Institute for
Interlaboratory Studies

Results of Proficiency Test
pH in Leather/Footwear
November 2022

Organized by: Institute for Interlaboratory Studies
Spijkenisse, the Netherlands

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1 INTRODUCTION

Since 2014 the Institute for Interlaboratory Studies (iis) organizes a proficiency scheme for the determination of pH in Leather/Footwear every year. During the annual proficiency testing program 2022/2023 it was decided to continue the proficiency test for the determination of pH in Leather/Footwear.

In this interlaboratory study 80 laboratories in 25 countries registered for participation, see appendix 3 for the number of participants per country. In this report the results of the pH in Leather/Footwear proficiency test are presented and discussed. This report is also electronically available through the iis website www.iisnl.com.

2 SET UP

The Institute for Interlaboratory Studies (iis) in Spijkenisse, the Netherlands, was the organizer of this proficiency test (PT). Sample analyzes for fit-for-use and homogeneity testing were subcontracted to an ISO/IEC17025 accredited laboratory.
It was decided to send one leather sample of approximately 10 grams labelled #22770.
The participants were requested to report rounded and unrounded test results. The unrounded test results were preferably used for the 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 organization of this proficiency test was the one as described for proficiency testing in the report 'iis Interlaboratory Studies: Protocol for the Organisation, Statistics and Evaluation' of June 2018 (iis-protocol, version 3.5). This protocol is electronically available through the iis website www.iisnl.com, from the FAQ page.

2.3 CONFIDENTIALITY STATEMENT

All data presented in this report must be regarded as confidential and for use by the participating companies only. Disclosure of the information in this report is only allowed by means of the entire report. Use of the contents of this report for third parties is only allowed by written permission of the Institute for Interlaboratory Studies. Disclosure of the identity of one or more of the participating companies will be done only after receipt of a written agreement of the companies involved.

2.4 SAMPLES

A batch of black leather was purchased on the local market and grinded. After homogenization 125 small plastic bags were filled with approximately 10 grams each and labelled #22770.
The homogeneity of the subsamples was checked by the determination of the pH of extract in accordance with ISO4045 on 8 stratified randomly selected subsamples.

	pH of extract
sample #22770-1	3.11
sample #22770-2	3.13
sample #22770-3	3.12
sample #22770-4	3.13
sample #22770-5	3.14
sample #22770-6	3.14
sample #22770-7	3.14
sample #22770-8	3.12

Table 1: homogeneity test results of subsamples #22770

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

	pH of extract
r (observed)	0.03
reference method	iis memo 2204
0.3 x R (reference method)	0.06

Table 2: evaluation of the repeatability of subsamples #22770

The calculated repeatability is in agreement with 0.3 times the reproducibility of the reference method. Therefore, homogeneity of the subsamples was assumed.

To each of the participating laboratories one leather sample labelled #22770 was sent on October 19, 2022.

2.5 ANALYZES

The participants were requested to determine the pH of extract and when applicable also pH of ten times diluted extract and the difference between the two pH measurements.
To ensure homogeneity it was requested not to use less than 0.5 gram per determination and not to age or dry the sample. It was also requested to report if the laboratory was accredited for the determined components and to report some analytical details.

It was explicitly requested to treat the sample as if it was a routine sample and to report the test results using the indicated units on the report form and not to round the test results but report as much significant figures as possible. It was also requested not to report ‘less than’ results, which are above the detection limit, because such results cannot be used for meaningful statistical evaluations.

To get comparable test results a detailed report form and a letter of instructions are prepared. On the report form the reporting units are given as well as the reference test methods (when applicable) that will be used during the evaluation. The detailed report form and the letter of instructions are both made available on the data entry portal www.kpmd.co.uk/sgs-iis-cts/. The participating laboratories are also requested to confirm the sample receipt on this data entry portal. The letter of instructions can also be downloaded from the iis website www.iisnl.com.

