Results of Proficiency Test
pH in Leather/Footwear
November 2021

Organized by: Institute for Interlaboratory Studies
Spijkenisse, the Netherlands

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1 INTRODUCTION

Since 2013 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 2021/2022 it was decided to continue the proficiency test for the determination of pH in Leather/Footwear.

In this interlaboratory study 94 laboratories in 26 different 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 labelled #21770.
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 brown leather was purchased on the local market and cut in pieces. After homogenization 125 small bags were filled with approximately 10 grams each and labelled #21770.
The homogeneity of the subsamples was checked by the determination of the pH of extract in accordance with ISO4045 on 10 stratified randomly selected subsamples.

	pH of extract
sample #21770-1	3.78
sample #21770-2	3.73
sample #21770-3	3.74
sample #21770-4	3.74
sample #21770-5	3.72
sample #21770-6	3.71
sample #21770-7	3.71
sample #21770-8	3.69
sample #21770-9	3.70
sample #21770-10	3.70

Table 1: homogeneity test results of subsamples #21770

From the above test results the relative standard deviation (RSD) was calculated and compared with 0.3 times the average relative standard deviation obtained from seven iis PTs of pH in leather test data from 2014 - 2020 in agreement with the procedure of ISO13528, Annex B2 in the next table.

	pH of extract
RSD% (observed)	0.71
reference method	iis PTs
0.3 x RSD% (reference method)	0.73

Table 2: evaluation of the relative standard deviation of subsamples #21770

The calculated relative standard deviation is in agreement with 0.3 times the average relative standard deviation obtained from the previous iis PTs. Therefore, homogeneity of the subsamples was assumed.

To each of the participating laboratories one leather sample #21770 was sent on October 20, 2021.

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.
It was also requested to report if the laboratory was accredited for the determined components that were determined 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 method (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. 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 (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. Nine participants reported test results after the final reporting date and two other participants did not report any test results. Not all participants were able to report all tests requested. In total 92 participants reported 267 numerical test results. Observed were 10 outlying test results, which is 3.7%. In proficiency tests outlier percentages of 3% - 7.5% are quite normal.

Not all original data sets proved to have a normal Gaussian distribution. These are referred as “not OK” or “suspect”. The statistical evaluation of these data should be used with due care, see also paragraph 3.1.

4.1 EVALUATION PER TEST

In this paragraph 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 reported test results 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. Therefore, the reproducibility of ASTM D2810 was taken to estimate the target reproducibility. This appears to be very strict. As a rule of thumb, the reproducibility of a method is three times the repeatability. However, in ASTM D2810, the repeatability is 0.03 pH units and the reproducibility is 0.06 pH units (thus factor of 2 instead of 3). Also, the repeatability and reproducibility are based on the values of duplicate measurements. Therefore, in this report the reproducibility for this test is calculated by three times the repeatability times the square root of two (3 x 0.03 x $\sqrt{2}$ = 0.127 pH units), assuming that the sample material was not sufficient for most participants to perform the determination at least in duplicate.

pH of extract: This determination may be problematic. Three statistical outliers were observed. The calculated reproducibility after rejection of the statistical outliers is not in agreement with the strict estimated requirements of ASTM D2810:18 but is in agreement with the average standard deviation as observed in previous iis PTs.

pH of ten times diluted extract: This determination may be problematic. Three statistical outliers were observed. The calculated reproducibility after rejection of the statistical outliers is not at all in agreement with the strict estimated requirements of ASTM D2810:18 but is in good agreement with the average standard deviation as observed in previous iis PTs.

Difference between pH of extract and pH ten times diluted extract: This determination was not problematic. Four statistical outliers were observed. The calculated reproducibility after rejection of the statistical outliers is in agreement with the estimated requirements of ASTM D2810:18.

4.2 PERFORMANCE EVALUATION FOR THE GROUP OF LABORATORIES

A comparison has been made between the reproducibility estimated from the target 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 target reproducibility derived from reference test methods (in casu ASTM and ISO test methods) are presented in the next table.

Parameter	unit	n	average	2.8 * sd	R(lit)
pH of extract	-	89	3.72	0.17	0.13
pH of extract ten times diluted	-	84	4.19	0.27	0.13
Difference in pH	-	84	0.47	0.18	0.18

Table 3: reproducibilities of test on sample #21770

Without further statistical calculations, it can be concluded that the group of participating laboratories have some difficulties with the determination of the pH. See also the discussions in paragraphs 4.1 and 5.

