioned in the report and it will have consequences for the evaluation of the test results.

Finally, the reproducibilities were calculated from the standard deviations by multiplying them with a factor of 2.8.

3.2 GRAPHICS

In order to visualise the data against the reproducibilities from literature, Gauss plots were made, using the sorted data for one determination (see appendix 1). On the Y-axis the reported analysis results are plotted. The corresponding laboratory numbers are under the X-axis. The straight horizontal line presents the consensus value (a trimmed mean). The four striped lines, parallel to the consensus value line, are the +3s, +2s, -2s and -3s target reproducibility limits of the selected standard. Outliers and other data, which were excluded from the calculations, are represented as a cross. Accepted data are represented as a triangle.
Furthermore, Kernel Density Graphs were made. This is a method for producing a smooth density approximation to a set of data that avoids some problems associated with histograms (see appendix 5; nos.13 and 14). Also a normal Gauss curve was projected over the Kernel Density Graph.

3.3 Z-SCORES

To evaluate the performance of the individual participating laboratories the z-scores were calculated. In order to be able to have an objective evaluation of the performance of the individual participants, it was decided to evaluate this performance against the literature requirements. Therefore the z-scores were calculated using a target standard deviation. This target standard deviation was calculated from the literature reproducibility by division with 2.8.
The $z_{(target)}$-scores were calculated according to:

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

The $z_{(target)}$-scores are listed in the result tables in appendix 1.

When a laboratory did use a test method with a reproducibility that is significantly different from the reproducibility of the reference test method used in this report, it is strongly advised to recalculate the z-score, while using the reproducibility of the actual test method used, this in order to evaluate the fit-for-useness of the reported test result.

Absolute values for z<2 are very common and absolute values for z>3 are very rare. The usual interpretation of z-scores is as follows:

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

4 EVALUATION

During the execution of this proficiency test some reporting problems occurred. Twenty one participants reported test results after the deadline and three participants did not report any test results. Finally, 129 participants did report 137 numerical results. Observed was 1 outlying result, which is 0.7% of the numerical results. In proficiency studies, outlier percentages of 3% - 7.5% are quite normal.
Only one aromatic amine present was detected by the majority of the participating laboratories. The data set of Benzidine did proof to have a normal Gaussian distribution.

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 92 mg/kg was not problematic. Only one statistical outlier was observed. One participant reported a false negative test result.
The test results reported by the participants vary from nd – 178 mg/kg. The observed reproducibility after rejection of the statistical outlier is in good agreement with the reproducibility requirement estimated from the standard test method ISO 17234-1:2010.

General: Nine participants reported also the presence of other aromatic amines at different concentration levels. A number of participants reported also the presence of Aniline.
Only one laboratory 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	126	91.74	50.45	53.29

Table 3: reproducibilities of aromatic amines in leather sample #14022

Without further statistical calculations, it can be concluded that the group of participating laboratories have no problem with the analysis of Benzidine 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 amine in the 2014 PT is in good agreement in comparison with the spread of the aromatic amine as observed in the previous PT's, see below table.

Parameter	*March 2014*	*March 2013*	*March 2012*	*March 2011*	*March 2010*	*March 2008*	*March 2007*	*April 2006*	*LMBG 82.02.3:97*
4-Aminodiphenyl	n.e.	n.e	69%	n.e.	n.e.	n.e.	n.e.	127%	Unknown
Benzidine	55%	77%	55%	n.e.	n.e.	105%	126%	133%	43 – 69%
3,3-Dimethylbenzidine	n.e.	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.	n.e.	140%	n.e.	n.e.	84– 103%
2,4-Xylidine	n.e.	100%	n.e.	53%	44%	n.e.	n.e.	n.e.	n.e.

