Institute for
Interlaboratory Studies

Results of Proficiency Test
Chromium (VI)
in Leather/Footwear
March 2022

Organized by: Institute for Interlaboratory Studies
Spijkenisse, the Netherlands

Author: ing. G.A. Oosterlaken-Buijs
Correctors: ing. R.J. Starink & ing. M. Meijer
Approved by: ing. A.S. Noordman-de Neef

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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 Of all Chromium compounds, primarily Chromium (VI) was used, but this has been replaced by the less hazardous Chromium (III) in most applications.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 2021/2022 it was decided to continue the proficiency test for the determination of Chromium (VI) in Leather/Footwear.

In this interlaboratory study 143 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 leather sample of 5 grams positive on Chromium (VI) and labelled #22540.
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 gray colored leather positive on Chromium (VI) was selected. The leather was grinded and aged. After homogenization about 185 plastic bags were filled with approximately 5 grams of leather each, vacuumed and labelled #22540.
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 #22540-1	5.4
sample #22540-2	4.6
sample #22540-3	5.2
sample #22540-4	5.4
sample #22540-5	4.8
sample #22540-6	5.3
sample #22540-7	5.4
sample #22540-8	4.8

Table 1: homogeneity test results of subsamples #22540

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)	0.9
reference test method	ISO17075-2:17
0.3 x R (reference test method)	0.9

Table 2: evaluation of the repeatability of subsamples #22540

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 sample labelled #22540 was sent on February 23, 2022.

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. Fourteen participants reported test results after the final reporting date and four other participants were not able to report any test results. Not all participants were able to report all tests requested.
In total 139 participants reported 189 numerical test results. Observed were 2 outlying test results, which is 1.1%. 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. No statistical outliers were observed. The calculated reproducibility is in full agreement with the requirements of ISO17075-1:17.

Chromium (VI) (chromatographic): 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 ISO17075-2:17.

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	123	8.02	3.31	3.60
Chromium (VI) (chromatographic)	mg/kg	64	7.79	2.75	3.39

Table 3: reproducibilities of tests on sample #22540

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 MARCH 2022 WITH PREVIOUS PTS

	March 2022	May 2021	May 2020	May 2019	April 2018
Number of reporting laboratories	139	152	142	148	162
Number of test results	189	204	193	192	190
Number of statistical outliers	2	5	8	7	2
Percentage of statistical outliers	1.1%	2.5%	4.1%	3.6%	1.1%

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, expressed as relative standard deviation (RSD) of the PTs, see next table.

Component	March 2022	May 2021	May 2020	May 2019	2015 - 2018	R(lit)*)
Chromium (VI) (colorimetric)	15%	10%	13%	11%	15-33%	14-18%
Chromium (VI) (chromatographic)	13%	11%	14%	6%	10-31%	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

The reported analytical details from the participants are listed in appendix 2.

- About 85% of the reporting participants mentioned to be accredited for the determination of Chromium (VI) in leather.
- About 90% of the reporting participants used a sample intake between 1 and 2 grams.
- A large difference was found for the time period between opening of the vacuum packed sample and extraction. About 60% of the participants analyzed the sample “immediately” or within 10 minutes. About 25% of the participants did the analyzes after 10 minutes and within one hour. About 15% of the participants started the extraction after 1 hour up to 20 days after opening of the vacuum packed sample.
- All participants, except one, reported to have measured a pH before and after extraction between pH 7 and pH 8, and thus in accordance with the test methods ISO17075-1:17 and ISO17075-2:17.

For Chromium (VI) colorimetric and Chromium (VI) chromatographic are the calculated reproducibilities in (full) 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.
Examples of regulations can be found in below table.

Chromium (VI)	Limit	Comment
OEKO-TEX® 100	<3 mg/kg	For all classes
EU: REGULATION No 301/2014 amending Annex XVII to Regulation (EC) No 1907/2006 of the (REACH)	<3 mg/kg	Implementation: 01-05-2014 Reported only as dry-weight

Table 6: Regulation on Chromium (VI)

When the results of this interlaboratory study were compared to these limits it may be noticed that almost all participants, except one, would make identical decisions about the acceptability of the leather. Almost all participants would have rejected sample #22540. Based on the colorimetric test result one participant would have released sample #22540.

