

Results of Proficiency Test  
Chromium(VI) in leather  
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Organised by: Institute for Interlaboratory Studies  
Spijkenisse, the Netherlands

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 Of all Chromium compounds, primarily Chromium(VI) was used, but this has been replaced by the less hazardous Chromium(III) in most applications.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

On request of several participants, the Institute of Interlaboratory Studies decided to organise an interlaboratory study for the determination of Chromium(VI) in leather in the 2013-2014 PT program.

In the interlaboratory study of February 2014, 123 laboratories from 29 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 Spijkensisse was the organizer of this proficiency test. It was decided to send 2 different samples (approximately 5 grams each, labelled #14501 and #14502), both positive in Chromium(VI). The analyses for fit-for-use and for homogeneity testing were subcontracted.

Participants were requested to report rounded and unrounded test results. The unrounded test results were preferably used for statistical evaluation. Also an inventory was made of the analytical details of the used test method, by means of a questionnaire, which was included in the report form.

### 2.1 QUALITY SYSTEM

The Institute for Interlaboratory Studies in Spijkensisse, the Netherlands, has implemented a quality system based on ISO/IEC 17043:2010. 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 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).

## 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

Two samples were used in this proficiency test, both positive on Chromium(VI).

The first sample, a red leather (#14501), 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 second sample, a blue leather (#14502), was supplied by a leather manufacturer. It was cut by means of a shredder in leather scraps and the material was mixed thoroughly. Five 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.

<i>Chromium(VI)</i>	<i>in #14501 (mg/kg)</i>	<i>in #14502 (mg/kg)</i>
sample 1	1.74	53.72
sample 2	1.49	50.05
sample 3	1.60	54.38
sample 4	1.61	53.05
sample 5	1.84	51.11
sample 6	1.66	
sample 7	1.72	

table 1: homogeneity test results of subsamples #14501 and #14502

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:

<i>Chromium(VI)</i>	<i>in #14501 (mg/kg)</i>	<i>in #14502 (mg/kg)</i>
r (observed)	0.32	5.10
reference method	ISO17075:2007	ISO17075:2007
0.3 x R (reference method)	0.36	6.15

table 2: evaluation of the repeatability of subsamples #14501

The repeatabilities of the results of the homogeneity tests for Chromium(VI) of sample #14501 and sample #14502 were in agreement with 0.3 times the reproducibility mentioned in the reference method ISO17075:2007. Therefore, homogeneity of the subsamples was assumed for both sample batches.

Approx. 5 grams of both samples #14501 and #14502 were sent to each of the participating laboratories on January 29, 2014.

## 2.5 ANALYSES

The participants were requested to determine the content of Chromium(VI) of two leather samples, applying the analysis procedure that is routinely used in the laboratory. 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 gathered. The original data are tabulated in the appendices of this report. The laboratories are presented by their code numbers.

Directly after the 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, see lit.5) found it to be an outlier. The laboratories that produced these suspect data were asked to check the results. Additional or corrected data are placed under 'Remarks' in the result tables in appendix 1. The analytical details from the questionnaire are summarized in Appendix 2. 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 Organization, Statistics and Evaluation' of January 2010 (iis-protocol, version 3.2).

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.

Prior to the statistical evaluation, the normality of the distribution of the data 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. In the case of an anormal distribution, the statistical evaluation should be used with care.

According to ISO 5725 (1986 and 1994, lit.2 and 3) the original results per determination were submitted subsequently to Dixon's and Grubbs' 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  $R(0.01)$  for Rosner General ESD test (lit. 9). 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 General ESD 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. 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 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. Also a normal Gauss curve was projected over the Kernel Density Graph for reference.

### 3.3 Z-SCORES

To evaluate the performance of the individual participating laboratories the z-scores were calculated. In order to be able to have an objective evaluation of the performance of the individual participants, it was decided to evaluate this performance against the literature requirements. Therefore the z-scores were calculated using a target standard deviation. This target standard deviation was calculated from the literature reproducibility by division with 2.8.

The  $z_{(\text{target})}$ -scores were calculated according to:

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

The  $z_{(\text{target})}$ -scores are listed in the result tables in appendix 1.

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.

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. Fourteen participants reported results after the final reporting date and four participants did not report any test results. One participant withdrew its test results due to use of a test for Total Chromium instead of Chromium(VI).

Finally, 118 participants did report 231 results. Observed were 14 outlying results, which is 6.1% of the numerical results. In proficiency studies, outlier percentages of 3% - 7.5% are quite normal.

Some laboratories submitted two sets of results, one based on the leather as received and the other on dry matter (see remark column in Appendix 1). Most participants did not state whether the result was based on dry matter or not. These results were used as they were reported, no corrections could be made without reported volatile content. Reported results on dry matter will be significantly higher than those based on the leather as received.

### 4.1 METHODS USED BY PARTICIPANTS

The majority of participants used the ISO17075 method for the determination of Chromium(VI). Some laboratories used §64 B LFGB 82.02-11 (from the Lebensmittel-, Bedarfsgegenstände- und Futtermittel Gesetzbuch) and BVL B 82.02-11 (from the Bundesamt für Verbraucherschutz und Lebensmittelsicherheit). These three tests appear to be similar (both in literature searches as in the results of this proficiency test). An in-house test was only used by two participants. Some participants explicitly mentioned that they did not age the sample on the report data sheet.