Table 4: development of relative reproducibilities over the years

6 DISCUSSION

From the reported test methods it appeared that almost all 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

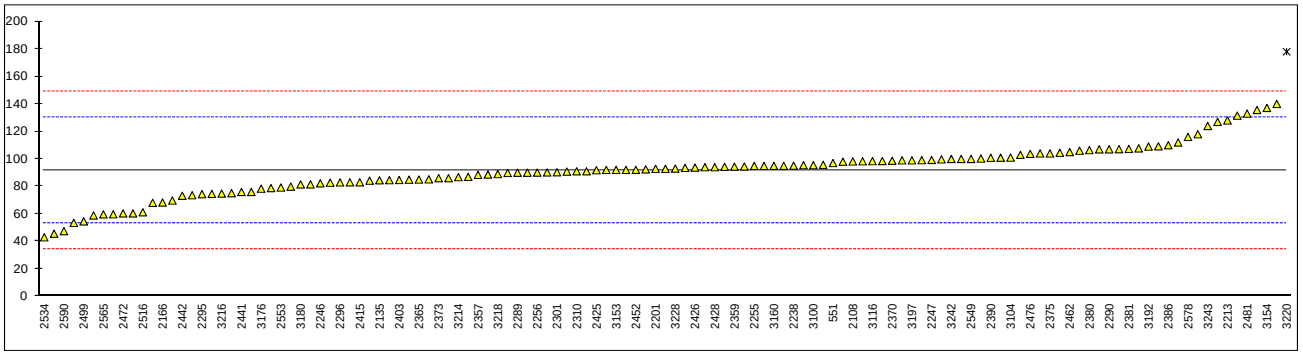
Determination of Benzidine (CASno.92-87-5) in sample #14022; results in mg/kg

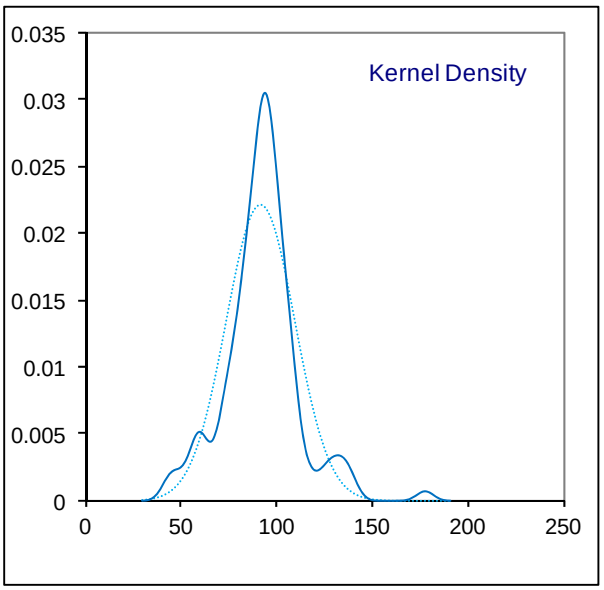
lab	method	value	mark	z(targ)	lab	method	value	mark	z(targ)
110		95.73		0.21	2489		104.46		0.67
213		92.4		0.03	2492		98		0.33
348		94.29		0.13	2493		-----		-----
551		97.00	C	0.28	2495		90.0		-0.09
623		107.1		0.81	2497		94.5		0.14
840		107		0.80	2499		54.61		-1.95
1911		82.714		-0.47	2511		98.48		0.35
2102		59.75		-1.68	2514		99.13		0.39
2108		98.2		0.34	2516		61.2		-1.60
2115		n.d.	false -?	-----	2532		100.3		0.45
2121		84.92		-0.36	2534		43		-2.56
2129		135.6		2.30	2540		79.86		-0.62
2132		118.0		1.38	2549		100.0		0.43
2135		84.5		-0.38	2553		79.2		-0.66
2137		104		0.64	2562		-----		-----
2139		131.5		2.09	2565		59.7		-1.68
2146		-----		-----	2566		94.9		0.17
2165		99		0.38	2570		90.20		-0.08
2166		68.3		-1.23	2578		116		1.27
2170		100.9		0.48	2581		68.1		-1.24
2172		73.6		-0.95	2582		85.16		-0.35
2184		94		0.12	2590		47.5		-2.32
2201		92.8		0.06	2592		69.76		-1.16
2213		128		1.91	2609		107.7		0.84
2217		126.95		1.85	3100		95.5		0.20
2238		95.1		0.18	3104		101		0.49
2246		82.28		-0.50	3116		98.4		0.35
2247		99.28		0.40	3117		76		-0.83
2255		94.9		0.17	3118		45.60		-2.42
2256		90.07		-0.09	3146		92		0.01
2289		90		-0.09	3150		60.4		-1.65
2290		107		0.80	3153		92		0.01
2291		100		0.43	3154		137.12		2.38
2295		74.4		-0.91	3160		94.98		0.17
2296		82.91		-0.46	3167		140		2.54
2297		78.8		-0.68	3172		89.8		-0.10
2301		90.3039		-0.08	3176		78.38		-0.70
2310		91		-0.04	3180		81.48		-0.54
2311		95		0.17	3182		81.50		-0.54
2352		84.2		-0.40	3185		88.7		-0.16
2357		88.4		-0.18	3190		93.5		0.09
2358		90.8		-0.05	3191		92		0.01
2359		94.40		0.14	3192		109		0.91
2364		91		-0.04	3197		99		0.38
2365		85		-0.35	3199		92.8		0.06
2366		75.1		-0.87	3200		103		0.59
2367		87		-0.25	3201		53.5		-2.01
2368		83		-0.46	3210		58.9		-1.73
2370		98.7		0.37	3214		86.80		-0.26
2372		112		1.06	3216		74.83		-0.89
2373		86		-0.30	3218		89		-0.14
2375		104.0		0.64	3220		178.0	C,R(0.01)	4.53
2379		98.3		0.34	3222		86.0		-0.30
2380		106.44		0.77	3228		93		0.07
2381		107.264		0.82	3237		109.1936		0.92
2386		110		0.96	3242		99.97		0.43
2390		100.856		0.48	3243		124		1.69
2403		84.65		-0.37	3248		106.0		0.75
2410		74.6		-0.90	8005		99.7		0.42
2413		-----		-----					
2415		83.0		-0.46					
2425		91.8		0.00					
2426		93.6815		0.10					
2428		94		0.12					
2429		84.54		-0.38					
2432		95.5		0.20					
2441		76		-0.83					
2442		73.19		-0.97					
2452		92.07		0.02					
2462		105		0.70					
2472		60.4		-1.65					
2476		103.7		0.63					
2481		133.0		2.17					

