Results of Proficiency Test
Chromium VI in leather
April 2016

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Report: iis16A05

June 2016

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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 Of all Chromium compounds, primarily Chromium VI was used, but this has been replaced by the less hazardous Chromium III in most applications.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 2015/2016, this proficiency test was continued.
In the interlaboratory study of April 2016, 147 laboratories from 29 different countries have registered for participation (see appendix 3). In this report, the results of the 2016 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 in Spijkenisse was the organizer of this proficiency test. Due to lack of a sufficient amount of suitable materials it was decided to use in this proficiency test only one leather sample without aging. Sample analyses for fit-for-use and homogeneity testing were subcontracted to an accredited laboratory. It was decided to send one sample of approximately 5 grams, labelled #16540.
The 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% confidentiality of participant's data. Feedback from the participants on the reported data is encouraged and customer's satisfaction is measured on regular basis by sending out questionnaires.

2.2 PROTOCOL

The protocol followed in the organisation of this proficiency test was the one as described for proficiency testing in the report 'iis Interlaboratory Studies: Protocol for the Organization, Statistics and Evaluation' of April 2014 (iis-protocol, version 3.3). This protocol can be downloaded from 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 leather sample, labelled (#16540), was prepared by a third party. It was cut in small 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	*#16540 (mg/kg)*
#16540-1	4.31
#16540-2	4.76
#16540-3	4.81
#16540-4	4.30
#16540-5	4.62
#16540-6	4.01
#16540-7	4.48

table 1: homogeneity test results of subsamples #16540

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

Chromium VI	*#16540 (mg/kg)*
r (observed)	0.80
reference test method	ISO17075:2007
r (reference test method)	0.81
0.3 x R (reference test method)	0.60

table 2: evaluation of the repeatability of subsamples #16540

The repeatability of the results of the homogeneity tests for Chromium VI of sample #16540 was not in agreement with 0.3 times the reproducibility mentioned in the reference method ISO17075:2007. However, it was in full agreement with the repeatability of the reference method ISO17075:2007. Therefore, homogeneity of the subsamples was assumed for sample #16540.

Approx. 5 grams of sample #16540 was sent to each of the participating laboratories on March 23, 2016.

2.5 ANALYSES

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, however without drying (or determination of volatile matter).
To get comparable results a detailed report form, on which the units were prescribed as well as the required standards and a letter of instructions were prepared and made available on the data entry portal www.kpmd.co.uk/sgs-iis/. The detailed report form was also made available for download on 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 reanalysis). Additional or corrected test results are used for data analysis and the original reported test results 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.
A list of abbreviations used in the tables can be found in appendix 4.

3.1 STATISTICS

The protocol followed in the organisation 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 April 2014 (iis-protocol, version 3.3).

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. The statistical evaluation of the test results should be used with due care in case that a data set does not prove to have a normal distribution.

In accordance to ISO 5725 the original test results per determination were submitted to Dixon's and 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. 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 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 of 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 some cases, a reproducibility based on former iis proficiency tests could be used.

When a laboratory did use a test method with a reproducibility that is significantly different from the reproducibility of the reference test method used in this report, it is strongly advised to recalculate the z-score, while using the reproducibility of the actual test method used, this in order to evaluate whether the reported test result is fit-for-use.

The z-scores were calculated according to:

$z_{(target)}$ = (test result - average of proficiency test) / target standard deviation

The $z_{(target)}$ scores are listed in the result tables of 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:

|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. Seven participants reported results after the final reporting date and two other participants did not report any test results.
Finally, 145 participants did report 144 numerical results (one laboratory reported <3 mg/kg). Observed were 6 outlying test results, which is 4.2% 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. 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. Only two laboratories reported to have measured a pH outside the acceptable range. Both test results were significantly low and one of the test results was excluded from the statistical evaluation as it appeared to be an outlier.

#16540: The determination of Chromium VI at a concentration level of 4 mg/kg was problematic. Six statistical outliers were observed. The calculated reproducibility after rejection of the statistical outliers is not in agreement with ISO17075:2007. The large dispersion of the reported test results is (partly) caused by the differences in the pre-treatment of the sample. The laboratories that did use the sample as received without cutting/grinding, reported significantly lower test results than the laboratories that did cut or grind the sample before the determination of the chromium VI content, see also the discussion in chapter 6.

4.2 PERFORMANCE EVALUATION FOR THE GROUP OF LABORATORIES

A comparison has been made between the reproducibility as declared by the relevant reference test method and the reproducibility 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	mg/kg	138	3.97	3.23	2.06

table 3: performance overview for sample #16540

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 requirement 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.

When using a limit of <3 mg/kg and applying it to the reported test results for sample #16540, the majority of the laboratories would not release this sample to the consumer market. However, 27 laboratories (=19%) reported a test result below the above mentioned limit 3 mg/kg and would have released the leather to the market.

NB: when the test results had been reported on “dry weight” according Regulation No 301/2014 the average chromium VI content of 3.97 would be higher!

5 COMPARISON WITH PREVIOUS INTERLABORATORY STUDIES

The observed variation in the test results for Chromium VI in the 2016 PT is in agreement in comparison with the variation as observed in the previous PTs, see below table.