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.

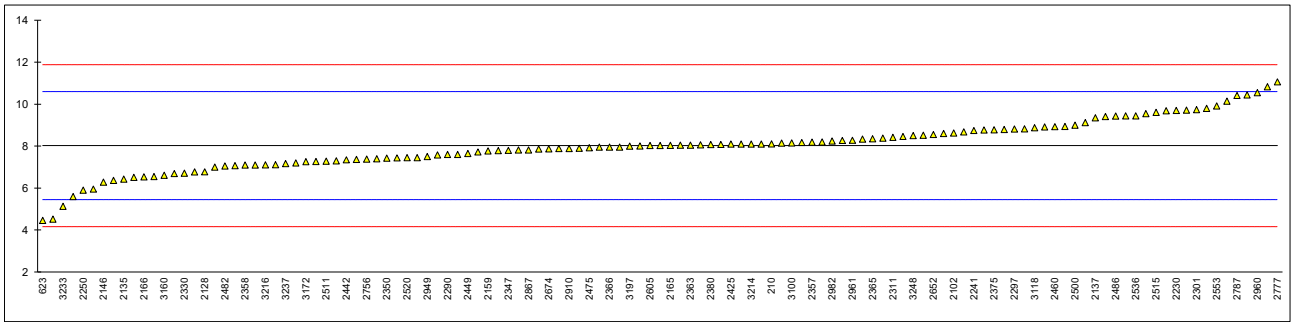
APPENDIX 1

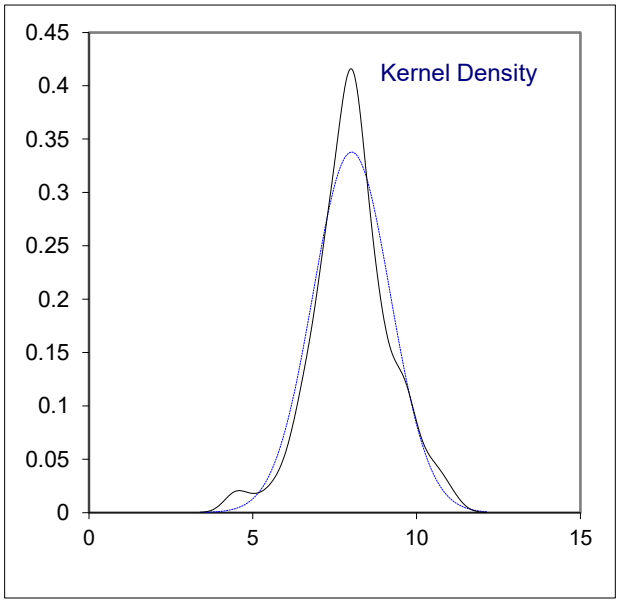
Determination of Chromium (VI) (colorimetric) in sample #22540; results in mg/kg

