Institute for
Interlaboratory Studies

Results of Proficiency Test
Heavy Metals by Perspiration
in Leather/Footwear
November 2023

Organized 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 leather consumer products. Laws and regulations impose some of these standards and requirements. In addition to mandatory environmental standards and requirements for leather some Ecolabelling schemes are imposing environmental requirements for leather products on a voluntary basis e.g. EU Ecolabel for footwear regulation 2016/1349/EU, OEKO-TEX® Standard, bluesign® and the American Apparel and Footwear Association.

Since 2020 the Institute for Interlaboratory Studies organizes a proficiency scheme for the determination of Heavy Metals by Perspiration in Leather/Footwear every year. During the annual proficiency testing program of 2023 it was decided to continue the proficiency test for the determination of Heavy Metals by Perspiration in Leather/Footwear.

In this interlaboratory study 49 laboratories in 21 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/Footwear proficiency test 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 a laboratory that has performed the tests in accordance with for ISO/IEC17043 relevant requirements of ISO/IEC17025.
It was decided to send one leather sample of approximately 6 grams labelled #23755.
The participants were requested to report rounded and unrounded test results. The unrounded test results were preferably used for 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

A batch of pink leather pieces was selected which was artificially fortified with some heavy metals. After homogenization 65 small plastic bags were filled with approximately 6 grams each and labelled #23755.
The homogeneity of the subsamples was checked by the determination of Antimony and Arsenic in accordance with ISO17072-1 on 8 stratified randomly selected subsamples.

	Antimony as Sb in mg/kg	Arsenic as As in mg/kg
sample #23755-1	60.0	9.4
sample #23755-2	57.3	9.1
sample #23755-3	60.3	9.4
sample #23755-4	51.1	8.5
sample #23755-5	57.4	8.9
sample #23755-6	57.1	9.5
sample #23755-7	59.6	9.9
sample #23755-8	54.9	8.8

Table 1: homogeneity test results of subsamples #23755

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

	Antimony as Sb in mg/kg	Arsenic as As in mg/kg
r (observed)	8.6	1.3
reference test method	EN16711-2:15	EN16711-2:15
0.3 x R (reference test method)	9.6	1.5

Table 2: evaluation of the repeatabilities of subsamples #23755

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

To each of the participating laboratories one leather sample labelled #23755 was sent on October 25, 2023.

2.5 ANALYZES

The participants were requested to determine: Antimony as Sb, Arsenic as As, Cadmium as Cd, Chromium as Cr, Cobalt as Co, Copper as Cu, Lead as Pb, Mercury as Hg and Nickel as Ni. To ensure homogeneity it was requested not to use less than 0.5 gram per determination, and not to age or dry the sample. It was also requested to report if the laboratory was accredited for the determined component 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 appendices 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 appendices 1 and 2. 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.

The assigned value is determined by consensus based on the test results of the group of participants after rejection of the statistical outliers and/or suspect data.

According to ISO13528 all (original received or corrected) results per determination were submitted to outlier tests. In the iis procedure for proficiency tests, outliers are detected prior to calculation of the mean, standard deviation and reproducibility. For small data sets, Dixon (up to 20 test results) or Grubbs (up to 40 test results) outlier tests can be used. For larger data sets (above 20 test results) Rosner’s outlier test can be used. 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. This 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 (dotted line) was projected over the Kernel Density Graph (smooth line) for reference. The Gauss curve is calculated from the consensus value and the corresponding standard deviation.

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 (derived from e.g. ISO or ASTM test methods), the z-scores were calculated using a target standard deviation. This results in an evaluation independent of the variation in 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, like Horwitz or an estimated reproducibility based on former iis proficiency tests.

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 proficiency test no problems were encountered with the dispatch of the samples. Three participants reported test results after the final reporting date and three other participants did not report any test results. Not all participants were able to report all elements requested.
In total 46 participants reported 131 numerical test results. Observed were 6 outlying test results, which is 4.6%. In proficiency tests outlier percentages of 3% - 7.5% are quite normal.

All data sets proved to have a normal Gaussian distribution.

4.1 EVALUATION PER ELEMENT

In this section 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 tables together

with the original data in appendix 1. The abbreviations, used in these tables, are explained in appendix 5.

