Results of Proficiency Test
AZO dyes in textile
March 2013

Organised by: Institute for Interlaboratory Studies
Spijkenisse, the Netherlands

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1 INTRODUCTION

The Institute for Interlaboratory Studies (iis) organizes every year a proficiency test for banned AZO dyes in textile since 1997.
In this interlaboratory study, 165 laboratories in 33 different countries have participated (see appendix 3). In this report, the results of the 2013 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 #13020 and #13021), each dyed with different banned AZO dyes. Sample #13020 was especially prepared by a third party. Sample #13021 was purchased on the local market. Both samples were tested for fit for use and 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/IEC 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 presented in this report must be regarded as confidential and for use by the participating companies only. Disclosure of the information in this report is only allowed by means of the entire report. Use of the contents of this report for third parties is only allowed by written permission of the Institute for Interlaboratory Studies. Disclosure of the identity of one or more of the participating companies will be done only after receipt of a written agreement of the companies involved.

2.4 SAMPLES

The two different bulk textile samples, a blue cotton (sample #13020) and a striped multicoloured curtain (sample #13021), each approximately 1 kg, were dyed with different banned AZO-dyes. Out of each bulk batch, 200 samples with an equal piece of fabric of approximately 4 gram were prepared. The samples were labelled and tested for homogeneity. The homogeneity of the subsamples #13020 and #13021 (testing was subcontracted) was checked by determination of an aromatic amine on respectively 8 and 4 stratified randomly selected samples. See the following tables for the test results.

	3,3'-Dimethoxybenzidine in mg/kg
sample #13020-1	58.9
sample #13020-2	57.4
sample #13020-3	56.6
sample #13020-4	54.1
sample #13020-5	56.1
sample #13020-6	54.2
sample #13020-7	52.4
sample #13020-8	54.7

table 1: homogeneity test results of subsamples #13020

	o-Toluidine *in mg/kg*
sample #13021-1	85
sample #13021-2	87
sample #13021-3	90
sample #13021-4	77

table 2: homogeneity test results of subsamples #13021

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	*o*-Toluidine *in mg/kg*
r (observed) #13020	5.9	--
r (observed) #13021	--	16
reference method	EN14362-1:2012	EN14362-1:2012
0.3 x R (reference method)	7.5	16

table 3: repeatabilities of subsamples #13020 and #13021

The calculated repeatabilities of the test results 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 #13020 and #13021 was sent to the participating laboratories on March 6, 2013.

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 in general 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:

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

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

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

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

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

4 EVALUATION

During the execution of this proficiency test some reporting problems occurred. Thirty-one participants reported the results after the deadline and six participants did not report any test result. Finally, 159 participants did report 427 numerical results. Observed were 19 outlying results, which is 4.4% of the numerical results. In proficiency studies, outlier percentages of 3% - 7.5% are quite normal.
Anomal data distributions were found for 3,3-Dimethoxybenzidine, *p*-Chloroaniline, 2,4-Diaminoanisol and *o*-Toluidine. Therefore, the statistical evaluations should be used with care.
There are no reproducibility requirements for *p*-Chloroaniline and 2,4-Diaminoanisol reported in EN14362-1:2012, therefore the target reproducibilities were estimated from the reproducibilities of all aromatic amine compounds mentioned in EN14362-1:2012.

4.1 EVALUATION PER SAMPLE AND PER 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.

Textile sample #13020:

3,3'-Dimethoxybenzidine (CASno.119-90-4):
The determination of this aromatic amine at a concentration level of 50 mg/kg was problematic. Seven statistical outliers were detected. The numerical test results reported by the participants vary from 6.73 – 139.30 mg/kg. However the vast majority of the test results was higher than 30 mg/kg.
The observed reproducibility after rejection of the statistical outliers is not in agreement with the reproducibility requirement estimated from the test method EN14362-1:2012.

Textile sample #13021:

p-Chloroaniline (CASno.106-74-8):
The determination of this aromatic amine was very problematic. Eighty-one laboratories reported 'less than' test results or 'not detected' or a test result near or below the limit of detection and twenty-five laboratories reported numerical test results in the range from

15.38 - 104.3 mg/kg. Therefore no significant conclusions were drawn. See also the discussion in chapter 5.

2,4-Diaminoanisol (CASno.615-05-4):
The determination of this aromatic amine at a concentration level of 28 mg/kg, was problematic. Six statistical outliers were detected. The numerical test results reported by the participants vary from 'n.d.' – 145.42 mg/kg. The observed reproducibility after rejection of the statistical outliers is not at all in agreement with the reproducibility requirement estimated from the test method EN14362-1:2012.

o-Toluidine (CASno.95-53-4) in sample #13021
The determination of this aromatic amine at a concentration level of 107.77 mg/kg was problematic for a number of participants. Six statistical outliers were observed.
The test results reported by the participants vary from 'n.d.'-235.5 mg/kg.
The observed reproducibility after rejection of the statistical outliers is almost in agreement with the reproducibility requirement estimated from the test method EN14362-1:2012.

General:
Three participants reported also the presence of other aromatic amines at different concentration levels in sample #13020 (see Appendix 2).
Two laboratories reported to have detected 3,3'-Dimethylbenzidine instead of 3,3'-Dimethoxybenzidine. Probably the compounds were wrongly identified or the results may have been reported in the wrong row of the report form

Twenty participants reported also the presence of other aromatic amines at different concentration levels in sample #13021 (see Appendix 2).

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.

Parameter	*unit*	*n*	*average*	*2.8 * sd*	R(target)
3,3'-Dimethoxybenzidine	mg/kg	149	50.4	23.3	17.7

table 4: reproducibility of the aromatic amine in textile sample #13020

Parameter	*unit*	*n*	*average*	*2.8 * sd*	R(target)
p-Chloroaniline *	mg/kg	27	50.5	79.3	22.9
2,4-Diaminoanisol	mg/kg	85	27.8	40.9	12.6
o-Toluidine	mg/kg	147	107.8	81.5	65.8

table 5: reproducibilities of the aromatic amines in textile sample #13021

* See the discussion in chapter 6

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 in line with the spreads as observed in previous PTs and almost in agreement with the target reproducibilities estimated from the standardized test method EN14362-1:2012, see below table.

