Results of Proficiency Test
Chromium VI in leather
April 2018

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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 Of all Chromium compounds, primarily Chromium VI was used, but this has been replaced by the less hazardous Chromium III in most applications.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. During the annual proficiency testing program 2017/2018, it was decided to continue the PT for the analysis Chromium VI in leather.
In this interlaboratory study, 164 laboratories in 36 different countries registered for participation (see appendix 3). In this report, the results of the 2018 proficiency test are presented and discussed. This report is also electronically available through the iis website www.iisnl.com.

2 SET UP

The Institute for Interlaboratory Studies (iis) in Spijkenisse was the organizer of this proficiency test (PT). Sample analyses for fit-for-use and homogeneity testing were subcontracted to an ISO/IEC 17025 accredited laboratory. Due to lack of a sufficient amount of suitable materials it was decided to send in this proficiency test only one aged leather sample, positive on Chromium VI, labelled #18545.
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 ISO/IEC17043:2010. This ensures strict adherence to protocols for sample preparation and statistical evaluation and 100% confidentiality of participant's data. Feedback from the participants on the reported data is encouraged and customer's satisfaction is measured on 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 March 2017 (iis-protocol, version 3.4). 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 grey leather sample was obtained from the local market. The batch was grinded and aged. After thoroughly mixing, 180 bags were filled with approximately 5 grams of leather each and vacuumed. The homogeneity of subsamples #18545 was checked by determination of Chromium VI in accordance with ISO17075 on eight stratified randomly selected samples, see table 1.

	Chromium VI in mg/kg
Sample #18545-1	6.84
Sample #18545-2	6.56
Sample #18545-3	7.56
Sample #18545-4	7.09
Sample #18545-5	7.27
Sample #18545-6	7.27
Sample #18545-7	6.03
Sample #18545-8	5.87

Table 1: homogeneity test results of subsamples #18545

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

	Chromium VI in mg/kg
r (observed)	1.7
reference test method	ISO17075:17
r (reference test method)	1.6

Table 2: evaluation of the repeatability of subsamples #18545

The repeatability of the test results of the homogeneity tests for Chromium VI of sample #18545 was in agreement with repeatability of the reference test method ISO17075:2017. Therefore, homogeneity of the subsamples was assumed for sample #18545.

To each of the participating laboratories one sample (labelled #18545) of approx. 5 grams was sent on April 4, 2018.

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.
It was explicitly requested to treat the sample as if it was a routine sample, but not to age nor to dry the sample (nor to determine volatile matter). The amount of sample was not sufficient to allow aging and/or determine the volatile matter content. Also, it was asked to keep the sample stored dark, dry and cool (4 – 10 °C) and keep sample packed until the start of extraction.

It was also requested to report the test results using the indicated units on the report form and not to round the test results, but to report as much significant figures as possible. It was also requested not to report 'less than' test results, which are above the detection limit, because such test results cannot be used for meaningful statistical evaluation.
Also, some analytical details were requested to be reported.

To get comparable test results a detailed report form and a letter of instructions are prepared. The detailed report form and the letter of instructions are both made available on the data entry portal www.kpmd.co.uk/sgs-iis-cts/. The participating laboratories were also requested to confirm the sample receipt on this data entry portal. The letter of instructions can also be downloaded from the iis website www.iisnl.com.

3 RESULTS

During five weeks after sample dispatch, the test results of the individual laboratories were gathered via the data entry portal www.kpmd.co.uk/sgs-iis-cts/. The reported test results are tabulated per sample and per component in the appendix 1 of this report. The laboratories are represented by their code numbers.

Directly after the deadline, a reminder was sent to those laboratories that did not report 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 reanalyses). Additional or corrected test results are used for the data analysis and the original test results are placed under 'Remarks' in the test result tables in appendix 1. Test results that came in after the deadline were not taken into account in this screening for suspect data and thus these participants were not requested for checks.

3.1 STATISTICS

The protocol followed in the 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 March 2017 (iis-protocol, version 3.4).

For the statistical evaluation the *unrounded* (when available) figures were used instead of the rounded test results. Test results reported as '<…' or '>…' were not used in the statistical evaluation.

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

In accordance to ISO 5725 the original test results per determination were submitted subsequently to Dixon's, 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 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 significant 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 in accordance with:

$z_{(target)}$ = (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 the samples. Two participants did not report any test results. Not all laboratories were able to report all analyses requested.
In total, 162 participants reported 190 numerical results. Observed were 2 outlying test results, which is 1.1% of the numerical results. In proficiency studies, outlier percentages of 3% - 7.5% are quite normal.

4.1 EVALUATION PER TEST

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

In 2017 a new version of test method ISO17075 was published. The 2017 version of ISO17075 was split up into two parts: colorimetric method (part 1) and chromatographic method (part 2). In the previous version of ISO17075 (2007 version) only the colorimetric method was described.

Cr VI - colorimetric: The determination of Chromium VI at a concentration level of 6.3 mg/kg was problematic. One statistical outlier was observed. The calculated reproducibility after rejection of the statistical outlier is not in agreement with ISO17075:2017 (part 1).

Cr VI - chromatographic: The determination of Chromium VI at a concentration level of 5.7 mg/kg was problematic. One statistical outlier was observed. The calculated reproducibility after rejection of the statistical outlier is not in agreement with ISO17075:2017 (part 2).

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 ISO17075:2017 are presented in the next table.

Parameter	unit	n	average	2.8 * sd	R(target)
Chromium VI – colorimetric	mg/kg	143	6.30	5.52	2.95
Chromium VI – chromatographic	mg/kg	45	5.75	4.94	3.04

Table 3: performance overview for sample #18545

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 (part, 1 and 2), for this sample.

