Results of Proficiency Test
AZO dyes in textile
March 2010

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, 121 laboratories in 30 different countries have participated (see appendix 4). In this report, the results of this proficiency test are presented and discussed.

2 SET UP

The Institute for Interlaboratory Studies in Spijkenisse was the organizer of this proficiency test. It was decided to use in this proficiency test 2 different textile samples (labelled #1019 and #1020), 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 and ILAC-G13:2007. This ensures 100% confidentiality of participant's data. Also customer's satisfaction is measured on a regular basis by sending out questionnaires.

2.2 PROTOCOL

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

2.3 CONFIDENTIALITY STATEMENT

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

2.4 SAMPLES

Two different bulk textile samples, each dyed with different AZO-dyes, were prepared by a third party. The first batch, labelled #1019, was a orange coloured yarn and the second batch, labelled #1020, was a purple coloured yarn.
Each bulk sample of approximately 500 grams of material was cut into pieces and after thorough mixing, divided over 100 subsamples of 4 gram each. The samples were labelled and tested for homogeneity. The homogeneity of the subsamples #1019 and #1020 (testing was subtracted) was checked by determination of aromatic amines of 13 stratified randomly selected samples. See the following tables for the test results.

orange coloured yarn	*o-toluidine in mg/kg*	*4,4-diaminodiphenylsulfide in mg/kg*
sample #1019-1	26.9	122.1
sample #1019-2	30.5	125.0
sample #1019-3	28.5	123.4
sample #1019-4	28.7	120.5
sample #1019-5	28.6	124.8
sample #1019-6	25.9	124.8
sample #1019-7	26.9	118.5
sample #1019-8	25.8	118.5
sample #1019-9	30.5	124.1
sample #1019-10	31.8	119.8
sample #1019-11	27.8	120.8
sample #1019-12	26.8	117.6
sample #1019-13	30.7	120.8

table 1: homogeneity test results of subsamples #1019

purple coloured yarn	*benzidine in mg/kg*
sample #1020-1	27.8
sample #1020-2	31.4
sample #1020-3	30.1
sample #1020-4	29.8
sample #1020-5	30.8
sample #1020-6	29.5
sample #1020-7	31.5
sample #1020-8	30.5
sample #1020-9	30.8
sample #1020-10	31.5
sample #1020-11	30.7
sample #1020-12	28.9
sample #1020-13	32.1

table 2: homogeneity test results of subsamples #1020

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:

	o-toluidine in mg/kg	*4,4-diaminodiphenylsulfide in mg/kg*
r (observed)	5.5	7.4
reference method	EN14362-1	EN14362-1
0.3 x R (reference method)	5.2	16.4

table 3: repeatabilities of subsamples #1019

	benzidine in mg/kg
r (observed)	3.3
reference method	EN14362-1
0.3 x R (reference method)	3.5

table 4: repeatabilities of subsamples #1020

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 #1019 and #1020 was sent to the participating laboratories on March 12, 2010.

2.5 ANALYSES

The participants were asked to determine the concentrations of 23 forbidden aromatic amines and o-anisidine, applying the analysis procedure that is routinely used in the laboratory. To get comparable results reported, a detailed report form, on which the requested amines and the units were pre-printed, was sent together with each set of samples. Furthermore, an extra report form for reporting of analysis details was enclosed. Also a letter of instructions was sent along.

3 RESULTS

During four weeks after sample despatch, the results of the individual laboratories were gathered. The original data are tabulated in the appendices of this report. The laboratories are presented by their code numbers.

Directly after the deadline, a reminder fax was sent to those laboratories that had not yet reported. Shortly after the deadline, the available results were screened for suspect data. A result was called suspect in case the Huber Elimination Rule (a robust outlier test) found it to be an outlier. The laboratories that produced these suspect data were asked to check the results. Additional or corrected data are placed under 'Remarks' in the result tables in appendix 1. A list of abbreviations used in the tables can be found in appendix 5.

3.1 STATISTICS

Statistical calculations were performed as described in the report 'i.i.s. Interlaboratory Studies: Protocol for the Organization, Statistics and Evaluation' of January 2010 (i.i.s.-protocol, version 3.2)

For the statistical evaluation the *unrounded* (when available) figures were used instead of the rounded results. Results reported as '<…' or '>…" were not used in the statistical evaluation.
Before further calculations, the normality of the distribution of the various data sets per determination was checked by means of the Lilliefors-test. In the case of an anormal distribution, the statistical evaluation should be used with care.

According to ISO 5725 (1986 and 1994, lit.7 and 8) the original results per determination were submitted subsequently to Dixon's and Grubbs' outlier tests. Outliers are marked by D(0.01) for the Dixon's test, by G(0.01) or DG(0.01) for the Grubbs' test. Stragglers are marked by D(0.05) for the Dixon's test, by G(0.05) or DG(0.05) for the Grubbs' test. Both outliers and stragglers were not included in the calculations of averages and standard deviations.

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

3.2 GRAPHICS

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

3.3 Z-SCORES

To evaluate the performance of the individual participating laboratories the z-scores were calculated. In order to be able to have an objective evaluation of the performance of the individual participants, it was decided to evaluate this performance against the literature requirements. Therefore the z-scores were calculated using a target standard deviation.

This target standard deviation was calculated from the literature reproducibility by division with 2.8.
The $z_{(target)}$-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. Thirteen participants reported the results after the deadline and seven participants did not report any results due to various reasons. Finally, 114 participants did report 572 numerical results. Observed were 32 outlying results, which is 5.6% 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 all aromatic amines, except for benzidine in sample #1020. 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.

Sample #1019:

4,4-Diaminodiphenylsulfide (CASno.139-65-1):

The determination of this aromatic amine at a very high concentration level of 3000 mg/kg, which is probably near or above the upper calibration limit, is only problematic for a number of laboratories. Six statistical outliers were detected and two laboratories reported a test result less than 30 mg/kg.
The numerical test results reported by the participants vary from 6.5 – 5600 mg/kg.
The observed reproducibility (51%) is, after rejection of the statistical outliers, not in full agreement with the estimated reproducibility limit of EN14362 (45%), but this may be caused by the high concentration level. The reproducibilities of EN14362 were determined at concentrations from 17.7 – 29.7 mg/kg.

o-Toluidine (CASno.95-53-4):

The determination of this aromatic amine at a concentration level of 490 mg/kg, is only problematic for a number of laboratories. Eight statistical outliers were detected and three laboratories reported a test result less than 30 mg/kg.
The numerical test results reported by the participants vary from 11 – 700 mg/kg. The observed reproducibility (52%) is, after rejection of the statistical outliers, in full agreement with the reproducibility for this amine as mentioned in EN14362 (61%).

Sample #1020:

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

The determination of this aromatic amine at a concentration level of 60 mg/kg, is only problematic for a number of laboratories. Six statistical outliers were detected and five laboratories reported a test result less than 30 mg/kg.
The numerical test results reported by the participants vary from 2.9 – 104 mg/kg. The observed reproducibility (50%) is, after rejection of the statistical outliers, almost in agreement with the estimated reproducibility limit of EN14362 (45%).

Benzidine (CASno.92-87-5):

The determination of this aromatic amine at a concentration level of 367 mg/kg is problematic. Five statistical outliers were detected and two laboratories reported a test result less than 30 mg/kg.
The numerical test results reported by the participants vary from 79 – 634 mg/kg. The observed reproducibility (54%) is, after rejection of the statistical outliers, not in agreement with the strict reproducibility as mentioned in EN14362 (39%).

3,3-Dimethylbenzidine (CASno.119-93-7):

The determination of this aromatic amine at a concentration level of 315 mg/kg, is only problematic for a number of laboratories. Seven statistical outliers were detected and three laboratories reported a test result less than 30 mg/kg.
The numerical test results reported by the participants vary from 3.8 – 613 mg/kg. The observed reproducibility (49%) is, after rejection of the statistical outliers, in full agreement with the reproducibility mentioned in EN14362 (49%).

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), in the next two tables.

