Results of Proficiency Test
pH and Formaldehyde
in leather
October 2014

Organised by: Institute for Interlaboratory Studies
Spijkenisse, the Netherlands

Author: ing. C.M. Nijssen-Wester
Correctors: dr. R. Visser & ing. N. Boelhouwer

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1 INTRODUCTION

Worldwide, many consumer products are produced from leather. During the production of leather products, many different types of auxiliary agents and dyes are used to process leather. Neither in the U.S. nor in the European Union there is general legislation that limits the presence of formaldehyde in leather. However, some individual countries have restricting limits on the concentration of free formaldehyde in leather that may vary from 20 mg/kg for leather used for young children to 100 mg/kg when the leather is in contact with the skin, 150 mg/kg for shoe uppers and 400 mg/kg for leather without permanent contact with the skin. In 2006, The China Leather Industry Standard Committee Organization established the Limit of Harmful Matters in Leather: GB20400-2006. This national mandatory standard was approved by the General Administration of P.R. of China for Quality Supervision and Inspection and Quarantine and implemented in December 2007.
Since several years, the Institute for Interlaboratory Studies (iis) organises a proficiency scheme for Formaldehyde in textile. On request of several participants, the institute decided to organize also a proficiency test for Formaldehyde in Leather in 2013. It was decided to continue this scheme as part of the proficiency testing program 2014/2015. The tests on the leather were extended with a test for pH value of leather.
In this interlaboratory study, 110 laboratories in 29 different countries participated. See appendix 3 for the number of participating laboratories per country.
In this report, the results of this 2014 proficiency test are presented and discussed. This report is also electronically available through the iis internet site www.iisnl.com.

2 SET UP

The Institute for Interlaboratory Studies in Spijkenisse was the organiser of this proficiency test. Analyses of fit for use and homogeneity were subcontracted to an ISO/IEC 17025 accredited laboratory. In this proficiency test, it was decided to use one sample (#14209, approx. 8 grams) which was positive on Formaldehyde content (free and released). Participants were requested to report results with one extra figure. These unrounded results were preferably used for the statistical evaluations.

2.1 QUALITY SYSTEM

The Institute for Interlaboratory Studies in Spijkenisse, the Netherlands, has implemented a quality system based on IEC/ISO17043:2010. 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 Organisation, Statistics and Evaluation' of April 2014 (iis-protocol, version 3.3), which can be downloaded from http://www.iisnl.com.

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 black leather sample was shreddered and after homogenisation divided over 120 subsamples of approx. 8 gram and labelled sample #14209.
The homogeneity of the subsamples was checked on Formaldehyde according to ISO17226-1 on 8 stratified randomly selected samples. The homogeneity testing was performed by a subcontracted ISO17025 accredited laboratory. See the following tables for the test results.

	Formaldehyde in mg/kg
Sample #14209-1	68.5
Sample #14209-2	72.2
Sample #14209-3	74.2
Sample #14209-4	72.3
Sample #14209-5	69.9
Sample #14209-6	71.1
Sample #14209-7	65.2
Sample #14209-8	69.4

Table 1: homogeneity test results of subsamples #14209

From the above test results, the repeatabilities were calculated and compared with 0.3 times the corresponding reproducibilities in agreement with the procedure of ISO 13528 (Annex B2) or with the repeatability of the reference method, in the next table:

	Formaldehyde in mg/kg
r	7.8
Reference test	ISO17226-1:08
$0.3*R_{(reference\ test)}$	12.7

Table 2: repeatability of subsamples #14209

From the above results of the homogeneity test, the repeatability was calculated.
The calculated repeatability for sample #14209 is in good agreement with 0.3 times the reproducibility of the reference test method. Therefore, homogeneity of all subsamples was assumed.

One sample of approx. 8 grams (labelled #14209) was sent to the participating laboratories on October 15, 2014.

2.5 ANALYSES

The participants were asked to determine on sample #14209, the content of Formaldehyde (HPLC), the content of Formaldehyde (colorimetric) and pH.
To get comparable results, detailed report forms were sent together with each set of samples. On the report form, the requested Formaldehyde content (both HPLC and colorimetric method) and pH value, including the units, were pre-printed. Also a letter of instructions was sent along.

3 RESULTS

During four weeks after sample despatch, the results of the individual laboratories were gathered. The original data are tabulated in the appendices of this report. The laboratories are presented by their code numbers.

Directly after the deadline, a reminder fax was sent to those laboratories that had not yet reported. Shortly after the deadline, the available results were screened for suspect data. A result was called suspect in case the Huber Elimination Rule (a robust outlier test, see lit.5) found it to be an outlier. The laboratories that produced these suspect data were asked to check the results. Additional or corrected data are placed under 'Remarks' in the result tables in appendix 1. A list of abbreviations used in the tables can be found in appendix 4.

3.1 STATISTICS

Statistical calculations were performed as described in the report 'iis Interlaboratory Studies: Protocol for the Organisation, Statistics and Evaluation' of April 2014 (iis-protocol, version 3.3). For the statistical evaluation the *unrounded* (when available) figures were used instead of the rounded results. Results reported as '<…' or '>…" were not used in the statistical evaluation.
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. Not all data sets proved to have a normal distribution, in which cases the statistical evaluation of the results should be used with due care.