4.3 COMPARISON OF THE PROFICIENCY TEST OF APRIL 2018 WITH PREVIOUS PTS

	April 2018	*April 2017*	*April 2016*	*February 2015*	*February 2014*
Number of reporting labs	162	163	145	141	118
Number of results reported	190	183	144	153	231
Number of statistical outliers	2	5	6	5	14
Percentage outliers	1.1%	2.7%	4.2%	3.3%	6.1%

Table 4: comparison with previous proficiency tests

In proficiency tests, outlier percentages of 3% - 7.5% are quite normal.

The observed variation in the test results for Chromium VI in the 2018 PT is in agreement in comparison with the variation as observed in the previous PTs, see below table.

Component	*April 2018*	*April 2017*	*April 2016*	*February 2015*	*February 2014*	*Target*
Cr VI (colorimetric)	31%	15%	29%	33%	19 – 31%	15%
Cr VI (chromatographic)	31%	10%	n.e.	n.e.	n.e.	10%

Table 5: development of the uncertainties over the years

The good variation of 2017 could not repeated in 2018. Presumable due to the amount of Chromium VI present in the sample. The Chromium VI content in sample of PT 2017 was almost three times higher. However, the variation observed in 2018 is in line with the PTs of 2014 and 2015.

4.4 EVALUATION OF THE ANALYTICAL DETAILS

For this Proficiency Test some analytical details were requested (see appendix 2).
Questions like: is your laboratory accredited in accordance with ISO/IEC17025 and some specific questions with regards to the analytical details of the test method used.
Based on the answers given by the participants the following can be summarized:
One hundred twenty-seven of the registered participants mentioned that they are accredited to report Chromium VI in leather. One hundred thirty-nine tested the leather samples according to the test method ISO17075, two participants used an in house method and two used GB/T22807. One hundred forty-six mentioned that they have used a test portion between 1.0 - 2.0 grams. One mentioned to have use less material (0.5 gram) for intake and two have used more testing material for intake (4 gram). The majority of the group mentioned: extraction time >180min and extraction temperature >20°C. The pH before and after extraction was in accordance with test method ISO17075:2017. The other analytical details asked was type and frequency of the shaker. The observed large variation could not be explained from the reported analytical details. It is remarkable that for the leather sample used in this proficiency test, all of the requested analytical details have no significant influence on the test result for this sample.

5 DISCUSSION

As Chromium VI is carcinogenic, mutagenic and toxic for reproduction, the regulations within countries tend to adopt a zero-tolerance policy. In actual practise this will mean below the detection limit of the widely accepted test method ISO17075:2017 (parts 1 and 2). Examples of regulations can be found in table 6.

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 6: 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 #18545 most of the laboratories would not release this sample to the consumer market. Six laboratories would have released sample #18545.

6 CONCLUSION

It can be concluded that the group of participants have problems with the determination of Chromium VI colorimetric and chromatographic in this sample. Each participating laboratory will have to evaluate its performance in this study and decide about any corrective actions if necessary.

Therefore, participation on a regular basis in this scheme could be helpful to improve the performance and thus increase of the quality of the analytical results.

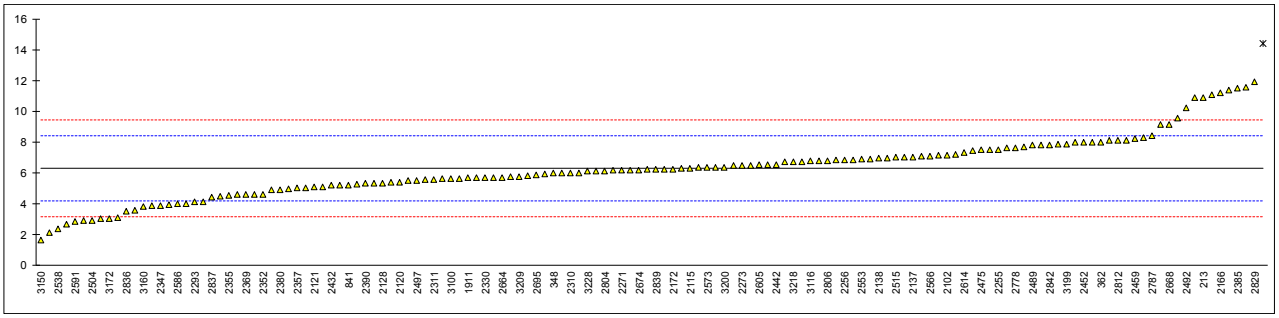
APPENDIX 1

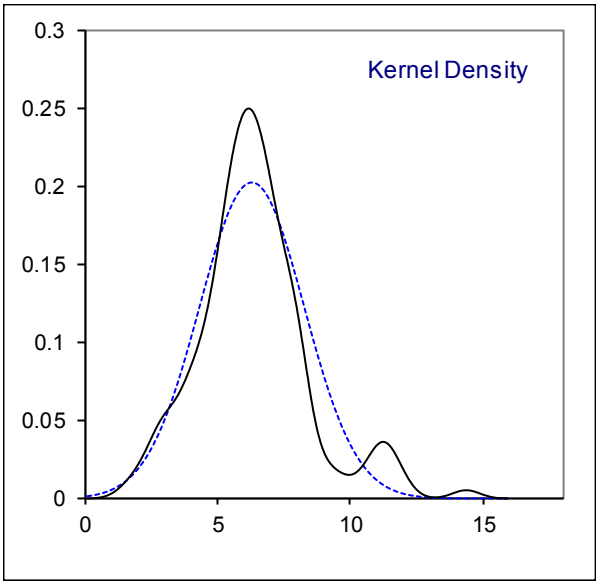
Determination of Chromium VI (colorimetric) in sample #18545; results in mg/kg