4.3 COMPARISON OF THE PROFICIENCY TEST OF NOVEMBER 2021 WITH PREVIOUS PTS

	November 2021	November 2020	November 2019	November 2018	November 2017
Number of reporting laboratories	92	106	136	114	102
Number of test results	267	356	441	396	378
Number of statistical outliers	10	14	17	12	16
Percentage of statistical outliers	3.7%	3.9%	3.9%	3.0%	4.2%

Table 4: comparison with previous proficiency tests

The performance of the determinations of the proficiency test was compared expressed as relative standard deviation (RSD) of the PTs, see below table.

Parameter	November 2021	November 2020	November 2019	2013-2018	Target pH 4.8-3.3	RSD iis PTs*
pH of extract	1.6%	2.3%	2.5%	1.7-3.2%	0.9-1.4%	2.4%
pH of extract ten times diluted	2.3%	3.3%	2.3%	2.3-3.0%	0.9-1.4%	2.6%

Table 5: development of uncertainties over the years

*) the average relative standard deviation obtained from seven iis PTs of pH in leather test data from 2014 - 2020

The uncertainties for the 2021 PT are smaller to the uncertainties of the PT of 2020. The determinations are not in agreement with the uncertainties as mentioned in the respective reference test method. These targets are most likely too strict to be met. However, both determinations are in agreement with the average relative standard deviation based on the iis PTs of previous years.

4.4 EVALUATION OF THE ANALYTICAL DETAILS

The reported details of the analytical test methods are listed in appendix 2. Eighty-seven participants reported the analytical details that were requested. The following can be summarized:

- About 85% of all laboratories reported to be accredited for the determination of pH in leather.
- About 55% used the sample as received and 45% further cut the sample.
- About 70% of the participants reported to have used 5 grams for intake. About 20% reported to have used less than 5 grams and about 10% reported to have used more.
- Over 90% of the participants did not use an additional step to wet the samples.

No effect was observed on the averages or variation between reported test results.

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. All participants reported a test result below 4.00. Four participants did not report a test result for the dilution of the extract (10 times), while three reported to have performed another test method than ISO4045. None of the participants mentioned to use method ASTM D2810.

6 CONCLUSION

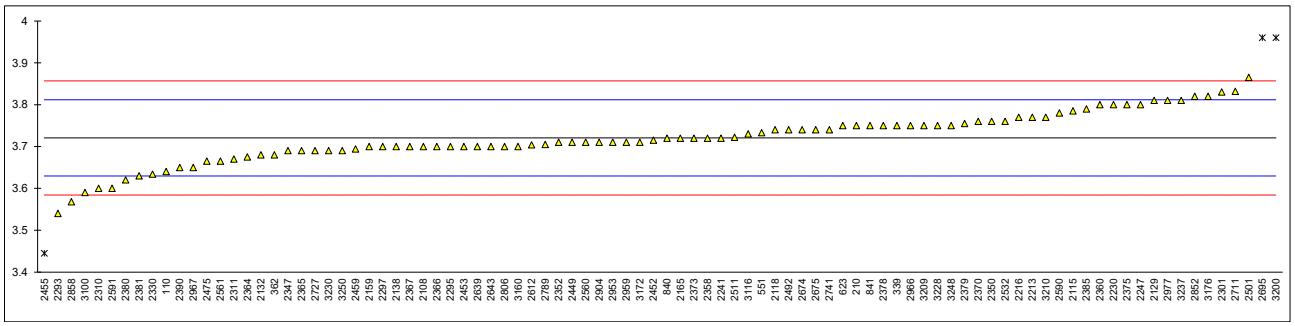
The variation observed for the determinations in this interlaboratory study can be caused by the pretreatment by the laboratories of the sample and/or by the performance of the analysis. Consequently, the reproducibility cannot be improved by only one change in the analysis. Each laboratory has to evaluate its performance in this study and make decisions about necessary corrective actions. 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.