According to ISO5725 the original results per determination were submitted to Dixon's and/or 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 (ref. 17). 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. Finally, the reproducibilities were calculated from the standard deviations by multiplying them with a factor of 2.8.

For each assigned value the uncertainty was determined in accordance with ISO13528. Subsequently the calculated uncertainty was evaluated against the respective requirement based on the target reproducibility in accordance with ISO13528. When the uncertainty passed the evaluation no remarks are made in the report. However, when the uncertainty failed the evaluation it is mentioned in the report and it will have consequences for the evaluation of the test results.

3.2 GRAPHICS

In order to visualise the data against the reproducibilities from literature, Gauss plots were made, using the sorted data for one determination (see appendix 1). On the Y-axis the reported analysis results are plotted. The corresponding laboratory numbers are under the X-axis. The straight horizontal line presents the consensus value (a trimmed mean). The four striped lines, parallel to the consensus value line, are the +3s, +2s, -2s and -3s target reproducibility limits of the selected standard. Outliers and other data, which were excluded from the calculations, are represented as a cross. Accepted data are represented as a triangle. Furthermore, Kernel Density Graphs were made. This method is producing a smooth density approximation to a set of data that avoids some problems associated with histograms. Also a normal Gauss curve was projected over the Kernel Density Graph for reference.

3.3 Z-SCORES

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

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

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

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

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

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

	$\lvert z \rvert < 1$	good
$1 <$	$\lvert z \rvert < 2$	satisfactory
$2 <$	$\lvert z \rvert < 3$	questionable
$3 <$	$\lvert z \rvert$	unsatisfactory

4 EVALUATION

During the execution of this proficiency test no problems occurred with the delivery of the samples. Two laboratories did not report any test results and twenty other laboratories reported results after the final reporting date.

Finally, the 108 reporting laboratories did send in total 224 numerical results. Observed were 7 statistical outlying results, which is 3.1% of the numerical results. In proficiency studies, outlier percentages of 3% - 7.5% are quite normal.

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

4.1 EVALUATION PER TEST

In this section, the sample #14209 is discussed. All statistical results reported on the leather sample are summarised in appendix 1.

Formaldehyde content (HPLC): This determination was problematic. No statistical outliers were observed, but one test result was excluded from the statistical evaluation as the reported test method is for textiles only. However the calculated reproducibility after rejection of suspect data is not in agreement agreement with the requirements of ISO17226-1:2008.

Formaldehyde content (colorimetric): This determination was very problematic. No statistical outliers were observed, however two test results may be excluded from the statistical evaluation as the reported test method is for textiles only.
As can be seen from the Kernel density graph, the data distribution curve appears to be multi-modal, with a peak around 50 mg/kg and a group of higher values lagging after this peak. ISO17226-2 states that it can be more easily interfered with, for example by absorbances caused by colourings of the leather (see also §6). Therefore it was decided to use the mean of group for ISO17226-1 (HPLC) as the target mean of the group for ISO17226-2 (colorimetric). Based on this mean, the target reproducibility according to ISO17226-2 and the z-scores were calculated.
The calculated reproducibility after rejection of the suspect data is not at all in agreement with the requirements of ISO17226-2:2008. This applies to all results of the group as well as the reproducibility based on the target mean of the HPLC method. For further information, see §6.

pH: This determination was very problematic. Seven (!) statistical outliers were observed and one test result was excluded from the statistical evaluation as the reported test method is for textiles only. The calculated reproducibility after rejection of the suspect data is not at all in agreement with the requirements of ASTM D2810:2013.
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. In general 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 (factor of 2 instead of 3). Also the repeatability and reproducibility are based on the values of duplicate tests. Therefore in this report the reproducibility for this test is calculated by three times the repeatability times the square root of two (0.127 pH units).

The majority of the laboratories reported according to either ASTM D2810 or ISO4045. Both methods were also evaluated separately. The group of 35 laboratories performing ASTM D2810 showed slightly better precision than the group performing ISO4045, however still the calculated reproducibilities of both groups after rejection of the statistical outliers are not at all in agreement with the estimated requirements of ASTM D2810:2013.
A possible reason for the larger reproducibility of the ISO4045 group may be that the ISO4045 method describes measuring a ten times diluted solution, when the pH measured is below 4. Only seven participants reported both results for pH. The pH difference for this leather sample was 0.5 pH units between the standard test and the ten times diluted one. It could be possible that some laboratories, that performed ISO4045, have reported the ten times diluted pH value instead of the pH value requested. ASTM D2810 does not describe this extra step and therefore the precision may be better, although the accuracy may be less than the ISO4045 method.

4.2 PERFORMANCE EVALUATION FOR THE GROUP OF LABORATORIES

A comparison has been made between the calculated reproducibilities estimated from ISO17226 and the reproducibilities as found for the group of participating laboratories. The number of significant results, the average results, the calculated reproducibilities (standard deviation*2.8) and the target reproducibilities (ISO17226), are compared in the next table.