Parameter	*unit*	*n*	*Average*	*2.8 * sd*	*EN14362-1*
4,4-Diaminodiphenylsulfide	mg/kg	103	3034	1556	1374
o-Toluidine	mg/kg	102	489	255	299

table 5: reproducibilities of the aromatic amines in textile sample #1019

Parameter	*unit*	*n*	*Average*	*2.8 * sd*	*EN14362-1*
4-Aminodiphenyl	mg/kg	106	60.3	30.1	27.3
Benzidine	mg/kg	105	367	199	142
3,3-Dimethylbenzidine	mg/kg	104	315	156	155

table 6: reproducibilities of the aromatic amines in textile sample #1020

Without further statistical calculations, it can be concluded that the group of participating laboratories has hardly any difficulties with the analysis at relatively high concentration levels (60-3000 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 small in comparison with the spreads as observed in previous PTs and almost in agreement with the reproducibilities mentioned in the standardized test method EN14362-1, see below table.

Parameter	*March 2010*	*March 2009*	*March 2008*	*March 2007*	*April 2006*	*April 2005*	*March 2004*	*EN 14362*
4-Aminodiphenyl	50%	n.a.	n.a.	100%	n.a.	n.a.	n.a.	n.a.
Benzidine	54%	n.a.	57%	71-99%	78%	78%	98%	39%
3,3-Dimethylbenzidine	49%	n.a.	90%	77%	n.a.	84%	65%	49%
3,3-Dimethoxybenzidine	n.a.	n.a.	n.a.	59-70%	83%	85%	86%	35%
o-Toluidine	52%	n.a.	n.a.	n.a	n.a.	106%	89-96%	61%
2,4-Diaminoanisol	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	66%	n.a.
2-Naphthylamine	n.a.	n.a.	75%	n.a.	n.a.	116%	78-108%	n.a.
4,4-Diaminodiph.methane	n.a.	58%	n.a.	n.a.	n.a.	92%	98%	42%
4,4-Diaminodiph.sulfide	51%	n.a.	73%	n.a.	n.a.	n.a.	n.a.	n.a.
o-Anisidine	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.
p-Chloroanailine	n.a.	76%	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.
4,4-Diamino-3,3-dichlorodiphenylmethane	n.a.	65%	n.a.	n.a.	119%	n.a.	n.a.	n.a.

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

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

6 DISCUSSION

From the reported test methods it is clear that most participants treated the yarn samples according identical test methods. A vast majority used EN14362-1 and most others used the (identical) method LFBG 82.02.2. Only seven times an in house method was reported. The majority of the laboratories used GC/MS for quantification and HPLC/DAD for confirmation. Most laboratories used MTBE for clean-up and remarkably, at least twelf laboratories did not do any clean-up (see appendix 3).

Regretfully too little information was received about the calibrants (brand, purity) as used by the participating laboratories to justify any significant conclusions on the effect of the calibrants used, but it is clear that most calibration ranges are approx 1 mg/L – 50 mg/L.
The concentration of the AZO dye, that gave 4,4'-diaminodephenylsulfide after reduction in sample #1019, clearly was –unexpectedly- very high and this may have resulted in an amine concentration outside the normal calibration range. Some laboratories may have retested the sample using a smaller amount of sample or a higher dilution of the amine solution, but in any case this high concentration will have caused quantification problems for several laboratories. And these problems may easily explain for the relatively high spread of the 4,4'-diaminodephenylsulfide in sample #1019 and also for the seven false positive 4,4'-diaminodephenylsulfide results on sample #1020 (see appendix 2).
Regretfully this high concentration was not discovered during the fit-for-use and homogeneity testing. Although is not clear what the reason has been, the testing procedure has been adjusted and fortified to ensure that similar will not recur with future samples.
In principle it is tried to prepare all PT samples in such a way that aromatic amine concentrations between 10 and 100 mg/kg are found during the PT.
In view of the above on the relatively high concentrations of aromatic amines present in this PT, it is remarkable that for o-toluidine, benzidine and 3,3'-dimethylamine relatively small spreads were found in this PT (much smaller than in previous PTs).

In total 10 participants corrected for recovery although this correction is not mentioned in any of the standardised test methods. The results of these 10 participants were not significantly different from the other test results.

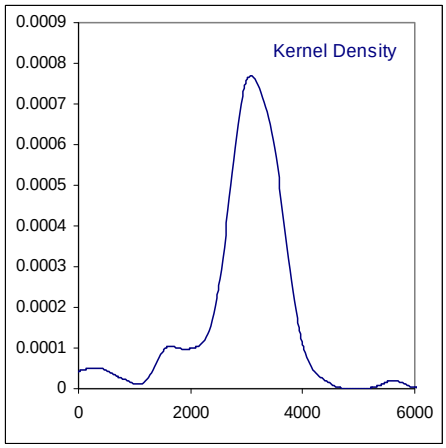
From the various above mentioned matters, it can be concluded that the spread observed in this interlaboratory study is not caused by just one critical point in the analysis. Each participating laboratory will have to evaluate its performance in this study and decide about any corrective actions if necessary.

APPENDIX 1

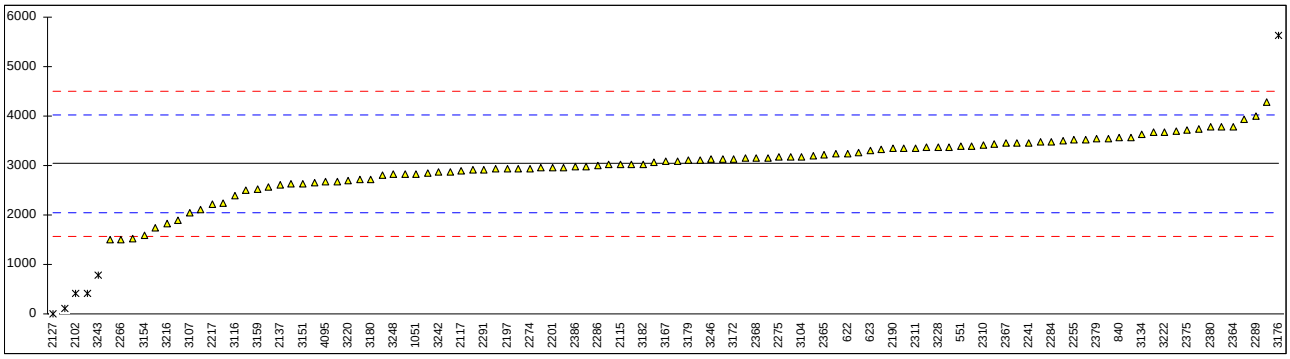
Determination of 4,4-Diaminodiphenylsulfide (CASno.139-65-1) in sample #1019; results in mg/kg

lab	method	value	mark	z(targ)	remarks
361	EN14362-1	3570.8458		1.09	
551	EN14362-1	3385.0		0.72	
622	EN14362-1	3246.20		0.43	
623	in house	3297.79		0.54	
840	EN14362-1	3556.02		1.06	
1051	EN14362-1	2822.7	C	-0.43	first reported 8267.9
1213	§64 LFGB B82.02-02	3253		0.45	
2102	EN14362-1	405	G(0.05)	-5.36	
2115	EN14362-1	3029.71		-0.01	
2117	§64 LFGB B82.02-02	2900		-0.27	
2121	EN14362-1	2643		-0.80	
2127	EN14362-1	6.493	DG(0.01)	-6.17	
2129	EN14362-1	>4000		> 1.97	
2132	EN14362-1	3936.7		1.84	
2137	§64 LFGB BVL B82.02-02	2605.5		-0.87	
2139	EN14362-1	1884.0		-2.34	
2146	EN14362-1	2680		-0.72	
2152	EN14362-1	107.0	G(0.05)	-5.97	
2156		-----		-----	
2160	B.82.02-2	2228.9		-1.64	
2165	EN14362-1	3089		0.11	
2166	EN14362-1	2103.5		-1.90	
2170	EN14362-1	3100.26	C	0.13	first reported n.d.
2172	EN14362-1	2930		-0.21	
2173	EN14362-1	2980.11		-0.11	
2184	EN14362-1	2490		-1.11	
2186	§64 LFBG 82.02-2	>150	C	-----	first reported ----
2190	EN14362-1	3340		0.62	
2196	EN14362-1	3059		0.05	
2197	EN14362-1	2936		-0.20	
2201	EN14362-1	2950		-0.17	
2213	EN14362-1	2822		-0.43	
2215	EN14362	2880		-0.31	
2217	EN14362-1	2227.59		-1.64	
2221	EN14362-1	1520		-3.09	
2227		-----		-----	
2235	EN14362-1	3142.5		0.22	
2236	in house	3531		1.01	
2239	EN14362-1	nd	C	-----	first reported 42041
2241	EN14362-1	3462		0.87	
2248	§64 LFGB B82.02-2	3134		0.20	
2252	EN14362-1	3158.3		0.25	
2255	EN14362-1	3529.0		1.01	
2256	EN14362-1	3030		-0.01	
2261	in house	2636		-0.81	
2265	§64 LFGB B82.02-2+4	n.d.		-----	false negative?
2266	EN14362-1	1504.6		-3.12	
2270	EN14362-1	2953.6		-0.16	
2272	EN14362-1	1495		-3.14	
2274	EN14362-1	2941.6		-0.19	
2275	EN14362-1	3172		0.28	
2276	§64 LFGB B82.02-2	4290		2.56	
2284	EN14362-1	3469.3		0.89	
2285	EN14362-1	3020		-0.03	
2286	EN14362-1	3000		-0.07	
2287	EN14362-1	2800		-0.48	
2289	EN14362-1	4000		1.97	
2291	EN14362-1	2915		-0.24	
2293		-----		-----	
2310	EN14362-1	3423		0.79	
2311	EN14362-1	3355		0.65	
2350	EN14362-1	3780		1.52	
2357	EN14362-1	3392		0.73	
2358	EN14362-1	3468		0.88	
2359	EN14362-1	3747		1.45	
2364	EN14362-1	3784		1.53	
2365	EN14362-1	3225		0.39	
2366	EN14362-1	3445		0.84	
2367	EN14362-1	3456		0.86	
2368	EN14362-1	3150		0.24	
2370	EN14362-1	3509		0.97	