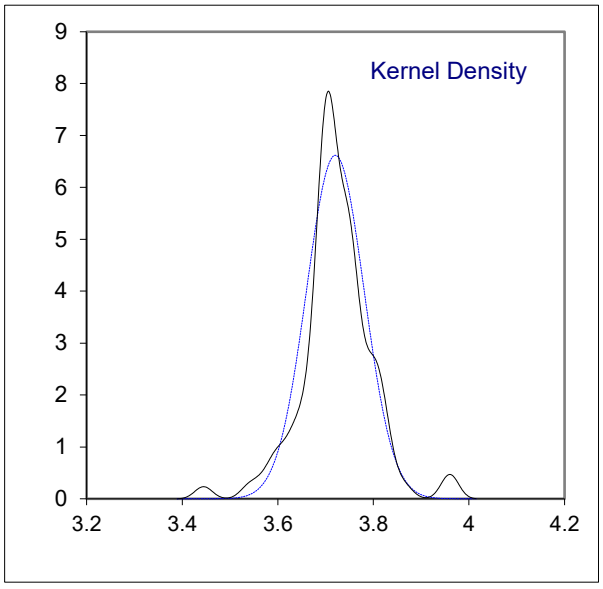
APPENDIX 1

Determination of pH of extract on sample #21770; unitless results

lab	method	value	mark	z(targ)	remarks
110	ISO4045	3.64		-1.77	
210	ISO4045	3.75		0.65	
339	ISO4045	3.75		0.65	
362	ISO4045	3.68		-0.89	
551	ISO4045	3.733		0.27	
623	ISO4045	3.75		0.65	
840	ISO4045	3.72		-0.01	
841	ISO4045	3.75		0.65	
2108	ISO3071	3.7		-0.45	
2115	ISO4045	3.785		1.42	
2118	ISO4045	3.74		0.43	
2129	ISO4045	3.81		1.97	
2132	ISO4045	3.68		-0.89	
2138	ISO4045	3.70		-0.45	
2159	ISO4045	3.70		-0.45	
2165	ISO4045	3.72		-0.01	
2213	ISO4045	3.77		1.09	
2216	ISO4045	3.77		1.09	
2220		-----		-----	
2230	ISO4045	3.8		1.75	
2241	ISO4045	3.720		-0.01	
2247	ISO4045	3.80		1.75	
2293	ISO4045	3.54		-3.97	
2295	ISO4045	3.7		-0.45	
2297	ISO4045	3.70		-0.45	
2301	ISO4045	3.83		2.41	
2310	ISO4045	3.6		-2.65	
2311	ISO4045	3.67		-1.11	
2330	ISO4045	3.634		-1.90	
2347	ISO4045	3.69		-0.67	
2350	ISO4045	3.76		0.87	
2352	ISO4045	3.71		-0.23	
2358	ISO4045	3.72		-0.01	
2360	ISO4045	3.80		1.75	
2364	ISO4045	3.675		-1.00	
2365	ISO4045	3.69		-0.67	
2366	ISO4045	3.70		-0.45	
2367	ISO4045	3.70		-0.45	
2370	ISO4045	3.76		0.87	
2373	ISO4045	3.72		-0.01	
2375	ISO4045	3.8		1.75	
2378	ISO4045	3.75		0.65	
2379	ISO4045	3.755		0.76	
2380	ISO4045	3.62		-2.21	
2381	ISO4045	3.63		-1.99	
2385	ISO4045	3.79		1.53	
2390	ISO4045	3.65		-1.55	
2449		3.71		-0.23	
2452	ISO4045	3.715		-0.12	
2453	ISO4045	3.7		-0.45	
2455	ISO4045	3.445	R(0.05)	-6.06	
2459	ISO4045	3.694		-0.58	
2475	ISO4045	3.665		-1.22	
2492	In house	3.74		0.43	
2501	ISO4045	3.865		3.18	
2511	ISO4045	3.722		0.03	
2532	ISO4045	3.76		0.87	
2560	ISO4045	3.71		-0.23	
2561	ISO4045	3.665		-1.22	
2590	ISO4045	3.78		1.31	
2591	ISO4045	3.6		-2.65	
2612	ISO4045	3.704		-0.36	
2639	QB/T2724	3.70		-0.45	
2643	ISO4045	3.70		-0.45	
2674	ISO4045	3.74		0.43	
2675	ISO4045	3.74		0.43	
2695	ISO4045	3.96	C,R(0.05)	5.27	first reported: 4.05
2711	ISO4045	3.832		2.45	
2727	ISO4045	3.69		-0.67	
2741	ISO4045	3.74		0.43	
2789	ISO4045	3.705		-0.34	
2806	ISO4045	3.70		-0.45	
2852	ISO4045	3.82		2.19	
2858	ISO4045	3.568		-3.36	

