Institute for
Interlaboratory Studies

Results of Proficiency Test
Chromium (VI) in Leather/Footwear
April 2023

Organized by: Institute for Interlaboratory Studies
Spijkenisse, the Netherlands

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1 INTRODUCTION

Chromium (VI) is a toxic and mutagenic substance. In the leather industry Chromium containing substances could be used in the production process. Of all Chromium compounds, primarily Chromium (VI) was used, but this has been replaced by the less hazardous Chromium (III) in most applications. The regulations for the presence of Chromium (VI) for leather continue to become stricter. But even if no Chromium (VI) is used in the production of leather, it can still be formed from Chromium (III), when production or end-use circumstances are not controlled.

Since 2014 the Institute for Interlaboratory Studies (iis) organizes a proficiency scheme for the determination of Chromium (VI) in Leather/Footwear every year. During the annual proficiency testing program 2022/2023 it was decided to continue the proficiency test for the determination of Chromium (VI) in Leather/Footwear.

In this interlaboratory study 156 laboratories in 34 countries registered for participation, see appendix 3 for the number of participants per country. In this report the results of the Chromium (VI) 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 an ISO/IEC17025 accredited laboratory.
It was decided to send one aged vacuum sealed leather sample of 5 grams labelled #23545. The participants were asked to report the 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 red colored leather positive on Chromium (VI) was selected. The leather was grinded and aged. After homogenization about 175 plastic bags were filled with approximately 5 grams of leather, vacuumed sealed and labelled #23545.
The homogeneity of the subsamples was checked by determination of Chromium (VI) in accordance with ISO17075-2 on 8 stratified randomly selected subsamples.

	Chromium (VI) in mg/kg
sample #23545-1	5.1
sample #23545-2	4.7
sample #23545-3	4.3
sample #23545-4	5.1
sample #23545-5	4.7
sample #23545-6	4.7
sample #23545-7	5.0
sample #23545-8	4.8

Table 1: homogeneity test results of subsamples #23545

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.

	Chromium (VI) in mg/kg
r (observed)	0.7
reference test method	ISO17075-2:17
0.3 x R (reference test method)	0.9

Table 2: evaluation of the repeatability of subsamples #23545

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

To each of the participating laboratories one leather sample labelled #23545 was sent on March 8, 2023.

2.5 ANALYZES

The participants were requested to determine Chromium (VI) (colorimetric and/or chromatographic). To ensure homogeneity it was requested not to use less than 0.5 grams of the sample per determination. It was also requested to report if the laboratory was accredited to determine the reported component and to report some analytical details.

It was explicitly requested to treat the sample as if it was a routine sample, but not to age nor to dry the sample nor to determine volatile matter. The amount of sample was not sufficient to allow aging and/or determine the volatile matter content. Also, it was requested to keep the sample stored dark, dry, cool (4 – 10 °C) and vacuum packed until the start of extraction.

Furthermore, it was also requested to report the test results using the indicated units on the report form and not to round the 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 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.

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 some problems were encountered with the dispatch of the samples. Eleven participants reported test results after the final reporting date and five other participants did not report any test results. Not all participants were able to report all tests requested.
In total 151 participants reported 216 numerical test results. Observed were 5 outlying test results, which is 2.3%. In proficiency tests outlier percentages of 3% - 7.5% are quite normal.

Not all data sets proved to have a normal Gaussian distribution. These are referred to as “not OK” or “suspect”. The statistical evaluation of these data sets should be used with due care, see also paragraph 3.1.

4.1 EVALUATION PER TEST

In this section the reported test results are discussed per test. 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 4.

Chromium (VI) (colorimetric): This determination was not problematic. Two statistical outliers were observed. The calculated reproducibility after rejection of the statistical outliers is in agreement with the requirements of ISO17075-1:17.

Chromium (VI) (chromatographic): This determination was not problematic. Three statistical outliers were observed. The calculated reproducibility after rejection of the statistical outliers is in agreement with the requirements of ISO17075-2:17.

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 reference methods are presented in the next table.

Parameter	unit	n	average	2.8 * sd	R(lit)
Chromium (VI) (colorimetric)	mg/kg	125	5.62	2.04	2.69
Chromium (VI) (chromatographic)	mg/kg	86	5.70	1.76	3.03

Table 3: reproducibilities of tests on sample #23545

Without further statistical calculations it can be concluded that there is a good compliance of the group of participating laboratories with the reference test methods.

