Results of Proficiency Test
Chromium(VI) in leather
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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 Of all Chromium compounds, primarily Chromium (VI) was used, but this has been replaced by the less hazardous Chromium (III) in most applications.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.

The Institute for Interlaboratory Studies organizes since 2014 an interlaboratory study for the determination of Chromium (VI) in leather. In the annual proficiency test program of 2014/2015, this proficiency test was continued.
In the interlaboratory study of February 2015, 147 laboratories from 30 different countries have participated (see appendix 3). In this report, the results of this proficiency test are presented and discussed. This report is also electronically available through the iis internet site http://www.iisnl.com.

2 SET UP

The Institute for Interlaboratory Studies in Spijkenisse was the organizer of this proficiency test. It was decided to send one sample (approximately 5 grams, labelled #15008), that is positive on Chromium (VI). The analyses for fit-for-use and for homogeneity testing were subcontracted.
On request a second of sample #15008 was send to a limited number of participants, for the determination of Chromium (VI) after the aging procedure. The aging procedure on the leather sample was performed by the laboratories themselves. Due to the lack of samples it was not possible to send a second sample #15008 to all participants.
Participants were requested to report rounded and unrounded test results. The unrounded test results were preferably used for statistical evaluation.

2.1 QUALITY SYSTEM

The Institute for Interlaboratory Studies in Spijkenisse, the Netherlands, has implemented a quality system based on IEC/ISO17043:2010. This ensures strict adherence to protocols for sample preparation and statistical evaluation and 100% confidentially 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 organisation was the one as described for proficiency testing in the report 'iis Interlaboratory Studies: Protocol for the Organisation, Statistics and Evaluation' of April 2014 (iis-protocol, version 3.3). This protocol can be downloaded from the iis website http://www.iisnl.com.

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 leather sample, labelled (#15008), was acquired from local retail. It was cut in small leather squares and the material was mixed thoroughly. Seven stratified randomly selected samples were tested using ISO17075 to check the homogeneity of the batch.
The test results of the homogeneity tests are shown in table 1.

Chromium(VI)	*#15008 (mg/kg)*
sample 1	1.74
sample 2	1.49
sample 3	1.60
sample 4	1.61
sample 5	1.84
sample 6	1.66
sample 7	1.72

table 1: homogeneity test results of subsamples #15008

From the above test results, the repeatability was calculated and compared with 0.3 times the corresponding reproducibility in agreement with the procedure of ISO13528, Annex B2, in the next table:

Chromium(VI)	*#15008 (mg/kg)*
r (observed)	0.32
reference method	ISO17075:2007
0.3 x R (reference method)	0.36

table 2: evaluation of the repeatability of subsamples #15008

The repeatability of the results of the homogeneity tests for Chromium(VI) of sample #15008 was in agreement with 0.3 times the reproducibility mentioned in the reference method ISO17075:2007. Therefore, homogeneity of the subsamples was assumed for sample #15008.

A number of participants agreed to test a second sample of #15008, for the determination of Chromium (VI) after the aging procedure.

Approx. 5 grams of sample #15008 (or 2 * 5 grams) was sent to each of the participating laboratories on January 21, 2015.

2.5 ANALYSES

The participants were requested to determine the content of Chromium (VI) before aging on a leather sample, applying the analysis procedure that is routinely used in the laboratory.
A number of participants that received the second sample was requested to determine the content of Chromium (VI) after aging the leather sample. To get comparable results reported, a detailed report form was sent together with the samples. The report form included a questionnaire about the test performance, in order to identify, if possible, analytical details that might have influence on the results of the test.
Also a letter of instructions was sent with the samples.

3 RESULTS

During four weeks after sample despatch, the results of the individual laboratories were received. The original reported results are tabulated per determination in appendix 1 of this report. The laboratories are presented by their code numbers.
Directly after deadline, a reminder fax was sent to those laboratories that had not yet reported.
Shortly after the deadline, the available results were screened for suspect data. A 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 (raw data of the) reported results.
Additional or corrected results have been used for data analysis and original results are placed under 'Remarks' in the result tables in appendix 1. A list of abbreviations used in the tables can be found in appendix 4.

3.1 STATISTICS

Statistical calculations were performed as described in the report ‘iis Interlaboratory Studies: Protocol for the Organisation, Statistics and Evaluation’ (iis-protocol, April 2014 version 3.3). For the statistical evaluation the *unrounded* (when available) figures were used instead of the rounded results. 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. Not all data sets proved to have a normal distribution, in which cases the statistical evaluation of the results should be used with due care.