For the determination of Heavy Metals by Perspiration in Leather/Footwear the ISO17072-1 is considered to be the official test method. 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 for the target reproducibilities the precision data from test method EN16117-2:15. Test method EN16117-2 is a method for the determination of heavy metals extracted by acidic artificial perspiration solution from textile. This method mentions the standard deviation and variation coefficient per element between laboratories. The reproducibility of each metal was calculated by multiplying the variation coefficient of the metal with 2.8.

Antimony as Sb: The group of participants met the target requirements. One statistical outlier was observed. The calculated reproducibility after rejection of the statistical outlier is in agreement with the requirements of EN16711-2:15.

Arsenic as As: The group of participants met the target requirements. Two statistical outliers were observed. The calculated reproducibility after rejection of the statistical outliers is in agreement with the requirements of EN16711-2:15.

Chromium as Cr: The group of participants had difficulty to meet the target requirements. Three statistical outliers were observed. The calculated reproducibility after rejection of the statistical outliers is not in agreement with the requirements of EN16711-2:15.

The participants agreed on a concentration near or below the limit of detection for all other elements mentioned in paragraph 2.5. Therefore, no z-scores are calculated for these elements. The reported 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 derived from the reference method are presented in the next table.

Element	unit	n	average	2.8 * sd	R(lit)
Antimony as Sb	mg/kg	42	54.2	29.2	30.4
Arsenic as As	mg/kg	42	8.44	4.93	4.73
Chromium as Cr	mg/kg	41	47.7	32.7	20.1

Table 3: reproducibilities of tests in sample #23755

Without further statistical calculations it can be concluded that for most tests there is a good compliance of the group of participants with the reference test method.

4.3 COMPARISON OF THE PROFICIENCY TEST OF NOVEMBER 2023 WITH PREVIOUS PTS

	November 2023	November 2022	November 2021	November 2020
Number of reporting laboratories	46	50	50	55
Number of test results	131	145	144	55
Number of statistical outliers	6	6	7	4
Percentage of statistical outliers	4.6%	4.1%	4.9%	7.3%

Table 4: comparison with previous proficiency tests

In proficiency tests outlier percentages of 3% - 7.5% are quite normal.

The performance of the determinations of the proficiency test was compared to uncertainties observed in PTs over the years, expressed as relative standard deviation (RSD) of the PTS, see next table.

Element	November 2023	November 2022	November 2021	November 2020
Antimony as Sb	19%	--	--	--
Arsenic as As	21%	--	--	--
Cadmium as Cd	--	8%	--	--
Chromium as Cr	24%	15%	22%	15%
Cobalt as Co	--	--	9%	--
Copper as Cu	--	15%	--	--
Lead as Pb	--	--	--	--
Mercury as Hg	--	--	--	--
Nickel as Ni	--	--	10%	--

Table 5: development of the uncertainties over the years

The uncertainties observed in this PT are comparable to the uncertainties observed in previous PTs.

4.4 EVALUATION OF THE ANALYTICAL DETAILS

For this PT some analytical details were requested and are listed in appendix 3. Based on the answers given by the participants the following can be summarized:

- 77% of the participants mentioned that they are ISO/IEC17025 accredited to determine the reported elements.
- 24% mentioned to use the sample as received and 76% did further cut or further grind the sample prior to analysis.
- 50% used a sample intake of 1 gram, 20% used 0.5 grams and 30% used 2 grams or more.

For most elements present in the sample the calculated reproducibility is in agreement with the requirements of the target reproducibility, therefore no separate statistical analysis has been performed.

5 DISCUSSION

Limits for Heavy Metals by Perspiration are specified in the Eco-labelling of 2016/1349/EU, the Leather Standard by OEKO-TEX® and the leather limits in bluesign®. When the test results of this interlaboratory study are compared to these limits (see table 6), it was noticed that all participants, except one, would have made identical decisions about the acceptability of the leather for the determined parameters.