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

	April 2023	March 2022	May 2021	May 2020	May 2019
Number of reporting laboratories	151	139	152	142	148
Number of test results	216	189	204	193	192
Number of statistical outliers	5	2	5	8	7
Percentage of statistical outliers	2.3%	1.1%	2.5%	4.1%	3.6%

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 tests was compared to uncertainties observed in PTs over the years, expressed as relative standard deviation (RSD) of the PTs, see next table.

Component	April 2023	March 2022	May 2021	May 2020	2014 - 2019	R(lit)*)
Chromium (VI) (colorimetric)	13%	15%	10%	13%	11-33%	14-18%
Chromium (VI) (chromatographic)	11%	13%	11%	14%	6-31%	9-21%

Table 5: development of the uncertainties over the years

*) R(lit) calculated at 5 and 25 mg/kg respectively

The relative standard deviations observed in this PT are in line with the relative standard deviations observed in previous PTs.

4.4 EVALUATION OF THE ANALYTICAL DETAILS

More than 90% of the participants reported to use test method ISO17075 part 1 for colorimetric measurement or ISO17075 part 2 for the chromatographic analysis for the determination of Chromium (VI). For this PT some analytical details were requested which are listed in appendix 2. Based on the answers given by the participants the following can be summarized:

- Eighty-eight percent of the participants mentioned to be accredited for the determination of Chromium (VI) in leather.
- About ninety percent of the reporting participants used a sample intake between 1 and 2 grams.
- All participants, except one, reported to have measured a pH after extraction between pH 7 and pH 8, and thus in accordance with the test methods ISO17075-1 or ISO17075-2.

For both Chromium (VI) colorimetric and Chromium (VI) chromatographic the calculated reproducibilities are in agreement the requirements of the reference test method, therefore no separate statistical analysis has been performed.

5 DISCUSSION

As Chromium (VI) is carcinogenic, mutagenic and toxic for reproduction, the regulations within countries tend to adopt a zero-tolerance policy. In actual practice this means below the detection limit of the widely accepted test method ISO17075:2017 parts 1 and 2 of 3 mg/kg. Examples of regulations can be found in below table.

Chromium (VI)	Limit in mg/kg	Comment
OEKO-TEX® Leather	<2	Class: baby
OEKO-TEX® Leather	<200	For all other classes
EU regulation No 301/2014 amending Annex XVII to Regulation (EC) No 1907/2006 of the (REACH)	<3	Reported as dry weight only

Table 6: Regulation on Chromium (VI) in leather

When the results of this interlaboratory study were compared to these limits it may be noticed that all participants, except two, would have made identical decisions about the acceptability of the leather. Almost all participants would have rejected the sample.

6 CONCLUSION

It can be concluded that the group of participants have no problems with the determination of Chromium (VI) colorimetric and chromatographic in this proficiency test. However, each 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 Chromium (VI) (colorimetric) in sample #23545; results in mg/kg