Component	*April 2016*	*February 2015*	*February 2014*	*Target*
Chromium VI	29%	33%	19 – 31%	19%

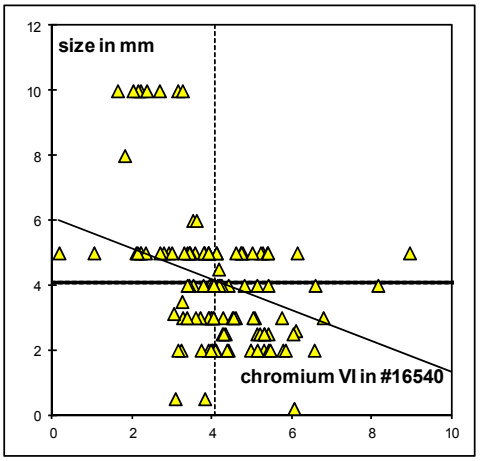
table 5: development of the uncertainties over the years

6 DISCUSSION

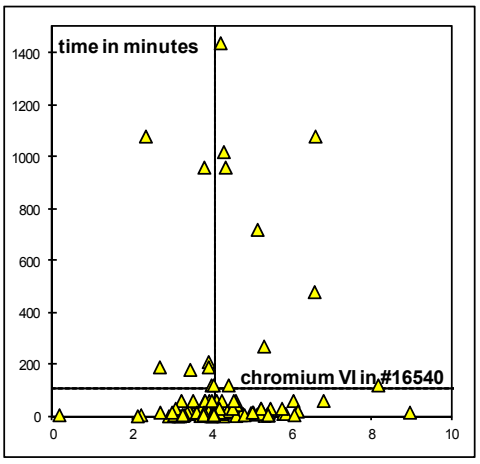
From the reported test methods it appeared that a large majority participants tested the leather samples according to the test method ISO17075:2007, a colorimetric test method, and five participants used §64 B LFGB 82.02-11. These two tests methods appear to be similar (both in literature searches as in the results of this proficiency test). Other used test methods are CPSD-AN-00044, DIN53314, GB/T22807 and ISO/DIS 17075-2:2015, a chromatographic test method.

The analytical details that were reported by the participants are summarized in appendix 2.

Sample pretreatment by cutting or grinding:
The samples were already cut to pieces before the homogenisation of the material.
A number of participants did cut the sample further; one participant used a milling procedure to powder the sample. The final particle size of the sample has a visible influence on the test results, see the graph. Cut/grinded samples are giving higher chromium VI test results than when tested without pre-treatment, see also the separate evaluations of the two sets of test results on page 13.



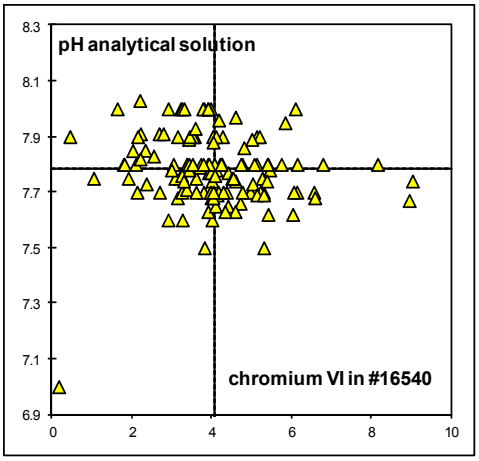
Time between cutting/grinding and extraction:
Another factor of influence may be the time between the cutting/grinding and the actual extraction with the buffer solution. Chromium VI is not very stable and may oxidize easily to Chromium III. In the graph it is visible that no correlation is present between the measured Chromium VI content and the actual time between cutting/grinding and extraction of the sample. The stability of Chromium VI under the test circumstances obviously is not critical.



pH:

Also the pH is an important factor in test method ISO17075:2007, as it states that the pH should be between 7.5 and 8.0. In the graph it is visible that no correlation is present between the pH of the analytical solution and the Chromium VI content of the sample.

Two laboratories reported to have measured a pH outside the acceptable range. Both test results were significantly low and one of the test results appeared to be a statistical outlier.