lab	method	value	mark	z(targ)	remarks
110	ISO17075-1	not analyzed		-----	
210	ISO17075-1	8.11		0.07	
362	ISO17075-1	9.545	C	1.18	first reported 12.53
523	ISO17075-1	7.88		-0.11	
551		-----		-----	
623	ISO17075-1	4.46	C	-2.77	first reported 3.43
840	ISO17075-1	7.9		-0.09	
841	ISO17075-1	7.44		-0.45	
1910	ISO17075-1	7.197		-0.64	
2102	ISO17075-1	8.621		0.47	
2115		-----		-----	
2120	ISO17075-1	5.60		-1.88	
2121	ISO17075-1	10.446		1.88	
2128	ISO17075-1	6.777		-0.97	
2132	ISO17075-1	7.9497		-0.06	
2135	ISO17075-1	6.43		-1.24	
2137	ISO17075-1	9.347		1.03	
2146	ISO17075-1	6.28		-1.35	
2159	ISO17075-1	7.77		-0.20	
2165	ISO17075-1	8.041		0.02	
2166	ISO17075-1	6.538		-1.15	
2201	ISO17075-1	8.334		0.24	
2215	ISO17075-1	8.772		0.58	
2223		-----		-----	
2228	ISO17075-1	8.169		0.11	
2230	ISO17075-1	9.7		1.30	
2232	ISO17075-1	9.685		1.29	
2241	ISO17075-1	8.74		0.56	
2250	ISO17075-1	5.9	C	-1.65	first reported 4.6
2256	ISO17075-1	8.045		0.02	
2290	ISO17075-1	7.6		-0.33	
2297	ISO17075-1	8.814		0.62	
2300	ISO17075-1	8.91		0.69	
2301	ISO17075-1	9.74		1.34	
2310	ISO17075-1	8.94		0.71	
2311	ISO17075-1	8.42		0.31	
2320	In house	6.766		-0.98	
2330	ISO17075-1	6.709		-1.02	
2347	ISO17075-1	7.8		-0.17	
2350	ISO17075-1	7.427		-0.46	
2352	ISO17075-1	7.720		-0.23	
2357	ISO17075-1	8.19		0.13	
2358	ISO17075-1	7.1		-0.72	
2363	ISO17075-1	8.046		0.02	
2365	ISO17075-1	8.35		0.26	
2366	ISO17075-1	7.95		-0.06	
2369	ISO17075-1	8.102		0.06	
2370	ISO17075-1	7.27		-0.58	
2375	ISO17075-1	8.78		0.59	
2378	GB/T22807	8.1		0.06	
2379	ISO17075-1	8.791		0.60	
2380	ISO17075-1	8.073		0.04	
2385	ISO17075-1	7.86		-0.13	
2390	ISO17075-1	8.146		0.10	
2425	ISO17075-1	8.10		0.06	
2426	ISO17075-1	8.01		-0.01	
2442	ISO17075-1	7.348		-0.52	
2449	ISO17075-1	7.65		-0.29	
2452	ISO17075-1	7.111		-0.71	
2460	ISO17075-1	8.929		0.71	
2475	ISO17075-1	7.927		-0.07	
2482	BVL B82-02-11	7.05		-0.75	
2486	ISO17075-1	9.437		1.10	
2500	ISO17075-1	9.0		0.76	
2504	ISO17075-1	10.829		2.18	
2511	ISO17075-1	7.2813		-0.58	
2515	ISO17075-1	9.613		1.24	
2520	ISO17075-1	7.45		-0.44	
2536	ISO17075-1	9.443		1.10	
2549	ISO17075-1	8.20		0.14	
2553	In house	9.912		1.47	
2561		-----		-----	
2566	ISO17075-1	9.44		1.10	
2573		-----		-----	

