Results of Proficiency Test Heavy Metals by Perspiration in Leather November 2020

Organized by: Institute for Interlaboratory Studies
Spijkenisse, the Netherlands

Author: ing. R.J. Starink
Corrector: ing. A.S. Noordman-de Neef
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CONTENTS

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 leathers products on a voluntary basis. Well known program is for instance Oeko-Tex Standard 100 (Germany)

The Institute for Interlaboratory Studies organizes since 2003 a scheme of proficiency test for the determination of Heavy Metals by Perspiration in Textile. On request of a number of participants the Institute of Interlaboratory Studies (iis) decided to organize a new proficiency scheme for the determination of Heavy Metals by Perspiration in Leather in 2020.
In this interlaboratory study 59 laboratories in 18 different countries registered for participation. See appendix 4 for the number of participants per country.
In this report the results of the Heavy Metals by Perspiration in Leather proficiency tests are presented and discussed. This report is also electronically available through the iis website www.iisnl.com.

2 SET UP

The Institute for Interlaboratory Studies (iis) in Spijkenisse, the Netherlands, was the organizer of this proficiency test (PT). Sample analyzes for fit-for-use and homogeneity testing were subcontracted to an ISO/IEC17025 accredited laboratory. It was decided to send one leather sample of approximately 6 grams and labelled #20710. The participants were requested to report rounded and unrounded test results. The unrounded test results were preferably used for the statistical evaluation.

2.1 QUALITY SYSTEM

The Institute for Interlaboratory Studies in Spijkenisse, the Netherlands, has implemented a quality system based on ISO/IEC17043:2010. 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 organization 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 June 2018 (iis-protocol, version 3.5). This protocol is electronically available through the iis website www.iisnl.com, from the FAQ page.

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 selected batch was a grey grinded leather. After homogenization 81 bags were filled with approximately 6 grams and labelled #20710.
The homogeneity of the subsamples was checked by the determination of Chromium content in accordance with ISO17072-1 test method on 8 stratified randomly selected subsamples.

	Perspirated Chromium in mg/kg
Sample #20710-1	188.9
Sample #20710-2	203.0
Sample #20710-3	187.2
Sample #20710-4	194.6
Sample #20710-5	201.9
Sample #20710-6	208.8
Sample #20710-7	192.0
Sample #20710-8	192.9

Table 1: homogeneity test results of subsamples #20710

From the above test results the repeatability was calculated and compared with 0.3 times the reproducibility of the reference test method in agreement with the procedure of ISO13528, Annex B2 in the next table.

	Perspirated Chromium in mg/kg
r (observed)	21.2
reference test method	EN16711-2:15 *)
0.3 x R (reference test method)	24.7

Table 2: evaluation of the repeatability of subsamples #20710

*) see paragraph 4.1

The calculated repeatability was in agreement with 0.3 times the estimated reproducibility of the reference test method. Therefore, homogeneity of the subsamples was assumed.

To each of the participating laboratories one subsample of #20710 was sent on October 21, 2020.

2.5 ANALYZES

The participants were requested to determine on sample #20710 the perspirated heavy metals: Antimony as Sb, Arsenic as As, Cadmium as Cd, Chromium as Cr, Cobalt as Co, Copper as Cu, Lead as Pb, Manganese as Mn, Mercury as Hg, Nickel as Ni and Zinc as Zn applying the analysis procedure that is routinely used in the laboratory. It was requested to use preferably a solid/liquid ratio of 1/50 g/mL. It was also requested to report if the laboratory was accredited for the requested components that were determined and to report some analytical details.

It was explicitly requested to treat the sample as if it was a routine sample and to report the test results using the indicated units on the report form and not to round the test results, but report as much significant figures as possible. It was also requested not to report ‘less than’ test results, which are above the detection limit, because such test results cannot be used for meaningful statistical evaluations.

To get comparable test results, a detailed report form and a letter of instructions are prepared. On the report form the reporting units are given as well as the reference test methods (when applicable) that will be used during the evaluation. The detailed report form and the letter of instructions are both made available on the data entry portal www.kpmd.co.uk/sgs-iis-cts/. The participating laboratories are also requested to confirm the sample receipt on this data entry portal. The letter of instructions can also be downloaded from the iis website www.iisnl.com.

