Results of Proficiency Test
pH and Formaldehyde
in leather
November 2016

Organised by: Institute for Interlaboratory Studies
Spijkenisse, the Netherlands

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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. Many countries have adopted environmental standards and requirements restricting the use of harmful chemicals. Laws and regulations impose some of these standards and requirements. In addition to mandatory environmental standards and requirements for leather, there are some Ecolabelling schemes imposing environmental requirements for textile & leather products on a voluntary basis. A well known organisation is for instance Bluesign® (Switzerland), which has created a Bluesign® system substances list (BSSL).
Since several years, the Institute for Interlaboratory Studies (iis) organises a proficiency scheme for Formaldehyde in textile. The institute decided to organize also a proficiency test for Formaldehyde and pH in Leather in 2013. During the annual proficiency testing program 2016/2017, it was decided to continue the round robin for the analysis of Free Formaldehyde and pH.
In this interlaboratory study, 109 laboratories in 28 different countries registered for participation. See appendix 3 for the number of participating laboratories per country.
In this report, the results of this 2016 proficiency test are presented and discussed. This report is also electronically available through the iis website site www.iisnl.com.

2 SET UP

The Institute for Interlaboratory Studies in Spijkenisse was the organiser of this proficiency test (PT). Sample preparation and analyses of fit-for-use and homogeneity were subcontracted to an ISO17025 accredited laboratory. It was decided to send in this Proficiency Test one sample (labelled #16335) positive on Free Formaldehyde and one sample (labelled #16336) especially for pH determination. Sample #16335 is approx. 3 grams and sample #16336 is approx. 5 grams. The participants were requested to report rounded and unrounded test results. These unrounded test 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 ISO/IEC 17043:2010. 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). This protocol can be downloaded from the iis website www.iisnl.com, from the FAQ page.

2.3 CONFIDENTIALITY STATEMENT

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

2.4 SAMPLES

A black leather sample was cut into small pieces and after homogenisation divided over 120 subsamples of approx. 3 gram and labelled sample #16635. Each sample was packed in aluminium foil. The homogeneity of the subsamples was checked on Formaldehyde according to ISO17226-1 on 8 stratified randomly selected samples. See the following table for the test results.

	Free Formaldehyde in mg/kg
Sample #16635-1	25.4
Sample #16635-2	24.6
Sample #16635-3	24.7
Sample #16635-4	26.9
Sample #16635-5	23.8
Sample #16635-6	23.7
Sample #16635-7	23.5
Sample #16635-8	26.1

Table 1: homogeneity test results of subsamples #16635

From the above results of the homogeneity test, the observed repeatability was calculated and compared with 0.3 times the proficiency target reproducibility in agreement with the procedure of ISO 13528, Annex B2 in the next table:

	Free Formaldehyde in mg/kg
r (observed)	3.4
Reference test method	ISO17226-1:08
0.3*R (ref. test method)	3.7

Table 2: repeatability of subsamples #16635

The calculated repeatability for sample #16635 is in good agreement with 0.3 times the reproducibility of the reference test method. Therefore, homogeneity of all subsamples was assumed.

The second sample, again a black leather sample, was shreddered and after homogenisation divided over 132 subsamples of approx. 5 gram (labelled #16636). Each sample was packed in aluminium foil. The homogeneity of the subsamples was checked on pH according to ASTM D2810 on 8 stratified randomly selected samples. See the following table for the test results.

	pH
Sample #16636-1	3.99
Sample #16636-2	3.98
Sample #16636-3	3.99
Sample #16636-4	4.00
Sample #16636-5	4.01
Sample #16636-6	4.01
Sample #16636-7	3.99
Sample #16636-8	4.01

Table 3: homogeneity test results of subsamples #16636

From the above results of the homogeneity test, the observed repeatability was calculated and compared with 0.3 times the proficiency target reproducibility in agreement with the procedure of ISO 13528, Annex B2 in the next table:

	pH
r (observed)	0.03
Reference test method	ASTM D2810:13
0.3*R (ref. test method)	0.04

Table 4: repeatability of subsamples #16636

The calculated repeatability for sample #16636 is in good agreement with 0.3 times the reproducibility of the reference test method. Therefore, homogeneity of all subsamples was assumed.

To the participants, a set of samples (1 sample labelled #16335 and 1 sample labelled #16336) was sent on October 12, 2016.

2.5 ANALYSES

The participants were asked to determine on sample #16635, the content of Formaldehyde (HPLC) and/or the content of Formaldehyde (colorimetric) and on sample #16636 the pH “undiluted” and/or pH “ten times diluted extract” with the analytical procedures that are routinely used in the laboratory
It was explicitly requested to treat the samples as if they were routine samples and to report the test results using the indicated units on the report form and not to round the results more, 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 calculations.

To get comparable results a detailed report form, on which the units were prescribed as well as the reference test methods and a letter of instructions were prepared and made available on the data entry portal www.kpmd.co.uk/sgs-iis-cts/. The laboratories were also requested to confirm the sample receipt on the same data entry portal together with some details of the test methods used. A letter of instructions was added to the sample package.

