Results of Proficiency Test
Chromium (VI) in Leather
May 2021

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 Of all Chromium compounds, primarily Chromium (VI) was used, but this has been replaced by the less hazardous Chromium (III) in most applications.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 2020/2021 it was decided to continue the proficiency test for the analysis of Chromium (VI) in Leather.

In this interlaboratory study 155 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 (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), labelled #21580. 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 gray colored leather positive on Chromium (VI) was obtained from a local supplier. The leather material was grinded and aged. After homogenization about 210 plastic bags were filled with approximately 5 grams of leather, vacuumed and labelled #21580. 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 #21580-1	3.931
Sample #21580-2	4.166
Sample #21580-3	3.625
Sample #21580-4	3.727
Sample #21580-5	4.422
Sample #21580-6	4.193
Sample #21580-7	3.922
Sample #21580-8	4.475

Table 1: homogeneity test results of subsamples #21580

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)	0.865
reference test method	ISO17075-2:17
0.3 * R (ref. test method)	0.826

Table 2: evaluation of the repeatability of subsamples #21580

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 #21580 was sent on April 14, 2021.

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 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 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 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, e.g. ISO reproducibilities, 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 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 test result tables in appendix 1.

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

	|z|	< 1	good
1 <	|z|	< 2	satisfactory
2 <	|z|	< 3	questionable
3 <	|z|		unsatisfactory

4 EVALUATION

In this interlaboratory study no problems were encountered with the dispatch of the samples. Seven participants reported after the final reporting date and three participants did not report any test results at all.
In total 152 participants reported 204 numerical test results. Observed were 5 outlying test results, which is 2.5%. 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 problematic for a number of laboratories at a concentration level of 4.7 mg/kg. Four 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 at a concentration level of 4.5 mg/kg. One statistical outlier was observed. The calculated reproducibility after rejection of the statistical outlier 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 literature reference test methods (in casu ISO test methods) are presented in the next table.

Parameter	unit	n	average	2.8 * sd	R(lit.)
Chromium (VI) (colorimetric)	mg/kg	133	4.67	1.29	2.33
Chromium (VI) (chromatographic)	mg/kg	66	4.55	1.39	2.84

Table 3: reproducibilities of tests on sample #21580

Without further statistical calculations it could 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 MAY 2021 WITH PREVIOUS PTS

	May 2021	May 2020	May 2019	April 2018	April 2017
Number of reporting laboratories	152	142	148	162	163
Number of test results	204	193	192	190	183
Number of statistical outliers	5	8	7	2	5
Percentage of statistical outliers	2.5%	4.1%	3.6%	1.1%	2.7%

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 2021	May 2020	May 2019	April 2018	2015 - 2017	Target
Chromium (VI) (colorimetric)	10%	13%	11%	31%	15-33%	15%
Chromium (VI) (chromatographic)	11%	14%	6%	31%	10%	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 some analytical details were requested which are 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 opening of the vacuum packed sample and extraction. About 60% 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 5% of the participants started the extraction after 1 hour up to 4 days after opening of the vacuum packed sample.
All participants, except one, reported to have used 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.
No effect was observed on the averages or variation between reported test results.

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 almost all participants (except one) 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 #21580 almost all participants would not release this sample to the consumer market. Based on the colorimetric test result one participant would release sample #21580.

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.