3 RESULTS

During five weeks after sample dispatch, the test results of the individual laboratories were gathered via the data entry portal www.kpmd.co.uk/sgs-iis-cts/. The reported test results are tabulated per determination in appendix 1 and 2 of this report. The laboratories are presented by their code numbers.

Directly after the deadline, a reminder was sent to those laboratories that had not reported test results at that moment. Shortly after the deadline, the available test results were screened for suspect data. A test 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 reported test results (no reanalyzes). Additional or corrected test results are used for data analysis and the original test results are placed under 'Remarks' in the result tables in appendix 1. Test results that came in after the deadline were not taken into account in this screening for suspect data and thus these participants were not requested for checks.

3.1 STATISTICS

The protocol followed in the organization 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 June 2018 (iis-protocol, version 3.5).

For the statistical evaluation the *unrounded* (when available) figures were used instead of the rounded test results. Test results reported as '<…' or '>…' were not used in the statistical evaluation.

First, the normality of the distribution of the various data sets per determination was checked by means of the Lilliefors-test, a variant of the Kolmogorov-Smirnov test and by the calculation of skewness and kurtosis. Evaluation of the three normality indicators in combination with the visual evaluation of the graphic Kernel density plot, lead to judgement of the normality being either 'unknown', 'OK', 'suspect' or 'not OK'. After removal of outliers, this check was repeated. If a data set does not have a normal distribution, the results of the statistical evaluation should be used with due care.

According to ISO5725 the original test results per determination were submitted to Dixon's, Grubbs' or Rosner's 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 and by R(0.01) for the Rosner's 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 and by R(0.05) for the Rosner's 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. In this PT, the criterion of ISO13528, paragraph 9.2.1. was met for all evaluated tests, therefore, the uncertainty of all assigned values may be negligible and need not be included in the PT report.

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

3.2 GRAPHICS

In order to visualize 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 test results are plotted. The corresponding laboratory numbers are on 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 reference test method. 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. The Kernel Density Graph is a method for producing a smooth density approximation to a set of data that avoids some problems associated with histograms. Also, a normal Gauss curve was projected over the Kernel Density Graph for reference.

3.3 Z-SCORES

To evaluate the performance of the participating laboratories the z-scores were calculated. As it was decided to evaluate the performance of the participants in this proficiency test (PT) against the literature requirements, e.g. EN reproducibilities, the z-scores were calculated using a target standard deviation. This results in an evaluation independent of the variation of this interlaboratory study.

The target standard deviation was calculated from the literature reproducibility by division with 2.8. In case no literature reproducibility was available, other target values were used. In some cases, a reproducibility based on former iis proficiency tests could be used.

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 whether the reported test result is fit-for-use.
The z-scores were calculated according to:

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

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

Absolute values for z<2 are very common and absolute values for z>3 are very rare. Therefore, 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

In this interlaboratory study some problems were encountered with the dispatch of the samples due to the COVID-19 pandemic. Therefore, the reporting time on the data entry portal was extended with one week. One participant reported the test results after this period and four participants did not report any test results. Not all participants were able to report all elements requested.
Finally, the 55 reporting laboratories reported 55 numerical test results. Observed were 4 outlying results, which is 7.3% of all reported numerical test results. In proficiency studies, outlier percentages of 3% - 7.5% are quite normal.

The data set proved to have a normal Gaussian distribution.

4.1 EVALUATION PER ELEMENT

In this paragraph the reported test results are discussed per element. The test methods which were used by the various laboratories were taken into account for explaining the observed differences when possible and applicable. These test methods are also in the table together with the reported test results in appendix 1. The abbreviations used in these tables are explained in appendix 5.

Test method ISO17072-1 is considered to be the official test method for the determination of perspirated metals in Leather. Regretfully only precision data for Lead are mentioned at a very low value of 0.6 mg/kg. Also, the use of the Horwitz equation is very strict. Therefore, it was decided to use the target reproducibilities which were estimated from the reproducibility data as mentioned in EN16117-2, Determination of metals extracted by acidic artificial perspiration solution.

