



Institute for  
Interlaboratory Studies

## Results of Proficiency Test pH in Leather/Footwear November 2023

**Organized by:** Institute for Interlaboratory Studies  
Spijkenisse, the Netherlands

**Author:** Mr. M. Meijer, BSc

**Correctors:** Mrs. A. Ouwerkerk, BSc & Mr. R.J. Starink, BSc

**Approved by:** Mr. R.J. Starink, BSc

**Report:** iis23A10

February 2024

**CONTENTS**

1	INTRODUCTION .....	3
2	SET UP .....	3
2.1	QUALITY SYSTEM.....	3
2.2	PROTOCOL.....	3
2.3	CONFIDENTIALITY STATEMENT .....	3
2.4	SAMPLES .....	4
2.5	ANALYZES .....	4
3	RESULTS .....	5
3.1	STATISTICS .....	5
3.2	GRAPHICS .....	6
3.3	Z-SCORES .....	6
4	EVALUATION .....	7
4.1	EVALUATION PER TEST .....	7
4.2	PERFORMANCE EVALUATION FOR THE GROUP OF LABORATORIES.....	8
4.3	COMPARISON OF THE PROFICIENCY TEST OF NOVEMBER 2023 WITH PREVIOUS PTS .....	8
4.4	EVALUATION OF THE ANALYTICAL DETAILS.....	9
5	DISCUSSION.....	9
6	CONCLUSION .....	9

## Appendices:

1.	Data, statistical and graphic results .....	10
2.	Analytical Details.....	12
3.	Number of participants per country.....	14
4.	Abbreviations and literature .....	15

## **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 of 2023 it was decided to continue the proficiency test for the determination of pH in Leather/Footwear.

In this interlaboratory study 73 laboratories in 24 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](http://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 a laboratory that has performed the tests in accordance with for ISO/IEC17043 relevant requirements of ISO/IEC17025.

It was decided to send one leather sample of approximately 10 grams labelled #23765.

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](http://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 115 small plastic bags were filled with approximately 10 grams each and labelled #23765.

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 #23765-1	3.53
sample #23765-2	3.53
sample #23765-3	3.53
sample #23765-4	3.55
sample #23765-5	3.50
sample #23765-6	3.48
sample #23765-7	3.50
sample #23765-8	3.47

Table 1: homogeneity test results of subsamples #23765

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)	0.08
reference method	iis memo 2204 *)
0.3 x R (reference method)	0.07

Table 2: evaluation of the repeatability of subsamples #23765

\*) see paragraph 4.1

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 #23765 was sent on October 25, 2023.

## 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 these determinations 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' test results, which are above the detection limit, because such test 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/](http://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](http://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/](http://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 in 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:

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

The  $z_{(\text{target})}$  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 no problems were encountered with the dispatch of the samples. One participant 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 72 participants reported 143 numerical test results. Observed were 2 outlying test results, which is 1.4%. In proficiency tests outlier percentages of 3% - 7.5% are quite normal.

Both 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 method ISO4045 is considered to be the official test method for the determination of pH in leather. Regretfully, ISO4045 does not provide precision data. 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 these iis PTs is 2.3% for pH of extract and 2.6% for pH of ten times diluted extract. This investigation is summarized in iis memo 2204 (see lit. 13).

pH of extract: The group of participants met the target requirements. Two 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: The group of participants met the target requirements. No statistical outliers were observed. The calculated reproducibility 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 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 the reference method are presented in the next table.

Parameter	unit	n	average	2.8 * sd	R(target)
pH of extract		70	3.55	0.18	0.23
pH of ten times diluted extract		71	4.06	0.28	0.30

Table 3: reproducibilities of tests on sample #23765

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

#### 4.3 COMPARISON OF THE PROFICIENCY TEST OF NOVEMBER 2023 WITH PREVIOUS PTS

	November 2023	November 2022	November 2021	November 2020	November 2019
Number of reporting laboratories	72	79	92	106	136
Number of test results	143	156	267	356	441
Number of statistical outliers	2	8	10	14	17
Percentage of statistical outliers	1.4%	5.1%	3.7%	3.9%	3.9%

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 2023	November 2022	November 2021	November 2020	November 2019
pH of extract	1.8%	1.7%	1.6%	2.3%	2.5%
pH of ten times diluted extract	2.4%	1.5%	2.3%	3.3%	2.3%

Table 5: development of the uncertainties over the years



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

#### **4.4 EVALUATION OF THE ANALYTICAL DETAILS**

All but one of the participants reported to have used test method ISO4045. None of the participants reported to have used test method ASTM D2810.