lab	method	value	mark	z(targ)	remarks
213	ISO17075-1	10.92		4.39	
230	ISO17075-1	11.39		4.84	
339	ISO17075Mod.	6.27		-0.02	
348	ISO17075-1	5.969		-0.31	
362	ISO17075-1	8.017		1.63	
551	ISO17075-1	9.565		3.11	
623	ISO17075-1	6.22		-0.07	
840	ISO17075-1	5.2		-1.04	
841	ISO17075-1	5.2		-1.04	
1911	ISO17075-1	5.664		-0.60	
2102	ISO17075-1	7.15		0.81	
2115	ISO17075-1	6.31		0.01	
2120	ISO17075-1	5.41		-0.84	
2121	ISO17075-1	5.064		-1.17	
2128	ISO17075-1	5.325		-0.92	
2129	ISO17075-1	4.96		-1.27	
2132	ISO17075-1	5.565		-0.69	
2137	ISO17075	7.03		0.70	
2138	ISO17075-1	6.963		0.63	
2159	In house	4.58		-1.63	
2165	ISO17075-1	5.82		-0.45	
2166	ISO17075-1	11.167		4.63	
2172	ISO17075-1	6.261		-0.03	
2184	ISO17075-1	6.21		-0.08	
2201	ISO17075-1	8.015		1.63	
2213	ISO17075-1	6.2		-0.09	
2215	ISO17075-1	6.339		0.04	
2228	ISO17075-1	3.8943		-2.28	
2230	ISO17075-1	7.85		1.48	
2232	ISO17075-1	7.213		0.87	
2241	ISO17075-1	6.47		0.17	
2247	ISO17075-1	7.49		1.13	
2250	ISO17075-1	5.314		-0.93	
2255	ISO17075-1	7.51		1.15	
2256	ISO17075-1	6.8644		0.54	
2266	ISO17075-1	8.1		1.71	
2271	ISO17075-1	6.2	C	-0.09	First reported 9.5
2272	ISO17075-1	5.6699		-0.60	
2273	ISO17075-1	6.5		0.19	
2290	ISO17075-1	7.82		1.45	
2293	ISO17075-1	4.114		-2.07	
2297	ISO17075-1	6.33		0.03	
2300	ISO17075-1	8.13		1.74	
2301	ISO17075-1	6.9		0.57	
2310	ISO17075-1	6.00		-0.28	
2311	ISO17075-1	5.59		-0.67	
2330	ISO17075-1	5.679		-0.59	
2347	ISO17075-1	3.9		-2.28	
2350	ISO17075-1	6.8659		0.54	
2352	ISO17075-1	4.61		-1.60	
2355	ISO17075-1	4.54		-1.67	
2357	ISO17075-1	5.00		-1.23	
2358	ISO17075-1	5.923		-0.35	
2363	ISO17075-1	4.9		-1.33	
2365		-----		-----	
2366	ISO17075-1	5.30		-0.95	
2369	ISO17075-1	4.6		-1.61	
2370	ISO17075-1	5.61		-0.65	
2375	ISO17075-1	8.3		1.90	
2378	ISO17075-1	4.51		-1.70	
2379	ISO17075-1	5.976		-0.30	
2380	ISO17075-1	4.912		-1.32	
2382	ISO17075-1	3.6		-2.56	
2385	ISO17075-1	11.5		4.94	
2389	ISO17075-1	5.73		-0.54	
2390	ISO17075-1	5.31		-0.94	
2426	ISO17075-1	6.110		-0.18	
2432	ISO17075-1	5.191		-1.05	
2442	In house	6.57		0.26	
2449	ISO17075-1	6.83		0.51	
2452	ISO17075-1	8.0		1.62	
2459	ISO17075-1	8.210		1.82	
2460	ISO17075-1	5.40		-0.85	
2475	ISO17075-1	7.479		1.12	
2485		-----		-----	

lab	method	value	mark	z(targ)	remarks
2486	ISO17075-1	6.9636		0.63	
2488		-----		-----	
2489	ISO17075-1	7.8		1.43	
2492	ISO17075-1	10.2		3.71	
2495		-----		-----	
2497	ISO17075-1	5.52		-0.74	
2499		-----		-----	
2500	ISO17075-1	6.534		0.23	
2501	ISO17075-1	4.13		-2.06	
2504	ISO17075-1	2.94		-3.19	
2511	ISO17075-1	3.12	C	-3.02	First reported 12.56
2515	ISO17075-1	6.997		0.67	
2523		-----		-----	
2538	ISO17075-1	2.353		-3.75	
2553	ISO17075-1	6.89		0.56	
2561		-----		-----	
2566	ISO17075-1	7.1		0.76	
2573	ISO17075-1	6.33		0.03	
2586	ISO17075-1	4.012		-2.17	
2590	ISO17075-1	5.6510		-0.61	
2591	ISO17075-1	2.84		-3.28	
2592	ISO17075-1	5.7	C	-0.57	First reported 11.3
2597	ISO17075-1	4.03		-2.15	
2605	ISO17075-1	6.52		0.21	
2614	ISO17075-1	7.31		0.96	
2624	ISO17075-1	7.027		0.69	
2637	ISO17075-1	5.5		-0.76	
2649	ISO17075-1	6.80		0.48	
2652	ISO17075-1	6.176		-0.11	
2656		-----		-----	
2664	ISO17075-1	5.705		-0.56	
2668	ISO17075-1	9.16		2.72	
2674	ISO17075-1	6.2		-0.09	
2675		-----		-----	
2695	ISO17075-1	5.882		-0.39	
2701	ISO17075-1	6.695		0.38	
2705	ISO17075-1	7.97		1.59	
2706		-----		-----	
2711		-----		-----	
2713	ISO17075-1	7.14		0.80	
2725		-----		-----	
2730		-----		-----	
2749		-----		-----	
2756	ISO17075-1	4.6		-1.61	
2773	ISO17075-1	6.5		0.19	
2777	GB22807	9.128		2.69	
2778	GB/T22807	7.651		1.29	
2783	ISO17075-1	11.5335		4.98	
2786	ISO17075-1	5.00	C	-1.23	First reported 1.29
2787	ISO17075-1	8.392		1.99	
2804	ISO17075-1	6.142		-0.15	
2806	ISO17075-1	6.8		0.48	
2812	ISO17075-1	8.12		1.73	
2813	ISO17075-1	14.368	C,R(0.05)	7.67	First reported 37.497
2823	ISO17075-1	2.106		-3.98	
2829	ISO17075-1	11.939	C	5.36	First reported 10.625
2836	ISO17075-1	3.5238		-2.63	
2837		4.4		-1.80	
2838	ISO17075-1	3.93		-2.25	
2839	ISO17075-1	6.21		-0.08	
2842	ISO17075-1	7.82		1.45	
2843		-----		-----	
2844	ISO17075-1	2.93		-3.20	
3100	ISO17075-1	5.64		-0.62	
3116	ISO17075-1	6.76		0.44	
3134	ISO17075-1	5.098		-1.14	
3146		-----		-----	
3150	ISO17075-1	1.66	C	-4.41	First reported 1.41
3154	ISO17075-1	2.70		-3.42	
3160	ISO17075-1	3.82		-2.35	
3163		-----		-----	
3172	ISO17075-1	3.053		-3.08	
3176		-----		-----	
3179	ISO17075-1	3.03		-3.10	
3185	ISO17075-1	6.026		-0.26	
3191		-----		-----	
3197	ISO17075-1	7.62		1.26	
3199	ISO17075-1	7.868		1.49	

