Results of Proficiency Test
AZO dyes in textile
March 2011

Organised by: Institute for Interlaboratory Studies
                 Spijkenisse, the Netherlands

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Appendices:

1   INTRODUCTION

The Institute for Interlaboratory Studies (iis) organizes every year a scheme of proficiency test for banned AZO dyes in textile since 1997.

In this interlaboratory study, 107 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. It was decided to use in this proficiency test 2 different textile samples (labelled #11018 and #11019), each dyed with different AZO dyes. The samples were prepared by a third party and tested for homogeneity by an accredited 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, ILAC-G13:2007 and ISO 17043:2010. 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

Two different bulk textile samples, each dyed with different AZO-dyes, were prepared by a third party. The first batch, labelled #11018, was a blue-grey coloured hosiery fabric and the second batch, labelled #11019, was a violet coloured hosiery fabric.

Each bulk sample of approximately 1 kg of material was cut into pieces and after thorough mixing, divided over 150 subsamples of 4 gram each. The samples were labelled and tested for homogeneity. The homogeneity of the subsamples #11018 and #11019 (testing was subcontracted) was checked by determination of aromatic amines on respectively 5 and 8 stratified randomly selected samples. See the following tables for the test results.

Blue-grey coloured hosiery fabric	3,3-Dimethoxybenzidine in mg/kg
sample #11018-1	190
sample #11018-2	210
sample #11018-3	200
sample #11018-4	200
sample #11018-5	210

table 1: homogeneity test results of subsamples #11018

violet coloured hosiery fabric	4,4-Diaminodiphenylether in mg/kg	4,4-Diamino-3,3-dichloro-diphenylmethane in mg/kg
sample #11019-1	39.2	94.9
sample #11019-2	37.9	97.2
sample #11019-3	37.8	93.4
sample #11019-4	39.3	97.3
sample #11019-5	38.1	93.2
sample #11019-6	40.1	97.8
sample #11019-7	40.3	95.1
sample #11019-8	39.4	92.0

table 2: homogeneity test results of subsamples #11019

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 tables:

	3,3-Dimethoxybenzidine in mg/kg
r (observed)	23.4
reference method	EN14362-1
0.3 x R (reference method)	26.1

table 3: repeatabilities of subsamples #11018

	4,4-Diaminodiphenylether in mg/kg	*4,4-Diamino-3,3-dichloro-diphenylmethane in mg/kg*
r (observed)	0.3	0.6
reference method	EN14362-1	EN14362-1
0.3 x R (reference method)	5.9	14.4

table 4: repeatabilities of subsamples #11019

The repeatabilities of the results of homogeneity test were in agreement with 0.3 times the reproducibilities mentioned in (or estimated from) the reference method EN14362-1. Therefore, homogeneity of the subsamples was assumed.

Approx. 4 grams of each of the samples #11018 and #11019 was sent to the participating laboratories on March 9, 2011.

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. 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) 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.

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.

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. Sixteen participants reported the results after the deadline and two participants did not report any results due to various reasons. Finally, 105 participants did report 476 numerical results. Observed were 25 outlying results, which is 5.3% of the numerical results. In proficiency studies, outlier percentages of 3% - 7.5% are quite normal.
Not all data sets proved to have a normal distribution. Anomal data distributions were found for 4-Aminodiphenyl, Benzidine and 3,3-Dimethoxybenzidine. Therefore, the statistical evaluations should be used with care.

4.1 EVALUATION PER SAMPLE AND COMPONENT

In this section, the results are discussed per sample. All statistical results reported on the textile samples are summarised in appendix 1 and all other reported results of the most relevant aromatic amines present are summarised in appendix 2.
For participants that reported results, of which more then 50% turned out to be statistical outliers, the other reported results were excluded, as they may be suspect too.

Sample #11018:

4-Aminodiphenyl (CASno.92-67-1):

The determination of this aromatic amine at the low concentration level of 5 mg/kg, which is probably near or below the lower detection limit, was only problematic for one laboratory that reported a false positive result. All other laboratories reported a test result less than 30 mg/kg. No further conclusions were drawn.
The numerical test results reported by the participants vary from 1.45 – 69.7 mg/kg.

Benzidine (CASno.92-87-5):

The determination of this aromatic amine at a concentration level of 73 mg/kg, was problematic. Five statistical outliers were detected and four laboratories reported a test result less than 30 mg/kg (or "not detected").
The numerical test results reported by the participants vary from 11.4 – 151.1 mg/kg.
The observed reproducibility (51%) is, after rejection of the statistical outliers, not in agreement with the reproducibility for this amine as mentioned in EN14362 (39%).

3,3-Dimethoxybenzidine (CASno.119-90-4):

The determination of this aromatic amine at a concentration level of 227 mg/kg, was problematic. Five statistical outliers were detected and six laboratories reported a test result less than 30 mg/kg (or "not detected").

The numerical test results reported by the participants vary from 23.2 – 413.4 mg/kg. The observed reproducibility (48%) is, after rejection of the statistical outliers, not in agreement with the estimated reproducibility limit of EN14362 (35%).

Sample #11019:

4,4-Diamino-3,3-dichlorodiphenylmethane (CASno.101-14-4):

The determination of this aromatic amine at a concentration level of 68.5 mg/kg was problematic. Four statistical outliers were detected and three laboratories reported a test result less than 30 mg/kg and one laboratory reported "not detected". The numerical test results reported by the participants vary from 1.6 – 110 mg/kg. The observed reproducibility (55%) is, after rejection of the statistical outliers, not in agreement with the strict estimated reproducibility as mentioned in EN14362 (45%).