	Eco-label 2016/1349/EU footwear for > 3 years in mg/kg	OEKO-TEX® leather direct skin contact in mg/kg	bluesign® leather next to skin use in mg/kg
Antimony as Sb	30.0	30.0	5
Arsenic as As	1.0	1.0	0.2
Cadmium as Cd	0.1	0.1	0.1
Chromium as Cr	--	200.0	--
Cobalt as Co	4.0	4.0	1.0
Copper as Cu	50.0	50.0	25
Lead as Pb	1.0	1.0	0.2
Mercury as Hg	0.02	0.02	0.02
Nickel as Ni	1.0	4.0	1.0

Table 6: Leather Standard by Oeko-Tex®

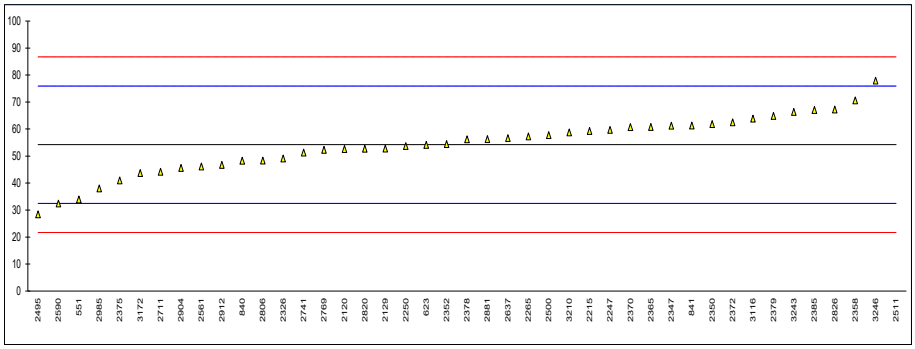
6 CONCLUSION

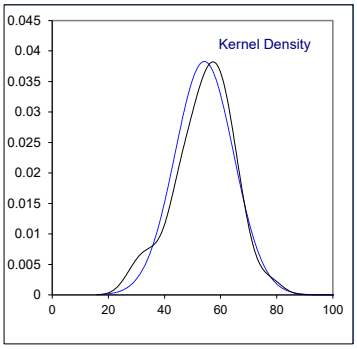
Each participating laboratory will have to evaluate its performance in this study and decide about any corrective actions if necessary. Therefore, participation on a regular basis in this scheme could be helpful to improve the performance and thus increase of the quality of the analytical results.

APPENDIX 1

Determination of Antimony as Sb on sample #23755; results in mg/kg

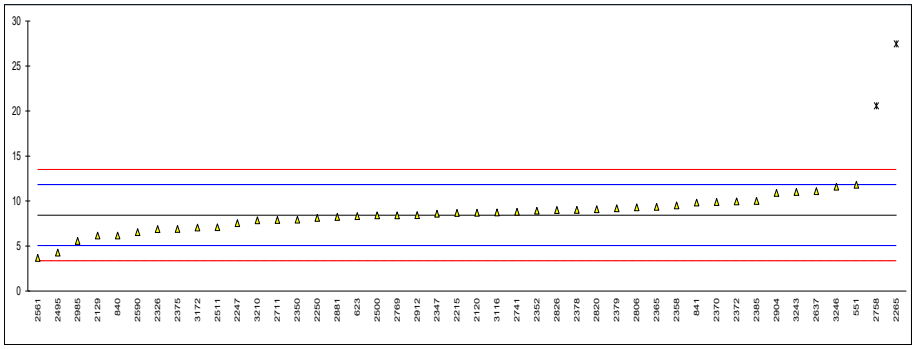
lab	method	value	mark	z(targ)	remarks
210		-----		-----	
551	In house	33.88		-1.88	
623	EN16711-2	54.12		-0.01	
840	ISO17072-1	48.2		-0.55	
841	ISO17072-1	61.3		0.65	
2120	ISO17072-1	52.6		-0.15	
2129	ISO17072-1	52.750		-0.13	
2215	ISO17072-1	59.304		0.47	
2247	ISO17072-1	59.65		0.50	
2250	ISO17072-1	53.66		-0.05	
2265	ISO17072-1	57.23		0.28	
2301	ISO17072-1	<5		<-4.54	possible a false negative test result
2326	EN16711-2	49.054		-0.48	
2347	ISO17072-1	61.2		0.64	
2350	EN16711-2	61.825		0.70	
2352	GB/T22930.1	54.380		0.02	
2358	ISO17072-1	70.617		1.51	
2365	ISO17072-1	60.72		0.60	
2370	ISO105E04	60.7		0.60	
2372	ISO17072-1	62.5		0.76	
2375	ISO17072-1	41		-1.22	
2378	ISO17072-1	56.21		0.18	
2379	ISO17072-1	64.8539		0.98	
2385	ISO17072-1	67		1.18	
2455		-----		-----	
2495	ISO17072-1	28.38		-2.38	
2500	ISO17072-1	57.72	C	0.32	first reported: 28
2511	ISO17072-1	213.15	R(0.01)	14.66	
2561	ISO17072-1	46.10		-0.75	
2590	ISO17072-1	32.42		-2.01	
2637	ISO17072-1	56.6		0.22	
2711	ISO17072-1	44.2	C	-0.92	first reported: 105.9
2741	ISO17072-1	51.26		-0.27	
2758	EN16711-2	-----		-----	
2769	ISO17072-1	52.3	C	-0.18	first reported: 4.59
2806	ISO17072-1	48.3		-0.55	
2820	ISO17072-1	52.68		-0.14	
2826	ISO17072-1	67.2		1.20	
2881	ISO17072-1	56.28		0.19	
2904	ISO17072-1	45.542		-0.80	
2912	ISO17072-1	46.746		-0.69	
2977		-----		-----	
2985	ISO17072-1	38		-1.50	
2989		-----		-----	
3116	ISO17072-1	63.8		0.88	
3172	ISO17072-1	43.7		-0.97	
3210	ISO17072-1	58.71907		0.42	
3243	ISO17072-1	66.3		1.11	
3246	ISO17072-1	77.886		2.18	
	normality	OK			
	n	42			
	outliers	1			
	mean (n)	54.2116			
	st.dev. (n)	10.42088	RSD = 19%		
	R(calc.)	29.1785			
	st.dev.(EN16711-2:15)	10.84232			
	R(EN16711-2:15)	30.3585			