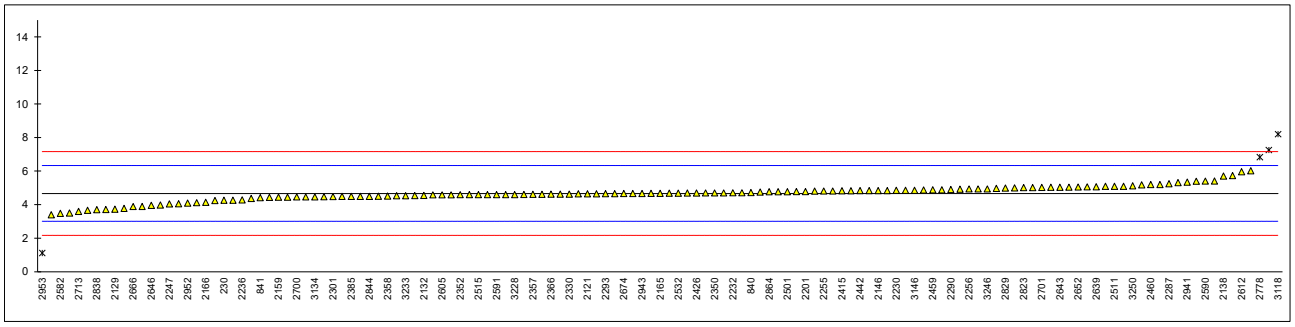
APPENDIX 1

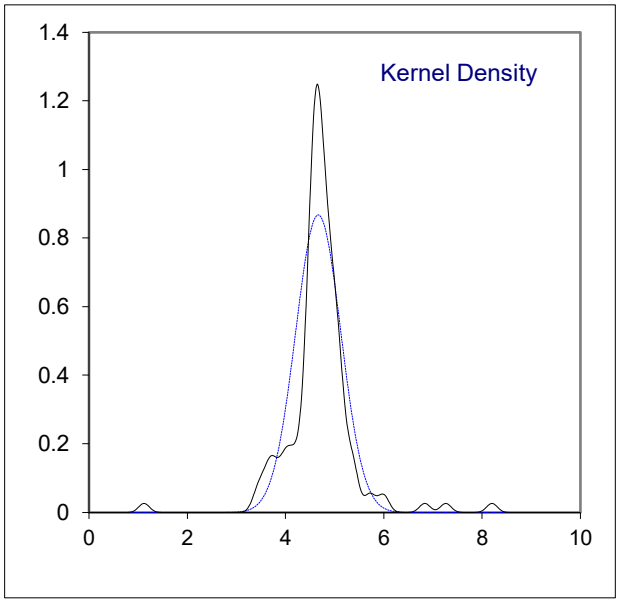
Determination of Chromium (VI) (colorimetric) in sample #21580; results in mg/kg

lab	method	value	mark	z(targ)	remarks
210	ISO17075-1	5.06		0.48	
230	ISO17075-1	4.26834		-0.48	
339		-----		-----	
348	ISO17075-1	7.26	R(0.01)	3.12	
362	ISO17075-1	5.398		0.88	
551	ISO17075-1	3.78		-1.06	
622	ISO17075-1	5.1861		0.63	
623	ISO17075-1	5.730		1.28	
840	ISO17075-1	4.729		0.08	
841	ISO17075-1	4.42		-0.29	
1213	ISO17075-1	4.940		0.33	
2115		-----		-----	
2118	ISO17075-1	4.25		-0.50	
2121	ISO17075-1	4.642		-0.03	
2129	ISO17075-1	3.73		-1.13	
2132	ISO17075-1	4.55		-0.14	
2137	ISO17075-1	5.317		0.79	
2138	ISO17075	5.7		1.25	
2146	ISO17075-1	4.84		0.21	
2159	ISO17075-1	4.44		-0.27	
2165	ISO17075-1	4.67		0.01	
2166	ISO17075-1	4.147		-0.62	
2201	ISO17075-1	4.782		0.14	
2215	ISO17075-1	4.873		0.25	
2228	ISO17075-1	3.6672		-1.20	
2230	ISO17075-1	4.86		0.24	
2232	ISO17075-1	4.705		0.05	
2236	In house	4.2818		-0.46	
2247	ISO17075-1	4.05		-0.74	
2250		-----		-----	
2255	ISO17075-1	4.81		0.17	
2256	ISO17075-1	4.94		0.33	
2287	ISO17075-1	5.244		0.70	
2289	ISO17075-1	4.84		0.21	
2290	ISO17075-1	4.9		0.28	
2293	ISO17075-1	4.652		-0.02	
2301	ISO17075-1	4.48		-0.22	
2310	ISO17075-1	5.2		0.64	
2311	ISO17075-1	4.6420		-0.03	
2320	In house	3.5	C	-1.40	First reported 7.124
2330	ISO17075-1	4.631		-0.04	
2347	GB/T22807	4.5		-0.20	
2350	ISO17075-1	4.7014		0.04	
2352	ISO17075-1	4.591		-0.09	
2357	ISO17075-1	4.62		-0.05	
2358	ISO17075-1	4.51		-0.19	
2363	ISO17075-1	4.588		-0.09	
2365	ISO17075-1	4.473		-0.23	
2366	ISO17075-1	4.63		-0.04	
2369	ISO17075-1	4.663		0.00	
2370	ISO17075-1	4.65		-0.02	
2375	ISO17075-1	4.6		-0.08	
2378	ISO17075-1	4.58		-0.10	
2379	ISO17075-1	4.655		-0.01	
2380	ISO17075-1	4.544		-0.15	
2382	ISO17075-1	4.669		0.01	
2385	ISO17075-1	4.5		-0.20	
2390	ISO17075-1	4.43		-0.28	
2410	ISO17075-1	5.0		0.40	
2415	ISO17075-1	4.83		0.20	
2425	ISO17075-1	4.77		0.13	
2426	ISO17075-1	4.69		0.03	
2442	ISO17075-1	4.84		0.21	
2449	ISO17075-1	3.71		-1.15	
2455	ISO17075-1	3.9	C	-0.92	First reported none detected
2459	ISO17075-1	4.88		0.26	
2460	ISO17075-1	5.199		0.64	
2475	ISO17075-1	4.71		0.05	
2486	ISO17075-1	5.1		0.52	
2489	ISO17075-1	4.68		0.02	
2495		-----		-----	
2500	ISO17075-1	4.921		0.31	
2501	ISO17075-1	4.77		0.13	
2511	ISO17075-1	5.1		0.52	