lab	method	value	mark	z(targ)	remarks
2904	ISO4045	3.71		-0.23	
2953	ISO4045	3.71		-0.23	
2959	ISO4045	3.71		-0.23	
2966	ISO4045	3.75		0.65	
2967	ISO4045	3.65		-1.55	
2977	ISO4045	3.81		1.97	
2985		-----		-----	
3100	ISO4045	3.59		-2.87	
3116	ISO4045	3.73		0.21	
3160	ISO4045	3.70		-0.45	
3172	ISO4045	3.71		-0.23	
3176	ISO4045	3.82		2.19	
3200	ISO4045	3.96	R(0.05)	5.27	
3209	ISO4045	3.75		0.65	
3210	ISO4045	3.77		1.09	
3228	ISO4045	3.75		0.65	
3230	ISO4045	3.69		-0.67	
3237	ISO4045	3.81		1.97	
3248	ISO4045	3.75		0.65	
3250	ISO4045	3.69		-0.67	
	normality	OK			
	n	89			
	outliers	3			
	mean (n)	3.721			
	st.dev. (n)	0.0603	RSD = 1.6%		
	R(calc.)	0.169			
	st.dev.(D2810:18)	0.0455			
	R(D2810:18)	0.127			
Comp					
	R(iis PTs)	0.253			



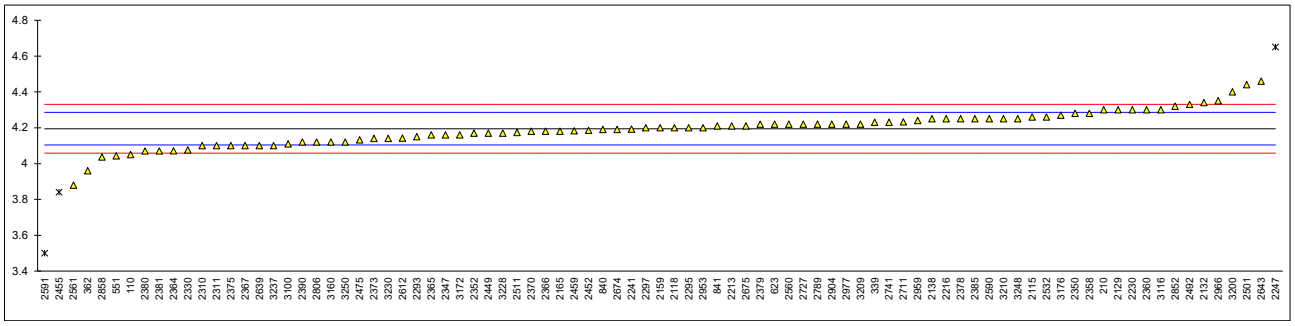


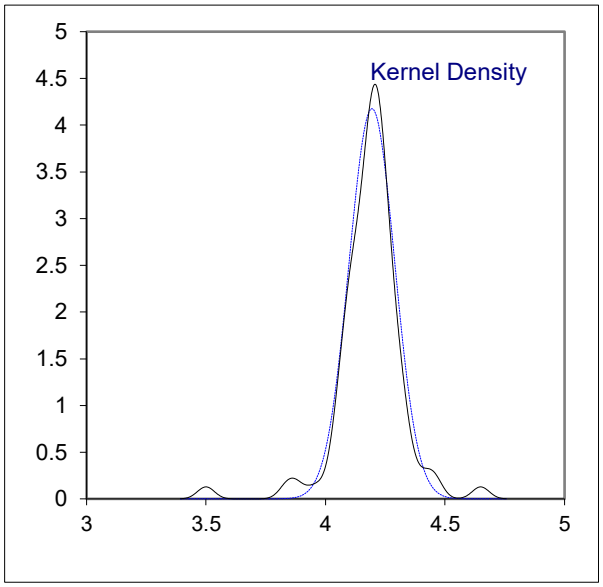
Determination of pH of ten times diluted extract on sample #21770; unitless results