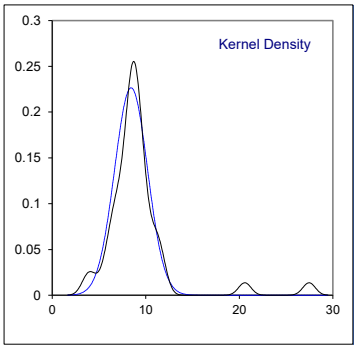




Determination of Arsenic as As on sample #23755; results in mg/kg

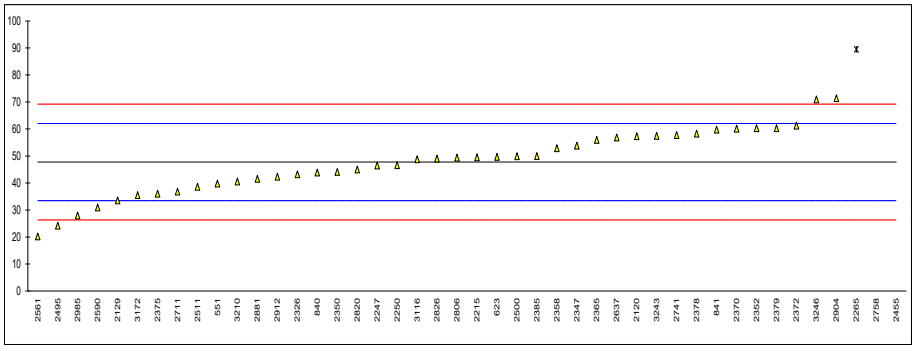
lab	method	value	mark	z(targ)	remarks
210		-----		-----	
551	In house	11.80		1.99	
623	EN16711-2	8.32		-0.07	
840	ISO17072-1	6.16		-1.35	
841	ISO17072-1	9.82		0.82	
2120	ISO17072-1	8.71		0.16	
2129	ISO17072-1	6.158		-1.35	
2215	ISO17072-1	8.688		0.15	
2247	ISO17072-1	7.54		-0.53	
2250	ISO17072-1	8.130		-0.18	
2265	ISO17072-1	27.45	R(0.01)	11.26	
2301	ISO17072-1	<0.5		<-4.70	possible a false negative test result
2326	EN16711-2	6.887		-0.92	
2347	ISO17072-1	8.6		0.10	
2350	EN16711-2	7.921		-0.31	
2352	GB/T22930.1	8.921		0.29	
2358	ISO17072-1	9.512		0.64	
2365	ISO17072-1	9.352		0.54	
2370	ISO105E04	9.88		0.85	
2372	ISO17072-1	9.95		0.90	
2375	ISO17072-1	6.9		-0.91	
2378	ISO17072-1	9.01		0.34	
2379	ISO17072-1	9.1871		0.44	
2385	ISO17072-1	10		0.93	
2455		-----		-----	
2495	ISO17072-1	4.272		-2.47	
2500	ISO17072-1	8.42	C	-0.01	first reported: 1.31
2511	ISO17072-1	7.08		-0.80	
2561	ISO17072-1	3.68		-2.82	
2590	ISO17072-1	6.55		-1.12	
2637	ISO17072-1	11.1		1.58	
2711	ISO17072-1	7.9		-0.32	
2741	ISO17072-1	8.81		0.22	
2758	EN16711-2	20.584	R(0.01)	7.20	
2769	ISO17072-1	8.42		-0.01	
2806	ISO17072-1	9.3		0.51	
2820	ISO17072-1	9.08		0.38	
2826	ISO17072-1	9.0		0.33	
2881	ISO17072-1	8.23		-0.12	
2904	ISO17072-1	10.887		1.45	
2912	ISO17072-1	8.430		-0.01	
2977		-----		-----	
2985	ISO17072-1	5.56		-1.71	
2989		-----		-----	
3116	ISO17072-1	8.74		0.18	
3172	ISO17072-1	7.05		-0.82	
3210	ISO17072-1	7.87324		-0.33	
3243	ISO17072-1	11.0		1.52	
3246	ISO17072-1	11.587		1.87	
	normality	OK			
	n	42			
	outliers	2			
	mean (n)	8.4385			
	st.dev. (n)	1.76111	RSD = 21%		
	R(calc.)	4.9311			
	st.dev.(EN16711-2:15)	1.68769			
	R(EN16711-2:15)	4.7255			