In accordance to ISO 5725 (1986 and 1994) the original results per determination were submitted subsequently to Dixon, Grubbs and Rosner outlier tests. Outliers are marked by D(0.01) for the Dixon test, by G(0.01) or DG(0.01) for the Grubbs test and by R(0.01) for the Rosner General ESD test (see appendix 4, no.10). Stragglers are marked by D(0.05) for the Dixon 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. When the uncertainty passed the evaluation, no remarks are made in the report. However, when the uncertainty failed the evaluation it is mentioned in the report and it will have consequences for the evaluation of the test results.

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

3.2 GRAPHICS

In order to visualise the data against the reproducibilities from literature, Gauss plots were made, using the sorted data for each determination (see appendix 1). On the Y-axis the reported analysis results are plotted. The corresponding laboratory numbers are under 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 standard. 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 (see appendix 4; nos 8 and 9). Also a normal Gauss curve was projected over the Kernel Density Graph.

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. ASTM reproducibilities, the z-scores were calculated using a target standard deviation. This results in an evaluation independent of the spread of this interlaboratory study. The target standard deviation was calculated from the literature reproducibility by division with 2.8.

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 in accordance with:

$$z_{(target)} = (\text{result} - \text{average of PT}) / \text{target standard deviation}$$

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.
Therefore the usual interpretation of z-scores maybe 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 samples. Eleven participants reported results after the final reporting date and six participants did not report any test results.

Finally, 141 participants did report 153 results. Observed were 5 outlying results, which is 3.3% of the numerical results. In proficiency studies, outlier percentages of 3% - 7.5% are quite normal.

4.1 EVALUATION PER SAMPLE

In this section, the results are discussed per sample. All statistical results reported on the leather samples are summarised in appendix 1.

In ISO17075 is mentioned that the pH of the solution after extraction and filtering through a membrane filter shall be between 7.5 and 8.0. If not, the complete procedure shall be start again. As this indicate to be an important parameter in the procedure. It was decided to exclude the reported results measured with a pH≥ 8.0 of the solution for statistical evaluation.

#15008: (non aging) The determination of Chromium (VI) at a low concentration level of 1.7 mg/kg appeared to be problematic. Six statistical outliers were observed and twenty results were excluded from the statistical evaluation. The calculated reproducibility after rejection of the statistical outliers is not in agreement with ISO17075:2007.

#15008: (after aging) The determination of Chromium (VI) at a concentration level of 7.8 mg/kg appeared to be problematic. No statistical outliers were observed. However, the calculated reproducibility is not in agreement with ISO17075:2007.

4.2 PERFORMANCE EVALUATION FOR THE GROUP OF LABORATORIES

A comparison has been made between the reproducibility as declared by the relevant standard method and the reproducibilities as found for the group of participating laboratories.

The number of significant test results, the average result, the calculated reproducibility (standard deviation*2.8) and the target reproducibility, derived from the official test method ISO17075:2007 are presented in the next table.

Parameter	unit	n	Average	2.8 * sd	R(target)
Chromium(VI) in #15008 (non aging)	mg/kg	111	1.66	1.53	1.18
Chromium(VI) in #15008 (after aging)	mg/kg	16	7.75	3.85	3.50

table 3: performance overview for samples #15008 (non aging and after aging)

From the above table, it can be concluded, without further statistical calculations, that the participating laboratories have problems with the analysis of Chromium (VI) in leather, when compared to the target reproducibility requirements of the ISO17075 method.

4.3 EVALUATION OF GROUP RESULTS AGAINST LIMITS FOR CHROMIUM (VI)

As Chromium (VI) is carcinogenic, mutagenic and toxic for reproduction, the regulations within countries tend to adopt a zero-tolerance policy. In actual practise this will mean below the detection limit of the widely accepted test method ISO17075:2007.
Examples of regulations can be found in table 4.

Chromium(VI)	**Limit**	**Comment**
Germany: SG (Schadestoff gepruft) – label	< 3 mg/kg	As well for aging as non-aging
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 4: Regulation on Chromium (VI)

When the results of this interlaboratory study were compared to this limit, it may be noticed that not all participants would make identical decisions about the acceptability of the leather.

NB: when the result was reported on “dry weight” according Regulation No 301/2014 the result of 1.66 will be higher!

