

Results of Proficiency Test
AZO dyes in textile
March 2012

Organised by: Institute for Interlaboratory Studies
Spijkenisse, the Netherlands

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1 INTRODUCTION

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

In this interlaboratory study, 143 laboratories in 34 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 #12030 and #12031), 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 ILAC G13 and ISO 17043:2010. This ensures strict adherence to protocols for sample preparation and statistical evaluation and 100% confidentiality of participant's data. Also customer's satisfaction is measured on a regular basis by sending out questionnaires.

2.2 PROTOCOL

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

2.3 CONFIDENTIALITY STATEMENT

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

2.4 SAMPLES

Two different bulk textile samples, each dyed with different AZO-dyes, were prepared by a third party. The first batch, labelled #12030, was a blue cotton and the second batch, labelled #12031, was a brown cotton.

Each bulk sample of approximately 1 kg of material was cut into pieces and after thorough mixing, divided over 160 subsamples of 4 gram each. The samples were labelled and tested for homogeneity. The homogeneity of the subsamples #12030 and #12031 (testing was subcontracted) was checked by determination of aromatic amines on 7 stratified randomly selected samples. See the following tables for the test results.

	<i>3,3-Dimethoxybenzidine in mg/kg</i>
sample #12030-1	94.03
sample #12030-2	94.87
sample #12030-3	94.16
sample #12030-4	94.53
sample #12030-5	94.67
sample #12030-6	94.35
sample #12030-7	94.42

table 1: homogeneity test results of subsamples #12030

	<i>Benzidine in mg/kg</i>
sample #12031-1	8.73
sample #12031-2	8.38
sample #12031-3	8.62
sample #12031-4	8.15
sample #12031-5	8.20
sample #12031-6	8.38
sample #12031-7	8.09

table 2: homogeneity test results of subsamples #12031

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:

	<i>3,3-Dimethoxybenzidine in mg/kg</i>	<i>Benzidine in mg/kg</i>
r (observed) #12030	0.81	--
r (observed) #12031	--	0.67
reference method	EN14362-1:03	EN14362-1:03
0.3 x R (reference method)	9.94	0.97

table 3: repeatabilities of subsamples #12030 and #12031

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 #12030 and #12031 was sent to the participating laboratories on March 7, 2012.

2.5 ANALYSES

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

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:

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

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-three participants reported the results after the deadline and six participants did not report any results due to various reasons. Finally, 135 participants did report 389 numerical results. Observed were 19 outlying results, which is 4.9% of the numerical results. In proficiency studies, outlier percentages of 3% - 7.5% are quite normal.

Anomal data distributions were found for 4-Aminodiphenyl, 3,3-Dimethoxybenzidine and Benzidine. 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.

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

The determination of this aromatic amine at a concentration level of 42.0 mg/kg was problematic for a number of participants. Four statistical outliers were observed.

The test results reported by the participants vary from 0.49 – 70.3 mg/kg.

The observed reproducibility after rejection of the statistical outliers is in full agreement with the reproducibility requirement estimated from the test method EN14362-1:03.

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

The determination of this aromatic amine at a concentration level of 34.7 mg/kg was problematic. Eight statistical outliers were detected.

The numerical test results reported by the participants vary from 'n.d.' – 51.5 mg/kg.

The observed reproducibility after rejection of the statistical outliers is not in agreement with the reproducibility requirement estimated from the test method EN14362-1:03.

Benzidine (CASno.92-87-5):

The determination of this aromatic amine at a concentration level of 17.4 mg/kg, was problematic. Seven statistical outliers were detected.

The numerical test results reported by the participants vary from 'n.d.' – 27.15 mg/kg.

The observed reproducibility after rejection of the statistical outliers is not in agreement with the reproducibility requirement estimated from the test method EN14362-1:03.

4.2 PERFORMANCE EVALUATION FOR THE GROUP OF LABORATORIES

A comparison has been made between the reproducibilities as declared by the relevant standard test methods 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.

<i>Parameter</i>	<i>unit</i>	<i>n</i>	<i>Average</i>	<i>2.8 * sd</i>	<i>EN14362-1</i>
4-Aminodiphenyl	mg/kg	130	42.00	20.65	19.02
3,3-Dimethoxybenzidine	mg/kg	122	34.73	17.07	12.19

table 4: reproducibilities of the aromatic amines in textile sample #12030

<i>Parameter</i>	<i>unit</i>	<i>n</i>	<i>Average</i>	<i>2.8 * sd</i>	<i>EN14362-1</i>
Benzidine	mg/kg	118	17.36	10.1	6.72

table 5: reproducibilities of the aromatic amines in textile sample #12031

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 for most 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 EN14362-1:2003, see below table.