4,4-Diaminodiphenylether (CASno.101-80-4):

The determination of this aromatic amine at a concentration level of 29 mg/kg, was problematic for a number of laboratories. Ten statistical outliers were detected and two laboratories reported "not detected". The numerical test results reported by the participants vary from 6.6 – 54.3 mg/kg. The observed reproducibility (41%) is, after rejection of the statistical outliers, in full agreement with the estimated reproducibility mentioned in EN14362 (45%).

4.2   PERFORMANCE EVALUATION FOR THE GROUP OF LABORATORIES

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

The number of significant results, the average results, the calculated reproducibilities (standard deviation*2.8) and the target reproducibilities, derived (or estimated) from the official test method EN14362-1 (equivalent to LFGB 82.02-2), are compared in the next two tables.

Parameter	unit	n	Average	2.8 * sd	EN14362-1
4-Aminodiphenyl	mg/kg	54	5.2	4.5	(2.4) *
Benzidine	mg/kg	95	72.7	37.1	28.1
3,3-Dimethoxybenzidine	mg/kg	91	228.1	108.6	80.1

table 5: reproducibilities of the aromatic amines in textile sample #11018

*) between brackets is near or below detection limit

Parameter	unit	n	Average	2.8 * sd	EN14362-1
4,4-Diamino-3,3-dichlorodiphenylmethane	mg/kg	98	68.9	38.0	31.2
4,4-Diaminodiphenylether	mg/kg	89	29.1	11.8	13.2

table 6: reproducibilities of the aromatic amines in textile sample #11019

Without further statistical calculations, it can be concluded that the group of participating laboratories has some difficulties with the analysis of the found concentration levels (5-227 mg/kg) for all aromatic amines. See also the discussion in paragraphs 4.1 and 6.

5   COMPARISON WITH PREVIOUS INTERLABORATORY STUDIES

The spreads in the results of the aromatic amines are all relatively small in comparison with the spreads as observed in previous PTs and almost in agreement with the (estimated) reproducibilities mentioned in the standardized test method EN14362-1, see below table.

Parameter	March 2011	March 2010	March 2009	March 2008	March 2007	April 2006	April 2005	EN 14362
4-Aminodiphenyl	(86%)*	50%	n.a.	n.a.	100%	n.a.	n.a.	45%.
Benzidine	51%	54%	n.a.	57%	71-99%	78%	78%	39%
3,3-Dimethylbenzidine	n.a.	49%	n.a.	90%	77%	n.a.	84%	49%
3,3-Dimethoxybenzidine	48%	n.a.	n.a.	n.a.	59-70%	83%	85%	35%
o-Toluidine	n.a.	52%	n.a.	n.a.	n.a	n.a.	106%	61%
2-Naphthylamine	n.a.	n.a.	n.a.	75%	n.a.	n.a.	116%	45%.
4,4-Diaminodiph.methane	n.a.	n.a.	58%	n.a.	n.a.	n.a.	92%	42%
4,4-Diaminodiph.sulfide	n.a.	51%	n.a.	73%	n.a.	n.a.	n.a.	45%.
p-Chloroaniline	n.a.	n.a.	76%	n.a.	n.a.	n.a.	n.a.	45%.
4,4-Diaminodiphenylether	41%	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	45%
4,4-Diamino-3,3-dichlorodiphenylmethane	55%	n.a.	65%	n.a.	n.a.	119%	n.a.	45%.

table 7: long term development of relative reproducibilities of aromatic amines in textile samples

* The concentration of percentage between brackets was near or below detection limit

The improvement over the years is continuing. This may be 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

From the reported test methods, it is clear that most participants treated the fabric samples according identical test methods. The majority used EN14362-1 and some others used the (identical) method LFBG 82.02.2. Only seven participants reported to have used a different test method.

One laboratory remarked that it did not find any of the requested amines, while five other participants reported 'not detected" for one of the detected amines.
The observed spreads of the test results is not yet in full agreement with the estimated target spread, based on EN14362-1. And from the Kernel graphic presentations in appendix 1, it may be concluded that still some quality improvement may be gained.

Sample #11018 was already used before, in PT iis02A02. When the data of both PTs are compared it is remarkable to notice that the consensus values for both rounds differ not significantly, while the spread has improved strongly, see table 8.
This implicates that the AZO dyes present in the material used for samples #0220 and #11018, were stable for this 9-year period and also that the quality of the analysis has improved significantly over the years. And also it may be concluded that the assigned values, determined as averages in the iis PTs, are consistent over the years.

	4-aminodiphenyl		Benzidine		3,3-Dimethoxybenzidine	
	iis02A02	iis11A01	iis02A02	iis11A01	iis02A02	iis11A01
number of results	28	55	39	95	37	92
average	4.0	5.1	72.5	72.7	237.1	227.1
2.8 * st.dev.	4.9	4.7	69.4	37.1	175.7	110.8
R (EN14362-1)	(1.1) *	(2.3) *	28.0	28.1	83.2	79.7

table 8: Comparison of aromatic amines in samples #0220 (in iis02A02) and #11018 (in iis11A01)

*) between brackets is near or below detection limit

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.
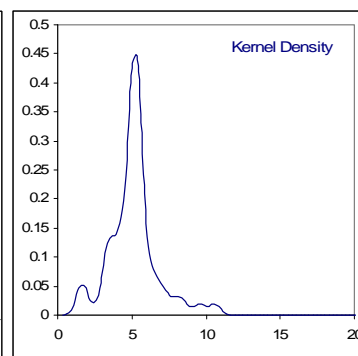
APPENDIX 1