When using a limit of <3 mg/kg and applying it to the non aging sample #15008 (Chromium (VI) of 1.7 mg/kg in this PT), the majority of the laboratories would release this sample to the consumer market. However, eleven laboratories reported a test result upon the above mentioned limit 3 mg/kg and would have rejected to release the leather to the market. Remarkably, all laboratories that tested the leather sample for Chromium (VI) after aging would reject to release the leather to the market, as the test results found for Chromium (VI) after aging were significant higher (7.8 mg/kg) then the limit of 3 mg/kg.

5 DISCUSSION

Non aging sample

From the reported test methods it appeared that most participants tested the leather samples according to the test method ISO17075 and six participants used §64 B LFGB 82.02-11. These two tests methods appear to be similar (both in literature searches as in the results of this proficiency test). Other used test methods are CPSD-AN-00044, DIN53314 and GB/T22807. The observed reproducibility for the non aged sample in this PT was not in agreement with the reproducibility of the reference method ISO17075:2007.

The analytical details that were requested from the participants are summarized in Appendix 2. The samples were already cut or shred before dispatch. Some participants did cut the leather sample a slightly smaller; another participant used a milling procedure to powder the sample. The final particle size of the leather sample seems not to have an influence on the test results.

The pH indicates to be an important factor in this test method ISO17075, as states that the pH should be between 7.5 and 8.0. For this reason the Chromium (VI) results were screened for pH and excluded when the pH of the solution, reported by the laboratory, was pH ≥8.0. In the graph it is visible that the majority of the group, which were excluded found high test results and biased the overall group performance.

The other analytical details mentioned in appendix 2 appeared to have no significant influence on the test result for this sample.

Aging sample:

On request of a number of participants a second sample of #15008 was sent, for the determination of Chromium (VI) after the aging procedure. Regretfully, test method ISO17075 does not describe ageing as such, but regulating bodies may have an ageing ‘preparation’ as part of the specification limit. Due to the lack of samples it was not possible to send a second of sample #15008 to all participants.

It is remarkably to notice that the consensus value of the group for non-aging is approximately 5 times smaller than to the consensus value of the group after aging for this level of Chromium (VI), (1.7 vs 7.8 mg/kg). This suggests that ageing is an important step and therefore, it should be clearly described if ageing is performed or not. Regretfully, not all regulations mention if the limit (3 mg Chromium VI /kg) is based on ageing or non-ageing.