normality	OK
n	126
outliers	1
mean (n)	91.744
st.dev. (n)	18.0195
R(calc.)	50.455
R(ISO17234-1:2010)	53.286

Compare R(Horwitz) = 20.819

Lab 551: first reported 374.10
Lab 3220: first reported 359.0





APPENDIX 2

Summary of other reported aromatic amines

lab	aromatic amines
2102	90.36 mg/kg 3.3-Dimethoxybenzidine;
2121	3.14mg/kg 4-Aminodiphenyl;
2217	2.22 mg/kg 4-Aminodiphenyl;
2413	2.45 mg/kg 2,4-Diaminoanisol; 5.37 mg/kg 2.4-Diaminotoluene
2497	1.33 mg/kg 4-Aminodiphenyl;
2534	36 mg/kg 4.4-Diaminodiphenylmethane;
2592	2.10 mg/kg 4-Aminodiphenyl;
3160	1.80 mg/kg 4-Aminodiphenyl;
3222	2.5 mg/kg 4-Aminodiphenyl;

APPENDIX 3

Analytical details

Lab	sample weight	degreasing	Reduction cleavage	column used	solvent used	Evap. temp.	solvent for dissolve residue	Chromatic analysis
110	1 g	n-hexane	10+10min	Diatomaceous earth	MTBE	45	Methanol	HPLC/DAD - GC/MSD
213	1 g	n-hexane	10+10min	quick meth	Ethylacetate	--	--	HPLC/DAD - GC/MSD
348	1 g	n-hexane	10+10min	--	ethylacetate	--	--	GC/MSD - HPLC/MS/MS
551	1 g	n-hexane	30 min	--	Ethylacetate	45	Methanol	GC/MSD
623	1.0 g	citrate	30 min	Diatomaceous earth	MTBE	60	Methanol	GC/MSD
840	1 g	n-hexane	30 min	--	MTBE	60	MTBE	--
1911	1 g	n-hexane	10+10min	Chromabond XTR	MTBE	40	Methanol	HPLC/DAD
2102	0.5 g	n-hexane	1.5 hrs	--	--	--	--	GC/MSD
2108	0.17 g	n-hexane	20min	Chromabond XTR	MTBE	50	Methanol	HPLC/DAD
2115	1 g	n-hexane	15+15min	Diatomaceous earth	MTBE	50	MTBE	GC/MSD
2121	0.75 g	n-hexane	10+10min	Extrelut NT20	MTBE	45	Methanol	LC-MS/DAD
2129	0.84 g	n-hexane	30 min	Chromabond XTR	MTBE	40	--	HPLC/DAD - GC/MSD
2132	1 g	n-hexane	20 min	Diatomaceous earth	MTBE	48	Methanol	HPLC/DAD
2135	1 g	n-hexane	30 min	Chromabond XTR	MTBE	50	MTBE	GC/MSD
2137	0.5 g	n-hexane	30 min	--	MTBE	50	MTBE	GC/MSD
2139	0.16 g	n-hexane	30 min	--	MTBE	60	Methanol	HPLC/DAD - GC/MSD
2146	--	--	--	--	--	--	--	--
2165	1 g	n-hexane	20 min	Kieselgur column	MTBE	50	Methanol	HPLC/DAD - GC/MSD
2166	0.5 g	--	30 min	Diatomaceous earth	MTBE	45	Phos. /methanol	HPLC/DAD
2170	1 g	n-hexane	10 min	Chromabond XTR	MTBE	40	--	--
2172	1 g	n-hexane	20 min	Kieselgur column	MTBE	40	Methanol	HPLC/DAD - GC/MSD
2184	1 g	n-hexane	20 min	Kieselgur column	MTBE	50	Methanol	HPLC/DAD - GC/MSD
2201	0.5 g	n-hexane	30+30min	Kieselgur column	MTBE	40	MTBE	HPLC/DAD - GC/MSD
2213	1 g	n-hexane	30min	Diatomaceous earth	MTBE	40	Methanol	HPLC/DAD - GC/MSD
2217	1 g	n-hexane	10+10min	--	MTBE	--	--	HPLC/MSD
2238	0.5 g	n-hexane	10+10min	Diatomaceous earth	MTBE	40	MTBE	HPLC/DAD - GC/MSD
2246	1 g	n-hexane	20 min	Chromabond XTR	MTBE	45	Methanol	HPLC/DAD - GC/MSD
2247	0.25 g	n-hexane	30 min	Chromabond XTR	MTBE	40	Methanol	HPLC/DAD - GC/MSD
2255	0.5 g	n-hexane	20 min	Kieselgur column	MTBE	50	MTBE	HPLC/DAD - GC/MSD
2256	1 g	n-hexane	20 min	Kieselgur column	MTBE	40	Methanol	HPLC/DAD - GC/MSD
