Results of Proficiency Test
Perspirated Metals in textile
October 2012

Organised by: Institute for Interlaboratory Studies
Spijkenisse, the Netherlands

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1 INTRODUCTION

Since the 1990's, many countries have adopted environmental standards and requirements restricting the use of harmful chemicals in the production of textiles and clothing. Laws and regulations impose some of these standards and requirements. In addition to mandatory environmental standards and requirements for textiles, there are some Ecolabelling schemes imposing environmental requirements for textile products on a voluntary basis. Well known programs are for instance Milieukeur (the Netherlands), Oeko-Tex Standard 100/200 (Germany) and Thai Green Label (Thailand).
Since 2002 the Institute for Interlaboratory Studies (iis) organizes a proficiency scheme for perspirated metals in textile. Also this year this scheme is part of the proficiency testing program 2012/2013.
In this interlaboratory study 79 laboratories in 25 different countries participated. See appendix 3 for the number of participants per country. 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 organiser of this proficiency test. Sample preparation and analyses were subcontracted.
It was decided to use 2 different textile samples in this round and to request to use a solid/liquid ratio of 1/50 by preference (see paragraph 6 and the report iis07A05).
Participants were requested to report results with one extra figure. These unrounded results were preferably used for the statistical evaluations.

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 ISO17043:2010.
This ensures strict adherence to protocols for sample preparation and statistical evaluation and 100% confidentiality of participant's data. Feedback from the participants on the reported data is encouraged and customer's satisfaction is measured on regular basis by sending out questionnaires.

2.2 PROTOCOL

The protocol followed in the organisation of this proficiency test was the one as described for proficiency testing in the report iis Interlaboratory Studies: Protocol for the Organisation, 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 materials used in this proficiency test were prepared by a subcontractor. The two different coloured finely cut textile samples, sample #12120 and sample #12121 were each well mixed and divided over 100 subsamples of approx. 3.5 grams. The samples were labelled and tested for homogeneity on 15 randomly selected samples. The homogeneity testing was performed by a subcontracted ISO17025 accredited laboratory. See the following tables for the homogeneity test results.

	Perspirated Cadmium in mg/kg	*Perspirated Cobalt in mg/kg*
Sample #12120-1	1.98	2.35
Sample #12120-2	1.99	2.28
Sample #12120-3	2.18	2.23
Sample #12120-4	2.12	2.16
Sample #12120-5	2.09	2.28
Sample #12120-6	2.17	2.31
Sample #12120-7	2.15	2.32
Sample #12120-8	2.13	2.28
Sample #12120-9	1.96	2.21
Sample #12120-10	1.94	2.21
Sample #12120-11	1.95	2.05
Sample #12120-12	1.98	2.32
Sample #12120-13	1.98	2.34
Sample #12120-14	2.12	2.33
Sample #12120-15	2.05	2.25

Table 1: homogeneity test results of subsamples #12120

	Perspirated Cadmium in mg/kg	*Perspirated Mercury in mg/kg*
Sample #12121-1	10.12	0.332
Sample #12121-2	9.98	0.337
Sample #12121-3	10.11	0.323
Sample #12121-4	10.10	0.333
Sample #12121-5	10.04	0.334
Sample #12121-6	10.04	0.325
Sample #12121-7	10.04	0.337
Sample #12121-8	9.86	0.331
Sample #12121-9	10.12	0.328
Sample #12121-10	10.01	0.339
Sample #12121-11	10.01	0.328
Sample #12121-12	9.87	0.326
Sample #12121-13	10.01	0.337
Sample #12121-14	9.87	0.325
Sample #12121-15	9.80	0.336

Table 2: homogeneity test results of subsamples #12121

From the above results of the homogeneity tests, the repeatabilities were calculated and compared with 0.3 times the corresponding reproducibility of the reference method in agreement with the procedure of ISO 13528, Annex B2 in the next table:

	Perspirated Cadmium in mg/kg	*Perspirated Cobalt in mg/kg*
r (observed)	0.25	0.22
reference method	Horwitz	Horwitz
0.3 x R (reference method)	0.25	0.27

Table 3: repeatabilities of subsamples #12120

	Perspirated Cadmium in mg/kg	*Perspirated Mercury in mg/kg*
r (observed)	0.29	0.015
reference method	Horwitz	Horwitz
0.3 x R (reference method)	0.95	0.053

Table 4: repeatabilities of subsamples #12121

The calculated repeatabilities are both in good agreement with 0.3 times the estimated target reproducibilities, calculated using the Horwitz equation. Therefore, homogeneity of all subsamples was assumed.

In total 2 samples, one of each sample #12120 and #12121 were sent to the participating laboratories on October 10, 2012.

2.5 ANALYSES

The participants were asked to determine the concentrations of perspirated heavy metals: Arsenic, Antimony, Cadmium, Chromium, Cobalt, Copper, Lead, Mercury and Nickel, applying the analysis procedure that is routinely used in the laboratory, but to use preferably a solid/liquid ration of 1/50 g/ml as prescribed in E-DIN54233-3:2010. To get comparable results, detailed report forms were sent together with each set of samples. On the report forms the requested heavy metals, including the units and questions about the analytical details, were pre-printed. Also a letter of instructions was sent along.

3 RESULTS

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

Directly after the deadline, a reminder fax was sent to those laboratories that had not yet reported. Shortly after the deadline the available results were screened for suspect data. A result was called suspect in case the Huber Elimination Rule (a robust outlier test, see lit.5) found it to be an outlier. The laboratories that produced these suspect data were asked to check the results. Additional or corrected data are placed under 'Remarks' in the result tables in appendix 1. A list of abbreviations used in the tables can be found in appendix 3.

3.1 STATISTICS

Statistical calculations were performed as described in the report 'iis Interlaboratory Studies: Protocol for the Organisation, 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.8 and 9) 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 method is producing a smooth density approximation to a set of data that avoids some problems associated with histograms (see appendix 3; nos.14 and 15).