lab	method	value	mark	z(targ)	remarks
3200	ISO17075-1	6.34		0.04	
3209	ISO17075-1	5.75		-0.52	
3210		-----		-----	
3216	ISO17075-1	10.88		4.36	
3218	ISO17075-1	6.700		0.38	
3222	ISO17075-1	7.7		1.33	
3228	ISO17075-1	6.1		-0.19	
3233	ISO17075-1	7.46		1.11	
3237	ISO17075-1	11.10		4.56	
3246	ISO17075-1	6.75	C	0.43	First reported 13.5
3248	ISO17075-1	7.093		0.76	
	normality	OK			
	n	143			
	outliers	1			
	mean (n)	6.296			
	st.dev. (n)	1.9707	RSD= 31.3%		
	R(calc.)	5.518			
	st.dev.(ISO17075-1:17)	1.0524			
	R(ISO17075-1:17)	2.947			



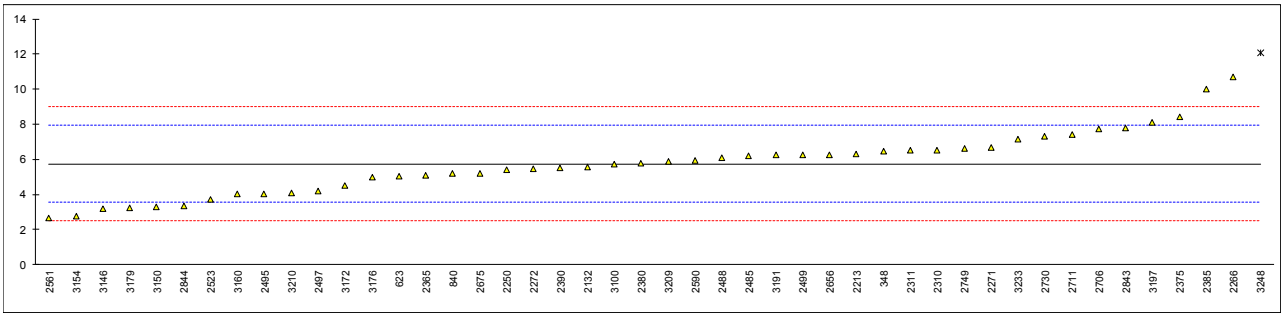


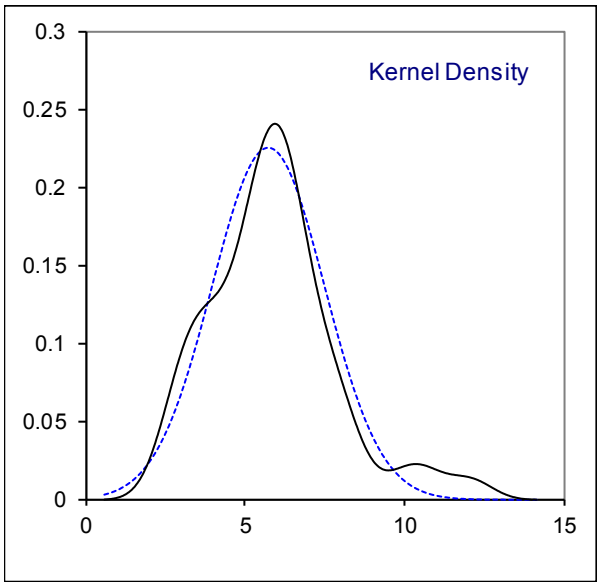
Determination of Chromium VI (chromatographic) in sample #18545; results in mg/kg