Parameter	unit	n	average	2.8 * sd	R (target)
Formaldehyde (HPLC)	mg/kg	70	50.61	42.50	29.39
Formaldehyde (colorimetric)	mg/kg	73	(67.21)*	62.99	(16.96)*
pH		70	3.29	0.28	0.13

Table 3: observed reproducibilities of leather samples #14209

*) not used to calculate z-scores, see §4.1 and §6

From the above tables it can be concluded that, without statistical calculations, the group of participating laboratories have difficulties with the Formaldehyde (HPLC) and pH, but have severe problems with the colorimetric analysis, when compared with the requirements of the target test methods.
See also the discussions in paragraphs 4.1 and 6.

5 COMPARISON OF THE PROFICIENCY TEST OF OCTOBER 2014 WITH PREVIOUS PTS

The uncertainties in the test results of determined Formaldehyde in leather in the iis14A05 PT are not in line with the uncertainties of the method or as observed in previous PTs (see below table).

Parameter	October 2014	October 2013	Est. ISO17226
Formaldehyde (HPLC)	30%	22%	21% (17226-1)
Formaldehyde (colorimetric)	33%	25%	9% (17226-2)

Table 4: Development of relative uncertainties over the years

6 DISCUSSION

The standard test method for formaldehyde content is ISO17226. Part 1 and part 2 describe the determination of the formaldehyde content by extraction of the free formaldehyde from the leather with a detergent solution. The difference between both parts of ISO17226 is the method of quantification. Quantification of the formaldehyde is done by HPLC in part 1 and by colorimetric analysis in part 2. Therefore part 2 is not selective for formaldehyde, whereas part 1 is selective. The test results from part 2 will in general be higher than the test results from part 1. In the case of dispute part 1 shall be used in preference.
Looking at the reproducibility statements of both methods, it is remarkable that the reproducibility of the colorimetric method is smaller than the reproducibility of the HPLC method. Maybe the precision data for the colorimetric method were obtained with samples and/or conditions that did not influence the test (as the method describes that the test could for example be influenced by absorbances from the leather colouring).

Analytical Details Colorimetric method
In this PT several analytical details were asked on the report form for test method ISO17226-2 (colorimetric). Especially about corrections for absorbances found in reagents and acetyl acetone colouring components (see Appendix 2 for the analytical details).

In total 68 participants completed this section of the report form. Three participants did not fill in the questions or only one. Thirty-one laboratories determined the corrections in absorbance needed to correct for colouring, which is not caused by the sample and made the correction. Nine laboratories determined the corrections needed, but did not correct the measured absorbances. And twenty-eight (!) laboratories did not determine nor correct the absorbance.

Looking at the absorbances reported for the determination of presence of formaldehyde in the reagents (ISO17226-2 section 7.2.4), four of the fifty participants found a higher absorbance than is acceptable. When testing other components for causing colouring with acetyl acetone (section 7.2.5), twelve (!) of the thirty-one participants found a higher absorbance than acceptable by the method (0.05). In this case the method states that ISO17226-1 should be done. This may be one of the reasons that the spread for this test is large.

Sample 14209 in comparison to formaldehyde limits

When the results of this interlaboratory study were compared to the Standard “Limit of Harmful Matters in Leather” of the Chinese Leather Industry Committee Organization: GB20400-2006 (table 4), it may be noticed that not all participants would make identical decisions about the acceptability of the leather.

GB20400	Category A Products for babies: underclothes, bedding, etc	Category B Products with **Direct** skin contact	Category C Products Without direct skin contact
Free Formaldehyde in mg/kg	<20	<75	<300

Table 5: Summary of limits from Standard GB20400:2006

When using ISO17226 part 1, all but two reporting laboratories (71) would reject this sample for category A and five laboratories would reject this sample also for category B. No laboratories would reject this sample for category C.
When using ISO17226 part 2, all but one, reporting laboratories (70) would reject this sample for category A, nineteen laboratories would reject this sample also for category B and no laboratories would reject this sample for category C.