<i>Parameter</i>	<i>March 2012</i>	<i>March 2011</i>	<i>March 2010</i>	<i>March 2009</i>	<i>March 2008</i>	<i>March 2007</i>	<i>April 2006</i>	<i>EN 14362</i>
4-Aminodiphenyl	49%	(86%)*	50%	n.e.	n.e.	100%	n.e.	45%
Benzidine	58%	51%	54%	n.e.	57%	71-99%	78%	39%
3,3-Dimethylbenzidine	n.e.	n.e.	49%	n.e.	90%	77%	n.e.	49%
3,3-Dimethoxybenzidine	49%	48%	n.e.	n.e.	n.e.	59-70%	83%	35%
o-Toluidine	n.e.	n.e.	52%	n.e.	n.e.	n.a	n.e.	61%
2-Naphthylamine	n.e.	n.e.	n.e.	n.e.	75%	n.e.	n.e.	45%
4,4-Diaminodiph.methane	n.e.	n.e.	n.e.	58%	n.e.	n.e.	n.e.	42%
4,4-Diaminodiph.sulfide	n.e.	n.e.	51%	n.e.	73%	n.e.	n.e.	45%
p-Chloroaniline	n.e.	n.e.	n.e.	76%	n.e.	n.e.	n.e.	45%
4,4-Diaminodiphenylether	n.e.	41%	n.e.	n.e.	n.e.	n.e.	n.e.	45%
4,4-Diamino-3,3-dichlorodiphenylmethane	n.e.	55%	n.e.	65%	n.e.	n.e.	119%	45%

table 6: 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. The relative reproducibility appears to stabilize around 50% for all aromatic amines.

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 ten participants reported to have used a different test method.

The observed spreads of the test results, except for 4-Aminodiphenyl are not in 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.

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.

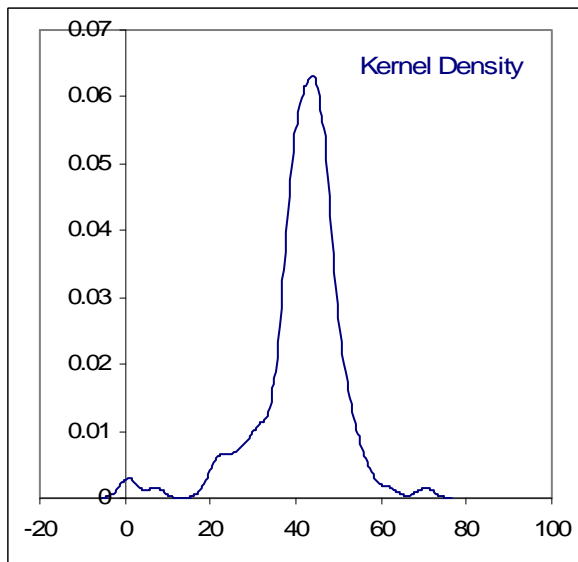
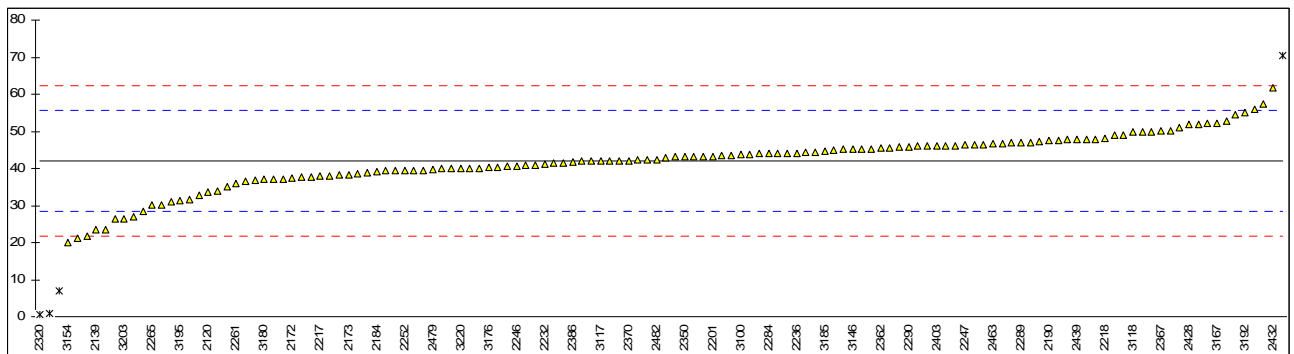
APPENDIX 1