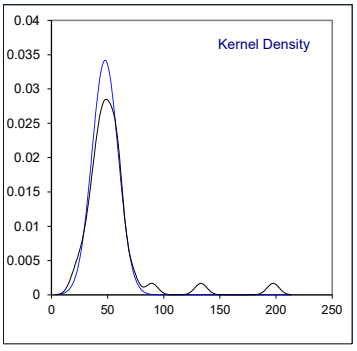




Determination of Chromium as Cr on sample #23755; results in mg/kg

lab	method	value	mark	z(targ)	remarks
210		-----		-----	
551	In house	39.78		-1.11	
623	EN16711-2	49.69		0.27	
840	ISO17072-1	43.9		-0.54	
841	ISO17072-1	59.7		1.67	
2120	ISO17072-1	57.3		1.34	
2129	ISO17072-1	33.534		-1.98	
2215	ISO17072-1	49.506		0.25	
2247	ISO17072-1	46.50		-0.17	
2250	ISO17072-1	46.61		-0.16	
2265	ISO17072-1	89.43	R(0.05)	5.82	
2301	ISO17072-1	<5		<-5.97	possible a false negative test result
2326	EN16711-2	43.207		-0.63	
2347	ISO17072-1	53.8		0.85	
2350	EN16711-2	44.049		-0.52	
2352	GB/T22930.1	60.260		1.75	
2358	ISO17072-1	52.901		0.72	
2365	ISO17072-1	55.94		1.15	
2370	ISO105E04	60.1		1.73	
2372	ISO17072-1	61.2		1.88	
2375	ISO17072-1	36		-1.64	
2378	ISO17072-1	58.27		1.47	
2379	ISO17072-1	60.2686		1.75	
2385	ISO17072-1	50		0.32	
2455	ISO17072-1	197.54	R(0.01)	20.92	
2495	ISO17072-1	24.18		-3.29	
2500	ISO17072-1	49.92	C	0.30	first reported: 5.78
2511	ISO17072-1	38.56		-1.28	
2561	ISO17072-1	20.20		-3.85	
2590	ISO17072-1	30.91		-2.35	
2637	ISO17072-1	56.8		1.27	
2711	ISO17072-1	36.8	C	-1.53	first reported: 88.6
2741	ISO17072-1	57.73		1.40	
2758	EN16711-2	133.164	R(0.01)	11.93	
2769		-----		-----	
2806	ISO17072-1	49.4		0.23	
2820	ISO17072-1	44.94		-0.39	
2826	ISO17072-1	49.0		0.18	
2881	ISO17072-1	41.49		-0.87	
2904	ISO17072-1	71.4	C	3.30	first reported: 108.006
2912	ISO17072-1	42.281		-0.76	
2977		-----		-----	
2985	ISO17072-1	28.00		-2.76	
2989		-----		-----	
3116	ISO17072-1	48.8		0.15	
3172	ISO17072-1	35.48		-1.71	
3210	ISO17072-1	40.54832		-1.00	
3243	ISO17072-1	57.4		1.35	
3246	ISO17072-1	70.965		3.24	
	normality	OK			
	n	41			
	outliers	3			
	mean (n)	47.7395			
	st.dev. (n)	11.66627	RSD = 24%		
	R(calc.)	32.6656			
	st.dev.(EN16711-2:15)	7.16093			
	R(EN16711-2:15)	20.0506			