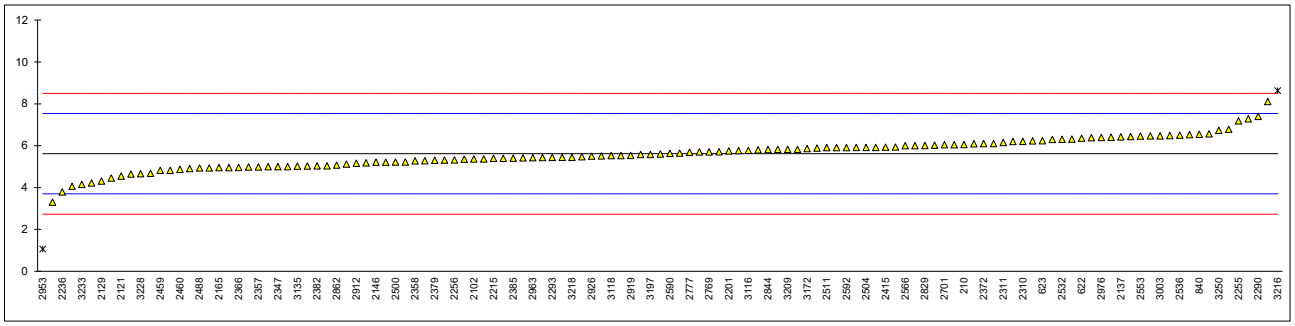
lab	method	value	mark	z(targ)	remarks
110		-----		-----	
210	ISO17075-1	6.05		0.45	
523		-----		-----	
551		5.525		-0.10	
622	ISO17075-1	6.35		0.76	
623	ISO17075-1	6.24		0.65	
840	ISO17075-1	6.54		0.96	
841	ISO17075-1	6.78		1.21	
2102	ISO17075-1	5.37		-0.26	
2115		-----		-----	
2121	ISO17075-1	4.548		-1.11	
2129	ISO17075-1	4.304		-1.37	
2131		-----		-----	
2132	ISO17075-1	5.82		0.21	
2137	ISO17075-1	6.418		0.83	
2146	ISO17075-1	5.21		-0.42	
2159	ISO17075-1	5.80		0.19	
2165	ISO17075-1	4.95		-0.70	
2201	ISO17075-1	5.746		0.13	
2215	ISO17075-1	5.395		-0.23	
2223		-----		-----	
2228		-----		-----	
2230	ISO17075-1	6.19		0.60	
2232	ISO17075-1	6.525		0.94	
2236	ISO17075-1	3.796		-1.90	
2247	ISO17075-1	6.23		0.64	
2250	ISO17075-1	5.435		-0.19	
2255	ISO17075-1	7.18		1.63	
2256	ISO17075-1	5.315		-0.32	
2287	ISO17075-1	5.438		-0.19	
2289	ISO17075-1	5.47		-0.15	
2290	ISO17075-1	7.4		1.86	
2291	ISO17075-1	5.88		0.27	
2293	ISO17075-1	5.436		-0.19	
2295	ISO17075-1	5		-0.64	
2310	ISO17075-1	6.2		0.61	
2311	ISO17075-1	6.15		0.55	
2326	ISO17075-1	5.023		-0.62	
2330	ISO17075-1	5.761		0.15	
2347	ISO17075-1	5.0		-0.64	
2350	ISO17075-1	6.3095		0.72	
2352	ISO17075-1	4.934		-0.71	
2357	ISO17075-1	4.98		-0.66	
2358	ISO17075-1	5.274		-0.36	
2363	ISO17075-1	5.033		-0.61	
2365	ISO17075-1	4.68		-0.98	
2366	ISO17075-1	4.96		-0.68	
2369	ISO17075-1	4.979		-0.67	
2370	ISO17075-1	5.18		-0.46	
2372	ISO17075-1	6.1		0.50	
2375	ISO17075-1	5.90		0.29	
2378	ISO17075-1	4.951		-0.69	
2379	ISO17075-1	5.300		-0.33	
2380	ISO17075-1	5.279		-0.35	
2382	ISO17075-1	5.03		-0.61	
2385	ISO17075-1	5.40		-0.23	
2410	ISO17075-1	7.28		1.73	
2415	ISO17075-1	5.925		0.32	
2449		-----		-----	
2459	ISO17075-1	4.82		-0.83	
2460	ISO17075-1	4.867		-0.78	
2475		-----		-----	
2486	ISO17075-1	6.405		0.82	
2488	ISO17075-1	4.931		-0.72	
2489	ISO17075-1	6.43		0.85	
2495		-----		-----	
2500	ISO17075-1	5.212		-0.42	
2504	ISO17075-1	5.908		0.30	
2511	ISO17075-1	5.9		0.29	
2515	ISO17075-1	6.092		0.49	
2523		-----		-----	
2532	ISO17075-1	6.3		0.71	
2536	ISO17075-1	6.497		0.92	
2538	ISO17075-1	5.91		0.30	