Determination of 4-Aminodiphenyl (CASno.92-67-1) in sample #12030; results in mg/kg

lab	method	value	mark	z(targ)	lab	method	value	mark	z(targ)
110	EN14362-1	47.79		0.85	2390	EN14362-1	26.922		-2.22
348	EN14362-1	46.10		0.60	2403	EN14362-1	46		0.59
362	EN14362-1	21.29		-3.05	2410	EN14362-1	44		0.29
551	EN14362-1	48.94		1.02	2413		-----		-----
622	EN14362-1	26.4922		-2.28	2420	EN14362-1	37.2	C	-0.71
623	EN14362-1	40.5		-0.22	2425	LFGB 82.02-2	36.6		-0.79
840	EN14362-1	42		0.00	2427	EN14362-1	39.56		-0.36
1213	INH-7619	46.7		0.69	2428		52		1.47
2102	in house	6.97	G(0.01)	-5.16	2429	EN14362-1	47.50		0.81
2115	EN14362	43.19		0.18	2432	in house	61.65		2.89
2120	EN14362-1	33.5		-1.25	2439	EN14362-1	47.8		0.85
2121	EN14362-1	49.9		1.16	2442	in house	46.43		0.65
2129	EN14362-1	51		1.33	2450	EN14362-1	37.8		-0.62
2131	EN14362-1	39.5		-0.37	2452	EN14362-1	44.28		0.34
2132	EN14362-1	45.7		0.55	2456	EN14362-1	21.81		-2.97
2137	EN14362-1	43.2		0.18	2463	EN14362-1	46.65		0.69
2139	EN14362-1	23.4		-2.74	2469	EN14362-1	70.3	G(0.05)	4.17
2146	EN14362-1	47.9		0.87	2472	EN14362-1	45		0.44
2165	GB/T 17592	40		-0.29	2479	EN14362-1	39.65		-0.35
2166	EN14362-1	40.3		-0.25	2481	EN14362-1	0.82	C,G(0.01)	-6.06
2172	EN14362-1	37.4		-0.68	2482	EN14362-1	42.25		0.04
2173	EN14362-1	38.40		-0.53	2483	INH-15205	43.50		0.22
2184	EN14362-1	39		-0.44	2484	in house	52		1.47
2186		-----		-----	2485	LFGB 82.02-2	36.7		-0.78
2190	EN14362-1	47.4		0.80	2486		-----		-----
2196	EN14362-1	44		0.29	2487	EN14362-1	54.50		1.84
2197		-----		-----	2488		-----		-----
2201	EN14362-1	43.2		0.18	2489	EN14362-1	45.5		0.52
2215	EN14362-1	39.3		-0.40	2492	EN14362-1	38.50		-0.51
2217	EN14362-1	38.0		-0.59	3100	EN14362-1	43.7		0.25
2218	EN14362-1	48.0		0.88	3104	EN14362-1	43.01		0.15
2221	EN14362-1	44		0.29	3107	EN14362-1	34.01		-1.18
2232	EN14362-1	41.03		-0.14	3116	EN14362-1	46		0.59
2236	EN14362-1	44.16		0.32	3117	EN14362-1	42		0.00
2238	EN14362-1	44.4		0.35	3118	EN14362-1	49.79		1.15
2245	EN14362-1	47.91		0.87	3134	EN14362-1	57.3		2.25
2246	EN14362-1	40.67		-0.20	3146	LFGB 82.02-2	45.1		0.46
2247	EN14362-1	46.4		0.65	3150	LFGB 82.02-2	50.1		1.19
2248	EN14362-1	38.8		-0.47	3151	EN14362-1	38.3		-0.54
2252	EN14362-1	39.5		-0.37	3153	EN14362-1	49.1		1.05
2255	EN14362-1	46.5		0.66	3154	BVL B82.02-2	20.05		-3.23
2256	EN14362-1	45.3		0.49	3160	EN17234	39.38		-0.39
2261	GB/T 17592	36		-0.88	3163		-----		-----
2265	LFGB B82.02.2	30.18		-1.74	3167	EN14362-1	52.3		1.52
2266	EN14362-1	23.6		-2.71	3172	EN14362-1	41.5		-0.07
2272	EN14362-1	28.4		-2.00	3176	EN14362-1	40.2		-0.26
2284	EN14362-1	44		0.29	3180	EN14362-1	37		-0.74
2286	EN14362-1	56		2.06	3182	EN14362-1	52.20		1.50
2287	EN14362-1	50		1.18	3183	LFGB B82.02-2	30.27		-1.73
2289	EN14362-1	47		0.74	3185	EN14362-1	44.5		0.37
2290	EN14362-1	45.9		0.57	3190	EN14362-1	45.2		0.47
2293		-----		-----	3191	EN14362-1	42		0.00
2295	EN14362-1	31.1		-1.60	3192	LFGB 82.02-2	55.1		1.93
2300	EN14362-1	47		0.74	3195	EN14362-1	31.33		-1.57
2301		-----		-----	3197	EN14362	46		0.59
2310	EN14362-1	41.9		-0.01	3199	EN14362-1	43.8		0.27
2311	EN14362-1	42.2		0.03	3200	EN14362-1	43.4		0.21
2313	EN14362-1	40.9		-0.16	3203	EN14362	26.5		-2.28
2320	EN14362-1	0.49	G(0.01)	-6.11	3209	EN14362-1	41.9		-0.01
2350	EN14362-1	43.1		0.16	3210	EN14362-1	32.8		-1.35
2359	EN14362-1	43.1		0.16	3212		-----		-----
2362	EN14362-1	45.4		0.50	3216	EN14362-1	31.46	C	-1.55
2364	EN14362-1	47		0.74	3218	EN14362-1	40		-0.29
2366	EN14362-1	45.1		0.46	3220	EN14362-1	40.0		-0.29
2367	EN14362-1	50.1		1.19	3222	EN14362-1	38.0		-0.59
2368	EN14362-1	40		-0.29	3228	EN14362-1	40		-0.29
2370	EN14362-1	42.1		0.02	3233	EN14362-1	42.2		0.03
2372	LMBG 82.02-2	41.58		-0.06	3237		47.102		0.75
2375	EN14362-1	52.61		1.56	3242	in house	37.60		-0.65
2379	EN14362-1	37.08		-0.72	3248	EN14362-1	35		-1.03
2380	EN14362-1	46.00		0.59	8008	in house	40.75		-0.18
2386	LFGB 82.02-2	41.8		-0.03					