lab	method	value	mark	z(targ)	remarks
213		-----		-----	
230		-----		-----	
339		-----		-----	
348	ISO17075-2	6.455		0.65	
362		-----		-----	
551		-----		-----	
623	ISO17075-2	5.01		-0.68	
840	ISO17075-2	5.2		-0.50	
841		-----		-----	
1911		-----		-----	
2102		-----		-----	
2115		-----		-----	
2120		-----		-----	
2121		-----		-----	
2128		-----		-----	
2129		-----		-----	
2132	In house	5.575		-0.16	
2137		-----		-----	
2138		-----		-----	
2159		-----		-----	
2165		-----		-----	
2166		-----		-----	
2172		-----		-----	
2184		-----		-----	
2201		-----		-----	
2213	ISO17075-2	6.3		0.51	
2215		-----		-----	
2228		-----		-----	
2230		-----		-----	
2232		-----		-----	
2241		-----		-----	
2247		-----		-----	
2250	ISO17075-2	5.421		-0.30	
2255		-----		-----	
2256		-----		-----	
2266	ISO17075-2	10.7		4.56	
2271	ISO17075-2	6.7	C	0.88	First reported 10.2
2272	ISO17075-2	5.478		-0.25	
2273		-----		-----	
2290		-----		-----	
2293		-----		-----	
2297		-----		-----	
2300		-----		-----	
2301		-----		-----	
2310	ISO17075-2	6.503		0.70	
2311	ISO17075-2	6.50		0.69	
2330		-----		-----	
2347		-----		-----	
2350		-----		-----	
2352		-----		-----	
2355		-----		-----	
2357		-----		-----	
2358	ISO17075-2	N/A		-----	
2363		-----		-----	
2365	ISO17075-2	5.07		-0.62	
2366	ISO17075-2	out of capability		-----	
2369		-----		-----	
2370		-----		-----	
2375	ISO17075-2	8.4		2.44	
2378		-----		-----	
2379		-----		-----	
2380	ISO17075-2	5.760		0.01	
2382		-----		-----	
2385	ISO17075-2	10.0		3.92	
2389		-----		-----	
2390	ISO17075-2	5.50		-0.23	
2426		-----		-----	
2432		-----		-----	
2442		-----		-----	
2449		-----		-----	
2452		-----		-----	
2459		-----		-----	
2460		-----		-----	
2475		-----		-----	
2485	ISO17075-2	6.198		0.41	

lab	method	value	mark	z(targ)	remarks
2486		-----		-----	
2488	ISO17075-2	6.1		0.32	
2489		-----		-----	
2492		-----		-----	
2495	ISO17075-2	4.024		-1.59	
2497	ISO17075-2	4.21		-1.42	
2499	ISO17075-2	6.262		0.47	
2500		-----		-----	
2501		-----		-----	
2504		-----		-----	
2511		-----		-----	
2515		-----		-----	
2523	ISO17075-2	3.736		-1.85	
2538		-----		-----	
2553		-----		-----	
2561	ISO17075-2	2.675		-2.83	
2566		-----		-----	
2573		-----		-----	
2586		-----		-----	
2590	ISO17075-2	5.9431		0.18	
2591		-----		-----	
2592		-----		-----	
2597		-----		-----	
2605		-----		-----	
2614		-----		-----	
2624		-----		-----	
2637		-----		-----	
2649		-----		-----	
2652		-----		-----	
2656	ISO17075-2	6.27		0.48	
2664		-----		-----	
2668		-----		-----	
2674		-----		-----	
2675	ISO17075-2	5.213		-0.49	
2695		-----		-----	
2701		-----		-----	
2705		-----		-----	
2706	ISO17075-2	7.747		1.84	
2711	ISO17075-2	7.39		1.51	
2713		-----		-----	
2725		-----		-----	
2730	ISO17075-2	7.29		1.42	
2749	ISO17075-2	6.636		0.82	
2756		-----		-----	
2773		-----		-----	
2777		-----		-----	
2778		-----		-----	
2783		-----		-----	
2786		-----		-----	
2787		-----		-----	
2804		-----		-----	
2806		-----		-----	
2812		-----		-----	
2813		-----		-----	
2823		-----		-----	
2829		-----		-----	
2836		-----		-----	
2837		-----		-----	
2838		-----		-----	
2839		-----		-----	
2842		-----		-----	
2843	ISO17075-2	7.81		1.90	
2844	ISO17075-2	3.36		-2.20	
3100	ISO17075-2	5.72		-0.03	
3116		-----		-----	
3134		-----		-----	
3146	ISO17075-2	3.17		-2.37	
3150	ISO17075-2	3.31		-2.25	
3154	ISO17075-2	2.78		-2.73	
3160	ISO17075-2	4.01		-1.60	
3163		-----		-----	
3172	ISO17075-2	4.52		-1.13	
3176	ISO17075-2	4.995		-0.69	
3179	ISO17075-2	3.23		-2.32	
3185		-----		-----	
3191	ISO17075-2	6.248		0.46	
3197	ISO17075-2	8.09		2.16	
3199		-----		-----	

lab	method	value	mark	z(targ)	remarks
3200		-----		-----	
3209	ISO17075-2	5.89		0.13	
3210	In house	4.100		-1.52	
3216		-----		-----	
3218		-----		-----	
3222		-----		-----	
3228		-----		-----	
3233	ISO17075-2	7.15		1.29	
3237		-----		-----	
3246		-----		-----	
3248	ISO17075-2	12.089	R(0.05)	5.84	
	normality	OK			
	n	45			
	outliers	1			
	mean (n)	5.748			
	st.dev. (n)	1.7656	RSD= 30.7%		
	R(calc.)	4.944			
	st.dev.(ISO17075-2:17)	1.0855			
	R(ISO17075-2:17)	3.039			