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, no problems occurred with sample dispatch and with the reporting of the test results. However, seven laboratories decided not to report any test results due to various reasons. Ten other laboratories reported test results after the final reporting date.
Finally, the 73 reporting laboratories did report in total 266 numerical results.
All participating laboratories, except three, did use a solid/liquid ratio of 1/50 as requested. The deviating laboratories used as solid/liquid ratios 1/20, 1/25 and 1/100 g/ml. Observed were 9 statistical outlying results, which is 3.4% of the numerical results. In proficiency studies, outlier percentages of 3% - 7.5% are quite normal.

All original data sets, except for Cadmium (#12120) proved to have a non-Gaussian distribution. Therefore, the statistical evaluation for these determinations should be used with care.

The majority of the participating laboratories used ISO105-E04, a method that regretfully does not mention any reproducibility. In 2010 the draft method DIN 54233-3 was issued. This method does mention the reproducibility for one concentration per metal (varying from 13-40%) only. As the actual reproducibility will be concentration dependent and as the concentrations in this PT are significantly different from the ones mentioned in DIN54233-3, the reproducibilities, estimated by the Horwitz equation, were used in this PT for evaluation.

4.1 EVALUATION PER METAL

In this section, the determinations per perspirated metal are discussed. All statistical results reported on the samples are summarised in appendix 1.

Cadmium: The determination of this metal was problematic for sample #12121 at a perspiration level of 11 mg/kg, but no analytical problems were observed for sample #12120 with a perspiration level of 2 mg/kg.
Only three statistical outliers were observed. The observed reproducibility after rejection of the statistical outliers is in agreement with the estimated target reproducibility calculated using the Horwitz equation for sample #12120, but not in agreement for sample #12121.

Cobalt: The determination of this metal was not problematic at a perspiration level of 2.4 mg/kg. Only two statistical outliers were observed and the calculated reproducibility after rejection of the statistical outliers is in full agreement with the estimated target reproducibility calculated using the Horwitz equation.

Mercury: The determination of this metal was very problematic at a perspiration level of 0.08 mg/kg. Four statistical outliers were observed and the calculated reproducibility after rejection of the statistical outliers is not at all in agreement with the estimated target reproducibility calculated using the Horwitz equation.

4.2 PERFORMANCE EVALUATION FOR THE GROUP OF LABORATORIES

A comparison has been made between the strict calculated reproducibilities using the Horwitz equation 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 (Horwitz equation), are compared in the next two tables.

Parameter	*Unit*	*n*	*average*	*2.8 * sd*	*R (target)*
Perspirated Cadmium	mg/kg	71	2.03	0.78	0.82
Perspirated Cobalt	mg/kg	70	2.42	0.77	0.95

Table 5: reproducibilities of perspirated metals in sample #12120

Parameter	*unit*	*n*	*average*	*2.8 * sd*	*R (target)*
Perspirated Cadmium	mg/kg	72	10.75	4.11	3.37
Perspirated Mercury	mg/kg	43	0.084	0.097	0.055

Table 6: reproducibilities of perspirated metals in sample #12121

From the above tables it can be concluded that, without statistical calculations, the group of participating laboratories have no difficulties with the analysis when compared with the strict target results calculated with the Horwitz equation. See also the discussions in paragraphs 4.1 and 6.

5 COMPARISON WITH THE PREVIOUS PROFICIENCY TESTS

The spreads that were found in the results during the present round are in agreement with the spreads as observed in previous rounds (see below table).

Parameter	*October 2012*	*October 2011*	*October 2010*	*October 2009*	*November 2008*	*November 2007*	*November 2006*
Arsenic	--	--	--	--	--	66%	--
Antimony	--	52%	--	41%	46%	--	--
Cadmium	38%	--	40%	--	--	--	85%
Chromium	--	53%	--	--	--	114%	47%
Cobalt	32%	23%	31%	--	28%	--	--
Copper	--	61%	--	48-46%	26%	64-80%	93-39
Lead	--	--	--	--	--	375%	138-172%
Mercury	116%	--	--	--	--	--	134%
Nickel	--	29-38%	19%	--	23%	41%	--

Table 7: Comparison of observed relative reproducibilities (since 2008 s/l ratio prescribed on 1:50)

The improvement of the results in the last five rounds is most probably caused by the use of a more uniform solid/liquid ratio then in rounds before 2008 (>90% of all participating laboratories reported results after use of a liquor ratio of 1:50 since 2008).

6 DISCUSSION

When the results of this interlaboratory study were compared to the Ecolabelling Standards and Requirements for Textiles in EU (table 9), it could be noticed that some participants would make different decisions about the acceptability of the textiles for the determined parameters, to the majority of the group. The detection limit reported by many laboratories does not meet the requirements of the Standards (reported detection limit is often larger than the maximum required concentration by the Ecolabelling standard).

Ecolabel	EU-adult clothes	EU-baby clothes	Öko-Tex 100 Class 1: baby clothes	Öko-Tex 100 Class 2: direct skin contact	Öko-Tex 100 Class 3 : non skin contact
Arsenic (As) mg/kg	1)	1)	0.2	1.0	1.0
Antimony (Sb) mg/kg	1)	1)	30.0	30.0	30.0
Cadmium (Cd) mg/kg	1)	1)	0.1	0.1	0.1
Chromium (Cr) mg/kg	1)	1)	1.0	2.0	2.0
Cobalt (Co) mg/kg	1)	1)	1.0	4.0	4.0
Copper (Cu) mg/kg	1)	1)	25.0	50.0	50.0
Lead (Pb) mg/kg	1)	1)	0.2	1.0	1.0
Mercury (Hg) mg/kg	1)	1)	0.02	0.02	0.02
Nickel (Ni) mg/kg	1)	1)	0.5	1.0	1.0

Table 8: Ecolabelling Standards and Requirements for Textiles in EU

1) No use of metals in dyes and pigments

Methods for determination of these Heavy Metals are specified in the Standards of the Ecolabelling Institutes. Unfortunately, only test methods for the release of heavy metals via perspiration is mentioned. The method for detection of the metals is specified as “Detection via A.A.S or ICP”.
It should be noticed that for the results reported in this proficiency test, all participants have performed the acid perspiration step according to almost the same conditions. Differences in sample intake and perspiration time and temperature may be parameters of importance. However, the liquor ratio (ml of perspiration liquid / gram of textile) appeared to be a parameter of utmost importance and without mentioning this ratio (or the respective test method), the test results may have little value (see previous reports iis07A05 and iis08A05 on “Perspirated Metals in Textile”). Therefore in this proficiency test the participating laboratories were advised to use preferably a ratio of 1:50 as in the latest available draft test method E DIN 54233-3:2010.