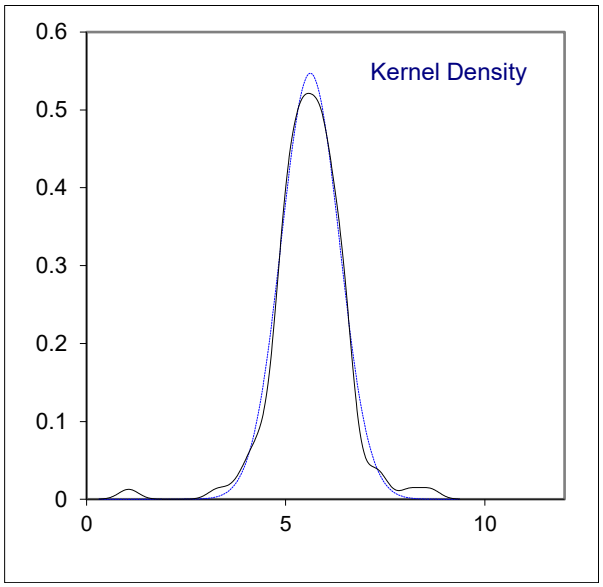
lab	method	value	mark	z(targ)	remarks
2549	ISO17075-1	5.907		0.30	
2553	In house	6.454		0.87	
2561		-----		-----	
2566	ISO17075-1	6.0		0.40	
2569	ISO17075-1	6.1		0.50	
2582		-----		-----	
2590	ISO17075-1	5.625		0.01	
2591	ISO17075-1	6.02		0.42	
2592	ISO17075-1	5.9018		0.30	
2605	ISO17075-1	5.42		-0.21	
2610		-----		-----	
2614		-----		-----	
2624	ISO17075-1	6.041		0.44	
2637	ISO17075-1	3.3		-2.41	
2643	ISO17075-1	5.51		-0.11	
2646	ISO17075-1	5.3514		-0.28	
2652	ISO17075-1	5.225		-0.41	
2656		-----		-----	
2666	ISO17075-1	6.48		0.90	
2668	ISO17075-1	5.64		0.02	
2674	ISO17075-1	4.82		-0.83	
2682	ISO17075-1	5.93		0.33	
2701	ISO17075-1	6.04		0.44	
2706		-----		-----	
2711		-----		-----	
2712	ISO17075-1	5.31		-0.32	
2734		-----		-----	
2743	ISO17075-1	5.21		-0.42	
2744	ISO17075-1	5		-0.64	
2749		-----		-----	
2751		4.45		-1.22	
2765	ISO17075-1	8.11		2.60	
2769	ISO17075-1	5.700		0.09	
2772	ISO17075-1	5.697		0.08	
2777		5.684		0.07	
2778	GB/T22807	6.383		0.80	
2806	ISO17075-1	6.298		0.71	
2823	ISO17075-1	5.578		-0.04	
2829	ISO17075-1	6.005		0.40	
2836		-----		-----	
2844	ISO17075-1	5.818		0.21	
2849	ISO17075-1	4.218		-1.46	
2858	ISO17075-1	6.46		0.88	
2862	ISO17075-1	5.07		-0.57	
2882	ISO17075-1	5.823		0.21	
2912	ISO17075-1	5.153		-0.48	
2919	ISO17075-1	5.531		-0.09	
2926	ISO17075-1	5.5	C	-0.12	first reported: 2.69
2953	ISO17075-1	1.06	R(0.01)	-4.75	
2963	ISO17075-1	5.425		-0.20	
2966		-----		-----	
2967		-----		-----	
2976	ISO17075-1	6.39		0.80	
2977		-----		-----	
2989	ISO17075-1	4.9001		-0.75	
2990	ISO17075-1	5.399		-0.23	
3003	ISO17075-1	6.46		0.88	
3016		-----		-----	
3100	ISO17075-1	5.37		-0.26	
3116	ISO17075-1	5.774		0.16	
3118	ISO17075-1	5.524		-0.10	
3135	In house	5.02		-0.62	
3146	ISO17075-1	5.711		0.10	
3153	ISO17075-1	5.12		-0.52	
3160	ISO17075-1	6.56		0.98	
3172	ISO17075-1	5.8624		0.25	
3179	ISO17075-1	6		0.40	
3192		-----		-----	
3197	ISO17075-1	5.58		-0.04	
3199	ISO17075-1	4.641210058		-1.02	
3209	ISO17075-1	5.82		0.21	
3210		-----		-----	
3216	ISO17075-1	8.62	C,R(0.01)	3.13	first reported: 9.18
3218	ISO17075-1	5.44		-0.18	
3228	ISO17075-1	4.66		-1.00	
3230	In house	4.0622		-1.62	
3233	ISO17075-1	4.15		-1.53	
3237		-----		-----	

lab	method	value	mark	z(targ)	remarks
3248	ISO17075-1	5.6		-0.02	
3250	ISO17075-1	6.73		1.16	
6191		-----		-----	
6428		-----		-----	

	normality	suspect
	n	125
	outliers	2
	mean (n)	5.618
	st.dev. (n)	0.7295
	R(calc.)	2.043
	st.dev.(ISO17075-1:17)	0.9602
	R(ISO17075-1:17)	2.689