Parameter	*March 2013*	*March 2012*	*March 2011*	*March 2010*	*March 2009*	*March 2008*	*March 2007*	*April 2006*	*EN 14362*
4-Aminodiphenyl	n.e.	49%	(86%)*	50%	n.e.	n.e.	100%	n.e.	45%
Benzidine	n.e.	58%	51%	54%	n.e.	57%	71-99%	78%	39%
3,3'-Dimethylbenzidine	n.e.	n.e.	n.e.	49%	n.e.	90%	77%	n.e.	49%
3,3'-Dimethoxybenzidine	46%	49%	48%	n.e.	n.e.	n.e.	59-70%	83%	35%
o-Toluidine	76%	n.e.	n.e.	52%	n.e.	n.e.	n.a	n.e.	61%
2-Naphthylamine	n.e	n.e.	n.e.	n.e.	n.e.	75%	n.e.	n.e.	45%
4,4'-Diaminodiph.methane	n.e.	n.e.	n.e.	n.e.	58%	n.e.	n.e.	n.e.	42%
4,4'-Diaminodiph.sulfide	n.e.	n.e.	n.e.	51%	n.e.	73%	n.e.	n.e.	45%
p-Chloroaniline	n.e.**	n.e.	n.e.	n.e.	76%	n.e.	n.e.	n.e.	45%
4,4'-Diaminodiphenylether	n.e.	n.e.	41%	n.e.	n.e.	n.e.	n.e.	n.e.	45%
4,4'-Diamino-3,3'-dichlorodiphenylmethane	n.e.	n.e.	55%	n.e.	65%	n.e.	n.e.	119%	45%
2,4-Diaminoanisol	147%	n.e.	n.e.	n.e.	n.e.	n.e.	n.e.	n.e.	45%

table 6: long term development of relative reproducibilities of aromatic amines in textile samples

* Concentration of this component was near or below detection limit

** See the discussion in chapter 6

From the above table it is clear that no quality improvement is visible for the detected banned dyes.

6 DISCUSSION

From the reported test methods, it is clear that most participants treated the fabric samples according identical test methods. The majority of the laboratories used EN14362-1 and some others used the (identical) method LFBG 64-82.02.2. A number of participants reported to have used a different test method.
However, the detection technique and the purity of the various calibration standards that were used may vary strongly.

The different type of samples used in this PT may (partly) explain the large spread. Sample #13020 is a fabric dyed on special request with only one pure AZO dye that is known to release 3,3'-Dimethoxybenzidine, while sample #13021 was purchased on the local market and obviously was dyed with a number of AZO dyes. This latter material was from a striped curtain with a regular pattern of different coloured stripes. Although every participant received an equal piece of fabric, cut perpendicular on the striped pattern, the division of the AZO dyes present in sample #13021 and the necessary pre-treatment (e.g. choice of a subsample) of the multicoloured sample #13021 by the laboratories may certainly be the cause of extra uncertainty in the test results in comparison with sample #13020.

Sample #13021 was used before in the 2001 PT iis01A01:

		#0061 in iis01A01			#13021 in iis13A01T		
Parameter	unit	n	average	uncertainty	n	average	uncertainty
p-Chloroaniline	mg/kg	17	30.1	16.1	*27*	*50.5*	*28.3*
2,4-Diaminoanisol	mg/kg	10	13.9	12.3	85	27.8	14.6
o-Toluidine	mg/kg	32	67.0	45.0	147	107.8	29.1

Table 7: comparison of results of identical samples in iis01A01 and iis13A01T

The desired quality improvement is not visible. Perhaps the increase in the number of participants (147 vs 32) may hamper to see this effect.
Although the averages of the two PTs are deviating, the uncertainty in the averages is so large that the observed differences are statistically not significant.
What cannot be seen from above table is that in 2001 no less than 16 laboratories reported the presence of p-Chloroaniline (10-53 mg/kg) and only 4 laboratories (20%) reported the absence of p-Chloroaniline (e.g. n.d.). In the 2013 PT only 25 laboratories reported the presence of p-Chloroaniline (15-104 mg/kg) and no less than 81 laboratories (76%) reported the absence of p-Chloroaniline (e.g. n.d.).
The cause for this difference between the 2001 and 2013 results is not clear.

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.
Therefore, participation on a regular basis in this scheme could be helpful to improve the performance and the quality of the analytical results.

APPENDIX 1

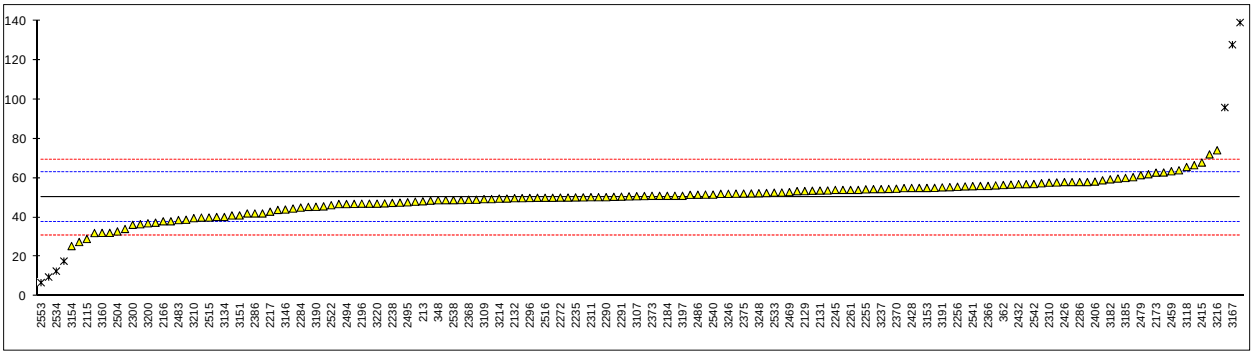
Determination of 3,3'-Dimethoxybenzidine (CASno.119-90-4) in sample #13020; results in mg/kg