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

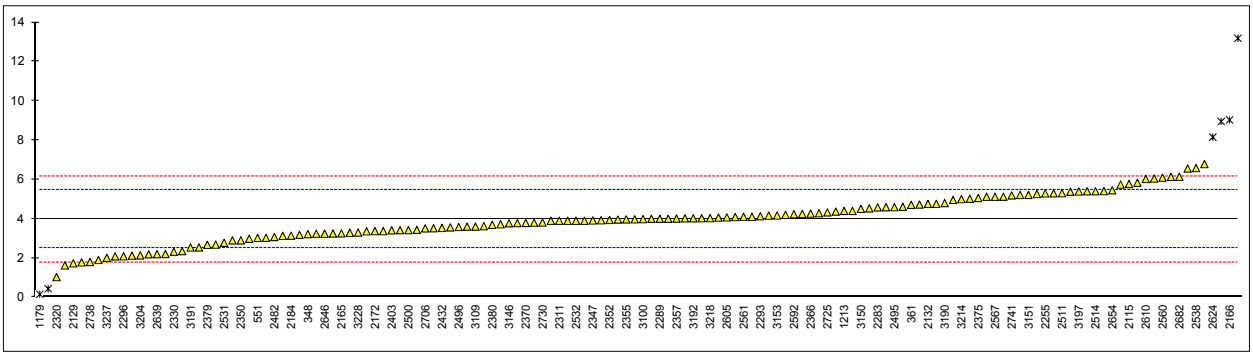
APPENDIX 1

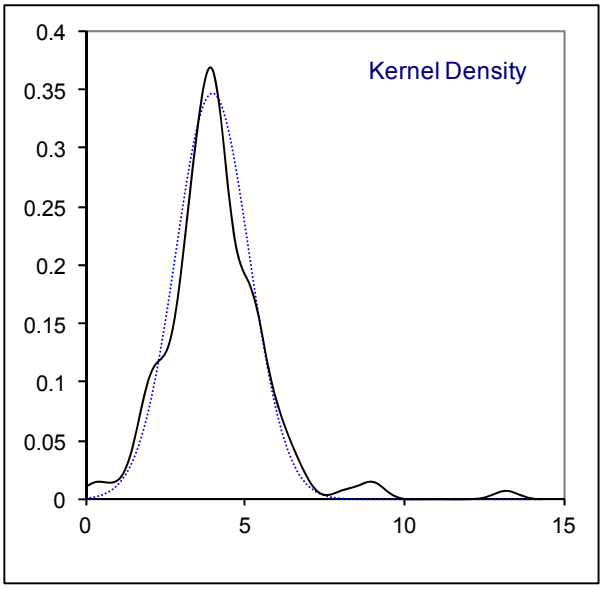
Determination of Chromium VI in sample #16540; results in mg/kg

lab	method	value	mark	z(targ)	remarks
110	ISO17075	6.784		3.82	
213	ISO17075	5.26		1.75	
339	ISO17075Mod.	1.9	C	-2.81	first reported <2.5
348	ISO17075	3.217		-1.02	
361	ISO17075	4.71		1.00	
551	ISO17075	3.0258		-1.28	
623	ISO17075	3.56		-0.56	
840	ISO17075	3.8		-0.23	
1179	EN71-3+A1	0.15365	R(0.05)	-5.18	
1213	ISO17075	4.4	C	0.58	first reported 11.183
2102		-----		-----	
2115	ISO17075	5.77		2.44	
2128	ISO17075	2.190		-2.42	
2129	ISO17075	1.73		-3.04	
2131	ISO17075	3.185		-1.07	
2132	ISO17075	4.76		1.07	
2165	ISO17075	3.2572		-0.97	
2166	ISO17075	9.031	R(0.05)	6.87	
2172	ISO17075	3.369		-0.82	
2184	ISO17075	3.137		-1.13	
2201	ISO17075	4.20		0.31	
2213	ISO17075	5.12		1.56	
2228	In house	2.2055		-2.40	
2232	ISO17075	2.0859		-2.56	
2238	ISO17075	4.104		0.18	
2246	ISO17075	4.725		1.02	
2247	ISO17075	4.96		1.34	
2255	ISO17075	5.29		1.79	
2272	ISO17075	6.5585		3.51	
2273		-----		-----	
2283	ISO17075	4.58		0.83	
2289	ISO17075	4.0		0.04	
2290	ISO17075	4.61		0.87	
2293	ISO17075	4.129		0.22	
2295	ISO17075	5.4		1.94	
2296	In house	2.09		-2.55	
2310	ISO17075	3.60		-0.50	
2311	ISO17075	3.9		-0.10	
2320		1.03		-3.99	
2330	ISO17075	2.3226		-2.24	
2347	ISO17075	3.9155		-0.07	
2350	ISO17075	2.9016		-1.45	
2352	ISO17075	3.94		-0.04	
2355	ISO17075	3.967		0.00	
2357	ISO17075	4.01		0.05	
2358	ISO17075	3.5176		-0.62	
2363	ISO17075	4.02		0.07	
2365	ISO17075	3.97		0.00	
2366	ISO17075	4.2634		0.40	
2369	ISO17075	3.9		-0.10	
2370	ISO17075	3.79		-0.25	
2375	ISO17075	5.06		1.48	
2379	ISO17075	2.6742		-1.76	
2380	ISO17075	3.6920		-0.38	
2385	ISO/DIS17075-2	4.25		0.38	
2389	ISO17075	5.21		1.68	
2390	ISO17075	3.42		-0.75	
2403	ISO17075	3.4136		-0.76	
2410	ISO17075	4.0		0.04	
2426	ISO17075	5.02		1.42	
2432	ISO17075	3.5375		-0.59	
2442	ISO17075	3.03		-1.28	
2449	ISO17075	3.438		-0.72	
2459	ISO17075	5.8339		2.53	
2460	ISO17075	5.408		1.95	
2462	ISO17075	3.37		-0.82	
2482	ISO17075	3.07		-1.22	
2489	ISO17075	4.0		0.04	
2495	ISO17075	4.59		0.84	
2496	ISO17075	3.5791		-0.53	
2497	ISO17075	6.13		2.93	
2500	ISO17075	3.421		-0.75	
2501	ISO17075	3.1333		-1.14	
2504	ISO17075	5.1261		1.57	
2511	ISO17075	5.3		1.81	
2514	ISO17075	5.4		1.94	