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:

- 89% reported to be accredited for the determination of pH in leather.
- 91% used the sample as received and 7% further cut or grinded the sample.
- 76% reported to have used a sample intake of around 5 grams while 20% have used less than 5 grams.
- 91% did not use additional steps to wet the samples.

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

### **5 DISCUSSION**

Test method ISO4045 is used to determine the pH in leather. In this test method the pH extract is diluted ten times 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 ten times diluted extract from the pH value of 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. In this PT all participants reported a test result below pH 4.00. One participant did not report a test result for the ten times dilution of the extract.

### **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 the quality of the analytical results.

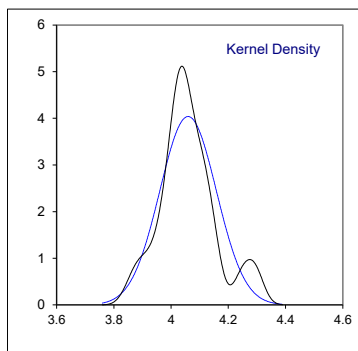
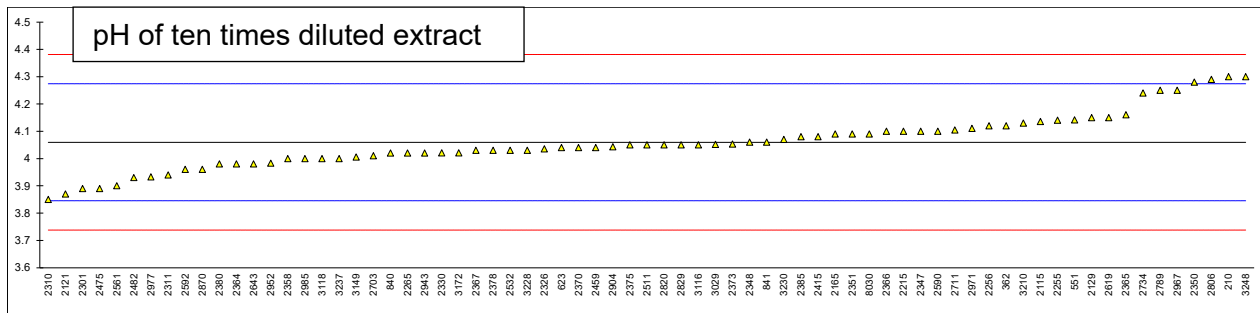
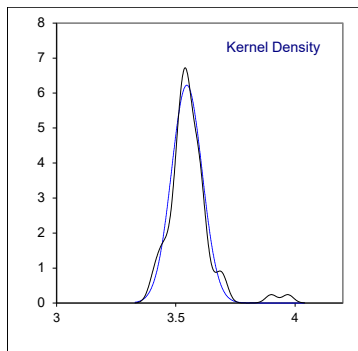
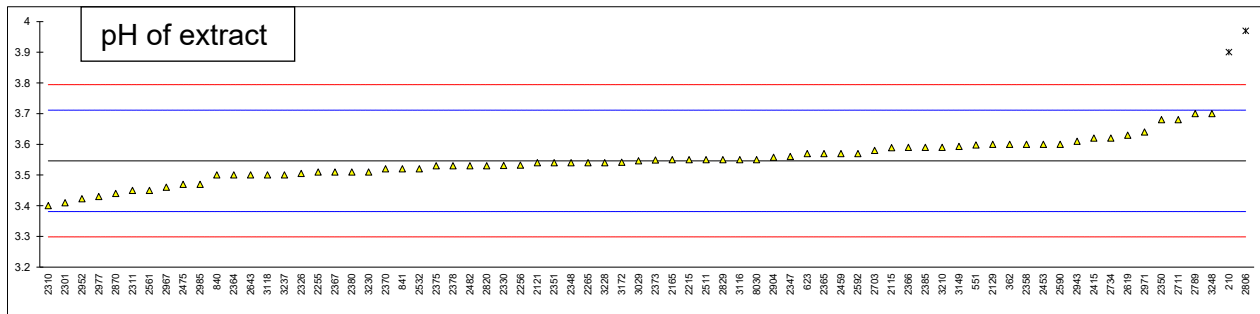
**APPENDIX 1**