lab	method	value	mark	z(targ)	remarks
110	ISO4045	4.05		-3.18	
210	ISO4045	4.30		2.32	
339	ISO4045	4.23	C	0.78	first reported: 20.4
362	ISO4045	3.96		-5.16	
551	ISO4045	4.043		-3.34	
623	ISO4045	4.22		0.56	
840	ISO4045	4.19		-0.10	
841	ISO4045	4.21		0.34	
2108		-----		-----	
2115	ISO4045	4.260		1.44	
2118	ISO4045	4.20		0.12	
2129	ISO4045	4.30		2.32	
2132	ISO4045	4.34		3.20	
2138	ISO4045	4.25		1.22	
2159	ISO4045	4.20		0.12	
2165	ISO4045	4.18		-0.32	
2213	ISO4045	4.21		0.34	
2216	ISO4045	4.25		1.22	
2220		-----		-----	
2230		4.3		2.32	
2241	ISO4045	4.192		-0.06	
2247	ISO4045	4.65	R(0.01)	10.02	
2293	ISO4045	4.15		-0.98	
2295	ISO4045	4.2		0.12	
2297	ISO4045	4.20		0.12	
2301		-----		-----	
2310	ISO4045	4.1		-2.08	
2311	ISO4045	4.10		-2.08	
2330	ISO4045	4.076		-2.61	
2347	ISO4045	4.16		-0.76	
2350	ISO4045	4.28		1.88	
2352	ISO4045	4.17		-0.54	
2358	ISO4045	4.28		1.88	
2360	ISO4045	4.30		2.32	
2364	ISO4045	4.071		-2.72	
2365	ISO4045	4.16		-0.76	
2366	ISO4045	4.18		-0.32	
2367	ISO4045	4.10		-2.08	
2370	ISO4045	4.18		-0.32	
2373	ISO4045	4.14		-1.20	
2375	ISO4045	4.1		-2.08	
2378	ISO4045	4.25		1.22	
2379	ISO4045	4.22		0.56	
2380	ISO4045	4.07		-2.74	
2381	ISO4045	4.07		-2.74	
2385	ISO4045	4.25		1.22	
2390	ISO4045	4.12		-1.64	
2449		4.17		-0.54	
2452	ISO4045	4.185		-0.21	
2453		-----		-----	
2455	ISO4045	3.840	R(0.05)	-7.80	
2459	ISO4045	4.183		-0.26	
2475	ISO4045	4.132		-1.38	
2492	In house	4.33		2.98	
2501	ISO4045	4.440		5.40	
2511	ISO4045	4.173		-0.48	
2532	ISO4045	4.26		1.44	
2560	ISO4045	4.22		0.56	
2561	ISO4045	3.88		-6.92	
2590	ISO4045	4.25		1.22	
2591	ISO4045	3.5	R(0.01)	-15.28	
2612	ISO4045	4.142		-1.16	
2639	QB/T2724	4.10		-2.08	
2643	ISO4045	4.46		5.84	
2674	ISO4045	4.19		-0.10	
2675	ISO4045	4.21		0.34	
2695		-----		-----	
2711	ISO4045	4.233		0.84	
2727	ISO4045	4.22		0.56	
2741	ISO4045	4.23		0.78	
2789	ISO4045	4.220		0.56	
2806	ISO4045	4.12		-1.64	
2852	ISO4045	4.32		2.76	
2858	ISO4045	4.036		-3.49	

lab	method	value	mark	z(targ)	remarks
2904	ISO4045	4.22		0.56	
2953	ISO4045	4.2		0.12	
2959	ISO4045	4.24		1.00	
2966	ISO4045	4.35	C	3.42	first reported: 4.85
2967		-----		-----	
2977	ISO4045	4.22		0.56	
2985		-----		-----	
3100	ISO4045	4.11		-1.86	
3116	ISO4045	4.30		2.32	
3160	ISO4045	4.12		-1.64	
3172	ISO4045	4.16		-0.76	
3176	ISO4045	4.27		1.66	
3200	ISO4045	4.40		4.52	
3209	ISO4045	4.22		0.56	
3210	ISO4045	4.25		1.22	
3228	ISO4045	4.17		-0.54	
3230	ISO4045	4.14		-1.20	
3237	ISO4045	4.10		-2.08	
3248	ISO4045	4.25		1.22	
3250	ISO4045	4.12		-1.64	

	normality	suspect	
	n	84	
	outliers	3	
	mean (n)	4.195	
	st.dev. (n)	0.0956	RSD = 2.3%
	R(calc.)	0.268	
	st.dev.(D2810:18)	0.0455	
	R(D2810:18)	0.127	
Comp			
	R(iis PTs)	0.311	