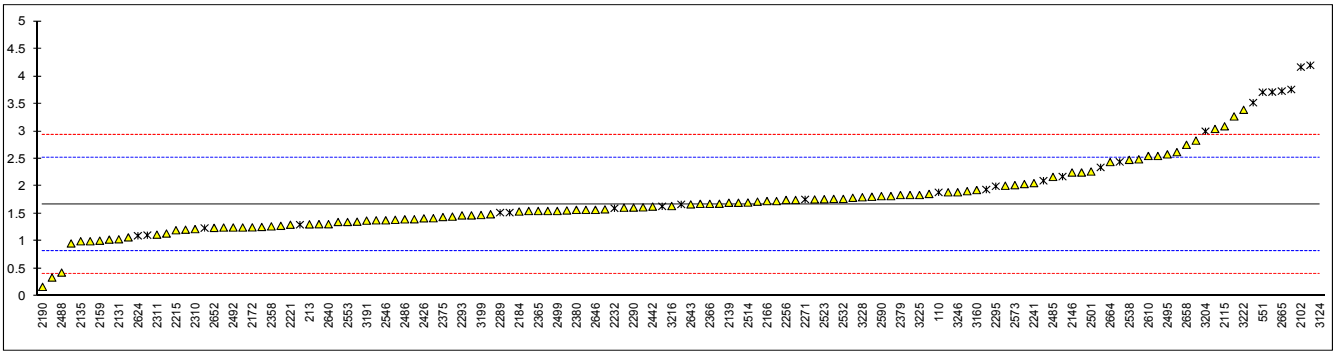
APPENDIX 1

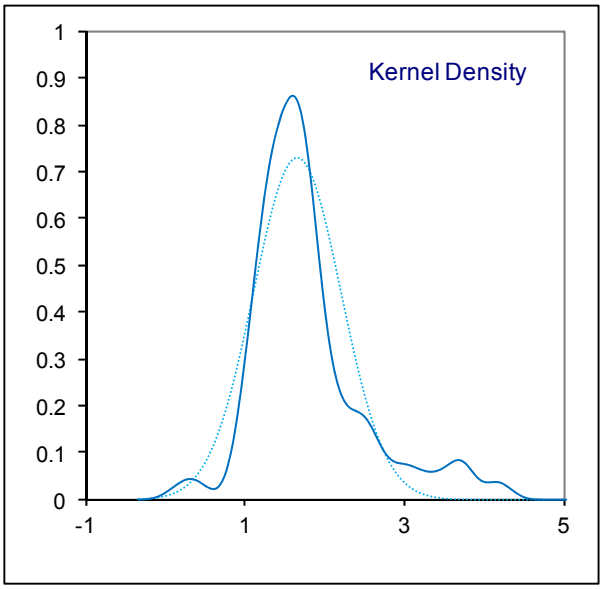
Determination of Chromium(VI) non aging in sample #15008; results in mg/kg

lab	method	value	mark	z(targ)	remarks
110	INH-3352	1.889	ex	0.54	Result excluded, see §4.1
213	ISO17075	1.307		-0.84	
361	ISO17075	1.55		-0.27	
551	ISO17075	3.71	ex	4.84	Result excluded, see §4.1
622		1.1097	ex	-1.31	Result excluded, see §4.1
623	ISO17075	1.39		-0.64	
2102	ISO17075	4.167	R(0.05)	5.92	
2108	ISO17075	2.04		0.89	
2115	ISO17075	3.09		3.38	
2129	ISO17075	0.34		-3.13	
2131	ISO17075	1.035		-1.48	
2132	ISO17075	1.448		-0.51	
2135	§64LFGB82.02.11	1.00		-1.57	
2138	ISO17075	1.38		-0.67	
2139	ISO17075	1.7		0.09	
2146	ISO17075	2.25		1.39	
2159	CPSD-AN-00044	1.01		-1.54	
2165	ISO17075	1.89		0.54	
2166	§64LFGB82.02.11	1.73		0.16	
2172	ISO17075	1.252		-0.97	
2184	ISO17075	1.54		-0.29	
2190	in house	0.17		-3.53	
2201	ISO17075	1.56		-0.24	
2215	ISO17075	1.20		-1.09	
2221	ISO17075	1.300		-0.86	
2228		-----		-----	
2230	ISO17075	1.21		-1.07	
2232	ISO17075	1.60	ex	-0.15	Result excluded, see §4.1
2238	ISO17075	1.61		-0.12	
2241	ISO17075	2.057		0.93	
2247	ISO17075	1.35		-0.74	
2255	ISO17075	1.617		-0.11	
2256	ISO17075	1.75		0.21	
2271	ISO17075	1.76	ex	0.23	Result excluded, see §4.1
2289	ISO17075	1.52	ex	-0.34	Result excluded, see §4.1
2290	ISO17075	1.612		-0.12	
2293	DIN53314	1.470		-0.46	
2295		2	ex	0.80	Result excluded, see §4.1
2296	ISO17075	1.77		0.25	
2301	ISO17075	1.84		0.42	
2310	ISO17075	1.22		-1.05	
2311	ISO17075	1.12		-1.28	
2320	INH-104	2.443	ex	1.85	Result excluded, see §4.1
2330	ISO17075	1.68		0.04	
2350	ISO17075	1.6348	ex	-0.07	Result excluded, see §4.1
2352	ISO17075	1.73		0.16	
2357	ISO17075	1.72		0.14	
2358	ISO17075	1.27		-0.93	
2363	GB/T22807	1.750		0.21	
2365	ISO17075	1.55		-0.27	
2366	ISO17075	1.68		0.04	
2369	ISO17075	1.67	ex	0.02	Result excluded, see §4.1
2370	ISO17075	1.58		-0.20	
2375	ISO17075	1.44		-0.53	
2379	ISO17075	1.84		0.42	
2380	ISO17075	1.57		-0.22	
2385	ISO17075	1.4		-0.62	
2389	ISO17075	1.26		-0.95	
2390	ISO17075	1.91		0.59	
2410	ISO17075	<3		-----	
2413		-----		-----	
2426	ISO17075	1.4169		-0.58	
2432	in house	3.713	R(0.05)	4.85	
2441	ISO17075	n.d.		-----	
2442	in house	1.63		-0.08	
2449	ISO17075	1.356		-0.72	
2450	CPSD-AN-00044	1.249		-0.98	
2452	ISO17075	1.3	ex	-0.86	Result excluded, see §4.1
2455		-----		-----	
2460	ISO17075	0.96		-1.66	
2477		-----		-----	
2481	ISO17075	3.042		3.26	
2482	ISO17075	2.01		0.82	
2485	ISO17075	2.17		1.20	