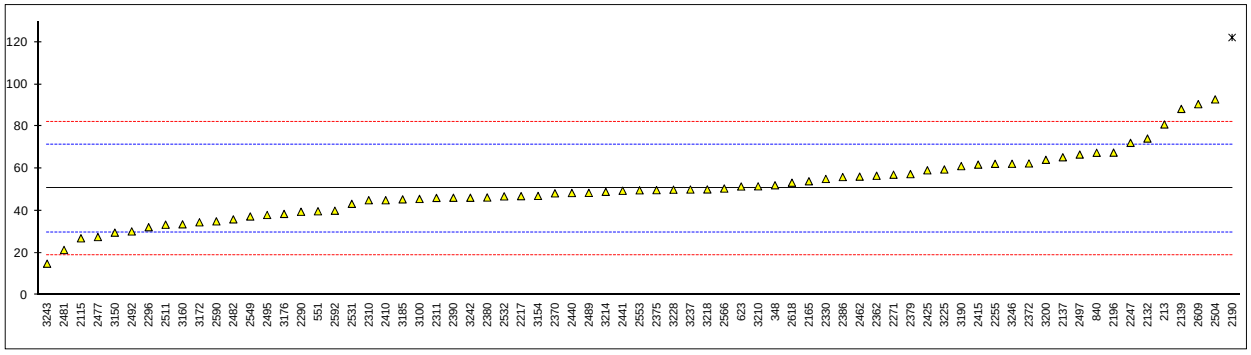
APPENDIX 1

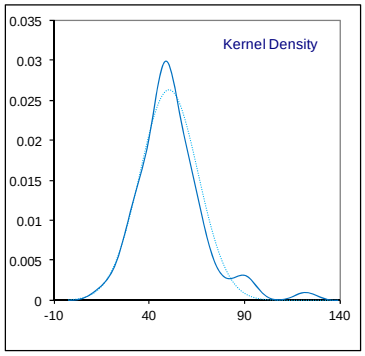
Determination of Formaldehyde content (HPLC)on sample #14209; results in mg/kg

lab	method	value	mark	z(targ)	remarks
110		-----		-----	
213	ISO17226-1	80.98		2.89	
348	in house	52.10		0.14	
361		-----		-----	
551	ISO17226-1	39.76		-1.03	
623	ISO17226-1	51.52		0.09	
840	ISO17226-1	67.53		1.61	
2108		-----		-----	
2115	ISO17226-1	26.94		-2.26	
2129		-----		-----	
2132	ISO17226-1	74.28		2.25	
2137	HPLC	65.4		1.41	
2139	ISO17226-1	88.34		3.59	
2165	ISO17226-1	54		0.32	
2172		-----		-----	
2190	ISO14184-1	122.23	ex	6.82	Result excluded, test method is for textile
2196	ISO17226-1	67.6		1.62	
2215		-----		-----	
2216		-----		-----	
2217	ISO17226-1	46.94		-0.35	
2247	ISO17226-1	72.25		2.06	
2255	ISO17226-1	62.3		1.11	
2256		-----		-----	
2261		-----		-----	
2271	ISO17226-1	57.11		0.62	
2290	ISO17226-1	39.53		-1.06	
2293		-----		-----	
2295		-----		-----	
2296	ISO17226-1	32.20		-1.75	
2310	ISO17226-1	45.0		-0.53	
2311	ISO17226-1	46.1		-0.43	
2330	ISO17226-1	55.11		0.43	
2362	ISO17226-1	56.62		0.57	
2367		-----		-----	
2368		-----		-----	
2370	ISO17226-1	48.29		-0.22	
2372	ISO17226-1	62.46		1.13	
2375	ISO17226-1	49.8		-0.08	
2379	ISO17226-1	57.40		0.65	
2380	ISO17226-1	46.30		-0.41	
2386	ISO17226-1	56.0		0.51	
2389		-----		-----	
2390	ISO17226-1	46.18		-0.42	
2403		-----		-----	
2410	ISO17226-1	45		-0.53	
2415	ISO17226-1	61.92		1.08	
2425	ISO17226-1	59.20		0.82	
2428		-----		-----	
2440	ISO17226-1	48.43		-0.21	
2441	ISO17226-1	49.5		-0.11	
2446		-----		-----	
2452		-----		-----	
2453		-----		-----	
2460		-----		-----	
2462	ISO17226-1	56.2		0.53	
2472		-----		-----	
2476		-----		-----	
2477	ISO17226-1	27.53		-2.20	
2481	ISO17226-1	21.4		-2.78	
2482	ISO17226-1	35.94		-1.40	
2489	ISO17226-1	48.5		-0.20	
2492	ISO17226-1	30.2		-1.94	
2495	ISO17226-1	38.0		-1.20	
2497	ISO17226-1	66.68		1.53	
2504	ISO17226-1	92.85		4.02	
2511	ISO17226-1	33.395		-1.64	
2518		-----		-----	
2519		-----		-----	
2531	ISO17226-1	43.29		-0.70	
2532	ISO17226-1	46.8333		-0.36	
2534		-----		-----	
2538		-----		-----	
2549	ISO17226-1	37.3		-1.27	
2553	ISO17226-1	49.7		-0.09	
2560		-----		-----	
2566	ISO17226-1	50.56		-0.01	
2590	ISO17226-1	34.98		-1.49	

2592	ISO17226-1	40.03	-1.01
2593		-----	-----
2609	ISO17226-1	90.59	3.81
2618	ISO17226-1	53.33	0.26
2624		-----	-----
2633		-----	-----
2639		-----	-----
2650		-----	-----
3100	ISO17226-1	45.62	-0.48
3146		-----	-----
3150	ISO17226-1	29.64	-2.00
3154	ISO17226-1	47.04	-0.34
3160	ISO17226-1	33.56	-1.62
3172	ISO17226-1	34.54	-1.53
3176	ISO17226-1	38.51	-1.15
3180		-----	-----
3183		-----	-----
3185	ISO17226-1	45.42	-0.49
3190	ISO17226-1	61.20	1.01
3197		-----	-----
3200	ISO17226-1	64.2	1.29
3210	ISO17226-1	51.6	0.09
3214	ISO17226-1	49	-0.15
3218	ISO17226-1	50.14	-0.05
3220		-----	-----
3222		-----	-----
3225	ISO17226-1	59.6	0.86
3228	ISO17226-1	50	-0.06
3237	ISO17226-1	50.09	-0.05
3242	ISO17226-1	46.197	-0.42
3243	ISO17226-1	14.9	-3.40
3246	ISO17226-1	62.31	1.11
3248		-----	-----

normality	OK
n	70
outliers	0 (+1ex)
mean (n)	50.614
st.dev. (n)	15.1774
R(calc.)	42.497
R(ISO17226-1:08)	29.394





