Results of Proficiency Test
Chromium (VI) in Leather
May 2020

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Organized by: Institute for Interlaboratory Studies
Spijkenisse, the Netherlands

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CONTENTS

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 Of all Chromium compounds, primarily Chromium (VI) was used, but this has been replaced by the less hazardous Chromium (III) in most applications.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 test for the determination of Chromium (VI) in Leather every year. During the annual proficiency testing program 2019/2020 it was decided to continue the proficiency test for the analysis of Chromium (VI) in Leather.

In this interlaboratory study 147 laboratories in 34 different countries registered for participation. See appendix 3 for the number of participating participants per country. In this report the results of this 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. 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), labelled #20585. 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 a 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 dark green colored leather positive on Chromium 6+ was obtained from a local market. The leather material was grinded and aged. After thoroughly mixing 170 plastic bags were filled with approximately 5 grams of leather, vacuumed and labelled #20585. The homogeneity of the subsamples was checked by determination of Chromium (VI) in accordance with ISO17075-1 on 8 stratified randomly selected subsamples.

	Chromium (VI) in mg/kg
Sample #20585-1	5.641
Sample #20585-2	5.563
Sample #20585-3	5.734
Sample #20585-4	6.016
Sample #20585-5	5.859
Sample #20585-6	5.938
Sample #20585-7	5.891
Sample #20585-8	5.859

Table 1: homogeneity test results of subsamples #20585

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)	0.431
reference test method	ISO17075-1:17
0.3 * R (ref. test method)	0.829

Table 2: evaluation of the repeatability of subsamples #20585

The calculated repeatability was 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 #20585 was sent on April 15, 2020.

2.5 ANALYZES

The participants were requested to determine the content of Chromium (VI) on a leather sample applying the analysis procedure that is routinely used in the laboratory.
It was requested, to ensure homogeneity, to not use less than 0.5 grams per determination.

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 and cool (4 – 10°C) and keep sample 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 and 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 appropriate 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 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 re-analyzes). Additional or corrected test results are used for data analysis and 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 in the report ’iis Interlaboratory Studies: Protocol for the Organization, 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 in general not used in the statistical evaluation.

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

According to ISO5725, the original test results per determination were submitted to Dixon's and/or Grubbs' and/or Rosner's outlier tests. Outliers are marked by D(0.01) for the Dixon's test, by G(0.01) or DG(0.01) for the Grubbs' test and by R(0.01) for the Rosner's test. Stragglers are marked by D(0.05) for the Dixon's test, by G(0.05) or DG(0.05) for the Grubbs' test and by R(0.05) for the Rosner's test. Both outliers and stragglers were not included in the calculations of the averages and the standard deviations.

For each assigned value, the uncertainty was determined in accordance with ISO13528. Subsequently the calculated uncertainty was evaluated against the respective requirement based on the target reproducibility in accordance with ISO13528. In this PT, the criterion of ISO13528, paragraph 9.2.1. was met for all evaluated tests, therefore, the uncertainty of all assigned values may be negligible and need not be included in the PT report.

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

3.2 GRAPHICS

In order to visualize the data against the reproducibilities from literature, Gauss plots were made, using the sorted data for one determination (see appendix 1). On the Y-axis the reported test results are plotted. The corresponding laboratory numbers are on the X-axis. The straight horizontal line presents the consensus value (a trimmed mean). The four striped lines, parallel to the consensus value line, are the +3s, +2s, -2s and -3s target reproducibility limits of the selected reference test method. Outliers and other data, which were excluded from the calculations, are represented as a cross. Accepted data are represented as a triangle.

Furthermore, Kernel Density Graphs were made. The Kernel Density Graph is a method for producing a smooth density approximation to a set of data that avoids some problems associated with histograms. Also, a normal Gauss curve was projected over the Kernel Density Graph for reference.

3.3 Z-SCORES

To evaluate the performance of the participating laboratories the z-scores were calculated. As it was decided to evaluate the performance of the participants in this proficiency test (PT) against the literature requirements, 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. In general, when no literature reproducibility is available, another target may be 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 results 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 result tables in appendix 1.

Absolute values for z<2 are very common and absolute values for z>3 are very rare. The usual interpretation of z-scores is as follows:

	$\lvert z \rvert < 1$	good
$1 <$	$\lvert z \rvert < 2$	satisfactory
$2 <$	$\lvert z \rvert < 3$	questionable
$3 <$	$\lvert z \rvert$	unsatisfactory

4 EVALUATION

In this interlaboratory study some problems were encountered with the dispatch of the samples due to the COVID-19 pandemic. Seven participants reported after the final reporting date and five participants did not report any test results at all.
In total 142 participants reported 193 numerical results. Observed were 8 outlying test results, which is 4.1% of the numerical results. In proficiency studies, outlier percentages of 3% - 7.5% are quite normal.