In EN16117-2 is mentioned the standard deviation and variation coefficient per element between laboratories. The reproducibility of each metal was calculated by multiplying the standard deviation (or variation coefficient) of the metal with 2.8.

Chromium: The determination of Chromium was not problematic. Four statistical outliers were observed. The calculated reproducibility after rejection of the statistical outliers is in full agreement with the requirements of EN16711-2:15.

Other Elements: The majority of the participants agreed on a content close to or below the quantification limits of all other requested elements. Therefore, no z-scores were calculated. The test results are given in appendix 2.

4.2 PERFORMANCE EVALUATION FOR THE GROUP OF LABORATORIES

A comparison has been made between the reproducibility as declared by the reference test method and the reproducibility as found for the group of participating laboratories. The number of significant test results, the average, the calculated reproducibility (2.8 * standard deviation) and the target reproducibility are compared in the next table.

Component	unit	n	average	2.8 * sd	R(target)
Chromium as Cr	mg/kg	51	129.1	55.9	54.2

Table 3: reproducibility of perspirated metals in sample #20710

From the table above it can be concluded that, without statistical calculations, the group of participating laboratories do not have difficulties to analyze Chromium. See also the discussion in paragraphs 4.1 and 5.

4.3 OVERVIEW OF THE PROFICIENCY TEST OF NOVEMBER 2020

The evolution of the uncertainty expressed as relative standard deviation for Perspirated heavy Metals in Leather as observed in this proficiency scheme is listed in table 4

Component	November 2020	EN16711-2
Antimony as Sb	--	20%
Arsenic as As	--	20%
Cadmium as Cd	--	10%
Chromium as Cr	15%	15%
Cobalt as Co	--	13%
Copper as Cu	--	16%
Lead as Pb	--	40%
Manganese as Mn	--	--
Mercury as Hg	--	31%
Nickel as Ni	--	10%
Zinc as Zn	--	--

Table 4: uncertainties overview

4.4 EVALUATION OF ANALYTICAL DETAILS

The reported details of the analytical test methods that were used by the participants are listed in appendix 3. About 85% of the participating laboratories reported to be accredited for the determination of perspirated metals in leather.
It should be noticed that differences in sample intake and the solid/liquid ratio (grams of leather per ml perspiration liquid) appeared to be a parameter of utmost importance (see reports iis07A05 and iis08A05 on “Perspirated Metals in Textile”). Therefore, in this proficiency test the laboratories were advised to use preferably a ratio of 1:50 and a sample intake of at least 0.5 gram. About 60% of the participants reported to have used the 1:50 ration.
About 60% of the participants used a sample intake of 0.5 - 1 grams and around 20% of the participants used a sample intake of 2 grams (as mentioned in ISO17072-1) or more.

5 DISCUSSION

In this PT the average of the homogeneity test results is not in line with the average (consensus value) from the PT result. There are several reasons for this. First, the goal of the homogeneity testing is different from the goal of the evaluation of the reported PT results. In order to prove the homogeneity of the PT samples, a test method is selected with a high precision (smallest variation). The accuracy (trueness) of the test method is less relevant. Secondly, the homogeneity testing is done by one laboratory only. The test results of this ISO/IEC17025 accredited laboratory will have a bias (systematic deviation) depending on the test method used. The desire to detect small variations between the PT samples leads to the use of a sensitive test method with high precision, which may be a test method with significant bias. Also, each test result reported by the laboratories that participate in the PT

will have a bias. However, some will have a positive bias and others a negative bias. These different biases compensate each other in the PT average (consensus value). Therefore, the PT consensus value may deviate from the average of the homogeneity test. At the same time the accuracy of the PT consensus value is more reliable than the accuracy of the average of the homogeneity test.