Two laboratories (code 2177 and 3239) used an IEC62321 method, which apparently is not equivalent. IEC62321 is a method to determine Chromium(VI) in plastics, metals and electronics using a strong alkaline solution. The results have not been excluded from the statistical evaluation, but were all statistically outlying results or false negative values.

## 4.2 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.

#14501: The determination of Chromium(VI) at a concentration level of 3.6 mg/kg was problematic. Ten statistical outliers were observed. The calculated reproducibility, after rejection of the statistical outliers, is not in agreement with ISO17075:2007.

#14502: The determination of Chromium(VI) at a concentration level of 19.6 mg/kg was problematic. Four statistical outliers were observed. The calculated reproducibility, after rejection of the statistical outliers, is not in agreement with ISO17075:2007.

## 4.3 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 #14501	mg/kg	106	3.61	2.65	1.93
Chromium(VI) in #14502	mg/kg	111	19.59	10.74	8.00

table 3: performance overview for samples #14501 and #14502

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 results of the ISO17075 method.

See also the discussion in paragraphs 4.1 and 5.



#### 4.4 EVALUATION OF GROUP RESULTS AGAINST LIMITS FOR CHROMIUM(VI)

Since 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: LFGB	< 3 mg/kg	
Germany: SG (Schadestoff geprüft) – label	< 3 mg/kg	
EU: REGULATION No 301/2014 amending Annex XVII to Regulation (EC) No 1907/2006 of the (REACH)	< 3 mg/kg	Implementation: 01-05-2014

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 sample #14501 (Chromium(VI) of 3.6 mg/kg in this PT), the majority of the laboratories would reject this sample for release to the consumer market. One laboratory has reported: “not detected” and would have released the leather to the market. The other laboratories that reported values <3 mg/kg, could have released the leather to the market, if the limit from the table above instead of zero-tolerance policy is applied.

Applying this limit to #14502 (Chromium(VI) of 19.6 mg/kg in this PT), it is remarkable to find two laboratories reported “non detected”. They might have released a leather with an amount of Chromium(VI) well above the limit.

## 5 DISCUSSION

From the reported test methods it appeared that most participants tested the leather samples according identical test methods: ISO17075 or §64 B LFGB 82.02-11 or BVL B 82.02-11. The observed reproducibilities in this PT were not in agreement with the reproducibility of the reference method ISO17075:2007, but close to this target reproducibility (for both samples approximately 35% higher).

Some influencing factors were found during the evaluation of this proficiency test.

The analytical details that were requested from the participants are summarized in Appendix 2. Looking at these details, the following test method details do not appear to be of a major influence on the test results in this proficiency test: extraction gas or method, extraction time, analysis technique, cell length (when using a spectrophotometer) and recovery.

Not enough information could be summarized out of the answers on analytical details of preparation/particle size of the leather. Since the samples were already cut or shred before dispatch, some labs added a milling procedure to powder the leather, whereas others used the material as it was or cut it slightly smaller.

The buffer solution used by most participants was dipotassium hydrogen phosphate. The pH after extraction with this solution should be between 7.5 and 8.0. The two laboratories which performed the non-equivalent method of IEC62321, used an alkaline solution for the extraction, which resulted in a pH around 13 and statistically outlying results.

Thus pH seems to be a factor in this test method. ISO17075 states that the pH should be between 7.5 and 8.0. For this reason the Chromium(VI) results for both tests were also statistically calculated using two groups: results from samples with pH after extraction  $>7.5$  and  $<8.0$  and results from samples having a pH  $\geq 8.0$ . The results of the statistical evaluation of these subgroups can be found in the table of results in Appendix 1.

For both samples, 12 participants reported a pH after extraction, which was  $\geq 8.0$ . The remaining participants (93-96) reported a pH  $<8.0$ .

Comparing the statistical evaluations of both groups, the important finding is that the average value of the small subgroup (pH $>8.0$ ) is higher than that of the other subgroup for both samples. This suggests that the higher pH after extraction could result in a higher value of Chromium(VI).

It also can be seen that repeatabilities as well as reproducibilities remain the same for the large group with pH $<8.0$  and is different for the small group of 12 with pH $\geq 8.0$ . Since this group is very small in comparison to the total group or the other subgroup, it is difficult to determine whether these differences are significant.

## 6 RECOMMENDATIONS

For a next proficiency test it might be valuable to reconsider the set-up (or the instructions) in order to avoid mixing of test results based on dry matter and test results that were not based on dry matter, in one evaluation. Possibly, the participants may report the Chromium content on both the leather as received as well as on dry matter.

There could be some confusion about the ageing of the leather before testing. Two participants especially commented that they did not age the sample before analysis. Test method ISO17075 does not describe ageing as such, but regulating bodies could have an ageing 'preparation' as part of the specification limit. For future proficiency tests for Chromium(VI) in leather it should be clear from the instructions that the sample should be tested for Chromium(VI) without ageing of the leather.