2522	ISO17075	3.9	C	-0.10	first reported 0.60
2531	ISO17075	2.7790		-1.62	
2532	ISO17075	3.9		-0.10	
2538		6.58		3.54	
2543	ISO17075	8.95	R(0.05)	6.76	
2553	ISO17075	2.12		-2.51	
2560	ISO17075	6.093		2.88	
2561	ISO17075	4.10		0.18	
2563	ISO17075	3.24		-0.99	
2567	ISO17075	5.12		1.56	
2569	ISO17075	4.06		0.12	
2586	ISO17075	4.0865		0.16	
2590	ISO17075	4.4011		0.58	
2592	ISO17075	4.23		0.35	
2605	ISO17075	4.07		0.13	
2610	ISO17075	6.026		2.79	
2612	ISO17075	4.365		0.54	
2624	ISO17075	8.155	R(0.05)	5.68	
2629	ISO17075	4.5888		0.84	
2637	ISO17075	2.9		-1.45	
2639	GB/T 22807	2.1995		-2.40	
2646	ISO17075	3.24		-0.99	
2654	ISO17075	5.45	C	2.01	first reported 12.76
2655	In house	<3		-----	
2656	ISO17075	2.9825		-1.34	
2662	ISO17075	3.9233		-0.06	
2664	ISO17075	1.7794		-2.98	
2668	ISO17075	3.72		-0.34	
2674	ISO17075	3.3604		-0.83	
2682	ISO17075	6.14		2.95	
2695	ISO17075	5.3757		1.91	
2702	ISO17075-2	4.16		0.26	
2705	ISO17075	13.19	R(0.01)	12.52	
2706	In house	3.51		-0.63	
2711	ISO17075-2	3.621		-0.47	
2713	ISO17075	3.2878		-0.93	
2716	ISO17075	0.435	R(0.05)	-4.80	
2721	In house	3.96		-0.01	
2725	ISO17075	4.3258		0.48	
2730	ISO17075-2	3.8106		-0.22	
2738	In house	1.8		-2.95	
2741	ISO17075	5.19		1.66	
3100	ISO17075	3.98		0.01	
3109	In house	3.6		-0.50	
3116	In house	3.78		-0.26	
3146	ISO17075 mod.	3.77		-0.27	
3150	ISO17075	4.50		0.72	
3151	ISO17075	5.215		1.69	
3153	ISO17075	4.169		0.27	
3154	ISO17075	2.54		-1.94	
3160	ISO17075	6.05		2.82	
3172	ISO17075	5.2959		1.80	
3183	ISO17075	2.6852		-1.75	
3185	ISO17075	4.03		0.08	
3190	ISO17075	4.8		1.13	
3191	ISO17075	2.5363		-1.95	
3192	In house	4.0250		0.07	also reported ISO/DIS17075-2 result: 3.895 mg/kg
3197	ISO17075	5.39		1.93	
3200	ISO17075	4.53		0.76	
3204		2.135		-2.49	
3209	ISO17075	5.74		2.40	
3210	In house	4.28		0.42	
3214	ISO17075	5.0		1.40	
3216	ISO17075	2.3532		-2.20	
3218	ISO17075	4.03		0.08	
3220	DIN53314	3.25		-0.98	
3222	ISO17075	4.761		1.07	
3228	ISO17075	3.30		-0.91	
3233	In house	1.6228		-3.19	
3237	ISO17075	2.01		-2.66	
3248	ISO17075	3.9		-0.10	

		only after cutting/grinding:	tested as received:
	normality	OK	OK
	n	106	32
	outliers	4	1
	mean (n)	4.320	2.763
	st.dev. (n)	0.9541	1.0735
	R(calc.)	2.671	3.006
	R(ISO17075:07)	2.195	1.603


14
12
10
8
6
4
2
0
1179 2320 2129 2738 3237 2296 3204 2639 2330 3191 2379 2531 2350 551 2482 2184 348 2646 2165 3228 2172 2403 2500 2706 2432 2496 3109 2380 3146 2370 2730 2311 2532 2347 2352 2355 3100 2289 2357 3192 3218 2605 2561 2293 3153 2592 2366 2725 1213 3150 2283 2495 361 2132 3190 3214 2375 2567 2741 3151 2255 2511 3197 2514 2654 2115 2610 2560 2682 2538 2624 2166