2372	EN14362-1	3350		0.64	
2375	EN14362-1	3727		1.41	
2379	EN14362-1	3535		1.02	
2380	EN14362-1	3775.139		1.51	
2386	LFGB 82.02-2	2970		-0.13	
2390	EN14362-1	3457.416		0.86	
3100	EN14362-1	3178		0.29	
3104	EN14362-1	3181		0.30	
3107	in house	2045		-2.02	
3116	EN14362-1	2400		-1.29	
3117	EN14362-1	2946		-0.18	
3118	EN14362-1	3697.78		1.35	
3134	EN14362-1	3627.7		1.21	
3149		-----		-----	
3150	64 LFGB 82.02.2	2558		-0.97	
3151	EN14362-1	2640		-0.80	
3153	EN14362-1	3540		1.03	
3154	BVL B82.02-2	1583.39		-2.96	
3159	EN14362-1	2520		-1.05	
3167	EN14362-1	3079		0.09	
3170		-----		-----	
3172	EN14362-1	3138		0.21	
3174	EN14362-1	3362.33		0.67	
3176		5629.6	C,G(0.05)	5.29	first reported 5281.42
3179	EN14362-1	3100		0.13	
3180		2720		-0.64	
3182	EN14362-1	3032.576		0.00	
3185	EN14362-1	3330		0.60	
3190	EN14362-1	2708		-0.66	
3195	EN14362-1	1749		-2.62	
3197	EN14362-1	2937.5		-0.20	
3203	EN14362-1	2849.50		-0.38	
3204		-----		-----	
3210	EN14362-1	present		-----	
3216	EN14362-1	1820.7		-2.47	
3218	EN14362-1	2910		-0.25	
3220	EN14362-1	2700		-0.68	
3222	EN14362-1	3684		1.32	
3226	EN14362-1	421.50	G(0.01)	-5.32	
3228	EN14362-1	3368		0.68	
3233	EN14362-1	3379		0.70	
3237	in house	3675.2		1.31	
3242	in house	2862.0		-0.35	
3243	§35 LMBG 82.02-2	790	G(0.05)	-4.57	
3246	EN14362-1	3130		0.20	
3247	EN14362-1	3235	C	0.41	first reported 3235 mg/kg 4,4'-diaminodiphenylether
3248	EN14362-1	2816		-0.44	
4095	EN14362-1	2672		-0.74	
5012		-----		-----	
8008	in house	3200		0.34	



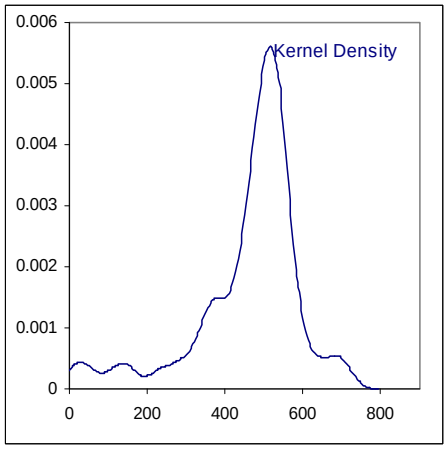
normality	not OK	
n	103	
outliers	6	
mean (n)	3034.70	
st.dev. (n)	555.888	
R(calc.)	1556.49	
R(EN14362-1)	1374.11	



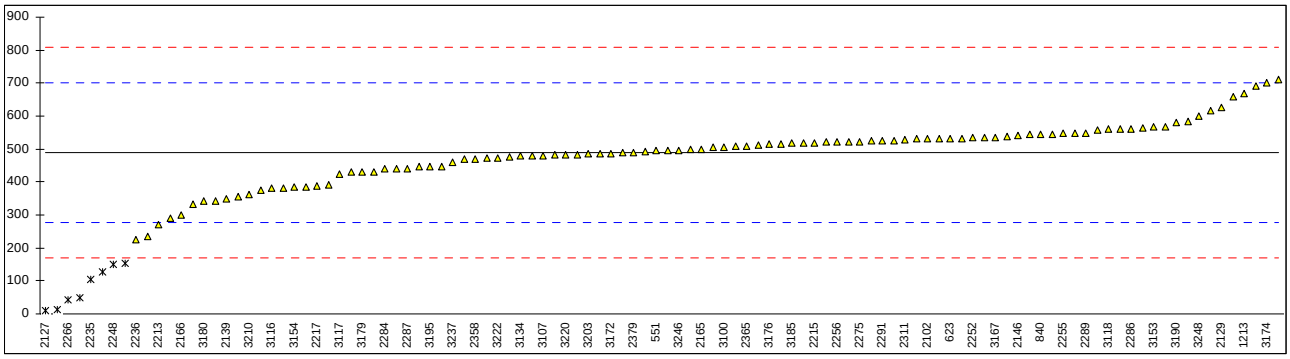
Determination of o-Toluidine (CASno.95-53-4) in sample #1019; results in mg/kg

lab	method	value	mark	z(targ)	remarks
361	EN14362-1	582.0796		0.87	
551	EN14362-1	495.4		0.06	
622	EN14362-1	384.85		-0.98	
623	in house	532.20		0.40	
840	EN14362-1	543.11		0.51	
1051	EN14362-1	290.2		-1.86	
1213	§64 LFGB B82.02-02	668		1.68	
2102	EN14362-1	531		0.39	
2115	EN14362-1	617.20		1.20	
2117	§64 LFGB B82.02-02	560		0.66	
2121		-----		-----	
2127	EN14362-1	11.108	DG(0.05)	-4.48	
2129	EN14362-1	627		1.29	
2132	EN14362-1	512.0	C	0.22	first reported 713.3
2137	§64 LFGB BVL B82.02-02	658.6	C	1.59	first reported 798.8
2139	EN14362-1	348.5		-1.32	
2146	EN14362-1	542		0.50	
2152	EN14362-1	153.6	DG(0.01)	-3.14	
2156		-----		-----	
2160	B.82.02-2	438.8		-0.47	
2165	EN14362-1	500		0.10	
2166	EN14362-1	299.7		-1.77	
2170	EN14362-1	520.66	C	0.30	
2172	EN14362-1	530		0.38	
2173	EN14362-1	488.25		-0.01	
2184	EN14362-1	430		-0.55	
2186	§64 LFBG 82.02-2	>150	C	-----	first reported ----
2190	EN14362-1	448		-0.38	
2196	EN14362-1	509		0.19	
2197		-----		-----	
2201	EN14362-1	519		0.28	
2213	EN14362-1	272	C	-2.03	first reported 1002
2215	EN14362	520		0.29	
2217	EN14362-1	386.53		-0.96	
2221	EN14362-1	448		-0.38	
2227		-----		-----	
2235	EN14362-1	103.6	C,DG(0.05)	-3.61	first reported ----
2236	in house	226		-2.46	
2239	EN14362-1	n.d.	C	-----	first reported 1477
2241	EN14362-1	546		0.53	
2248	§64 LFGB B82.02-2	151	DG(0.01)	-3.17	
2252	EN14362-1	533.9		0.42	
2255	EN14362-1	546.6		0.54	
2256	EN14362-1	521		0.30	
2261	in house	521		0.30	
2265	§64 LFGB B82.02-2+4	235.5	C	-2.38	first reported n.d.
2266	EN14362-1	41.8	DG(0.01)	-4.19	
2270	EN14362-1	491.9		0.03	
2272	EN14362-1	12.78	DG(0.05)	-4.46	
2274	EN14362-1	504.2		0.14	
2275	EN14362-1	523		0.32	
2276	§64 LFGB B82.02-2	690		1.88	
2284	EN14362-1	438.7		-0.47	
2285	EN14362-1	480		-0.08	
2286	EN14362-1	560		0.66	
2287	EN14362-1	440		-0.46	
2289	EN14362-1	548		0.55	
2291	EN14362-1	524		0.33	
2293		-----		-----	
2310	EN14362-1	486		-0.03	
2311	EN14362-1	527		0.36	
2350	EN14362-1	568		0.74	
2357	EN14362-1	524		0.33	
2358	EN14362-1	470		-0.18	
2359	EN14362-1	537		0.45	
2364	EN14362-1	531		0.39	
2365	EN14362-1	509		0.19	
2366	EN14362-1	533		0.41	
2367	EN14362-1	526		0.35	
2368	EN14362-1	482		-0.07	
2370	EN14362-1	558		0.65	
2372	EN14362-1	496		0.07	
2375	EN14362-1	565		0.71	