lab	method	value	mark	z(targ)	remarks
2515	ISO17075-1	4.60		-0.08	
2532	ISO17075-1	4.68		0.02	
2536	ISO17075-1	4.972		0.37	
2538	ISO17075-1	4.60		-0.08	
2549	ISO17075-1	4.81		0.17	
2561	ISO17075-1	3.39		-1.53	
2569	ISO17075-1	4.5		-0.20	
2573	ISO17075-1	4.37		-0.35	
2582	ISO17075-1	3.4804		-1.43	
2590	ISO17075-1	5.4		0.88	
2591	ISO17075-1	4.60		-0.08	
2605	ISO17075-1	4.58		-0.10	
2610		-----		-----	
2612	ISO17075-1	5.9619		1.56	
2624		-----		-----	
2639	GB/T22807	5.07		0.49	
2643	ISO17075-1	5.035		0.45	
2646	ISO17075-1	3.96		-0.85	
2650	ISO17075-1	4.608		-0.07	
2652	ISO17075-1	5.049		0.46	
2656		-----		-----	
2666	ISO17075-1	3.890		-0.93	
2668	ISO17075-1	4.84		0.21	
2674	ISO17075-1	4.66		-0.01	
2682		4.12		-0.66	
2695	ISO17075-1	not analyzed		-----	
2700	ISO17075-1	4.457		-0.25	
2701	ISO17075-1	5.026		0.43	
2711		-----		-----	
2713	ISO17075-1	3.6		-1.28	
2716	ISO17075-1	4.63		-0.04	
2734		-----		-----	
2741	ISO17075-1	4.86		0.24	
2743	ISO17075-1	4.271		-0.47	
2765	ISO17075-1	6.02		1.63	
2777		4.623		-0.05	
2778	GB/T22807	6.833	R(0.01)	2.61	
2789	ISO17075-1	4.70		0.04	
2806	ISO17075-1	5.1		0.52	
2823	ISO17075-1	5.018		0.43	
2829	ISO17075-1	4.99		0.39	
2838	ISO17075-1	3.7	C	-1.16	First reported 6.45
2839	ISO17075-1	4.702		0.04	
2844	ISO17075-1	4.50		-0.20	
2864	ISO17075-1	4.766		0.12	
2866		-----		-----	
2892	ISO17075-1	4.833		0.20	
2918	§64 LFGB B82.02-11	4.052		-0.74	
2919		-----		-----	
2941	ISO17075-1	5.34		0.81	
2943	ISO17075-1	4.665		0.00	
2949	ISO17075-1	4.446	C	-0.26	First reported 2.766
2952	ISO17075-1	4.09		-0.69	
2953	ISO17075-1	1.12	R(0.01)	-4.27	
2959	ISO17075-1	4.806		0.17	
2961		-----		-----	
2963	ISO17075-1	4.88		0.26	
2964	ISO17075-1	4.459		-0.25	
2966		-----		-----	
2967		-----		-----	
3100	ISO17075-1	4.68845		0.03	
3116	ISO17075-1	4.507		-0.19	
3118	ISO17075-1	8.2	C,R(0.01)	4.26	First reported 22.92
3134	ISO17075-1	4.46		-0.25	
3135	In house	5.41		0.90	
3146	ISO17075-1	4.861		0.24	
3153	ISO17075-1	5.019		0.43	
3154		-----		-----	
3160	ISO17075-1	4.75		0.10	
3172	ISO17075-1	5.033		0.44	
3176	ISO17075-1	4.533		-0.16	
3192		-----		-----	
3199	ISO17075-1	3.97247		-0.83	
3210		-----		-----	
3216	ISO17075-1	4.774		0.13	
3218	ISO17075-1	4.600		-0.08	
3228	ISO17075-1	4.60		-0.08	
3233	ISO17075-1	4.535		-0.16	