Not all original 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 problematic for a number of laboratories at a concentration level of 5.9 mg/kg. Six statistical outliers were observed. However, 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 at a concentration level of 6.0 mg/kg. Two statistical outliers were observed. However, 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 found for the group of participating laboratories and the target reproducibility as derived from the reference test method. The number of significant test results, the average, the calculated reproducibility (2.8 * standard deviation) and the target reproducibility derived from literature reference test methods are presented in the next table.

Parameter	unit	n	average	2.8 * sd	R(lit.)
Chromium (VI) (colorimetric)	mg/kg	124	5.86	2.11	2.78
Chromium (VI) (chromatographic)	mg/kg	61	6.00	2.32	3.09

Table 3: reproducibilities of tests on sample #20585

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

4.3 COMPARISON OF THE PROFICIENCY TEST OF MAY 2020 WITH PREVIOUS PTS

	May 2020	May 2019	April 2018	April 2017	April 2016
Number of reporting laboratories	142	148	162	163	145
Number of test results	193	192	190	183	144
Number of statistical outliers	8	7	2	5	6
Percentage of statistical outliers	4.1%	3.6%	1.1%	2.7%	4.2%

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	May 2019	May 2019	April 2018	April 2017	2015 - 2016	Target
Chromium (VI) (colorimetric)	13%	11%	31%	15%	29-33%	15%
Chromium (VI) (chromatographic)	14%	6%	31%	10%	n.e.	18%

Table 5: development of the uncertainties over the years

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 test methods ISO17075-1 and ISO17075-2 are used by almost all of the reporting participants for the determination of Chromium (VI) with colorimetric and chromatographic method respectively.
For this PT also some analytical details were requested, the data is given in appendix 2.
Based on the answers given by the participants the following can be summarized:
About 85% of the reporting participants mentioned that they are accredited for the determination of Chromium (VI) in Leather.
About 95% of the reporting participants used a test portion between 1 and 2 grams.
A large different was found for the time period between grinding/cutting and extraction.
About 55% of the participants analyzed the sample “immediately” or within 10 minutes. About 35% of the participants did the analyzes after 10 minutes but within the hour. About 10% of the participants started with analyzing the sample after 1 hour up to 3 days after grinding/cutting the sample and extraction.
All participants, except two, reported to have found the pH before and after extraction between pH 7 and pH 8 and thus in accordance with the test methods ISO17075-1:2017 and ISO17075-2:2017.
Also, the type and frequency of the shaker were requested to report. Several types of shakers were mentioned. For example, “horizontal”, “orbital” or “mechanical”. About 80% of the reporting participants used a frequency of 100 ±10 rpm.

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 will mean 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
Germany: SG (Schadestoff gepruft) – label	< 3 mg/kg	As well for aging as non-aging
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 this limit, it may be noticed that all participants would make identical decisions about the acceptability of the leather. When using a limit of <3 mg/kg and applying it to the reported test results for sample #20585 all participants would not release this sample to the consumer market.

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.

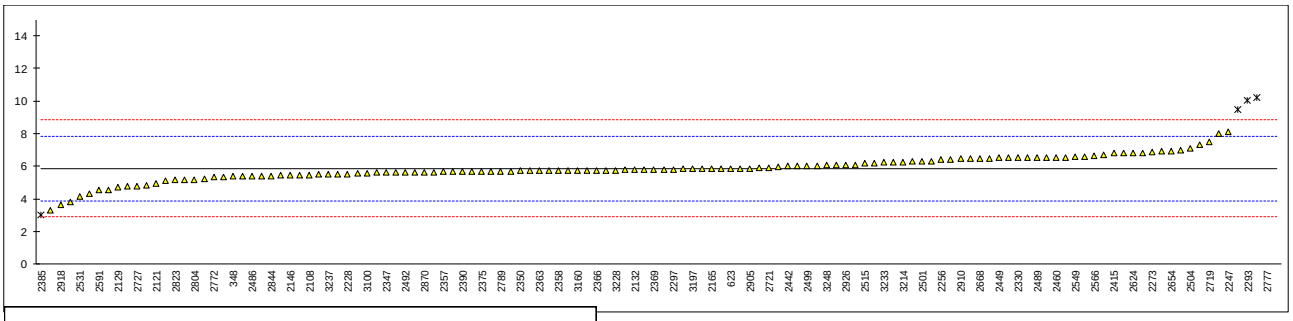
APPENDIX 1

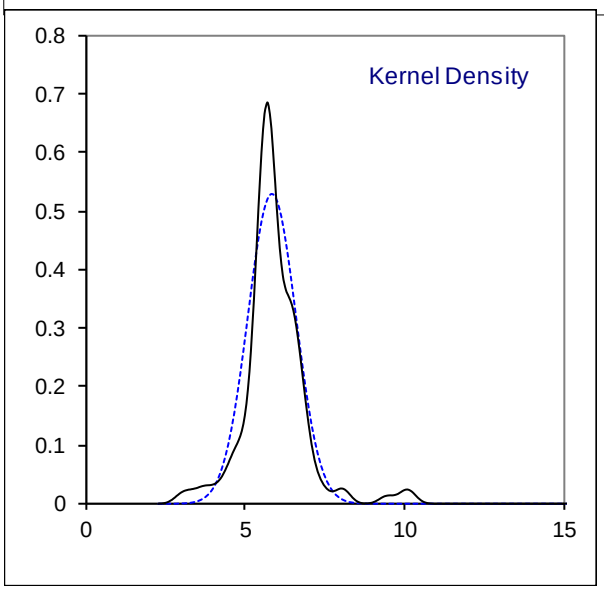
Determination of Chromium (VI) (colorimetric) in sample #20585; results in mg/kg