3 RESULTS

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

Directly after the deadline, a reminder was sent to those laboratories that did not report test results at that moment.
Shortly after the deadline, the available test results were screened for suspect data. A test result was called suspect in case the Huber Elimination Rule (a robust outlier test) found it to be an outlier. The laboratories that produced these suspect data were asked to check the reported test results. Additional or corrected test results are used for the data analysis and the original 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 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).

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. 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.

In accordance to ISO 5725 the original test results per determination were submitted subsequently to Dixon’s, Grubbs’ and or Rosner’s outlier tests. Outliers are marked by D(0.01) for the Dixon test, by G(0.01) or DG(0.01) for the Grubbs test and by R(0.01) for the Rosner test. Stragglers are marked by D(0.05) for the Dixon test, by G(0.05) or DG(0.05) for the Grubbs test and by R(0.05) for the Rosner test. Both outliers and stragglers were not included in the calculations of averages and standard deviations.

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

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

3.2 GRAPHICS

In order to visualise the data against the reproducibilities from literature, Gauss plots were made, using the sorted data for one determination (see appendix 1). On the Y-axis the reported analysis 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 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. The Kernel Density Graph is a method for producing a smooth density approximation to a set of data that avoids some problems associated with histograms. Also a normal Gauss curve was projected over the Kernel Density Graph for reference.

3.3 Z-SCORES

To evaluate the performance of the participating laboratories the z-scores were calculated. As it was decided to evaluate the performance of the participants in this proficiency test (PT) against the literature requirements, the z-scores were calculated using a target standard deviation. This results in an evaluation independent of the spread of this interlaboratory study.

The target standard deviation was calculated from the target reproducibility (preferably taken from a standardized test method) by division with 2.8. In case no literature reproducibility was available, other target values were used.

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 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. This should be done in order to evaluate whether the reported test results are fit-for-purpose.

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

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

4 EVALUATION

During the execution of this proficiency test, no problems occurred with the delivery of the samples. Three laboratories did not report any test results and one laboratories reported results after the final reporting date.
Finally, the 106 reporting laboratories sent in total 240 numerical test results. Observed were 17 outlying test results, which is 7.1% of the numerical test results. In proficiency studies, outlier percentages of 3% - 7.5% are quite normal.

For the determination of Formaldehyde in Leather the test methods ISO17226-1 and ISO17226-2 are considered to be the official test methods. Therefore, the target reproducibilities were estimated from the reproducibility data as mentioned in the annexes of ISO17226-1 and ISO17226-2.

A number of participants reported that the amount of material was not sufficient for testing the pH and/or to perform the test in duplicate as required according ISO4045 and/or ISO17226-1.

4.1 EVALUATION ANALYSIS DETAILS

For this PT some analysis details were requested (see appendix 2). Questions like: were the reagents checked for absence of formaldehyde and were the reagents tested for other compounds which caused a colouring with acetylacetone?

Looking at the answers given by the participants the following can be summarized:
46 participants checked the reagents for absence of formaldehyde, 27 participants did not. 24 participants tested for other compounds that may cause a colouring with acetylacetone, 38 participants did not.
When evaluating the above differences in the execution of the test, no relation was found between these test conditions and the reported test results.

4.2 EVALUATION PER SAMPLE AND PER TEST

In this section, the results on sample #16635 and #16636 are discussed. All statistical results reported on the leather sample are summarised in appendix 1.

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.

Sample #16635

Formaldehyde content (HPLC): This determination was problematic for a number of laboratories. Five statistical outliers were observed. However, the calculated reproducibility after rejection of statistical outliers is almost in agreement with the requirements of ISO17226-1:2008.

Formaldehyde content (colorimetric): This determination was very problematic. Two statistical outliers were observed and one result was excluded as the used test method is for textile. The calculated reproducibility after rejection of the suspect data is not at all in agreement with the requirements of ISO17226-2:2008.

Sample #16636

pH of extract: This determination was problematic. Nine statistical outliers were observed. The calculated reproducibility after rejection of the statistical outliers is not 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), assuming that the sample material was not sufficient for most participants to perform the determination in duplicate.

The majority of the laboratories reported according to either ISO4045 or ASTM D2810. Both methods were also evaluated separately. The group of 13 laboratories performing ASTM D2810 showed slightly better precision than the group of 76 laboratories performing ISO4045. However, the calculated reproducibilities of both groups after rejection of the statistical outliers are not in agreement with the estimated requirements of ASTM D2810:2013.

pH of ten times diluted extract: This determination may be problematic. No less than seventeen test results (=85% of all reported test results) were excluded for various reasons (see page 20 and 21). The calculated reproducibility after rejection of the suspect data is not in agreement with the requirements of ASTM D2810:2013. This may be due to the low number of valid test results.
It was remarkable that none of the reporting laboratories mentioned the test method used.

4.3 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 and ASTM D2810), are compared in the next table.