lab	method	value	mark	z(targ)	remarks
3237	ISO17075-1	5.03932		0.45	
3246	ISO17075-1	4.9414		0.33	
3250	ISO17075-1	5.12		0.55	
	normality	suspect			
	n	133			
	outliers	4			
	mean (n)	4.665			
	st.dev. (n)	0.4599	RSD =10%		
	R(calc.)	1.288			
	st.dev.(ISO17075-1:17)	0.8308			
	R(ISO17075-1:17)	2.326			



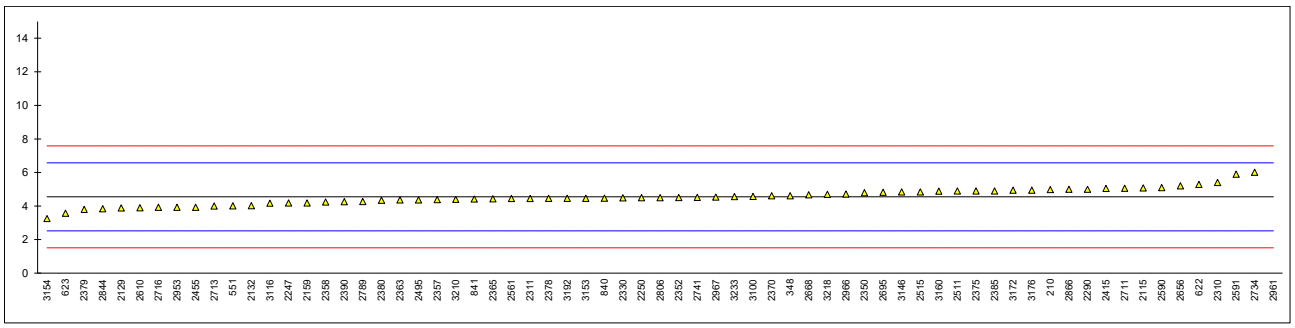


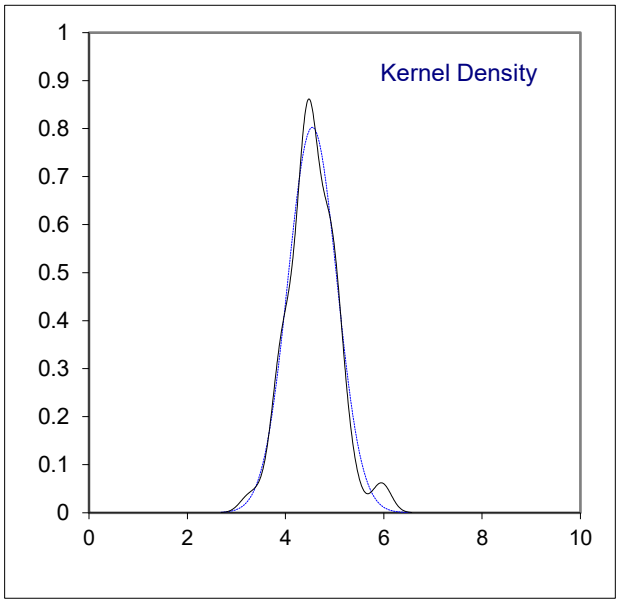
Determination of Chromium (VI) (chromatographic) in sample #21580; results in mg/kg