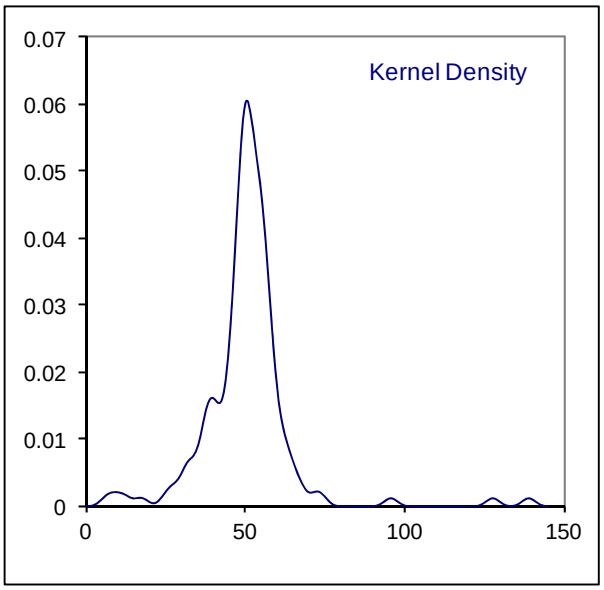
lab	method	value	mark	z(targ)	remarks
110	EN14362	37.3		-2.07	
213	EN14362	48.20		-0.34	
348	EN14362	48.76		-0.25	
362	EN14362	56.5	C	0.97	first reported 19.2
551	ISO14362	52.65	C	0.36	first reported 131.02
1911	EN14362	46.859		-0.55	
2102	in house	139.30	C, G(0.01)	14.09	first reported 278.60
2115		29.02		-3.38	
2121	EN14362	44.5		-0.93	
2129	EN14362	53.4		0.48	
2131	in house	53.66		0.52	
2132	EN14362	49.8		-0.09	
2135	LFGB 64-82.02.2	36.5		-2.20	
2138	EN14362	50.3		-0.01	
2139	EN14362	50.7		0.05	
2146	EN14362	55.8		0.86	
2152		-----		-----	
2165	EN14362	50		-0.06	
2166	EN14362	38		-1.96	
2170	EN14362	66.60		2.57	
2172	EN14362	38.8		-1.83	
2173	EN14362	62.8		1.97	
2184	EN14362	51		0.10	
2187	EN14362	62		1.84	
2190	EN14362	40.2		-1.61	
2196	EN14362	47		-0.53	
2201	EN14362	53.7		0.53	
2213	EN14362	54		0.58	
2217	EN14362	42.9		-1.18	
2232	EN14362	9.58	G(0.01)	-6.46	
2235	EN14362	50.18		-0.03	
2236	INH-009	56.93		1.04	
2238	EN14362	47.4		-0.47	
2245	EN14362	54		0.58	
2246	EN14362	48.836		-0.24	
2247	EN14362	51		0.10	
2255	EN14362	54.3		0.62	
2256	EN14362	55.6		0.83	
2261	GB/T17592	54		0.58	
2272	EN14362	50.1		-0.04	
2283	EN14362	32.1		-2.89	
2284	EN14362	45.0		-0.85	
2286	EN14362	58		1.21	
2287	EN14362	56		0.89	
2289	EN14362	51		0.10	
2290	EN14362	50.3		-0.01	
2291	EN14362	50.56688		0.03	
2293	EN14362	59.812		1.50	
2295	EN14362	58.9		1.35	
2296	ISO14362	49.9		-0.07	
2297	EN14362	41		-1.48	
2300	EN14362	36.22		-2.24	
2310	EN14362	57.7		1.16	
2311	EN14362	50.3		-0.01	
2313	EN14362	54.5		0.66	
2359	EN14362	46.8		-0.56	
2364	EN14362	52		0.26	
2366	EN14362	56		0.89	
2367	EN14362	49.6		-0.12	
2368	EN14362	49		-0.22	
2370	EN14362	54.6		0.67	
2372	ISO17234	50.5		0.02	
2373	EN14362	51		0.10	
2375	EN14362	52.14		0.28	
2379	EN14362	47.00		-0.53	
2380	EN14362	51.50		0.18	
2381	EN14362	55.40		0.80	
2386	DIN14362	42.0		-1.32	
2390	EN14362	62.882		1.98	
2403	EN14362	58		1.21	
2406	EN14362	58.23		1.25	
2410	EN14362	48.8		-0.25	

2415	EN14362	67.95		2.79	
2425	EN14362	52.087		0.27	
2426	EN14362	57.99		1.21	
2428	GB/T17592	55		0.73	
2429		-----		-----	
2432	in house	56.9		1.04	
2442	in house	53.37		0.48	
2452	EN14362	27.448		-3.63	
2453		-----		-----	
2456	EN14362	49	C	-0.22	first reported 79
2459	EN14362	63.517		2.08	
2469	EN14362	52.88		0.40	
2472	EN14362	42		-1.32	
2475	EN14362	50.87		0.08	
2476		-----		-----	
2479	EN14362	61.5		1.76	
2481	in house	55.0		0.73	
2482	EN14362	32.03		-2.90	
2483	INH-15205	38.63		-1.86	
2486	EN14362	51.56		0.19	
2489	EN14362	48.0		-0.37	
2492	in house	57.8		1.18	
2493		-----		-----	
2494	EN14362	46.80		-0.56	
2495	EN14362	47.7		-0.42	
2496	EN14362	55.03		0.74	
2497	EN14362	34.1		-2.58	
2504	EN14362	32.83		-2.78	
2511	EN14362	39.9		-1.66	
2514	EN14362	53.6		0.51	
2515	EN14362	39.92		-1.65	
2516	EN14362	50		-0.06	
2520		-----		-----	
2521		-----		-----	
2522	EN14362	46.2		-0.66	
2523	EN14362	47.135		-0.51	
2524		-----		-----	
2526	EN14362	50.2		-0.03	
2527	EN14362	38		-1.96	
2528	EN14362	64		2.16	
2533	EN14362	52.6		0.35	
2534	EN14362	12.6	G(0.01)	-5.98	
2536	EN14362	54.93		0.72	
2538	in house	48.8		-0.25	
2539	GB/T17592	56.3	C	0.94	first reported 22.52
2540	EN14362	51.61		0.20	
2541	EN14362	55.9		0.88	
2542	EN14362	57.0		1.05	
2549	EN14362	56.71		1.01	
2553	EN14362	6.732	G(0.01)	-6.91	
3100	EN14362	54.4		0.64	
3104	EN14362	45.34		-0.80	
3107	EN14362	50.79		0.07	
3109	LFGB 64-82.02.2	49.3		-0.17	
3116	EN14362	50.1		-0.04	
3117	EN14362	58		1.21	
3118	EN14362	65.68		2.43	
3134	EN14362	40.2		-1.61	
3145	LFGB 64-82.02.2	52.2		0.29	
3146	EN14362	44		-1.01	
3150	EN14362	51.6		0.20	
3151	EN14362	41		-1.48	
3153	EN14362	55.0		0.73	
3154	BVLV 82.02.2	25.39		-3.96	
3160	EN14362	32.09		-2.89	
3167	EN14362	128	G(0.01)	12.30	
3172	EN14362	49.8		-0.09	
3176		47.5		-0.45	
3180	EN14362	17.69	G(0.05)	-5.18	
3182	EN14362	59.4		1.43	
3183	64 LFGB B82.02.2	49.31		-0.17	
3185	EN14362	60.1		1.54	
3190	EN14362	45.4		-0.79	
3191	EN14362	55.3		0.78	
3192	64 LFGB B82.02.2	72.1		3.44	
3197	EN14362	51		0.10	
3199	CPSD AN 00607	43.8		-1.04	