normality	not OK
n	130
outliers	4
mean (n)	41.998
st.dev. (n)	7.3732
R(calc.)	20.645
R(EN14362-1:03)	19.016

Lab 2420: First reported 62.7
 Lab 2481: First reported 1.12
 Lab 3216: First reported n.d.

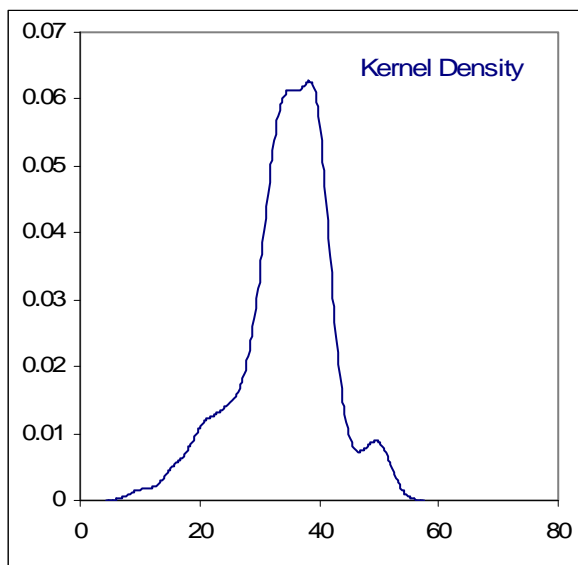
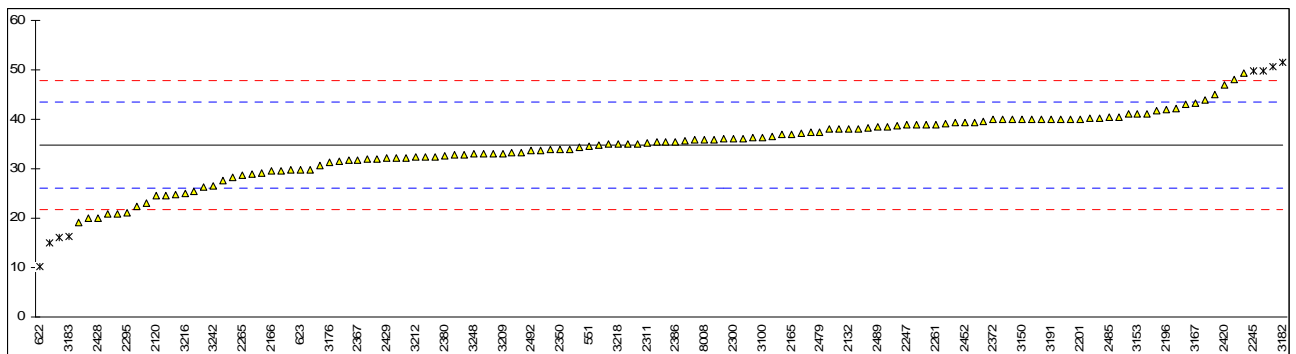