Methods for determination of these Heavy Metals via perspiration are specified in the Standards of the Ecolabelling Institutes.
Some participants would make different decisions about the acceptability of the leather for the determined parameters, when the test results of this interlaboratory study are compared to the Ecolabelling Standards and Requirements for Leather in EU (see table 5). In this PT all reporting laboratories would made the same decision and would reject the sample for class 1 (baby clothes). Two laboratories would have rejected the sample for all classes also.

Ecolabel	Class 1: baby clothes in mg/kg	Class 2: direct skin contact in mg/kg	Class 3: no direct skin contact in mg/kg	Class 4: decoration material in mg/kg
Antimony as Sb	30.0	30.0	30.0	--
Arsenic as As	0.2	1.0	1.0	1.0
Cadmium as Cd	0.1	0.1	0.1	0.1
Chromium as Cr	2.0	200.0	200.0	200.0
Cobalt as Co	1.0	4.0	4.0	4.0
Copper as Cu	25.0	50.0	50.0	50.0
Lead as Pb	0.2	1.0	1.0	1.0
Manganese as Mn	--	--	--	--
Mercury as Hg	0.02	0.02	0.02	0.02
Nickel as Ni	1.0	4.0	4.0	4.0
Zinc as Zn	--	--	--	--

Table 5: Ecolabelling Standards and Requirements for Leathers in EU

6 CONCLUSION

In this proficiency test the Heavy Metal content by perspiration in Leather was determined. The variation observed for the perspirated metal in this interlaboratory study is in line with the observations of the heavy metals by perspiration in textile proficiency tests (see iis20A12 chapter 4.3).

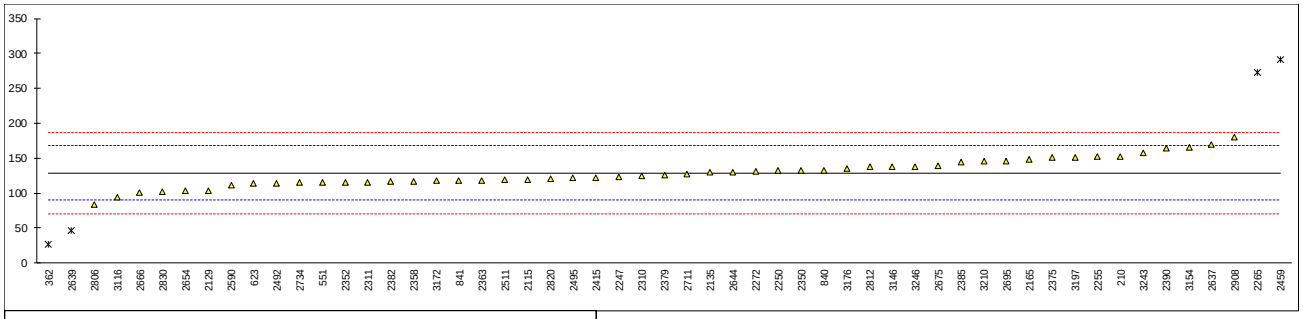
A possible explanation for the variation could be the preparation or the conditioning of the sample and/or by the performance of the analysis by the laboratory. Each laboratory should evaluate its performance in this study and make decisions about necessary corrective actions. Therefore, participation on a regular basis in this scheme could be helpful to improve the performance and thus increase of the quality of the analytical results.