3200	EN14362	37		-2.12	
3210	EN14362	39.6		-1.70	
3214	EN14362	49.58		-0.12	
3216	EN14362	74.2	C	3.78	first reported 13.69
3218	EN14362	54		0.58	
3220	EN14362	47.0		-0.53	
3222	EN14362	57.4		1.11	
3225	EN14362	45.62		-0.75	
3228	EN14362	50		-0.06	
3233	EN14362	48.54		-0.29	
3237		54.40		0.64	
3242	EN14362	60.5		1.61	
3243	EN14362	96	G(0.01)	7.23	
3246	EN14362	52		0.26	
3248	EN14362	52.3		0.31	
8008		-----		-----	

normality	not OK
n	149
outliers	7
mean (n)	50.361
st.dev. (n)	8.3177
R(calc.)	23.290
R(EN14362-1:2012)	17.677





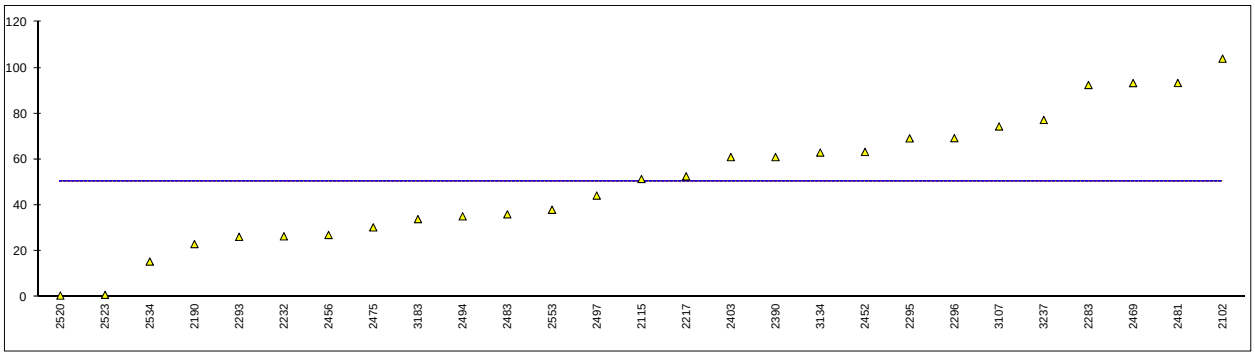
Determination of *p*-Chloroaniline (CASno.106-74-8) in sample #13021; results in mg/kg

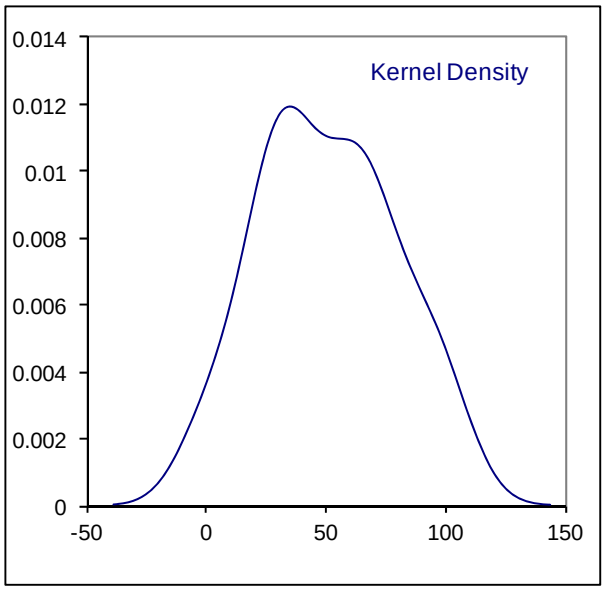
lab	method	value	mark	z(targ)	remarks
110	EN14362	n.d.		-----	
213	EN14362	n.d.		-----	
348	EN14362	n.d.		-----	
362	EN14362	<5.0		-----	
551	ISO14362	n.d.		-----	
1911		-----		-----	
2102	in house	104.03		-----	
2115		51.45		-----	
2121		-----		-----	
2129		-----		-----	
2131		-----		-----	
2132	EN14362	<5		-----	
2135		-----		-----	
2138		-----		-----	
2139	EN14362	<5		-----	
2146		-----		-----	
2152		-----		-----	
2165	EN14362	n.d.		-----	
2166	EN14362	n.d.		-----	
2170		-----		-----	
2172	EN14362	n.d.		-----	
2173	EN14362	n.d.		-----	
2184	EN14362	<5		-----	
2187	EN14362	n.d.		-----	
2190	EN14362	23.0		-----	
2196	EN14362	n.d.		-----	
2201	EN14362	<5		-----	
2213		-----		-----	
2217	EN14362	52.6		-----	
2232	EN14362	26.4		-----	
2235		-----		-----	
2236		-----		-----	
2238	EN14362	<5		-----	
2245	EN14362	n.d.		-----	
2246	EN14362	n.d.		-----	
2247	EN14362	n.d.		-----	
2255		-----		-----	
2256	EN14362	n.d.		-----	
2261		-----		-----	
2272		-----		-----	
2283	EN14362	92.5		-----	
2284	EN14362	<5.0		-----	
2286	EN14362	<10		-----	
2287	EN14362	<10		-----	
2289		-----		-----	
2290	EN14362	n.d.		-----	
2291	EN14362	n.d.		-----	
2293	EN14362	26.182		-----	
2295	EN14362	69.2		-----	
2296	ISO14362	69.3		-----	
2297	EN14362	<5		-----	
2300		-----		-----	
2310	EN14362	n.d.		-----	
2311	EN14362	n.d.		-----	
2313		-----		-----	
2359	EN14362	n.d.		-----	
2364	EN14362	n.d.		-----	
2366	EN14362	n.d.		-----	
2367	EN14362	n.d.		-----	
2368	EN14362	n.d.		-----	
2370	EN14362	n.d.		-----	
2372	ISO17234	n.d.		-----	
2373	EN14362	n.d.		-----	
2375	EN14362	n.d.		-----	
2379	EN14362	n.d.		-----	
2380	EN14362	n.d.		-----	
2381	EN14362	n.d.		-----	
2386	DIN14362	<5		-----	
2390	EN14362	61.015		-----	
2403	EN14362	61		-----	
2406	EN14362	<10		-----	
2410		-----		-----	