General

The spreads observed in this interlaboratory study are not caused by just one critical point in the analysis. Consequently, the reproducibilities cannot be improved by only one change in the analysis. Each laboratory has to evaluate its performance in this study and make decisions about necessary corrective actions. Therefore, participation on a regular basis in this scheme could be helpful to improve the performance and thus increase of the quality of the analytical results.

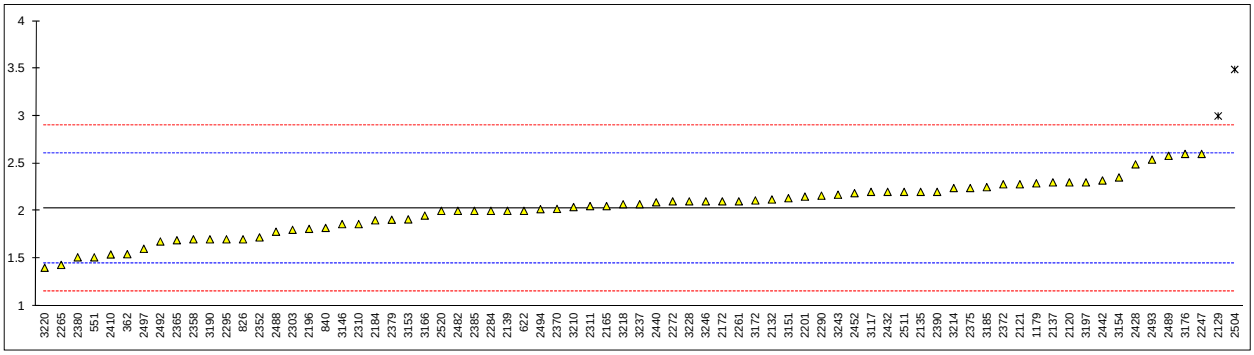
APPENDIX 1

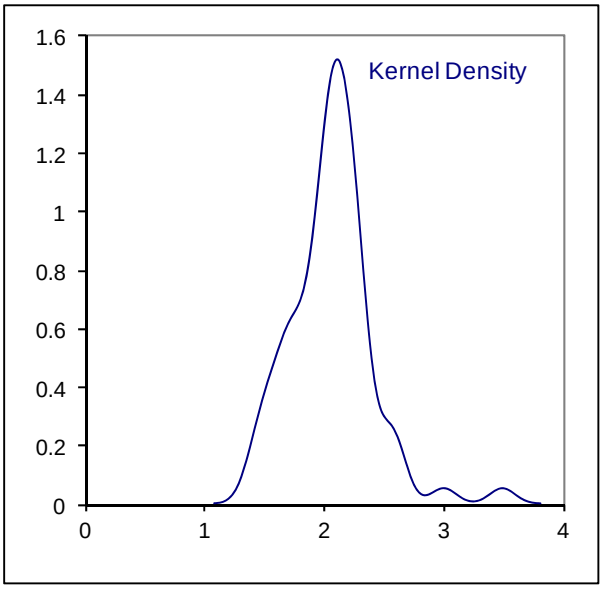
Determination of perspirated Cadmium (s/l ratio = 1/50) on sample #12120; results in mg/kg

lab	method	value	mark	z(targ)	remarks
348		-----		-----	
362	INH-103	1.543	C	-1.66	Used s/l ratio 1/25
551	ISO11885	1.51		-1.77	
622	DIN54020	2.0		-0.09	
826	ISO104-E04	1.7	C	-1.12	Used s/l ratio 1/20
840	ISO150-E04	1.82		-0.71	
1179	DIN54233-3	2.29		0.90	
2120	in house	2.3	C	0.94	Used s/l ratio 1/100
2121		2.28		0.87	
2129	ISO105-E04/ISO17294-2	3.0	G(0.05)	3.34	
2132	in house	2.12		0.32	
2135	in house	2.2		0.59	
2137	ISO105-E04	2.3		0.94	
2139	OEKO-Tex Std.100/200	2.0		-0.09	
2165	ISO105-E04	2.05		0.08	
2172	in house	2.10		0.25	
2184	ISO105-E04	1.9		-0.44	
2196	DIN54233	1.81		-0.74	
2201	DIN54233-3	2.15		0.42	
2247	ISO105-E04	2.6	C	1.97	First reported 3.0
2256		-----		-----	
2261	G/T17593.2	2.1		0.25	
2265	DIN54233-3	1.43		-2.05	
2272	ISO17072-1	2.1		0.25	
2284	DIN54233-3	2.0		-0.09	
2290	ISO105-E04	2.16		0.46	
2293		-----		-----	
2295	DIN54233	1.7	C	-1.12	First reported 0.5
2303	in house	1.80		-0.78	
2310	ISO105-E04	1.86		-0.57	
2311	ISO105-E04	2.05		0.08	
2352	ISO105-E04	1.72		-1.05	
2358	ISO105-E04	1.7		-1.12	
2365	ISO105-E04	1.69		-1.16	
2370	ISO105-E04	2.02		-0.02	
2372	ISO105-E04	2.28		0.87	
2375	OEKO-Tex Std.100/200/ISO105	2.24		0.73	
2379	ISO105-E04	1.906		-0.41	
2380	ISO105-E04	1.51		-1.77	
2385	in house	2.00		-0.09	
2390	ISO105-E04	2.2		0.59	
2410	DIN54233	1.54		-1.67	
2428	G/T17593	2.49		1.59	
2432	in house	2.2		0.59	
2440	BG/T17593.2	2.09		0.22	
2442	in house	2.32		1.00	
2447		-----		-----	
2452	DIN54233-3	2.1865		0.55	
2453		-----		-----	
2482	DIN54233-3	2.0		-0.09	
2488	ISO105-E04	1.78		-0.85	
2489	ISO105-E04	2.58	C	1.90	First reported 3.12
2492	OEKO-Tex Std.200	1.677		-1.20	
2493	DIN54233	2.54		1.76	
2494	ISO105-E04	2.0176		-0.03	
2497	INH-030	1.6		-1.46	
2504	DIN54233	3.49	G(0.01)	5.02	
2511	DIN54233-3	2.2		0.59	
2520	ISO105-E04	2		-0.09	
3117	G/T17593.2	2.20		0.59	
3146	DIN54233/ISO11885/ISO1483	1.86		-0.57	
3151	DIN54233-3	2.133		0.36	
3153	ISO105-E04	1.91		-0.40	
3154	ISO17072	2.352		1.11	
3166	in house	1.95		-0.26	
3172	DIN54233	2.11		0.28	
3176	DIN54233-3	2.6		1.97	
3185	DIN54233	2.25		0.76	
3190	OEKO-Tex Std.100/200	1.70		-1.12	
3197	ISO105-E04	2.3		0.94	
3210	ISO17072-1	2.04		0.04	
3214	DIN54233-3	2.24		0.73	
3218	DIN54233	2.07		0.15	
3220	DIN54233/54020	1.4	C	-2.15	First reported 3.0
3228	in house	2.1		0.25	
3232		-----		-----	