RSD = 13%



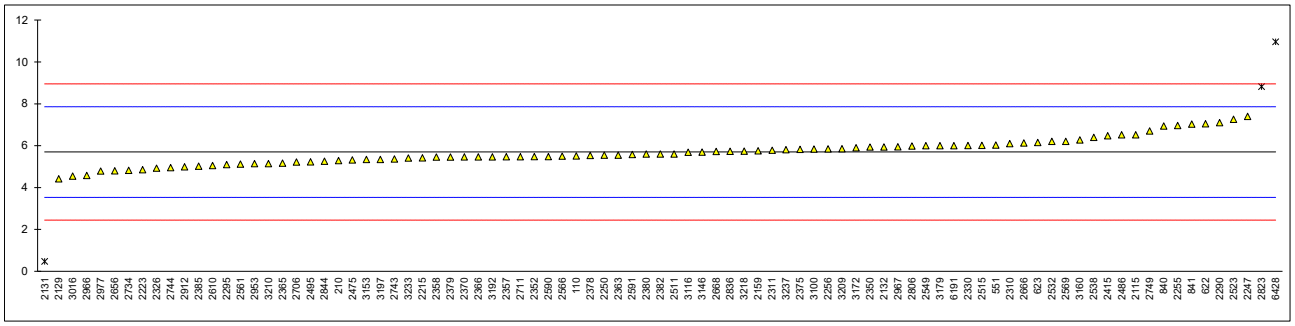


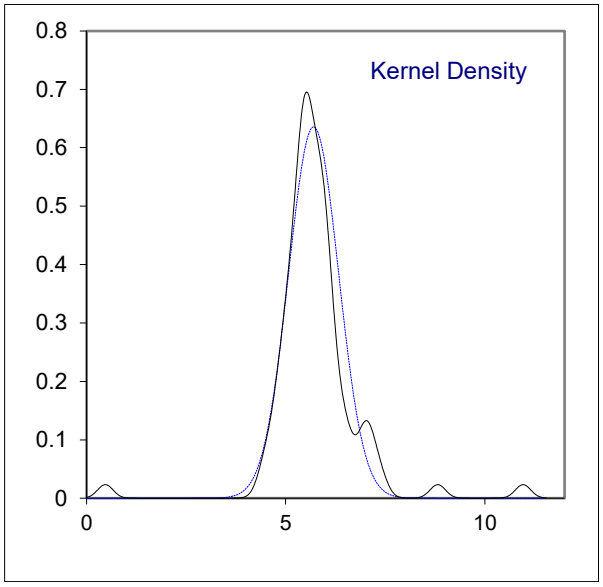
Determination of Chromium (VI) (chromatographic) in sample #23545; results in mg/kg

lab	method	value	mark	z(targ)	remarks
110	ISO17075-2	5.512		-0.17	
210	ISO17075-2	5.29		-0.38	
523		-----		-----	
551		6.026		0.30	
622	ISO17075-2	7.04		1.24	
623	ISO17075-2	6.15		0.42	
840	ISO17075-2	6.94		1.15	
841	ISO17075-2	7.03		1.23	
2102		-----		-----	
2115	ISO17075-2	6.52		0.76	
2121		-----		-----	
2129	ISO17075-2	4.418		-1.18	
2131	In house	0.47	R(0.01)	-4.83	
2132	ISO17075-2	5.94		0.22	
2137		-----		-----	
2146		-----		-----	
2159	ISO17075-2	5.75		0.05	
2165		-----		-----	
2201		-----		-----	
2215	ISO17075-2	5.420		-0.26	
2223	In house	4.85		-0.78	
2228		-----		-----	
2230		-----		-----	
2232		not analyzed		-----	
2236		-----		-----	
2247	ISO17075-2	7.40		1.57	
2250	ISO17075-2	5.5465		-0.14	
2255	ISO17075-2	6.96		1.16	
2256	ISO17075-2	5.842		0.13	
2287		-----		-----	
2289		-----		-----	
2290	ISO17075-2	7.1		1.29	
2291		-----		-----	
2293		-----		-----	
2295	ISO17075-2	5.1		-0.55	
2310	ISO17075-2	6.1		0.37	
2311	ISO17075-2	5.78		0.07	
2326	ISO17075-2	4.923		-0.72	
2330	ISO17075-2	6.008		0.28	
2347		-----		-----	
2350	ISO17075-2	5.9358		0.22	
2352	ISO17075-2	5.478		-0.20	
2357	ISO17075-2	5.47		-0.21	
2358	ISO17075-2	5.454		-0.23	
2363	ISO17075-2	5.547		-0.14	
2365	ISO17075-2	5.16		-0.50	
2366	ISO17075-2	5.46		-0.22	
2369		-----		-----	
2370	ISO17075-2	5.46		-0.22	
2372		-----		-----	
2375	ISO17075-2	5.82		0.11	
2378	ISO17075-2	5.535		-0.15	
2379	ISO17075-2	5.455		-0.23	
2380	ISO17075-2	5.599		-0.09	
2382	ISO17075-2	5.60		-0.09	
2385	ISO17075-2	5.02		-0.63	
2410		-----		-----	
2415	ISO17075-2	6.470		0.71	
2449		-----		-----	
2459		-----		-----	
2460		-----		-----	
2475	ISO17075-2	5.313		-0.36	
2486	ISO17075-2	6.517		0.75	
2488		-----		-----	
2489		-----		-----	
2495	ISO17075-2	5.23		-0.43	
2500		-----		-----	
2504		-----		-----	
2511	ISO17075-2	5.6		-0.09	
2515	ISO17075-2	6.015		0.29	
2523	ISO17075-2	7.260		1.44	
2532	ISO17075-2	6.2		0.46	
2536		-----		-----	
2538	ISO17075-2	6.4		0.65	