Determination of 4-Aminodiphenyl (CASno.92-67-1) in sample #11018; results in mg/kg

lab	method	value	mark	z(targ)	remarks
1213	TCVN7619-1	3.45		-----	
2102		-----		-----	
2115		4.75		-----	
2120		-----		-----	
2121		-----		-----	
2129	EN14362-1	5		-----	
2131		-----		-----	
2132	EN14362-1	<5		-----	
2135		4		-----	
2146	EN14362-1	3.8		-----	
2152		4.33		-----	
2160		-----		-----	
2166	EN14362-1	<10		-----	
2172	EN14362-1	5.36		-----	
2173		5.800		-----	
2184	EN14362-1	5		-----	
2190	EN14362	8.0		-----	
2196	EN14362-1	4		-----	
2197		69.7	G(0.01)	-----	False positive result?
2201	EN14362-1	<5		-----	
2215	EN14362-1	5.5		-----	
2218		-----		-----	
2221	EN14362-1	n.d.		-----	
2235		-----		-----	
2236	EN14362-1	4.490		-----	
2239		-----		-----	
2241	EN14362-1	n.d.		-----	
2246		<10		-----	
2247	EN14362-1	4.4		-----	
2248	EN14362-1	<10		-----	
2255	EN14362-1	6.5		-----	
2256	EN14362-1	5.36		-----	
2260	EN14362-1	5.0		-----	
2261		-----		-----	
2266		-----		-----	
2271		n.d.		-----	
2272	EN14362-1	n.d.		-----	
2275	EN14362-1	5		-----	
2284	EN14362-1	<10		-----	
2286	EN14362-1&2	<10		-----	
2287	EN14362-1&2	<10		-----	
2289		-----		-----	
2290	EN14362-1	5.6		-----	
2292		-----		-----	
2295	EN14362-1	4.8		-----	
2297	EN14362-1	<10		-----	
2405	EN14362-1&2	2.8		-----	
2410	EN14362-1	<20		-----	
2413	EN14362-1	10.58		-----	
2415	EN14362-1	n.d.		-----	
2419	EN14362-1	1.45	ex	-----	Result excluded, see paragraph 4.1
2421		1.648		-----	
2427		-----		-----	
2428		-----		-----	
2432		-----		-----	
2434	EN14362-1	9.56	C	-----	First reported 2.73 mg/kg
2436	EN14362-1	5.3		-----	
2437	EN14362-1	5.2		-----	
2439	LMGB B82.02-2	5.1		-----	
2440	GB/T 17592	3.4		-----	
3100		5.2		-----	
3101	EN14362-1	n.d.		-----	
3104		<10		-----	
3107		3.4		-----	
3116	EN14362-1	5.4		-----	
3117	EN14362-1	5		-----	
3118		6.18		-----	
3134		-----		-----	
3146		3.5		-----	
3149	LFGB B82.02-2	6.75		-----	
3150	LFGB B82.02-2	5.8		-----	
3151		-----		-----	
3153	EN14362-1	6.9		-----	

3154	EN14362-1	n.d.	-----
3159	EN14362-1	5.2	-----
3160	EN14362-1	4.25	-----
3163	TD-GC-MS	n.d.	-----
3167	EN14362-1	5.49	-----
3170		-----	-----
3172	EN14362-1	<10	-----
3174	EN14362-1	7.42	-----
3176		3.4	-----
3180		-----	-----
3182	EN14362-1	<5	-----
3185	EN14362-1	5.1	-----
3190	EN14362-1	<5	-----
3191	EN14362-1	<10	-----
3195	EN14362-1	4.853	-----
3197	EN14362-1	5.9	-----
3199	CPSD-AN-00017	<10	-----
3200	EN14362-1	5.4	-----
3204	LFGB B82.02-2	<10	-----
3209	EN14362-1	5.5	-----
3210	EN14362-1	1.87	-----
3214	EN14362-1	5.3	-----
3218	EN14362-1	n.d.	-----
3220	EN14362-1	5.0	-----
3225		-----	-----
3228		-----	-----
3232	EN14362-1	n.d.	-----
3233	EN14362-1	n.d.	-----
3237	EN14362-1/2	5.45	-----
3243		-----	-----
3246		5.3	-----
3247	EN14362-1	8.5	-----
3248		5.0	-----
8008		<10	-----

normality	not OK
n	54
outliers	1
mean (n)	5.20
st.dev. (n)	1.596
R(calc.)	4.47
R(EN14362-1)	(2.35)
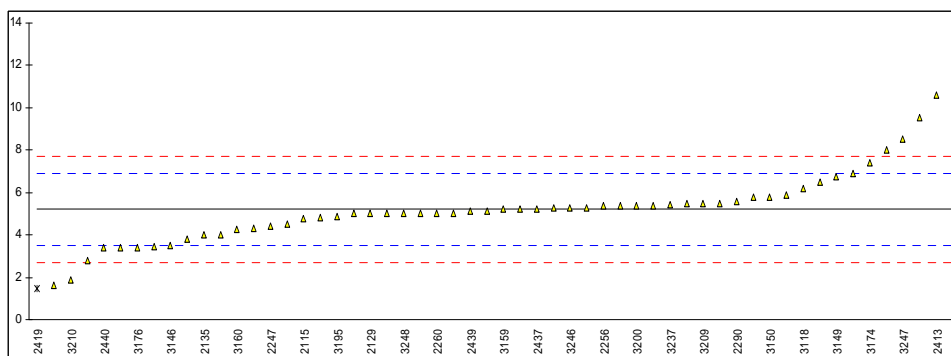
Determination of Benzidine (CASno.92-87-5) in sample #11018; results in mg/kg