2379	EN14362-1	489.94		0.01	
2380	EN14362-1	471.537		-0.16	
2386	LFGB 82.02-2	534	C	0.42	first reported 267
2390	EN14362-1	546.620		0.54	
3100	EN14362-1	506		0.16	
3104	EN14362-1	483		-0.06	
3107	in house	480		-0.08	
3116	EN14362-1	380		-1.02	
3117	EN14362-1	423		-0.62	
3118	EN14362-1	559.66		0.66	
3134	EN14362-1	479.4		-0.09	
3149		-----		-----	
3150	64 LFGB 82.02.2	500		0.10	
3151	EN14362-1	390		-0.93	
3153	EN14362-1	566		0.72	
3154	BVL B82.02-2	384.28		-0.98	
3159	EN14362-1	430		-0.55	
3167	EN14362-1	535		0.43	
3170		-----		-----	
3172	EN14362-1	486.2		-0.03	
3174	EN14362-1	701.86		1.99	
3176		514.4		0.24	
3179	EN14362-1	430		-0.55	
3180		342		-1.38	
3182	EN14362-1	373.461		-1.08	
3185	EN14362-1	518		0.27	
3190	EN14362-1	582		0.87	
3195	EN14362-1	448		-0.38	
3197	EN14362-1	357	C	-1.24	first reported 204.8
3203	EN14362-1	484.25		-0.04	
3204		-----		-----	
3210	EN14362-1	361		-1.20	
3216	EN14362-1	128.4	DG(0.05)	-3.38	
3218	EN14362-1	543		0.51	
3220	EN14362-1	483.0	C	-0.06	first reported 1050
3222	EN14362-1	474		-0.14	
3226	EN14362-1	709.96		2.07	
3228	EN14362-1	515		0.24	
3233	EN14362-1	343		-1.37	
3237	in house	459.9		-0.27	
3242	in house	470.0		-0.18	
3243	§35 LMBG 82.02-2	49	C,DG(0.01)	-4.12	first reported n.d.
3246	EN14362-1	496		0.07	
3247	EN14362-1	333		-1.46	
3248	EN14362-1	599		1.03	
4095	EN14362-1	381.3		-1.01	
5012		-----		-----	
8008	in house	475		-0.13	



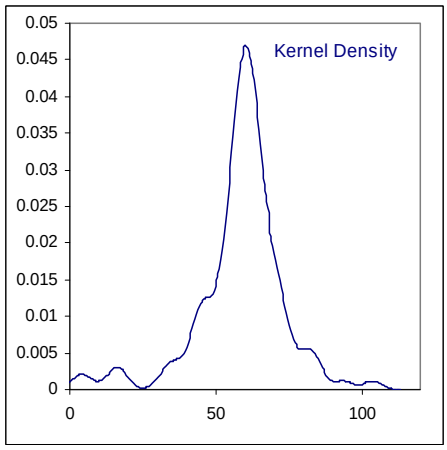
	normality	not OK
	n	102
	outliers	8
	mean (n)	489.05
	st.dev. (n)	91.135
	R(calc.)	255.18
	R(EN14362-1)	298.81



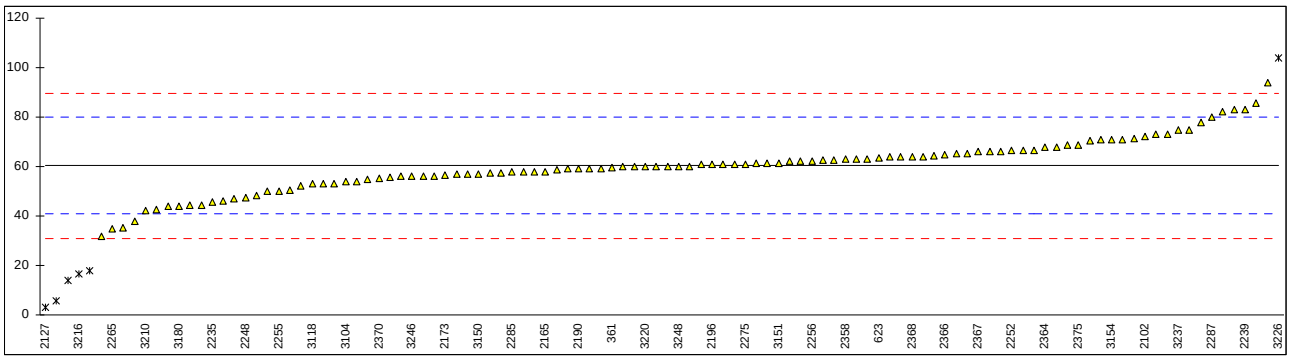
Determination of 4-Aminodiphenyl (CASno.92-67-1) in sample #1020; results in mg/kg

lab	method	value	mark	z(targ)	remarks
361	EN14362-1	59.3532		-0.10	
551	EN14362-1	62.7		0.25	
622	EN14362-1	48.12		-1.25	
623	in house	63.33		0.31	
840	EN14362-1	64.20		0.40	
1051	EN14362-1	57.5		-0.29	
1213	§64 LFGB B82.02-02	61.5	C	0.12	first reported 32.7
2102	EN14362-1	72		1.20	
2115	EN14362-1	57.57		-0.28	
2117	§64 LFGB B82.02-02	66		0.59	
2121	EN14362-1	83		2.33	
2127	EN14362-1	2.932	G(0.05)	-5.88	
2129	EN14362-1	78		1.82	
2132	EN14362-1	59.1	C	-0.12	first reported 94.5
2137	§64 LFGB BVL B82.02-02	74.9		1.50	
2139	EN14362-1	44.2		-1.65	
2146	EN14362-1	68		0.79	
2152	EN14362-1	5.5	G(0.05)	-5.62	
2156		-----		-----	
2160	B.82.02-2	53.1		-0.74	
2165	EN14362-1	58		-0.23	
2166	EN14362-1	43.7		-1.70	
2170	EN14362-1	58.52	C	-0.18	first reported n.d.
2172	EN14362-1	61.1		0.08	
2173	EN14362-1	56.55		-0.38	
2184	EN14362-1	60		-0.03	
2186	§64 LFBG 82.02-2	42.59	C	-1.82	first reported ----
2190	EN14362-1	59		-0.13	
2196	EN14362-1	61		0.07	
2197		-----		-----	
2201	EN14362-1	53		-0.75	
2213	EN14362-1	57.0		-0.34	
2215	EN14362	60		-0.03	
2217	EN14362-1	44.4	C	-1.63	first reported 26.13
2221	EN14362-1	46		-1.47	
2227		-----		-----	
2235	EN14362-1	45.8	C	-1.49	first reported ----
2236		-----		-----	
2239	EN14362-1	83		2.33	
2241	EN14362-1	58		-0.23	
2248	§64 LFGB B82.02-2	47.6		-1.30	
2252	EN14362-1	66.4		0.63	
2255	EN14362-1	50.2		-1.03	
2256	EN14362-1	62		0.18	
2261	in house	54		-0.64	
2265	§64 LFGB B82.02-2+4	34.9	C	-2.60	first reported n.d.
2266	EN14362-1	31.8		-2.92	
2270	EN14362-1	54.80		-0.56	
2272	EN14362-1	93.84	C	3.44	first reported n.d.
2274	EN14362-1	66.4		0.63	
2275	EN14362-1	61		0.07	
2276	§64 LFGB B82.02-2	85.5		2.59	
2284	EN14362-1	71.3		1.13	
2285	EN14362-1	58		-0.23	
2286	EN14362-1	71		1.10	
2287	EN14362-1	80		2.02	
2289	EN14362-1	64		0.38	
2291	EN14362-1	62		0.18	
2293		-----		-----	
2310	EN14362-1	57		-0.34	
2311	EN14362-1	66.0		0.59	
2350	EN14362-1	68.6		0.85	
2357	EN14362-1	56		-0.44	
2358	EN14362-1	62.9		0.27	
2359	EN14362-1	64		0.38	
2364	EN14362-1	68		0.79	
2365	EN14362-1	64		0.38	
2366	EN14362-1	65		0.48	
2367	EN14362-1	66		0.59	
2368	EN14362-1	64		0.38	
2370	EN14362-1	55.3		-0.51	
2372	EN14362-1	66.6		0.65	
2375	EN14362-1	68.8		0.87	