3 RESULTS

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

Directly after the deadline, a reminder was sent to those laboratories that had not reported test results at that moment. Shortly after the deadline, the available test results were screened for suspect data. A test result was called suspect in case the Huber Elimination Rule (a robust outlier test) found it to be an outlier. The laboratories that produced these suspect data were asked to check the reported test results (no reanalyzes). Additional or corrected test results are used for data analysis and the original test results are placed under 'Remarks' in the result tables in appendix 1. Test results that came in after the deadline were not taken into account in this screening for suspect data and thus these participants were not requested for checks.

3.1 STATISTICS

The protocol followed in the organization of this proficiency test was the one as described for proficiency testing in the report ‘iis Interlaboratory Studies: Protocol for the Organisation, Statistics and Evaluation’ of June 2018 (iis-protocol, version 3.5).
For the statistical evaluation the *unrounded* (when available) figures were used instead of the rounded test results. Test results reported as ‘<…’ or ‘>…’ were not used in the statistical evaluation.

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

The assigned value is determined by consensus based on the test results of the group of participants after rejection of the statistical outliers and/or suspect data.

According to ISO13528 all (original received or corrected) results per determination were submitted to outlier tests. In the iis procedure for proficiency tests, outliers are detected prior to calculation of the mean, standard deviation and reproducibility. For small data sets, Dixon (up to 20 test results) or Grubbs (up to 40 test results) outlier tests can be used. For larger data sets (above 20 test results) Rosner's outlier test can be used. Outliers are marked by D(0.01) for the Dixon's test, by G(0.01) or DG(0.01) for the Grubbs' test and by R(0.01) for the Rosner's test. Stragglers are marked by D(0.05) for the Dixon's test, by G(0.05) or DG(0.05) for the Grubbs' test and by R(0.05) for the Rosner's test. Both outliers and stragglers were not included in the calculations of averages and standard deviations.

For each assigned value, the uncertainty was determined in accordance with ISO13528. Subsequently the calculated uncertainty was evaluated against the respective requirement based on the target reproducibility in accordance with ISO13528. In this PT, the criterion of ISO13528, paragraph 9.2.1. was met for all evaluated tests, therefore, the uncertainty of all assigned values may be negligible and need not be included in the PT report.

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

3.2 GRAPHICS

In order to visualize the data against the reproducibilities from literature, Gauss plots were made, using the sorted data for one determination (see appendix 1). On the Y-axis the reported test results are plotted. The corresponding laboratory numbers are on the X-axis. The straight horizontal line presents the consensus value (a trimmed mean). The four striped lines, parallel to the consensus value line, are the +3s, +2s, -2s and -3s target reproducibility limits of the selected reference test method. Outliers and other data, which were excluded from the calculations, are represented as a cross. Accepted data are represented as a triangle.

Furthermore, Kernel Density Graphs were made. This is a method for producing a smooth density approximation to a set of data that avoids some problems associated with histograms. Also, a normal Gauss curve (dotted line) was projected over the Kernel Density Graph (smooth line) for reference. The Gauss curve is calculated from the consensus value and the corresponding standard deviation.

3.3 Z-SCORES

To evaluate the performance of the participating laboratories the z-scores were calculated. As it was decided to evaluate the performance of the participants in this proficiency test (PT) against the literature requirements (derived from e.g. ISO or ASTM test methods), 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, like Horwitz or an estimated reproducibility based on former iis proficiency tests.

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

The z-scores were calculated according to:

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

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

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

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

4 EVALUATION

In this proficiency test some problems were encountered with the dispatch of the samples. Six participants reported test results after the final reporting date and one other participant did not report any test results. Not all participants were able to report all tests requested. In total 79 participants reported 156 numerical test results. Observed were 8 outlying test results, which is 5.1%. In proficiency tests outlier percentages of 3% - 7.5% are quite normal.

All data sets proved to have a normal Gaussian distribution.

4.1 EVALUATION PER TEST

In this section the reported test results are discussed per test. The test methods which were used by the various laboratories were taken into account for explaining the observed differences when possible and applicable. These test methods are also in the tables together with the original data in appendix 1. The abbreviations, used in these tables, are explained in appendix 4.

Test methods ASTM D2810 and ISO4045 are considered to be the official test methods for the determination pH in leather. Regretfully, ISO4045 does not provide precision data and the reproducibility of ASTM D2810 appears to be very strict. It has been observed that the group of participants are not able to meet the (strict) requirements of test method ASTM D2810 over the years.