**Determination of pH on sample #23765; 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	3.9	R(0.01)	4.28	4.3		2.24	0.4	
362	ISO4045	3.60		0.65	4.12		0.56	0.52	
551	ISO4045	3.598		0.63	4.142		0.77	-0.544	
623	ISO4045	3.57		0.29	4.04		-0.18	0.47	
840	ISO4045	3.5		-0.56	4.02		-0.37	0.51	
841	ISO4045	3.52		-0.32	4.06		0.00	0.52	
2115	ISO4045	3.589		0.52	4.136		0.71	0.552	
2121	ISO4045	3.54		-0.08	3.87		-1.77	0.4	E
2129	ISO4045	3.60		0.65	4.15		0.84	0.55	
2165	ISO4045	3.55		0.05	4.09		0.28	0.54	
2215	ISO4045	3.55		0.05	4.10		0.38	0.55	
2255	ISO4045	3.51		-0.44	4.14		0.75	0.63	
2256	ISO4045	3.532		-0.17	4.120		0.56	0.588	
2265	ISO4045	3.54		-0.08	4.02		-0.37	0.48	
2301	ISO4045	3.41		-1.65	3.89		-1.58	0.48	
2310	ISO4045	3.4		-1.77	3.85		-1.96	0.45	
2311	ISO4045	3.45	C	-1.16	3.94	C	-1.12	0.49	C
2326	ISO4045	3.505		-0.50	4.035		-0.23	0.53	
2330	ISO4045	3.531		-0.18	4.021		-0.36	0.49	
2347	ISO4045	3.56		0.17	4.10		0.38	0.54	
2348	ISO4045	3.54		-0.08	4.06		0.00	0.52	
2350	ISO4045	3.68		1.62	4.28		2.06	0.60	
2351	ISO4045	3.54		-0.08	4.09		0.28	0.55	
2358	ISO4045	3.6	C	0.65	4.0	C	-0.56	0.4	C
2364	ISO4045	3.50		-0.56	3.98		-0.74	0.48	
2365	ISO4045	3.57		0.29	4.16		0.94	-0.59	
2366	ISO4045	3.59		0.53	4.10		0.38	-0.51	
2367	ISO4045	3.51		-0.44	4.03		-0.28	0.52	
2370	ISO4045	3.52		-0.32	4.04		-0.18	0.52	
2373	ISO4045	3.549		0.03	4.053		-0.06	0.504	
2375	ISO4045	3.53		-0.20	4.05		-0.09	0.52	
2378	QB/T2724	3.53		-0.20	4.03		-0.28	0.50	
2380	ISO4045	3.51		-0.44	3.98		-0.74	0.47	
2385	ISO4045	3.59		0.53	4.08		0.19	-0.49	
2415	ISO4045	3.62		0.89	4.08		0.19	0.46	
2453	ISO4045	3.6		0.65	-----		-----	-----	