2486	ISO17075	1.3987		-0.62	
2488	ISO17075	0.43		-2.91	
2489	ISO17075	1.55		-0.27	
2492	ISO17075	1.25		-0.98	
2495	ISO17075	2.58		2.17	
2497	ISO17075	1.76		0.23	
2499	ISO17075	1.55		-0.27	
2501	ISO17075	2.26778		1.43	
2504	ISO17075	<2		-----	
2511	ISO17075	2.25		1.39	
2514	ISO17075	1.704		0.10	
2515	ISO17075	1.809		0.35	
2523	ISO17075	1.764		0.24	
2532	ISO17075	1.77		0.25	
2536	ISO17075	1.31		-0.83	
2538	B82.02.11	2.48		1.93	
2546	ISO17075	1.38		-0.67	
2549	in house	1.79		0.30	
2553	ISO17075	1.35		-0.74	
2563	ISO17075	1.28		-0.90	
2566	ISO17075	1.24	ex	-1.00	Result excluded, see §4.1
2567	ISO17075	1.47		-0.46	
2573	ISO17075	2.02		0.85	
2578	ISO17075	3.27		3.80	
2590	ISO17075	1.82		0.37	
2592	ISO17075	1.57		-0.22	
2605	ISO17075	1.00		-1.57	
2610	ISO17075	2.55		2.10	
2614	ISO17075	1.1		-1.33	
2624	ISO17075	1.099	ex	-1.33	Result excluded, see §4.1
2637	ISO17075	4.2	R(0.05)	6.00	
2640	ISO17075	1.31		-0.83	
2643	ISO17075	1.67		0.02	
2646	§64LFGB82.02.11	1.5700		-0.22	
2649	DIN53314	1.94	ex	0.66	Result excluded, see §4.1
2650	ISO17075	1.25		-0.98	
2652	ISO17075	1.243		-0.99	
2655	INH-17075	1.682		0.05	
2656		-----		-----	
2658	ISO17075	2.754		2.58	
2664	ISO17075	2.44		1.84	
2665	ISO17075	3.73	R(0.05)	4.89	
2666	ISO17075	3.76	R(0.05)	4.96	
2677	ISO17075	1.77		0.25	
3109	DIN53314	2.62		2.26	average of two results; 2.60 and 2.63
3116	ISO17075	1.419		-0.58	
3118	ISO17075	2.49		1.96	
3124	in house	10.059549	ex	19.86	Result excluded, see §4.1
3146	§64LFGB-B82.02.11	1.07		-1.40	
3149	ASU82.02.11	2.83		2.76	
3150	ISO17075	1.70	C	0.09	first reported: 0.10
3151	ISO17075	2.175	ex	1.21	Result excluded, see §4.1
3154	ISO17075	1.03		-1.50	
3160	ISO17075	1.93		0.63	
3172	ISO17075	2.343	ex	1.61	Result excluded, see §4.1
3180		-----		-----	
3190	ISO17075	1.49		-0.41	
3191	ISO17075	1.375		-0.68	
3192	ISO17075	1.14		-1.24	
3197	ISO17075	2.1	ex	1.03	Result excluded, see §4.1
3199	ISO17075	1.47659363		-0.44	
3204	ASU§64B82.02.11	2.999	ex	3.16	Result excluded, see §4.1
3210	INH-01	<3.0		-----	
3216	ISO17075	1.64		-0.05	
3218	ISO17075	1.52	ex	-0.34	Result excluded, see §4.1
3220	ISO17075	3.52	ex	4.39	Result excluded, see §4.1
3222	ISO17075	3.39		4.08	
3225	ISO17075	1.84		0.42	
3228	ISO17075	1.8		0.32	
3233	in house	1.86		0.47	average of two results; 1.76 and 1.97
3237	ISO17075	2.55		2.10	
3242	ISO17075	1.82		0.37	
3246	ISO17075	1.89		0.54	

Normality	suspect
N	111
Outliers	5 (+ 21 excl)
mean (n)	1.663
st.dev. (n)	0.5457
R(calc.)	1.528
R(ISO17075:07)	1.184