APPENDIX 2

Summary of reported analytical details

Lab	ISO/IEC17025 accredited	Sample intake used	Extraction time (min)	Extraction temperature (°C)
213	No	2,0017g	180 min	Ambient temperature
230	Yes	2.0077	180	ambient
339	No	2g	180	Room temperature
348	No	2 g	180	20
362	Yes	2.0026	3h	room temperature 21C
551	Yes	1.0030g	180	22
623	Yes	1 g	180 minutes	25 C
840	Yes	1	3h	25
841	Yes			
1911	Yes	about 2	180	22,1
2102	Yes	2	3 hours	20
2115	Yes	1 g	180 min	25°C
2120	No	1 g/ 50 ml	180	23ºC
2121	Yes	2.103 g and 2,008 g	3h00	Ambient
2128	Yes	appr. 2 g	240	20
2129	Yes			
2132	Yes	1.0g	180	21
2137	Yes	2.007 g	180 min	25
2138	No	2.0004 g	180 minutes	22 degrees
2159	Yes	1 g	180 min	24°C
2165	Yes	1.0	180	22
2166	Yes	1.1	180	20 +/-2
2172	Yes	2g	180 mins	25°C
2184	Yes	1	180	25°C
2201	Yes	1.0g	180mins	24°C
2213	Yes	2gm	4hrs	room temperature
2215	Yes	2.0078	180min	25°C
2228	Yes	1.0006 g	180 min	22.5 °C
2230	Yes	1.0055g	3hrs	Room temperature
2232	Yes	2.0023	180	23.5
2241	Yes	1	180	23
2247	---			
2250	Yes	0,5 g 1 g	180 min	20 °C
2255	Yes	1.002	180	25
2256	Yes	1.0208	180	26.8
2266	Yes	2.0072	180	20
2271	Yes	2.0014	180	23.2
2272	Yes	2.0062	180	around 25°C
2273	Yes	2.002	180	22.4
2290	---			
2293	No	2.00	180 minutes	Room temperature
2297	Yes	2.0011	3hr	25
2300	Yes	2grams	180 minutes	32°C
2301	Yes	1	3hours	28
2310	No	2.00g	3 hrs±5 mins	25°C
2311	Yes	2	180	22 °C
2330	Yes	1	180	27.13
2347	Yes	2g	180minutes	25°C
2350	Yes	2 g	3 hours	room temperature
2352	Yes	2g	180min	25.1°C
2355	Yes	2	180mins	25°C
2357	Yes			
2358	Yes	2 g	180 mins	22.2 degree C
2363	Yes	1g	180min	22°C
2365	Yes	2g	180min	23.0°C
2366	Yes	2g	180min	25°C
2369	Yes	1g	180min	23°C
2370	Yes	2 g	180 minutes	25°C
2375	Yes	2 gr	180 mins	22.2C
2378	Yes	2g	180min	25.0°C
2379	Yes	1.0019	180 min	24.98 degree
2380	Yes	1.0 g	180 minutes	20 °C
2382	No	2	180	22.3°C
2385	Yes	1 g	180	20
2389	Yes	2 grams	180 min	22
2390	Yes	2.0018 gm	3 Hours (180 minutes)	20.8 - 21.0
2426	Yes	0.5072	3 Hours	Room Temperature
2432	No	2	180	

Lab	ISO/IEC17025 accredited	Sample intake used	Extraction time (min)	Extraction temperature (°C)
2442	No	2.0065	180 min	24
2449	Yes	1	180	22
2452	Yes	1.99 g	180 minutes	25 °C
2459	Yes	2.0 g	180 min	25
2460	Yes	2	180	20
2475	No	0.9921	180	room temperature
2485	Yes	2	180	23
2486	Yes	0.5048	180 minutes	18 to 25 °C
2488	Yes	2	180	
2489	Yes	2.001g	3 hrs	RT
2492	Yes	1	3 hours	Room Temperature
2495	No	1	180	24
2497	Yes	2	180	24
2499	Yes	2.000 grams	180 minutes	Room temperature (23 °C)
2500	Yes	1g	180 minutes	25 °C
2501	Yes	one is 2.0001g, the other is 1.993 g	180 minutes	20°C
2504	Yes	2.0000 g	180 minutes	25 C
2511	---			
2515	Yes	1.0003	180	24
2523	Yes	1.5035g	180 minutes	25°C
2538	Yes	1,5 and 1,7	180	24
2553	Yes	1.034	180mins	23.8
2561	Yes	2.01	180	
2566	Yes	1.0021 gm	180min	24
2573	Yes	2g	180min	22
2586	Yes	2 g	180 min	23 °C
2590	Yes	0,9954	180	20,4
2591	No	2.0	180 minutes	Room Temperature
2592	Yes	2 g	180 min	rt
2597	---			
2605	Yes	2g	180min	25°C
2614	Yes	1.0016 grams	3 hrs	24 c
2624	No	2,00	180	room temperature
2637	Yes	1	180	20
2649	---			
2652	Yes	1.0045g	3h	20
2656	No	2g	180min	21°C
2664	Yes	2	180	RT
2668	Yes	1.0 grams	180 minutes	Room temperature
2674	Yes	1g	180 minutes	about 22°C
2675	Yes	1,0001	180	21,5 °C
2695	Yes	2	180 minutes	20°C
2701	---			
2705	No	2g	180	RT
2706	Yes	1	180	23
2711	No	0.995	180	25
2713	Yes	2 gram	180 min	-
2725	---			
2730	No	2,00	180 minutes	ambient temperature
2749	No	1	180	23
2756	Yes	2GRAM	180MINUTES	ROOM TEMPERATURE
2773	Yes	1.0	180	23.0
2777	No	4.119	180 minutes	23.3
2778	Yes	4g	180 minutes	25°C
2783	Yes	2.001	180	22
2786	Yes	2	180	25
2787	Yes	2	180	room temperature
2804	No	2	180	25
2806	No	2,03	180	24
2812	No	2	180	23
2813	Yes	2.00156	180	23
2823	No	2.0	180	Ambient - uncontrolled
2829	Yes	2.0066 g	180 minutes	23 °C
2836	Yes	2.0339 and 2.0198	180	25ºC
2837	Yes	2g	3h	20
2838	Yes	2,0004/2,0005	180	23
2839	Yes	2.002	180	25°C
2842	No	2 GRAMS	APPROX 4 HOURS	ROOM TEMPERATURE
2843	---			
2844	No	2.0000 +/- 0.02	180 min +/- 5 min	22 ºC
3100	Yes	2 grams	180 minutes	24.4°C
3116	Yes	1.0083	180	20
3134	Yes	2,00 g	180 min	20°C