lab	method	value	mark	z(targ)	remarks
2549	ISO17075-2	6.000		0.28	
2553		-----		-----	
2561	ISO17075-2	5.12		-0.54	
2566	ISO17075-2	5.5		-0.18	
2569	ISO17075-2	6.2		0.46	
2582		-----		-----	
2590	ISO17075-2	5.478		-0.20	
2591	ISO17075-2	5.58		-0.11	
2592		-----		-----	
2605		-----		-----	
2610	ISO17075-2	5.05		-0.60	
2614		-----		-----	
2624		-----		-----	
2637		-----		-----	
2643		-----		-----	
2646		-----		-----	
2652		-----		-----	
2656	In house	4.8		-0.83	
2666	ISO17075-2	6.13		0.40	
2668	ISO17075-2	5.72		0.02	
2674		-----		-----	
2682		-----		-----	
2701		-----		-----	
2706	ISO17075-2	5.220		-0.44	
2711	ISO17075-2	5.47		-0.21	
2712		-----		-----	
2734	ISO17075-2	4.822		-0.81	
2743	ISO17075-2	5.37		-0.30	
2744	ISO17075-2	4.95		-0.69	
2749	ISO17075-2	6.70		0.92	
2751		-----		-----	
2765		-----		-----	
2769		-----		-----	
2772		-----		-----	
2777		-----		-----	
2778		-----		-----	
2806	ISO17075-2	5.984		0.26	
2823	ISO17075-2	8.817	R(0.01)	2.88	
2829		-----		-----	
2836	ISO17075-2	5.730		0.03	
2844	ISO17075-2	5.257		-0.41	
2849		-----		-----	
2858		-----		-----	
2862		-----		-----	
2882		-----		-----	
2912	ISO17075-2	4.991		-0.65	
2919		-----		-----	
2926		-----		-----	
2953	ISO17075-2	5.14		-0.52	
2963		-----		-----	
2966	ISO17075-2	4.575		-1.04	
2967		5.947		0.23	
2976		-----		-----	
2977	ISO17075-2	4.7848		-0.85	
2989		-----		-----	
2990		-----		-----	
3003		-----		-----	
3016	ISO17075-2	4.545		-1.07	
3100	ISO17075-2	5.84		0.13	
3116	ISO17075-2	5.685		-0.01	
3118		-----		-----	
3135		-----		-----	
3146	ISO17075-2	5.692		-0.01	
3153	ISO17075-2	5.34		-0.33	
3160	ISO17075-2	6.27		0.53	
3172	ISO17075-2	5.894		0.18	
3179	ISO17075-2	6		0.28	
3192	ISO17075-2	5.46		-0.22	
3197	ISO17075-2	5.34		-0.33	
3199		-----		-----	
3209	ISO17075-2	5.85		0.14	
3210	In house	5.144		-0.51	
3216		-----		-----	
3218	ISO17075-2	5.74		0.04	
3228		-----		-----	
3230		-----		-----	
3233	ISO17075-2	5.41	C	-0.27	first reported: 3.68
3237	ISO17075-2	5.81		0.10	

lab	method	value	mark	z(targ)	remarks
3248		-----		-----	
3250		-----		-----	
6191	ISO17075-2	6.0	C	0.28	first reported: 3.4
6428	ISO17075-2	10.960	R(0.01)	4.86	
	normality	OK			
	n	86			
	outliers	3			
	mean (n)	5.700			
	st.dev. (n)	0.6275	RSD = 11%		
	R(calc.)	1.757			
	st.dev.(ISO17075-2:17)	1.0826			
	R(ISO17075-2:17)	3.031			