lab	method	value	mark	z(targ)	remarks
210	ISO17075-2	4.98		0.43	
230		-----		-----	
339		-----		-----	
348	ISO17075-2	4.61		0.06	
362		-----		-----	
551	ISO17075-2	4.01		-0.53	
622	ISO17075-2	5.2922		0.74	
623	ISO17075-2	3.570		-0.97	
840	ISO17075-2	4.467		-0.08	
841	ISO17075-2	4.42		-0.13	
1213		-----		-----	
2115	ISO17075-2	5.08		0.53	
2118		-----		-----	
2121		-----		-----	
2129	ISO17075-2	3.89		-0.65	
2132	ISO17075-2	4.02		-0.52	
2137		-----		-----	
2138		-----		-----	
2146		-----		-----	
2159	ISO17075-2	4.19		-0.35	
2165		-----		-----	
2166		not analyzed		-----	
2201	ISO17075-2	NA		-----	
2215		-----		-----	
2228		Not applicable		-----	
2230		-----		-----	
2232		-----		-----	
2236	In house	Not Tested		-----	
2247	ISO17075-2	4.19		-0.35	
2250	ISO17075-2	4.5		-0.05	
2255		-----		-----	
2256		-----		-----	
2287		-----		-----	
2289		-----		-----	
2290	ISO17075-2	5.0		0.45	
2293	ISO17075-2	Not Analyzed		-----	
2301		-----		-----	
2310	ISO17075-2	5.4		0.84	
2311	ISO17075-2	4.4558		-0.09	
2320		-----		-----	
2330	ISO17075-2	4.488		-0.06	
2347		-----		-----	
2350	ISO17075-2	4.796		0.25	
2352	ISO17075-2	4.502		-0.05	
2357	ISO17075-2	4.38		-0.17	
2358	ISO17075-2	4.24		-0.30	
2363	ISO17075-2	4.363		-0.18	
2365	ISO17075-2	4.432		-0.11	
2366	ISO17075-2	out of capability		-----	
2369		-----		-----	
2370	ISO17075-2	4.61		0.06	
2375	ISO17075-2	4.9		0.35	
2378	ISO17075-2	4.46		-0.09	
2379	ISO17075-2	3.80		-0.74	
2380	ISO17075-2	4.348		-0.20	
2382	ISO17075-2	not applicable		-----	
2385	ISO17075-2	4.9015		0.35	
2390	ISO17075-2	4.26		-0.28	
2410		-----		-----	
2415	ISO17075-2	5.05		0.50	
2425		-----		-----	
2426		-----		-----	
2442		-----		-----	
2449		-----		-----	
2455	ISO17075-2	3.9210		-0.62	
2459		-----		-----	
2460		-----		-----	
2475		-----		-----	
2486		-----		-----	
2489		-----		-----	
2495	ISO17075-2	4.368		-0.18	
2500		-----		-----	
2501		-----		-----	
2511	ISO17075-2	4.9		0.35	
2515	ISO17075-2	4.84		0.29	

lab	method	value	mark	z(targ)	remarks
2532		-----		-----	
2536		-----		-----	
2538		-----		-----	
2549		Not feasible		-----	
2561	ISO17075-2	4.45		-0.10	
2569		-----		-----	
2573		-----		-----	
2582		-----		-----	
2590	ISO17075-2	5.1		0.55	
2591	ISO17075-2	5.90		1.34	
2605		-----		-----	
2610	ISO17075-2	3.90		-0.64	
2612		-----		-----	
2624		-----		-----	
2639		-----		-----	
2643	ISO17075-2	not analyzed		-----	
2646		-----		-----	
2650		-----		-----	
2652		-----		-----	
2656	In house	5.2		0.64	
2666		-----		-----	
2668	ISO17075-2	4.67		0.12	
2674		-----		-----	
2682		-----		-----	
2695	ISO17075-2	4.82		0.27	
2700		-----		-----	
2701		-----		-----	
2711	ISO17075-2	5.06		0.51	
2713	ISO17075-2	4.0		-0.54	
2716	ISO17075-2	3.92		-0.62	
2734	ISO17075-2	6.01		1.44	
2741	ISO17075-2	4.51		-0.04	
2743		-----		-----	
2765		-----		-----	
2777		-----		-----	
2778		-----		-----	
2789	ISO17075-2	4.27		-0.27	
2806	ISO17075-2	4.5		-0.05	
2823		-----		-----	
2829		-----		-----	
2838		-----		-----	
2839		-----		-----	
2844	ISO17075-2	3.84		-0.70	
2864		-----		-----	
2866	ISO17075-2	4.9988		0.45	
2892		-----		-----	
2918		-----		-----	
2919		-----		-----	
2941		-----		-----	
2943		-----		-----	
2949		-----		-----	
2952		-----		-----	
2953	ISO17075-2	3.92		-0.62	
2959		-----		-----	
2961	ISO17075-2Mod.	192.591	R(0.01)	185.69	
2963		-----		-----	
2964		-----		-----	
2966	ISO17075-2	4.715		0.17	
2967	ISO17075-2	4.527		-0.02	
3100	ISO17075-2	4.5773		0.03	
3116	ISO17075-2	4.171		-0.37	
3118		-----		-----	
3134		-----		-----	
3135		-----		-----	
3146	ISO17075-2	4.838		0.29	
3153	ISO17075-2	4.462		-0.08	
3154	ISO17075-2	3.25		-1.28	
3160	ISO17075-2	4.89		0.34	
3172	ISO17075-2	4.945		0.39	
3176	ISO17075-2	4.950		0.40	
3192	ISO17075-2	4.46		-0.09	
3199		-----		-----	
3210	In house	4.397		-0.15	
3216		-----		-----	
3218	ISO17075-2	4.700		0.15	
3228		-----		-----	
3233	ISO17075-2	4.568		0.02	
3237		-----		-----	