2379	EN14362-1	60.66		0.04	
2380	EN14362-1	65.015		0.48	
2386	LFGB 82.02-2	56		-0.44	
2390	EN14362-1	62.487		0.23	
3100	EN14362-1	61		0.07	
3104	EN14362-1	54		-0.64	
3107	in house	38		-2.29	
3116	EN14362-1	60		-0.03	
3117	EN14362-1	62		0.18	
3118	EN14362-1	52.84		-0.76	
3134	EN14362-1	82.2		2.25	
3149		-----		-----	
3150	64 LFGB 82.02.2	57		-0.34	
3151	EN14362-1	61.5		0.12	
3153	EN14362-1	70.3		1.03	
3154	BVL B82.02-2	70.96		1.09	
3159	EN14362-1	63.1		0.29	
3167	EN14362-1	73		1.30	
3170		-----		-----	
3172	EN14362-1	65.4		0.52	
3174	EN14362-1	50.42		-1.01	
3176		35.35		-2.56	
3179	EN14362-1	63		0.28	
3180		44		-1.67	
3182	EN14362-1	52.147		-0.84	
3185	EN14362-1	60		-0.03	
3190	EN14362-1	59		-0.13	
3195	EN14362-1	17.9	G(0.05)	-4.35	
3197	EN14362-1	50.0		-1.06	
3203	EN14362-1	59.16		-0.12	
3204		-----		-----	
3210	EN14362-1	42.3		-1.85	
3216	EN14362-1	16.5	DG(0.01)	-4.49	
3218	EN14362-1	60		-0.03	
3220	EN14362-1	60		-0.03	
3222	EN14362-1	73		1.30	
3226	EN14362-1	103.82	G(0.05)	4.47	
3228	EN14362-1	58		-0.23	
3233	EN14362-1	70.8		1.08	
3237	in house	74.6		1.47	
3242	in house	47.0		-1.36	
3243	§35 LMBG 82.02-2	14	C,DG(0.01)	-4.75	first reported n.d.
3246	EN14362-1	56		-0.44	
3247	EN14362-1	61		0.07	
3248	EN14362-1	60		-0.03	
4095	EN14362-1	56.3		-0.41	
5012		-----		-----	
8008	in house	55.8		-0.46	



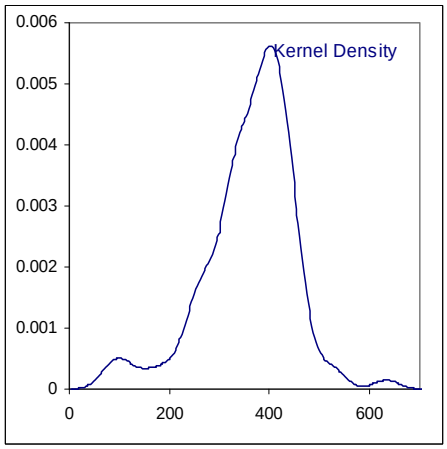
normality	not OK
n	106
outliers	6
mean (n)	60.288
st.dev. (n)	10.7341
R(calc.)	30.056
R(EN14362-1)	27.298



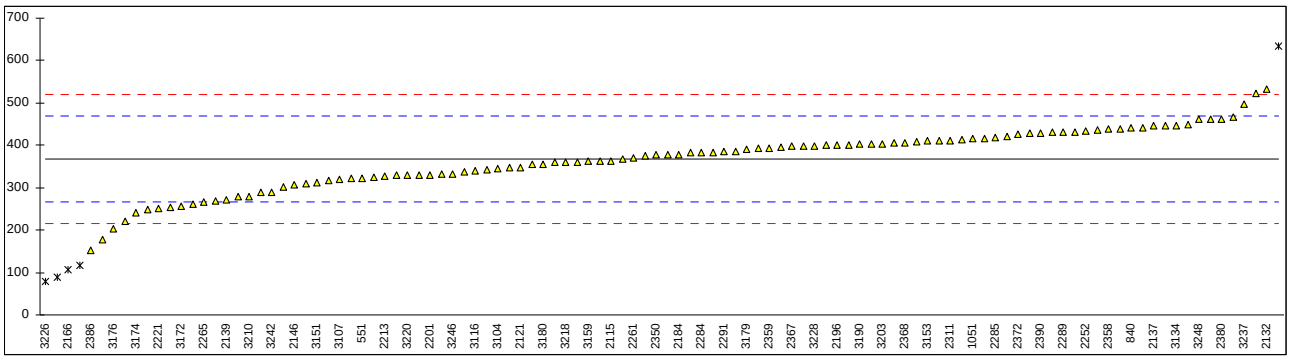
Determination of Benzidine (CASno.92-87-5) in sample #1020; results in mg/kg

lab	method	value	mark	z(targ)	remarks
361	EN14362-1	386.3682		0.37	
551	EN14362-1	323.0		-0.87	
622	EN14362-1	252.91		-2.25	
623	in house	413.59		0.91	
840	EN14362-1	441.16		1.45	
1051	EN14362-1	415.3		0.94	
1213	§64 LFGB B82.02-02	268		-1.96	
2102	EN14362-1	363		-0.09	
2115	EN14362-1	363.16		-0.08	
2117	§64 LFGB B82.02-02	260		-2.11	
2121	EN14362-1	348		-0.38	
2127		-----		-----	
2129	EN14362-1	466		1.94	
2132	EN14362-1	532.8		3.26	
2137	§64 LFGB BVL B82.02-02	445.4		1.54	
2139	EN14362-1	270.3		-1.91	
2146	EN14362-1	308		-1.17	
2152		-----		-----	
2156		-----		-----	
2160	B.82.02-2	347.3		-0.39	
2165	EN14362-1	402		0.68	
2166	EN14362-1	105.5	DG(0.05)	-5.16	
2170	EN14362-1	328.58	C	-0.76	first reported 21.48
2172	EN14362-1	325		-0.83	
2173	EN14362-1	395.58		0.56	
2184	EN14362-1	378		0.21	
2186	§64 LFBG 82.02-2	<15		<-6.94	false negative?
2190	EN14362-1	435		1.33	
2196	EN14362-1	401		0.66	
2197	EN14362-1	522		3.05	
2201	EN14362-1	330		-0.74	
2213	EN14362-1	328.41		-0.77	
2215	EN14362	330		-0.74	
2217	EN14362-1	249.25		-2.33	
2221	EN14362-1	252		-2.27	
2227		-----		-----	
2235	EN14362-1	447.0		1.57	
2236	in house	432.4		1.28	
2239	EN14362-1	n.d.	C	-----	first reported 1605
2241	EN14362-1	417		0.98	
2248	§64 LFGB B82.02-2	377		0.19	
2252	EN14362-1	432.8		1.29	
2255	EN14362-1	397.0		0.58	
2256	EN14362-1	332		-0.70	
2261	in house	371		0.07	
2265	§64 LFGB B82.02-2+4	267.5	C	-1.97	first reported n.d.
2266	EN14362-1	303.0		-1.27	
2270	EN14362-1	309.0		-1.15	
2272	EN14362-1	87.64	DG(0.05)	-5.51	
2274	EN14362-1	383.7		0.32	
2275	EN14362-1	318		-0.97	
2276	§64 LFGB B82.02-2	634	G(0.05)	5.25	
2284	EN14362-1	382.6		0.30	
2285	EN14362-1	418		1.00	
2286	EN14362-1	430		1.23	
2287	EN14362-1	450		1.63	
2289	EN14362-1	432		1.27	
2291	EN14362-1	385		0.35	
2293		-----		-----	
2310	EN14362-1	410		0.84	
2311	EN14362-1	412		0.88	
2350	EN14362-1	377		0.19	
2357	EN14362-1	442		1.47	
2358	EN14362-1	438		1.39	
2359	EN14362-1	394		0.52	
2364	EN14362-1	420		1.04	
2365	EN14362-1	400		0.64	
2366	EN14362-1	406		0.76	
2367	EN14362-1	397		0.58	
2368	EN14362-1	407		0.78	
2370	EN14362-1	401		0.66	
2372	EN14362-1	426		1.16	
2375	EN14362-1	408		0.80	