lab	method	value	mark	z(targ)	remarks
2582		-----		-----	
2590	ISO17075-1	8.08		0.05	
2591	ISO17075-1	7.07		-0.74	
2602	§ 64 BVL B82-02-11, mod	7.3		-0.56	
2605	ISO17075-1	8.03		0.01	
2610		-----		-----	
2624	ISO17075-1	7.396		-0.49	
2637	ISO17075-1	5.95		-1.61	
2643	ISO17075-1	8.033		0.01	
2649	ISO17075-1	7.6		-0.33	
2652	ISO17075-1	8.555		0.41	
2656		-----		-----	
2668	ISO17075-1	8.27		0.19	
2674	ISO17075-1	7.87		-0.12	
2675	ISO17075-1	9.127		0.86	
2695	ISO17075-1	not analyzed		-----	
2701	ISO17075-1	9.72		1.32	
2703		-----		-----	
2711		-----		-----	
2734		-----		-----	
2737	ISO17075-1	8.5150		0.38	
2749		-----		-----	
2756	ISO17075-1	7.38		-0.50	
2765	ISO17075-1	6.55		-1.14	
2777		11.066		2.37	
2778		10.150		1.65	
2787	ISO17075-1	10.416	C	1.86	first reported 20.738
2806	ISO17075-1	9.8		1.38	
2823	ISO17075-1	6.3649		-1.29	
2826	ISO17075-1	8.06		0.03	
2829	ISO17075-1	7.367		-0.51	
2844	ISO17075-1	7.1		-0.72	
2860	ISO17075-1	7.82		-0.16	
2867	ISO17075-1	7.82		-0.16	
2882	ISO17075-1	Not detectable		-----	possibly a false negative test result?
2910	ISO17075-1	7.886		-0.11	
2917	ISO17075-1	6.693		-1.03	
2926	ISO17075-1	7.785		-0.18	
2949	ISO17075-1	7.505		-0.40	
2955	ISO17075-1	8.6		0.45	
2960	ISO17075-1	10.550		1.97	
2961	ISO17075-1	8.280		0.20	
2963	ISO17075-1	8.82		0.62	
2967		-----		-----	
2977	ISO17075-1	not determined		-----	
2980	ISO17075-1	7		-0.79	
2982	ISO17075-1	8.24		0.17	
2989	ISO17075-1	7.4508		-0.44	
2990	ISO17075-1	8.383		0.28	
2994		8.68		0.51	
3100	ISO17075-1	8.1476		0.10	
3116	ISO17075-1	8.4643		0.34	
3118	ISO17075-1	8.8796		0.67	
3153	ISO17075-1	6.512		-1.17	
3154		-----		-----	
3160	ISO17075-1	6.61		-1.10	
3172	ISO17075-1	7.261		-0.59	
3197	ISO17075-1	8.0		-0.02	
3209	ISO17075-1	7.58		-0.34	
3210		-----		-----	
3214	ISO17075-1	8.1		0.06	
3216	ISO17075-1	7.11		-0.71	
3218		-----		-----	
3228	ISO17075-1	7.95		-0.06	
3230	In house	4.51552		-2.72	
3233	ISO17075-1	5.129		-2.25	
3237	ISO17075-1	7.17		-0.66	
3248	ISO17075-1	8.5		0.37	
3250	ISO17075-1	9.41		1.08	

normality	OK	
n	123	
outliers	0	
mean (n)	8.021	
st.dev. (n)	1.1808	RSD = 15%
R(calc.)	3.306	
st.dev.(ISO17075-1:17)	1.2868	
R(ISO17075-1:17)	3.603	





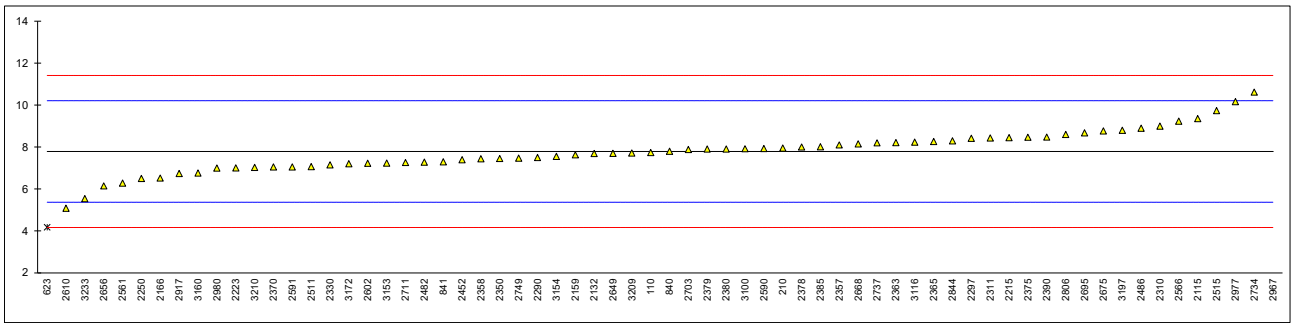
Determination of Chromium (VI) (chromatographic) in sample #22540; results in mg/kg