lab	method	value	mark	z(targ)	remarks
3246		-----		-----	
3250		-----		-----	
	normality	OK			
	n	66			
	outliers	1			
	mean (n)	4.548			
	st.dev. (n)	0.4971	RSD = 11%		
	R(calc.)	1.392			
	st.dev.(ISO17075-2:17)	1.0127			
	R(ISO17075-2:17)	2.835			





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
210	Yes				
230	Yes	4.0 grams (Extraction was performed twice with a mass of 2 grams each time)	6-8 minutes	7.99	7.61
339	---				
348	Yes	2		8.0±0.1	7,53
362	Yes	2 g	5 min		7.58
551	Yes	1g	Less than 30 minutes.	8.083.	7.685.
622	Yes	2 grams	Immediately after pack was opened about 5 minutes.	8.00	7.96
623	Yes	1	10	8.01	8.03
840	Yes	1.0040	10 minutes	8.02	7.87
841	Yes	2 grams	1 minutes	7.99	7.82
1213	Yes	2g		pH= 8.03	
2115	---				
2118	Yes	1.65g	5	7.99	7.63
2121	Yes	1.5005g, 1.5724g and 2.0093g	1 min, 6min and 11 min	8 +/- 0.1	7.71, 7.69, 7.61
2129	Yes				
2132	Yes	2.0008g	<30 min	7.96	7.61
2137	Yes	1	3	8.03	7.9
2138	Yes	2 g	10 min	8.0	8.0
2146	No	2 g	about 20 min	7,996	7,642/7,634
2159	Yes	2,0 gram	30 min	8,0	7,9
2165	Yes	1 g	5 min	8.0	7.6
2166	Yes	2,0068	16 Minutes	7,96	7,63
2201	Yes	1.013g	1hour	PH:7.56	PH:7.58
2215	Yes	2.001g	180min	8.0	7.9
2228	Yes	1.0046	3 minutes	7.98	7.62
2230	Yes	1.004g	5 min	8.00	7.60
2232	Yes	2 grams	immediately	7.97	7.65
2236	Yes	2.0042	<60	8.01	7.29
2247	Yes	2.0	5.0	8.01	7.66
2250	Yes	2	immediately	8	8
2255	Yes	1.009	25	8	7.9
2256	Yes	1.0028	1min	7.936	7.442
2287	No	1g	7 min	pH8.0	pH8.0
2289	Yes	2.0 g	5 minutes	8.01	7.82
2290	Yes				
2293	Yes	2.0	180	8.00	7.78
2301	Yes	1.0038	2.5 minutes	7.99	7.82
2310	Yes	2		8	7.6
2311	Yes	2		8	7.7
2320	Yes	1g	60 minutes	8.03	7.95
2330	Yes	1 g	Within 2 hours	8.0	7.7
2347	Yes	1g		8.06	7.68
2350	Yes	2 g	immediately	7.52	7.53
2352	Yes	1g	24h	8.03	7.68
2357	Yes				
2358	Yes	2 grams	1 minutes	7.3	7.3
2363	Yes	4g	30min	8.0	7.0~8.0
2365	Yes	2.0123g	2h	7.97	7.54