Determination of 3,3-Dimethoxybenzidine (CASno.119-90-4) in sample #12030; results in mg/kg

lab	method	value	mark	z(targ)	lab	method	value	mark	z(targ)
110	EN14362-1	39.26		1.04	2390	EN14362-1	19.201		-3.57
348	EN14362-1	38.75		0.92	2403	EN14362-1	38		0.75
362		----		----	2410	EN14362-1	35		0.06
551	EN14362-1	34.53		-0.05	2413		----		----
622	EN14362-1	10.3015	C,G(0.05)	-5.61	2420	EN14362-1	46.9		2.80
623	EN14362-1	29.8		-1.13	2425	LFGB 82.02-2	27.6		-1.64
840	EN14362-1	37		0.52	2427	EN14362-1	37.19		0.57
1213	INH-7619	40.0		1.21	2428		20		-3.38
2102	in house	31.63		-0.71	2429	EN14362-1	32.14		-0.59
2115	EN14362	35.65		0.21	2432	in house	50.60	DG(0.05)	3.65
2120	EN14362-1	24.5		-2.35	2439	EN14362-1	29.1		-1.29
2121	EN14362-1	49.4		3.37	2442	in house	24.5		-2.35
2129	EN14362-1	41		1.44	2450	EN14362-1	32.4		-0.53
2131	EN14362-1	20.9		-3.18	2452	EN14362-1	39.32		1.05
2132	EN14362-1	38.0		0.75	2456	EN14362-1	16.05	G(0.05)	-4.29
2137	EN14362-1	<5		----	2463	EN14362-1	38.54		0.88
2139	EN14362-1	22.5		-2.81	2469	EN14362-1	49.8	DG(0.05)	3.46
2146	EN14362-1	38.1		0.77	2472	EN14362-1	33	C	-0.40
2165	GB/T 17592	37		0.52	2479	EN14362-1	37.5		0.64
2166	EN14362-1	29.6		-1.18	2481	EN14362-1	traces		----
2172	EN14362-1	33.2		-0.35	2482	EN14362-1	25.49		-2.12
2173	EN14362-1	38.28		0.82	2483	INH-15205	36.21		0.34
2184	EN14362-1	35		0.06	2484	in house	48		3.05
2186		----		----	2485	LFGB 82.02-2	40.4		1.30
2190		----		----	2486		----		----
2196	EN14362-1	42		1.67	2487	EN14362-1	34.45		-0.06
2197		----		----	2488		----		----
2201	EN14362-1	40.1		1.23	2489	EN14362-1	38.5		0.87
2215	EN14362-1	33.8		-0.21	2492	EN14362-1	33.66		-0.25
2217	EN14362-1	28.2		-1.50	3100	EN14362-1	36.4		0.38
2218	EN14362-1	40.2		1.26	3104	EN14362-1	35.47		0.17
2221	EN14362-1	39		0.98	3107	EN14362-1	29.88		-1.11
2232	EN14362-1	23.07	C	-2.68	3116	EN14362-1	40		1.21
2236	EN14362-1	19.98		-3.39	3117	EN14362-1	41		1.44
2238	EN14362-1	36.1		0.32	3118	EN14362-1	43.85		2.10
2245	EN14362-1	49.75	DG(0.05)	3.45	3134	EN14362-1	24.7		-2.30
2246	EN14362-1	36.57		0.42	3146	LFGB 82.02-2	33.2		-0.35
2247	EN14362-1	38.9		0.96	3150	LFGB 82.02-2	40.0		1.21
2248	EN14362-1	35.9		0.27	3151	EN14362-1	32.2		-0.58
2252	EN14362-1	32.4		-0.53	3153	EN14362-1	41.0		1.44
2255	EN14362-1	39.4		1.07	3154	BVL B82.02-2	20.78		-3.20
2256	EN14362-1	39.2		1.03	3160	EN17234	32.15		-0.59
2261	GB/T 17592	39	C	0.98	3163		----		----
2265	LFGB B82.02.2	28.78		-1.37	3167	EN14362-1	43.2		1.95
2266	EN14362-1	31.7		-0.70	3172	EN14362-1	41.7		1.60
2272	EN14362-1	29.6		-1.18	3176	EN14362-1	31.3		-0.79
2284	EN14362-1	34		-0.17	3180	EN14362-1	15	G(0.05)	-4.53
2286	EN14362-1	43		1.90	3182	EN14362-1	51.53	DG(0.05)	3.86
2287	EN14362-1	45		2.36	3183	LFGB B82.02-2	16.37	G(0.05)	-4.22
2289	EN14362-1	40		1.21	3185	EN14362-1	40.0		1.21
2290	EN14362-1	39.0		0.98	3190	EN14362-1	35.4		0.15
2293		----		----	3191	EN14362-1	40		1.21
2295	EN14362-1	21.1		-3.13	3192	LFGB 82.02-2	42.1		1.69
2300	EN14362-1	36	C	0.29	3195	EN14362-1	32.86	C	-0.43
2301		----		----	3197	EN14362	38		0.75
2310	EN14362-1	32.8		-0.44	3199	EN14362-1	39.5		1.10
2311	EN14362-1	35.2		0.11	3200	EN14362-1	37.4		0.61
2313	EN14362-1	34.8		0.02	3203	EN14362	29		-1.32
2320	EN14362-1	n.d.		----	3209	EN14362-1	33.1		-0.37
2350	EN14362-1	33.9		-0.19	3210	EN14362-1	30.7		-0.93
2359	EN14362-1	40.1		1.23	3212	EN14362-1	32.3		-0.56
2362	EN14362-1	40.4		1.30	3216	EN14362-1	24.90	C	-2.26
2364	EN14362-1	32		-0.63	3218	EN14362-1	35		0.06
2366	EN14362-1	35.8		0.25	3220	EN14362-1	40.0		1.21
2367	EN14362-1	31.8		-0.67	3222	EN14362-1	26.3		-1.94
2368	EN14362-1	33		-0.40	3228	EN14362-1	36		0.29
2370	EN14362-1	35.1		0.09	3233	EN14362-1	32.0		-0.63
2372	LMBG 82.02-2	39.90		1.19	3237		33.895		-0.19
2375	EN14362-1	40.20		1.26	3242	in house	26.60		-1.87
2379	EN14362-1	29.68		-1.16	3248	EN14362-1	33		-0.40
2380	EN14362-1	32.65		-0.48	8008	in house	35.84		0.26
2386	LFGB 82.02-2	35.5		0.18					