Lab	ISO/IEC17025 accredited	Sample intake used	Extraction time (min)	Extraction temperature (°C)
3146	Yes	2 g	3 hour	room temperature
3150	---			
3154	Yes			
3160	Yes	1 g	180	23 °C
3163	---			
3172	Yes			
3176	Yes	1	180	21
3179	Yes	3 samples with 1g, 1 sample 2 g	180	21
3185	Yes	2.0g	180 min	23°C
3191	Yes	1g	180 minutes	25
3197	Yes	2,0002 g	180 minutes	22C
3199	Yes	1.0080	180 minutes	22.5 degrees C
3200	Yes	2.0017	180	25
3209	Yes	2.0053	180	23
3210	Yes	2.001	180	20.5
3216	Yes	2,03 and 2,04	180	Room Temperature
3218	Yes	1g	180min	23.2°C
3222	Yes	2	180	21
3228	Yes	2.0	180min	22
3233	No	1.0088	180	20
3237	Yes	2 gram	180 minutes	25
3246	Yes	1.00	180	25°C
3248	Yes	2.0	180	25

Summary of reported analytical details, continued

Lab	pH before the extraction	pH after the extraction	Type of shaker used	Frequency of the shaker
213	8	7,85	Orbital shaker	100 rpm
230	8.0	7.2	orbital shaker	150 rpm
339	8	7.75	Orbital shaking table	160 rpm
348	8.15	7.5-8.0	orbital	100 rpm
362	8.0	7.8	Mechanical orbital shaker	100 +/- 10 min-1
551	8.02	8.01	Orbital Shaker	150rpm
623	7.8	8.0	Mechanical Shaker	100 min-1
840	8.0	7.7	Orbital	100
841				
1911	8,01	7,76	horizontal	100 / minute
2102	8	7.9	shaker able to perform circular movement	slow frequency
2115	8.0	7.8	horizontal	60 rpm /min
2120	8,0	7,8	EDMUND BUHLER TH 10, orbital shaker	100 rpm +/- 10 rpm
2121	8	7,74	horizontal and circular	100 rpm
2128	pH 8	pH 7,7 - pH 8	horizontal shaker	50 turns per minute
2129				
2132	7.9	7.9	Mech. Shaker	100 r.p.m
2137	8.06	7.81		
2138	8.00	7.99	open air shaker	110 rpm
2159	9,5	8	Orbital shaker	100 rpm
2165	8.0	7.70/7.74	Reciprocating	100 rpm
2166	8.0	7.6	horizontal	150/Min.
2172	8.0	7.5	Mechanical shaker	100 min-1
2184	7.9	7.8	Mechanical orbital shaker	100 rpm
2201	8.00	7.69	Linear shaker	100 per min
2213	8.01	7.78	Orbital	110
2215	7.5	7.4	mechanical orbital shaker	100
2228	8.01	7.5 - 10	Reciprocal shaking bath	170 rpm
2230	7.99	8.00	mechanical shaker	100 /min
2232	8.0	7.73	mechanical orbital shaker	100 ± 10 min- I.
2241	8.0	7.8	Excella E2, open air shaker	100
2247				
2250	8,0	8,0	Heidolph	120 rpm
2255	8.0	7.9	Orbital	100 rpm
2256	8.00	7.84	Mechanical shaker	100
2266		7	rotatest	100 +/- 10 tour/min
2271	8.0	7.8	Orbital	100
2272	8.0	7.61	orbital shaker	100rpm
2273	8.0	7.61	Back and forward	100 rpm
2290				
2293		7.74	reciprocant	90 RPM
2297	8.03	7.78		105min-1
2300	8.0 (± 0.1)	7.5	Vibrator	
2301	7.97	7.85	mechanical shaker	100RPM
2310	8.0pH	7.7pH	Orbittal motion	110 rpm
2311	8	7.8	Mechnical shaker	100rpm
2330	8.038	7.636	Horizontal shaker	100
2347	8.05	7.74		100/minute
2350	8.0	7.5	Orbital shaker	100/min
2352	8.0	7.5	water bath	100 times/min
2355	8.0	7.8	Reciprocating	100 per min
2357				
2358	pH 8.0	pH 7.9	Mechanical Orbital shaker	100 rpm
2363	8.0	7.0-8.0		100r/min
2365	7.98	7.73	Circular movement orbital shaker.	100
2366	8	7.5	orbital shaker	100
2369	8	7.5	rotating shaker	100r/min
2370	8.0	7.6	Horizontal oscillator	120 rpm
2375	8	7.8	Mechanical	100 rpm
2378	8.0	7.8	water bath	100 times/min
2379	8.00	7.70	Rotary Shaker	100
2380	8.0	7.7	Mechanical	100 RPM
2382	8.093	7.689	THZ-C-1 shaker	100RPM
2385	8,0	7,8	horizontal shaker	100
2389	8.02	7.69	Orbital	100 rpm
2390	8.0	7.76	orbital Shaker	100 rpm
2426	8.0	7.68	Orbital	100 Rpm
2432	8.02	7.78	mechanical orbital shaker	100rpm
2442	8.01	7.84	Horizontal	100 rpm
2449	8	7.9	mechanical	110