Therefore, iis decided to use the iis PT data gathered from 2014 to 2021 to estimate a more realistic target reproducibility for the evaluation of the quality of the test results for the determination of pH in Leather/Footwear. The average relative standard deviation over all iis PTs of pH in Leather for pH of extract is 2.3% and for pH of ten times diluted extract is 2.6%. This investigation is summarized in iis memo 2204 (see lit. 13).

pH of extract: This determination was not problematic. Three statistical outliers were observed. The calculated reproducibility after rejection of the statistical outliers is in agreement with the target reproducibility as derived from iis memo 2204.

pH of ten times diluted extract: This determination was not problematic. Five statistical outliers were observed. The calculated reproducibility after rejection of the statistical outliers is in agreement with the target reproducibility as derived from iis memo 2204.

4.2 PERFORMANCE EVALUATION FOR THE GROUP OF LABORATORIES

A comparison has been made between the reproducibility estimated from the reference test method and the reproducibility as found for the group of participating laboratories. The number of significant results, the average, the calculated reproducibility (2.8 * standard deviation) and the reproducibility derived from reference methods are presented in the next table.

Parameter	unit	n	average	2.8 * sd	R(target)
pH of extract		76	3.61	0.17	0.24
pH of extract ten times diluted		72	4.05	0.18	0.30

Table 3: reproducibilities of tests on sample #22770

Without further statistical calculations it can be concluded that for both parameters there is a good compliance of the group of participating laboratories with the reference method.

4.3 COMPARISON OF THE PROFICIENCY TEST OF NOVEMBER 2022 WITH PREVIOUS PTS

	November 2022	November 2021	November 2020	November 2019	November 2018
Number of reporting laboratories	79	92	106	136	114
Number of test results	156	267	356	441	396
Number of statistical outliers	8	10	14	17	12
Percentage of statistical outliers	5.1%	3.7%	3.9%	3.9%	3.0%

Table 4: comparison with previous proficiency tests

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

The performance of the determinations of the proficiency test was compared to uncertainties observed in PTs over the years, expressed as relative standard deviation (RSD) of the PTS, see next table.

Parameter	November 2022	November 2021	November 2020	2014-2019	Target
pH of extract	1.7%	1.6%	2.3%	1.7-3.2%	2.3%
pH of extract ten times diluted	1.5%	2.3%	3.3%	2.3-3.0%	2.6%

Table 5: development of the uncertainties over the years

The uncertainties observed in this PT are comparable or better to the uncertainties observed in previous PTs.

4.4 EVALUATION OF THE ANALYTICAL DETAILS

For this PT some analytical details were requested which are listed in appendix 2. Based on the answers given by the participants the following can be summarized:

- About 80% reported to be accredited for the determination of pH in leather.
- About 85% used the sample as received and 15% further cut or grinded the sample.
- About 75% reported to have used 5 grams for intake. About 20% reported to have used less than 5 grams and about 5% reported to have used more.
- Over 95% of the participants did not use an additional step to wet the samples.

As the majority of the group follow the same analytical procedures no separate statistical analysis has been performed.

5 DISCUSSION

Two different test methods are available to determine the pH in leather, ASTM D2810 and ISO4045. The difference between both test methods is the dilution of the extract (10 times) in ISO4045 when the pH of the undiluted extract is not between 4.00 and 10.00. According to ISO4045 the difference figure is then calculated by subtracting the pH value of the 10 times diluted extract from the pH value from the undiluted extract. Remarkably, most of the participants reported an absolute value for the difference between pH of extract and pH of ten times diluted extract.
All participants reported a test result below 4.00, except one. Two participants did not report a test result for the dilution of the extract (10 times), while two reported to have performed another test method than ISO4045. None of the participants reported to use method ASTM D2810.

6 CONCLUSION

Although it can be concluded that most of the participants have no problem with the determination on pH in this PT, 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.