normality	not OK
n	122
outliers	8
mean (n)	34.728
st.dev. (n)	6.0953
R(calc.)	17.067
R(EN14362-1:03)	12.189

- Lab 622: First reported 8.1865
- Lab 2232: First reported 71.69
- Lab 2261: First reported 17
- Lab 2300: First reported 18.52
- Lab 2472: First reported 54
- Lab 3195: First reported 69.57
- Lab 3216: First reported n.d.

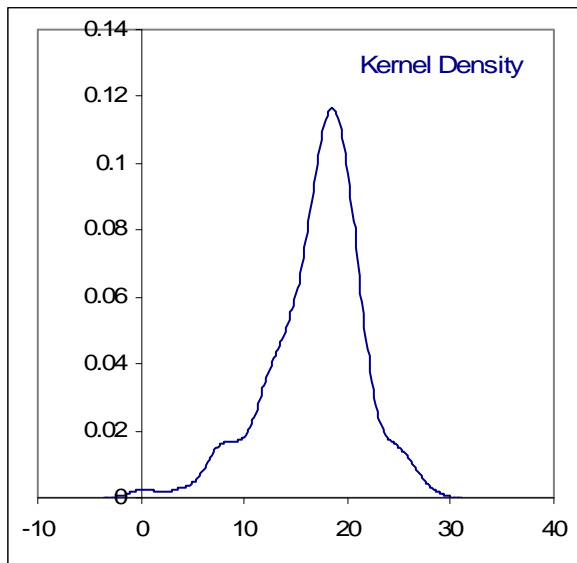
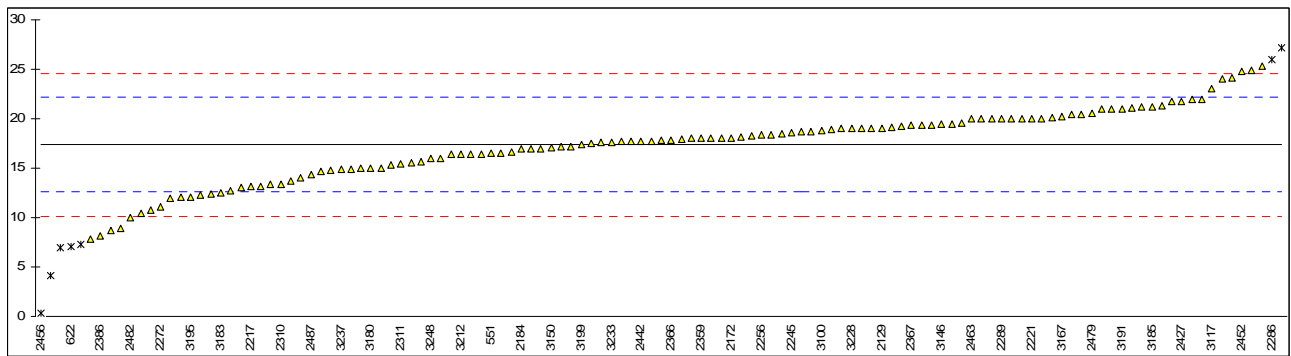