3237	in house	2.070	0.15
3243	DIN54233	2.17	0.49
3246	DIN54233-3	2.1	0.25

normality	not OK
n	71
outliers	2
mean (n)	2.027
st.dev. (n)	0.2801
R(calc.)	0.784
R(Horwitz)	0.816



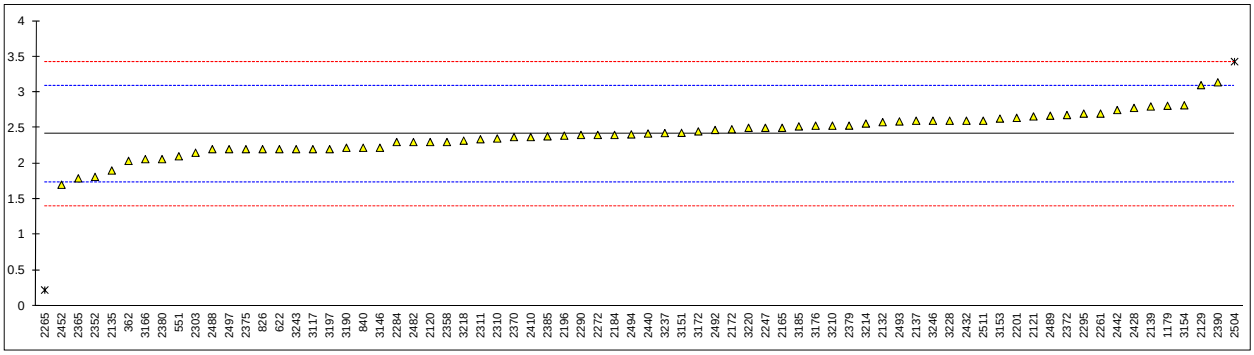


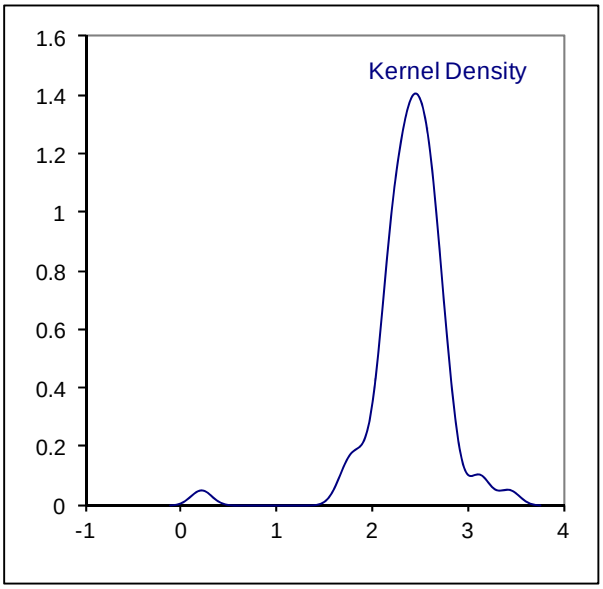
Determination of perspirated Cobalt (s/l ratio = 1/50) on sample #12120; results in mg/kg