2289	1 g	n-hexane	10+10min	Diatomaceous earth	MTBE	40	MTBE	HPLC/DAD - GC/MSD
2290	0.5 g	n-hexane	20 min	Chromabond XTR	MTBE	45	MTBE	HPLC/DAD - GC/MSD
2291	0.5 g	n-hexane	30 min	Chromabond XTR	MTBE	40	Acetonitril	HPLC/DAD - GC/MSD
2295	1 g	n-hexane	10+10min	Diatomaceous earth	MTBE	--	Nitrogen gas	GC/MSD
2296	1 g	n-hexane	30 min	Agilent ChemElt	MTBE	46	Methanol	HPLC/DAD - GC/MSD
2297	1 g	n-hexane	30 min	Kieselgur column	MTBE	40	Methanol	GC/MSD
2301	0.5 g	n-hexane	20 min	Kieselgur column	MTBE	40	Methanol	HPLC/DAD - GC/MSD
2310	1 g	n-hexane	30 min	Chem Elut HDPE	MTBE	40	Acetonitril	HPLC/DAD - GC/MSD
2311	1 g	n-hexane	30 min	Chem Elut HDPE	MTBE	30	Methanol	HPLC/DAD - GC/MSD
2352	0.5 g	n-hexane	20 min	Diatomaceous earth	MTBE	45	Methanol	GC/MSD
2357	1 g	n-hexane	30 min	Diatomaceous earth	MTBE	35	Methanol	HPLC/DAD
2358	0.9 g	n-hexane	30 min	Diatomaceous earth	MTBE	40	Methanol	HPLC/DAD - GC/MSD
2359	0.5 g	n-hexane	25 min	Diatomaceous earth	MTBE	45	Methanol	GC/MSD
2364	1 g	n-hexane	30 min	--	--	50	Ethylacetate	HPLC/DAD - GC/MSD
2365	0.5 g	n-hexane	10+10min	Diatomaceous earth	MTBE	40	Methanol	GC/MSD
2366	0.5 g	n-hexane	25 min	Diatomaceous earth	MTBE	45	MTBE	GC/MSD
2367	1 g	n-hexane	30 min	--	--	50	Ethylacetate	HPLC/DAD - GC/MSD
2368	0.5 g	n-hexane	30 min	--	--	50	Ethylacetate	HPLC/DAD - GC/MSD
2370	0.5 g	n-hexane	30 min	Diatomaceous earth	MTBE	40	Methanol	HPLC/DAD - GC/MSD
2372	1 g	n-hexane	30 min	--	MTBE	--	--	HPLC/DAD - GC/MSD
2373	1 g	n-hexane	10+10min	--	--	445	MTBE	HPLC/DAD - GC/MSD
2375	0.35 g	n-hexane	--	Chem Elut HDPE	MTBE	--	--	HPLC/DAD - GC/MSD
2379	1 g	n-hexane	30 min	Extrelut NT20	MTBE	40	Acetonitril	HPLC/DAD - GC/MSD
2380	1 g	n-hexane	20 min	--	--	--	--	--
2381	1 g	n-hexane	20 min	--	--	--	--	HPLC/DAD - GC/MSD
2386	0.1 g	citrate	30 min	TOX - Elut	MTBE	30	Methanol	HPLC/DAD
2390	0.5 g	n-hexane	10+10min	--	--	--	--	GC/MSD
2403	0.5 g	n-hexane	25 min	Kieselgur column	MTBE	35	Methanol	GC/MSD
2410	0.5 g	n-hexane	20 min	--	MTBE	50	MTBE	HPLC/DAD - GC/MSD
2413	1.0 g	n-hexane	20 min	Kieselgur column	MTBE	40	Methanol	GC/MSD
2415	0.5 g	n-hexane	30 min	--	MTBE	40	Methanol	HPLC/DAD - GC/MSD
2425	1 g	n-hexane	30 min	Diatomaceous earth	MTBE	49	Methanol	HPLC/DAD - GC/MSD
2426	0.5 g	n-hexane	20 min	Diatomaceous earth	MTBE	40	MTBE	GC/MSD
2428	1 g	n-hexane	30 min	Kieselgur column	MTBE	35	Methanol	HPLC/DAD
2429	1 g	n-hexane	20 min	Chromabond XTR	MTBE	40	MTBE	HPLC/DAD - GC/MSD
2432	0.5 g	n-hexane	30 min	--	MTBE	--	--	GC/MSD
2441	0.5 g	n-hexane	30 min	--	MTBE	40	Methanol	GC/MSD
2442	0.5 g	n-hexane	30 min	--	--	--	--	HPLC/DAD - GC/MSD
2452	1 g	n-hexane	10+10min	--	MTBE	40	MTBE	GC/MSD
2462	1 g	n-hexane	10 min	Diatomaceous earth	MTBE	46	Methanol	TLC - GC/MSD
2472	1 g	n-hexane	10 min	Diatomaceous earth	MTBE	38	Methanol	HPLC/DAD - GC/MSD
2476	1 g	n-hexane	20 min	Diatomaceous earth	MTBE	50	MTBE	HPLC/DAD - GC/MSD