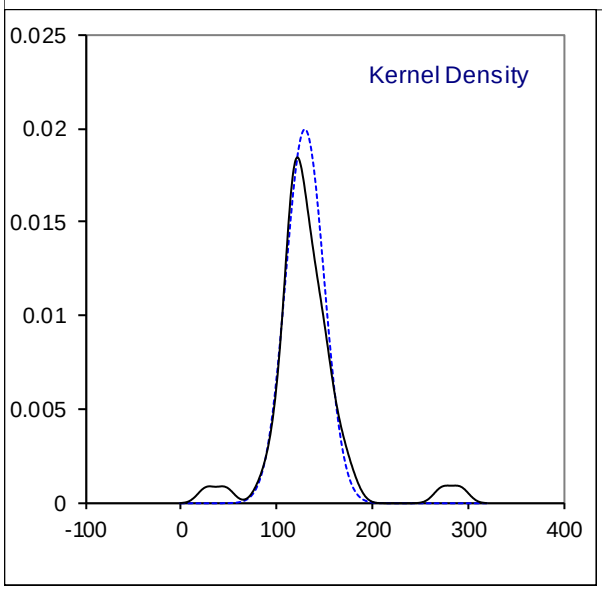
APPENDIX 1

Determination of Chromium as Cr on sample #20710; results in mg/kg

lab	method	value	mark	z(targ)	remarks
110		-----		-----	
210	ISO17072-1	152.97		1.24	
362	In house	26.3	R(0.01)	-5.31	
551	ISO105E04	114.816		-0.74	
623	ISO17072-1	114.270		-0.76	
840	ISO105E04	133.075		0.21	
841	EN16711-2	117.81		-0.58	
2115	EN16711-2	119.6		-0.49	
2129	EN16711-2	103.69		-1.31	
2135	ISO17072-1	130.00		0.05	
2165	ISO17072-1	147.9		0.97	
2247	ISO17072-1	123.79		-0.27	
2250	ISO17072-1	132.89		0.20	
2255	ISO17072-1	151.7		1.17	
2265	ISO17072-1	272.50	R(0.01)	7.41	
2272	ISO17072-1	130.6		0.08	
2310	ISO17072-1	125		-0.21	
2311	ISO105E04	115.34		-0.71	
2350	ISO17072-2/ISO105E04	132.96		0.20	
2352	In house	115.2		-0.72	
2358	ISO17072-1	117.2		-0.61	
2363	ISO17072-1	118		-0.57	
2375	ISO17072-1	150.5		1.11	
2379	ISO17072-1	126.5227		-0.13	
2382	ISO17072-1	116.2		-0.66	
2385		144		0.77	
2390	ISO105E04	164.85		1.85	
2415	ISO17072-1	122.41		-0.34	
2459	ISO17072-1	291.25	R(0.01)	8.38	
2492	In house	114.5		-0.75	
2495	ISO17072-1	121.5		-0.39	
2511	ISO17072-1	119.1		-0.51	
2514		-----		-----	
2563		-----		-----	
2590	ISO17072-1	111.29		-0.92	
2637	ISO17072-1	170		2.12	
2639	GB/T22930	46.14585	R(0.01)	-4.28	
2644		130		0.05	
2654		103.500		-1.32	
2666	ISO17072-1	100.9		-1.45	
2675	ISO17072-1	138.57		0.49	
2695	ISO105E04/ISO17072-1	146.32993		0.89	
2711	ISO17072-1	126.8		-0.12	
2734		114.7		-0.74	
2806		83.8		-2.34	
2812	ISO17072-1	137.33		0.43	
2820	ISO105E04/ISO17072-1	120.1		-0.46	
2830	ISO17072-1	102.0821		-1.39	
2908	ISO17072-1	179.56		2.61	
3116	ISO17072-1	93.6		-1.83	
3146	EN16711-2	138		0.46	
3154	EN16711-2	165.16		1.87	
3172	ISO17072-1	117.4		-0.60	
3176	ISO17072-1	134.91		0.30	
3197	ISO17072-1	150.5		1.11	
3210	In house	145.3	C	0.84	First reported 23490
3237		-----		-----	
3243	ISO17072-1	157		1.44	
3246		138.38		0.48	

	normality	OK	
	n	51	
	outliers	4	
	mean (n)	129.051	
	st.dev. (n)	19.9607	RSD = 15%
	R(calc.)	55.890	
	st.dev.(EN16711-2:15)	19.3577	
	R(EN16711-2:15)	54.201	
Compare			
	R(Horwitz)	27.819	


350
300
250
200
150
100
50
0
362 2639 2806 3116 2666 2830 2654 2129 2590 623 2492 2734 551 2352 2311 2382 2358 3172 841 2363 2511 2115 2820 2495 2415 2247 2310 2379 2711 2135 2644 2272 2250 2350 840 3176 2812 3146 3246 2675 2385 3210 2695 2165 2375 3197 2255 210 3243 2390 3154 2637 2908 2265 2459