lab	method	value	mark	z(targ)	remarks
210	ISO17075-1	4.57		-1.30	
230		-----		-----	
339		-----		-----	
348	ISO17075-1	5.369		-0.49	
362	ISO17075-1	5.71		-0.15	
551	ISO17075-1	6.4558		0.60	
623	ISO17075-1	5.85		-0.01	
840	ISO17075-1	5.56		-0.30	
841	ISO17075-1	6.9		1.05	
2102	ISO17075-1	3.819		-2.05	
2108	ISO17075-1	5.47		-0.39	
2115	ISO17075-1	6.20		0.34	
2118	ISO17075-1	5.944		0.09	
2121	ISO17075-1	4.924		-0.94	
2128	ISO17075-1	6.282		0.43	
2129	ISO17075-1	4.73		-1.14	
2132	ISO17075-1	5.775		-0.08	
2146	ISO17075-1	5.4484		-0.41	
2159	ISO17075-1	6.50		0.65	
2165	ISO17075-1	5.84		-0.02	
2201	ISO17075-1	5.828		-0.03	
2215	ISO17075-1	6.70		0.85	
2228	ISO17075-1	5.520		-0.34	
2230	ISO17075-1	5.359		-0.50	
2232	ISO17075-1	5.80		-0.06	
2236	ISO17075-1	3.3071		-2.57	
2247	ISO17075-1	8.12		2.28	
2250		-----		-----	
2256	ISO17075-1	6.403		0.55	
2273	ISO17075-1	6.89		1.04	
2290	ISO17075-1	6.8		0.95	
2293	ISO17075-1	10.02	R(0.01)	4.19	
2297	ISO17075-1	5.81		-0.05	
2301	ISO17075-1	5.40		-0.46	
2310	ISO17075-1	6.30		0.44	
2311	ISO17075-1	5.6		-0.26	
2330	ISO17075-1	6.508		0.65	
2347	ISO17075-1	5.6		-0.26	
2350	ISO17075-1	5.7077		-0.15	
2352	ISO17075-1	5.6		-0.26	
2357	ISO17075-1	5.65		-0.21	
2358	ISO17075-1	5.73		-0.13	
2363	ISO17075-1	5.72		-0.14	
2365	ISO17075-1	5.66		-0.20	
2366	ISO17075-1	5.74		-0.12	
2369	ISO17075-1	5.80		-0.06	
2370	ISO17075-1	5.68		-0.18	
2375	ISO17075-1	5.7		-0.16	
2378	ISO17075-1	5.5		-0.36	
2379	ISO17075-1	5.098		-0.77	
2380	ISO17075-1	6.52		0.67	
2382	ISO17075-1	5.77		-0.09	
2385	ISO17075-1	3.01	R(0.05)	-2.87	
2390	ISO17075-1	5.68		-0.18	
2410	ISO17075-1	10.2	R(0.01)	4.37	
2415	ISO17075-1	6.80		0.95	
2425	ISO17075-1	6.49		0.64	
2442	ISO17075-1	6.01		0.15	
2449	ISO17075-1	6.5		0.65	
2460	ISO17075-1	6.521		0.67	
2462	ISO17075-1	6.26		0.40	
2475		-----		-----	
2482	ISO17075-1	6.10		0.24	
2486	ISO17075-1	5.4		-0.46	
2489	ISO17075-1	6.52		0.67	
2492	ISO17075-1	5.62		-0.24	
2499	ISO17075-1	6.02		0.16	
2500	ISO17075-1	6.61		0.76	
2501	ISO17075-1	6.29		0.43	
2504	ISO17075-1	7.10		1.25	
2508	ISO17075-1	7.32		1.47	
2511	ISO17075-1	5.7		-0.16	
2515	ISO17075-1	6.17		0.31	
2523		-----		-----	