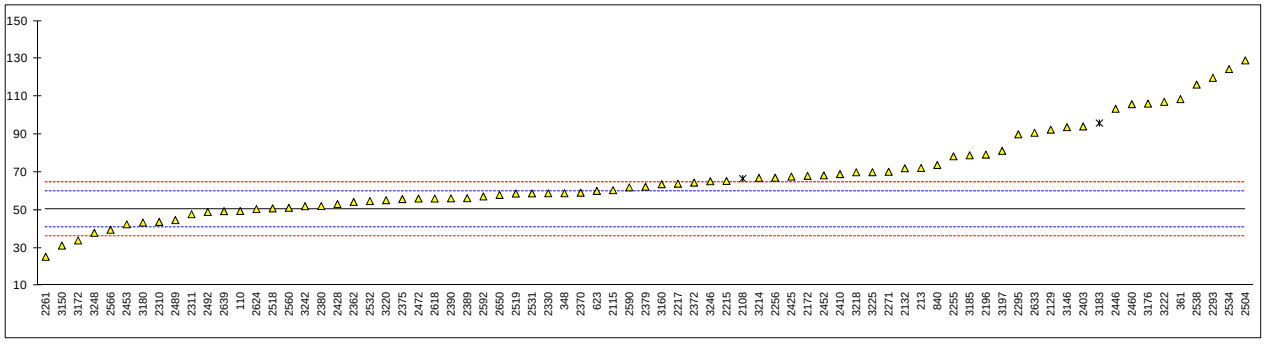
Determination of Formaldehyde content (colorimetric) on sample #14209; results in mg/kg

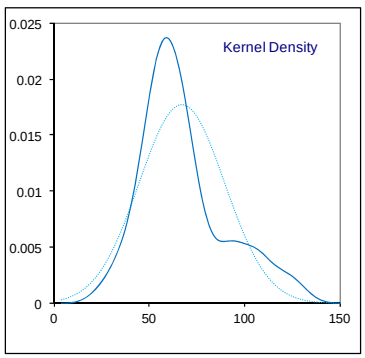
lab	method	value	mark	z(targ)	remarks
110	ISO17226-2	49.48		-0.24	
213	ISO17226-2	72.22		4.55	
348	in house	58.91		1.75	
361	ISO17226-2	108.63		12.21	
551		-----		-----	
623	ISO17226-2	60.11		2.00	
840	ISO17226-2	73.82		4.88	
2108	JAP Law 112	66.6	ex	3.36	Result excluded, test method is for textile
2115	ISO17226-2	60.50		2.08	
2129	ISO17226-2	92.5		8.82	
2132	ISO17226-2	72.09		4.52	
2137		-----		-----	
2139		-----		-----	
2165		-----		-----	
2172	ISO17226-2	68.05		3.67	
2190		-----		-----	
2196	ISO17226-2	79.3		6.04	
2215	ISO17226-2	65.4		3.11	
2216		-----		-----	
2217	ISO17226-2	63.92		2.80	
2247		-----		-----	
2255	ISO17226-2	78.4		5.85	
2256	ISO17226-2	67.1		3.47	
2261	ISO17226-2	25.3375		-5.32	
2271	ISO17226-2	70.24		4.13	
2290		-----		-----	
2293	ISO17226-2	119.892		14.58	
2295	ISO17226-2	90		8.29	
2296		-----		-----	
2310	ISO17226-2	43.7		-1.46	
2311	ISO17226-2	47.8		-0.59	
2330	ISO17226-2	58.89		1.74	
2362	ISO17226-2	54.3		0.78	
2367		-----		-----	
2368		-----		-----	
2370	ISO17226-2	59.19		1.81	
2372	ISO17226-2	64.51		2.92	
2375	ISO17226-2	55.8		1.09	
2379	ISO17226-2	62.34		2.47	
2380	ISO17226-2	52.13		0.32	
2386		-----		-----	
2389	ISO17226-2	56.29		1.19	
2390	ISO17226-2	56.17		1.17	
2403	ISO17226-2	94.20		9.17	
2410	ISO17226-2	69		3.87	
2415		-----		-----	
2425	ISO17226-2	67.67		3.59	
2428	ISO17226-2	53.22		0.55	
2440		-----		-----	
2441		-----		-----	
2446	ISO17226-2	103.53		11.14	
2452	ISO17226-2	68.33		3.73	
2453	ISO17226-2	42.48		-1.71	
2460	ISO17226-2	105.96		11.65	
2462		-----		-----	
2472	ISO17226-2	56.09		1.15	
2476		-----		-----	
2477		-----		-----	
2481		-----		-----	
2482		-----		-----	
2489	ISO17226-2	44.7		-1.24	
2492	ISO17226-2	49.0		-0.34	
2495		-----		-----	
2497		-----		-----	
2504	ISO17226-2	129.10		16.52	
2511		-----		-----	
2518	ISO17226-2	50.9		0.06	
2519	ISO17226-2	58.73		1.71	
2531	ISO17226-2	58.83		1.73	
2532	ISO17226-2	54.7705		0.87	
2534	ISO17226-2	124.5		15.55	
2538	ISO17226-2	116.30		13.83	
2549		-----		-----	
2553		-----		-----	
2560	ISO17226-2	51.20		0.12	
2566	ISO17226-2	39.6		-2.32	
2590	ISO17226-2	62.02		2.40	
2592	ISO17226-2	57.20		1.39	