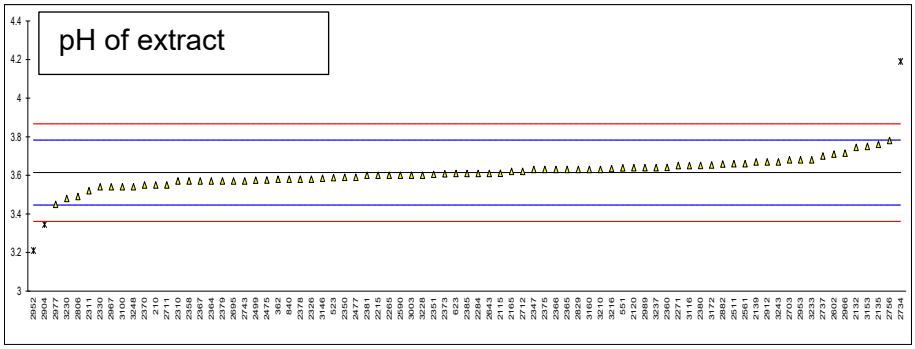
APPENDIX 1

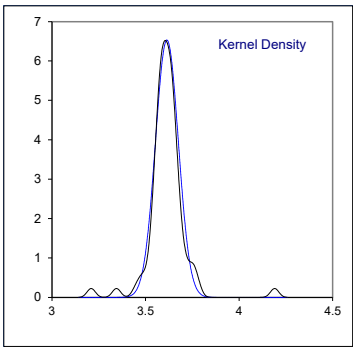
Determination of pH on sample #22770; unitless results