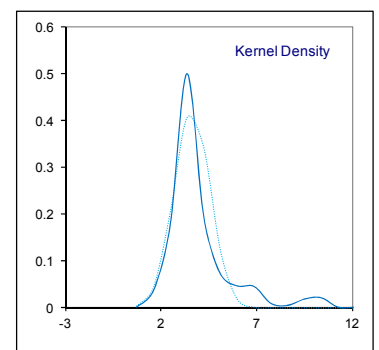
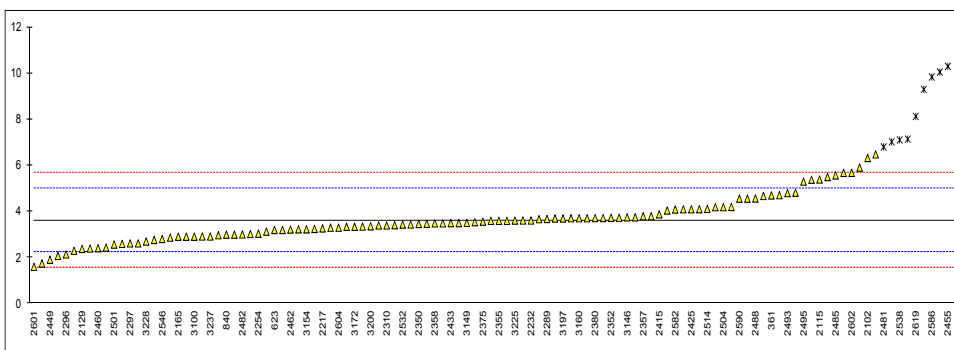
**APPENDIX 1****Determination of Chromium(VI) in sample #14501; results in mg/kg**

lab	method	Value	Mark	z(targ)	remarks
361	ISO17075	4.7		1.58	
623	ISO17075	3.2		-0.60	
840	ISO17075	3.0		-0.89	
1557		----	W	----	Withdrawn: first reported 31665.0 as Total Chromium
2102	ISO17075	6.326		3.94	
2115	ISO17075	5.39		2.58	
2121	ISO17075	2.436		-1.71	
2129	ISO17075	2.38		-1.79	
2132	ISO17075	3.47		-0.21	
2135	§64 LFGB 82.02-11	2.08		-2.23	
2139	ISO17075	3.0		-0.89	
2165	ISO17075	2.91		-1.02	
2166	§64 LFGB 82.02-11	1.75		-2.71	
2177	IEC62321	n.d.		----	
2184	ISO17075	2.77		-1.23	
2215	ISO17075	2.6		-1.47	
2217	ISO17075	3.27		-0.50	
2232	ISO17075	3.614		0.00	
2235	ISO17075	3.733		0.17	
2236	ISO17075	2.621		-1.44	
2247	ISO17075	4.047		0.63	
2254	ISO17075	3.04		-0.83	
2255	ISO17075	4.19		0.84	
2271	ISO17075	3.23		-0.56	
2272	ISO17075	3.4		-0.31	
2273	ISO17075	3.67		0.08	
2284	ISO17075	3.71		0.14	
2289	ISO17075	3.68		0.10	
2290	ISO17075	4.103		0.71	
2293	ISO17075	10.05	C,G(0.01)	9.35	First reported: 0.9275
2296	ISO17075	2.14		-2.14	
2297	ISO17075	2.62		-1.44	
2300	ISO17075	5.68		3.00	
2303		----		----	
2307		----		----	
2310	ISO17075	3.4		-0.31	
2311	ISO17075	3.6		-0.02	
2350	ISO17075	3.4629		-0.22	
2352	ISO17075	3.73		0.17	Result based on dry matter
2355	ISO17075	3.60		-0.02	Result based on dry matter
2357	ISO17075	3.8		0.27	Result based on dry matter
2358	ISO17075	3.49		-0.18	
2359	ISO17075	2.87		-1.08	
2363	ISO17075	3.72		0.15	Result based on dry matter
2365	GB/T22807	4.10		0.71	
2366	ISO17075	3.13		-0.70	
2370	ISO17075	3.49		-0.18	
2372	ISO17075	3.614		0.00	
2375	ISO17075	3.56		-0.08	
2379	ISO17075	3.2		-0.60	
2380	ISO17075	3.72		0.15	
2385	BVL 82.02-11	5.5		2.74	Also submitted result with method ISO17075: 8.8
2390	ISO17075	4.71		1.59	
2410	ISO17075	3.3		-0.46	
2415	ISO17075	3.88		0.39	
2425	ISO17075	4.1		0.71	
2432		----		----	
2433	ISO17075	3.5		-0.17	
2449	ISO17075	1.9104		-2.48	
2452	ISO17075	5.38		2.57	
2455	ISO17075	10.3	C,G(0.01)	9.72	First reported: 8.613
2460	ISO17075	2.41		-1.75	
2462	ISO17075	3.22		-0.57	
2481	ISO17075	6.8	DG(0.05)	4.63	
2482	ISO17075	3.01		-0.88	
2485	ISO17075	5.57		2.84	
2488	ISO17075	4.57		1.39	
2489	ISO17075	3.44		-0.25	
2492	in house	<3.00		----	
2493	ISO17075	4.8		1.72	
2494	ISO17075	3.35		-0.38	
2495	ISO17075	5.3		2.45	
2497	ISO17075	4.82		1.75	