lab	method	value	mark	z(targ)	remarks
348		-----		-----	
362	INH-103	2.035	C	-1.12	Used s/l ratio 1/25
551	ISO11885	2.10		-0.93	
622	DIN54020	2.2		-0.64	
826	ISO104-E04	2.2	C	-0.64	Used s/l ratio 1/20
840	ISO150-E04	2.22		-0.58	
1179	DIN54233-3	2.81		1.17	
2120	in house	2.3	C	-0.34	Used s/l ratio 1/100
2121		2.66		0.72	
2129	ISO105-E04/ISO17294-2	3.1		2.02	
2132	in house	2.58		0.49	
2135	in house	1.9		-1.52	
2137	ISO105-E04	2.6		0.55	
2139	OEKO-Tex Std.100/200	2.8		1.14	
2165	ISO105-E04	2.5		0.25	
2172	in house	2.48		0.19	
2184	ISO105-E04	2.4		-0.05	
2196	DIN54233	2.39		-0.08	
2201	DIN54233-3	2.64		0.66	
2247	ISO105-E04	2.5		0.25	
2256		-----		-----	
2261	G/T17593.2	2.7		0.84	
2265	DIN54233-3	0.22	G(0.01)	-6.49	
2272	ISO17072-1	2.4		-0.05	
2284	DIN54233-3	2.3		-0.34	
2290	ISO105-E04	2.40		-0.05	
2293		-----		-----	
2295	DIN54233	2.7	C	0.84	First reported nd
2303	in house	2.15		-0.78	
2310	ISO105-E04	2.35		-0.19	
2311	ISO105-E04	2.34		-0.22	
2352	ISO105-E04	1.81		-1.79	
2358	ISO105-E04	2.3		-0.34	
2365	ISO105-E04	1.79		-1.85	
2370	ISO105-E04	2.37		-0.13	
2372	ISO105-E04	2.68		0.78	
2375	OEKO-Tex Std.100/200/ISO105	2.20		-0.64	
2379	ISO105-E04	2.531		0.34	
2380	ISO105-E04	2.06		-1.05	
2385	in house	2.38		-0.10	
2390	ISO105-E04	3.14		2.14	
2410	DIN54233	2.37		-0.13	
2428	G/T17593	2.78		1.08	
2432	in house	2.6		0.55	
2440	BG/T17593.2	2.42		0.01	
2442	in house	2.75		0.99	
2447		-----		-----	
2452	DIN54233-3	1.7		-2.11	
2453		-----		-----	
2482	DIN54233-3	2.3		-0.34	
2488	ISO105-E04	2.2		-0.64	
2489	ISO105-E04	2.67		0.75	
2492	OEKO-Tex Std.200	2.47		0.16	
2493	DIN54233	2.59		0.52	
2494	ISO105-E04	2.4078		-0.02	
2497	INH-030	2.2		-0.64	
2504	DIN54233	3.43	G(0.05)	3.00	
2511	DIN54233-3	2.6		0.55	
2520	ISO105-E04	<0.1		<-6.84	False negative?
3117	G/T17593.2	2.20		-0.64	
3146	DIN54233/ISO11885/ISO1483	2.22		-0.58	
3151	DIN54233-3	2.43		0.04	
3153	ISO105-E04	2.63		0.63	
3154	ISO17072	2.817		1.19	
3166	in house	2.06		-1.05	
3172	DIN54233	2.45		0.10	
3176	DIN54233-3	2.53		0.34	
3185	DIN54233	2.52		0.31	
3190	OEKO-Tex Std.100/200	2.22		-0.58	
3197	ISO105-E04	2.2		-0.64	
3210	ISO17072-1	2.53		0.34	
3214	DIN54233-3	2.56		0.43	
3218	DIN54233	2.32		-0.28	
3220	DIN54233/54020	2.5		0.25	
3228	in house	2.6		0.55	
3232		-----		-----	

3237	in house	2.426	0.03
3243	DIN54233	2.20	-0.64
3246	DIN54233-3	2.6	0.55

normality	OK
n	70
outliers	2
mean (n)	2.416
st.dev. (n)	0.2733
R(calc.)	0.765
R(Horwitz)	0.948



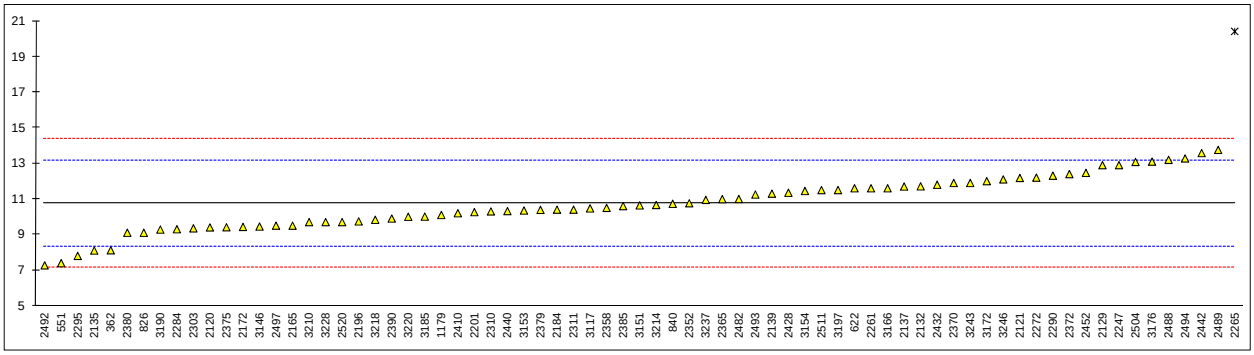


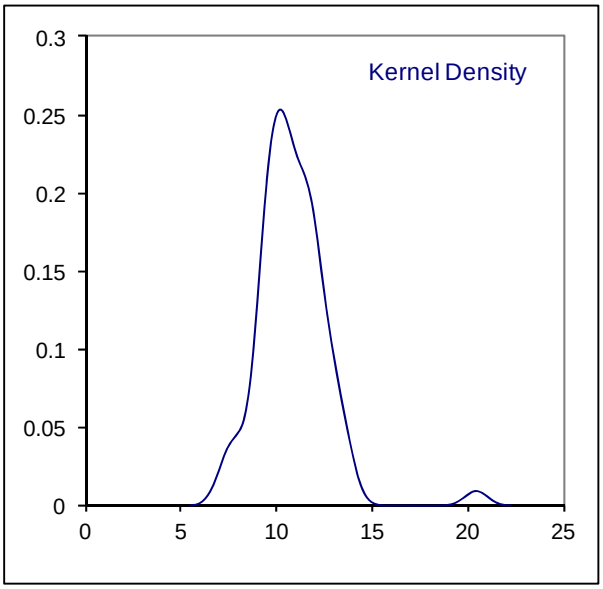
Determination of perspirated Cadmium (s/l ratio = 1/50) on sample #12121; results in mg/kg