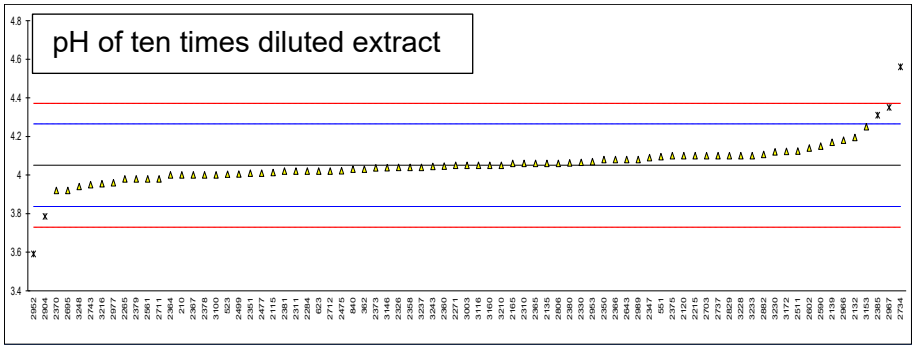
lab	method	pH of extract	mark	z(targ)	pH ten times diluted	mark	z(targ)	pH of extract - pH 10x diluted	mark
210	ISO4045	3.55		-0.77	4		-0.48	0.45	
362	ISO4045	3.58		-0.41	4.03		-0.20	0.45	
523	ISO4045	3.588		-0.32	4.004		-0.44	0.416	
551	ISO4045	3.639		0.29	4.095		0.41	0.456	
623	ISO4045	3.61		-0.05	4.02		-0.29	0.41	
840	ISO4045	3.58		-0.41	4.03		-0.20	0.45	
2115	ISO4045	3.611		-0.04	4.013		-0.36	0.402	
2120	ISO4045	3.64		0.30	4.10		0.46	0.46	
2132	ISO4045	3.745		1.55	4.195		1.34	0.45	
2135	ISO4045	3.76		1.73	4.06	C	0.08	0.44	C, E
2139	ISO4045	3.67		0.66	4.17		1.11	0.50	
2165	ISO4045	3.62		0.06	4.06		0.08	0.44	
2215	ISO4045	3.60		-0.17	4.10		0.46	0.50	
2265	ISO4045	3.60		-0.17	3.98		-0.67	0.38	
2271	ISO4045	3.65		0.42	4.05		-0.01	0.40	
2284	ISO4045	3.61		-0.05	4.02		-0.29	0.41	
2310	ISO4045	3.57		-0.53	4.06	C	0.08	0.49	C
2311	ISO4045	3.52		-1.12	4.02		-0.29	0.50	
2326	ISO4045	3.58		-0.41	4.04		-0.10	0.46	
2330	ISO4045	3.54		-0.89	4.066		0.14	0.526	
2347	ISO4045	3.63		0.18	4.09		0.36	-0.46	
2350	ISO4045	3.59		-0.29	4.08		0.27	0.49	
2351	ISO4045	3.605		-0.11	4.010		-0.39	0.405	
2358	ISO4045	3.57		-0.53	4.04	C	-0.10	0.47	C
2360	ISO4045	3.641		0.31	4.046		-0.05	0.405	
2364	ISO4045	3.57		-0.53	4.00		-0.48	0.43	
2365	ISO4045	3.63		0.18	4.06		0.08	-0.43	
2366	ISO4045	3.63		0.18	4.08		0.27	-0.45	
2367	ISO4045	3.57		-0.53	4.00		-0.48	0.43	
2370	ISO4045	3.55		-0.77	3.92		-1.23	0.37	
2372		-----		-----	-----		-----	-----	
2373	ISO4045	3.608		-0.08	4.037		-0.13	0.429	
2375	ISO4045	3.63		0.18	4.10		0.46	0.47	
2378	ISO4045	3.58		-0.41	4.00		-0.48	0.42	
2379	ISO4045	3.57		-0.53	3.98		-0.67	0.41	
2380	ISO4045	3.651		0.43	4.062		0.10	0.411	
2381	ISO4045	3.60		-0.17	4.02		-0.29	0.42	
2385	ISO4045	3.61		-0.05	4.31	R(0.01)	2.42	-0.70	
2475	ISO4045	3.576		-0.46	4.022		-0.27	0.45	
2477	ISO4045	3.59		-0.29	4.01		-0.39	0.42	
2499	ISO4045	3.575		-0.47	4.005		-0.43	0.43	
2511	ISO4045	3.66		0.54	4.124		0.68	0.464	
2561	ISO4045	3.66		0.54	3.98		-0.67	0.32	
2590	ISO4045	3.60		-0.17	4.15		0.92	0.55	
2602	ISO4045	3.71		1.13	4.14		0.83	0.43	
2643	ISO4045	3.61		-0.05	4.08		0.27	0.47	
2695	ISO4045	3.57	C	-0.53	3.92	C	-1.23	0.35	
2703	ISO4045	3.68		0.78	4.10		0.46	-0.42	
2711	ISO4045	3.55		-0.77	3.98		-0.67	0.43	
2712	ISO4045	3.62		0.06	4.02		-0.29	0.40	
2734	ISO4045	4.19	R(0.01)	6.83	4.56	R(0.01)	4.76	0.37	
2737	ISO4045	3.70		1.01	4.10		0.46	0.40	
2743	ISO4045	3.57		-0.53	3.95		-0.95	0.38	
2756	SLC13	3.78		1.96	-----		-----	-----	
2806	ISO4045	3.49		-1.48	4.06		0.08	0.57	
2829	ISO4045	3.63		0.18	4.10		0.46	0.47	
2882	ISO4045	3.658	C	0.52	4.107	C	0.52	0.448	C
2904	ISO4045	3.345	R(0.01)	-3.20	3.785	R(0.01)	-2.49	0.44	
2912	ISO4045	3.67		0.66	-----		-----	-----	
2952	ISO4045	3.21	C,R(0.01)	-4.80	3.59	C,R(0.01)	-4.31	0.38	
2953	ISO4045	3.68		0.78	4.07		0.18	0.39	
2966	ISO4045	3.715		1.19	4.180		1.20	0.465	
2967	ISO4045	3.54		-0.89	4.35	R(0.01)	2.79	0.8	
2977	ISO4045	3.45	C	-1.95	3.96	C	-0.85	0.31	E
2989	ISO4045	3.64		0.30	4.08		0.27	0.44	
3003	ISO4045	3.6		-0.17	4.05		-0.01	0.45	
3100	ISO4045	3.54		-0.89	4.00		-0.48	0.46	
3116	ISO4045	3.65		0.42	4.05		-0.01	0.40	
3146	ISO4045	3.585		-0.35	4.038		-0.12	0.453	
3153	ISO4045	3.75	C	1.61	4.25	C	1.86	0.50	C
3160	ISO4045	3.63		0.18	4.05		-0.01	0.42	
3172	ISO4045	3.6532		0.46	4.1223		0.66	0.4691	
3210	ISO4045	3.63		0.18	4.05		-0.01	0.42	