Parameter	unit	n	average	2.8 * sd	R (target)
Formaldehyde (HPLC)	mg/kg	61	25.46	14.54	12.69
Formaldehyde (colorimetric)	mg/kg	55	63.55	45.91	16.15
pH of extract		87	4.14	0.25	0.13
pH of extract ten times diluted		3	(4.55)	(0.29)	(0.13)

Table 5: observed reproducibilities of leather samples #16635 and #16636

From the above tables it can be concluded that, without statistical calculations, the group of participating laboratories has severe difficulties with the determination of formaldehyde (colorimetric) and pH, but have no problems with the HPLC analysis, when compared with the requirements of the target test methods for this sample.

See also the discussions in paragraphs 4.2 and 5.

4.4 COMPARISON OF THE PROFICIENCY TEST OF NOVEMBER 2016 WITH PREVIOUS PTS

Parameter	November 2016	October 2015	October 2014	October 2013
Number of reporting labs	106	116	108	48
Number of results reported	240	239	224	52
Number of statistical outliers	16	7	7	6
Percentage outliers	6.7%	2.9%	3.1%	11.5%

Table 6: Comparison with previous PTs

The uncertainty in the test result of determined Formaldehyde in leather (HPLC) in the iis16A09 PT is in line with the uncertainty of the target test method. However, the uncertainty in the test result of the colorimetric determination of Formaldehyde in leather is not in line with the uncertainty of the target test method. Some improvement is visible in comparison with the results in previous PTs (see below table).

Parameter	November 2016	October 2015	October 2014	October 2013	Est. from target test method
Formaldehyde (HPLC)	20%	23%	30%	22%	22% (17226-1)
Formaldehyde (colorimetric)	26%	22%	33%	25%	9% (17226-2)
pH (undiluted)	2.1%	2.6%	3.2%	n.e.	0.9% (D2810)
pH (10x diluted)	2.3%	n.e.	n.e.	n.e.	0.9% (D2810)

Table 7: Development of relative uncertainties over the years

5 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, which is the case with the leather sample in this PT. 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 63 participants completed this section of the report form. Regretfully, the reported details are inconsistent and therefore it was impossible to draw significant conclusions.

Sample #16635 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 7), 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 8: Summary of limits from Standard GB20400:2006

When using ISO17226 part 1, all, except seven, reporting laboratories would reject this sample for category A. For category B, three laboratories would reject this sample, while all other reporting laboratories would accept this sample. None of the reporting laboratories would reject this sample for category C.
When using ISO17226 part 2, all, except two reporting laboratories would reject this sample for category A. Forty-six laboratories would accept this sample for category B, while none of the reporting laboratories would reject this sample for category C.

Compared to other labelling standards different decisions would be made concerning the acceptance or rejection of the sample.

Sample #16636 was chosen to determine the pH only as the leather was not positive on formaldehyde. Two different test methods are available to determine the pH of leather, ASTM D2810 and ISO4045. The difference between the two test methods is the dilution of the extract (10 times) in ISO4045, in case the pH of the undiluted extract is not between 4.00 and 10.00.
Remarkably, a large number of participants reported a test value for pH “10 times diluted”, although there was no reason for (e.g. test method used was ASTM D2810 and/or the pH of the undiluted extract was >4.00 and <10.00). These 17 test results were excluded for statistical evaluation.

In this proficiency test the Free Formaldehyde content and pH were determined. The variation observed for the Free Formaldehyde content (HPLC and colorimetric) and pH in this interlaboratory study are in line with the previous proficiency tests. The variations observed in this interlaboratory study can be caused by the preparation or the conditioning 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.