lab	method	value	mark	z(targ)	remarks
1213	TCVN7619-1	45.8		-2.68	
2102		74.19		0.15	
2115		77.14		0.44	
2120	EN14362-1	77		0.43	
2121		-----		-----	
2129	EN14362-1	58		-1.46	
2131		31.1	DG(0.05)	-4.14	
2132	EN14362-1	98.5		2.57	
2135		63		-0.96	
2146	EN14362-1	81.5		0.88	
2152		78.67		0.59	
2160		-----		-----	
2166	EN14362-1	55.67		-1.69	
2172	EN14362-1	74.0		0.13	
2173		73.86		0.12	
2184	EN14362-1	78		0.53	
2190	EN14362	84.0		1.13	
2196	EN14362-1	60		-1.26	
2197		151.1	G(0.01)	7.80	
2201	EN14362-1	75.0		0.23	
2215	EN14362-1	72.6		-0.01	
2218	EN14362-1&2	57.14		-1.55	
2221	EN14362-1	76		0.33	
2235	EN14362-1	67.9		-0.48	
2236	EN14362-1	84.60		1.18	
2239		63.2		-0.94	
2241	EN14362-1	73.2		0.05	
2246		74.48		0.18	
2247	EN14362-1	75.0		0.23	
2248	EN14362-1	65.2		-0.75	
2255	EN14362-1	78.0		0.53	
2256	EN14362-1	74.1		0.14	
2260	EN14362-1	65.0		-0.77	
2261		-----		-----	
2266	EN14362-1	46.60		-2.60	
2271		73.1		0.04	
2272	EN14362-1	41.8		-3.07	
2275	EN14362-1	82		0.93	
2284	EN14362-1	74.0		0.13	
2286	EN14362-1&2	79		0.63	
2287	EN14362-1&2	54		-1.86	
2289		85		1.22	
2290	EN14362-1	81.7		0.90	
2292	EN14362-1	42.65	C	-2.99	First reported 38.35 mg/kg
2295	EN14362-1	90		1.72	
2297	EN14362-1	80		0.73	
2405	EN14362-1&2	78.3		0.56	
2410	EN14362-1	72.5		-0.02	
2413	EN14362-1	82.30		0.96	
2415	EN14362-1	76.3419		0.36	
2419	EN14362-1	11.41	G(0.05)	-6.10	
2421		40.443		-3.21	
2427	EN14362-1	80.12		0.74	
2428		-----		-----	
2432	in house	78.6		0.59	
2434	EN14362-1	46.45		-2.61	
2436	EN14362-1	94.6		2.18	
2437	EN14362-1	82.5		0.98	
2439	LMGB B82.02-2	75.8		0.31	
2440	GB/T 17592	55.6		-1.70	
3100		80.7		0.80	
3101	EN14362-1	n.d.		-----	False negative?
3104		66.08		-0.66	
3107		56.7		-1.59	
3116	EN14362-1	73		0.03	
3117	EN14362-1	74		0.13	
3118		83.64		1.09	
3134		-----		-----	
3146		54		-1.86	
3149	LFGB B82.02-2	77.3		0.46	
3150	LFGB B82.02-2	81		0.83	
3151	EN14362-1	69		-0.37	
3153	EN14362-1	88.1		1.53	

3154	EN14362-1	53.40		-1.92	
3159	EN14362-1	77.6		0.49	
3160	EN14362-1	74.71		0.20	
3163	TD-GC-MS	n.d.		-----	False negative?
3167	EN14362-1	97.9		2.51	
3170		20.42	DG(0.05)	-5.20	
3172	EN14362-1	76.3		0.36	
3174	EN14362-1	45.57		-2.70	
3176		52.3		-2.03	
3180		52.6		-2.00	
3182	EN14362-1	83.507		1.08	
3185	EN14362-1	82.5		0.98	
3190	EN14362-1	66.4		-0.63	
3191	EN14362-1	79		0.63	
3195	EN14362-1	87.284		1.45	
3197	EN14362-1	77.3		0.46	
3199	CPSD-AN-00017	70.9		-0.18	
3200	EN14362-1	91.7		1.89	
3204	LFGB B82.02-2	32.2	G(0.05)	-4.03	
3209	EN14362-1	75.8		0.31	
3210	EN14362-1	60.0		-1.26	
3214	EN14362-1	90.8		1.80	
3218	EN14362-1	77		0.43	
3220	EN14362-1	80.0		0.73	
3225	EN14362-1	76.2		0.35	
3228		80		0.73	
3232	EN14362-1	87		1.42	
3233	EN14362-1	64.87		-0.78	
3237	EN14362-1/2	69.0		-0.37	
3243	LFGB B82.02-2	97.9		2.51	
3246		65.4		-0.73	
3247	EN14362-1	96		2.32	
3248		75.0		0.23	
8008		64.32		-0.83	

|	
normality	not OK
n	95
outliers	5
mean (n)	72.69
st.dev. (n)	13.232
R(calc.)	37.05
R(EN14362-1)	28.13
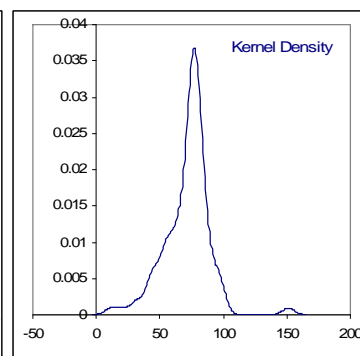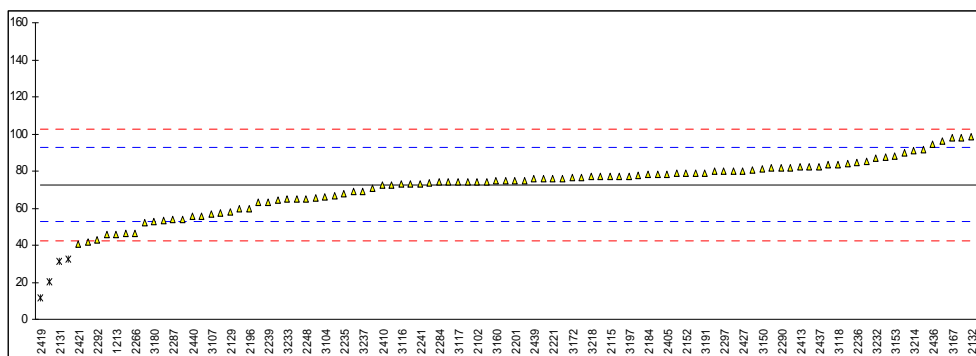
Determination of 3,3-Dimethoxybenzidine (CASno.119-90-4) in sample #11018; results in mg/kg