2415		-----	-----
2425		-----	-----
2426	EN14362	n.d.	-----
2428	GB/T17592	n.d.	-----
2429	EN14362	n.d.	-----
2432		-----	-----
2442		-----	-----
2452	EN14362	63.255	-----
2453		-----	-----
2456	EN14362	27	-----
2459	EN14362	n.d.	-----
2469	EN14362	93.35	-----
2472	EN14362	<5	-----
2475	EN14362	30.30	-----
2476		-----	-----
2479	EN14362	n.d.	-----
2481	in house	93.4	-----
2482		-----	-----
2483	INH-15205	36.01	-----
2486	EN14362	n.d.	-----
2489	EN14362	n.d.	-----
2492		-----	-----
2493		-----	-----
2494	EN14362	35.13	-----
2495		-----	-----
2496	EN14362	n.d.	-----
2497	EN14362	44.2	-----
2504		-----	-----
2511	EN14362	<5	-----
2514		-----	-----
2515	EN14362	<5	-----
2516	EN14362	<5	-----
2520	EN14362	0.528	-----
2521		-----	-----
2522		-----	-----
2523	EN14362	0.826	-----
2524		-----	-----
2526	EN14362	n.d.	-----
2527	EN14362	n.d.	-----
2528	EN14362	<10	-----
2533	EN14362	n.d.	-----
2534	EN14362	15.381	-----
2536	EN14362	n.d.	-----
2538		-----	-----
2539	GB/T17592	n.d.	-----
2540		-----	-----
2541		-----	-----
2542		-----	-----
2549	EN14362	n.d.	-----
2553	EN14362	37.982	-----
3100	EN14362	n.d.	-----
3104	EN14362	<5	-----
3107	EN14362	74.39	-----
3109		-----	-----
3116	EN14362	<5	-----
3117		-----	-----
3118		-----	-----
3134	EN14362	63.0	-----
3145		-----	-----
3146	EN14362	<10	-----
3150		-----	-----
3151		-----	-----
3153	EN14362	n.d.	-----
3154		-----	-----
3160		-----	-----
3167	EN14362	<3	-----
3172		-----	-----
3176		-----	-----
3180		-----	-----
3182		-----	-----
3183	64 LFGB B82.02.2	33.90	-----
3185	EN14362	n.d.	-----
3190	EN14362	<5	-----
3191	EN14362	<10	-----
3192	64 LFGB B82.02.2	<30	-----
3197		-----	-----
3199	CPSD AN 00607	<10	-----

3200	EN14362	n.d.	-----
3210		-----	-----
3214	EN14362	n.d.	-----
3216		-----	-----
3218	EN14362	n.d.	-----
3220		-----	-----
3222		-----	-----
3225		-----	-----
3228	EN14362	n.d.	-----
3233	EN14362	n.d.	-----
3237		77.2222	-----
3242	EN14362	n.d.	-----
3243		-----	-----
3246	EN14362	n.d.	-----
3248		-----	-----
8008		-----	-----

normality	OK
n	27
outliers	0
mean (n)	50.465
st.dev. (n)	28.3141
R(calc.)	79.279
R(EN14362-1:2012)	22.850





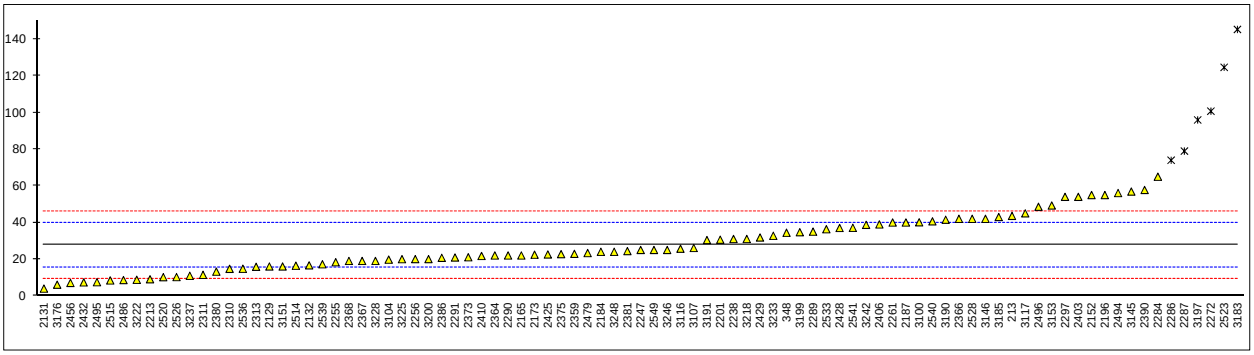
Determination of 2,4-Diaminoanisol (CASno.615-05-4) in sample #13021; results in mg/kg

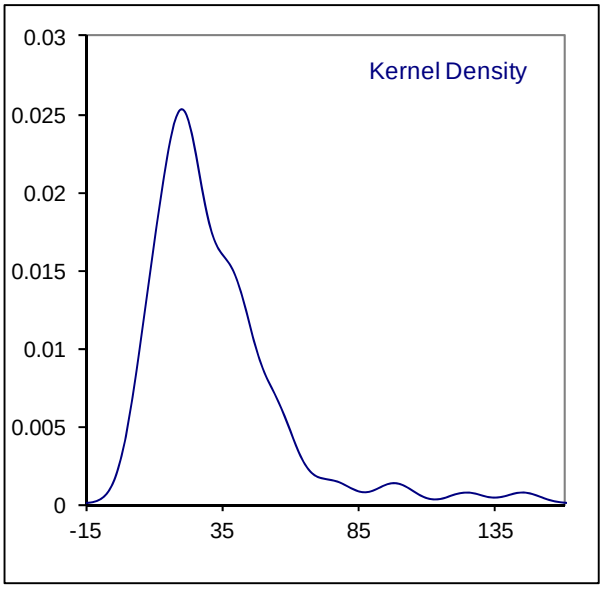
lab	method	value	mark	z(targ)	remarks
110	EN14362	n.d.		-----	False negative?
213	EN14362	43.6		3.53	
348	EN14362	34.39		1.48	
362	EN14362	<5.0		<-5.07	False negative?
551	ISO14362	n.d.		-----	False negative?
1911		-----		-----	
2102		-----		-----	
2115		-----		-----	
2121		-----		-----	
2129	EN14362	16.0		-2.62	
2131	in house	3.90		-5.31	
2132	EN14362	16.6		-2.48	
2135		-----		-----	
2138		-----		-----	
2139	EN14362	<5		<-5.07	False negative?
2146		-----		-----	
2152	EN14362	55		6.07	
2165	EN14362	22		-1.28	
2166	EN14362	n.d.		-----	False negative?
2170		-----		-----	
2172	EN14362	n.d.		-----	False negative?
2173	EN14362	22.4		-1.19	
2184	EN14362	24		-0.84	
2187	EN14362	40		2.73	
2190		-----		-----	
2196	EN14362	55		6.07	
2201	EN14362	30.6		0.63	
2213	EN14362	9		-4.18	
2217	EN14362	n.d.		-----	False negative?
2232		-----		-----	
2235		-----		-----	
2236		-----		-----	
2238	EN14362	31.0		0.72	
2245	EN14362	n.d.		-----	False negative?
2246	EN14362	n.d.		-----	False negative?
2247	EN14362	25.0		-0.61	
2255	EN14362	18.3		-2.11	
2256	EN14362	20.0		-1.73	
2261	GB/T17592	40		2.73	
2272	EN14362	100.8	G(0.05)	16.28	
2283		-----		-----	
2284	EN14362	65.0		8.30	
2286	EN14362	74	DG(0.05)	10.31	
2287	EN14362	79	DG(0.05)	11.42	
2289	EN14362	35		1.61	
2290	EN14362	22.0		-1.28	
2291	EN14362	20.87630		-1.53	
2293	EN14362	n.d.		-----	False negative?
2295		-----		-----	
2296		-----		-----	
2297	EN14362	54		5.85	
2300		-----		-----	
2310	EN14362	14.7		-2.91	
2311	EN14362	11.4		-3.64	
2313	EN14362	15.8		-2.66	
2359	EN14362	22.9		-1.08	
2364	EN14362	22		-1.28	
2366	EN14362	42		3.17	
2367	EN14362	19.0		-1.95	
2368	EN14362	19		-1.95	
2370	EN14362	n.d.		-----	False negative?
2372	ISO17234	n.d.		-----	False negative?
2373	EN14362	21		-1.50	
2375	EN14362	22.72		-1.12	
2379	EN14362	n.d.		-----	False negative?
2380	EN14362	13.17		-3.25	
2381	EN14362	24.38		-0.75	
2386	DIN14362	20.7		-1.57	
2390	EN14362	57.763		6.69	
2403	EN14362	54		5.85	
2406	EN14362	38.96		2.50	
2410	EN14362	21.7		-1.35	