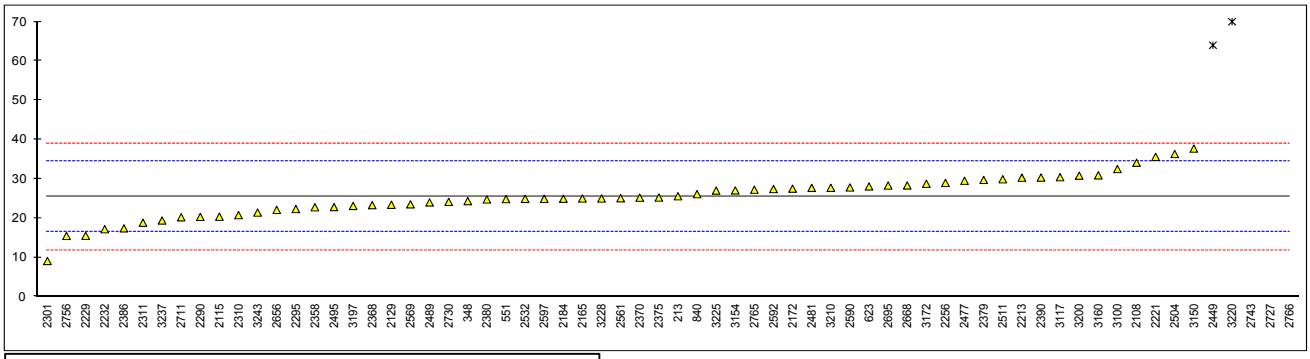
APPENDIX 1

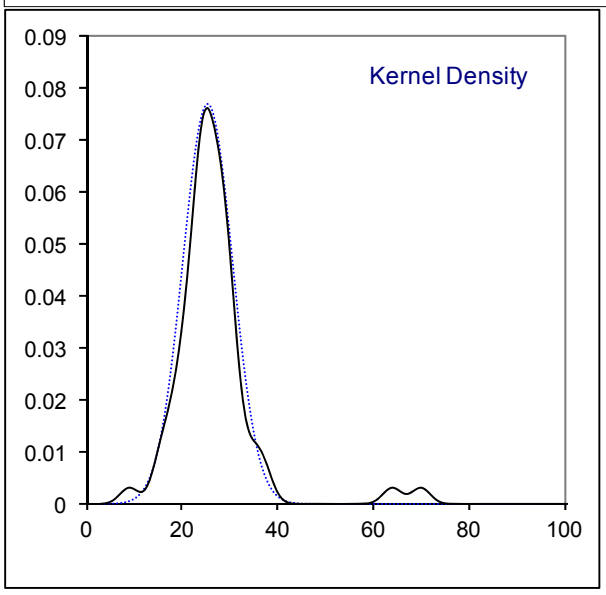
Determination of Formaldehyde content (HPLC) on sample #16635; results in mg/kg

lab	method	value	mark	z(targ)	remarks
110		-----		-----	
213	ISO17226-1	25.56		0.02	
348	In house	24.33	C	-0.25	First reported 78.166
362		-----		-----	
551	ISO17226-1	24.827		-0.14	
622		-----		-----	
623	ISO17226-1	28.07		0.58	
840	ISO17226-1	26.1		0.14	
2108	ISO17226-1	34.1		1.91	
2115	ISO17226-1	20.35		-1.13	
2129	ISO17226-1	23.39		-0.46	
2131		-----		-----	
2132		-----		-----	
2138		-----		-----	
2165	ISO17226-1	25		-0.10	
2172	ISO17226-1	27.5		0.45	
2184	ISO17226-1	24.93		-0.12	
2213	ISO17226-1	30.3		1.07	
2221	ISO17226-1	35.58		2.23	
2229	ISO17226-1	15.5		-2.20	
2232	ISO17226-1	17.17		-1.83	
2246		-----		-----	
2247		-----		-----	
2256	ISO17226-1	28.95		0.77	
2290	ISO17226-1	20.3		-1.14	
2293		-----		-----	
2295	ISO17226-1	22.3		-0.70	
2296		-----		-----	
2301	ISO17226-1	9.078		-3.61	
2310	ISO17226-1	20.76		-1.04	
2311	ISO17226-1	18.82		-1.46	
2330		-----		-----	
2351		-----		-----	
2358	ISO17226-1	22.76		-0.59	
2360		-----		-----	
2364		-----		-----	
2367		-----		-----	
2368	ISO17226-1	23.30		-0.48	
2370	ISO17226-1	25.20		-0.06	
2373		-----		-----	
2375	ISO17226-1	25.23		-0.05	
2379	ISO17226-1	29.71		0.94	
2380	ISO17226-1	24.74		-0.16	
2381		-----		-----	
2383		-----		-----	
2386	In house	17.395		-1.78	
2389		-----		-----	
2390	ISO17226-1	30.32		1.07	
2446		-----		-----	
2449	ISO17226-1	64.008	R(0.01)	8.51	
2453		-----		-----	
2460		-----		-----	
2477	ISO17226-1	29.5073		0.89	
2481	ISO17226-1	27.7		0.50	
2489	ISO17226-1	24		-0.32	
2495	ISO17226-1	22.81		-0.58	
2497		-----		-----	
2504	ISO17226-1	36.32		2.40	
2511	ISO17226-1	29.89		0.98	
2519		-----		-----	
2532	ISO17226-1	24.9		-0.12	
2540		-----		-----	
2561	ISO17226-1	25.06		-0.09	
2563		-----		-----	
2569	ISO17226-1	23.5		-0.43	
2572		-----		-----	
2590	ISO17226-1	27.796		0.52	
2592	ISO17226-1	27.40		0.43	
2597	ISO17226-1	24.92		-0.12	
2612		-----		-----	
2619		-----		-----	
2643		-----		-----	
2649		-----		-----	
2656	ISO17226-1	22.10		-0.74	
2668	ISO17226-1	28.31		0.63	
2674		-----		-----	
2695	ISO17226-1	28.29		0.63	