lab	method	value	mark	z(targ)	remarks
1213	TCVN7619-1	256		0.98	
2102		156.40		-2.51	
2115		234.19		0.21	
2120	EN14362-1	217		-0.39	
2121		-----		-----	
2129	EN14362-1	n.d.		-----	False negative?
2131		144.28	ex	-2.93	Result excluded, see paragraph 4.1
2132	EN14362-1	302.4		2.60	
2135		225		-0.11	
2146	EN14362-1	248		0.70	
2152		261.28		1.16	
2160		-----		-----	
2166	EN14362-1	111.43	G(0.05)	-4.08	
2172	EN14362-1	251		0.80	
2173		254.4		0.92	
2184	EN14362-1	240		0.42	
2190	EN14362	249.9		0.76	
2196	EN14362-1	170		-2.03	
2197		413.4	G(0.05)	6.48	
2201	EN14362-1	214.6		-0.47	
2215	EN14362-1	237.0		0.31	
2218	EN14362-1&2	157.52		-2.47	
2221	EN14362-1	236		0.28	
2235	EN14362-1	213.0		-0.53	
2236	EN14362-1	250.5		0.79	
2239		253.7		0.90	
2241	EN14362-1	229.9		0.06	
2246		239.58		0.40	
2247	EN14362-1	244.0		0.56	
2248	EN14362-1	201.5		-0.93	
2255	EN14362-1	241.6		0.47	
2256	EN14362-1	231		0.10	
2260	EN14362-1	179.2		-1.71	
2261	GB/T 17592	292		2.24	
2266	EN14362-1	149.80		-2.74	
2271		231		0.10	
2272	EN14362-1	132.2		-3.35	
2275	EN14362-1	261		1.15	
2284	EN14362-1	240.0		0.42	
2286	EN14362-1&2	249		0.73	
2287	EN14362-1&2	293		2.27	
2289		260		1.12	
2290	EN14362-1	244.8		0.59	
2292		-----		-----	
2295	EN14362-1	293		2.27	
2297	EN14362-1	210		-0.63	
2405	EN14362-1&2	208.2		-0.69	
2410	EN14362-1	223		-0.18	
2413	EN14362-1	n.d.		-----	False negative?
2415	EN14362-1	264.0954		1.26	
2419		-----		-----	
2421		23.221	G(0.05)	-7.16	
2427	EN14362-1	224.84		-0.11	
2428		-----		-----	
2432	in house	277.3		1.72	
2434	EN14362-1	159.04		-2.41	
2436	EN14362-1	246.1		0.63	
2437	EN14362-1	285.5		2.01	
2439	LMGB B82.02-2	275.0		1.64	
2440	GB/T 17592	179.7		-1.69	
3100		248.0		0.70	
3101	EN14362-1	167.4		-2.12	
3104		261.52		1.17	
3107		174.7		-1.87	
3116	EN14362-1	243		0.52	
3117	EN14362-1	250		0.77	
3118		240.71		0.44	
3134		-----		-----	
3146		137		-3.18	
3149	LFGB B82.02-2	222.5		-0.19	
3150	LFGB B82.02-2	230		0.07	
3151	EN14362-1	210		-0.63	
3153	EN14362-1	232.5		0.16	

3154	EN14362-1	164.27		-2.23	
3159	EN14362-1	235		0.24	
3160	EN14362-1	189.97		-1.33	
3163	TD-GC-MS	n.d.		-----	False negative?
3167	EN14362-1	249		0.73	
3170		24.47	G(0.01)	-7.12	
3172	EN14362-1	234.4		0.22	
3174	EN14362-1	150.84		-2.70	
3176		181.6		-1.62	
3180		174.7	C	-1.87	First reported 140.8 mg/kg
3182	EN14362-1	264.798		1.29	
3185	EN14362-1	237		0.31	
3190	EN14362-1	225.5		-0.09	
3191	EN14362-1	226		-0.07	
3195	EN14362-1	249.267		0.74	
3197	EN14362-1	267.7		1.39	
3199	CPSD-AN-00017	211.5		-0.58	
3200	EN14362-1	277.8		1.74	
3204	LFGB B82.02-2	215.4		-0.44	
3209	EN14362-1	223.9		-0.15	
3210	EN14362-1	164		-2.24	
3214	EN14362-1	229.3		0.04	
3218	EN14362-1	260		1.12	
3220	EN14362-1	248.0		0.70	
3225	EN14362-1	248.3		0.71	
3228		250		0.77	
3232	EN14362-1	n.d.		-----	False negative?
3233	EN14362-1	143.65		-2.95	
3237	EN14362-1/2	217.5		-0.37	
3243	LFGB B82.02-2	264		1.26	
3246		264.1		1.26	
3247	EN14362-1	348	G(0.01)	4.20	
3248		213.4		-0.51	
8008		260.98		1.15	