2501	ISO17075	2.57		-1.52	
2504	ISO17075	4.19		0.84	
2514	ISO17075	4.12		0.74	
2532	ISO17075	3.4358		-0.26	
2538	B82.02-11	7.11	DG(0.05)	5.08	
2540	ISO17075	3.54		-0.11	
2546	ISO17075	2.81		-1.17	
2563	ISO17075	3.5		-0.17	
2566	ISO17075	3.7		0.13	
2582	ISO17075	4.089		0.69	
2583	§64 LFGB B82.02-11	3.25		-0.53	
2586	EN17075	9.84	C,G(0.01)	9.05	First reported: 6.67
2590	ISO17075	4.56		1.38	
2592	ISO17075	3.34		-0.40	Result based on dry matter
2593	ISO17075	4.56		1.38	
2600	§64 LFGB 82.02-11	7.025	DG(0.05)	4.96	
2601	§64 LFGB B82.02-11	1.6		-2.93	
2602	§64 LFGB B82.02-11	5.68		3.00	
2604		3.3		-0.46	
2605	ISO17075	2.91		-1.02	
2610	ISO17075	6.48		4.17	
2619	ISO17075	8.13	G(0.05)	6.56	
3100	ISO17075	2.91		-1.02	
3107	ISO17075	2.40		-1.76	
3118		----		----	
3144	§64 LFGB 82.02-11	2.30		-1.91	
3146	ISO17075	3.75		0.20	
3149	82.02-11	3.51		-0.15	
3154	ISO17075	3.23		-0.56	
3160	ISO17075	3.71		0.14	
3172	ISO17075	3.34		-0.40	
3179	ISO17075	3.8		0.27	
3180	ISO17075	2.975		-0.93	
3185	ISO17075	3.03	C	-0.85	First reported: 20.16
3190	ISO17075	3.41		-0.30	
3192	§64 LFGB 82.02-11	2.92		-1.01	
3197	ISO17075	3.7		0.13	
3200	ISO17075	3.36		-0.37	
3204	§64 B82.02-11	7.140	DG(0.05)	5.13	
3209	ISO17075	3.71		0.14	
3210	ISO17075	3.6	C	-0.02	First reported: 9.38
3216	ISO17075	9.30	G(0.01)	8.26	
3220	ISO17075	4.2		0.85	
3222	ISO17075	5.91		3.34	Result based on dry matter
3225	ISO17075	3.61		-0.01	
3228	ISO17075	2.7		-1.33	
3237	ISO17075	2.92		-1.01	
3239	IEC62321	223.6	C,G(0.01)	319.74	First reported: 60.2
3243	INH-226	4.675		1.54	
3246	ISO17075	3.75		0.20	

		<u>pH of solution after extraction</u>	
		pH < 8.0	pH ≥ 8.0
normality	not OK	OK	not OK
n	106	94	13
outliers	10	8	1
mean (n)	3.614	3.589	4.190
st.dev. (n)	0.9446	0.9207	1.7103
R(calc.)	2.645	2.578	4.789
R(ISO17075:07)	1.926	1.917	2.145



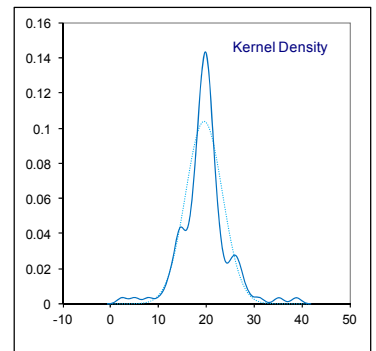
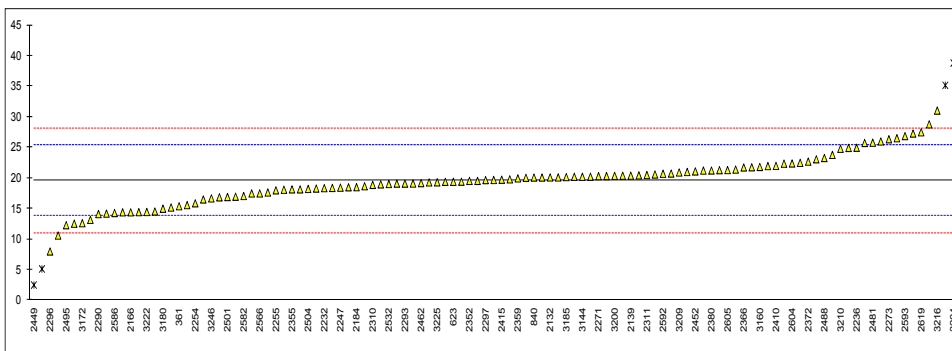
## Determination of Chromium(VI) in sample #14502; results in mg/kg