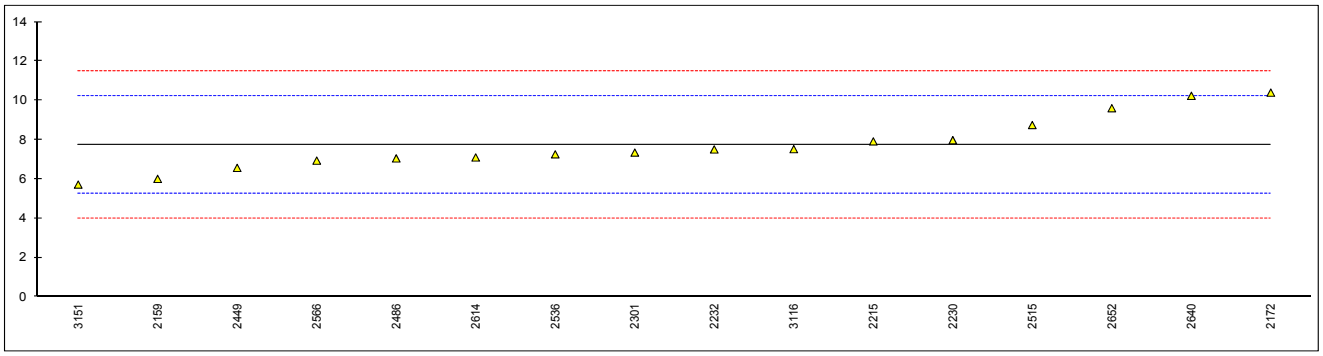


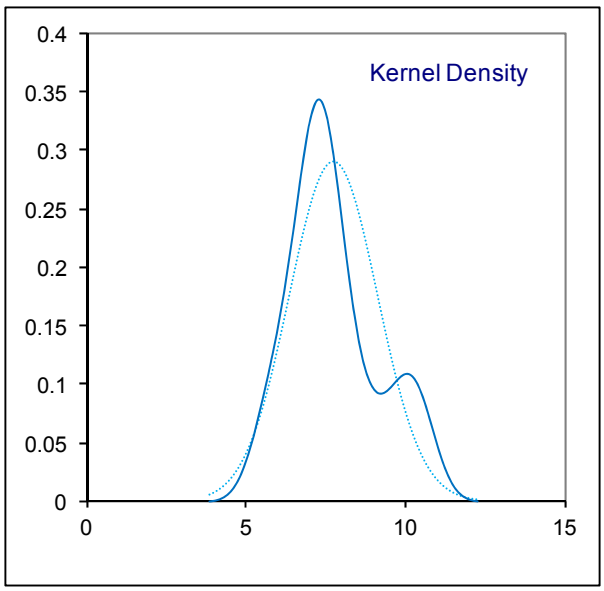


Determination of Chromium(VI) after aging in sample #15008; results in mg/kg

lab	method	Value	mark	z(targ)	remarks
2159	CPSD-AN-00044	6.01		-1.39	
2172	ISO17075	10.402		2.13	
2215	ISO17075	7.92		0.14	
2230	ISO17075	7.98		0.19	
2232	ISO17075	7.51		-0.19	
2301	ISO17075	7.35		-0.32	
2449	ISO17075	6.57		-0.94	
2486	ISO17075	7.0524		-0.56	
2515	ISO17075	8.75		0.80	average of two results; 8.69 and 8.80
2536	ISO17075	7.26		-0.39	
2566	ISO17075	6.94		-0.65	
2614	ISO17075	7.1		-0.52	
2640	ISO17075	10.24		2.00	
2652	ISO17075	9.608		1.49	
3116	ISO17075	7.523		-0.18	
3151	ISO17075	5.720		-1.62	

normality	OK
n	16
outliers	0
mean (n)	7.746
st.dev. (n)	1.4126
R(calc.)	3.852
R(ISO17075:07)	3.498