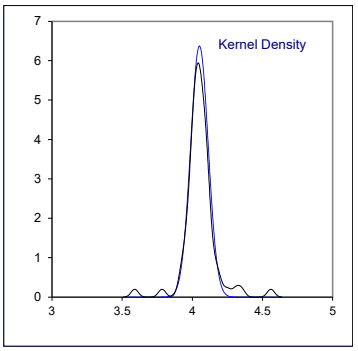
lab	method	pH of extract	mark	z(targ)	pH ten times diluted	mark	z(targ)	pH of extract - pH 10x diluted	mark
3216	ISO4045	3.635		0.24	3.955		-0.90	0.32	
3228	ISO4045	3.60		-0.17	4.10		0.46	0.50	
3230	In house	3.48	C	-1.60	4.12	C	0.64	0.64	C
3233	ISO4045	3.68		0.78	4.10		0.46	0.42	
3237	ISO4045	3.64		0.30	4.04		-0.10	0.4	
3243	ISO4045	3.67		0.66	4.045		-0.06	0.375	
3248	ISO4045	3.54		-0.89	3.94		-1.04	0.4	
	normality	OK			OK				
	n	76			72				
	outliers	3			5				
	mean (n)	3.615			4.051				
	st.dev. (n)	0.0611	RSD=1.7%		0.0626	RSD=1.5%			
	R(calc.)	0.171			0.175				
	st.dev.(R(iis memo 2204))	0.0842			0.1070				
	R(iis memo 2204)	0.236			0.299				

Lab 2135 first reported respectively 4.41; 0.65. E: Calculation difference, iis calculated -0.30
Lab 2310 first reported respectively 4.14; 0.57
Lab 2358 first reported respectively 4.37; 0.80
Lab 2695 first reported respectively 3.92; 3.57
Lab 2882 first reported respectively 4.349; 5.022; 0.673
Lab 2952 first reported respectively 3.17; 3.55
Lab 2977 first reported respectively 3.35; 3.66. E: Calculation difference, iis calculated -0.51
Lab 3153 first reported respectively 3.35; 3.55; 0.20
Lab 3230 first reported respectively 3.21; 3.92; 0.71