2593		-----		-----	
2609		-----		-----	
2618	ISO17226-2	56.09		1.15	
2624	ISO17226-2	50.497		-0.02	
2633	ISO17226-2	90.87		8.47	
2639	GB/T19941	49.40		-0.26	
2650	ISO17226-2	58		1.55	
3100		-----		-----	
3146	ISO17226-2	93.80		9.09	
3150	ISO17226-2	31.25		-4.08	
3154		-----		-----	
3160	ISO17226-2	63.67		2.75	
3172	ISO17226-2	33.95		-3.51	
3176	ISO17226-2	106.26		11.71	
3180	ISO17226-2	43.4		-1.52	
3183	JAP Law 112	95.94	ex	9.54	Result excluded, test method is for textile
3185	ISO17226-2	78.95		5.96	
3190		-----		-----	
3197	ISO17226-2	81.28		6.45	
3200		-----		-----	
3210		-----		-----	
3214	ISO17226-2	67		3.45	
3218	ISO17226-2	69.96		4.07	
3220	ISO17226-2	55.2		0.97	
3222	ISO17226-2	107.19		11.91	
3225	ISO17226-2	70.0		4.08	
3228		-----		-----	
3237		-----		-----	
3242	ISO17226-2	52.05		0.30	
3243		-----		-----	
3246	ISO17226-2	65.2		3.07	
3248	GB/T19941	38		-2.66	

		All results
normality		OK
n		73
outliers		0 (+2ex)
mean (n)	50.614*	67.211
st.dev. (n)		22.4969
R(calc.)		62.991
R(ISO17226-2:08)	13.302**	16.955

*) mean used from ISO17226-1 (HPLC).
**) R(ISO17226-2) and z-scores are based on this mean (see §4.1)





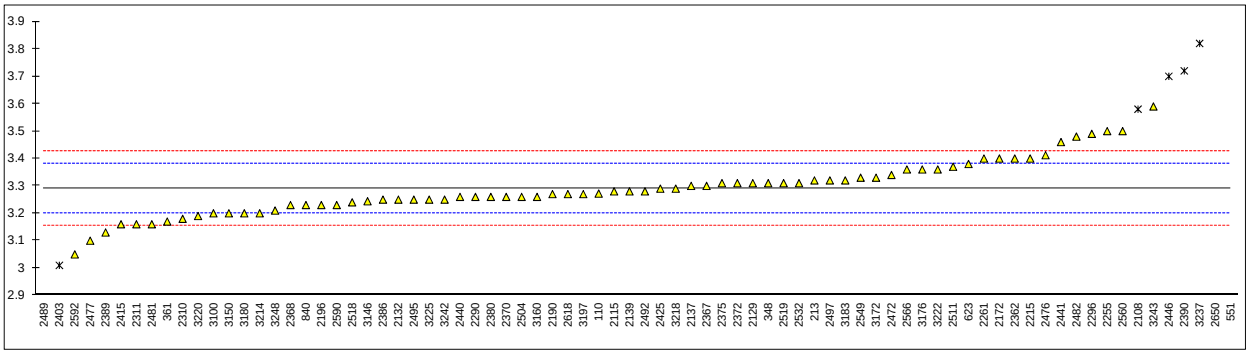
Determination of pH on sample #14209; unitless results