2415		-----		-----	
2425	EN14362	22.54		-1.16	
2426	EN14362	n.d.		-----	False negative?
2428	GB/T17592	37		2.06	
2429	EN14362	31.80		0.90	
2432	in house	7.28		-4.56	
2442		-----		-----	
2452		-----		-----	
2453		-----		-----	
2456	EN14362	7		-4.62	
2459	EN14362	n.d.		-----	False negative?
2469		-----		-----	
2472	EN14362	<5		<-5.07	False negative?
2475	EN14362	n.d.		-----	False negative?
2476		-----		-----	
2479	EN14362	23.3		-0.99	
2481		-----		-----	
2482		-----		-----	
2483	INH-15205	n.d.		-----	False negative?
2486	EN14362	8.57		-4.27	
2489	EN14362	n.d.		-----	False negative?
2492		-----		-----	
2493		-----		-----	
2494	EN14362	56.07	C	6.31	first reported 415.58
2495	EN14362	7.4		-4.53	
2496	EN14362	48.59		4.64	
2497		-----		-----	
2504		-----		-----	
2511	EN14362	<5		<-5.07	False negative?
2514	EN14362	16.4		-2.53	
2515	EN14362	8.36		-4.32	
2516	EN14362	<5		<-5.07	False negative?
2520	EN14362	10.152		-3.92	
2521		-----		-----	
2522		-----		-----	
2523	EN14362	124.751	G(0.01)	21.61	
2524		-----		-----	
2526	EN14362	10.2		-3.91	
2527	EN14362	n.d.		-----	False negative?
2528	EN14362	42		3.17	
2533	EN14362	36.3		1.90	
2534	EN14362	n.d.		-----	False negative?
2536	EN14362	14.74		-2.90	
2538		-----		-----	
2539	GB/T17592	17.19		-2.35	
2540	EN14362	40.65		2.87	
2541	EN14362	37.1		2.08	
2542		-----		-----	
2549	EN14362	25		-0.61	
2553	EN14362	<5		<-5.07	False negative?
3100	EN14362	40.1		2.75	
3104	EN14362	19.72		-1.79	
3107	EN14362	26.07		-0.37	
3109		-----		-----	
3116	EN14362	25.7		-0.46	
3117	EN14362	45		3.84	
3118		-----		-----	
3134		-----		-----	
3145	LFGB 64-82.02.2	56.9		6.49	
3146	EN14362	42		3.17	
3150		-----		-----	
3151	EN14362	16		-2.62	
3153	EN14362	49.3		4.80	
3154		-----		-----	
3160		-----		-----	
3167	EN14362	<3		<-5.52	False negative?
3172		-----		-----	
3176		6.02		-4.84	
3180		-----		-----	
3182		-----		-----	
3183	64 LFGB B82.02.2	145.42	G(0.01)	26.22	
3185	EN14362	43.0		3.40	
3190	EN14362	41.5		3.06	
3191	EN14362	30.4		0.59	
3192	64 LFGB B82.02.2	<30		-----	
3197	EN14362	96	G(0.01)	15.21	
3199	CPSD AN 00607	34.7		1.55	

3200	EN14362	20	-1.73	
3214	EN14362	n.d.	-----	False negative?
3216		-----	-----	
3218	EN14362	31	0.72	
3220		-----	-----	
3222	EN14362	8.7	-4.25	
3225	EN14362	19.96	-1.74	
3228	EN14362	19	-1.95	
3233	EN14362	32.74	1.11	
3237		10.9027	-3.75	
3242	EN14362	38.71	2.44	
3243		-----	-----	
3246	EN14362	25	-0.61	
3248	EN14362	24.0	-0.84	
8008		-----	-----	

normality	not OK
n	85
outliers	6
mean (n)	27.752
st.dev. (n)	14.605
R(calc.)	40.895
R(EN14362-1:2012)	12.566





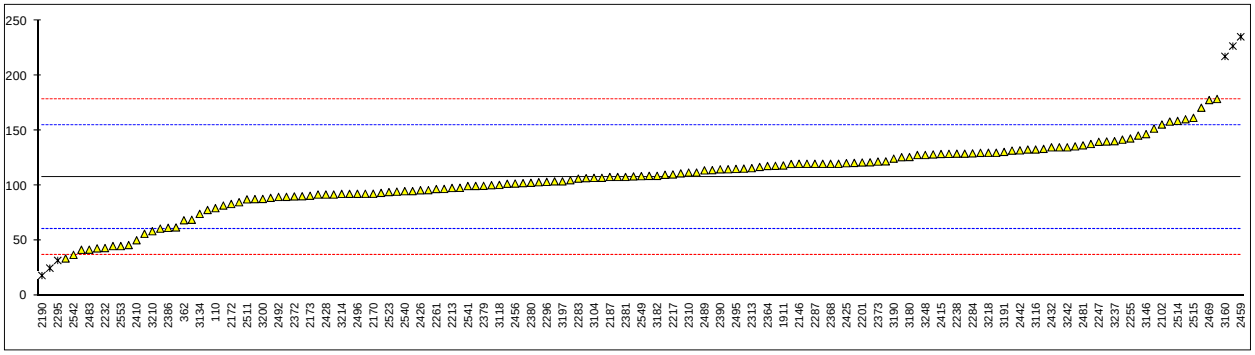
Determination of *o*-Toluidine (CASno.95-53-4) in sample #13021; results in mg/kg