Kernel Density
0.025
0.02
0.015
0.01
0.005
0
-100
0
100
200
300
400

APPENDIX 2 Reported test results of Antimony, Arsenic, Cadmium, Cobalt, Copper, Lead, Manganese, Mercury, Nickel and Zinc on sample #20710; results in mg/kg

lab	Sb	As	Cd	Co	Cu	Pb	Mn	Hg	Ni	Zn
110	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----
210	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----
362	-----	-----	-----	-----	11.8	-----	-----	-----	-----	-----
551	-----	1.3469	-----	0.5141	0.8336	-----	3.1511	-----	0.5591	1.585
623	Not det.	Not det.	Not det.	Not det.	Not det.	Not det.	1.150	Not det.	Not det.	Not det.
840	<0.3	<0.03	<0.01	0.160	<1	<0.03	<2	<0.006	0.168	<2
841	<0.2	<0.025	<0.025	0.15	<5	<0.1	<5	<0.005	0.24	<5
2115	-----	-----	-----	-----	-----	-----	1.94	-----	-----	1.69
2129	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----
2135	-----	-----	-----	0.128	-----	-----	1.13	-----	0.288	-----
2165	<RL	<RL	<RL	<RL	<RL	<RL	1.266	<RL	<RL	<RL
2247	Not det.	Not det.	Not det.	Not det.	Not det.	Not det.	Not det.	Not det.	Not det.	Not det.
2250	Not det.	Not det.	Not det.	0.1539	Not det.	Not det.	1.246	Not det.	0.2258	Not det.
2255	Not det.	Not det.	Not det.	Not det.	Not det.	Not det.	Not det.	Not det.	Not det.	Not det.
2265	Not det.	Not det.	Not det.	0.21	Not det.	Not det.	1.62	Not det.	0.38	1.90
2272	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----
2310	Not det.	Not det.	Not det.	Not det.	Not det.	Not det.	1.12	Not det.	Not det.	Not det.
2311	Not det.	Not det.	Not det.	Not det.	Not det.	Not det.	0.9835	Not det.	Not det.	Not det.
2350	<0.5	<0.02	<0.02	0.1544	<5	<0.1	-----	<0.005	0.2009	-----
2352	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----
2358	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	N/A	n.d.	n.d.	n.d.
2363	<1	<0.1	<0.05	<0.5	<5	<0.1	NA	<0.01	<0.5	<5
2375	0.12	<0.02	<0.02	0.18	<0.5	<0.05	1.25	<0.005	0.27	0.9
2379	Not det.	Not det.	Not det.	Not det.	Not det.	Not det.	Not det.	Not det.	Not det.	Not det.
2382	<1.0	<0.10	<0.050	<0.50	<5.0	<0.10	<10.0	<0.010	<0.50	<10.0
2385	< 0.1	< 0.1	< 0.05	0.2	< 0.5	< 0.1	1.75	< 0.01	< 0.5	51
2390	n.d	n.d	n.d	n.d	n.d	n.d	-----	n.d	n.d	-----
2415	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----
2459	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
2492	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----
2495	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1
2511	-----	-----	-----	0.12	-----	-----	-----	-----	0.27	-----
2514	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----
2563	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----
2590	Not det.	Not det.	Not det.	Not det.	Not det.	Not det.	Not det.	Not det.	Not det.	-----
2637	<0.01	<0.02	<0.005	0.21	0.23	<0.01	1.55	<0.001	0.27	0.95
2639	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----
2644	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----
2654	1.680	Not det.	Not det.	Not det.	Not det.	Not det.	Not det.	Not det.	Not det.	Not det.
2666	Not det.	Not det.	Not det.	0.14	0.06	Not det.	0.97	Not det.	0.73	Not det.
2675	< 0,1	< 0,1	< 0,1	0.18	< 0,1	< 0,1	1.34	<0,1	0.31	<1
2695	Not det.	Not det.	Not det.	Not det.	Not det.	Not det.	2.27013	Not det.	Not det.	1.33763
2711	Not det.	Not det.	Not det.	<1.0	4.0	-----	1.3	-----	<1.0	1.6
2734	2.3	Not det.	Not det.	Not det.	Not det.	Not det.	2.1	Not det.	Not det.	Not det.
2806	< 0,1	< 0,1	< 0,1	< 0,1	0.1	< 0,1	0.6	0.001	0.1	1.4
2812	0.12	Not det.	Not det.	0.18	0.54	Not det.	1.21	Not det.	0.26	1.10
2820	-----	-----	-----	0.1	0.3	-----	2.3	-----	-----	1.0
2830	Not det.	Not det.	Not det.	Not det.	Not det.	Not det.	-----	Not det.	Not det.	-----
2908	ND	ND	ND	ND	ND	ND	-----	ND	ND	-----
3116	-----	-----	-----	0.138	-----	-----	-----	-----	0.228	-----
3146	Not det.	Not det.	Not det.	Not det.	Not det.	Not det.	1.24	Not det.	Not det.	0.752
3154	-----	0.026	-----	0.174	1.66	0.043	1.50	-----	0.289	1.39
3172	< 5	< 0.05	< 0.02	0.17	< 5	< 0.1	--	< 0.01	0.26	< 5
3176	-----	-----	-----	0.159	-----	-----	2.04	-----	0.232	-----
3197	<5	<1	<0,1	<1	<5	<0,1	<5	<0,01	<1	<5
3210	<25	<25	<10	<10	<10	<25	<10	0.0208	<10	<10
3237	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----
3243	2.1	n.d.	n.d.	n.d.	0.43	n.d.	2.0	n.d.	n.d.	1.2
3246	Not det.	Not det.	Not det.	0.146	Not det.	Not det.	1.097	Not det.	0.282	Not det.