2701		-----		-----	
2702		-----		-----	
2711	ISO17226-1	20.21		-1.16	
2712		-----		-----	
2727	ISO17226-1	147.0	R(0.01)	26.82	
2730	ISO17226-1	24.13		-0.29	
2741		-----		-----	
2743	ISO17226-1	111.26	C,R(0.01)	18.93	First reported 55.63
2749		-----		-----	
2752		-----		-----	
2756	ISO17226-1	15.45975		-2.21	
2765	ISO17226-1	27.23		0.39	
2766	ISO17226-1	180.0	C,R(0.01)	34.10	First reported 256.7
3100	ISO17226-1	32.480		1.55	
3117	ISO17226-1	30.41		1.09	
3146		-----		-----	
3150	ISO17226-1	37.7		2.70	
3154	ISO17226-1	27.05		0.35	
3160	ISO17226-1	30.89		1.20	
3172	ISO17226-1	28.75		0.73	
3176		-----		-----	
3197	ISO17226-1	23.1		-0.52	
3200	ISO17226-1	30.8		1.18	
3210	In house	27.71		0.50	
3214		-----		-----	
3220	ISO17226-1	70	C,R(0.01)	9.83	First reported 96.4
3225	ISO17226-1	27.0		0.34	
3228	ISO17226-1	25.0		-0.10	
3237	ISO17226-1	19.38		-1.34	
3238		-----		-----	
3243	ISO17226-1	21.41		-0.89	
3248		-----		-----	

normality	suspect
n	61
outliers	5
mean (n)	25.455
st.dev. (n)	5.1936
R(calc.)	14.542
R(ISO17226-1:08)	12.689



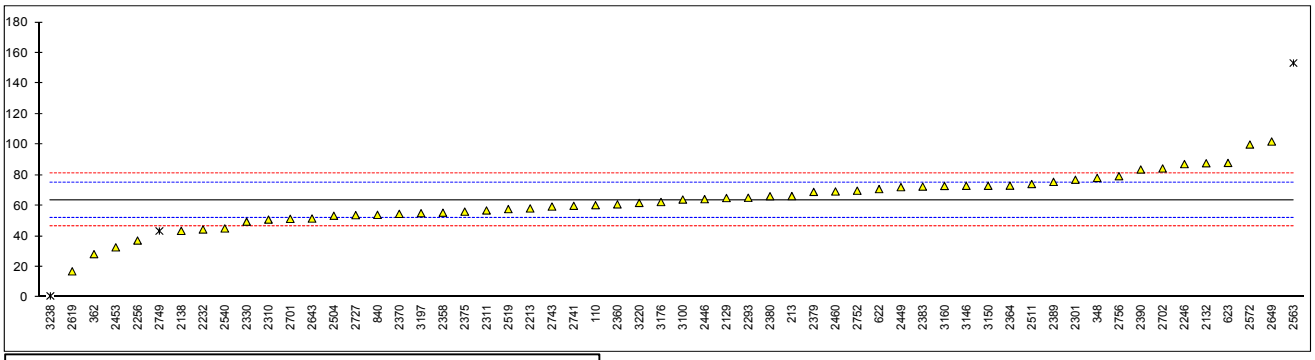


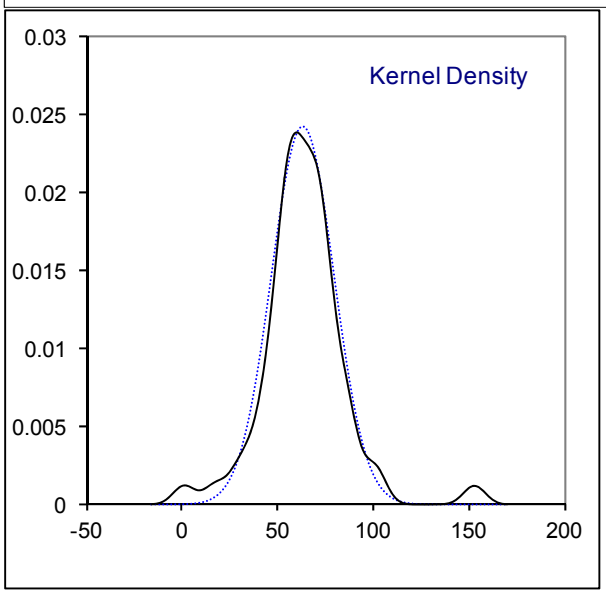
Determination of Formaldehyde content (colorimetric) on sample #16635; results in mg/kg