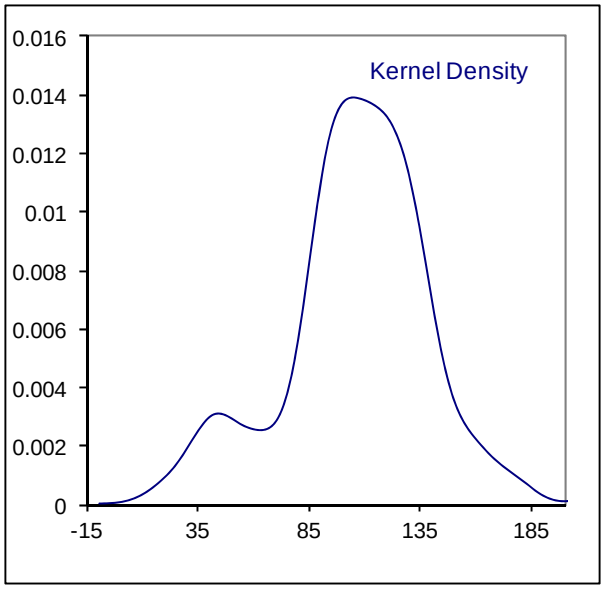
lab	method	value	mark	z(targ)	
110	EN14362	79.6		-1.19	
213	EN14362	111.3		0.15	
348	EN14362	121.35		0.57	
362	EN14362	68.6	C	-1.66	first reported 22.7
551	ISO14362	114.22		0.27	
1911	EN14362	118.468		0.45	
2102	in house	155.74		2.03	
2115		87.86		-0.84	
2121	EN14362	25	G(0.05)	-3.50	
2129	EN14362	227.15	G(0.05)	5.05	
2131	in house	99.82		-0.34	
2132	EN14362	128.0	C	0.86	first reported 212.0
2135	LFGB 64-82.02.2	120.0		0.52	
2138	EN14362	102.4		-0.23	
2139	EN14362	117.1		0.39	
2146	EN14362	120.0		0.52	
2152	EN14362	92		-0.67	
2165	EN14362	135		1.15	
2166	EN14362	43		-2.74	
2170	EN14362	92.71		-0.64	
2172	EN14362	83.4		-1.03	
2173	EN14362	90.9		-0.71	
2184	EN14362	129		0.90	
2187	EN14362	108		0.01	
2190	EN14362	18.3	G(0.05)	-3.78	
2196	EN14362	85		-0.96	
2201	EN14362	121.2	C	0.57	first reported 30.6
2213	EN14362	98		-0.41	
2217	EN14362	110.3		0.11	
2232	EN14362	43.3		-2.73	
2235	EN14362	62.06		-1.93	
2236		-----		-----	
2238	EN14362	129.2		0.91	
2245	EN14362	179		3.01	
2246	EN14362	90.451		-0.73	
2247	EN14362	140.0		1.36	
2255	EN14362	143.04		1.49	
2256	EN14362	109		0.05	
2261	GB/T17592	97		-0.46	
2272	EN14362	158.4		2.14	
2283	EN14362	106.5		-0.05	
2284	EN14362	129.5		0.92	
2286	EN14362	133		1.07	
2287	EN14362	120		0.52	
2289	EN14362	115		0.31	
2290	EN14362	140.3		1.38	
2291	EN14362	133.56665		1.09	
2293	EN14362	n.d.		-----	false negative?
2295	EN14362	32	C, G(0.05)	-3.21	first reported 30
2296	ISO14362	103.5		-0.18	
2297	EN14362	120		0.52	
2300	EN14362	129.97		0.94	
2310	EN14362	112		0.18	
2311	EN14362	108		0.01	
2313	EN14362	116		0.35	
2359	EN14362	126		0.77	
2364	EN14362	118		0.43	
2366	EN14362	105		-0.12	
2367	EN14362	119.8		0.51	
2368	EN14362	120		0.52	
2370	EN14362	112		0.18	
2372	ISO17234	90.3		-0.74	
2373	EN14362	122		0.60	
2375	EN14362	118.11		0.44	
2379	EN14362	99.94		-0.33	
2380	EN14362	102.67		-0.22	
2381	EN14362	108.0		0.01	
2386	DIN14362	61.7		-1.95	
2390	EN14362	114.961		0.30	
2403	EN14362	132		1.02	
2406	EN14362	171.01		2.67	
2410	EN14362	50.4		-2.43	

2415	EN14362	128.93		0.89	
2425	EN14362	120.55		0.54	
2426	EN14362	95.89		-0.50	
2428	GB/T17592	92		-0.67	
2429	EN14362	115.58		0.33	
2432	in house	135		1.15	
2442	in house	132.19		1.03	
2452	EN14362	77.948		-1.26	
2453		-----		-----	
2456	EN14362	102		-0.24	
2459	EN14362	235.550	C, G(0.05)	5.40	first reported 311.750
2469	EN14362	178		2.97	
2472	EN14362	92		-0.67	
2475	EN14362	106.93		-0.04	
2476		-----		-----	
2479	EN14362	92.7		-0.64	
2481	in house	136.8		1.23	
2482	EN14362	45.07		-2.65	
2483	INH-15205	41.83		-2.79	
2486	EN14362	145.7		1.60	
2489	EN14362	114.0		0.26	
2492	in house	89.8		-0.76	
2493		-----		-----	
2494	EN14362	n.d.		-----	false negative?
2495	EN14362	115.3		0.32	
2496	EN14362	92.68		-0.64	
2497	EN14362	93.5		-0.60	
2504		-----		-----	
2511	EN14362	87.6		-0.85	
2514	EN14362	159.0		2.17	
2515	EN14362	161.8		2.29	
2516	EN14362	110		0.09	
2520	EN14362	103.2		-0.19	
2521		-----		-----	
2522	EN14362	94.6		-0.56	
2523	EN14362	94.238		-0.57	
2524		-----		-----	
2526	EN14362	100.5		-0.31	
2527	EN14362	104		-0.16	
2528	EN14362	152		1.87	
2533	EN14362	95.1		-0.54	
2534	EN14362	33.799		-3.13	
2536	EN14362	135.82		1.19	
2538	in house	120.8		0.55	
2539	GB/T17592	69.06		-1.64	
2540	EN14362	95.09		-0.54	
2541	EN14362	99.7		-0.34	
2542	EN14362	37.1		-2.99	
2549	EN14362	108.78		0.04	
2553	EN14362	45.076		-2.65	
3100	EN14362	129.2		0.91	
3104	EN14362	107.17		-0.03	
3107	EN14362	92.62		-0.64	
3109	LFGB 64-82.02.2	<10		<-4.16	false negative?
3116	EN14362	133		1.07	
3117	EN14362	89		-0.79	
3118	EN14362	100.76		-0.30	
3134	EN14362	74.4		-1.41	
3145	LFGB 64-82.02.2	98.1		-0.41	
3146	EN14362	147		1.66	
3150	EN14362	97.1		-0.45	
3151	EN14362	142		1.45	
3153	EN14362	120		0.52	
3154		-----		-----	
3160	EN14362	217.69	G(0.05)	4.65	
3167	EN14362	96		-0.50	
3172	EN14362	82		-1.09	
3176		46.0		-2.61	
3180	EN14362	126.16		0.78	
3182	EN14362	109.0		0.05	
3183	64 LFGB B82.02.2	56.29		-2.18	
3185	EN14362	122.2		0.61	
3190	EN14362	124.7		0.72	
3191	EN14362	130.8		0.97	
3192	64 LFGB B82.02.2	89.9		-0.76	
3197	EN14362	104		-0.16	
3199	CPSD AN 00607	128.5		0.88	