APPENDIX 2 Analytical details

lab	ISO/IEC 17025 accredited	sample intake (g)	pH before extraction	pH after extraction
110	Yes	2.01g	8.1	9
210	Yes	2g	8	7,7
523	---	---	---	---
551	---	---	---	---
622	Yes	Simplo: 2.0034 g Duplo: 2.0028 g Quality control: 1.0019 g	7.98	7.66
623	Yes	1	7.99	7.71
840	Yes	1g	8.0	7.64
841	Yes	2g	8.0	7.8
2102	No	2 gram	7.96	7.75
2115	Yes	2 g	8	
2121	Yes	2g	8	7,7
2129	Yes	0,8 g	7,93	7,93
2131	No	2	---	---
2132	Yes	2	8.0	7.7
2137	Yes	1	8	7.6
2146	No	about 2 g	8,0	8,0
2159	Yes	1	8,0	7,9
2165	Yes	1.0g	8.0	7.7
2201	Yes	1.0127 g	pH=7.91	pH=7.68
2215	Yes	1.0009g	8.0	7.5
2223	Yes	2	8	7.5
2228	---	---	---	---
2230	Yes	1.0219g	8.0	7.5
2232	Yes	2.0018	8.00	7.64
2236	Yes	2.0114	7.97	7.96
2247	Yes	2gm	8.0	7.8
2250	Yes	2,0 g	8,0	7,7
2255	Yes	1.0	8.0	7.9
2256	Yes	ISO 17075-1: 1.0052g ISO 17075-2: 1.0040g	ISO 17075-1: 8.023 ISO 17075-2: 8.002	ISO 17075-1: 7.812 ISO 17075-2: 7.731
2287	Yes	1.0g	---	---
2289	Yes	1g	8.0	8.0
2290	Yes	---	---	---
2291	Yes	1.2007g and 1.0702g	8.00	7.98
2293	Yes	2.02	8.00	7.68
2295	Yes	2 grams	8 pH	8 pH
2310	Yes	2	8	7.8
2311	Yes	1	8	7.8
2326	Yes	2.0008	8.01	7.68
2330	Yes	1 g	8.0	7.7
2347	Yes	1g	8.0	7.9
2350	Yes	2.0048g	pH 7.96	pH 7.5
2352	Yes	1.0027g	8.0	7.9
2357	Yes	---	---	---
2358	Yes	2.0	7.9	7.7
2363	Yes	2g	8	7-8
2365	Yes	2.0g	7.99	7.71
2366	Yes	1g	---	---
2369	Yes	---	---	---
2370	Yes	0.5 g	pH 7.99	pH 7.66
2372	Yes	2g	7.929	7.537
2375	Yes	1 gram	8.0	7.8
2378	Yes	2g	8.0	7.8
2379	Yes	1 g/50 ml	pH= 8.00	pH= 7.92
2380	Yes	1.0 g	8.0	7.7
2382	Yes	1g	8.05	7.98
2385	Yes	1 g	8,0	7,8
2410	Yes	1 g	8.0	7.8
2415	Yes	1 GRAM	PH = 8.0	PH = 7.8
2449	Yes	1.02g	8.0	7.72
2459	---	---	---	---
2460	Yes	2 g	8.01	7.68
2475	No	1.002	8	7.5
2486	Yes	1.0081	8	7.9
2488	Yes	2	7.62	8.01
2489	Yes	1.02	8.0	7.72
2495	Yes	1	8.00	7.76
2500	Yes	1g	8.00	7.81