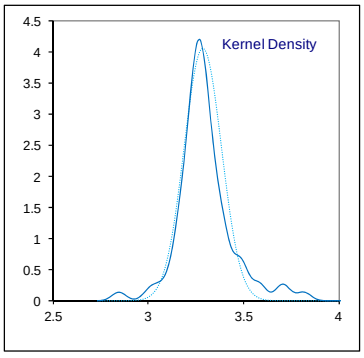
lab	method	value	mark	z(targ)	remarks
110	ASTM D2810	3.272		-0.40	
213	ASTM D2810	3.32		0.66	
348	ISO4045	3.31		0.44	
361	ISO4045	3.17		-2.64	
551	ASTM D2810	6.43	C,R(0.01)	69.07	First reported: 2.43
623	ISO4045	3.38		1.98	
840	ISO4045	3.23		-1.32	
2108	EN3071	3.58	ex	6.38	Result excluded, test method for textile only
2115	ISO4045	3.28		-0.22	
2129	ISO4045	3.31		0.44	
2132	ASTM D2810	3.25		-0.88	
2137		3.3		0.22	
2139	ASTM D2810	3.28		-0.22	
2165		-----		-----	
2172	ASTM D2810	3.40		2.42	
2190	ASTM D2810	3.27		-0.44	
2196	ASTM D2810	3.23		-1.32	
2215	ASTM D2810	3.4		2.42	
2216		-----		-----	
2217		-----		-----	
2247		-----		-----	
2255	ISO4045	3.5		4.62	
2256		-----		-----	
2261	QB/T2724	3.40		2.42	
2271		-----		-----	
2290	ASTM D2810	3.26		-0.66	
2293		-----		-----	
2295		-----		-----	
2296	ISO4045	3.49		4.40	
2310	ISO4045	3.18		-2.42	
2311	ISO4045	3.16		-2.86	
2330		-----		-----	
2362	ASTM D2810	3.4		2.42	
2367	ISO4045	3.30		0.22	
2368	ISO4045	3.23		-1.32	
2370	ISO4045	3.26		-0.66	
2372	ASTM D2810	3.31		0.44	
2375	ASTM D2810	3.31		0.44	
2379		-----		-----	
2380	ASTM D2810	3.26		-0.66	
2386	ISO4045	3.25		-0.88	
2389	ISO4045	3.13		-3.52	
2390	ISO4045	3.72	R(0.01)	9.46	
2403	ASTM D2810	3.01	R(0.01)	-6.16	
2410		-----		-----	
2415	ASTM D2810	3.16		-2.86	
2425	ASTM D2810	3.29		0.00	
2428		-----		-----	
2440	ASTM D2810	3.26		-0.66	
2441	ASTM D2810	3.46		3.74	
2446		3.7	R(0.01)	9.02	
2452		-----		-----	
2453		-----		-----	
2460		-----		-----	
2462		-----		-----	
2472	ASTM D2810	3.34		1.10	
2476	ISO4045	3.412		2.68	
2477	ASTM D2810	3.10		-4.18	
2481		3.16		-2.86	
2482	ISO4045	3.48		4.18	
2489	ASTM D2810	2.85	R(0.01)	-9.68	
2492	ISO4045	3.28		-0.22	
2495	ASTM D2810	3.25		-0.88	
2497	ISO4045	3.32		0.66	
2504	ASTM D2810	3.26		-0.66	
2511	ISO4045	3.370		1.76	
2518	ASTM D2810	3.24		-1.10	
2519	ASTM D2810	3.31		0.44	
2531		-----		-----	
2532	ASTM D2810	3.31		0.44	
2534		-----		-----	
2538		-----		-----	
2549	ASTM D2810	3.33		0.88	
2553		-----		-----	
2560	ASTM D2810	3.50		4.62	
2566	ASTM D2810	3.36		1.54	
2590	ISO4045	3.23		-1.32	
2592	ISO4045	3.05		-5.28	

2593		-----		-----
2609		-----		-----
2618	ASTM D2810	3.27		-0.44
2624		-----		-----
2633		-----		-----
2639		-----		-----
2650		5.01	R(0.01)	37.84
3100	ISO4045	3.20		-1.98
3146	ISO4045	3.244		-1.01
3150	ASTM D2810	3.20		-1.98
3154		-----		-----
3160	ISO4045	3.26		-0.66
3172	ASTM D2810	3.33		0.88
3176	ISO4045	3.36		1.54
3180	ISO4045	3.2		-1.98
3183	ISO4045	3.32		0.66
3185		-----		-----
3190		-----		-----
3197	ISO4045	3.27		-0.44
3200		-----		-----
3210		-----		-----
3214	ASTM D2810	3.20		-1.98
3218	ASTM D2810	3.290		0.00
3220	ISO4045	3.19		-2.20
3222	ISO4045	3.36		1.54
3225	ISO4045	3.25		-0.88
3228		-----		-----
3237	ISO4045	3.82	R(0.01)	11.66
3242	ASTM D2810	3.25		-0.88
3243	ASTM D2810	3.59		6.60
3246		-----		-----
3248	ASTM D2810	3.21		-1.76

		Only ASTM D2810	Only ISO4045
normality	OK	not OK	OK
n	70	35	32
outliers	7 (+1 ex)	3	2
mean (n)	3.290	3.299	3.280
st.dev. (n)	0.0983	0.0941	0.1033
R(calc.)	0.275	0.263	0.289
R(D2810:13)*	0.127	0.127	n.a.