lab	method	value	Mark	z(targ)	Remarks
361	ISO17075	15.4		-1.47	
623	ISO17075	19.4		-0.07	
840	ISO17075	20.1		0.18	
1557		----	W	----	Withdrawn: first reported 33817.5 as Total Chromium
2102	ISO17075	21.771		0.76	
2115	ISO17075	23.08		1.22	
2121	ISO17075	14.427		-1.81	
2129	ISO17075	17.5		-0.73	
2132	ISO17075	20.11		0.18	
2135	§64 LFGB 82.02-11	14.40		-1.82	
2139	ISO17075	20.4		0.28	
2165	ISO17075	18.16		-0.50	
2166	§64 LFGB 82.02-11	14.4		-1.82	
2177	IEC62321	n.d.		----	False negative?
2184	ISO17075	18.51		-0.38	
2215	ISO17075	19.8		0.07	
2217	ISO17075	18.30		-0.45	
2232	ISO17075	18.356		-0.43	
2235	ISO17075	22.362		0.97	
2236	ISO17075	24.970		1.88	
2247	ISO17075	18.44		-0.40	
2254	ISO17075	15.88		-1.30	
2255	ISO17075	18.00		-0.56	
2271	ISO17075	20.32		0.25	
2272	ISO17075	21.3		0.60	
2273	ISO17075	26.36		2.37	
2284	ISO17075	16.96		-0.92	
2289	ISO17075	21.24		0.58	
2290	ISO17075	14.124		-1.91	
2293	ISO17075	19.10	C	-0.17	First reported: 5.6139
2296	ISO17075	8.00		-4.05	
2297	ISO17075	19.68		0.03	
2300	ISO17075	15.19		-1.54	
2303		----		----	
2307		----		----	
2310	ISO17075	18.9		-0.24	
2311	ISO17075	20.5		0.32	
2350	ISO17075	22.501		1.02	
2352	ISO17075	19.54		-0.02	Result based on dry matter
2355	ISO17075	18.16		-0.50	Result based on dry matter
2357	ISO17075	19.1		-0.17	Result based on dry matter
2358	ISO17075	20.23		0.22	
2359	ISO17075	19.96		0.13	
2363	ISO17075	18.67		-0.32	Result based on dry matter
2365	GB/T22807	19.42		-0.06	
2366	ISO17075	21.75		0.76	
2370	ISO17075	18.4		-0.42	
2372	ISO17075	22.70		1.09	
2375	ISO17075	18.98		-0.21	
2379	ISO17075	n.d.		----	False negative?
2380	ISO17075	21.25		0.58	
2385	BVL 82.02-11	27.3		2.70	Also submitted result with method ISO17075: 32.1
2390	ISO17075	20.39		0.28	
2410	ISO17075	22		0.84	
2415	ISO17075	19.74		0.05	
2425	ISO17075	20.1		0.18	
2432		----		----	
2433	ISO17075	19.3		-0.10	
2449	ISO17075	2.5113	G(0.05)	-5.97	
2452	ISO17075	21.10		0.53	
2455	ISO17075	10.608		-3.14	
2460	ISO17075	14.19		-1.89	
2462	ISO17075	19.18		-0.14	
2481	ISO17075	25.8		2.17	
2482	ISO17075	20.75		0.41	
2485	ISO17075	26.53		2.43	
2488	ISO17075	23.29		1.29	
2489	ISO17075	18.10		-0.52	
2492	in house	16.86		-0.96	
2493	ISO17075	28.8		3.22	
2494	ISO17075	14.55		-1.76	
2495	ISO17075	12.3	C	-2.55	First reported: 30.4
2497	ISO17075	16.51		-1.08	

2501	ISO17075	16.91		-0.94	
2504	ISO17075	18.23		-0.48	
2514	ISO17075	17.65		-0.68	
2532	ISO17075	19.0361		-0.19	
2538	B82.02-11	35.18	G(0.05)	5.45	
2540	ISO17075	20.60		0.35	
2546	ISO17075	5.14	G(0.05)	-5.06	
2563	ISO17075	12.543		-2.47	
2566	ISO17075	17.5		-0.73	
2582	ISO17075	17.07		-0.88	
2583	§64 LFGB B82.02-11	21.0		0.49	
2586	EN17075	14.29		-1.85	
2590	ISO17075	20.45		0.30	
2592	ISO17075	20.72		0.39	
2593	ISO17075	26.88		2.55	
2600	§64 LFGB 82.02-11	20.216		0.22	
2601	§64 LFGB B82.02-11	19.55		-0.01	
2602	§64 LFGB B82.02-11	24.95		1.87	
2604		22.4		0.98	
2605	ISO17075	21.32		0.60	
2610	ISO17075	25.75		2.15	
2619	ISO17075	27.50		2.77	
3100	ISO17075	20.34		0.26	
3107	ISO17075	13.17		-2.25	Remark by lab: Suspected reducing agents present in sample
3118		----		----	
3144	§64 LFBG 82.02-11	20.22		0.22	
3146	ISO17075	26.0		2.24	
3149	82.02-11	20.11		0.18	
3154	ISO17075	21.97		0.83	
3160	ISO17075	21.83		0.78	
3172	ISO17075	12.63		-2.44	
3179	ISO17075	20.05		0.16	
3180	ISO17075	15.0		-1.61	
3185	ISO17075	20.16	C	0.20	First reported: 3.03
3190	ISO17075	19.39		-0.07	
3192	§64 LFBG 82.02-11	23.8		1.47	
3197	ISO17075	19.7		0.04	
3200	ISO17075	20.37		0.27	
3204	§64 B82.02-11	38.826	G(0.01)	6.73	
3209	ISO17075	20.93		0.47	
3210	ISO17075	24.8	C	1.82	First reported: 40.65
3216	ISO17075	31.05		4.01	
3220	ISO17075	15.58		-1.40	
3222	ISO17075	14.46		-1.80	Result based on dry matter
3225	ISO17075	19.32		-0.09	
3228	ISO17075	18.5		-0.38	
3237	ISO17075	19.12		-0.16	
3239	IEC62321	<5.0		< -5.10	False negative?
3243	INH-226	21.402		0.63	
3246	ISO17075	16.69		-1.01	

normality	not OK
n	111
outliers	4
mean (n)	19.591
st.dev. (n)	3.8352
R(calc.)	10.739
R(ISO17075:07)	8.004

pH of solution after extraction		
	pH < 8.0	pH ≥ 8.0
normality	not OK	OK
n	96	15
outliers	3	1
mean (n)	19.714	21.640
st.dev. (n)	3.8414	3.2004
R(calc.)	10.756	8.961
R(ISO17075:07)	7.885	8.784