lab	method	value	mark	z(targ)	remarks
2531	ISO17075-1	4.13		-1.74	
2538	ISO17075-1	5.84		-0.02	
2549	ISO17075-1	6.6		0.75	
2553	ISO17075-1	6.82		0.97	
2561		-----		-----	
2563	ISO17075-1	4.81		-1.06	
2566	ISO17075-1	6.65		0.80	
2573	ISO17075-1	5.82		-0.04	
2590	ISO17075-1	4.767		-1.10	
2591	ISO17075-1	4.53		-1.34	
2605	ISO17075-1	5.49		-0.37	
2610		-----		-----	
2624	ISO17075-1	6.809		0.96	
2652	ISO17075-1	6.42		0.56	
2654	ISO17075-1	6.92		1.07	
2656		-----		-----	
2664	ISO17075-1	5.25		-0.61	
2668	ISO17075-1	6.46		0.61	
2674	ISO17075-1	5.73		-0.13	
2682	ISO17075-1	6.04		0.18	
2695	ISO17075-1	5.6225		-0.24	
2701	ISO17075-1	9.4693	R(0.01)	3.64	
2703		-----		-----	
2711		-----		-----	
2712	ISO17075-1	5.858		0.00	
2719	ISO17075-1	7.5		1.65	
2721	ISO17075-1	5.92		0.06	
2727	ISO17075-1	4.78		-1.09	
2730		-----		-----	
2737	ISO17075-1	6.51		0.66	
2749		-----		-----	
2772	ISO17075-1	5.326		-0.54	
2777	GB/T22807	15.741	R(0.01)	9.95	
2778	GB/T22807	5.150		-0.71	
2789	ISO17075-1	5.7		-0.16	
2804	ISO17075-1	5.19		-0.67	
2806	ISO17075-1	7.0		1.15	
2810	ISO17075-1	5.467		-0.39	
2812	ISO17075-1	5.72		-0.14	
2813	ISO17075-1	8.02	C	2.18	First reported 36.54
2823	ISO17075-1	5.148		-0.72	
2826	DIN11083	5.7958		-0.06	
2829	ISO17075-1	5.620		-0.24	
2839	ISO17075-1	6.015		0.16	
2844	ISO17075-1	5.41		-0.45	
2870	ISO17075-1	5.62		-0.24	
2905	ISO17075-1	5.86		0.00	
2908	ISO17075-1	4.327		-1.54	
2910	ISO17075-1	6.45		0.60	
2912		-----		-----	
2913		-----		-----	
2918	§LFGB B82.02-11	3.656		-2.22	
2920	ISO17075-1	25.88	R(0.01)	20.16	
2926	ISO17075-1	6.07		0.21	
3100	ISO17075-1	5.56		-0.30	
3116	ISO17075-1	5.743		-0.12	
3154		-----		-----	
3160	ISO17075-1	5.73		-0.13	
3172	ISO17075-1	6.552		0.70	
3176	ISO17075-1	5.40		-0.46	
3185	ISO17075-1	5.43		-0.43	
3197	ISO17075-1	5.82		-0.04	
3199	ISO17075-1	6.068379842		0.21	
3210		-----		-----	
3214	ISO17075-1	6.26		0.40	
3216	ISO17075-1	5.91	C	0.05	First reported 11.49
3218	ISO17075-1	5.70		-0.16	
3228	ISO17075-1	5.75		-0.11	
3233	ISO17075-1	6.23		0.37	
3237	ISO17075-1	5.49		-0.37	
3248	ISO17075-1	6.054		0.20	
3250	ISO17075-1	5.73		-0.13	
8005		-----		-----	

normality	suspect	
n	124	
outliers	6	
mean (n)	5.859	
st.dev. (n)	0.7544	RSD = 13%
R(calc.)	2.112	
st.dev.(ISO17075-1:17)	0.9930	
R(ISO17075-1:17)	2.781	