Determination of Benzidine (CASno.92-87-5) in sample #12031; results in mg/kg

lab	method	value	mark	z(targ)	lab	method	value	mark	z(targ)
110	EN14362-1	17.69		0.14	2390		----		----
348	EN14362-1	21.95		1.91	2403	EN14362-1	19		0.68
362	EN14362-1	n.d.		----	2410	EN14362-1	17		-0.15
551	EN14362-1	16.47		-0.37	2413		----		----
622	EN14362-1	7.0212	C,DG(0.05)	-4.31	2420		----		----
623	EN14362-1	14.7		-1.11	2425	LFGB 82.02-2	13.1		-1.78
840	EN14362-1	15		-0.98	2427	EN14362-1	21.78		1.84
1213		----		----	2428		7	DG(0.05)	-4.32
2102	in house	15.60		-0.73	2429	EN14362-1	21.27		1.63
2115	EN14362	n.d.		----	2432	in house	27.15	G(0.05)	4.08
2120		----		----	2439	EN14362-1	12.4		-2.07
2121	EN14362-1	19.1		0.72	2442	in house	17.72		0.15
2129	EN14362-1	19		0.68	2450	EN14362-1	19.4		0.85
2131		----		----	2452	EN14362-1	24.80		3.10
2132	EN14362-1	21.0		1.52	2456	EN14362-1	0.32	G(0.05)	-7.10
2137	EN14362-1	18.3		0.39	2463	EN14362-1	19.96		1.08
2139	EN14362-1	7.3	G(0.05)	-4.19	2469	EN14362-1	8.9		-3.53
2146	EN14362-1	20.4		1.27	2472	EN14362-1	20		1.10
2165	GB/T 17592	18		0.27	2479	EN14362-1	20.50		1.31
2166	EN14362-1	18.9		0.64	2481	EN14362-1	4.11	C,G(0.05)	-5.52
2172	EN14362-1	18.0		0.27	2482	EN14362-1	9.97	C	-3.08
2173	EN14362-1	21.2		1.60	2483	INH-15205	13.68		-1.53
2184	EN14362-1	17		-0.15	2484	in house	24		2.77
2186		----		----	2485	LFGB 82.02-2	19.5		0.89
2190	EN14362-1	10.4		-2.90	2486		----		----
2196	EN14362-1	22		1.93	2487	EN14362-1	14.33		-1.26
2197		----		----	2488		----		----
2201	EN14362-1	20.1		1.14	2489	EN14362-1	18.0		0.27
2215	EN14362-1	18.2		0.35	2492	EN14362-1	14.92	C	-1.02
2217	EN14362-1	13.1		-1.78	3100	EN14362-1	18.8		0.60
2218	EN14362-1	16.0		-0.57	3104	EN14362-1	17.16		-0.08
2221	EN14362-1	20		1.10	3107	EN14362-1	12.73		-1.93
2232	EN14362-1	13.39	C	-1.65	3116	EN14362-1	18		0.27
2236	EN14362-1	17.67		0.13	3117	EN14362-1	23		2.35
2238	EN14362-1	17.8		0.18	3118	EN14362-1	24.86		3.13
2245	EN14362-1	18.64		0.53	3134	EN14362-1	n.d.		----
2246	EN14362-1	17.49		0.05	3146	LFGB 82.02-2	19.5		0.89
2247	EN14362-1	17.6		0.10	3150	LFGB 82.02-2	17.1		-0.11
2248	EN14362-1	21.1		1.56	3151	EN14362-1	14.0		-1.40
2252	EN14362-1	17.0		-0.15	3153	EN14362-1	18.7		0.56
2255	EN14362-1	17.72		0.15	3154	BVL B82.02-2	18.40		0.43
2256	EN14362-1	18.4		0.43	3160	EN17234	16.50		-0.36
2261	GB/T 17592	20	C	1.10	3163		----		----
2265	LFGB B82.02.2	16.38	C	-0.41	3167	EN14362-1	20.2		1.18
2266	EN14362-1	7.8		-3.98	3172	EN14362-1	19.6		0.93
2272	EN14362-1	11.1		-2.61	3176	EN14362-1	15.5		-0.78
2284	EN14362-1	20		1.10	3180	EN14362-1	15		-0.98
2286	EN14362-1	26	G(0.05)	3.60	3182	EN14362-1	24.17		2.84
2287	EN14362-1	20		1.10	3183	LFGB B82.02-2	12.52		-2.02
2289	EN14362-1	20		1.10	3185	EN14362-1	21.2		1.60
2290	EN14362-1	19.21		0.77	3190	EN14362-1	20.4		1.27
2293		----		----	3191	EN14362-1	21		1.52
2295	EN14362-1	8.7		-3.61	3192	LFGB 82.02-2	25.3		3.31
2300	EN14362-1	12		-2.23	3195	EN14362-1	12.1		-2.19
2301		----		----	3197	EN14362	19		0.68
2310	EN14362-1	13.4		-1.65	3199	EN14362-1	17.4		0.02
2311	EN14362-1	15.4		-0.82	3200	EN14362-1	18.5		0.47
2313	EN14362-1	14.8		-1.07	3203	EN14362	12.3		-2.11
2320	EN14362-1	n.d.		----	3209	EN14362-1	19.4		0.85
2350	EN14362-1	16.4		-0.40	3210	EN14362-1	10.8	C	-2.73
2359	EN14362-1	18.0		0.27	3212	EN14362-1	16.4		-0.40
2362	EN14362-1	17.9		0.22	3216	EN14362-1	12.09	C	-2.20
2364	EN14362-1	21		1.52	3218	EN14362-1	20		1.10
2366	EN14362-1	17.8		0.18	3220	EN14362-1	15.0		-0.98
2367	EN14362-1	19.4		0.85	3222	EN14362-1	n.d.		----
2368	EN14362-1	19		0.68	3228	EN14362-1	19		0.68
2370	EN14362-1	16.6		-0.32	3233	EN14362-1	17.6		0.10
2372	LMBG 82.02-2	15.36		-0.83	3237		14.848		-1.05
2375	EN14362-1	21.71		1.81	3242	in house	13.04		-1.80
2379	EN14362-1	17.13		-0.10	3248	EN14362-1	16		-0.57
2380	EN14362-1	16.40		-0.40	8008	in house	18.72		0.57
2386	LFGB 82.02-2	8.1		-3.86					