## APPENDIX 2

## Summary of reported analytical details

Lab	Method	Extraction solvent	Extr. gas	Extr. time (min.)	pH after extract. #14501	pH after extract. #14502	Analysis technique	Cell length (cm)	Recovery #14501 (%)	Recovery #14502 (%)
361	ISO17075	K2HPO4	N2	5	7.67	7.77	Spectrophotometer	4	92.1	89.2
623	ISO17075	Buffer Phosphate		180	7.9	7.9	Spectrophotometer	4	96	97
840	ISO17075	K2HPO4	Ar	180	7.69	7.76	Spectrophotometer	5	94.2	90.1
1557										
2102	ISO17075	K2HPO4	Ar	180	7.7	7.8	LC-ICP-MS		99.14	
2115	ISO17075	Buffer ISO17075	N2	180	7.91	7.95	Spectrophotometer	5	108	85
2121	ISO17075	K2HPO4	N2	180	7.7	7.9	Spectrophotometer	1	62	74
2129	ISO17075	K2HPO4		180	7.7	7.8	Spectrophotometer	1		
2132	ISO17075	K2HPO4	N2	180	7.5	7.5	Spectrophotometer	4		
2135	§64 LFGB 82.02-11	Buffer Phosphate	N2	180	7.78	7.84	Spectrophotometer	1		
2139	ISO17075	K2HPO4		180	7.6	7.6	Spectrophotometer	1		
2165	ISO17075	K2HPO4	Ar	180	8.0	8.0	Spectrophotometer	4		
2166	§64 LFGB 82.02-11	Buffer Phosphate	Ar	180	7.8	7.9	Spectrophotometer	1	95	65.9
2177	IEC62321	Alkaline solution		60	13	13	Spectrophotometer	1		
2184	ISO17075	K2HPO4	N2	180	8	8	Spectrophotometer	4	104	92
2215	ISO17075	K2HPO4	N2	180	7.7	7.8	Spectrophotometer	2		
2217	ISO17075	K2HPO4	N2	180	7.8	8	Spectrophotometer	5	57.07	47.0
2232	ISO17075	K2HPO4	Ar	180	7.54	7.67	Spectrophotometer	1	97.9	97.9
2235	ISO17075	K2HPO4	Ar	180	7.77	7.82	Spectrophotometer	2	89.0	86.0
2236	ISO17075	K2HPO4		180	8.0	8.0		5	112	99
2247	ISO17075	K2HPO4	Ar	180	7.80	7.89	Spectrophotometer	5	90	88
2254	ISO17075	K2HPO4		180	7.74	7.92	Spectrophotometer	1		
2255	ISO17075	K2HPO4	N2	180	7.92	7.98	Spectrophotometer	5	98.3	98.75
2271	ISO17075	K2HPO4	N2	180	8.0	8.0	Spectrophotometer	5	97	97
2272	ISO17075	K2HPO4	N2	180	7.73	7.85	Spectrophotometer	4	91	86
2273	ISO17075	K2HPO4	N2	180	7.52	7.61	Spectrophotometer	4	101	94
2284	ISO17075	K2HPO4	N2	180	7.84	7.90	Spectrophotometer	1	99.0	99.0
2289	ISO17075	Phosphate buffer	Ar	180	8.0	8.0	Spectrophotometer	5	95	95
2290	ISO17075	K2HPO4	Ar	180	7.9	7.9	Spectrophotometer	5	95	103
2293	ISO17075	K2HPO4	Ar	180	7.76	7.82	Spectrophotometer	5	105.79	117.54
2296	ISO17075	Phosphate buffer	N2	180	7.7	7.9	Spectrophotometer	1	85.74	81.14
2297	ISO17075	K2HPO4	Ar	180	7.82	7.87	Spectrophotometer	1	86.7	87.6
2300	ISO17075	K2HPO4	Ar	180	7.65	7.62	Spectrophotometer	1		
2303										
2307										
2310	ISO17075	K2HPO4	Ar	180	7.9	8.1	Spectrophotometer	2	93	89
2311	ISO17075	K2HPO4	Ar	180	7.6	7.7	Spectrophotometer	5	103	98
2350	ISO17075	K2HPO4	N2	180	8	8	Spectrophotometer	4	MS/MSD	MS/MSD
2352	ISO17075	K2HPO4	N2	180	7.8	7.9	Spectrophotometer	5	98.8	94.5
2355	ISO17075	K2HPO4	Ar	180	7.6	7.8	Spectrophotometer	1	95	108
2357	ISO17075	K2HPO4	Ar	180	8.0	7.8	Spectrophotometer	1	103	
2358	ISO17075	K2HPO4	N2	180	7.60	7.82	Spectrophotometer	5	100	102
2359	ISO17075	K2HPO4	N2	180	7.8	7.9	Spectrophotometer	5	103.8	104.8
2363	ISO17075	K2HPO4	N2	180	7.6	7.7	Spectrophotometer	4	97.9	99.8
2365	GB/T22807	K2HPO4	N2	180	7.75	7.78	Spectrophotometer	2	101	88
2366	ISO17075	K2HPO4	N2	180	7 - 8	7 - 8	Spectrophotometer	2	100.5	100.2
2370	ISO17075	K2HPO4	Ar	180	7.77	7.83	Spectrophotometer	2	3.35	19.5
2372	ISO17075	Phosphate buffer	Ar	180	7.57	7.61	Spectrophotometer	1		
2375	ISO17075	K2HPO4		180	7.8	7.7	Spectrophotometer	5	98.3	99.9
2379	ISO17075	K2HPO4	N2	180	7.79	7.82	Spectrophotometer	5	106	107
2380	ISO17075	K2HPO4	N2	180	7.87	7.9	Spectrophotometer	5	97	98
2385	BVL 82.02-11	Phosphate buffer		34			Ion Chromatography			
2390	ISO17075	K2HPO4	N2	180	7.74	7.94	Spectrophotometer	4	94.2	103.6
2410	ISO17075	Phosphate buffer	N2	180	7.66	7.67	Spectrophotometer	5	77	N/A
2415	ISO17075	K2HPO4		180	7.8	7.9	Spectrophotometer	1		
2425	ISO17075	Phosphate buffer		180	8.0	8.0	Spectrophotometer	5	97	83
2432										
2433	ISO17075	K2HPO4	N2	180	7.96	7.9	Spectrophotometer	4		91.00
2449	ISO17075									
2452	ISO17075	K2HPO4	N2	180	7.82	7.89	Spectrophotometer	5	118.6087	105.0166
2455	ISO17075	K2HPO4	N2	180	7.70	7.76	Spectrophotometer	1	116 / 97	116 / 97
2460	ISO17075	K2HPO4	Ar	180	7.84	7.87	Spectrophotometer	4	96.0	88.4
2462	ISO17075	Phosphate buffer	Ar	180	7.7	7.8	Spectrophotometer	1	91.4	93.2
2481	ISO17075	K2HPO4		180	7.7	7.8	Spectrophotometer	1	87	80
2482	ISO17075	K2HPO4	Ar	180	7.8	7.8	IC-PCR-UV/Vis		98	95
2485	ISO17075	K2HPO4	Ar	180	8	8	Spectrophotometer	5	81	99
2488	ISO17075	Phosphate buffer	N2	180	7.8	7.9	Spectrophotometer	1	99.2	99.2
2489	ISO17075	K2HPO4	N2	180	7.81	7.84	Spectrophotometer	5	97.1	97.0