2481	0.5 - 1 g	n-hexane	30 min	Chromabond XTR	Ethylacetate	30	Dichloromethane	GC/MSD
2489	0.2 g	n-hexane	30 min	Chromabond XTR	MTBE	40	Methanol	HPLC/DAD - GC/MSD
2492	0.25 g	citrate	30 min	Diatomaceous earth	MTBE	35	Methanol	HPLC/MSD
2493	--	--	--	--	--	--	--	--
2495	1 g	n-hexane	20 min	Chem Elut HDPE	MTBE	40	MTBE	HPLC/DAD - GC/MSD
2497	0.5 g	--	10 min	Extrelut NT20	MTBE	50	MTBE	HPLC/MSD
2499	1 g	n-hexane	10+10min	Extrelut NT20	MTBE	35	Ethylacetate	GC/MSD
2511	1 g	n-hexane	20 min	Agilent ChemElt	MTBE	45	Methanol	GC/MSD
2514	0.5 g	n-hexane	20 min	Kieselgur column	MTBE	50	MTBE	HPLC/DAD - GC/MSD
2516	1.0 g	n-hexane	10+10min	Diatomaceous earth	MTBE	35	Methanol	HPLC/DAD - GC/MSD
2532	0.4 g	n-hexane	30 min	Chromabond XTR	MTBE	40	Methanol	HPLC/DAD - GC/MSD
2534	1 g	MTBE	20 min	Hypersep SLE	MTBE	45	--	GC/MSD
2540	1 g	n-hexane	20 min	Diatomaceous earth	MTBE	35	MTBE	GC/MSD
2549	0.5 g	n-hexane	30 min	Extrelut NT20	MTBE	50	Methanol	UPLC-PDA
2553	1 g	n-hexane	10+10min	Extrelut NT20	MTBE	40	Acetonitril	HPLC/DAD - GC/MSD
2562	--		--	--	--	--	--	--
2565	1 g	n-hexane	10+10min	Diatomaceous earth	MTBE	35	Methanol	HPLC/DAD - GC/MSD
2566	1 g	n-hexane	20 min	Kieselgur column	MTBE	40	Methanol	HPLC/DAD - GC/MSD
2570	1 g	n-hexane	30 min	Diatomaceous earth	MTBE	45	Methanol	HPLC/DAD - GC/MSD
2578	0.23 g	n-hexane	30 min	Diatomaceous earth	MTBE	40	MTBE	GC/MSD
2581	0.5 g	n-hexane	10 min	--	MTBE	50	Methanol	GC/MSD
2582	0.3 g	n-hexane	30 min	Chem Elut HDPE	MTBE	52	MTBE	HPLC/DAD - GC/MSD
2590	1 g	n-hexane	--	Chem Elut HDPE	MTBE	30	Methanol	HPLC/DAD - GC/MSD
2592	0.8 g	n-hexane	10+10min	Extrelut NT20	MTBE	42	Methanol	GC/MSD
2609	1 g	n-hexane	20 min	Kieselgur column	MTBE	42	Methanol	HPLC/DAD
3100	0.5 g	n-hexane	30 min	Diatomaceous earth	MTBE	35	MTBE	HPLC/DAD - GC/MSD
3104	0.5 g	n-hexane	30 min	--	MTBE	--	--	HPLC/DAD - GC/MSD
3116	1 g	n-hexane	20 min	Kieselgur column	MTBE	40	Methanol	HPLC/DAD - GC/MSD
3117	1 g	n-hexane	30 min	Diatomaceous earth	MTBE	34	Ethylacetate	HPLC/DAD - GC/MSD
3118	1 g	n-hexane	10+10min	Kieselgur column	MTBE	35	MTBE	GC/MSD