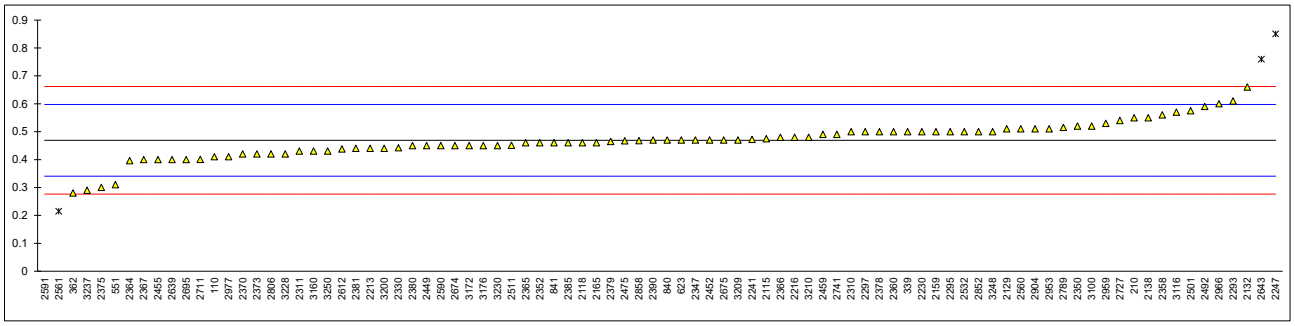


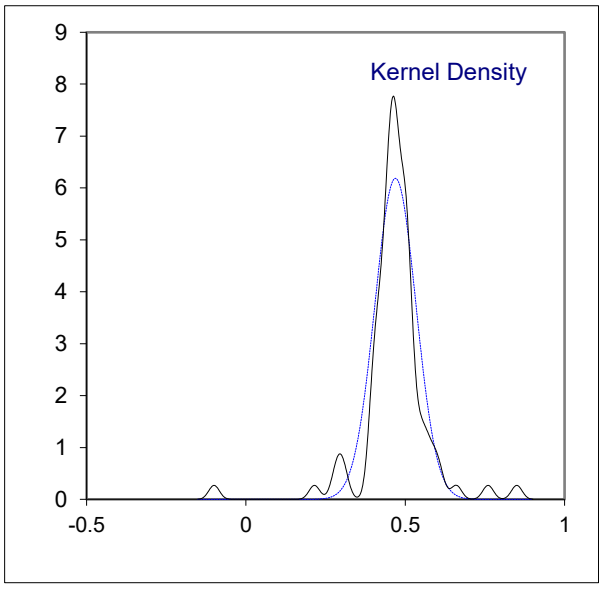
Determination of difference between pH of extract and pH of ten times diluted extract on sample #21770; unitless results

lab	method	value	mark	z(targ)	remarks
110	ISO4045	0.41		-0.92	
210	ISO4045	0.55		1.26	
339	ISO4045	0.5		0.48	
362	ISO4045	0.28		-2.94	
551	ISO4045	0.310		-2.48	
623	ISO4045	0.47		0.01	
840	ISO4045	0.47		0.01	
841	ISO4045	0.46		-0.14	
2108		-----		-----	
2115	ISO4045	0.475		0.09	
2118	ISO4045	0.46	C	-0.14	reported: -0.46, iis calculated 0.46
2129	ISO4045	0.51		0.63	
2132	ISO4045	0.66		2.97	
2138	ISO4045	0.55		1.26	
2159	ISO4045	0.5		0.48	
2165	ISO4045	0.46		-0.14	
2213	ISO4045	0.44	C	-0.45	reported: -0.44, iis calculated 0.44
2216	ISO4045	0.48		0.17	
2220		-----		-----	
2230		0.5		0.48	
2241	ISO4045	0.472		0.04	
2247	ISO4045	0.85	R(0.01)	5.92	
2293	ISO4045	0.61		2.19	
2295	ISO4045	0.5		0.48	
2297	ISO4045	0.5		0.48	
2301		-----		-----	
2310	ISO4045	0.5		0.48	
2311	ISO4045	0.43		-0.61	
2330	ISO4045	0.442		-0.42	
2347	ISO4045	0.47	C	0.01	reported: -0.47, iis calculated 0.47
2350	ISO4045	0.52		0.79	
2352	ISO4045	0.46		-0.14	
2358	ISO4045	0.56		1.41	
2360	ISO4045	0.50		0.48	
2364	ISO4045	0.396		-1.14	
2365	ISO4045	0.46	C	-0.14	reported: -0.46, iis calculated 0.46
2366	ISO4045	0.48	C	0.17	reported: -0.48, iis calculated 0.48
2367	ISO4045	0.40		-1.08	
2370	ISO4045	0.42		-0.77	
2373	ISO4045	0.42		-0.77	
2375	ISO4045	0.3		-2.63	
2378	ISO4045	0.50		0.48	
2379	ISO4045	0.465		-0.07	
2380	ISO4045	0.45		-0.30	
2381	ISO4045	0.44		-0.45	
2385	ISO4045	0.46		-0.14	
2390	ISO4045	0.47		0.01	
2449		0.45		-0.30	
2452	ISO4045	0.470		0.01	
2453		-----		-----	
2455	ISO4045	0.400		-1.08	
2459	ISO4045	0.49		0.32	
2475	ISO4045	0.467		-0.03	
2492	In house	0.59		1.88	
2501	ISO4045	0.575		1.65	
2511	ISO4045	0.451		-0.28	
2532	ISO4045	0.5		0.48	
2560	ISO4045	0.51		0.63	
2561	ISO4045	0.215	R(0.05)	-3.95	
2590	ISO4045	0.45		-0.30	
2591	ISO4045	-0.1	C,R(0.01)	-8.85	reported: 0.1, iis calculated -0.1
2612	ISO4045	0.438		-0.49	
2639	QB/T2724	0.40		-1.08	
2643	ISO4045	0.76	R(0.01)	4.52	
2674	ISO4045	0.45		-0.30	
2675	ISO4045	0.47		0.01	
2695	ISO4045	0.4		-1.08	
2711	ISO4045	0.401		-1.06	
2727	ISO4045	0.54		1.10	
2741	ISO4045	0.49		0.32	
2789	ISO4045	0.515		0.71	
2806	ISO4045	0.42		-0.77	
2852	ISO4045	0.5		0.48	
2858	ISO4045	0.468		-0.02	