lab	method	value	mark	z(targ)	remarks
110	ISO17226-2	60.342		-0.56	
213	ISO17226-2	66.27		0.47	
348	In house	78.166	C	2.53	First reported 24.33
362	ISO17226-2	28.25		-6.12	
551		-----		-----	
622	DIN53315	70.86		1.27	
623	ISO17226-2	88.0		4.24	
840	ISO17226-2	53.99		-1.66	
2108		-----		-----	
2115		-----		-----	
2129	ISO17226-2	65.0		0.25	
2131		-----		-----	
2132	ISO17226-2	87.77		4.20	
2138	ISO17226-2	43.53		-3.47	
2165	ISO17226-2	NA		-----	
2172		-----		-----	
2184		-----		-----	
2213	ISO17226-2	58.2		-0.93	
2221		-----		-----	
2229		-----		-----	
2232	ISO17226-2	44.42		-3.32	
2246	ISO17226-2	87.23		4.10	
2247		-----		-----	
2256	ISO17226-2	37.16		-4.58	
2290		-----		-----	
2293	ISO17226-2	65.185		0.28	
2295		-----		-----	
2296		-----		-----	
2301	ISO17226-2	77.000		2.33	
2310	ISO17226-2	50.89		-2.20	
2311	ISO17226-2	56.857		-1.16	
2330	ISO17226-2	49.54		-2.43	
2351		-----		-----	
2358	ISO17226-2	55.4		-1.41	
2360	ISO17226-2	60.87		-0.47	
2364	ISO17226-2	73.10		1.66	
2367		-----		-----	
2368		-----		-----	
2370	ISO17226-2	54.64		-1.55	
2373		-----		-----	
2375	ISO17226-2	56.1		-1.29	
2379	ISO17226-2	69.033		0.95	
2380	ISO17226-2	66.20		0.46	
2381		-----		-----	
2383	ISO17226-2	72.5		1.55	
2386		-----		-----	
2389	ISO17226-2	75.6		2.09	
2390	ISO17226-2	83.7		3.49	
2446	In house	64.27		0.12	
2449	ISO17226-2	72.142		1.49	
2453	ISO17226-2	32.7		-5.35	
2460	ISO17226-2	69.31		1.00	
2477		-----		-----	
2481		-----		-----	
2489		-----		-----	
2495		-----		-----	
2497		-----		-----	
2504	ISO17226-2	53.41		-1.76	
2511	ISO17226-2	74.15		1.84	
2519	ISO17226-2	57.76		-1.00	
2532		-----		-----	
2540	ISO17226-2	45.09		-3.20	
2561		-----		-----	
2563	ISO17226-2	153.4	C,R(0.01)	15.58	First reported 12.9
2569		-----		-----	
2572	ISO17226-2	100.03		6.32	
2590		-----		-----	
2592		-----		-----	
2597		-----		-----	
2612		-----		-----	
2619	ISO17226-2	17.01		-8.07	
2643	ISO17226-2	51.58		-2.08	
2649	ISO17226-2	102	C	6.67	First reported 181.14
2656		-----		-----	
2668		-----		-----	
2674		-----		-----	
2695		-----		-----	
2701	ISO17226-2	51.39		-2.11	

2702	ISO17226-2	84.36		3.61	
2711		-----		-----	
2712		-----		-----	
2727	ISO17226-2	53.8		-1.69	
2730		-----		-----	
2741	ISO17226-2	59.9		-0.63	
2743	ISO17226-2	59.42		-0.72	
2749	ISO14184-2	43.4	ex	-3.49	Result excluded, test method is for textile
2752	GB/T19941	69.8		1.08	
2756	ISO17226-2	79.3		2.73	
2765		-----		-----	
2766		-----		-----	
3100	ISO17226-2	64.02		0.08	
3117		-----		-----	
3146	ISO17226-2	73.0		1.64	
3150	ISO17226-2	73		1.64	
3154		-----		-----	
3160	ISO17226-2	72.89		1.62	
3172		-----		-----	
3176	ISO17226-2	62.40		-0.20	
3197	ISO17226-2	55.1		-1.47	
3200		-----		-----	
3210		-----		-----	
3214		-----		-----	
3220	ISO17226-2	61.8		-0.30	
3225		-----		-----	
3228		-----		-----	
3237		-----		-----	
3238	In house	0.90	R(0.05)	-10.86	
3243		-----		-----	
3248		-----		-----	

normality	OK
n	55
outliers	2 (+1 excl)
mean (n)	63.553
st.dev. (n)	16.3960
R(calc.)	45.909
R(ISO17226-2:08)	16.150