2379	EN14362-1	427.92		1.19	
2380	EN14362-1	461.042		1.85	
2386	LFGB 82.02-2	153		-4.22	
2390	EN14362-1	428.495		1.20	
3100	EN14362-1	376		0.17	
3104	EN14362-1	344		-0.46	
3107	in house	320		-0.93	
3116	EN14362-1	340		-0.54	
3117	EN14362-1	343		-0.48	
3118	EN14362-1	360.88		-0.13	
3134	EN14362-1	447.5		1.58	
3149		-----		-----	
3150	64 LFGB 82.02.2	367		-0.01	
3151	EN14362-1	313		-1.07	
3153	EN14362-1	410		0.84	
3154	BVL B82.02-2	279.27		-1.73	
3159	EN14362-1	363		-0.09	
3167	EN14362-1	461		1.84	
3170		-----		-----	
3172	EN14362-1	255.1		-2.21	
3174	EN14362-1	239.88		-2.51	
3176		202.94	C	-3.24	first reported 138.81
3179	EN14362-1	390		0.45	
3180		356		-0.22	
3182	EN14362-1	359.182		-0.16	
3185	EN14362-1	355		-0.24	
3190	EN14362-1	402		0.68	
3195	EN14362-1	177		-3.75	
3197	EN14362-1	321.4		-0.90	
3203	EN14362-1	402.92		0.70	
3204		-----		-----	
3210	EN14362-1	280		-1.72	
3216	EN14362-1	116.0	DG(0.05)	-4.95	
3218	EN14362-1	360		-0.14	
3220	EN14362-1	329		-0.76	
3222	EN14362-1	382		0.29	
3226	EN14362-1	79.04	DG(0.05)	-5.68	
3228	EN14362-1	399		0.62	
3233	EN14362-1	440		1.43	
3237	in house	497.9		2.57	
3242	in house	290.0		-1.52	
3243	§35 LMBG 82.02-2	220	C	-2.90	first reported 94
3246	EN14362-1	332		-0.70	
3247	EN14362-1	288		-1.56	
3248	EN14362-1	461		1.84	
4095	EN14362-1	337.7		-0.58	
5012		-----		-----	
8008	in house	394		0.52	



normality	OK
n	105
outliers	5
mean (n)	367.35
st.dev. (n)	71.200
R(calc.)	199.36
R(EN14362-1)	142.16

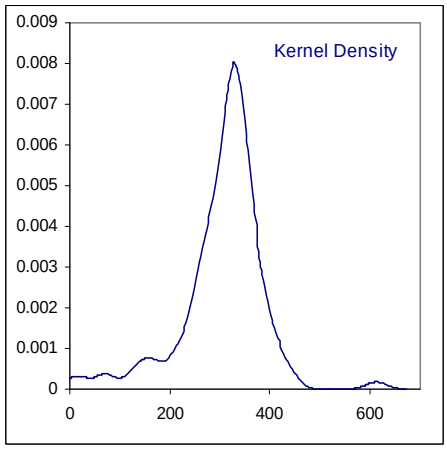


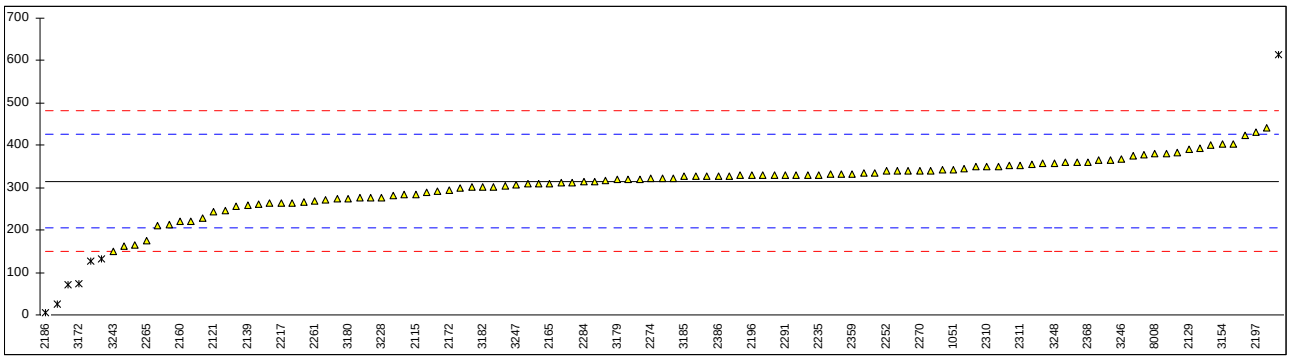
Determination of 3,3-Dimethylbenzidine (CASno.119-93-7) in sample #1020; results in mg/kg

lab	method	value	mark	z(targ)	remarks
361	EN14362-1	304.7761		-0.19	
551	EN14362-1	351.0		0.64	
622	EN14362-1	229.23	C	-1.56	first reported 4723.31
623	in house	322.76		0.13	
840	EN14362-1	360.90		0.82	
1051	EN14362-1	343.2		0.50	
1213	§64 LFGB B82.02-02	245		-1.27	
2102	EN14362-1	291		-0.44	
2115	EN14362-1	285.13		-0.55	
2117	§64 LFGB B82.02-02	320		0.08	
2121	EN14362-1	243		-1.31	
2127		-----		-----	
2129	EN14362-1	390		1.35	
2132	EN14362-1	400.3		1.53	
2137	§64 LFGB BVL B82.02-02	320.2	C	0.09	first reported 485.6
2139	EN14362-1	258.4		-1.03	
2146	EN14362-1	317		0.03	
2152		-----		-----	
2156		-----		-----	
2160	B.82.02-2	219.4		-1.74	
2165	EN14362-1	310		-0.10	
2166	EN14362-1	210.1		-1.90	
2170	EN14362-1	328.24	C	0.23	first reported 12.52
2172	EN14362-1	294		-0.39	
2173	EN14362-1	328.53		0.24	
2184	EN14362-1	302		-0.24	
2186	§64 LFBG 82.02-2	3.8315	C,G(0.05)	-5.63	first reported 9.104
2190	EN14362-1	336		0.37	
2196	EN14362-1	329		0.25	
2197	EN14362-1	431		2.09	
2201	EN14362-1	300		-0.28	
2213	EN14362-1	334.17		0.34	
2215	EN14362	290		-0.46	
2217	EN14362-1	263.4	C	-0.94	first reported 151.00
2221	EN14362-1	126	DG(0.05)	-3.42	
2227		-----		-----	
2235	EN14362-1	330.2		0.27	
2236	in house	403.2		1.59	
2239	EN14362-1	n.d.	C	-----	first reported 902
2241	EN14362-1	366		0.91	
2248	§64 LFGB B82.02-2	366		0.91	
2252	EN14362-1	338.9		0.42	
2255	EN14362-1	314.0		-0.03	
2256	EN14362-1	282		-0.60	
2261	in house	268		-0.86	
2265	§64 LFGB B82.02-2+4	176.1	C	-2.52	first reported n.d.
2266	EN14362-1	263.0		-0.95	
2270	EN14362-1	339.6		0.44	
2272	EN14362-1	132.28	DG(0.05)	-3.31	
2274	EN14362-1	321.2		0.10	
2275	EN14362-1	312		-0.06	
2276	§64 LFGB B82.02-2	613	G(0.05)	5.38	
2284	EN14362-1	313.4		-0.04	
2285	EN14362-1	313		-0.04	
2286	EN14362-1	350		0.63	
2287	EN14362-1	330		0.26	
2289	EN14362-1	310		-0.10	
2291	EN14362-1	330		0.26	
2293		-----		-----	
2310	EN14362-1	350		0.63	
2311	EN14362-1	353		0.68	
2350	EN14362-1	375		1.08	
2357	EN14362-1	341		0.46	
2358	EN14362-1	327		0.21	
2359	EN14362-1	333		0.32	
2364	EN14362-1	331		0.28	
2365	EN14362-1	329		0.25	
2366	EN14362-1	328		0.23	
2367	EN14362-1	333		0.32	
2368	EN14362-1	361		0.82	
2370	EN14362-1	384		1.24	
2372	EN14362-1	357		0.75	
2375	EN14362-1	339		0.43	