|	
normality	not OK
n	91
outliers	5
mean (n)	228.05
st.dev. (n)	38.792
R(calc.)	108.62
R(EN14362-1)	80.05
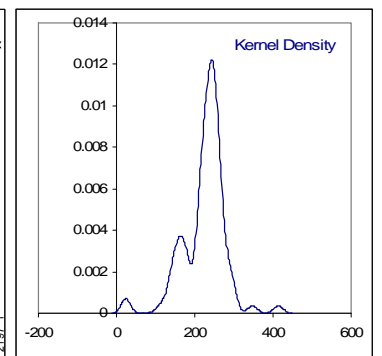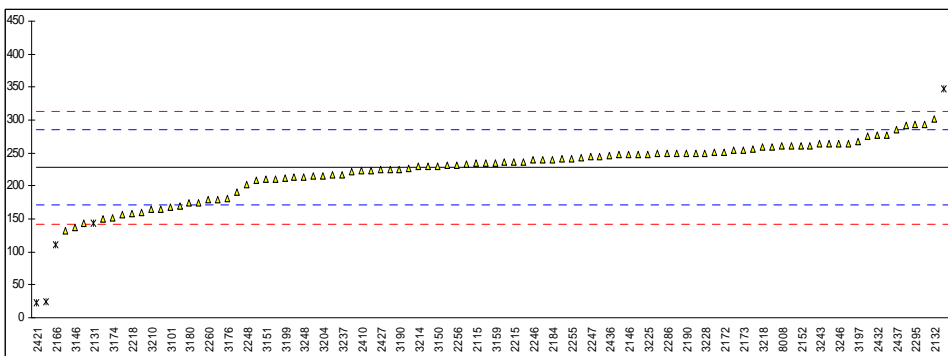
Determination of 4,4-Diamino-3,3-dichlorodiphenylmethane (CASno.101-14-4) in sample #11019; results in mg/kg

lab	method	value	mark	z(targ)	remarks
1213	TCVN7619-1	110	G(0.05)	3.70	
2102		45.43		-2.10	
2115		64.52		-0.39	
2120	EN14362-1	80		1.00	
2121		-----		-----	
2129	EN14362-1	57		-1.06	
2131		19.8	DG(0.05)	-4.41	
2132		98.4		2.65	
2135		56		-1.15	
2146	EN14362-1	56.8		-1.08	
2152		66.09		-0.25	
2160		-----		-----	
2166	EN14362-1	33.36		-3.19	
2172	EN14362-1	82.6		1.23	
2173		63.57		-0.47	
2184	EN14362-1	69		0.01	
2190	EN14362	74.3		0.49	
2196	EN14362-1	54		-1.33	
2197		17.0	DG(0.05)	-4.66	
2201	EN14362-1	74.2		0.48	
2215	EN14362-1	77.9		0.81	
2218	EN14362-1&2	62.53		-0.57	
2221	EN14362-1	82		1.18	
2235	EN14362-1	54.4		-1.30	
2236	EN14362-1	75.65		0.61	
2239		63.7		-0.46	
2241	EN14362-1	71.4		0.23	
2246		76.11		0.65	
2247	EN14362-1	70.0		0.10	
2248	EN14362-1	60.2	C	-0.78	First reported 11.2 mg/kg
2255	EN14362-1	73.5		0.42	
2256	EN14362-1	72.5		0.33	
2260	EN14362-1	56.7		-1.09	
2261	GB/T 17592	84		1.36	
2266	EN14362-1	36.20		-2.93	
2271		84.6		1.41	
2272	EN14362-1	78.3		0.85	
2275	EN14362-1	82		1.18	
2284	EN14362-1	78.6		0.88	
2286	EN14362-1&2	67		-0.17	
2287	EN14362-1&2	64	C	-0.44	First reported 136 mg/kg
2289		76		0.64	
2290	EN14362-1	81.8		1.16	
2292	EN14362-1	38.15	C	-2.76	First reported 34.67 mg/kg
2295	EN14362-1	54		-1.33	
2297	EN14362-1	65		-0.35	
2405	EN14362-1&2	42.8		-2.34	
2410	EN14362-1	85.4		1.49	
2413	EN14362-1	78.52		0.87	
2415	EN14362-1	76.8199		0.72	
2419	EN14362-1	1.60	G(0.01)	-6.04	
2421		89.009		1.81	
2427	EN14362-1	84.65	C	1.42	First reported 105.54 mg/kg
2428	GB/T 17592	56.0		-1.15	
2432	in house	92.5		2.12	
2434	EN14362-1	48.83		-1.80	
2436	EN14362-1	63.8		-0.45	
2437	EN14362-1	85.5		1.50	
2439	LMGB B82.02-2	75.7		0.62	
2440	GB/T 17592	54.9		-1.25	
3100		72.4		0.32	
3101	EN14362-1	75.6		0.61	
3104		70.18		0.12	
3107		50.2		-1.68	
3116	EN14362-1	76		0.64	
3117	EN14362-1	72		0.28	
3118		84.4		1.40	
3134		79.8		0.98	
3146		53		-1.42	
3149	LFGB B82.02-2	53.2		-1.41	
3150	LFGB B82.02-2	59		-0.88	
3151	EN14362-1	72		0.28	
3153	EN14362-1	77.2		0.75	

3154	EN14362-1	66.87		-0.18	
3159	EN14362-1	71.3		0.22	
3160	EN14362-1	41.34		-2.47	
3163	TD-GC-MS	n.d.		-----	False negative?
3167	EN14362-1	67.5		-0.12	
3170		32.71	ex	-3.25	Result excluded, see paragraph 4.1
3172	EN14362-1	69.8		0.09	
3174	EN14362-1	49.39		-1.75	
3176		86.2		1.56	
3180		46.1		-2.04	
3182	EN14362-1	97.103		2.54	
3185	EN14362-1	74.4		0.50	
3190	EN14362-1	77.0		0.73	
3191	EN14362-1	70		0.10	
3195	EN14362-1	67.232		-0.15	
3197	EN14362-1	69.1		0.02	
3199	CPSD-AN-00017	64.9		-0.35	
3200	EN14362-1	89.2		1.83	
3204	LFGB B82.02-2	43.6		-2.27	
3209	EN14362-1	78.1		0.83	
3210		-----		-----	
3214	EN14362-1	66.2		-0.24	
3218	EN14362-1	75		0.55	
3220	EN14362-1	73.0		0.37	
3225	EN14362-1	76.8		0.71	
3228		68		-0.08	
3232	EN14362-1	73		0.37	
3233	EN14362-1	57.92		-0.98	
3237	EN14362-1/2	71.8		0.26	
3243	LFGB B82.02-2	91.2		2.01	
3246		74.66		0.52	
3247	EN14362-1	58		-0.97	
3248		68.5		-0.03	
8008		73.27		0.40	