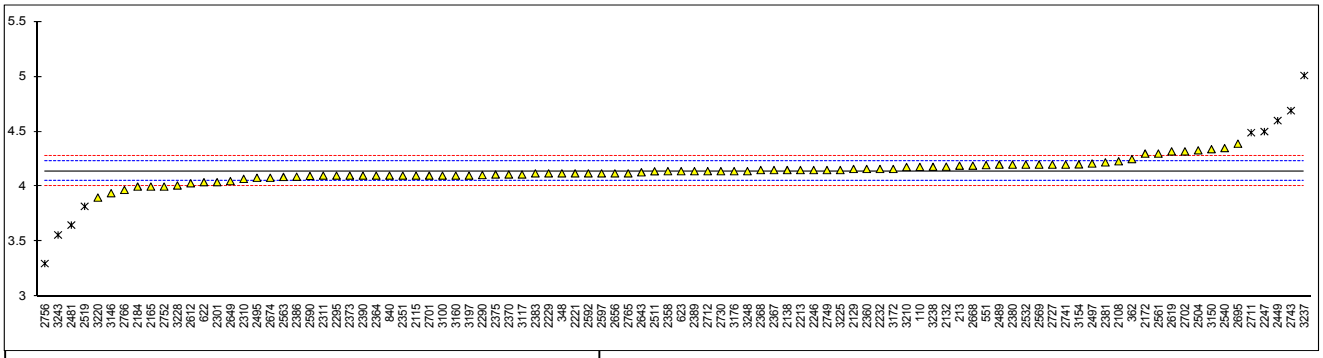


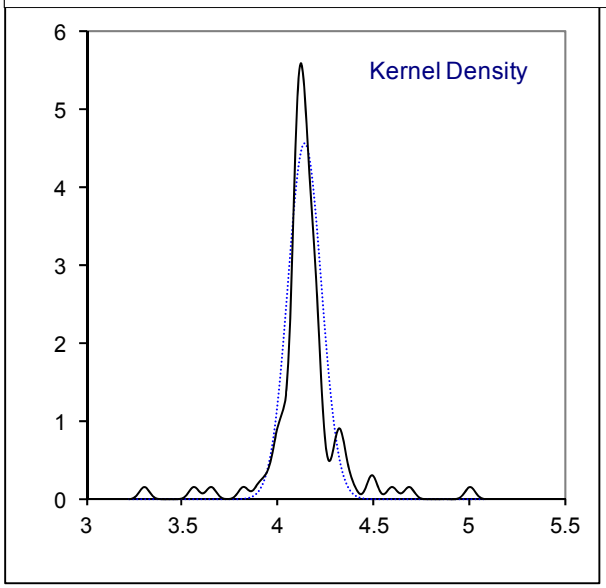
Determination of pH of extract on sample #16636; unitless results

lab	method	value	mark	z(targ)	remarks
110	ASTM D2810	4.179		0.83	
213	ISO4045	4.19		1.08	
348	ISO4045	4.12		-0.46	
362	ISO4045	4.25		2.40	
551	ISO3071	4.195		1.19	
622	ISO3071	4.04		-2.22	
623	ISO4045	4.14		-0.02	
840	ISO4045	4.1		-0.90	
2108	ISO4045	4.23		1.96	
2115	ISO4045	4.1	C	-0.90	First reported 4.5
2129	ISO4045	4.16		0.42	
2131		-----		-----	
2132	ISO4045	4.181		0.88	
2138	ISO4045	4.15		0.20	
2165	ISO4045	4.00		-3.10	
2172	ISO4045	4.3		3.50	
2184	ISO4045	4.00		-3.10	
2213	ISO4045	4.15		0.20	
2221	ISO4045	4.12	C	-0.46	First reported 4.51
2229	ISO4045	4.12		-0.46	
2232	ISO4045	4.16		0.42	
2246	ISO4045	4.15		0.20	
2247	ASTM D2810	4.5	R(0.05)	7.90	
2256		-----		-----	
2290	ISO4045	4.105		-0.79	
2293		-----		-----	
2295	ASTM D2810	4.1		-0.90	
2296		-----		-----	
2301	ASTM D2810	4.04		-2.22	
2310	ISO4045	4.07		-1.56	
2311	ISO4045	4.1		-0.90	
2330		-----		-----	
2351	ISO4045	4.10		-0.90	
2358	ISO4045	4.14		-0.02	
2360	ISO4045	4.16		0.42	
2364	ISO4045	4.10		-0.90	
2367	ISO4045	4.15		0.20	
2368	ISO4045	4.15		0.20	
2370	ISO4045	4.11		-0.68	
2373	ISO4045	4.10		-0.90	
2375	ISO4045	4.11		-0.68	
2379		-----		-----	
2380	ISO4045	4.20		1.30	
2381	ISO4045	4.22		1.74	
2383	ISO4045	4.12		-0.46	
2386	In house	4.09		-1.12	
2389	ISO4045	4.14		-0.02	
2390	ASTM D2810	4.1		-0.90	
2446		-----		-----	
2449	ASTM D2810	4.6	R(0.01)	10.10	
2453		-----		-----	
2460		-----		-----	
2477		-----		-----	
2481	ISO4045	3.65	R(0.01)	-10.80	
2489	ISO4045	4.2		1.30	
2495	ISO4045	4.08		-1.34	
2497	ISO4045	4.21		1.52	
2504	ASTM D2810	4.33		4.16	
2511	ISO4045	4.139		-0.05	
2519	ASTM D2810	3.82	R(0.05)	-7.06	
2532	ISO4045	4.2		1.30	
2540	ISO4045	4.35		4.60	
2561	ISO4045	4.30		3.50	
2563	ISO4045	4.0875		-1.18	
2569	ISO4045	4.2		1.30	
2572		-----		-----	
2590	ISO4045	4.097		-0.97	
2592	ISO4045	4.12		-0.46	
2597	ASTM D2810	4.12		-0.46	
2612	ISO4045	4.03		-2.44	
2619	ISO4045	4.32	C	3.94	First reported 5.7
2643	ASTM D2810	4.13		-0.24	
2649	ASTM D2810	4.05		-2.00	
2656	ISO4045	4.12		-0.46	
2668	ISO4045	4.19		1.08	
2674	ISO4045	4.08		-1.34	
2695	ISO4045	4.39		5.48	
2701	ISO4045	4.1		-0.90	