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
2366	Yes	2gram	less than 2 minutes	7.9-8.1	7.0-8.0
2369	---				
2370	Yes	2 g	40 mins	pH = 7.96	pH = 7.67
2375	Yes	1 gram	30 minutes	7.9	7.8
2378	Yes	2.001g	10min	8.0	7.6
2379	Yes	1 g / 50 mL	Time opening = 10 minutes Time extraction = 180 minutes	pH= 8.00	pH= 7.72
2380	Yes	1.00 g	3 Minute	8.0	7.68
2382	Yes	2.0214g	30min	7.99	7.0~8.0
2385	Yes	1 g	10 - 20 min	8.00	7.61
2390	Yes	2.0028 gram	test immediate perform after opening the sample.	8.01	7.74
2410	Yes	1g	immediately	8.0	7.7
2415	Yes	1g	15 mins	8.0	7.7
2425	Yes	1.0 g	15 minutes	8.0	7.8
2426	Yes	1.0009g	5min	8.00	7.92
2442	Yes	2.00 g	5 min	8.01	7.80
2449	---				
2455	Yes	2.04 grams	~ 15 minutes	7.98	7.71
2459	Yes	2gm	Immediate after opening	7.75	7.75
2460	Yes	2.2 g	15 min	9.34	7.63
2475	No	2.002	few minutes	8	7.7
2486	Yes	1.0053 gram	10 minutes	8	7.9
2489	Yes	1 g	10 minutes/3 hrs	8	7.8
2495	Yes	1.00g	5 minutes	pH = 8.00	pH = 7.60
2500	Yes	1g	30min	7.9	7.8
2501	Yes	1、2.0012g 2、2.0029g	5 mins	PH 8.00	PH 7.62
2511	---				
2515	Yes	1.0063	2 to 3 minutes	8.01	7.67
2532	Yes	2g	<10 minutes	pH- 8	pH - 7.58
2536	Yes	1.0090	Extraction started Immediately	8.0	7.9
2538	Yes	2 grams		pH 8.03 and pH 7.94	pH 7.57 and pH 7.69
2549	Yes	2	30	7.81	7.83
2561	Yes	2 g	5-10	8	8
2569	Yes	2 gm	10	8	7.8
2573	Yes	2g	5mins	7.6	
2582	Yes	2.0017 g	20 min	8.01 pH	8.00 pH
2590	Yes	1.0	5 min.	7.86	8.0
2591	Yes	2.00 grams	5 minutes	7.63	7.66
2605	Yes	4g	30min	8.03	8.00
2610	Yes	2.0037	5 minutes	8.00	7.57
2612	Yes	1. 2,0030g 2. 2,0009g	1:34 min	8,065	7,837
2624	---				
2639	No	2.0001g	5 minutes	8.02	7.40
2643	Yes	2 g	about 10 min	8.0	7.9
2646	Yes	2,000 g	approximately 30 min	pH: 8,02	pH: 7,50
2650	Yes	2 samples of 2g and 1 sample of 1,25g	30 minutes	-	7,57
2652	Yes	1.0052g	5min	8.0	7.8
2656	No	1 gram	1 hour	8	
2666	Yes	2,0048	10 minutes	7,9	7,54
2668	Yes	1.0	Immediately	8.01	7.68
2674	Yes	2g*2	20min	8.07	7.64
2682	Yes	2.0003	4 hours approximately	8.04	7.78