3200	EN14362	88		-0.84	
3214	EN14362	92.57	C	-0.64	first reported 292.01
3216	EN14362	41.73		-2.79	
3218	EN14362	130		0.94	
3220	EN14362	101.8		-0.25	
3222	EN14362	107.2		-0.02	
3225	EN14362	108.5		0.03	
3228	EN14362	130		0.94	
3233	EN14362	160.54		2.23	
3237		140.5555		1.39	
3242	EN14362	135.0		1.15	
3243	EN14362	61.0		-1.98	
3246	EN14362	138		1.28	
3248	EN14362	128.0		0.86	
8008		-----		-----	

normality	not OK
n	147
outliers	6
mean (n)	107.77
st.dev. (n)	29.110
R(calc.)	81.509
R(EN14362-1:2012)	65.850





APPENDIX 2

Summary of other reported aromatic amines in sample #13020

lab	method
2152	42 mg/kg 3,3'-Dimethylbenzidine
2429	52.41 mg/kg 3,3'-Dimethylbenzidine
2521	2.93 mg/kg *o*-aminoazotoluene; 0.83 mg/kg Diaminodiphenylmethane; 0.92 mg/kg 4,4-Diaminodiphenylether; 0.39 mg/kg 4,4-Diaminodiphenylsulfide; 2.5 mg/kg 2,4-Diaminotoluene; 3.25 mg/kg 4-Amino-azobenzene

Summary of other reported aromatic amines in sample #13021

lab	method
2102	17.99 mg/kg Benzidine, 20.48 mg/kg 3,3-Dimethoxybenzidine
2287	17 mg/kg 2-Naphtylamine
2293	3.203 mg/kg 4-Chloro-*o*-toluidine; 8.579 mg/kg Naphtylamine;0.747 mg/kg 2,4-Diaminotoluene; 1.849 mg/kg *o*-Aniside; 1.111 mg/kg 2,6-Xylidine
2295	9.1 mg/kg 4-Aminodiphenyl
2372	14.3 mg/kg *o*-Aminoazotoluene
2390	49.825 mg/kg *o*-Aminoazotoluene
2403	66 mg/kg *o*-Aminoazotoluene
2452	77.948 mg/kg 3,3-Dimethoxybenzidine
2456	15.3 mg/kg 2-Naphtylamine; 28 mg/kg *o*-Aminoazotoluene
2494	9.64 mg/kg 2-Nahtylamine; 49.66 mg/kg *o*-Aminoazotoluene
2495	2.6 mg/kg 2-Napthtylamine
2515	6.53 mg/kg Napthylamine
2521	31.85 mg/kg *o*-aminoazotoluene; 1.2 mg/kg Diaminodiphenylmethane; 0.9 mg/kg 3,3-Dimethyl-4,4diphenylmethane 1.33 mg/kg 4,4-Diaminodiphenylether; 0.61 mg/kg 4,4-Diaminodiphenylsulfide; 7.0 mg/kg 2,4-Diaminotoluene; 5.0 mg/kg 4-Amino-azobenzene
2523	1.463 mg/kg 2-Napthylamine; 0.220 mg/kg *o*-Aminoazotoluene
2293	4.760 mg/kg 4-chloro-*o*-toluidine; 7.344 mg/kg 2-Naptylamine 50.709 mg/kg 2,4-Diaminotoluene; 2.651 mg/kg *o*-Anisidine; 1.873 mg/kg mg/kg 2,6-Xylidine
3107	2.07 mg/kg 2-Napthylamine; 7.41 mg/kg *o*-Aminoazotoluene
3134	4.5 mg/kg 2-Napthylamine; 39.7 mg/kg *o*-Aminoazotoluene; 3.7 mg/kg 3,3-Dimethylbenzidine
3176	5.98 mg/kg 2-Napthylamine; 8.41 mg/kg *o*-Aminoazotoluene
3222	6.1 mg/kg 4-Chloro-*o*-toluidine; 13.2 mg/kg 2-Napthylamine; 31.5 mg/kg *o*-Aminoazotoluene
3237	7.7777 mg/kg *o*-Aminoazotoluene;

APPENDIX 3

Number of participants per country

8 labs in	BANGLADESH
1 lab in	BRAZIL
1 lab in	BULGARIA
2 labs in	EGYPT
1 lab in	FINLAND
6 labs in	FRANCE
14 labs in	GERMANY
1 lab in	GREECE
1 lab in	GUATAMALA
14 labs in	HONG KONG
2 labs in	HUNGARY
11 labs in	INDIA
2 labs in	INDONESIA
9 labs in	ITALY
4 labs in	JAPAN
5 labs in	KOREA
1 lab in	MOROCCO
41 labs in	P.R. of CHINA
3 labs in	PAKISTAN
1 lab in	POLAND
1 lab in	PORTUGAL
2 labs in	SINGAPORE
4 labs in	SPAIN
1 lab in	SRI LANKA
3 labs in	SWITZERLAND
5 labs in	TAIWAN
3 labs in	THAILAND
1 lab in	THE NETHERLANDS
2 labs in	TUNISIA
6 labs in	TURKEY
3 labs in	U.S.A.
2 labs in	UNITED KINGDOM
4 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
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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)