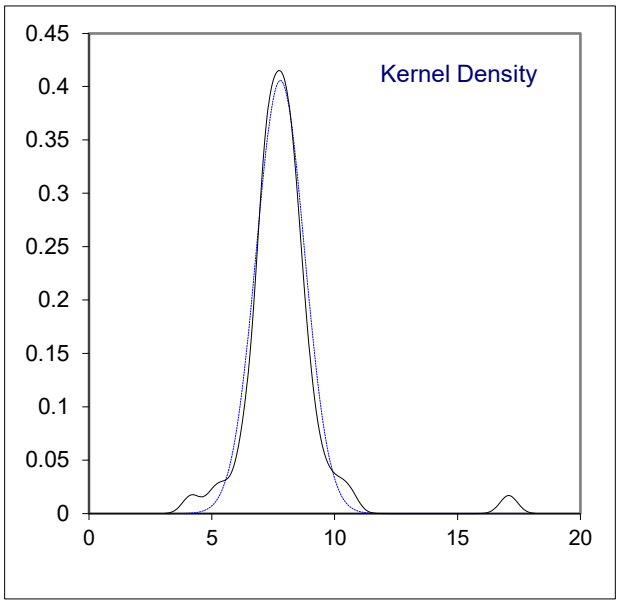
lab	method	value	mark	z(targ)	remarks
110	ISO17075-2	7.74		-0.04	
210	ISO17075-2	7.95		0.13	
362		-----		-----	
523		-----		-----	
551		-----		-----	
623	ISO17075-2	4.17	C,R(0.05)	-2.99	first reported 3.15
840	ISO17075-2	7.8		0.01	
841	ISO17075-2	7.3		-0.41	
1910		-----		-----	
2102		-----		-----	
2115	ISO17075-2	9.36		1.30	
2120		-----		-----	
2121		-----		-----	
2128		-----		-----	
2132	ISO17075-2	7.69		-0.08	
2135		-----		-----	
2137		-----		-----	
2146		-----		-----	
2159	ISO17075-2	7.63		-0.13	
2165		-----		-----	
2166	In house	6.519		-1.05	
2201	ISO17075-2	N/A		-----	
2215	ISO17075-2	8.444		0.54	
2223	In house	7.007		-0.65	
2228		-----		-----	
2230		-----		-----	
2232		-----		-----	
2241		-----		-----	
2250	ISO17075-2	6.5	C	-1.07	first reported 4.6
2256		-----		-----	
2290	ISO17075-2	7.5		-0.24	
2297	ISO17075-2	8.421		0.52	
2300		not analyzed		-----	
2301		-----		-----	
2310	ISO17075-2	9		1.00	
2311	ISO17075-2	8.43		0.53	
2320		-----		-----	
2330	ISO17075-2	7.147		-0.53	
2347		-----		-----	
2350	ISO17075-2	7.449		-0.28	
2352		-----		-----	
2357	ISO17075-2	8.10		0.26	
2358	ISO17075-2	7.44		-0.29	
2363	ISO17075-2	8.213		0.35	
2365	ISO17075-2	8.26		0.39	
2366		out of capability		-----	
2369		-----		-----	
2370	ISO17075-2	7.05		-0.61	
2375	ISO17075-2	8.47		0.56	
2378	GB/T38402	8.0		0.17	
2379	ISO17075-2	7.902		0.09	
2380	ISO17075-2	7.907		0.10	
2385	ISO17075-2	8.02		0.19	
2390	ISO17075-2	8.475		0.57	
2425		-----		-----	
2426		-----		-----	
2442		-----		-----	
2449		-----		-----	
2452	ISO17075-2	7.394		-0.33	
2460		-----		-----	
2475		-----		-----	
2482	ISO17075-2	7.28		-0.42	
2486	ISO17075-2	8.897		0.92	
2500		-----		-----	
2504		not applicable		-----	
2511	ISO17075-2	7.0609		-0.60	
2515	ISO17075-2	9.737		1.61	
2520		-----		-----	
2536		-----		-----	
2549		-----		-----	
2553		-----		-----	
2561	ISO17075-2	6.28		-1.25	
2566	ISO17075-2	9.24		1.20	
2573		-----		-----	