normality	not OK
n	118
outliers	7
mean (n)	17.361
st.dev. (n)	3.6000
R(calc.)	10.080
R(EN14362-1:03)	6.719

- Lab 622: First reported 4.2426
- Lab 2232: First reported 34.19
- Lab 2261: First reported 4
- Lab 2265: First reported 27.38
- Lab 2481: First reported 1.59
- Lab 2482: First reported 6.35
- Lab 2492: First reported 5.84
- Lab 3210: First reported 7.8
- Lab 3216: First reported n.d.



APPENDIX 2

Summary of all other reported aromatic amines in sample #12030; results in mg/kg

lab	method
2137	Benzidine = 45.4
2265	4.4-diaminodiphenylsulfide = 23.28
2456	12 other aromatic amines with concentrations between 0.16 – 1.08
2481	Benzidine = 6.14

Summary of all other reported aromatic amines in sample #12031; results in mg/kg

lab	method
622	4-aminodiphenyl = 0.9512
2190	4-aminodiphenyl = 5.2
2245	4-aminodiphenyl = 1.18
2420	4.4-diamino-3.3-dichlorodiphenylmethane = 15
2432	4-aminodiphenyl = 3.10
2442	4-aminodiphenyl = 3.99
2456	15 other aromatic amines with concentrations between 0.15 – 1.72
2481	4-aminodiphenyl = 0.51
2485	4-aminodiphenyl = 0.94

APPENDIX 3

Number of participants per country

5 labs in BANGLADESH
1 lab in BELGIUM
1 lab in CROATIA
1 lab in BULGARIA
1 lab in CROATIA
1 lab in CYPRUS
1 lab in FINLAND
6 labs in FRANCE
13 labs in GERMANY
1 lab in GREECE
1 lab in GUATEMALA
13 labs in HONG KONG
1 lab in HUNGARY
8 labs in INDIA
3 labs in INDONESIA
5 labs in ITALY
2 labs in JAPAN
4 labs in KOREA
38 labs in P.R. of CHINA
1 lab in PAKISTAN
1 lab in PORTUGAL
1 lab in SINGAPORE
1 lab in SLOVENIA
3 labs in SPAIN
1 lab in SRI LANKA
3 labs in SWITZERLAND
3 labs in TAIWAN R.O.C.
2 labs in THAILAND
2 labs in THE NETHERLANDS
1 lab in TUNESIA
6 labs in TURKEY
5 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.e.	= not evaluated
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 2003
- 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)