APPENDIX 2 Analytical details

lab	ISO/IEC17025 accredited	Sample Preparation	Sample intake (in grams)	Additional steps to wet the sample
210	---	Used as received		No
362	Yes	Used as received	5g	No
523	No	Used as received	5 g	No
551	Yes	Used as received	10 grams	No
623	Yes	Further cut	2.5	No
840	Yes	Used as received	5 grams	No
2115	Yes	Used as received	5 grams	No
2120	No	Used as received	2,5 g	No
2132	No	Used as received	5g	No
2135	No	Used as received	1	No
2139	Yes	Used as received	5.005 g, 5.005 g	No
2165	Yes	Used as received	2.0g	No
2215	Yes	Used as received	5g	No
2265	No	Used as received	5	No
2271	Yes	Used as received	5g	No
2284	Yes	Used as received	5g	No
2310	Yes	Used as received	5	No
2311	Yes	Used as received	5	No
2326	Yes	Used as received	5.0008	No
2330	Yes	Used as received	5.00 g	No
2347	Yes	Used as received	2.5g	No
2350	Yes	Used as received	5.0 g	No
2351	Yes	Used as received		---
2358	Yes	Used as received	5g	No
2360	Yes	Used as received	5.0g	No
2364	Yes	Used as received	5.00g*2	No
2365	Yes	Used as received	2g	No
2366	No	Used as received	5g	No
2367	Yes	Used as received	5.000	No
2370	Yes	Further cut	5.0043 g	No
2372	---	---		---
2373	Yes	Used as received	5g	No
2375	Yes	Further cut	2.5 gram	Yes: mixing with water in a disintegrator (eg Waring Blender)
2378	Yes	Used as received	5g	No
2379	Yes	Used as received	5.00 g /flask	No
2380	Yes	Used as received	5.0 g	No
2381	Yes	Used as received	5 grams.	No
2385	Yes	Used as received	ca. 2.5 g	No
2475	No	Used as received	4.9627	No
2477	Yes	Used as received	5.0014 and 5.0025	No
2499	Yes	Used as received	4.9936 g	No
2511	---	---		---
2561	Yes	Used as received	5g	No
2590	Yes	Used as received	1.25g	No
2602	No	Used as received	1,0 g	No
2643	Yes	Used as received	5.00 g / Sample	No
2695	Yes	Further grinded	4.8109	No
2703	Yes	Used as received	5g	No
2711	No	Used as received	5,0	No
2712	Yes	Used as received	5.0007g	No
2734	Yes	Used as received	10 g	No
2737	Yes	Used as received	2.5g	No
2743	Yes	Used as received	ABOUT 5g FOR EACH TEST	No
2756	Yes	Used as received		shaked continuously for 16 hours
2806	Yes	Used as received		No
2829	No	Further cut	5.0	No
2882	Yes	Used as received	5 grams	No
2904	Yes	Further grinded	2 aliquots of 4.54 g were used to carry out the duplicate test required by the ISO 4045 standard	No
2912	Yes	Used as received	5,005	No
2952	Yes	Used as received	5.0027 g	No
2953	Yes	Further cut	1	No
2966	Yes	Further cut	5.000	No
2967	No	Used as received	5 grams	No
2977	Yes	Further grinded	2.5	No
2989	No	Used as received	5g	No
3003	No	Used as received	5 grm	No
3100	Yes	Used as received	5g	No
3116	Yes	Used as received	5 grams	No

lab	ISO/IEC17025 accredited	Sample Preparation	Sample intake (in grams)	Additional steps to wet the sample
3146	Yes	Used as received	2 * 2.00g	No
3153	No	Used as received	5 grams	No
3160	Yes	Used as received	5 g	No
3172	Yes	---		---
3210	Yes	Used as received	5.0025	No
3216	Yes	Used as received		No
3228	Yes	Used as received	2.5g	No
3230	Yes	Further cut	5 grams	No
3233	No	Used as received	2 * 5g	No
3237	Yes	Used as received	5	No
3243	Yes	Used as received		No
3248	Yes	Used as received	5.0000	No

APPENDIX 3

Number of participants per country

3 labs in BANGLADESH
1 lab in BRAZIL
1 lab in BULGARIA
1 lab in CAMBODIA
1 lab in ETHIOPIA
4 labs in FRANCE
6 labs in GERMANY
5 labs in HONG KONG
2 labs in INDIA
1 lab in INDONESIA
15 labs in ITALY
3 labs in KOREA, Republic of
1 lab in MAURITIUS
3 labs in MEXICO
1 lab in MOROCCO
16 labs in P.R. of CHINA
3 labs in PAKISTAN
1 lab in PORTUGAL
2 labs in SPAIN
3 labs in TAIWAN
1 lab in THAILAND
1 lab in TUNISIA
2 labs in TURKEY
2 labs in UNITED KINGDOM
1 lab in VIETNAM

APPENDIX 4

Abbreviations

C	= final test result after checking of first reported suspect test result
D(0.01)	= outlier in Dixon's outlier test
D(0.05)	= straggler in Dixon's outlier test
G(0.01)	= outlier in Grubbs' outlier test
G(0.05)	= straggler in Grubbs' outlier test
DG(0.01)	= outlier in Double Grubbs' outlier test
DG(0.05)	= straggler in Double Grubbs' outlier test
R(0.01)	= outlier in Rosner's outlier test
R(0.05)	= straggler in Rosner's outlier test
E	= calculation difference between reported test result and result calculated by iis
W	= test result withdrawn on request of participant
ex	= test result excluded from statistical evaluation
n.a.	= not applicable
n.e.	= not evaluated
n.d.	= not detected
fr.	= first reported
f+?	= possibly a false positive test result?
f-?	= possibly a false negative test result?

Literature

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