APPENDIX 2

Reported test results of other requested elements on sample #23755; results in mg/kg

lab	Cd	Co	Cu	Pb	Hg	Ni
210	-----	-----	-----	-----	-----	-----
551	-----	-----	-----	-----	-----	-----
623	not detected	not detected	not detected	not detected	not detected	0.17
840	<0.01	<0.1	<1	<0.1	<0.006	<0.1
841	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1
2120	< 0,05	< 0.25	< 1.25	< 0,05	< 0,010	0.33
2129	not detected	not detected	not detected	not detected	not detected	not detected
2215	<0.02	<0.1	<5	<0.1	<0.005	<0.1
2247	<0.05	<0.3	<1.0	<1.0	<0.02	<0.1
2250	not detected	not detected	not detected	not detected	not detected	not detected
2265	not detected	not detected	not detected	not detected	not detected	not detected
2301	Not Detected	Not Detected	Not Detected	Not Detected	Not Detected	Not Detected
2326	ND	ND	ND	ND	ND	ND
2347	<0.05	<0.5	<5	<0.1	<0.01	<5
2350	< 0.02	< 0.1	< 5	< 0.06	< 0.005	0.159
2352	-----	-----	-----	-----	-----	-----
2358	not detected	not detected	not detected	not detected	not detected	not detected
2365	<0.03	<0.3	<5	<0.06	<0.02	<0.1
2370	<0.1	<0.1	<5	<0.2	<0.05	<0.5
2372	< 0.1	< 0.1	< 5	< 0.2	< 0.02	< 0.5
2375	<0.03	<0.3	<5	<0.06	<0.006	<0.1
2378	<0.03	<0.3	<5	<0.06	<0.02	<0.1
2379	Not detected	Not detected	Not detected	Not detected	Not detected	Not detected
2385	<0.1	<0.1	<5	<0.1	<0.01	<0.5
2455	2.02	-----	-----	ND <0.5	-----	-----
2495	<0.1	<0.1	<5	<1	<0.02	<0.1
2500	<0.05	<0.25	<5	<0.1	<0.02	<0.25
2511	-----	-----	-----	-----	-----	-----
2561	-----	-----	-----	-----	-----	-----
2590	< L.O.Q.	< L.O.Q.	< L.O.Q.	< L.O.Q.	< L.O.Q.	< L.O.Q.
2637	<0,005	0.005	0.17	<0,01	<0,005	0.16
2711	<5	<5	<5 C	<5	not analyzed	<5
2741	<0.05	<0.5	<5.0	<0.1	<0.02	<0.1
2758	not detected	not detected	not determined	not detected	not determined	0.903
2769	0.08	< 0,3 [LD]	< 0,3 [LD]	0.06	-----	< 0,3 [LD]
2806	not detected	not detected	0.1	not detected	not detected	not detected
2820	-----	-----	0.10	-----	-----	0.21
2826	Not detected	Not detected	Not detected	Not detected	Not detected	Not detected
2881	0	0	0.67	0	0	0.92
2904	0.9947	not detected	not detected	not detected	not detected	not detected
2912	<0.1	<0.1	<0.1	<0.1	<0.01	<0.1
2977	-----	-----	-----	-----	-----	-----
2985	not detected	not detected	0.06	not detected	not detected	not detected
2989	-----	-----	-----	-----	-----	-----
3116	<0.02	<0.1	<5	<0.1	<0.005	<0.1
3172	< 0.01	< 0.1	< 1	< 0.1	< 0.01	0.29
3210	<0.1	<1	<5	<0.2	<0.02	<1
3243	0.003	0.0058	0.42	0.071	0.007	0.115
3246	not detected	not detected	not detected	not detected	not detected	not detected