Kernel Density
0.4
0.35
0.3
0.25
0.2
0.15
0.1
0.05
0
0
5
10
15

APPENDIX 2

Summary of reported analytical details

Lab	Analysis method	Pretreatment	article size before analysis	time between grinding and extraction
110	RSTS-Chem-104-1	Cut	3 x 3 mm	< 1 hr
213	ISO 17075	Cut	5 x 5 mm	
339	UV absorbance (540 nm)	Used as received		n/a
348	ISO 17075	Cut	2 x 2 mm	<1 min
361	ISO 17075:2007	Cut	5 x 5 mm	~ 5 min
551	ISO 17075	Cut		
623	ISO 17075	Cut	5 x 5 mm	30 min
840	ISO 17075	Cut	0.5 cm	1 hour
1179	EN 71-3+A1	Grinded	0.5 mm	5 min
1213	ISO 17075	Cut	< 4mm	2 h
2102		---		
2115	ISO17075	Cut	2 mm	10 min
2128	ISO17075	Used as received	ca. 5 mm	n/a
2129	ISO17075	Used as received		
2131	ISO 17075	Cut		1 minute
2132	ISO 17075	Cut	5 x 5 mm	10 min
2165	ISO 17075:2007	Cut	3 x 3 mm	3 min
2166	ISO17075	Used as received		
2172	ISO 17075	Cut	5 x 5 mm	10 min
2184	ISO 17075	Cut	2 x 2 mm	immediately
2201	iso17075	Cut	4 x 4 mm	in 24 hours
2213	ISO 17075	Cut	2 mm to 3 mm	5 to 10 minutes
2228	CPSD-AN-00044-MTHD	Used as received	5 x 5 mm	5 min
2232	ISO 17075	Used as received	5 x 5 mm	n/a
2238	official method	Used as received	5 x 5 mm	5 min
2246	ISO 17075	Cut	5 x 5 mm	10 min
2247	ISO 17075	Cut	2 x 2 mm	10 to 15
2255	ISO 17075	Cut	2 x 2 mm	4.5 hours
2272		Cut	2 x 2 mm	<8 hours
2273		---		
2283	ISO 17075:2008	Cut	0.3*0.3 cm	60 min
2289	ISO 17075:2007	Cut	2 x 2 mm	immediately
2290	ISO17075	Cut		
2293	ISO17075	Cut	4 x 4 mm	15 min
2295	ISO 17075	Grinded	2-3	5 min
2296		---		
2310	ISO 17075	Used as received		
2311	ISO 17075	Cut	(5X5)±2 mm	30 min
2320	RSTS-CHEM-104-1	Used as received	5 x 5 mm	n/a
2330	ISO 17075	Cut	5 x 5 mm	1080 min
2347	ISO17075	Cut	3 x 3 mm	60 min
2350	ISO 17075	Cut	5 x 5 mm	immediately
2352	ISO 17075:2007	Cut	4 x 4 mm	30 min
2355	ISO17075	Cut	3 x 3 mm	30 min
2357		Used as received		
2358	ISO 17075	Cut	4 x 4 mm	15 min
2363	ISO 17075:2007	Cut	3 x 3 mm	15 min
2365	ISO17075:2007	Cut	3 x 3 mm	less than 2h
2366	ISO 17075	Cut	3 x 3 mm	immediately
2369		Cut	3 x 3 mm	3.5h
2370	ISO 17075	Cut	5 x 5 mm	16 hours
2375	ISO 17075-2007	Cut	3 x 3 mm	
2379	ISO 17075:2007	Used as received	1 cm X 1 cm	around 190 min
2380	ISO 17075:2007	Cut	3 x 3 mm	2 min
2385	Draft ISO 17075-2	Cut	2 - 3 mm	10 min
2389	ISO 17075	Cut	5 x 5 mm	30 min
2390	ISO 17075	Cut	5 x 5 mm	15 min
2403	ISO 17075:2007	Cut	4mm	10 min
2410	ISO 17075	Cut	4 x 4 mm	10 min
2426	ISO17075	Cut	3 x 3 mm	15 min
2432		Used as received		
2442	ISO 17075:2007	Cut	3.13 mm	5 min
2449		Cut	5 x 5 mm	180 min
2459		Cut	2 mm²	10 min
2460	ISO 17075:2007	Cut	2 x 2 mm	15 min
2462	ISO 17075	Cut	4 x 4 mm	15min
2482	BVL B 82.02-11	Cut	< 0,5 mm	~ 30 min
2489	ISO 17075	Cut	2 x 2 mm	10 min
2495	ISO 17075:2007	Cut	5 x 5 mm	45 min
2496	ISO 17075	Cut	3mm	15 min
2497	ISO 17075	Cut	5mm	20 min
2500	ISO17075	Cut	5 x 5 mm	20 min
2501	ISO17075:2007	Used as received	1cm x 1cm	n/a
2504	ISO17075	Cut	2*2 mm	720 min
2511	ISO 17075	Cut	2mm to 3 mm	few minutes
2514	ISO17075	Cut	4 x 4 mm	3min - 5 min