2379	EN14362-1	354.06		0.70	
2380	EN14362-1	381.063		1.19	
2386	LFGB 82.02-2	328		0.23	
2390	EN14362-1	321.674		0.11	
3100	EN14362-1	359		0.79	
3104	EN14362-1	352		0.66	
3107	in house	264		-0.93	
3116	EN14362-1	260		-1.00	
3117	EN14362-1	273		-0.77	
3118	EN14362-1	272.16		-0.78	
3134	EN14362-1	423.1		1.95	
3149		-----		-----	
3150	64 LFGB 82.02.2	303		-0.22	
3151	EN14362-1	255		-1.09	
3153	EN14362-1	343		0.50	
3154	BVL B82.02-2	402.85		1.58	
3159	EN14362-1	283		-0.59	
3167	EN14362-1	393		1.40	
3170		-----		-----	
3172	EN14362-1	73.6	C,G(0.05)	-4.37	first reported 489.1
3174	EN14362-1	211.89		-1.87	
3176		276.56		-0.70	
3179	EN14362-1	320		0.08	
3180		273		-0.77	
3182	EN14362-1	302.524		-0.23	
3185	EN14362-1	326		0.19	
3190	EN14362-1	344		0.52	
3195	EN14362-1	163		-2.76	
3197	EN14362-1	275.8		-0.72	
3203	EN14362-1	309.91		-0.10	
3204		-----		-----	
3210	EN14362-1	165		-2.72	
3216	EN14362-1	71.3	G(0.05)	-4.41	
3218	EN14362-1	330		0.26	
3220	EN14362-1	330		0.26	
3222	EN14362-1	339		0.43	
3226	EN14362-1	25.59	G(0.01)	-5.24	
3228	EN14362-1	277		-0.69	
3233	EN14362-1	378		1.13	
3237	in house	440.6		2.26	
3242	in house	220.0		-1.73	
3243	§35 LMBG 82.02-2	150	C	-2.99	first reported 122
3246	EN14362-1	368		0.95	
3247	EN14362-1	307		-0.15	
3248	EN14362-1	357		0.75	
4095	EN14362-1	265.2		-0.91	
5012		-----		-----	
8008	in house	380		1.17	

normality	not OK
n	104
outliers	7
mean (n)	315.41
st.dev. (n)	55.669
R(calc.)	155.87
R(EN14362-1)	154.87





APPENDIX 2

Summary of all other reported aromatic amines in sample #1019; results in mg/kg

lab	method
2127	o-aminoazotoluene 0.957 mg/kg
2186	1,4-phenylendiamine + analin detected and 4-aminoazotoluene suspected
2239	4-aminodiphenyl 29 mg/kg, benzidine 39 mg/kg, 3,3'-dimethylbenzidine 11 mg/kg, 4,4'-diamino-3,3'-dichlorodiphenylmethane 62 mg/kg
2276	2,4-diaminotoluene 25 mg/kg, o-aminoazotoluene 114 mg/kg
3107	p-cresidine 5 mg/kg
3118	4-aminodiphenyl 60.96 mg/kg, benzidine 309.81 mg/kg, 3,3'-dimethylbenzidine 249.85 mg/kg
3174	4-aminodiphenyl 3.05 mg/kg, benzidine 19.00 mg/kg, p-chloraniline, 3,3'-dimethylbenzidine 17.20 mg/kg, p-cresidine 10.15 mg/kg, 4,4'-diaminodiphenylether 22.00 mg/kg

Summary of all other reported aromatic amines in sample #1020; results in mg/kg

lab	method
622	4,4'-diaminodiphenylsulfide 17.01 mg/kg, o-toluidine 0.97mg/kg
2139	4,4'-diaminodiphenylsufide 15.1 mg/kg
2186	4,4'-diaminodiphenylmethane 18.96 mg/kg
2213	4,4'-diaminodiphenylsulfide 45.85 mg/kg
2217	4,4'-diaminodiphenylsulfide 4.8 mg/kg
3118	4,4'-diaminodiphenylsulfide 20.94 mg/kg
3174	4,4'-diaminodiphenylsulfide 46.68 mg/kg
3220	4,4'-diaminodiphenylsulfide 46 mg/kg

APPENDIX 3

Details of the analysis methods used by the participants

lab	solvents	detection methods	Calibration standards	Corr. Rec.
361	MTBE	GC/MS	1,5,10,15,20,30 mg/L mix A,B&C + ISTD Mix 10mg/L	no
551		GC/MS	RM, grade chromatographic	no
622			exstd. for quantification 12-68 mg/kg	
623		GC/MS+HPLC/UV-DAD	cal. curve 1,5,10,15,20,30 mg/L	no
840		GC/MS	cal. curve 5,10,15,20,30 ppm	no
1051	MTBE	GC/MS+HPLC/DAD	Sigma, Chemservice	no
1213	MTBE	GC/MS	Dr. Ehrenstorfer, ISTD	no
2102		GC/MS	Dr. Ehrenstorfer, Sigma/Aldrich, ISTD	no
2115	MTBE	GC/MS	Dr. Ehrenstorfer, Aldrich, technical purity salts	no
2117	MTBE		mix 9, Dr. Ehrenstorfer 100ug/ul	no
2121	MTBE	UPLC/MS+HPLC/UV	4,10,20,80mg/kg	no
2127	MTBE	HPLC/MS	in house std.	no
2129	MTBE	GC/MS+LC/TOF	Fluka, Riedel, ABCR	no
2132	MTBE	GC/MS+HPLC/DAD	Accustandard, Chemservice, Sigma (96-99%)	no
2137	MTBE	GC/MS+HPLC/DAD	ample type Accustandard (1-20mg/L)	yes
2139	methanol	HPLC/UV	Accustandard 100ug/mL	no
2146		HPLC/DAD		no
2152		GC/MS		no
2156				
2160	MTBE	GC/MS	Dr. Ehrenstorfer/10,20,30,40,50ppm	yes
2165		GC/MS, TLC	butylated hydroxytoluene	no
2166	MTBE	HPLC/DAD	2.5-50 mg/L	no
2170	methanol	GC/MS	2,4,10,15 ppm	no
2172	MTBE	GC/MS+HPLC/DAD	5-10mg/L	no
2173	methanol	GC/MS+LC/MS	Dr. Ehrenstorfer Mix 6: 50mg/L	no
2184		GC/MS	Naphthalene-d8	no
2186	MTBE	HPLC/DAD	15,30,50,100,150 mg/L	no
2190		GC/MS	ISTD	no
2196	MTBE	GC/MS+HPLC/DAD		no
2197	MTBE	HPLC/MS	6, 15, 30, 60 ppm	yes
2201	none	GC/MS+HPLC/UV	Dr. Ehrenstorfer (99.0-99.5%)	no
2213	methanol	GC/MS+HPLC	Dr. Ehrenstorfer 5,15,30ppm	no
2215	MTBE	GC/MS+HPLC/DAD	5,15,30ppm	yes
2217	MTBE	GC/MS	Dr. Ehrenstorfer pure standards	no
2221	none	GC/MS+HPLC/DAD	pure compounds (98.2-99.7%)	no
2227				
2235	MTBE	TLC,HPLC/DAD,GC/MS	Aldrich	no
2236	MTBE	HPLC/PDA	mixture of suspected amines 1,2,4,6,10ppm	no
2239		GC/MS	ISTD	no
2241	MTBE	GC/MS+UPLC/PDA/SQD	ISTD 10 mg/L	no
2248	MTBE	HPLC/UV+MS/MS	Sigma Aldrich (96.2-99.5%)	no
2252	MTBE	GC/MS+HPLC/DAD	some AZO ESTD othe AZO ISTD	no
2255	MTBE	GC/MS+HPLC/DAD	ISTD, 4 points cal 1,5,15,30mg/L	no
2256	MTBE	GC/MS+HPLC/DAD	conc.	yes
2261	DEE	GC/MS+HPLC/DAD	single standards	yes
2265	MTBE	HPLC/DAD	20,50,80,100mg/L	no
2266	MTBE	TLC+HPLC/DAD/UV+HPLC/MS	ESTD	no
2270	MTBE	GC/MS+HPLC/UV	Chemservice 15-100 mg/L	no
2272		GC/MS+HPLC/DAD	Dr. Ehrenstorfer 5-50 mg/kg	no
2274	MTBE	GC/MS+HPLC/DAD	4 points calibrations	no
2275	MTBE	GC/MS+HPLC/DAD	calib 0.6, 3, 15 ppm, ESTD	no
2276	acetonitrile	LC/MS-MS	Dr. Ehrenstorfer + Riedel de Haen 50-500ppb	no
2284	MTBE	GS/MS	certified st. mix 1-5ug/mL	yes
2285	MTBE	GC/MS	4 points calibrations & D10 ISTD	no
2286	MTBE	GC/MS+HPLC/DAD	24 mix st. solution (5,15,30ppm)	no
2287	MTBE	GC/MS+HPLC/DAD	24 mix st. solution (5,15,30ppm)	no
2289	MTBE	GC/MS + HPLC	calib 0.6,1.5,3.0,10mg/L	no
2291	MTBE	GC/MS+HPLC	5 points calibrations	no
2293				