lab	method	value	mark	z(targ)	remarks
2904	ISO4045	0.51		0.63	
2953	ISO4045	0.51		0.63	
2959	ISO4045	0.53		0.95	
2966	ISO4045	0.60	C	2.03	first reported: 1.10
2967		-----		-----	
2977	ISO4045	0.41		-0.92	
2985		-----		-----	
3100	ISO4045	0.52		0.79	
3116	ISO4045	0.57		1.57	
3160	ISO4045	0.43		-0.61	
3172	ISO4045	0.45		-0.30	
3176	ISO4045	0.45		-0.30	
3200	ISO4045	0.44		-0.45	
3209	ISO4045	0.47		0.01	
3210	ISO4045	0.48		0.17	
3228	ISO4045	0.42		-0.77	
3230	ISO4045	0.45		-0.30	
3237	ISO4045	0.29		-2.79	
3248	ISO4045	0.5		0.48	
3250	ISO4045	0.43		-0.61	

normality	suspect
n	84
outliers	4
mean (n)	0.469
st.dev. (n)	0.0645
R(calc.)	0.181
st.dev.(D2810:18)	0.0643
R(D2810:18)	0.180





APPENDIX 2 Analytical details

lab	ISO/IEC17025 accredited	Sample Preparation	Sample intake (in grams)	Additional steps to wet the sample
110	Yes	Used as received	5.0	No
210	Yes	---		---
339	Yes	---		---
362	Yes	Used as received	5g	No
551	No	Used as received	5g	No
623	Yes	Further cut	2.5 gram	No
840	Yes	Used as received	10 grams	No
841	Yes	Further cut	5 grams	No
2108	---	---		---
2115	Yes	Used as received	5 g	No
2118	Yes	Used as received	4,99g	No
2129	Yes	---		No
2132	Yes	Used as received	5.0241 gram	No
2138	Yes	Used as received	5 g	No
2159	Yes	Used as received	2,5 gram	No
2165	Yes	Further cut	2g	No
2213	Yes	Used as received	5	No
2216	No	Further cut	7.5 grams	No
2220	---	---		---
2230	Yes	Used as received	5g	Yes: a vacuum step
2241	Yes	Used as received	5.0065g / 4.9929g	No
2247	Yes	Further cut	ten grams	No
2293	No	Used as received	5.00	No
2295	Yes	Used as received	5 grams	No
2297	Yes	Used as received	2.5	---
2301	Yes	Used as received	5.0010	No
2310	Yes	Used as received	5	No
2311	Yes	Used as received	5	No
2330	Yes	Used as received	5 g	No
2347	Yes	Further cut	5.0g	No
2350	Yes	Further cut	5.00 g	Yes: mixing with water in a disintegrator (eg Waring Blender)
2352	Yes	Used as received		No
2358	Yes	Further cut	2.0 grams	No
2360	Yes	Used as received	5.0015	No
2364	Yes	Used as received	2.50g	No
2365	Yes	Used as received	2.0g	No
2366	No	Further cut	2.5g	No
2367	Yes	Used as received	5.0013g 5.0017g	No
2370	Yes	Further cut	5g	No
2373	Yes	Further cut	5g	No
2375	Yes	Further cut	2.5	No
2378	Yes	Further cut	5g	No
2379	Yes	Further cut	5.00 g / Sample	No
2380	Yes	Further cut	7.50 g	No
2381	Yes	Further cut	5 gm	No
2385	Yes	Used as received	5	No
2390	Yes	Further cut	5.0008 g	No
2449	---	---		---
2452	No	Used as received	5	Yes: mixing with water in a disintegrator (eg Waring Blender)
2453	---	---		---
2455	Yes	Used as received	5.027 g / 4.986 g	No
2459	Yes	Further cut	5 gram	No
2475	No	Used as received	5	No
2492	Yes	Further cut	5g	No
2501	Yes	Further cut	5g	No
2511	---	---		---
2532	Yes	Further cut	2.5 g in 50 ml water	No
2560	Yes	Used as received	5 gm	No
2561	Yes	Used as received	10	No
2590	Yes	Used as received	1.25g	No
2591	Yes	Further cut	5 grams	No
2612	Yes	Further cut	2x 2,5g & 2x 1,25 g	No
2639	No	Used as received	5.0003g	No
2643	Yes	Used as received	5 g	No
2674	Yes	Further cut	5g	No
2675	No	Used as received	4,99 / 4,91	No
2695	Yes	Further cut	5g	No
2711	No	Further cut	5.016g	No
2727	Yes	Further cut	2.50g	Yes: mixing with water in a disintegrator (eg Waring Blender)
2741	Yes	Used as received	5.0	No
2789	Yes	Used as received	10	No
2806	Yes	---		---
2852	---	---		---