3146	0.5 g	n-hexane	30 min	--	MTBE	45	Methanol	HPLC/DAD - GC/MSD
3150	0.5 g	n-hexane	30 min	Kieselgur column	MTBE	40	MTBE	GC/MSD
3153	0.5 g	n-hexane	20 min	Chromabond XTR	MTBE	35	MTBE	HPLC/DAD - GC/MSD
3154	0.3 g	citrate	30 min	alkaline silicate	MTBE	60	MTBE	HPLC/DAD
3160	0.8 g	n-hexane	20 min	Chem Elut HDPE	MTBE	50	Ethylacetate	GC/MSD
3167	1 g	n-hexane	30 min	Diatomaceous earth	MTBE	40	Methanol	HPLC/DAD - GC/MSD
3172	1 g	n-hexane	30 min	--	MTBE	35	Ethylacetate	HPLC/MSD - GC/MSD
3176	0.5 g	n-hexane	30 min	--	MTBE	50	Methanol	LC/MS-MS
3180	0.75 g	--	30 min	--	--	50	Methanol	HPLC/DAD - GC/MSD
3182	0.5 g	n-hexane	25 min	Agilent ChemElt	MTBE	50	MTBE	GC/MSD
3185	1 g	n-hexane	30 min	--	MTBE	--	--	HPLC/MSD - GC/MSD
3190	0.5 g	n-hexane	10+10min	Diatomaceous earth	MTBE	40	MTBE	HPLC/DAD - GC/MSD
3191	1 g	n-hexane	25 min	Diatomaceous earth	MTBE	50	Methanol	HPLC/DAD - GC/MSD
3192	1 g	n-hexane	20 min	Extrelut NT20	MTBE	45	Methanol	CE/DAD
3197	1 g	n-hexane	10+10min	Chem Elut HDPE	MTBE	40	Methanol	GC/MSD
3199	0.5 g	n-hexane	20 min	Agilent ChemElt	MTBE	40	Acetonitril	HPLC/DAD - GC/MSD
3200	0.5 g	n-hexane	30 min	Diatomaceous earth	MTBE	50	Methanol	HPLC/DAD
3201	1 g	n-hexane	20 min	Extrelut NT20	MTBE	40	Ethylacetate	HPTLC - GC/MSD
3210	1 g	n-hexane	30 min	--	MTBE	--	Methanol	HPLC/DAD - GC/MS/MS
3214	0.5 g	n-hexane	30 min	Chromabond XTR	MTBE	35	MTBE	HPLC/DAD - GC/MSD
3216	1 g	n-hexane	20 min	siliceous earth	MTBE	40	Methanol	HPLC/MS - GC/MSD
3218	1 g	--	30 min	Kieselgur column	MTBE	40	MTBE	HPLC/DAD - GC/MSD
3220	1 g	n-hexane	60 min	Chem Elut HDPE	--	40	Methanol	HPLC/DAD - GC/MSD
3222	1 g	n-hexane	20 min	Diatomaceous earth	MTBE	46	Acetonitril	GC/MSD
3228	1 g	n-hexane	20 min	Kieselgur column	MTBE	50	Methanol	HPLC/DAD - GC/MSD
3237	0.33 g	n-hexane	30 min	--	MTBE	--	--	HPLC/DAD - GC/MSD
3242	0.5 g	n-hexane	30 min	Extrelut NT20	MTBE	45	Methanol	HPLC/DAD
3243	1 g	n-hexane	30 min	Nucleodur C18	MTBE	50	MTBE	HPLC/DAD - GC/MSD
3248	1 g	--	30 min	Kieselgur column	MTBE	40	Acetonitril	HPLC/DAD - GC/MSD
8005	1 g	n-hexane	20 min	Kieselgur column	MTBE	40	Methanol	HPLC/DAD