lab	method	value	mark	z(targ)	remarks
348		-----		-----	
362	INH-103	8.116	C	-2.19	Used s/l ratio 1/25
551	ISO11885	7.39		-2.79	
622	DIN54020	11.6		0.71	
826	ISO104-E04	9.1	C	-1.37	Used s/l ratio 1/20
840	ISO150-E04	10.73		-0.01	
1179	DIN54233-3	10.1		-0.54	
2120	in house	9.4	C	-1.12	Used s/l ratio 1/100
2121		12.18		1.19	
2129	ISO105-E04/ISO17294-2	12.9		1.79	
2132	in house	11.71		0.80	
2135	in house	8.1		-2.20	
2137	ISO105-E04	11.7		0.79	
2139	OEKO-Tex Std.100/200	11.3		0.46	
2165	ISO105-E04	9.5		-1.04	
2172	in house	9.43		-1.09	
2184	ISO105-E04	10.4		-0.29	
2196	DIN54233	9.74		-0.84	
2201	DIN54233-3	10.26		-0.40	
2247	ISO105-E04	12.9		1.79	
2256		-----		-----	
2261	G/T17593.2	11.6	C	0.71	Used s/l ratio 1/200
2265	DIN54233-3	20.42	G(0.01)	8.04	
2272	ISO17072-1	12.2		1.21	
2284	DIN54233-3	9.3		-1.20	
2290	ISO105-E04	12.31		1.30	
2293		-----		-----	
2295	DIN54233	7.8	C	-2.45	First reported 2.7
2303	in house	9.35		-1.16	
2310	ISO105-E04	10.3		-0.37	
2311	ISO105-E04	10.4		-0.29	
2352	ISO105-E04	10.76		0.01	
2358	ISO105-E04	10.5		-0.20	
2365	ISO105-E04	10.99		0.20	
2370	ISO105-E04	11.9		0.96	
2372	ISO105-E04	12.4		1.38	
2375	OEKO-Tex Std.100/200/ISO105	9.41		-1.11	
2379	ISO105-E04	10.386		-0.30	
2380	ISO105-E04	9.10		-1.37	
2385	in house	10.6		-0.12	
2390	ISO105-E04	9.9		-0.70	
2410	DIN54233	10.2		-0.45	
2428	G/T17593	11.35		0.50	
2432	in house	11.8		0.88	
2440	BG/T17593.2	10.32		-0.35	
2442	in house	13.58		2.36	
2447		-----		-----	
2452	DIN54233-3	12.467		1.43	
2453		-----		-----	
2482	DIN54233-3	11		0.21	
2488	ISO105-E04	13.2		2.04	
2489	ISO105-E04	13.76		2.51	
2492	OEKO-Tex Std.200	7.269		-2.89	
2493	DIN54233	11.25		0.42	
2494	ISO105-E04	13.2782		2.11	
2497	INH-030	9.5		-1.04	
2504	DIN54233	13.08		1.94	
2511	DIN54233-3	11.5		0.63	
2520	ISO105-E04	9.7		-0.87	
3117	G/T17593.2	10.47		-0.23	
3146	DIN54233/ISO11885/ISO1483	9.45		-1.08	
3151	DIN54233-3	10.64		-0.09	
3153	ISO105-E04	10.35		-0.33	
3154	ISO17072	11.45		0.59	
3166	in house	11.6		0.71	
3172	DIN54233	12.0		1.04	
3176	DIN54233-3	13.1	C	1.96	First reported 17.2
3185	DIN54233	10.01		-0.61	
3190	OEKO-Tex Std.100/200	9.28		-1.22	
3197	ISO105-E04	11.5		0.63	
3210	ISO17072-1	9.7		-0.87	
3214	DIN54233-3	10.66		-0.07	
3218	DIN54233	9.83		-0.76	
3220	DIN54233/54020	10.0		-0.62	
3228	in house	9.7		-0.87	
3232		-----		-----	

3237	in house	10.948	0.17
3243	DIN54233	11.9	0.96
3246	DIN54233-3	12.1	1.13

normality	OK
n	73
outliers	1
mean (n)	10.746
st.dev. (n)	1.4666
R(calc.)	4.106
R(Horwitz)	3.367



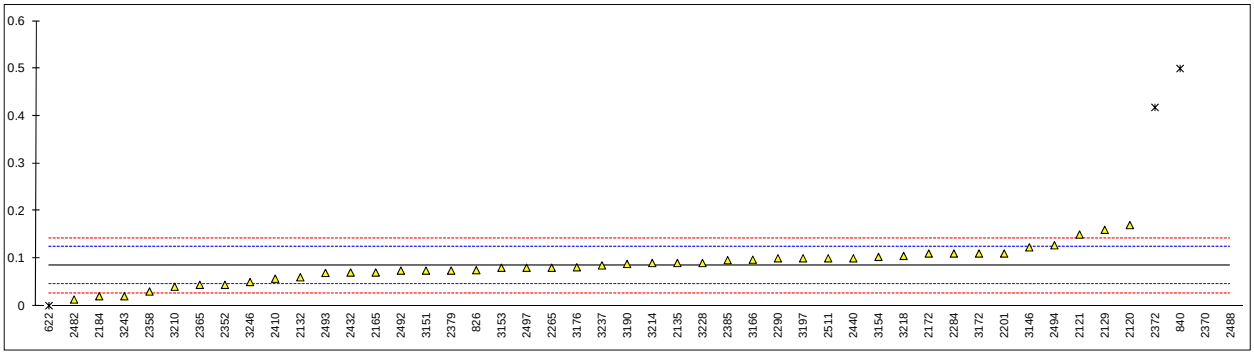


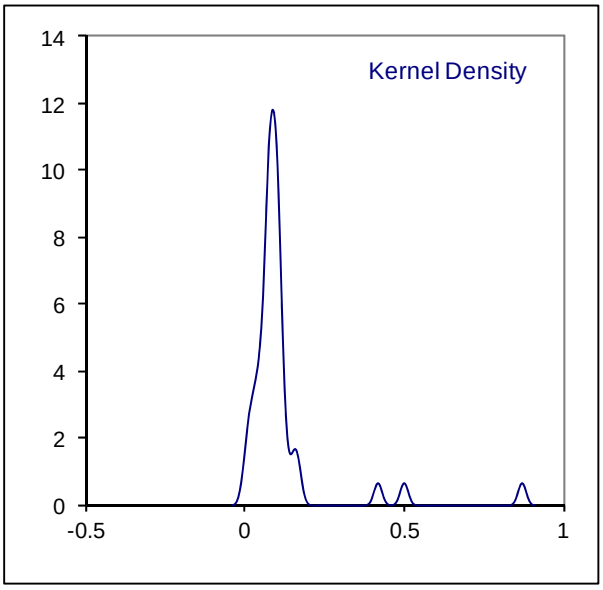
Determination of perspirated Mercury (s/l ratio = 1/50) on sample #12121; results in mg/kg