Lab	Analysis method	Pretreatment	article size before analysis	time between grinding and extraction
2522	ISO 17075	Cut	5 mm	20 min
2531	ISO 17075	Used as received	0,5 cm	n/a
2532	ISO17075-2008	Cut	2 mm	10 min and 3 hrs shaking
2538	B82.02-11	Cut	3 x 5 mm	approx. 18 h
2543	ISO 17075	Grinded	70% powder and 30% ar	15 min
2553	ISO 17075	Cut	5 x 5 mm	<1 min
2560	ISO 17075-1	Cut	3. 2mmX2mm	n/a
2561	ISO 17075	Cut	5X5mm	1 hour
2563	ISO 17075	Cut	ca. 3 x 4 mm	5 min
2567	ISO 17075	Cut	4 x 4 mm	--
2569	ISO 17075	Cut	4mm	10 min
2586	ISO 17075	Cut	2 mm	
2590	ISO 17075	Cut	2 x 2 mm	15 min
2592	ISO 17075	Cut	< 4 mm	1 hour
2605	ISO17075	Cut	2mm	10min
2610	ISO 17075	Cut	2-3 x 2-3 mm	60 min
2612	ISO17075	Cut	< 2x2 mm	20 min
2624	ISO 17075	Grinded	<4 mm	2 hours
2629	ISO 17075	Cut		2
2637	ISO 17075	Used as received		
2639	GB/T 22807-2008	Used as received	1cm x 1cm	n/a
2646	§ 64 82.02-11 (Stand 10/2008)	Used as received		
2654	ISO 17075	Grinded	2 mm	30 min
2655	In house method	Grinded	<2 mm	200 min
2656	ISO17075	Used as received	5 x 5 mm	15 min
2662	ISO 17075	Used as received	4 mm ± 0,5 mm	n/a
2664	ISO 17075:2007	Used as received		
2668	ISO 17075	Cut	2 x 2 mm	30 min
2674	ISO 17075	Cut	3 x 3 mm	15 min
2682		Grinded	N/A	20 min
2695	ISO 17075	Cut	2x10 mm	10 min
2702	17075-2	Cut	4-5 mm	15
2705	ISO 17075	Grinded	<5mm	~45
2706	In house method	Cut	ca. 0.3x1 cm	max. 1 h
2711	ISO/DIS 17075-2	Used as received		n/a
2713	ISO 17075	Cut	0.5 cmX0.5 cm	5 min
2716	ISO 17075	Used as received		
2721	In house method	Cut	2 x 2 mm	immediately
2725	ISO 17075	Cut	2-3mm	960 min
2730	ISO/DIS 17075-2	Cut	0.5 mm x 0.5 mm	<60 min
2738	in house method	Used as received	7-10mm * 7-10mm	
2741	ISO 17075	Cut	2-3mm	10 min
3100	ISO 17075	Cut	4 x 4 mm	1 hours
3109	In house method	Cut	5 mm x 7 mm	15 min
3116	In house method	Cut	5 x 5 mm	15 min
3146	ISO 17075 modified	Cut	3 x 5 mm	5 min
3150	ISO 17075	Cut	3 x 3 mm	30 min
3151	ISO 17075	Cut		30 min
3153	ISO 17075:2007	Cut	4 x 4 mm	30 min
3154	ISO 17075	Used as received		
3160	ISO 17075	Cut	0,2 x 0,2 mm	5 min
3172	ISO 17075	Cut	2-3mm	
3183	§64 LFGB 82.02-11	Cut	0,5 x 0,5 cm	15 min
3185	ISO17075:2007	Cut	4 x 4 mm	10 min
3190	ISO 17075	Cut	4 x 4 mm	5 min
3191	ISO17075	Used as received	not measured	n/a
3192	§64 LFGB 82.02-11	Cut	3 x 3 mm	120 min
3197	ISO 17075	Used as received	5 mm	5 min
3200	ISO 17075	Cut	3 x 3 mm	60 min
3204	§64B82.02.11	Used as received	1 x 1 cm	
3209	ISO17075	Cut	3 x 3 mm	30 min
3210	In house method	Cut	2*3mm	1020 min
3214	ISO 17075	Cut	0.5 cm x 0.5 cm	15 min
3216	ISO 17075:2007	Used as received	(10x10)mm	
3218	ISO 17075	Cut	4 x 4 mm	5 min
3220	DIN 53314	Cut	1cm square	5 min
3222	ISO 17075	Used as received		
3228	ISO 17075	Used as received		
3233	In house method	Used as received	1 cm x 1 cm	
3237	ISO 17075	Used as received	1 cm x 1 cm	
3248	ISO 17075	Used as received	5 x 5 mm	n/a