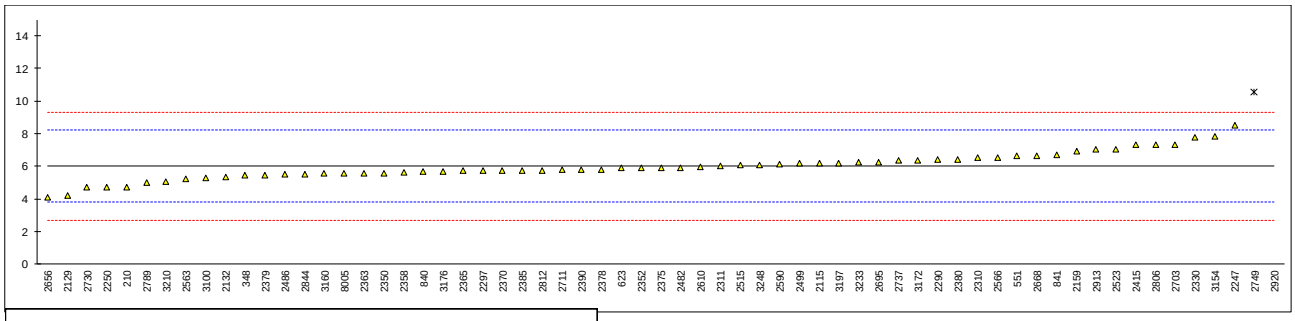


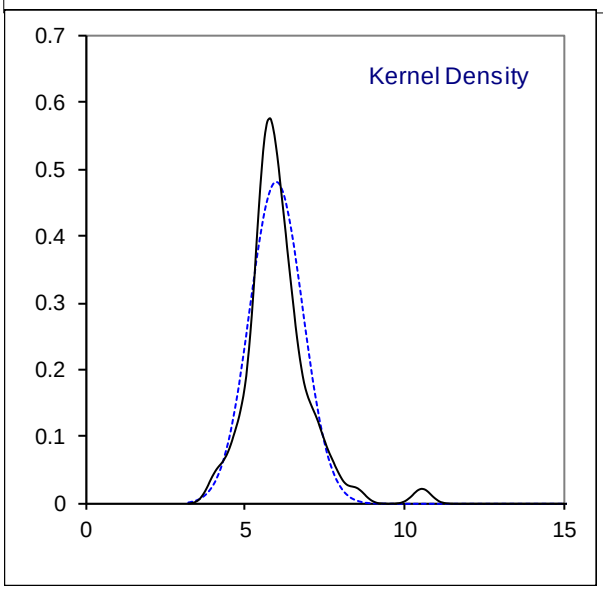
Determination of Chromium (VI) (chromatographic) in sample #20585; results in mg/kg

lab	method	value	mark	z(targ)	remarks
210	ISO17075-2	4.74		-1.15	
230		-----		-----	
339		-----		-----	
348	ISO17075-2	5.44		-0.51	
362		-----		-----	
551	In house	6.614		0.56	
623	ISO17075-2	5.89		-0.10	
840	ISO17075-2	5.67		-0.30	
841	ISO17075-2	6.7		0.63	
2102		-----		-----	
2108		-----		-----	
2115	ISO17075-2	6.2		0.18	
2118		-----		-----	
2121		-----		-----	
2128		-----		-----	
2129	ISO17075-2	4.20		-1.64	
2132	ISO17075-2	5.35		-0.59	
2146		-----		-----	
2159	ISO17075-2	6.91		0.83	
2165		-----		-----	
2201	ISO17075-2	NA		-----	
2215		-----		-----	
2228		N/A		-----	
2230		-----		-----	
2232		-----		-----	
2236		-----		-----	
2247	ISO17075-2	8.49		2.26	
2250	ISO17075-2	4.73		-1.16	
2256		-----		-----	
2273		-----		-----	
2290	ISO17075-2	6.4		0.36	
2293		-----		-----	
2297	ISO17075-2	5.73		-0.25	
2301		-----		-----	
2310	ISO17075-2	6.54		0.49	
2311	ISO17075-2	6.0		0.00	
2330	ISO17075-2	7.759		1.60	
2347		-----		-----	
2350	ISO17075-2	5.590		-0.37	
2352	ISO17075-2	5.9		-0.09	
2357		-----		-----	
2358	ISO17075-2	5.63		-0.34	
2363	ISO17075-2	5.59		-0.37	
2365	ISO17075-2	5.73		-0.25	
2366	ISO17075-2	out of cap.		-----	
2369		-----		-----	
2370	ISO17075-2	5.74		-0.24	
2375	ISO17075-2	5.9		-0.09	
2378	ISO17075-2	5.8		-0.18	
2379	ISO17075-2	5.465		-0.49	
2380	ISO17075-2	6.41		0.37	
2382		-----		-----	
2385	ISO17075-2	5.74		-0.24	
2390	ISO17075-2	5.79		-0.19	
2410		-----		-----	
2415	ISO17075-2	7.30		1.18	
2425		-----		-----	
2442		-----		-----	
2449		-----		-----	
2460		-----		-----	
2462		-----		-----	
2475		-----		-----	
2482	ISO17075-2	5.92		-0.07	
2486	ISO17075-2	5.5		-0.46	
2489		-----		-----	
2492		-----		-----	
2499	ISO17075-2	6.165		0.15	
2500		-----		-----	
2501		-----		-----	
2504		-----		-----	
2508		-----		-----	
2511		-----		-----	
2515	ISO17075-2	6.06		0.05	
2523	ISO17075-2 mod.	7.06		0.96	