APPENDIX 3 Analytical Details

lab	accredited	Sample intake (grams)	Ratio gram textile per ml
110	---		---
210	---		---
362	Yes		1 gram leather per 50 mL perspiration liquid
551	No	1g	1 gram leather per 50 mL perspiration liquid
623	Yes	1 gram	1 gram leather per 50 mL perspiration liquid
840	Yes	0.5 grams	1 gram leather per 50 mL perspiration liquid
841	Yes	0.5 grams	1 gram leather per 50 mL perspiration liquid
2115	Yes	1 g	1 gram leather per 50 mL perspiration liquid
2129	Yes	1,0 g	1 gram leather per 50 mL perspiration liquid
2135	Yes	2 g	1 gram leather per 50 mL perspiration liquid
2165	Yes	1.0g	1 gram leather per 50 mL perspiration liquid
2247	No	1gm	1 gram leather per 50 mL perspiration liquid
2250	Yes	0,5	1 gram leather per 50 mL perspiration liquid
2255	Yes	0.90	1 gram leather per 50 mL perspiration liquid
2265	No	1,5 g	Other, 1 gram leather per 30 mL perspiration liquid
2272	Yes	2gram	1 gram leather per 50 mL perspiration liquid
2310	Yes	1	1 gram leather per 50 mL perspiration liquid
2311	Yes	0.5	1 gram leather per 50 mL perspiration liquid
2350	Yes	1 g	1 gram leather per 50 mL perspiration liquid
2352	Yes	1g	1 gram leather per 50 mL perspiration liquid
2358	Yes	1 g	1 gram leather per 50 mL perspiration liquid
2363	Yes	2g	1 gram leather per 50 mL perspiration liquid
2375	---		---
2379	Yes	1 grams/ 50 mL	1 gram leather per 50 mL perspiration liquid
2382	Yes	2g	---
2385	Yes	1 g	1 gram leather per 50 mL perspiration liquid
2390	Yes	1.0033g	1 gram leather per 50 mL perspiration liquid
2415	Yes	1.0	1 gram leather per 50 mL perspiration liquid
2459	Yes	1.0 gram	---
2492	Yes	0.85 g	1 gram leather per 50 mL perspiration liquid
2495	Yes	1.0	1 gram leather per 50 mL perspiration liquid
2511	---		---
2514	---		---
2563	---		---
2590	Yes	1g	1 gram leather per 50 mL perspiration liquid
2637	Yes	1000 mg	1 gram leather per 50 mL perspiration liquid
2639	No	2.0008g	Other, 1 gram leather per 25 mL perspiration liquid
2644	No	2 g	1 gram leather per 50 mL perspiration liquid
2654	Yes	2	1 gram leather per 50 mL perspiration liquid
2666	Yes	4 gr	Other, 2 gram leather per 25 mL perspiration liquid
2675	Yes	about 1g per extraction	1 gram leather per 50 mL perspiration liquid
2695	Yes	6 g	1 gram leather per 50 mL perspiration liquid
2711	No	2.025g	1 gram leather per 50 mL perspiration liquid
2734	Yes	4 g	1 gram leather per 50 mL perspiration liquid
2806	Yes		---
2812	Yes	2	1 gram leather per 50 mL perspiration liquid
2820	Yes	2	1 gram leather per 50 mL perspiration liquid
2830	Yes	1.00 gram	1 gram leather per 50 mL perspiration liquid
2908	Yes	2 grams	1 gram leather per 50 mL perspiration liquid
3116	Yes	1g	1 gram leather per 50 mL perspiration liquid
3146	Yes	0.7 gram	1 gram leather per 50 mL perspiration liquid
3154	Yes	1	1 gram leather per 50 mL perspiration liquid
3172	Yes	1	1 gram leather per 50 mL perspiration liquid
3176	Yes	1	1 gram leather per 50 mL perspiration liquid
3197	Yes	1 g	1 gram leather per 50 mL perspiration liquid
3210	Yes	0.1	Other 0.1 gram leather per 100 mL perspiration liquid
3237	---		---
3243	Yes	0,750 g (2x)	1 gram leather per 50 mL perspiration liquid
3246	Yes	1.00	1 gram leather per 50 mL perspiration liquid