## Summary of reported analytical details (continued)

Lab	Method	Extraction solvent	Extr. gas	Extr. time (min.)	pH after extract. #14501	pH after extract. #14502	Analysis technique	Cell length (cm)	Recovery #14501 (%)	Recovery #14502 (%)
2492	in house	K2HPO4	N2	20	7.9	7.9	Spectrophotometer	1	93	98
2493	ISO17075	K2HPO4	N2	180	7.84	7.81	Spectrophotometer		97.4	89.9
2494	ISO17075	K2HPO4	N2	180	7.82	7.93	Spectrophotometer			
2495	ISO17075	Phosphate buffer	N2	180	7.7	7.9	Spectrophotometer	4		
2497	ISO17075	Phosphate buffer		180	7.8	7.8	Spectrophotometer	5	93	91
2501	ISO17075	K2HPO4	Ar	180	7.6	7.7	Spectrophotometer	4	108	108
2504	ISO17075	K2HPO4	N2	180	7.64	7.87	Spectrophotometer	1	107.0	107.0
2514	ISO17075	K2HPO4	N2	180	7.98	7.98	Spectrophotometer	5	99.3	98.75
2532	ISO17075	K2HPO4	N2	180	7.73	7.80	Spectrophotometer	5	93	96
2538	B82.02-11	Phosphate buffer	N2	180	7.7	7.7	Spectrophotometer	2	108.4	104.5
2540	ISO17075	Phosphate buffer	N2	180	7.74	7.80	Spectrophotometer	1		
2546	ISO17075	K2HPO4	N2	180	7.9	7.9	Spectrophotometer	4	92	106
2563	ISO17075	K2HPO4		180	7.74	7.84	Spectrophotometer	5		
2566	ISO17075	K2HPO4	Ar		7.94	7.96	Spectrophotometer	1	0.059 mg/l	0.059 mg/l
2582	ISO17075	K2HPO4	N2	180	7.9	7.6	Spectrophotometer	5	83	82
2583	§64LFBG B82.02-11	K2HPO4	N2	180	7.67	7.73	Spectrophotometer	2		
2586	EN17075	K2HPO4	Ultra	180	7.51	7.57	Spectrophotometer	4	85	91
2590	ISO17075	K2HPO4	N2	180	7.7	7.8	Spectrophotometer	4	86	87
2592	ISO17075	K2HPO4	N2	180	7.8	7.8	Spectrophotometer	1	97	95
2593	ISO17075	K2HPO4	N2	180	7.81	7.84	Spectrophotometer	4	94	91
2600	§64LFBG 82.02-11	K2HPO4	N2	180	7.66	7.76	Spectrophotometer	5	100.12	107.13
2601	§64LFBG B82.02-11	Phosphate buffer	N2	180	7.83	7.95	Spectrophotometer	1		
2602	§64LFBG B82.02-11	K2HPO4	N2	180	7.85	7.88	Spectrophotometer	1	92.8/85.5	79.6/42.2
2604		K2HPO4	N2	180	7.5 - 8.0	7.5 - 8.0	Spectrophotometer	4	95.7/103.2	102.7/101.8
2605	ISO17075	Phosphate buffer	N2	180	7.75	7.81	Spectrophotometer	5	101	96
2610	ISO17075	K2HPO4	Ultra	180	7.73	7.8	Spectrophotometer	4	113.7	106.1
2619	ISO17075	K2HPO4	N2	180	8.0	8.0	Spectrophotometer	2		
3100	ISO17075	Phosphate buffer	N2	180	7.70	7.79	Spectrophotometer	5	99.5	91.0
3107	ISO17075	K2HPO4	Ar	180	7.70	7.83	Spectrophotometer	4	104	72
3118										
3144	§64 LFBG 82.02-11	Phosphate buffer	N2	180	7.9	7.8	Spectrophotometer	1		
3146	ISO17075	K2HPO4	N2	180	8	8			93	95
3149	82.02-11	K2HPO4	N2	180	7.8	7.9	Spectrophotometer	5	102	81
3154	ISO17075	K2HPO4	N2	180			Spectrophotometer	4	136.6	155.2
3160	ISO17075	K2HPO4	Vac.	180	7.75	7.77	Spectrophotometer	4	94.0	75.8
3172	ISO17075	K2HPO4	N2	180	7.8	7.9	Spectrophotometer	5	>80	>80