|	
normality	OK
n	98
outliers	5
mean (n)	68.85
st.dev. (n)	13.583
R(calc.)	38.03
R(EN14362-1)	31.18
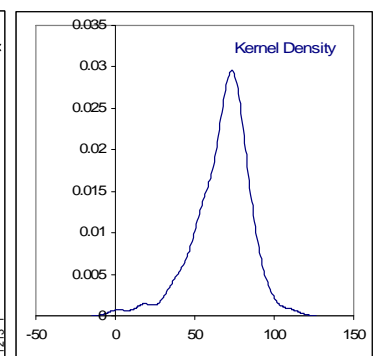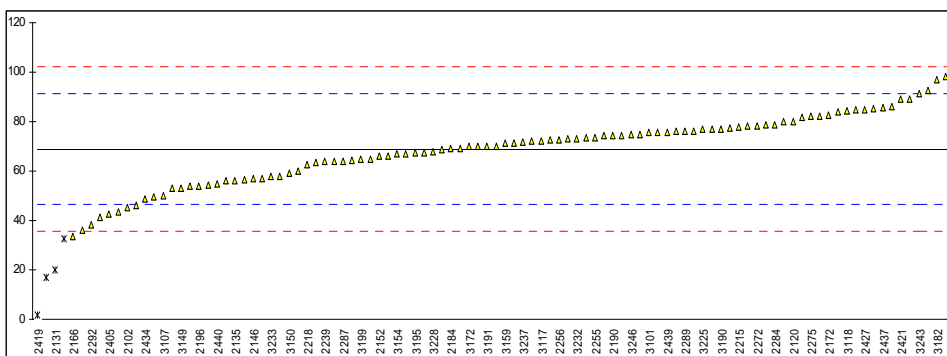
Determination of 4,4-Diaminodiphenylether (CASno.101-80-4) in sample #11019; results in mg/kg

lab	method	value	mark	z(targ)	remarks
1213	TCVN7619-1	26.6		-0.52	
2102		48.55	G(0.05)	4.15	
2115		30.92		0.40	
2120	EN14362-1	27		-0.44	
2121		-----		-----	
2129	EN14362-1	24		-1.08	
2131		14.7	DG(0.05)	-3.06	
2132		<5		-----	False negative?
2135		28		-0.23	
2146	EN14362-1	31.5		0.52	
2152		13.3	CDG(0.05)	-3.35	First reported 10.90 mg/kg
2160		-----		-----	
2166	EN14362-1	13.71	G(0.01)	-3.27	
2172	EN14362-1	25.8		-0.69	
2173		29.42		0.08	
2184	EN14362-1	30		0.20	
2190	EN14362	36.8		1.65	
2196	EN14362-1	24		-1.08	
2197		31.4	ex	0.50	Result excluded, see paragraph 4.1
2201	EN14362-1	28.5		-0.12	
2215	EN14362-1	28.5		-0.12	
2218	EN14362-1&2	33.98		1.05	
2221	EN14362-1	35		1.26	
2235	EN14362-1	25.4		-0.78	
2236	EN14362-1	33.10		0.86	
2239		21.5		-1.61	
2241	EN14362-1	30.5		0.31	
2246		35.95		1.47	
2247	EN14362-1	25.0		-0.86	
2248	EN14362-1	11.2	CDG(0.05)	-3.80	First reported 60.2 mg/kg
2255	EN14362-1	28.8		-0.05	
2256	EN14362-1	31.7		0.56	
2260	EN14362-1	23.5		-1.18	
2261		-----		-----	
2266		-----		-----	
2271		29.5		0.09	
2272	EN14362-1	12.8	G(0.01)	-3.46	
2275	EN14362-1	32		0.63	
2284	EN14362-1	30.7		0.35	
2286	EN14362-1&2	31		0.41	
2287	EN14362-1&2	30		0.20	
2289		34		1.05	
2290	EN14362-1	30.5		0.31	
2292	EN14362-1	18.05		-2.34	
2295	EN14362-1	6.6	CG(0.05)	-4.78	First reported 13.6 mg/kg
2297		30		0.20	
2405	EN14362-1&2	23.2		-1.25	
2410	EN14362-1	34.8		1.22	
2413	EN14362-1	54.34	G(0.01)	5.38	
2415	EN14362-1	24.0961		-1.06	
2419		-----		-----	
2421		30.423		0.29	
2427	EN14362-1	27.43		-0.35	
2428	GB/T 17592	26.8		-0.48	
2432	in house	24.9		-0.88	
2434	EN14362-1	18.23		-2.30	
2436	EN14362-1	34.2		1.09	
2437	EN14362-1	22.0		-1.50	
2439	LMGB B82.02-2	31.5		0.52	
2440	GB/T 17592	22.8		-1.33	
3100		32.2		0.67	
3101	EN14362-1	22.8		-1.33	
3104		26.14		-0.62	
3107		33.3		0.90	
3116	EN14362-1	28		-0.23	
3117	EN14362-1	35		1.26	
3118		26.4		-0.57	
3134		25.6		-0.74	
3146		25		-0.86	
3149	LFGB B82.02-2	32.4		0.71	
3150	LFGB B82.02-2	32		0.63	
3151	EN14362-1	23		-1.29	
3153	EN14362-1	34.8		1.22	