Lab	pH before the extraction	pH after the extraction	Type of shaker used	Frequency of the shaker
2452	8.0	7.8	orbital	110 r/minute
2459	8.05	7.80	Mechanical shaker	100 ± 10 rpm
2460	9.17	7.98	circle	100 rpm
2475			straight shaker	100rpm
2485	7.5	8.0	GFL 3017 Orbital shaker	150
2486	8.00	7.90	Mechanical shaker - (to and fro)	100 rpm
2488		7.76	orbital	100
2489	8	7.92	Orbital shaker	100 RPM
2492	8.0	8.0	Mechanical Shaker (Circular Movement)	100 rpm
2495	8.00	7.87	linear	150
2497	8.03	7.22	orbital shaker	100 / min
2499	7.9	7.5	Mechanical orbital shaker	101 (1/min)
2500	8.6	7.8	Mechanical shaker with speed	100/min
2501	8.00	7.66	orbital shaker	100 r/min
2504	8.01	7.67	Orbital shaker	100 rpm/min
2511				
2515	8.00	7.71	Combi-shaker	100 RPM
2523	8.00	7.71	Low temperature shaking Incubator (E-450L)	100 rpm
2538	7,97	7,72	Horizontal shaking device	80/min
2553	8.7	7.8	Mechanical Shaker	100
2561	8.01			
2566	8.01	7.96	mechanical	100
2573	8.0	7.8	orbital shaker	100r/min
2586	8,08	7,71	OS-20 Boeco Germany	100
2590	7,97	7,71	Orbital shaker	100
2591	7.5-8.0	7.5-8.0	Orbital	Continuous
2592		7.8	mechanical stirrer	90-110 min-1
2597				
2605	8.07	7.87	ZD-8802	100r/min
2614	pH 8	pH 7.8	Mechanical shaker	100/min
2624	8,0	/	/	/
2637	7,8	7,8		
2649				
2652	7.6	8.05	Reciprocating oscillator	100 ± 10min-1
2656	8,01	7,73	mechanical overhead shaker	12rpm
2664	8.0	7.8	orbital shaker	160
2668	8.0	7.9	Orbital shaker	100 RPM
2674	7.85	7.75	mechanical orbital shaker(Reciprocating)	100Hz
2675	8,0	7,7 / 7,7 / 7,7	circular shaker	100 min-1
2695	8,0	7,70	horizontal shaker	120 rpm
2701				
2705	8.0	8.0	Rotary flask shaker	100 min-1
2706	8.0	7.9	horizontal	80rpm
2711	8.1	7.7	Orbital	170
2713	8.01	7.75	orbital	100 min-1
2725				
2730	pH=8 +/- 0.1	pH= 7.7	orbital shaker	100 rpm
2749	-	-	-	-
2756	8.01	7.78	ORBITAL	80RPM
2773	8.0	7.9	orbital	150
2777	8.00	8.00	water bathing and waving shaker	50rmp
2778	pH=8.0	pH=7.6	Mechanical	120 times / minutes
2783	7.93	7.62	Orbital shaker	175 RPM
2786	7.26			100 rpm
2787	8	7.95	horizontal shaker	100rpm
2804	8	7.8	Mechnical Shaker	100 rpm
2806	8,0	7,8	orbital	100
2812	8.0	7.5	orbital	100 rpm
2813	8.00	7.74	mechanical shaker	100 ± 10
2823	7.98	7.80	GFL 3005 - Orbital shaker	100rpm
2829	8.01	7.85	orbital shaker	100 min^-1
2836	8.01	7.76	orbital shaker	100 rpm
2837	no need according to GB/T 22807-2008	7.5	Vortex generator	100r/min
2838	-	7,80/7,78	orbital	100
2839	8.0	7.6	SHAKER	105
2842	PH 7,9-8,1	7-8	MECHANİCAL ORBİTAL SHAKER	90-110 RPM
2843				
2844	8.00	7.76	Orbital shaker	110 rpm
3100	8.02	7.80	HY-6D	100 r/min
3116	7.9	7.6	Mechanical shaker	100 rpm
3134	8,0	7,7	Orbital shaker	110 rpm
3146	7,0 and 8,0	7,0 and 8,0	orbital shaker	100 min -1

Lab	pH before the extraction	pH after the extraction	Type of shaker used	Frequency of the shaker
3150				
3154				
3160	7,95	7,7	orbital shaker	100 rpm
3163				
3172				
3176	8,0	7,5	orbital shaker	100 cycle/minutes
3179	8		Edmund Bühler SM-30	75/min
3185	8.0	7.7	Orbital shaker	100 r/min
3191	7.98	7.55	reciprocating shaker	100 rpm
3197	8,0	7,76	Mechanical orbital shaker	100 rpm
3199	8.01	7.61	Shaking Waterbath	100 rpm
3200	8.0	7.8	mechanical orbital shaker	100min-1
3209	7.8	7.6	rotary type	50Z/min
3210	8.07	7.84	Agitateur rotatif	14 tours/min
3216	7,8	7,81	Mechanical shaker	100+/-10min-1
3218	8.03	7.85	HY-8	100r/min
3222	8.0	7.8	HORIZONTAL MECHANICAL SHAKER	100/min
3228	8.0	7.7	orbital shaker	100rpm
3233	8	8	mechanical shaker "IKA HS 260 basic"	90 shots per minute
3237	8,05	7,74	orbital	100 rpm
3246	7.94	7.77	Orbital Shaker	100 rpm
3248	8.0	7.7	mechanical shaker	RPM 110

APPENDIX 3

Number of participants per country

5 labs in BANGLADESH
2 labs in BRAZIL
2 labs in BULGARIA
1 lab in CAMBODIA
1 lab in ETHIOPIA
8 labs in FRANCE
12 labs in GERMANY
1 lab in GREECE
1 lab in GUATEMALA
10 labs in HONG KONG
10 labs in INDIA
2 labs in INDONESIA
13 labs in ITALY
4 labs in KOREA
1 lab in LUXEMBOURG
1 lab in MAURITIUS
2 labs in MEXICO
1 lab in MOROCCO
36 labs in P.R. of CHINA
5 labs in PAKISTAN
1 lab in POLAND
1 lab in PORTUGAL
1 lab in ROMANIA
1 lab in SERBIA
1 lab in SINGAPORE
7 labs in SPAIN
1 lab in SRI LANKA
4 labs in SWITZERLAND
3 labs in TAIWAN R.O.C.
2 labs in THAILAND
2 labs in THE NETHERLANDS
2 labs in TUNISIA
11 labs in TURKEY
2 labs 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
W	= test result withdrawn on request of participant
ex	= test result excluded from statistical evaluation
n.a.	= not applicable
n.e.	= not evaluated
n.d.	= not detected

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