3179	ISO17075	K2HPO4		180	7.9	8.0	Spectrophotometer	5	99.6	76.4
3180	ISO17075	Phosphate buffer	Ar	180	<8	<8	Spectrophotometer			
3185	ISO17075	K2HPO4	N2	180	7.8	7.8	Spectrophotometer	1	90.3	106.7
3190	ISO17075	K2HPO4	N2	180	7.83	7.92	Filterphotometer	5	102	103
3192	§64 LFBG 82.02-11	Phosphate buffer	Ar	180	7.79	7.86	Spectrophotometer	4	98.6/102.0	103.0/99.4
3197	ISO17075	K2HPO4	N2	180	7.8	7.9	Spectrophotometer	5	98	96
3200	ISO17075	K2HPO4	Ar	180	7.75	7.88	Spectrophotometer	4	93	81
3204	§64 B82.02-11	K2HPO4		180	8.0	8.1	Spectrophotometer	5	100.4	104.2
3209	ISO17075	K2HPO4	N2	180	7.8	7.9	Spectrophotometer	4	97.7	99.5
3210	ISO17075	K2HPO4	N2	240	7.80	7.81	Ion Chromatography			
3216	ISO17075	K2HPO4	N2	180	7.90	7.91	Spectrophotometer	1	93.6	73.2
3220	ISO17075	Phosphate buffer		180	7.9	7.8	Spectrophotometer	4		
3222	ISO17075	Phosphate buffer	N2	180	7.7	7.8	Spectrophotometer	1	90.9	90.5
3225	ISO17075	K2HPO4	N2	180	7.7	7.8	Spectrophotometer	4	105	95
3228	ISO17075	K2HPO4	N2	180			Spectrophotometer	4		
3237	ISO17075	K2HPO4	Ar	180	7.93	8.03	Spectrophotometer	1	95.18	97.69
3239	IEC62321	Digestion solution		180	12.75	13.05	Spectrophotometer	1	99	63
3243	INH-226	Phosphate buffer	Ar	34	7.78	7.84	Spectrophotometer	2	84.1	86.8
3246	ISO17075	Phosphate buffer	Ar	180	7.5	7.6	Spectrophotometer	1	95.5	94.2



## APPENDIX 3

### Number of participants per country

4 labs in BANGLADESH  
3 labs in BULGARIA  
3 labs in FRANCE  
20 labs in GERMANY  
1 lab in GUATEMALA  
7 labs in HONG KONG  
2 labs in HUNGARY  
8 labs in INDIA  
3 labs in INDONESIA  
10 labs in ITALY  
1 lab in JAPAN  
4 labs in KOREA  
1 lab in MEXICO  
24 labs in P.R. of CHINA  
2 labs in PAKISTAN  
1 lab in PHILIPPINES  
1 lab in SERBIA  
2 labs in SINGAPORE  
3 labs in SPAIN  
1 lab in SRI LANKA  
2 labs in SWITZERLAND  
2 labs in TAIWAN R.O.C.  
2 labs in THAILAND  
1 lab in THE NETHERLANDS  
1 lab in TUNISIA  
4 labs in TURKEY  
3 labs in U.S.A.  
3 labs in UNITED KINGDOM  
4 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

### Literature:

- 1 iis-Interlaboratory Studies: Protocol for the Organisation, Statistics and Evaluation, April 2014
- 2 ISO 5725, (1986)
- 3 ISO 5725, parts 1-6, (1994)
- 4 P.L. Davies, *Fr Z. Anal. Chem*, 351, 513, (1988)
- 5 W.J. Conover, *Practical; Nonparametric Statistics*, J. Wiley&Sons, NY, p.302, (1971)
- 6 M. Thompson and R. Wood, *J. AOAC Int*, 76, 926, (1993)
- 7 W.J. Youden and E.H. Steiner, *Statistical Manual of the AOAC*, (1975)
- 8 Analytical Methods Committee Technical Brief, No4 January 2001
- 9 Bernard Rosner, Percentage Points for a Generalized ESD Many-Outlier Procedure, *Technometrics*, 25(2), pp. 165-172, (1983)