2459	ISO4045	3.57		0.29	4.04		-0.18	0.47	
2475	ISO4045	3.47		-0.92	3.89		-1.58	-0.42	
2482	ISO4045	3.53		-0.20	3.93		-1.21	-0.40	
2511	ISO4045	3.55		0.05	4.05		-0.09	0.5	
2532	ISO4045	3.52		-0.32	4.03		-0.28	0.51	
2561	ISO4045	3.45		-1.16	3.90		-1.49	0.45	
2590	ISO4045	3.60		0.65	4.10		0.38	0.50	
2592	ISO4045	3.57		0.29	3.96		-0.93	0.39	
2619	ISO4045	3.63		1.01	4.15		0.84	0.52	
2643	ISO4045	3.50		-0.56	3.98		-0.74	0.48	
2703	ISO4045	3.58		0.41	4.01		-0.46	0.43	
2711	ISO4045	3.680		1.62	4.105		0.42	0.425	
2734	ISO4045	3.62		0.89	4.24		1.68	0.62	
2789	ISO4045	3.70		1.86	4.25		1.78	0.55	
2806	ISO4045	3.97	C,R(0.01)	5.13	4.29		2.15	0.50	E
2820	ISO4045	3.53	C	-0.20	4.05	C	-0.09	0.52	C
2829	ISO4045	3.55		0.05	4.05		-0.09	0.50	
2870	ISO4045	3.44		-1.29	3.96		-0.93	0.52	
2904	ISO4045	3.558		0.14	4.043		-0.15	0.485	
2943	ISO4045	3.61		0.77	4.02		-0.37	0.42	
2952	ISO4045	3.423		-1.49	3.983		-0.71	0.560	
2967	ISO4045	3.46		-1.04	4.25		1.78	0.81	
2971	ISO4045	3.64		1.13	4.11		0.47	0.47	
2977	ISO4045	3.430		-1.41	3.933		-1.18	0.503	
2985	ISO4045	3.47		-0.92	4.0		-0.56	-0.53	
2989		-----		-----	-----		-----	-----	
3029	ISO4045	3.546		0.00	4.052		-0.07	0.506	
3116	ISO4045	3.55		0.05	4.05		-0.09	-0.50	
3118	ISO4045	3.50		-0.56	4.00		-0.56	0.50	
3149	ISO4045	3.593		0.57	4.005		-0.51	-0.412	
3172	ISO4045	3.542		-0.05	4.021		-0.36	0.480	
3210	ISO4045	3.59		0.53	4.13		0.66	0.54	
3228	ISO4045	3.54		-0.08	4.03	C	-0.28	0.49	C
3230	ISO4045	3.51	C	-0.44	4.07		0.10	0.57	C
3237	ISO4045	3.5		-0.56	4.0		-0.56	0.5	
3248	ISO4045	3.7		1.86	4.3		2.24	0.6	
8030	ISO4045	3.55		0.05	4.09		0.28	0.54	