lab	method	value	mark	z(targ)	remarks
2582		-----		-----	
2590	ISO17075-2	7.93		0.12	
2591	ISO17075-2	7.05		-0.61	
2602	ISO17075-2	7.23		-0.46	
2605		-----		-----	
2610	ISO17075-2	5.08		-2.24	
2624		-----		-----	
2637		-----		-----	
2643		-----		-----	
2649	ISO17075-2	7.7		-0.07	
2652		-----		-----	
2656	In house	6.15		-1.36	
2668	ISO17075-2	8.15		0.30	
2674		-----		-----	
2675	ISO17075-2	8.768		0.81	
2695	ISO17075-2	8.6798		0.74	
2701		-----		-----	
2703	ISO17075-2	7.884646525		0.08	
2711	ISO17075-2	7.26		-0.44	
2734	ISO17075-2	10.62		2.34	
2737	ISO17075-2	8.200		0.34	
2749	ISO17075-2	7.47		-0.26	
2756		-----		-----	
2765		-----		-----	
2777		-----		-----	
2778		-----		-----	
2787		-----		-----	
2806	ISO17075-2	8.6		0.67	
2823		-----		-----	
2826		-----		-----	
2829		-----		-----	
2844	ISO17075-2	8.3		0.42	
2860		-----		-----	
2867		-----		-----	
2882		-----		-----	
2910		-----		-----	
2917	In house	6.738		-0.87	
2926		-----		-----	
2949		-----		-----	
2955		-----		-----	
2960		-----		-----	
2961		-----		-----	
2963		-----		-----	
2967	ISO17075-2	17.08	R(0.01)	7.68	
2977	ISO17075-2	10.17		1.97	
2980	ISO17075-2	7		-0.65	
2982		-----		-----	
2989		NA		-----	
2990		-----		-----	
2994		-----		-----	
3100	ISO17075-2	7.9176		0.11	
3116	ISO17075-2	8.2379		0.37	
3118		-----		-----	
3153	ISO17075-2	7.231		-0.46	
3154	ISO17075-2	7.56		-0.19	
3160	ISO17075-2	6.76		-0.85	
3172	ISO17075-2	7.203		-0.49	
3197	ISO17075-2	8.8		0.83	
3209	ISO17075-2	7.71		-0.07	
3210	In house	7.028		-0.63	
3214		-----		-----	
3216	ISO17075-2	Not Analyzed		-----	
3218		-----		-----	
3228		-----		-----	
3230	In house	not applicable		-----	
3233	ISO17075-2	5.537		-1.86	
3237		-----		-----	
3248		-----		-----	
3250		-----		-----	

normality	suspect
n	64
outliers	2
mean (n)	7.790
st.dev. (n)	0.9832
R(calc.)	2.753
st.dev.(ISO17075-2:17)	1.2095
R(ISO17075-2:17)	3.387