APPENDIX 2

Summary of reported analytical details

Lab	Sample grinded or cut	Final Particle Size	Extraction. time (min.)	pH after extract. #15008	pH after extract. after aging #15008	Recovery checked	Recovery #15008 (%)
110	as received	6	180	8.0		yes	100
213	as received	< 5 * 5	180	7.76		yes	126
361	as received	± 5 * 5	180	7.7		yes	90.9
551	as received	± 6.2 * 4.6	180	8.02		yes	103
622	grinded/cut		180	±8		yes	103
623	cut	5 * 5	180	7.91		yes	97
2102	as received	3	180	7.6		yes	104.57
2108	as received	5 * 5	180	7.86		yes	90.8
2115	grinded/cut		180	7.81		yes	92.2
2129	as received		180			no	
2131	as received	5 * 5	180	7.73/ 7.71		yes	111 and 88
2132	cut	± 1	180	7.9		yes	94.09
2135							
2138	as received	± 5 * 5	180	7.8		yes	94.06
2139		3	180	7.8			
2146	as received	5 * 5	180			yes	73.3
2159	as received	5 * 5	180	7.8	7.9	yes	100
2165	cut	1	180	7.5		yes	96
2166	as received	5 * 5	180	7.7		yes	92.7
2172			180	7.8	7.9	yes	93
2184	cut	1 * 1	180	7.9		yes	95.8
2190	as received		180	7.5		no	
2201	cut	4 * 4	180	7.8		yes	95.8
2215	as received	5 * 5	180	7.9	7.9	no	
2221	as received	4 * 6	180	7.63		yes	89
2228							
2230	as received	5 * 5	180	7.9	7.90	yes	84.0
2232	as received	5 * 5	180	8.12	8.06	yes	90.3
2238	as received	original size	180	7.85		no	
2241	grinded	2 * 2	180	7.79		yes	98.3
2247		4 * 4	180	7.92		yes	85
2255	as received	5 * 5	180	7.76		yes	91.6
2256							
2271	as received	5 * 5	180	8.0		yes	97
2289	cut	< 4 * 4	180	8.0		yes	96.1
2290	cut	4 * 4	180	7.7		yes	95
2293		5 * 5	180	7.61		yes	89
2295	as received		180	8		no	
2296	as received	5 * 5	180	7.86		yes	102.94
2301	as received	5 * 5	180	7.7	7.8	yes	97.37
2310	cut	5 * 5	180	7.8		yes	92
2311	cut	(5 * 5) ± 2	180	7.80		yes	92
2320	as received	5 * 5	180	8.0		no	
2330	as received	5 * 5	180	7.68		yes	94.5
2350	cut	5± 2 * 5 ± 2	180	8		yes	96.3/95.7
2352	cut	5 * 5	180	7.7		yes	102.6
2357	as received	5 * 5	180	7.93		yes	84.1
2358	cut	5 * 5	180	7.5-8.0		no	
2363	as received	±5 * 5	180	7.6		yes	97.7
2365							
2366	as received	as received	180	7.58		yes	95.5
2369		5 * 5	180	8.0		yes	100.2
2370							
2375	cut	5 * 5	180	7.8		yes	101
2379	as received	5 * 5	180	7.74		yes	111.00
2380	as received	5	180±5	7.78		yes	96
2385	as received	5 * 5	180	7.8		yes	96
2389	cut	5	180	7.77		yes	102.2
2390	as received		180	7.59		yes	103.1
2410	as received		180	7.80		yes	94
2413							
2426	cut	1.5	180	7.8		yes	103.6
2432	as received		180	7.8		yes	99
2441			180	7.8			100
2442	cut	5 * 5	180	7.7		no	
2449	as received	5 * 5	180	7.9	7.9		
2450	as received		180	7.6		no	