lab	ISO/IEC 17025 accredited	sample intake (g)	pH before extraction	pH after extraction
2504	Yes	1 gram	8.04	7.77
2511	---	2 g	9.023	7.986
2515	Yes	About 1 g	8.0	7.80
2523	Yes	1.5 grams.	8.0	7.69
2532	Yes	1 gram	8.0	7.81
2536	Yes	1.0004	8.0	7.9
2538	Yes	2/2/1 g	8,00 / 8,00 / 8,00	7,70 / 7,70 / 7,68
2549	Yes	2 grams	8.04	7.75
2553	Yes	1.0005	7.96	7.90
2561	Yes	2g	---	---
2566	Yes	1.0089gm	8.01	7.92
2569	Yes	1 gm	8	7.7
2582	---	---	---	---
2590	Yes	1g	7.50	7.37
2591	Yes	2.0 grams	---	---
2592	Yes	2	7.96	7.69
2605	Yes	4.0g	8.02	7.63
2610	Yes	2.0142	8.00	7.71
2614	---	---	---	---
2624	No	1,999	8,02	7,88
2637	---	---	---	---
2643	Yes	1 g	8.0	8.0
2646	Yes	2	8,066	7,62
2652	Yes	1.0052	8.0	7.8
2656	No	1 gram	8	not measured
2666	---	---	---	---
2668	Yes	1.0 gms	7.66	7.63
2674	Yes	1g	8.05	7.84
2682	Yes	2.001 gram	7.92	8.02
2701	No	5 g	8.01	7.92
2706	Yes	2	8.0	7.8
2711	No	1g	7.98	---
2712	Yes	2.0010 g	7.72	7.72
2734	Yes	4g	8,00	7,65
2743	Yes	1g	8,0	7,8
2744	Yes	2	8	7,60
2749	---	2 x 1 g	8.0	Zwischen 7 und 8
2751	Yes	2,0006	---	7,51
2765	Yes	2 g	8.0	7.7
2769	Yes	2,003	8,04	7,72
2772	Yes	5 grams	pH:8.03	pH:7.93
2777	Yes	1 gram	pH 8	pH 7.8
2778	No	4g	8.0±0.1	7.5
2806	Yes	About 2,0 gram	---	---
2823	No	2.0168g.	pH7.99.	pH7.68.
2829	Yes	2.01 g	8.00	7.64
2836	No	About 1.000g	pH= 8.0 +/- 0.1	pH= 7.67
2844	Yes	2.0085 2.0058	8.02	7.67
2849	Yes	2,00049	8,02	7,56
2858	Yes	2.0 gm	7.99	7.66
2862	Yes	2 x 1g	not determined	7,8
2882	Yes	2.003 GRAMS	8.00	7.61
2912	Yes	2 g	7.97	---
2919	No	2g	8,096	7,7
2926	No	2g	8,0	7,702
2953	Yes	1 grams	8.04	7.78
2963	Yes	1.0020g	8.02	7.79
2966	Yes	2,009	8,00	7,95
2967	No	2	8.07	7.77
2976	Yes	2.00g	8.00	7.86
2977	Yes	1g	8,01	8,01
2989	No	2gm	7.58	7.51
2990	Yes	1.0321g	8.0	7.7
3003	---	---	---	---
3016	No	I 1,0023 g, II 1,5050 g III 1,9947 g, IV 0,8719 g	8,00	I 7,80 II 7,74 III 7,7 IV 7,86
3100	Yes	2g	7.98	7.73
3116	Yes	1	7.9	7.6
3118	Yes	0.5	7.95	7.76
3135	Yes	Appr. 2 g	8.00	7.69
3146	Yes	One time 1.0020 g One time 2.0052 g and One time 2.0059 g	pH 8.0	pH 7.0 - 8.0

lab	ISO/IEC 17025 accredited	sample intake (g)	pH before extraction	pH after extraction
3153	Yes	0.5 gram	7.56	7.45
3160	Yes	1g/50 ml buffer	8.00	7.8
3172	Yes	1	8.00	7.68
3179	Yes	2g	---	---
3192	Yes	2g	8,0	7,6
3197	Yes	2g	8.00	7.67
3199	Yes	1.0124	7.94	7.77
3209	Yes	1g	7.9	7.9
3210	Yes	1.0044	8.03	7.76
3216	Yes	1st replicated=2,0044g / 2nd replicated=2,0014g	pH=8,00	pH=7,99
3218	Yes	2g	8.06	7.77
3228	Yes	2.0	7.8	7.0-8.0
3230	Yes	Duplicate analysis: 2.0244g/2.0160g	8.10	7.90
3233	No	1.0672	8	8.01
3237	Yes	2 gr	8,00	7,41
3248	Yes	2.0083 g	8.0	7.9
3250	Yes	1.0021	8.001	8.002
6191	Yes	2,0114 g	8,0	7,7
6428	Yes	1,955	8,05	7,8

APPENDIX 3

Number of participants per country

1 lab in	AUSTRIA
6 labs in	BANGLADESH
2 labs in	BRAZIL
2 labs in	CAMBODIA
1 lab in	CYPRUS
1 lab in	FINLAND
8 labs in	FRANCE
10 labs in	GERMANY
1 lab in	GUATEMALA
7 labs in	HONG KONG
10 labs in	INDIA
3 labs in	INDONESIA
17 labs in	ITALY
1 lab in	JAPAN
5 labs in	KOREA, Republic of
1 lab in	MAURITIUS
3 labs in	MEXICO
1 lab in	MOROCCO
25 labs in	P.R. of CHINA
6 labs in	PAKISTAN
3 labs in	POLAND
1 lab in	PORTUGAL
1 lab in	SINGAPORE
5 labs in	SPAIN
2 labs in	SRI LANKA
4 labs in	SWITZERLAND
6 labs in	TAIWAN
2 labs in	THAILAND
1 lab in	THE NETHERLANDS
1 lab in	TUNISIA
8 labs in	TURKEY
3 labs in	U.S.A.
2 labs in	UNITED KINGDOM
6 labs in	VIETNAM

APPENDIX 4

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
fr.	= first reported
f+?	= possibly a false positive test result?
f-?	= possibly a false negative test result?
SDS	= Safety Data Sheet

Literature

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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)
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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)