RSD = 13%





APPENDIX 2 Analytical details

lab	ISO/IEC 17025 accredited	sample intake (g)	time between opening of the vacuum packed sample and extraction (min)	pH before extraction	pH after extraction
110	Yes	2.0 gram	less than an hour	8.5	8.5
210	Yes				
362	Yes	2g	immediately	8.03	7.62
523	No	1.0 g	1.0 h	8.0	8.0
551	---				
623	Yes	1	5	7.99	7.72
840	Yes	1 gram	30 mins	8.0	7.85
841	Yes	1 grams	5 minutes	8.0	7.8
1910	Yes	2,00	7 min	8,01	7,60
2102	No	2 gram	12 hours	8.0	8.0
2115	Yes	1 g	immediately	8.0 pH	8.0 pH
2120	No	0,5 g	15 min	8,05	7,78
2121	Yes	m = 2.0089 g	5 minutes	pH = 8	pH = 7,6
2128	Yes	1-2 g	<5 min	pH 8,0	pH 7,9
2132	Yes ISO 17075-1 only	2 grams	less than 60 minutes	8.00	7.64
2135	Yes	1	10 min.	8,0	not tested
2137	Yes	1	1 min	8.01	7.92
2146	No	2,5 g	30 min	8,0	7,5
2159	Yes	1,0 g	90 minutes	7.9	7.7
2165	Yes	1.000g	immediately	8.0	7.6
2166	Yes	2 g	5 Min	8.09	7.66
2201	---	1.0124g	1hour	pH=7.90	pH=7.61
2215	Yes	1.0089	180min	8.0	7.5
2223	Yes	2 g		8	7.5 - 8
2228	Yes	1.0598	20	7.87	7.91
2230	Yes	1.0043	immediatly	pH=8.0	pH=7.7
2232	Yes	2grams	less than 1 minute	7.97	7.55
2241	Yes	2.0032 g	5 minutes	pH=7.98	pH=7.68
2250	Yes	2	24 h	8	8
2256	Yes	1.0032	1 minute	7.989	7.678
2290	Yes				
2297	Yes	1.0028	5	8.02	8.05
2300	Yes	2gram.	15 minutes	8.07	7.65
2301	Yes	1.0030	4 min	7.98	7.96
2310	Yes	1	Sample used as such	8	7.7
2311	Yes	2g		8	7.7
2320	Yes	1 g	15 Minutes	8.05	7.95
2330	Yes	1g	30 min	8.00	7.68
2347	---				
2350	Yes	2.0008g	immediately	pH 8.01	pH 7.81
2352	Yes	2.0060g	30min	8.01	7.65
2357	---				
2358	Yes	2.0 g	N/A	7.8	7.6
2363	Yes	2g*2	30mins	8	7-8
2365	Yes	2.0g	60min	7.96	7.85
2366	Yes	1	within 10minutes	7.9-8.1	7.0-8.0
2369	Yes	1g	less than 5 minutes	7.8	8
2370	Yes	2 g	30 min	pH = 8.0	pH = 7.7
2375	Yes	1g	5hours	8	7.7
2378	Yes	2g	30min	8	7.8
2379	Yes	1 g / 50 ml	Time opening = 10 minute Time extraction = 180 minute	pH = 8.00	pH = 7.86
2380	Yes	1.0 g	2 Minute	8.0	7.7
2385	Yes	2	5	8,0	7,6
2390	Yes	2.0020g	5 min	8.00	7.62
2425	Yes	1.0 g	10 minutes		
2426	Yes	2.0073	within 30 min	8.01	7.6
2442	Yes	2g	5 minutes	8.01	7.9
2449	Yes	1.0 GRAM	01 HOUR	8.0	7.6
2452	Yes	1	60	8	7.7
2460	Yes	2 g	5 min then 180 min in extraction	8.02	7.64
2475	No	2.11g	Few minutes	8	7.6
2482	Yes	1.0 g	up to 30 min		
2486	Yes	1.008 g	10 minutes	8.0	7.90
2500	Yes	about 1 g	30min	8.2	7.8
2504	Yes	1.00 g	20 minutes	8.02	7.7
2511	Yes				
2515	Yes	About 1 g	30 minutes	8.0	7.69
2520	No	2gm	240 minutes	8	7.23
2536	No	1.0033	Immediately within 5 minuets	8.0	7.9
2549	Yes	2 grams	10 mins	8.0	7.9
2553	Yes	1g	180mins	8.0	8.0
2561	Yes	2	10	8	8