Summary of reported analytical details, continued

Lab	extraction solution degassed	analytical solution degassed	pH extraction solution	pH analytical solution	extraction time and temperature
110	not degassed	not degassed	8.01	7.8	3hr @ 24C
213	Argon	Argon		7,5 - 8,0	3 hrs at 18~28 °C
339	not degassed	not degassed		7,5 - 8,0	180 min RT (20°C)
348	Nitrogen	Nitrogen	8.0 ± 0.05	close to 8.0	180 min
361	Nitrogen	not degassed	8.0	7.66	180 min / 21,2°C
551	Nitrogen	Nitrogen			180 min / 22 ºC
623	Nitrogen	Nitrogen	7.8	7.9	180 min at 25 C
840	Argon	Argon	8	8	
1179	not degassed	not degassed	< 2	+/- 7	60 min / 50°
1213	Nitrogen	Nitrogen	8.0	7.65	180 min, 30°C
2102	---	---			
2115	Nitrogen	Nitrogen	8.0		180 min 25°C
2128	Nitrogen	Nitrogen	8,00	8,03	180 min; RT 21,0 °C
2129	Argon	Argon			
2131	Nitrogen	Nitrogen		7.5-8.0	180 min, RT
2132	Nitrogen	Nitrogen	7.8	7.8	180 min & RT(25°C)
2165	Argon	Argon	8.0	7.6	180 min, 25.1°C
2166	Argon	Argon	8,00	7,74	180 min. 20 °C
2172	Argon O2-free)	Argon (O2-free)	8.0	7.8	180 min , 22 °C
2184	Nitrogen	Nitrogen	7.5	7.9	180 min, 23 deg C
2201	Nitrogen	not degassed	8.0	7.8	23°C at 180 min
2213	Argon O2-free)	Argon (O2-free)	8	7.8	180 min & temp is 23
2228	Argon O2-free)	not degassed	7.99	7.91	180 min and 26°C
2232	Argon	Argon (O2-free)	8.0	7.8	180 min and 24°C
2238	Nitrogen	Nitrogen	8.0	7.78	180 min RT
2246	Nitrogen	Nitrogen	7.8	7.8	180 min @ 25°C
2247	Argon	Argon	8.00	7.70	180 and 24
2255	Nitrogen	Nitrogen	8.0	7.7	3 hrs ; RT
2272	Nitrogen	Nitrogen	8.0	7.7	3hours 25°C
2273	---	---			
2283	Argon	not degassed	8.0	7.63	180 min and 22°C
2289	Argon O2-free)	Argon (O2-free)	7.7	7.7	180 min 20°C
2290					
2293	Nitrogen	Nitrogen	8.01	7.69	3 hrs +/- 5 min at RT
2295	Nitrogen	Nitrogen	8.05	7.8	180 min 23.6
2296	---	---			
2310	Argon		8.0±0.1	7.5 -8.0	180 min and 25±1ºC
2311	Argon	Argon	8.0	7.8	3 Hour
2320	Nitrogen	not degassed	7.5-8.0	7.5-8.0	180 min 28°C
2330	Nitrogen	Nitrogen	7.998	7.851	180 min and 25-30 °C
2347	Nitrogen	not degassed	8.01	7.77	180 min at 23°C
2350	Nitrogen	Nitrogen	8.0	8.0	3 hours , 20 °C
2352	Nitrogen	Nitrogen	8.01	7.72	3 hours 25°C
2355	Argon O2-free)	Argon (O2-free)	8.0	8.0	180 min and 25°C
2357					
2358	Nitrogen	Nitrogen	8.0	7.9	180 min, 22 °C
2363	Nitrogen	Nitrogen	8.0	7.9	3 hours and 22 °C
2365	Nitrogen	Nitrogen	8.01	7.77	3h, 23°C
2366	Nitrogen	not degassed	8.0	7,9	180 min and 23°C
2369	Nitrogen	Nitrogen	8.0	8.0	3h,23°C
2370	Argon	Argon	7.95	7.70	3 hours and 24 °C
2375			8.0	7.8	180 min - 22 C
2379	Nitrogen	Nitrogen	8.00	7.91	180 min , 24.1 °C
2380	Argon	not degassed	8.0	7.79	180+/-5 min at 22 °C
2385	Nitrogen	Nitrogen	8,0	7,8	180 min; 21 °C
2389	Nitrogen	Nitrogen	8.0	7.7	180 min , 25 °C
2390	Nitrogen	not degassed	8.01	7.78	180 min at 20.4 °C
2403	Nitrogen	Nitrogen	8.02	7.89	3hours, RT
2410	Nitrogen	not degassed	7.99	7.74	180 min
2426	Nitrogen	not degassed	8.01	7.73	180m / 25.2°C
2432					
2442	Argon O2-free)	Argon (O2-free)	8.01	7.8	180 min, 25°C
2449	Nitrogen	Nitrogen	7.67	7.9	180 min
2459	Argon	Argon	8.0	7.95	3 hours at 25 °C
2460	Argon O2-free)	Argon (O2-free)	7.97	7.62	180 min, 21°C
2462	Argon	Argon	8.0	7.8	180 min/ 23°C
2482	Argon O2-free)	Argon (O2-free)	8,0	7,5 - 8,0	3 hrs, 20 °C
2489	Nitrogen	Nitrogen	8	7.6	3 hrs/ 22°C
2495	Nitrogen	Nitrogen	8.04	7.74	3h, RT (22°C)
2496	Argon O2-free)	Argon (O2-free)	8.01	7.93	3h 2 min/23°C
2497	Nitrogen	Nitrogen	8.0	7.7	180 min / 23°C
2500	Argon O2-free)	Argon (O2-free)	8.0	7.8	25 °C for 3 hrs ¡À 5 min
2501	Argon O2-free)	Argon (O2-free)	8,01	7.68	30 min, 23°C
2504	Argon	Argon	8.01	7.69	180 min , RT
2511	Argon O2-free)	Argon (O2-free)	8.1	7.5	3 hours at 21 C