*) Calculation of R(D2810:13) see §4.1





APPENDIX 2

Analytical Details ISO17226-2

	Reagents checked for formaldehyde?	if yes, absorbance measured?	Tested for other comp. causing coloring with acetylacetone?	if yes, absorbance measured:	Was abs. corrected for above abs.?	if yes, abs. before correction:	if yes, abs. after correction:
110	Y	0.0008	N		Y	0.2656	0.0148
213	Y	-0.0002	Y	0.037	Y	0.425	0.3882
348	Y	0.33	N				
361	N		N		N		
551							
623	Y	0.0000	N		N		
840	Y	0.008	N		Y	0.449	0.414
2108	Y	0.0000	Y	0.0133	Y	0.1054	0.0921
2115	Y		N		N		
2129			N				
2132	N		Y	0.005	Y	0.474	0.469
2137							
2139							
2165							
2172	Y		Y	0.0551	Y	0.3847	0.3296
2190	N		N		N		
2196	Y	0.011	N		N		
2215	N		N		N		
2216							
2217	N		N		N		
2247							
2255	Y		Y		Y		
2256							
2261	N		N		N		
2271	Y	0.126	N		Y	0.8386	0.826
2290	Y	50 mAu	N		N		
2293	Y	0.000/-0.008	Y	0.038/0.125	Y	0.355	0.317
2295	Y	-0.00087	Y	0.0207	N		
2296							
2310	Y	0.0063	Y	0.0111	Y	0.2481	0.237
2311	Y	0.0040	Y	0.0947	Y	0.3618	0.2671
2330	Y	0.0024	Y	0.0435	Y	0.3596	0.3137
2362	Y	0.005	N		N		
2367							
2368							
2370	Y	0.001	Y	0.043	Y	0180	0.348
2372	Y	0.0001					
2375	Y	0.0004	Y	-0.037	N		
2379	Y	0.0094	Y	0.0120	Y	0.7783	0.7569
2380	N		N		N		
2386							
2389	N		N		Y	0.385	0.28
2390	N		N		N		
2403	Y	0.0191	N		Y	0.2652	0.2461
2410	Y	0.0012	Y	0.0037	Y		
2415							
2425	N		Y	0.0222	Y	0.1225	0.1003
2428							
2440							
2441							
2446	Y	0.0	N		N		
2452	Y	0.005	Y	0.154	N		
2453	Y	0.00	Y	0.05	Y	0.10	0.05

	Reagents checked for formaldehyde?	if yes, absorbance measured?	Tested for other comp. causing coloring with acetylacetone?	if yes, absorbance measured:	Was abs. corrected for above abs.?	if yes, abs. before correction:	if yes, abs. after correction:
2460	Y	0	Y	0.198+0.078	N		
2462							
2472	N		N		N		
2476							
2477							
2481							
2482							
2489	Y	0.0002	N		N		
2492	Y	0.0022	Y	0.0319	N		
2495							
2497							
2504	N		N		N		
2511							
2518	N		N		N		
2519	N		N		N		
2531	Y	0.009	Y	0.064	N		
2532	Y	0.004	N		N		
2534	Y	0.0021	N		N		
2538	Y	0.001	N		N		
2549							
2553							
2560	Y	0.0500	Y	0.0841	Y	0.3659	0.2818
2566	Y	0.001	Y	0.115	Y	0.325	0.210
2590	Y	0.001	Y	0.045	Y	0.379	0.334
2592	Y	0.020	Y	0.040	N		
2593							
2609							
2618							
2624	Y	0.0071	Y	0.0626	Y	0.3594	0.2968
2633					Y	3.8975	0.099
2639							
2650							
3100	N		N		N		
3146	N		N		N		
3150	Y	0.009	Y	0.026	Y	0.123	0.088
3154							
3160	Y	0.022	Y	0.172	N		
3172							
3176	Y	0.000	Y	0.013	Y	379	0.075
3180	N		N		N		
3183	Y		N		Y		
3185	Y	0.0029	Y	0.0050	Y	0.4166	0.4137
3190							
3197							
3200							
3210							
3214	N		N		N		
3218	Y	0.0009	N		N		
3220	Y	0.720	Y	0.163	Y	0.720	0.557
3222	Y	0.022	Y	0.033	N		
3225	Y	0.0026	N		Y	0.1157	
3228							
3237							
3242	Y	0.00	N		N		
3243							
3246	Y	0.024	N		Y	0.676	0.652
3248							

APPENDIX 3

Number of participants per country

5 labs in BANGLADESH
1 lab in BRAZIL
1 lab in BULGARIA
1 lab in CAMBODIA
1 lab in EGYPT
3 labs in FRANCE
11 labs in GERMANY
1 lab in GUATEMALA
5 labs in HONG KONG
1 lab in HUNGARY
9 labs in INDIA
1 lab in INDONESIA
11 labs in ITALY
3 labs in KOREA
2 labs in MEXICO
1 lab in MOROCCO
26 labs in P.R. of CHINA
2 labs in PAKISTAN
1 lab in PORTUGAL
3 labs in SPAIN
1 lab in SRI LANKA
1 lab in SWITZERLAND
3 labs in TAIWAN R.O.C.
2 labs in THAILAND
2 labs in TUNISIA
5 labs in TURKEY
2 labs in U.S.A.
1 lab in UNITED KINGDOM
4 labs in VIETNAM

APPENDIX 4

Abbreviations:

C = final result after checking of first reported suspect result
D(0.01) = outlier in Dixon's outlier test
D(0.05) = straggler in Dixon's outlier test
G(0.01) = outlier in Grubbs' outlier test
G(0.05) = straggler in Grubbs' outlier test
DG(0.01) = outlier in Double Grubbs' outlier test
DG(0.05) = straggler in Double Grubbs' outlier test
R(0.01) = outlier in Rosner outlier test
R(0.05) = straggler in Rosner outlier test
n.a. = not applicable
n.d. = not detected
W = withdrawn

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