Lab 2711 first reported: 9.3

APPENDIX 3 Analytical details

lab	ISO/IEC17025 accredited	Sample preparation	Sample intake (grams)
210	---	---	
551	---	---	
623	Yes	Further cut	1 gram
840	Yes	Further cut	3.0g
841	Yes	Further cut	0.5 grams
2120	No	Further cut	2g
2129	---	---	
2215	Yes	Further cut	1.0054g
2247	Yes	Further cut	4.5gm
2250	Yes	Further cut	0,5
2265	No	Further cut	1 gram
2301	Yes	Further cut	1.0010
2326	Yes	Further cut	1.0091 GM
2347	No	Further cut	1g
2350	Yes	Further cut	approximately 1.0 g
2352	Yes	Further cut	2g
2358	Yes	Further cut	1.0
2365	Yes	Further cut	1g
2370	Yes	Further cut	1 g
2372	No	Further cut	1g
2375	Yes	Used as received	0.50 gram
2378	Yes	Further cut	2g
2379	Yes	Used as received	1 gram :50 ml
2385	Yes	Further cut	1 g
2455	No	Further grinded	2.0241 and 2.0064 grams
2495	Yes	Further cut	0.5
2500	No	Used as received	1.0103g
2511	Yes	Further cut	
2561	Yes		
2590	Yes	Used as received	1 g
2637	Yes	Further cut	0,5 g
2711	No	Further cut	1,0
2741	Yes	Further cut	2g
2758	No	Further grinded	1
2769	No	Used as received	2,0 g
2806	Yes	Further cut	2
2820	Yes	Used as received	2 g
2826	Yes	Used as received	0.5002g
2881	Yes	Further cut	1g
2904	No	Used as received	2 g x 2 replicates
2912	Yes	Used as received	1g
2977	---	---	
2985	Yes	Further cut	6g
2989	---	---	
3116	Yes	Further cut	0.5
3172	Yes	---	
3210	Yes	Further cut	1.0047
3243	Yes	Further cut	1.001g
3246	Yes	Used as received	0.3g

APPENDIX 4

Number of participants per country

1 lab in BRAZIL
1 lab in FRANCE
6 labs in GERMANY
3 labs in HONG KONG
1 lab in INDIA
2 labs in INDONESIA
9 labs in ITALY
1 lab in KOREA, Republic of
2 labs in MOROCCO
6 labs in P.R. of CHINA
2 labs in PAKISTAN
1 lab in POLAND
2 labs in PORTUGAL
1 lab in SWITZERLAND
2 labs in TAIWAN
1 lab in THAILAND
1 lab in TUNISIA
1 lab in TURKEY
1 lab in U.S.A.
1 lab in UNITED KINGDOM
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
E	= calculation difference between reported test result and result calculated by iis
W	= test result withdrawn on request of participant
ex	= test result excluded from statistical evaluation
n.a.	= not applicable
n.e.	= not evaluated
n.d.	= not detected
f+?	= possibly a false positive test result?
f-?	= possibly a false negative test result?

Literature

1 iis Interlaboratory Studies, Protocol for the Organisation, Statistics & Evaluation, June 2018
2 ISO5725:86
3 ISO5725 parts 1-6:94
4 ISO13528:05
5 M. Thompson and R. Wood, J. AOAC Int, 76, 926, (1993)
6 W.J. Youden and E.H. Steiner, Statistical Manual of the AOAC, (1975)
7 P.L. Davies, Fr. Z. Anal. Chem, 331, 513, (1988)
8 J.N. Miller, Analyst, 118, 455, (1993)
9 Analytical Methods Committee, Technical Brief, No 4, January 2001
10 P.J. Lowthian and M. Thompson, The Royal Society of Chemistry, Analyst, 127, 1359-1364, (2002)
11 W. Horwitz and R. Albert, J. AOAC Int, 79.3, 589-621, (1996)
12 Bernard Rosner, Percentage Points for a Generalized ESD Many-Outlier Procedure, Technometrics, 25(2), 165-172, (1983)

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