lab	method	pH of extract	mark	z(targ)	pH ten times diluted	mark	z(targ)	pH of extract - pH 10x diluted	mark
	normality	OK			OK				
	n	70			71				
	outliers	2			0				
	mean (n)	3.546			4.060				
	st.dev. (n)	0.0641	RSD=1.8%		0.0988	RSD=2.4%			
	R(calc.)	0.179			0.277				
	st.dev.(iis memo 2204)	0.0826			0.1072				
	R(iis memo 2204)	0.231			0.300				

Lab 2121 calculation difference, iis calculated -0.33  
 Lab 2311 first reported 3.34, 3.80 and 0.46 respectively  
 Lab 2358 first reported 3.7, 4.5 and 0.8 respectively  
 Lab 2806 first reported 3.77. Calculation difference, iis calculated -0.32  
 Lab 2820 first reported 3.69, 4.58 and 0.89 respectively  
 Lab 3228 first reported 4.26 and 0.72 respectively  
 Lab 3230 first reported 3.27 and 0.80 respectively



## APPENDIX 2 Analytical details

lab	ISO/IEC17025 accredited	Sample Preparation	Sample intake (in grams)	Additional steps to wet the sample
210	Yes	Used as received	5g	No
362	Yes	Used as received	5g	No
551	No	Used as received	2.5001g	No
623	Yes	Further cut	1	No
840	Yes	Used as received	5g	No
841	Yes	Used as received	5g	No
2115	Yes	Used as received	5 g	No
2121	Yes	Used as received	5g	No
2129	Yes	Further cut	5g	No
2165	Yes	Used as received	2.0g	No
2215	Yes	Used as received	5.0024	No
2255	Yes	Used as received	5	No
2256	---	---	---	---
2265	No	Used as received	5 grams	No
2301	Yes	Used as received	5.0034	No
2310	Yes	Used as received	5	No
2311	Yes	Used as received	5	No
2326	Yes	Used as received	5.0037	No
2330	Yes	Used as received	---	No
2347	Yes	Used as received	2.5g	No
2348	Yes	Used as received	5 grams	Yes: mixing with water in a disintegrator (eg Waring Blender)
2350	Yes	Used as received	5g	No
2351	Yes	Used as received	---	No
2358	Yes	Used as received	5.0g	No
2364	Yes	Used as received	5g	No
2365	Yes	Used as received	5.0g	No
2366	No	Used as received	5g	No
2367	Yes	Used as received	4.9935	No
2370	Yes	Used as received	5 g	No
2373	Yes	Used as received	5.0g	No
2375	Yes	Used as received	2,5 gram	No
2378	Yes	Used as received	5G	No
2380	Yes	Used as received	5.0 g	No
2385	Yes	Further cut	5.0 g /100 ml	No
2415	Yes	Used as received	2.5 grams	No
2453	No	Further cut	---	No
2459	Yes	Used as received	5 grams	No
2475	No	Used as received	2.5g	No
2482	No	Further grinded	5	No
2511	Yes	Used as received	5 grams	No
2532	Yes	Used as received	2.5 g in 50ml	Yes: Soxhlet extraction
2561	Yes	Used as received	5g	No
2590	Yes	Used as received	2.5g	No
2592	Yes	Used as received	5.004	No
2619	Yes	Used as received	5g	No
2643	Yes	Used as received	5.00	No
2703	Yes	Used as received	2x (5.0+/- 0.1)g	No
2711	No	Used as received	5.011	No
2734	Yes	Used as received	5g	Yes: mixing with water in a disintegrator (eg Waring Blender)
2789	Yes	Used as received	5	No
2806	Yes	Used as received	10	No
2820	Yes	Used as received	5 g	No
2829	Yes	Used as received	5.0	Yes: Shake by hand for about 30s
2870	Yes	Used as received	5.00 gm x 2	No
2904	Yes	Used as received	5g x2 replicates	No
2943	Yes	Used as received	2	Yes: Orbital shaker
2952	Yes	Used as received	5.0035 g	No
2967	---	---	---	---
2971	Yes	Used as received	2g	No
2977	Yes	Used as received	5g	No
2985	Yes	Used as received	10g	No
2989	---	---	---	---
3029	Yes	Used as received	10 gr	No
3116	Yes	Used as received	5	No
3118	No	Used as received	2,5 gram	No
3149	Yes	Used as received	2* 5 g	No
3172	Yes	---	---	---
3210	Yes	Used as received	5.0077	No
3228	Yes	Used as received	5g	---
3230	Yes	Used as received	2grams	No
3237	Yes	Used as received	5g	No
3248	Yes	Pre-dry sample in oven temp. not higher 50°C	5	No

ISO/IEC17025		Sample Preparation	Sample intake (in grams)	Additional steps to wet the sample
lab	accredited			
8030	Yes	for 4 hours, then condition sample 20°C 65% relative humidity for 20 hours prior testing Used as received	5 g:1 flask	No

## APPENDIX 3

### Number of participants per country

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

- 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)
- 13 iis memo 2204: Reproducibility of pH in Leather/Footwear in iis PTs

Address: Malledijk 18, P.O. Box 200, 3200 AE Spijkensisse, The Netherlands  
Telephone number: +31 (0)88 214 45 41  
Email address: [nl.iis@sgs.com](mailto:nl.iis@sgs.com)  
Website: [www.iisnl.com](http://www.iisnl.com)

Institute for Interlaboratory Studies is a full member of SGS Nederland B.V. and registered at the Chamber of Commerce under number: 24226722. Unless otherwise agreed, all orders are executed in accordance with the SGS general conditions.