2310		GC/MS+HPLC/DAD	5,10,20 ppm	no
2311		GC/MS+HPLC/DAD	2,5,10,15,20,30mg/L	no
2350	MTBE	GC/MS+HPLC/DAD	5,10,20,30,50mg/L	no
2357	MTBE	GC/MS+HPLC/DAD	ISTD D10:10mg/kg	no
2358	MTBE	GC/MS+HPLC/DAD	2.5,5,10,15,20,30mg/L	no
2359	MTBE	GC/MS	1,2.5,5,10,20,30ug/mL ISTD	no
2364	MTBE	GC/MS+HPLC/DAD	5,10,15,20,30mg/L ISTD	no
2365	MTBE	GC/MS+HPLC/DAD	2.5,5,10,15,30mg/L	no
2366	MTBE	GC/MS+HPLC/DAD	2.5,5,10,20,30mg/L ISTD	no
2367	MTBE	GC/MS+HPLC/DAD	2.5,5,10,20,30mg/L	no
2368	MTBE	GC/MS	ISTD	no
2370	MTBE	GC/MS	3,5,10,20,30,40,50ug/mL	no
2372	no	GC/MS	4,8,16,24,32,40ug/mL	no
2375	no clean-up	GC/MS+HPLC/DAD	1-30mg/L	no
2379	MTBE	GC/MS+HPLC/DAD	3,5,10,20,30,50,100ug/mL	no
2380	Ethyl Acetate	GC/MS+HPLC/DAD	ISTD d10 & d8: 10mg/L	no
2386	MTBE	HPLC/UV	5,10,20,30,40,60ug/kg	instd.
2390	MTBE	GC/MS	1,5,10,15,20,30ppm	yes
3100	MTBE	GC/MS+HPLC/UV	3,15,30ppm	no
3104	nil	GC/MS+HPLC/DAD	Chemservice 5,10,20,30mg/L	no
3107		GC/MS+HPLC/UV	ISTD	no
3116		GC/MS+HPLC/DAD	ISTD	no
3117	none	GC/MS	ISTD	no
3118	MTBE	GC/MS+HPLC/DAD	0.6, 3.0 ppm	no
3134	MTBE	GC/MS+GC/FID	exstd.	no
3149				
3150	no clean-up	GC/MS	3,7.5,15,30mg/L	no
3151	MTBE	GC/MS+LC/MS	aromatic amines multistd. 10,25,50ppm	no
3153	MTBE	GC/MSD+HPLC/DAD	0.6,3,10,20ppm	no
3154	MTBE	HPLC/DAD	Dr. Ehrenstorfer single std., Ultra Scientific multi std.	no
3159	nil	GC/MS+HPLC/UV	5,10,30mg/L Chem Service	no
3167	MTBE	GC/MS+HPLC/DAD	Amines mix std. 30mg/kg	no
3170				
3172		HPLC/UV	each amine single st. 100mg/L	no
3174	MTBE	GC/MS	5-30ug/mL	yes
3176				
3179	MTBE	GC/MS+HPLC	0.3-9ug/mL ISTD	no
3180		GC/MS+HPLC/DAD		no
3182	MTBE	HPLC/UV	1,3,10ppm	no
3185	MTBE	HPLC/DAD	0.6,3,15,30ppm	no
3190	none	GC/MS+HPLC/UV	0.1,1,3,5,10,50ppm	no
3195	MTBE	HPLC/UV	Dr. Ehrenstorfer, AZO-mix16, 50mg/L	no
3197	MTBE	GC/MS+HPLC	5ppm, 10ppm, 20ppm, 30ppm, ISTD	no
3203	MTBE	HPLC/UV	2,4mg/L	no
3204				
3210				no
3216	methanol	HPLC/UV	Sigma Aldrich std. 5-160ppm	yes
3218	MTBE	GC/MS+HPLC/UV	3ppm	no
3220	extrelute	GC/MS+HPLC	Dr. Ehrenstorfer	no
3222	MTBE	GC/MS	commercial mix of amines 10mg/L	no
3226	MTBE	GC/MS	Std of AA 100µg/ml (ready to use), ISTD	no
3228	none	GC/MS	Dr. Ehrenstorfer + Supelco	no
3233	no clean-up	GC/MS	solutions 5-50 mg/l, ISTD	no
3237	MTBE	GC/MS	Dr. Ehrenstorfer 10,20,30ppm	no
3242	MTBE	GC/MS+HPLC/DAD	5,10,15,20,50ppm	no
3243	DEE	GC/MS+HPLC/UV	Accustandard 10-100ppm, st. addition	no
3246		GC/MS+HPLC/UV	ind. amines RM, ISTD	no
3247	MTBE	GC/MS	Isotec, Merck, Dr.Ehrenstorfer,Supelco,Fluka,Aldrich,1-50ppm	no
3248	methanol	GC/MS+HPLC/UV	Dr. Ehrenstorfer 5,10,20ppm	no
4095			Riedel de Haen, Sigma-Aldrich (96.2-99.9%)	no
5012				
8008	nil	GC/MS+HPLC/DAD	Chem service 5,10,20,30mg/L	no

APPENDIX 4

List of participants on alphabetical country order

2 labs in	BANGLADESH
1 lab in	BRASIL
1 lab in	BULGARIA
1 lab in	CYPRUS
1 lab in	FINLAND
5 labs in	FRANCE
16 labs in	GERMANY
1 lab in	GREECE
1 lab in	GUATEMALA
13 labs in	HONG KONG
2 labs in	HUNGARY
6 labs in	INDIA
3 labs in	INDONESIA
5 labs in	ITALY
2 labs in	JAPAN
3 labs in	KOREA
1 lab in	MALAYSIA
33 labs in	P.R. of CHINA
1 lab in	PAKISTAN
1 lab in	SINGAPORE
1 lab in	SLOVENIA
1 lab in	SPAIN
2 labs in	SWITZERLAND
2 labs in	TAIWAN R.O.C.
3 labs in	THAILAND
2 labs in	THE NETHERLANDS
5 labs in	TURKEY
2 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
n.a. = not applicable
n.d. = not detected

Literature:

1 DIN 53316
2 LMBG 82.02-2:98
3 LMBG 82.02-3:97
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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)