lab	method	value	mark	z(targ)	remarks
348		-----		-----	
362		-----		-----	
551	ISO11885	n.d.		-----	
622	DIN54020	0	ex	-4.31	Result excluded, zero is not a real result
826	ISO104-E04	0.075		-0.47	Used s/l ratio 1/20
840	ISO150-E04	0.50	G(0.01)	21.27	
1179	DIN54233-3	<0.1		-----	
2120	in house	0.17		4.39	Used s/l ratio 1/100
2121		0.15		3.37	
2129	ISO105-E04/ISO17294-2	0.16		3.88	
2132	in house	0.06		-1.24	
2135	in house	0.09		0.30	
2137	ISO105-E04	n.d.		-----	
2139	OEKO-Tex Std.100/200	<0.02		<-3.29	False negative?
2165	ISO105-E04	0.07		-0.73	
2172	in house	0.110		1.32	
2184	ISO105-E04	0.02		-3.28	
2196	DIN54233	n.d.		-----	
2201	DIN54233-3	0.1100		1.32	
2247		-----		-----	
2256		-----		-----	
2261		-----		-----	
2265	DIN54233-3	0.08		-0.21	
2272	ISO17072-1	<1		-----	
2284	DIN54233-3	0.11		1.32	
2290	ISO105-E04	0.10		0.81	
2293		-----		-----	
2295	DIN54233	n.d.		-----	
2303	in house	<0.05		-----	
2310	ISO105-E04	n.d.		-----	
2311	ISO105-E04	n.d.		-----	
2352	ISO105-E04	0.04400		-2.06	
2358	ISO105-E04	0.03		-2.77	
2365	ISO105-E04	0.044		-2.06	
2370	ISO105-E04	0.869	G(0.01)	40.15	
2372	ISO105-E04	0.418	G(0.01)	17.08	
2375	OEKO-Tex Std.100/200/ISO105	<0.01		<-3.80	False negative?
2379	ISO105-E04	0.074		-0.52	
2380	ISO105-E04	n.d.		-----	
2385	in house	0.0960		0.61	
2390	ISO105-E04	n.d.		-----	
2410	DIN54233	0.057		-1.39	
2428	G/T17593	n.d.		-----	
2432	in house	0.07		-0.73	
2440	BG/T17593.2	0.100		0.81	
2442	in house	n.d.	C	-----	First reported 0.2
2447		-----		-----	
2452	DIN54233-3	n.d.		-----	
2453		-----		-----	
2482	DIN54233-3	0.013		-3.64	
2488	ISO105-E04	0.98	G(0.01)	45.83	
2489		-----		-----	
2492	OEKO-Tex Std.200	0.074		-0.52	
2493	DIN54233	0.069		-0.78	
2494	ISO105-E04	0.1274		2.21	
2497	INH-030	0.08		-0.21	
2504	DIN54233	n.d		-----	
2511	DIN54233-3	0.1		0.81	
2520	ISO105-E04	<0.025		<-3.03	False negative?
3117		-----		-----	
3146	DIN54233/ISO11885/ISO1483	0.123		1.99	
3151	DIN54233-3	0.074		-0.52	
3153	ISO105-E04	0.08		-0.21	
3154	ISO17072	0.103		0.96	
3166	in house	0.097		0.66	
3172	DIN54233	0.11		1.32	
3176	DIN54233-3	0.081		-0.16	
3185	DIN54233	<1.0		-----	
3190	OEKO-Tex Std.100/200	0.088		0.20	
3197	ISO105-E04	0.1		0.81	
3210	ISO17072-1	0.04		-2.26	
3214	DIN54233-3	0.09	C	0.30	First reported 1.00
3218	DIN54233	0.105		1.07	
3220	DIN54233/54020	n.d.		-----	
3228	in house	0.09		0.30	
3232		-----		-----	

3237	in house	0.085	0.04
3243	DIN54233	0.02	-3.28
3246	DIN54233-3	0.05	-1.75

normality	OK
n	43
outliers	4
mean (n)	0.0842
st.dev. (n)	0.03474
R(calc.)	0.0973
R(Horwitz)	0.0547





Determination of other perspirated metals on sample #12120 and #12121; results in mg/kg

	#12120							#12121						
lab	As	Sb	Cr	Cu	Pb	Hg	Ni	As	Sb	Cr	Co	Cu	Pb	Ni
348	--	--	--	--	--	--	--	--	--	--	--	--	--	--
362	--	--	--	--	--	--	--	--	--	--	--	--	--	--
551	--	--	--	0.239	--	--	--		--	--	0.239	--	--	--
622	0.1	0.1	--	--	--	--	--	0.1	--	--	--	--	--	--
826	--	--	--	--	--	--	--	--	--	--	--	--	--	--
840	--	--	--	--	--	--	--	--	--	--	--	--	--	--
1179	--	--	--	--	--	--	--	--	--	--	--	--	--	--
2120	--	--	--	--	--	--	--	--	--	--	--	--	--	--
2121	--	--	--	--	--	--	0.13	--	--	--	--	--	--	0.10
2129	--	--	--	--	--	--	--	--	--	--	--	--	--	0.4
2132	--	--	--	--	--	--	--	--	--	--	--	--	--	--
2135	--	--	--	--	--	--	--	--	--	--	--	--	--	--
2137	--	--	--	--	--	--	--	--	--	--	--	--	--	--
2139	--	--	--	1.1	--	--	--	--	--	--	--	1.0	--	--
2165	--	--	--	--	--	--	--	--	--	--	--	--	--	--
2172	--	--	--	--	--	--	--	--	--	--	--	--	--	--
2184	--	--	--	--	--	--	--	--	--	--	--	--	--	--
2196	--	--	--	--	--	--	--	--	--	--	--	--	--	--
2201	--	--	--	--	--	--	--	--	--	--	--	--	--	--
2247	--	--	--	--	--	--	--	--	--	--	--	--	--	--
2256	--	--	--	--	--	--	--	--	--	--	--	--	--	--
2261	--	--	--	--	--	--	--	--	--	--	--	--	--	--
2265	0.56	--	--	0.69	--	--	--	0.51	--	--	--	1.11	--	--
2272	--	--	--	--	--	--	--	--	--	--	--	--	--	--
2284	--	--	--	--	--	--	--	--	--	--	--	--	--	--
2290	--	--	--	--	--	--	--	--	--	--	--	--	--	--
2293	--	--	--	--	--	--	--	--	--	--	--	--	--	--
2295	--	--	--	--	--	--	--	--	--	--	--	--	--	--
2303	--	--	--	--	--	--	--	--	--	--	--	--	--	0.05
2310	--	--	--	--	--	--	--	--	--	--	--	--	--	--
2311	--	--	--	--	--	--	--	--	--	--	--	--	--	--
2352	--	--	--	--	--	--	--	--	--	--	--	--	--	--
2358	--	--	--	--	--	--	--	--	--	--	--	--	--	--
2365	--	--	--	--	--	--	--	--	--	--	--	--	--	--
2370	--	--	--	--	--	--	--	--	--	--	--	--	--	--
2372	--	--	--	--	--	--	--	--	--	--	--	--	--	--
2375	--	--	--	--	--	--	--	--	--	--	--	--	--	--
2379	--	--	--	--	--	--	--	--	--	--	--	--	--	--
2380	--	--	--	--	--	--	--	--	--	--	--	--	--	--
2385	--	--	--	--	--	--	--	--	--	--	--	--	--	--
2390	--	--	--	--	--	--	--	--	--	--	--	--	--	--
2410	--	--	--	--	--	--	--	--	--	--	--	--	--	--
2428	--	--	--	--	--	--	--	--	--	--	--	--	--	--
2432	--	--	--	--	--	--	--	--	--	--	--	--	--	--
2440	--	--	--	0.29	--	--	0.11	--	--	--	--	0.24	--	0.14
2442	--	--	--	--	--	--	--	--	--	--	--	--	--	--
2447	--	--	--	--	--	--	--	--	--	--	--	--	--	--
2452	--	--	0.034	0.074	--	--	--	--	--	0.029	--	0.33	--	--