lab	ISO/IEC 17025 accredited	sample intake (g)	time between opening of the vacuum packed sample and extraction (min)	pH before extraction	pH after extraction
2566	Yes	1.0002 gm	within minute	8.0	7.6
2573	---				
2582	---				
2590	Yes	1g	10 min	8.01	7.7
2591	Yes	2.0 grams	30 mins	7.6	7.6
2602	Yes	1,00 g	about 30 min	8,03	7,65
2605	Yes	4g	30min	8.02	7.80
2610	Yes	2.0499	5 minutes	8.00	7.56
2624	No	4	30	8.04	8
2637	Yes	500 mg	1 h		
2643	Yes	1 g	about 5 minutes	7.9	7.9
2649	Yes	2 grams	10 mins	7.0 to 8.0	7.0 to 8.0
2652	Yes	1.0080g	10mins	8.04	8.01
2656	No	1 gram	30 min	8	-
2668	Yes	1.0 gms	Immediately after open	8.0	7.7
2674	Yes	1g*2	30min	8.01	7.68
2675	Yes	2 g	5 Minuten	8,00	7,58
2695	Yes	2	10 minutes	7.94	7.64
2701	Yes	1g	3.5 hour	8.00	7.94
2703	Yes	2.0157g	Unrecorded	pH 8.0 +/- 0.1	7.65
2711	No	1.019g	Abaut 10 minutes	8.034	7.657
2734	Yes	2g	10	8,0	
2737	Yes	1g	120min	8.01	7.98
2749	No	2 x 1 g	5 Minuten	8.0	7 - 8
2756	Yes				
2765	Yes	2	15	7.6	7.7
2777	Yes	1.0gram	1 hour	7.99	7.94
2778	Yes	4g	20mins	8.0±0.1	7.6
2787	Yes	2 g	1 min	7,9	7,7
2806	Yes				
2823	Yes	2.0089g	Less than 5 minutes.	pH 8.07.	pH 7.65.
2826	Yes	2g	1 week	8.0	7.5
2829	Yes	2	5	8	7.7
2844	Yes ISO17025-2 only	2.0201 g/ 2.0250 g	30 min	8.010	7.651
2860	Yes	1,0000 g	30 min	7,91	7,77
2867	Yes	2.0g	one hour	8.00	7.77
2882	Yes	2 gram	5 min	8.01	between 7 & 8
2910	Yes	1.0g	30minutes	8.0	7.6
2917	Yes	1) 2.0183 2) 2.0466	less than 5 minutes	pH 8,00	pH 7,59/ pH 7,48
2926	No	2.01g	5 minutes	7.92	7.55
2949	No	2.0 g	5 min	8.01	7.55
2955	Yes	1.0		8.0	8.0
2960	Yes	4.0 gram	Within 30 minutes	8.04	7.67
2961	No	1 g	5 min	8	7.5-8
2963	Yes	2.0076g	2min	7.95	7.69
2967	No	2,0 grams	10 minutes	8.03	7.63
2977	No	4 g	20 days	8,00	7,98
2980	No	2	10	8.0	7.6
2982	Yes	2.0g	5 mins	7.9	7.7
2989	No	2 gms	2 min	8.0	7.5
2990	Yes	about 4 grams	5 minutes	7.94	7.58
2994	No	0.5045g	5 days	8.00	7.73
3100	Yes	2g	2min	8.00	7.72
3116	Yes	1 gram	Immediately	7.9	7.6
3118	Yes	1 gram	15 minutes	7.99	7.77
3153	Yes	0.5 gram	10 minutes	7.6	7.41
3154	Yes	1			
3160	Yes	1 gram	10 minutes	8,0	7,8
3172	---	1	5	8.00	7.62
3197	Yes	2	10	8,0	7,7
3209	Yes	1g	2min	7.9	7.5
3210	Yes	1,001	14	7,98	7,72
3214	Yes	1g	10mins	7.938	7.620
3216	Yes	2,046g / 2,026g	time to weigh the sample	pH = 8,01	pH = 7,99
3218	---				
3228	---	2.0	Less than 10min	8.0	7.0 - 8.0
3230	Yes	2.0052g / 2.0056g	6-8 minutes	8.02	7.55
3233	No	1.0698g	Less than 15 min	8.01	8.02
3237	Yes	2g	the same time	8,02	7,72
3248	Yes	2	4 minutes	8.03	7.60
3250	Yes	1	5-10 mins	8	8

APPENDIX 3

Number of participants per country

8 labs in	BANGLADESH
2 labs in	BRAZIL
1 lab in	BULGARIA
2 labs in	CAMBODIA
2 labs in	EGYPT
1 lab in	ETHIOPIA
1 lab in	FINLAND
7 labs in	FRANCE
11 labs in	GERMANY
8 labs in	HONG KONG
6 labs in	INDIA
3 labs in	INDONESIA
11 labs in	ITALY
4 labs in	KOREA, Republic of
1 lab in	MAURITIUS
4 labs in	MEXICO
1 lab in	MOROCCO
29 labs in	P.R. of CHINA
5 labs in	PAKISTAN
1 lab in	POLAND
1 lab in	PORTUGAL
2 labs in	SERBIA
1 lab in	SINGAPORE
5 labs in	SPAIN
3 labs in	SRI LANKA
3 labs in	SWITZERLAND
3 labs in	TAIWAN
2 labs in	THAILAND
1 lab in	THE NETHERLANDS
2 labs in	TUNISIA
4 labs in	TURKEY
1 lab in	U.S.A.
3 labs in	UNITED KINGDOM
4 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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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)