3154	EN14362-1	22.17		-1.47	
3159	EN14362-1	26.7		-0.50	
3160	EN14362-1	24.62		-0.94	
3163	TD-GC-MS	n.d.		-----	False negative?
3167	EN14362-1	30.5		0.31	
3170		13.21	DG(0.05)	-3.37	
3172	EN14362-1	25.7		-0.71	
3174	EN14362-1	31.17		0.45	
3176		29.5		0.09	
3180		15	CG(0.05)	-2.99	First reported 11 mg/kg
3182	EN14362-1	29.730		0.14	
3185	EN14362-1	33.8		1.01	
3190	EN14362-1	25.3		-0.80	
3191	EN14362-1	32		0.63	
3195	EN14362-1	34.967		1.26	
3197	EN14362-1	32.2		0.67	
3199	CPSD-AN-00017	28.7		-0.08	
3200	EN14362-1	27.3		-0.37	
3204	LFGB B82.02-2	30.5		0.31	
3209	EN14362-1	30.7		0.35	
3210	EN14362-1	29.5		0.09	
3214	EN14362-1	36.6		1.60	
3218	EN14362-1	27		-0.44	
3220	EN14362-1	30.0		0.20	
3225	EN14362-1	31.2		0.46	
3228		35		1.26	
3232	EN14362-1	29		-0.01	
3233	EN14362-1	30.07		0.22	
3237	EN14362-1/2	28.0		-0.23	
3243	LFGB B82.02-2	36.5		1.58	
3246		31.86		0.60	
3247	EN14362-1	30		0.20	
3248		24.1		-1.06	
8008		33.56		0.96	

normality	OK
n	89
outliers	10
mean (n)	29.06
st.dev. (n)	4.205
R(calc.)	11.77
R(EN14362-1)	13.16
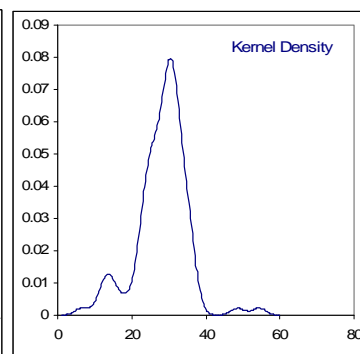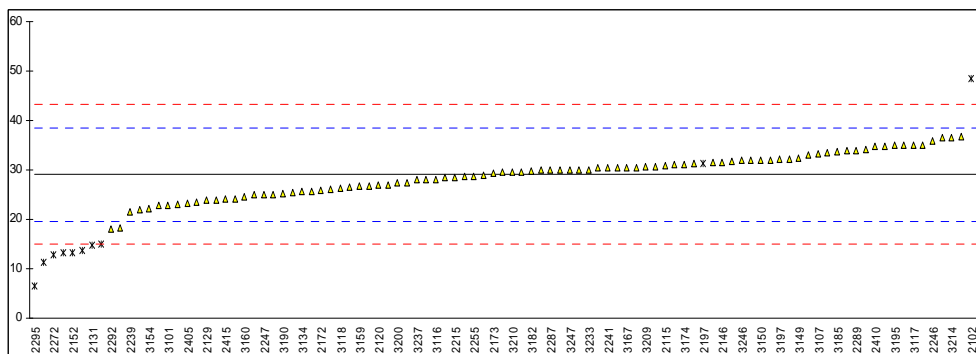
APPENDIX 2

Summary of all other reported aromatic amines in sample #11018; results in mg/kg

lab	method
2129	3,3-Dichlorobenzidine: 195 mg/kg
2146	2-Methoxyaniline : traces
2413	2,4-Diaminoanisol: 9.43 mg/kg, 3,3-Dimethylbenzidine: 254.36 mg/kg
2419	2,4-Diaminoanisol: 3.65 mg/kg; 4,4-Diamino-3,3-Dichlorodiphenylmethane: 1.48 mg/kg, 4,4-Oxydianiline: 2.90 mg/kg
2434	3,3-Dichlorobenzidine: 10.89 mg/kg, 3,3-Dimethyl-4,4-diaminodiphenylmethane: 3.96 mg/kg
2440	2-Methoxyaniline: 0.6 mg/kg
3101	4-Chloro-o-toluidine: 52.9 mg/kg
3195	2-Methoxyaniline: 0.821 mg/kg
3247	2-Methoxyaniline: 3 mg/kg

Summary of all other reported aromatic amines in sample #11019; results in mg/kg

lab	method
2132	4,4-Thiodianiline: 36.3 mg/kg
2415	2-Naphtylamine: 5.97 mg/kg, p-Chloroaniline: 5.13 mg/kg
2419	4-Aminodiphenyl: 2.12 mg/kg, 2-Naphtylamine: 4.27 mg/kg, 3,3-Dimethylbenzidine: 2.47 mg/kg
2434	4,4-Diaminodiphenylmethane: 2.17 mg/kg

APPENDIX 3

Number of participants per country

1 lab in	BANGLADESH
1 lab in	BULGARIA
1 lab in	CROATIA
1 lab in	CYPRUS
1 lab in	FINLAND
5 labs in	FRANCE
11 labs in	GERMANY
1 lab in	GREECE
14 labs in	HONG KONG
4 labs in	INDIA
1 lab in	INDONESIA
4 labs in	ITALY
2 labs in	JAPAN
1 lab in	KOREA
33 labs in	P.R. of CHINA
1 lab in	PORTUGAL
1 lab in	SLOVENIA
2 labs in	SPAIN
3 labs in	SWITZERLAND
1 lab in	TAIWAN R.O.C.
1 lab in	THAILAND
2 labs in	THE NETHERLANDS
5 labs in	TURKEY
3 labs in	U.S.A.
1 lab in	UNITED KINGDOM
5 labs in	VIETNAM

APPENDIX 4

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   LMBG 82.02-2:98
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
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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)