APPENDIX 4

Number of participants per country

6 labs in	BANGLADESH
1 lab in	BRAZIL
1 lab in	EGYPT
1 lab in	FINLAND
3 labs in	FRANCE
11 labs in	GERMANY
12 labs in	HONG KONG
2 labs in	HUNGARY
11 labs in	INDIA
3 labs in	INDONESIA
9 labs in	ITALY
2 labs in	JAPAN
4 labs in	KOREA
1 lab in	MOROCCO
35 labs in	P.R. of CHINA
2 labs in	PAKISTAN
1 lab in	POLAND
1 lab in	SINGAPORE
3 labs in	SPAIN
2 labs in	SRI LANKA
1 lab in	SWITZERLAND
3 labs in	TAIWAN R.O.C.
2 labs in	THAILAND
1 lab in	THE NETHERLANDS
2 labs in	TUNISIA
5 labs in	TURKEY
3 labs in	U.S.A.
1 lab in	UNITED KINGDOM
3 labs in	VIETNAM

APPENDIX 5

Abbreviations:

C = final result after checking of first reported suspect result
D(0.01) = outlier in Dixon's outlier test
D(0.05) = straggler in Dixon's outlier test
G(0.01) = outlier in Grubbs' outlier test
G(0.05) = straggler in Grubbs' outlier test
DG(0.01) = outlier in Double Grubbs' outlier test
DG(0.05) = straggler in Double Grubbs' outlier test
R(0.01) = outlier in Rosner' outlier test
R(0.05) = straggler in Rosner' outlier test
n.e. = not evaluated
n.d. = not detected

Literature:

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2 ISO 17234:2010
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