lab	method	value	mark	z(targ)	remarks
2531		-----		-----	
2538		-----		-----	
2549		-----		-----	
2553		-----		-----	
2561		-----		-----	
2563	ISO17075-2	5.24		-0.69	
2566	ISO17075-2	6.55		0.50	
2573		-----		-----	
2590	ISO17075-2	6.134		0.12	
2591		-----		-----	
2605		-----		-----	
2610	ISO17075-2	5.95		-0.05	
2624		-----		-----	
2652		-----		-----	
2654		-----		-----	
2656	ISO17075-2	4.1		-1.73	
2664		-----		-----	
2668	ISO17075-2	6.64		0.58	
2674		-----		-----	
2682		-----		-----	
2695	ISO17075-2	6.24		0.22	
2701		-----		-----	
2703	ISO17075-2	7.306		1.18	
2711	ISO17075-2	5.78		-0.20	
2712		-----		-----	
2719		-----		-----	
2721		-----		-----	
2727		-----		-----	
2730	ISO17075-2	4.72		-1.16	
2737	ISO17075-2	6.34		0.31	
2749	In house	10.5662	R(0.01)	4.15	
2772		-----		-----	
2777		-----		-----	
2778		-----		-----	
2789	ISO17075-2	5.0		-0.91	
2804		-----		-----	
2806	ISO17075-2	7.3		1.18	
2810		-----		-----	
2812	ISO17075-2	5.75		-0.23	
2813		-----		-----	
2823		-----		-----	
2826		-----		-----	
2829		-----		-----	
2839		-----		-----	
2844	ISO17075-2	5.51		-0.45	
2870		-----		-----	
2905		-----		-----	
2908		-----		-----	
2910		-----		-----	
2912		-----		-----	
2913	ISO17075-2	7.055		0.96	
2918		-----		-----	
2920	ISO17075-2	24.95	R(0.01)	17.21	
2926		-----		-----	
3100	ISO17075-2	5.30		-0.64	
3116		-----		-----	
3154	ISO17075-2	7.808		1.64	
3160	ISO17075-2	5.54		-0.42	
3172	ISO17075-2	6.363		0.33	
3176	ISO17075-2	5.69		-0.28	
3185		-----		-----	
3197	ISO17075-2	6.21		0.19	
3199		-----		-----	
3210	In house	5.072		-0.84	
3214		-----		-----	
3216		-----		-----	
3218		-----		-----	
3228		-----		-----	
3233	ISO17075-2	6.22		0.20	
3237		-----		-----	
3248	ISO17075-2	6.063		0.06	
3250		-----		-----	
8005	ISO17075-2	5.571		-0.39	

normality	OK	
n	61	
outliers	2	
mean (n)	6.002	
st.dev. (n)	0.8279	RSD = 14%
R(calc.)	2.318	
st.dev.(ISO17075-2:17)	1.1009	
R(ISO17075-2:17)	3.086	





APPENDIX 2 Analytical details

lab	ISO/IEC 17025 accredited	sample intake (g)	time between grinding/ cutting and extraction (min)	pH before extraction	pH after extraction	type shaker used	frequency shaker
210	No	2		8	7.64	Orbital shaker	100 rpm
230	---						
339	---						
348	Yes	2	30	7.98	7.69	Orbital shaker	100 rpm
362	Yes	2		8.00	7.58		
551	No	2	65	7.95	7.72	Orbital Shaker	100 rpm
623	Yes	2	30	8.00	7.97	Mechanical Shaker	100 rpm
840	Yes	1	5	7.97	7.68	Orbital Shaker	100 rpm
841	Yes	1		7.98	7.80	Shaking incubator	100 rpm
2102	No	2	< 5	8.0	8.0	horizontal shaker	110 rpm
2108	Yes	2	120	8.10	7.80	Horizontal Shaker	100 rpm
2115	Yes	1	immediately	8.0	7.9	Horizontal Sahker	60 rpm
2118	Yes	5	10	8.0	7.71	WiggenHauser shaker	100 rpm
2121	Yes	1.5	immediately	7.7		Orbital Shaker	
2128	Yes	2	< 10	8.0	7.7	Horizontal	50 / min
2129	Yes	1					
2132	No	1	30	7.8	7.8	Orbital Shaker	75 rpm
2146	Yes						
2159	Yes	1	immediately	8.0	7.9	Mechanical Shaker	100 rpm
2165	Yes	1	15	8.00	7.8	Mechanical orbital shaker.	100 rpm
2201	Yes	1	10	7.93	7.71	Straight line shaker	100 rpm
2215	Yes	0.5	180	8.0	7.8	Mechanical shaker	100 rpm
2228	No	1	60 - 120	8	7.66	DSR-10	300 rpm
2230	Yes	1	immediately	8.00	7.80	mechanical shaker	100 rpm
2232	Yes	2	Immediately	7.98	7.71	Orbital shaker	100 rpm
2236	Yes	2	1230	8.00	7.44	Wrist action	110 rpm
2247	Yes	2	5 – 10	8.01	7.90	Orbital shaker	100 rpm
2250	Yes	2	30	8.0	8.0	horizontal, mechanical shaker	100 rpm
2256	Yes	1	1	7.697	7.790	Shaking water bath	100 rpm
2273	Yes	2	10	8.0	7.87	Horizontal Shaker	100 rpm
2290	Yes						
2293	No	2	15	8.02	7.70	Linear shaker	100 rpm
2297	Yes	2	5	8.0	7.6	Mechanical orbital shaker	100 rpm
2301	Yes	2	15	8.0	7.5	Mechanical shaker	100 rpm
2310	Yes	2		8	7.7	Orbital Shaker	110 rpm
2311	Yes	1		8	7.9	Mechanical shaker	100 rpm
2330	Yes	1	60	8.001	7.65	Horizontal Shaker	100 rpm
2347	Yes	1	10	8.0	7.8		
2350	Yes	2	5	7.5	7.5	Orbital Shaker	100 rpm
2352	Yes	1	10	7.98	7.81	Thermostatic oscillator	100 rpm
2357	Yes						
2358	Yes	1	5	8.0	7.8	Mechanical orbital shaker	100 rpm
2363	Yes	4	30	8.0	7.0-8.0	smooth circular movement	100 rpm
2365	Yes	2	180	8.01	7.75	Shaking Table	100 rpm
2366	Yes	2	immediately	8.0	7.5	Orbital Shaker	100 rpm
2369	Yes	1	10	8.0	7.0-8.0	Rorating	100 rpm
2370	Yes	2	10	8.00	7.75	Horizontal oscillator	100 rpm
2375	Yes						
2378	Yes	2	10	8.0	7.7	Horizontal oscillator	100 rpm
2379	Yes	1	20	8.00	7.68	Horizontal Shakerl	100 rpm
2380	Yes	1	5	8.0	7.57	Mechanical Shaker	100 rpm
2382	Yes	2	30	8.0	7.9	concentric oscillator	100 rpm
2385	Yes	1	20	8.03	7.65	Horizontal	100 rpm
2390	Yes	2	10	8.00	7.64	Orbital Shaker	100 rpm
2410	Yes	1		8.0	7.7	Orbital Shaker	100 rpm
2415	Yes	2	30	8.0	7.8	Orbital Shaker	100 rpm
2425	Yes	1	15	8.01	7.88	Orbital Shaker	100 rpm
2442	Yes	1	5	8	7.86	Mechanical orbital shaker	100 rpm
2449	Yes	1	182	7.65	7.71	Mechanical Shaker	110 rpm
2460	No	2	10	7.96	7.61	Orbital Shaker	100 rpm
2462	Yes	2	30	8.0	7.8	Orbital Shaker	100 rpm
2475	---						
2482	Yes	0.5	10	8.0	7.7	Orbital Shaker	105 rpm
2486	Yes	1	10	8	7.9	Mechanical Shaker	100 rpm