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
2695	Yes	2,0038g	3 minutes	7,64	7,61
2700	No	1.0012	30	8.01	7.68
2701	Yes	1g	40 mins	7.85	7.62
2711	No	2.072	20 minutes	8,073	7.496
2713	Yes: ISO17075-1 only	2 g	5 min	8.0	7.8
2716	Yes: ISO17075-1 only	two times 2,0 g of sample were extracted in 100 mL solution, 1 time 1,0 g of sample was extracted in 50 mL of solution	less 30 minutes	pH 8,0	pH 7,7
2734	Yes	4,5 g	10	8,0	
2741	Yes	1gr	15 minutes	8.0	7.76
2743	Yes	1 g	30 min	8.0	8.0
2765	Yes	2 g	5 min	8.08	7.56
2777	No	2.0011g	1 hour	8.00	7.83
2778	Yes	4g	20mins	8.0±0.1	7.6
2789	Yes	2	15 min	8.0	7.8
2806	Yes				
2823	Yes	2.0042g	2 minutes	pH 8.03	pH 7.73
2829	Yes	2.0 g	5 min	pH 8.00	pH 7.76
2838	Yes	2,0054	180 min		7,65
2839	Yes	2.0005g	1 minutes	8.0	7.8
2844	No	First replicate: 2.0338 Second replicate: 2.0033	30 minutes	8.016	
2864	No	1 g	10 min	8.0	7.8
2866	Yes	2	5	8,0	7,63 and 7,60
2892	Yes	2.0	30 minutes	8.02	7.67
2918	Yes	1 g/50 ml	16 min	8,0	7,6
2919	---				
2941	No	2 g	2 min	8,06	7,70
2943	Yes	2 g	60 minutes		
2949	No	2.0050	4 days	8.1	7.8
2952	Yes	2 grams	10 minutes	8.00	7.81
2953	No	2	20	5,6	7,5
2959	No	2.025g	15min	8.0	7.7
2961	No	0.5 g	4-8 min	8-8.5	8-8.5
2963	Yes	2.0040g	1min	8.00	7.92
2964	No	2,008 g	4 minutes	8,0	7,6
2966	No	2,0013	15 minutes	8,01	7,95
2967	No	2 grams	15 minutes	8,07	7,72
3100	Yes	2.0003g	5 minutes	8.03	7.61
3116	Yes: ISO17075-1 only	1g	Immediately	7.98	7.65
3118	Yes	1.0078	10 minutes	8.0	7.8
3134	Yes	1 sample of 2 g/100ml extraction solution, 1 sample of 1.5g/75ml extraction solution	15 minutes	8.01	7.60 at 21°C
3135	Yes	Appr. 2 g	Appr. 1 hour	8.01	7.66
3146	Yes	one time 1.0017g and one time 2.0067g	5-10 minutes	pH 8.0	pH 7.0 - 8.0
3153	Yes	1 gram per trial	within 5 minutes	7.91	7.59-7.64
3154	Yes	2	30	8,0	7,7
3160	Yes	1 g	10 min	7,95; 8,1	7,5
3172	Yes				
3176	Yes	1	5	8	7,65
3192	Yes	2 g	5 minutes	8,00	7,60
3199	Yes	1.0063	10 minutes	8.01	7.61

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
3210	Yes	1.0017	100	8.03	7.62
3216	Yes	4g approx.	1min. approx.	7.88	7.51
3218	Yes	2g	<1h	7.5	7.6
3228	Yes	2.0g	Less than 10 min	8.0	7.0-8.0
3233	No	1.0033	30 min	8.00	7.65
3237	Yes	2 gr	5 min	8.02	7,92
3246	Yes	2.0g	5 min	8.01	7.66
3250	Yes	1	5-10 minutes	7.9	8

APPENDIX 3

Number of participants per country

1 lab in	AUSTRIA
6 labs in	BANGLADESH
1 lab in	BELGIUM
1 lab in	BRAZIL
2 labs in	BULGARIA
2 labs in	CAMBODIA
1 lab in	CYPRUS
1 lab in	FINLAND
7 labs in	FRANCE
13 labs in	GERMANY
1 lab in	GREECE
1 lab in	GUATEMALA
6 labs in	HONG KONG
8 labs in	INDIA
4 labs in	INDONESIA
16 labs in	ITALY
1 lab in	JAPAN
1 lab in	MAURITIUS
4 labs in	MEXICO
1 lab in	MOROCCO
27 labs in	P.R. of CHINA
5 labs in	PAKISTAN
1 lab in	SINGAPORE
6 labs in	SOUTH KOREA
9 labs in	SPAIN
2 labs in	SRI LANKA
1 lab in	SWITZERLAND
3 labs in	TAIWAN
1 lab in	THAILAND
1 lab in	TUNISIA
6 labs in	TURKEY
3 labs in	U.S.A.
2 labs in	UNITED KINGDOM
10 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

Literature

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7 M. Thompson and R. Wood, J. AOAC Int, 76, 926, (1993)
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