2453	--	--	--	--	--	--	--	--	--	--	--	--	--	--
2482	--	--	--	0.19	--	--	0.93	--	--	--	--	0.22	--	0.076
2488	--	--	1.1	--	--	--	1.2	--	--	0.45	--	--	--	0.89
2489	--	--	--	--	--	--	--	--	--	--	--	--	--	--
2492	--	--	--	--	--	--	--	--	--	--	--	--	--	--
2493	--	--	--	0.164	--	--	0.099	0.05	--	--	--	0.10	--	0.064
2494	1.0214	--	--	--	--	--	--	13.1554	--	--	--	--	--	--
2497	0.03	0.1	0.3	0.3	0.5	0.002	0.2	0.005	0.1	0.1	0.005	0.4	0.03	0.2
2504	--	--	--	--	0.62	0.22	0.33	--	--	--	0.12	0.17	0.20	0.33
2511	--	--	--	0.77	--	--	0.2	--	--	--	--	0.41	--	0.19
2520	--	--	--	0.1	--	--	2.7	--	--	--	--	0.104	--	2
3117	--	--	--	2.39	--	--	--	--	--	--	--	2.99	--	--
3146	--	--	--	--	--	--	--	--	--	--	--	--	--	--
3151	--	--	--	--	--	--	--	--	--	--	--	--	--	--
3153	--	--	--	--	--	--	--	--	--	--	--	--	--	--
3154	--	--	--	--	--	--	--	--	--	--	--	--	--	--
3166	--	--	0.05	0.19	0.041	--	0.10	0.008	--	0.05	0.011	0.15	0.049	0.13
3172	--	--	--	0.47	--	--	0.18	--	--	--	--	0.46	--	0.16
3176	--	--	--	--	--	--	--	--	--	--	--	--	--	0.52
3185	--	--	--	--	--	--	--	--	--	--	--	--	--	--
3190	--	--	--	--	--	--	--	--	--	--	--	--	--	--
3197	--	--	--	--	--	--	--	--	--	--	--	--	--	--
3210	--	--	--	--	--	--	--	--	--	--	--	--	--	--
3214	--	--	--	--	--	--	--	--	--	--	--	--	--	--
3218	--	--	--	--	--	--	--	--	--	--	--	--	--	--
3220	--	--	--	--	--	--	--	--	--	--	--	--	--	--
3228	--	--	--	--	--	--	--	--	--	--	--	--	--	--
3232	--	--	--	--	--	--	--	--	--	--	--	--	--	--
3237	--	--	--	--	0.037	--	--	--	--	--	--	--	0.047	--
3243	--	--	--	--	--	--	--	--	--	--	--	--	--	--
3246	--	--	--	--	--	--	--	--	--	--	--	--	--	--

APPENDIX 2

Number of participants per country:

2 labs in	BANGLADESH
1 lab in	BRAZIL
1 lab in	BULGARIA
1 lab in	EGYPT
2 labs in	FRANCE
9 labs in	GERMANY
1 lab in	GUATEMALA
6 labs in	HONG KONG
1 lab in	HUNGARY
6 labs in	INDIA
2 labs in	INDONESIA
2 labs in	ITALY
4 labs in	KOREA
18 labs in	P.R. of CHINA
1 lab in	PAKISTAN
1 lab in	PORTUGAL
1 lab in	SPAIN
3 labs in	TAIWAN R.O.C.
2 labs in	THAILAND
1 lab in	THE NETHERLANDS
2 labs in	TUNISIA
6 labs in	TURKEY
1 lab in	U.S.A.
1 lab in	UNITED KINGDOM
3 labs in	VIETNAM

APPENDIX 3

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:

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2 Öko-Tex Standard 100; January 2011
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10 ISO105 E4: 1994
11 ISO14184-1: 1994
12 ISO13528-05
13 M. Thompson and R. Wood. J. AOAC Int. 76. 926. (1993)
14 Analytical Methods Committee Technical brief, No4 January 2001.
15 The Royal Society of Chemistry 2002, Analyst 2002, 127 page 1359-1364, P.J. Lowthian and M. Thompson (see http://www.rsc.org/suppdata/an/b2/b205600n/).
16 Official Journal of the European Communities L133/29 : May 2002
17 E DIN 54233-3:2010