lab	ISO/IEC17025 accredited	Sample Preparation	Sample intake (in grams)	Additional steps to wet the sample
2858	Yes	Further cut	5 gm	No
2904	Yes	Used as received	5 grams	No
2953	No	Further cut	5	Yes: hand shake
2959	Yes	Further cut	4.960g	No
2966	Yes	Further cut	5.000	No
2967	No	Further cut	5 grams	No
2977	No	Used as received	8	No
2985	---	---		---
3100	Yes	Further cut	5g	No
3116	Yes	Used as received	5 grams	No
3160	Yes	Further cut	5g	No
3172	Yes	---		---
3176	Yes	Used as received		No
3200	Yes	Further cut	5 g	No
3209	Yes	Used as received	5g	No
3210	Yes	Used as received	5	No
3228	Yes	Used as received	2.5	No
3230	Yes	Further cut	5grams	No
3237	Yes	Used as received	5 gr	No
3248	Yes	Used as received	5.0053	No
3250	Yes	Used as received	10g	No

APPENDIX 3

Number of participants per country

4 labs in BANGLADESH
1 lab in BELGIUM
1 lab in BRAZIL
1 lab in BULGARIA
2 labs in CAMBODIA
4 labs in FRANCE
5 labs in GERMANY
1 lab in GUATEMALA
5 labs in HONG KONG
5 labs in INDIA
2 labs in INDONESIA
10 labs in ITALY
1 lab in MAURITIUS
3 labs in MOROCCO
20 labs in P.R. of CHINA
3 labs in PAKISTAN
2 labs in PORTUGAL
3 labs in SOUTH KOREA
3 labs in SPAIN
2 labs in TAIWAN
1 lab in THAILAND
2 labs in TUNISIA
5 labs in TURKEY
4 labs in U.S.A.
1 lab in UNITED KINGDOM
3 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 the statistical evaluations
n.a.	= not applicable
n.d.	= not detected
n.e.	= not evaluated

Literature

1 iis Interlaboratory Studies, Protocol for the Organisation, Statistics & Evaluation, June 2018
2 ISO5725:86
3 ISO5725 parts 1-6:94
4 ISO13528:05
5 M. Thompson and R. Wood, J. AOAC Int, 76, 926, (1993)
6 W.J. Youden and E.H. Steiner, Statistical Manual of the AOAC, (1975)
7 P.L. Davies, Fr. Z. Anal. Chem, 331, 513, (1988)
8 J.N. Miller, Analyst, 118, 455, (1993)
9 Analytical Methods Committee, Technical Brief, No 4, January 2001
10 P.J. Lowthian and M. Thompson, The Royal Society of Chemistry, Analyst, 127, 1359-1364, (2002)
11 W. Horwitz and R. Albert, J. AOAC Int, 79.3, 589-621, (1996)
12 Bernard Rosner, Percentage Points for a Generalized ESD Many-Outlier Procedure, Technometrics, 25(2), 165-172, (1983)