lab	ISO/IEC 17025 accredited	sample intake (g)	time between grinding/ cutting and extraction (min)	pH before extraction	pH after extraction	type shaker used	frequency shaker
2489	Yes	1	5	8.0	7.7	Orbital Shaker	100 rpm
2492	Yes	1				Orbital Shaker	100 rpm
2499	Yes	2	One day	8.00	7.70	Orbital Shaker	100 rpm
2500	Yes	1	30	8.1	7.8	Mechanical Shaker	100 rpm
2501	Yes	2	7	8.0	7.6	Orbital Shaker	100 rpm
2504	Yes	2	180	8	7.8	Orbital Shaker	100 rpm
2508	Yes	1	10				
2511	---						
2515	Yes	1	immediately	7.98	7.70	Combi-shaker	100 rpm
2523	Yes	1.5	35	7.99	7.95	Horizontal Shaker	100 rpm
2531	Yes	2	10	7.9	7.9	Orbital Shaker	100 rpm
2538	Yes	2		8	7.7	Horizontal shaker	100 rpm
2549	Yes	2	15	8	7.72	Orbital Shaker	100 rpm
2553	Yes	1	immediately	8.05	7.82	Horizontal Shaker	100 rpm
2561	---						
2563	Yes	2	10	--	7,7	Orbital Shaker	100 rpm
2566	Yes	1	immediately	8.00	7.80	SK-600,LAB	100 rpm
2573	Yes	1	40	8.03	7.85	Orbital Shaker	100 rpm
2590	Yes	1	5	8.04	7.98	Orbital Shaker	100 rpm
2591	Yes	2	30	7.6	7.6	Orbital Shaker	100 rpm
2605	Yes	4	10	8.02	7.83	Orbital Shaker	100 rpm
2610	Yes	2	7	8.00	7.64	Orbital Shaker	100 rpm
2624	No	2	10		8	Orbital Shaker	100 rpm
2652	Yes	1	2	8.0	7.9	/	100 rpm
2654	Yes	2	immediately	8.00	7.63	Rotary Shaker	30 tour/s
2656	No	1	20	8	6.7	Overhead Shaker	12 rpm
2664	Yes	2	-	8	8	Orbital Shaker	160 rpm
2668	Yes	1	immediately	7.8	7.9	Orbital Shaker	100 rpm
2674	Yes	1	10	8.02	7.56	Orbital Shaker	100 rpm
2682	Yes	2	40	7.98	7.56	Orbital Shaker	100 rpm
2695	Yes	2	10	7.99	7.7	Orbital Shaker	100 rpm
2701	No	1	120	8.04	7.78	Orbital Shaker	100 rpm
2703	Yes	2		8.01	7.71	Circular shaker	100 rpm
2711	No	2	30	8.014	7.608	Orbital Shaker	100 rpm
2712	Yes	2	1500	8.02	7.65	Baths-reciprocal shaker	100 rpm
2719	Yes	1					
2721	Yes	1 / 2	< 5	8.0	7 and 8	Horizontal Shaker	110 rpm
2727	Yes	2	15	8.0	7.7	Orbital Shaker	100 rpm
2730	No	2	45	8.0	7.66	Orbital Shaker	100 rpm
2737	Yes	1	3 days	8.05		Orbital Shaker	110 r/min
2749	Yes	1	60	8.0	7.1	Horizontal Shaker	100 rpm
2772	Yes	5	30	8.02	7.92	(ST-0):TS-520D	100 rpm
2777	No	4	30	9.62	8.08	Horizontal Shaker	50 rpm
2778	Yes	4	20	8.0±0.1	7.8	Mechanical Shaker	120 rpm
2789	No	2	10	8.0	7.8	Orbital Shaker	100 rpm
2804	No	2	5	8.0	7.7	Orbital Shaker	100 rpm
2806	No						
2810	Yes	2	10	8.02	7.98	Orbital Shaker	100 rpm
2812	Yes	1	2	7.7	7.8	Orbital Shaker	100 rpm
2813	Yes	2	13	8.078	7.795	Mechanical Shaker	60 rpm
2823	Yes	2	2	7.98	7.69	Orbital Shaker	100 rpm
2826	Yes	2	immediate	8.05	7.9	Orbital Shaker	100 rpm
2829	Yes	2	15	8.0	7.6	Orbital Shaker	100 rpm
2839	Yes	2	2	8.0	7.5	Orbital Shaker	100 rpm
2844	No	2	60	8.35	7.68	Orbital Shaker	110 rpm
2870	Yes	2	5	8.1	7.9	Orbital Shaker	105 rpm
2905	No	2	20	8.05	7.90	Orbital Shaker	100 rpm
2908	Yes	2	30	7.98	7.25	Orbital Shaker	100 rpm
2910	Yes	2	20	8.05	7.63	Cyclotron Shaker	100 rpm
2912	---						
2913	No	1	15	8,0	8,0	IKA KS 130 basic	160 rpm
2918	Yes	2	7	8.0	7.7	Horizontal Shaker	170 rpm
2920	No	2	10	8.01	7.75	GFL 3017	100 rpm
2926	No	2	15	8.00	7.68	Mechanical Agitator	100 rpm
3100	Yes	2	1	7.98	7.66	Orbital Shaker	100 rpm
3116	Yes	1	immediately	7.9	7.9	Mechanical shaker	100 rpm
3154	Yes	1	15	8.05	7 - 8	Circle	100 rpm