APPENDIX 4

Number of participants per country

2 labs in	BANGLADESH
1 lab in	BRAZIL
1 lab in	BULGARIA
1 lab in	FRANCE
11 labs in	GERMANY
3 labs in	HONG KONG
3 labs in	INDIA
1 lab in	INDONESIA
11 labs in	ITALY
4 labs in	MOROCCO
6 labs in	P.R. of CHINA
2 labs in	PAKISTAN
1 lab in	SOUTH KOREA
1 lab in	THAILAND
1 lab in	TUNISIA
5 labs in	TURKEY
1 lab in	U.S.A.
4 labs in	VIETNAM

APPENDIX 5

Abbreviations

C	= final test result after checking of first reported suspect test 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
R(0.01)	= outlier in Rosner's outlier test
R(0.05)	= straggler in Rosner's outlier test
W	= test result withdrawn on request of participant
ex	= test result excluded from statistical evaluations
n.a.	= not applicable
n.e.	= not evaluated
n.d.	= not detected
fr.	= first reported

Literature

1 iis Interlaboratory Studies, Protocol for the Organisation, Statistics & Evaluation, June 2018
2 Oeko-Tex Standard 100; January 2019
3 AAFA (American Apparel & Footwear Association) March 2013, 12th edition
4 Impacts of Environmental Standards and requirements in EU Countries. August 1999
5 Horwitz. Journal of AOAC International, 79.3, (1996)
6 P.L. Davies. Fr. Z. Anal. Chem. 351. 513. (1988)
7 W.J. Conover. Practical; Nonparametric Statistics. J. Wiley&Sons. NY., 302, (1971)
8 ISO5725:86
9 ISO5725. parts 1-6. (1994)
10 ISO105-E4:94
11 ISO13528:05
12 M. Thompson and R. Wood. J. AOAC Int. 76. 926. (1993)
13 Analytical Methods Committee, Technical brief, No 4, January 2001.
14 P.J. Lowthian and M. Thompson, The Royal Society of Chemistry, Analyst, 127, 1359-1364, (2002)
15 Official Journal of the European Communities L133/29: May 2002
16 Bernard Rosner, Percentage Points for a Generalized ESD Many-Outlier Procedure, Technometrics,25(2), 165-172, (1983)