Lab	Sample grinded or cut	Final Particle Size	Extaction. time (min.)	pH after extract. #15008 non aging	pH after extract. #15008 after aging	Recovery checked	Recovery #15008 (%)
2452	cut	1	180	8.04		yes	80
2455							
2460	as received	as received		7.74		yes	127.3
2477							
2481	as received	5.0	180	7.70		yes	103.3
2482	as received	as received	180	7.5-8		no	
2485	as received		180	7.8		yes	89
2486	as received	as received	180	7.78	7.93	no	
2488	as received	5 * 5	180	7.82		no	
2489	cut	±1.5 * 1.5	180	7.80		yes	100
2492	as received	NA	180	7.881		yes	99
2495	as received	no	180	7.83		no	
2497	cut	<0.5	180	7.7		yes	>90
2499	as received	as received	180	7.8		yes	78
2501	as received	3	180	7.63		yes	1
2504	as received	4 * 4	180	7.72		yes	96
2511	grinded or cut	grinded	180	7.8			
2514	as received	±5 * 5	180	7.95		yes	95
2515	as received	8 * 8	180	7.79	7.76	yes	96.4
2523		4 * 4	180	7.81		yes	88
2532	cut	1.5 * 1.5	180	7.86		yes	99.66
2536		5 * 5	180	7.8	7.9	yes	99
2538							
2546	as received	<4	180	7.7		yes	98.06
2549	cut	4 * 4	180	7.92		yes	90
2553	as received	5 * 5	180	7.9		yes	96.55
2563	cut	5 * 5	180	7.68-7.71		no	
2566		as received	180	8.02	8.02		
2567	cut	4 * 4	180	7.90		no	
2573	cut	4.8 * 5.3	180	7.90		yes	93.9
2578	as received	5 * 5	180	7.81		yes	85.3
2590	cut	no	180	7.8		yes	97
2592	as received		180	7.78		yes	97
2605	as received	5 * 5	180	7.74		yes	92
2610	as received		180	7.65		yes	95.9
2614	cut	5 * 5	180	7.84	7.85	yes	94
2624	as received	as received	180	8.04		yes	105.0
2637	grinded	1 * 1	180			no	
2640	as received	5 * 5	180	7.75	7.85	yes	97.9
2643	as received		180	7.8		yes	98.7
2646	as received	as received	180	7.7		yes	99
2649	as received	as received	180	8.0		yes	85
2650	as received	0.8	180	7.75		no	
2652		5	180	7.68	7.76	yes	91.15
2655	cut	2	180	7.64/7.66		yes	96.08/99.09
2656							
2658	as received	as received	180	7.8		yes	94
2664	as received	as received	180	7.7		yes	100.3
2665	cut	4	180	7.9		yes	95
2666	grinded or cut	3 - 5	180	7.8			
2677	as received		180	7.95		yes	116
3109	as received	<0.25*0.25	180	7.73		no	
3116	as received	5 * 5	180	7.8	7.9	no	
3118	cut	5 * 5	180	7.84		yes	105
3124	as received	2 * 2	180	10		no	
3146	as received		180	7.5		yes	99
3149	cut	2 * 4	180±5	7.8		yes	100
3150	as received	5 * 5	180			no	
3151	as received		180	8	8	yes	98
3154	as received		180	7.8		yes	104.0
3160	cut	2 - 3	180	7.75		yes	88.3
3172	as received		180	8.0		yes	>80
3180	as received	original size	180	7.90		no	
3190							
3191	cut	2 * 4	180	7.83		no	
3192	as received	3 - 8	180	7.85		no	
3197	as received	5	180	8.0		yes	89
3199	as received	5 * 5	180	7.82		no	
3204	as received	5 * 5	180	8.0		yes	101.2
3210	as received		180			no	
3216	as received		180	7.75		yes	94.4

Lab	Sample grinded or cut	Final Particle Size	Extaction. time (min.)	pH after extract. #15008 non aging	pH after extract. #15008 after aging	Recovery checked	Recovery #15008 (%)
3218	as received	2 * 2	180	8.0		yes	85
3220	as received	taken as it is	180	8.0		no	
3222	as received	±5 * 5	180	7.75		yes	87.5
3225	as received	6 * 6	180	7.8		yes	98.2
3228	as received	4	180				
3233	as received	5 * 5	180	7.70/7.72		no	
3237	as received		180	7.85		yes	105.4
3242	cut	2	180	7.8		yes	91.6
3246	as received		180	7.8		yes	91.5

APPENDIX 3

Number of participants per country

7 labs in	BANGLADESH
1 lab in	BRAZIL
1 lab in	BULGARIA
1 lab in	CAMBODIA
1 lab in	CAMBODIA, Kingdom of
1 lab in	DENMARK
1 lab in	FINLAND
5 labs in	FRANCE
18 labs in	GERMANY
1 lab in	GUATEMALA
6 labs in	HONG KONG
10 labs in	INDIA
4 labs in	INDONESIA
12 labs in	ITALY
5 labs in	KOREA
3 labs in	MEXICO
1 lab in	MOROCCO
28 labs in	P.R. of CHINA
4 labs in	PAKISTAN
1 lab in	SINGAPORE
4 labs in	SPAIN
2 labs in	SRI LANKA
5 labs in	SWITZERLAND
3 labs in	TAIWAN R.O.C.
3 labs in	THAILAND
1 lab in	THE NETHERLANDS
2 labs in	TUNISIA
7 labs in	TURKEY
4 labs in	U.S.A.
2 labs in	UNITED KINGDOM
3 labs in	VIETNAM

APPENDIX 4

Abbreviations:

C = final result after checking of first reported suspect 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
n.e. = not evaluated
n.d. = not detected

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