Lab	extraction solution degassed	analytical solution degassed	pH extraction solution	pH analytical solution	extraction time and temperature
2514	Nitrogen	Nitrogen	8	7.8	185 min & 22°C
2522	not degassed	not degassed	9.3	8.0	180 min 23 °C
2531	Nitrogen	not degassed	8.00	7.91	3h 23°C
2532	Nitrogen	Nitrogen	8.0	7.63	180 min and 25 °C
2538	Nitrogen	not degassed	8	7,70 - 7,66	180 and RT
2543	Nitrogen	Nitrogen	8,06	7,67	180 min / 25ºC
2553	Argon	Argon	8.0	7.7	180 min and 24 °C
2560	Nitrogen	Nitrogen	8	8	180±5 min at 25 °C
2561	Nitrogen	Nitrogen	8.01	7.9	180 at 25°C
2563	Argon O2-free)	Argon (O2-free)	8,0	7,7	3 hours at RT
2567	Argon	Argon	8.0	7.9	--
2569	Nitrogen	Nitrogen	8 (Buffer)	7.8	180 min , 24°C
2586	Argon O2-free)	Argon (O2-free)	8,07	7,65	180 min 23 °C
2590	Argon O2-free)	Argon (O2-free)	8.07	7.77	180 min and RT
2592	Nitrogen	Nitrogen	7,8	7,8	180 min , RT
2605	Nitrogen	not degassed	8.0	7.76	3h
2610	Argon	not degassed	8.00	7.62	3 h, 22.8 ºC
2612	Nitrogen	Nitrogen	7,9	7,7	3 hours RTs
2624	not degassed	not degassed	8.0	7,8	3 hours RT 20-26 °C
2629	Argon	Argon	8.04	7.97	3h at 25C
2637	Argon	Argon	8	7,6	3 Hours
2639	Argon O2-free)	Argon (O2-free)	8.06	7.82	180 min£¬22.3°C
2646	not degassed	not degassed	8,03	7,76	180 min, RT
2654	Nitrogen	Nitrogen	8	7.78	180 min/21.8°C
2655	Argon O2-free)	Argon (O2-free)	8.00	7.52, 7.52	180 min. no control temp.
2656	Nitrogen	not degassed	7,98	7,78	180 min at RT (20°C)
2662	Nitrogen	Nitrogen	8.0	7.8	180 min, 26°C
2664	Nitrogen	Nitrogen	8.0	7.8	180 min
2668	Argon	Argon	7.7	7.8	3 hrs and RT
2674	Argon O2-free)	Argon (O2-free)	8.00	7.71	3hours 24.6°C
2682	Nitrogen	Nitrogen	8.03	7.8	180 min at 21°C
2695	Nitrogen	Nitrogen	8.00	7.74	180 min at 20°C
2702	Nitrogen	Nitrogen	8.0	7.7	180 and 23.5
2705	Argon O2-free)	Argon (O2-free)	8.00	8	180 min, 23 °C
2706	Argon	Argon	8.0	7.8	180 / room temp.
2711	Nitrogen	Nitrogen	8.0		180 min, 23°C
2713	Argon O2-free)	Argon (O2-free)	8.0	7.74	180 min RT
2716	Argon O2-free)	not degassed	8,0	7,9	180 min, 23°C
2721	Argon O2-free)	not degassed	8.0	7.7	180 at RT
2725	ultrasonic	not degassed	8,00	7,63	180 min / 20-23ºC
2730	Nitrogen	not degassed	8 +/- 0.1	7 – 8	180 min at RT
2738	Argon	Argon	8.0	7.8	180 min
2741	not degassed	not degassed	7.7	7.9	180 and 27
3100	Nitrogen	Nitrogen	7.94	7.68	180 min 22.7°C
3109	Nitrogen	not degassed	8.0	7.7	180 min at 24°C
3116	Argon O2-free)	Argon (O2-free)	7.9	7.8	180 min at RT (15-28°C)
3146	Nitrogen	not degassed	8	8	3h / RT
3150	Argon	not degassed	8,0	7,5 - 8,0	180 min RT
3151	Argon O2-free)	Argon (O2-free)			180 min at RT
3153	not degassed	not degassed	8.06	7.96	180 min, 22oC
3154	Nitrogen				180 min RT
3160	Nitrogen	Nitrogen	7,99	7,70	180 min, 23ºC
3172			7.99	7.69	3h-25°C
3183	Nitrogen	not degassed	8,0	7,6-7,8	180 min at RT
3185	Nitrogen	Nitrogen	8.00	7.88	3hours,25°C
3190	Nitrogen	Nitrogen	8.00	7.86	180 min 24℃
3191	Nitrogen	Nitrogen	8.03	7.83	180 min, RT
3192	Argon O2-free)	Argon (O2-free)	8,0	7,68	180 min at RT (about 23°C)
3197	Nitrogen	Nitrogen	7,9	7,8	180 min and 22C
3200	Argon	Argon	8.00	7.75	25°C 3h
3204	Nitrogen	not degassed		7,9	180 min, 22 °C
3209	Nitrogen	Nitrogen	8.0	7.8	3Hour, 21.0 °C
3210	Nitrogen	Nitrogen	8	7.7	2h 21°C
3214	Nitrogen	Nitrogen	8.00	7.89	180 min, 22.1 °C
3216	Nitrogen	Nitrogen	7,9	7,73	180 min at 22ºC
3218	Nitrogen	Nitrogen	8.0	7.7	180 min,20¡ãC
3220	not degassed	not degassed	8	8	3 hours and 25°C
3222	Nitrogen	Nitrogen	8,0	7,7	182 min - 22°C
3228	Nitrogen	not degassed	8.0	8.0	3 hours at 23 °C
3233	Argon	Argon	8.00	8.00	180 min / 20.1°C
3237	Nitrogen	not degassed	8,03	7,85	180 min
3248	not degassed	not degassed	8	8	180 min RT

APPENDIX 3

Number of participants per country

5 labs in	BANGLADESH
2 labs in	BRAZIL
2 labs in	BULGARIA
2 labs in	CAMBODIA
5 labs in	FRANCE
17 labs in	GERMANY
1 lab in	GUATEMALA
8 labs in	HONG KONG
10 labs in	INDIA
1 lab in	INDONESIA
10 labs in	ITALY
2 labs in	KOREA
1 lab in	LUXEMBOURG
2 labs in	MEXICO
2 labs in	MOROCCO
34 labs in	P.R. of CHINA
6 labs in	PAKISTAN
1 lab in	SINGAPORE
5 labs in	SPAIN
2 labs in	SRI LANKA
6 labs in	SWITZERLAND
2 labs in	TAIWAN R.O.C.
3 labs in	THAILAND
2 labs in	THE NETHERLANDS
1 lab in	TUNISIA
5 labs in	TURKEY
1 lab in	U.S.A.
2 labs in	UNITED KINGDOM
5 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
n.e.	= not evaluated
n.d.	= not detected

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