lab	ISO/IEC 17025 accredited	sample intake (g)	time between grinding/ cutting and extraction (min)	pH before extraction	pH after extraction	type shaker used	frequency shaker
3160	Yes	1	10		7.5	Orbital Shaker	100 rpm
3172	Yes	1	1	8.0	7.7	Overhead rotating shaker	100 rpm
3176	Yes	1	30	9.0	7.77	Mechanical shaker	100 rpm
3185	Yes	1	180	8.0	7.8	Orbital Shaker	100 rpm
3197	Yes	2	3	7.9	8.0	Orbital Shaker	100 rpm
3199	Yes	1	10	7.97	7.66	Reciprocal Shaking Bath	100 rpm
3210	Yes	2	60	8.02	7.83	Agitateur rotatif	14 tours/min
3214	Yes	1	5	7.936	7.657	Orbital Shaker	100 rpm
3216	Yes	2	5	7.8	7.8	Liquid stirrer	100 rpm
3218	Yes	2	10	8.0	7.6	Orbital Shaker	100 rpm
3228	Yes	2	10	8.0	7.0 - 8.0	Orbital Shaker	100 rpm
3233	No	1	30	8.01	7.64	Mechanical shaker	100 rpm
3237	Yes	2	60	8.01	7.72	circular moving	100 rpm
3248	Yes	2	immediately	8.0	7.7	Mechanical shaker	60 rpm
3250	Yes	1	10	7.9	8.0	Mechanical shaker	100 rpm
8005	Yes	1	immediately	7.9	7.9	Mechanical shaker	100 rpm

APPENDIX 3

Number of participants per country

4 labs in	BANGLADESH
1 lab in	BELGIUM
1 lab in	BRAZIL
1 lab in	BULGARIA
2 labs in	CAMBODIA
1 lab in	ESTONIA
1 lab in	FINLAND
8 labs in	FRANCE
12 labs in	GERMANY
1 lab in	GUATEMALA
11 labs in	HONG KONG
8 labs in	INDIA
2 labs in	INDONESIA
12 labs in	ITALY
1 lab in	MAURITIUS
2 labs in	MEXICO
3 labs in	MOROCCO
28 labs in	P.R. of CHINA
3 labs in	PAKISTAN
2 labs in	PORTUGAL
1 lab in	ROMANIA
1 lab in	SINGAPORE
3 labs in	SOUTH KOREA
7 labs in	SPAIN
1 lab in	SRI LANKA
3 labs in	SWITZERLAND
6 labs in	TAIWAN R.O.C.
2 labs in	THAILAND
1 lab in	THE NETHERLANDS
1 lab in	TUNISIA
6 labs in	TURKEY
2 labs in	U.S.A.
3 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
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

Literature

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