2702	ISO4045	4.32		3.94	
2711	ISO4045	4.49	R(0.05)	7.68	
2712	ISO4045	4.14		-0.02	
2727	ISO4045	4.20		-----	
2730	ISO4045	4.14		-0.02	
2741	ISO4045	4.2		1.30	
2743	ISO4045	4.69	R(0.01)	12.08	
2749	ISO4054	4.150		0.20	
2752	QB/T2724	4.0		-3.10	
2756		3.3	C,R(0.01)	-18.50	First reported 4.48
2765	ISO4045	4.12		-0.46	
2766	ISO4045	3.97		-3.76	
3100	ASTM D2810	4.10		-0.90	
3117	ISO4045	4.11		-0.68	
3146	ISO4045	3.94		-4.42	
3150	ISO4045	4.34		4.38	
3154	ASTM D2810	4.202		1.34	
3160	ISO4045	4.10		-0.90	
3172	ISO4045	4.16		0.42	
3176	ISO4045	4.14		-0.02	
3197	ISO4045	4.10		-0.90	
3200		-----		-----	
3210	ISO4045	4.178		0.81	
3214		-----		-----	
3220	ISO4045	3.9	C	-5.30	First reported 3.3
3225	ISO4045	4.15		0.20	
3228	ISO4045	4.01		-2.88	
3237	ISO4045	5.01	R(0.01)	19.12	
3238	ISO4045	4.18		0.86	
3243	ISO4045	3.56	C,R(0.01)	-12.78	First reported 3.92
3248	GB/T7573	4.14		-0.02	

			Only ASTM D2810	Only ISO4045
	normality	suspect	not OK	suspect
	n	87	10	72
	outliers	9	3	5
	mean (n)	4.141	4.135	4.145
	st.dev. (n)	0.0876	0.0847	0.0887
	R(calc.)	0.245	0.237	0.248
	R(D2810:13)	0.127	0.127	Unknown



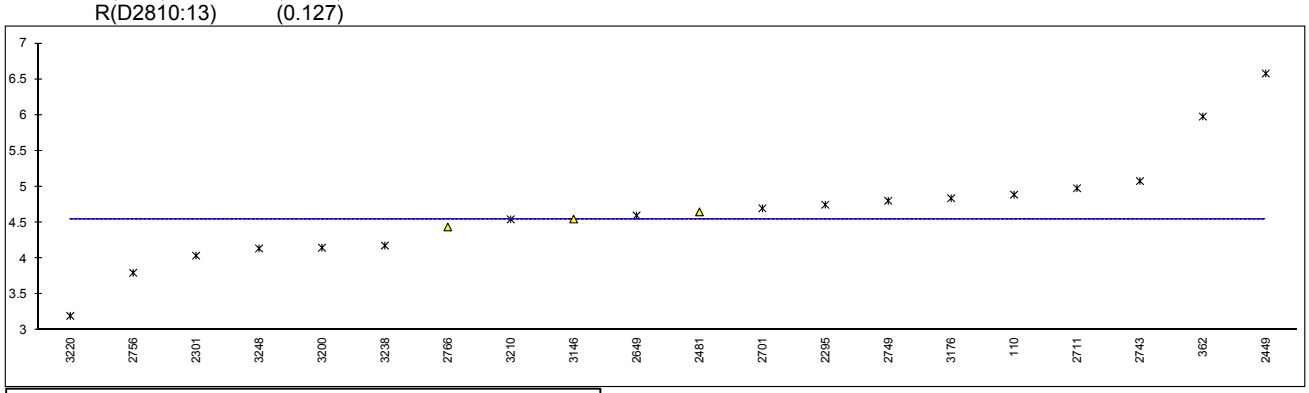


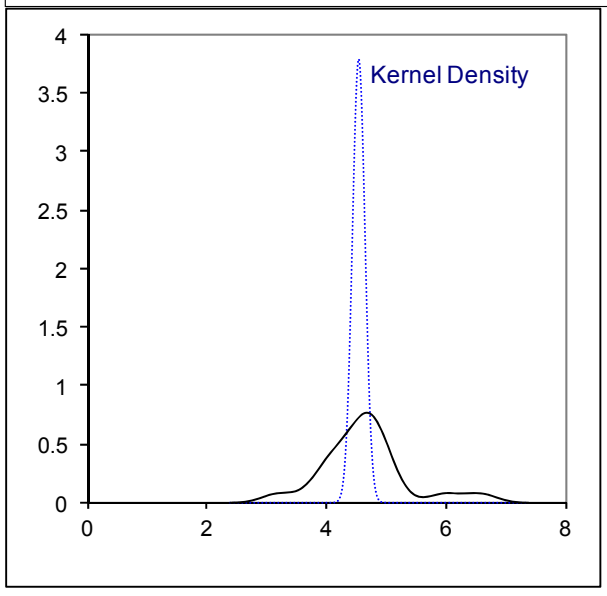
Determination of pH of ten times diluted extract on sample #16636; unitless results

lab	method	value	mark	z(targ)	remarks
110		4.8895	ex	-----	ASTM D2810 does not mention dilution & pH “undiluted” >4.00
213		-----		-----	
348		-----		-----	
362		5.98	ex	-----	pH “undiluted” >4.00, not necessary to dilute 10x
551		-----		-----	
622		-----		-----	
623		-----		-----	
840		-----		-----	
2108		-----		-----	
2115		-----		-----	
2129		-----		-----	
2131		-----		-----	
2132		-----		-----	
2138		-----		-----	
2165		-----		-----	
2172		-----		-----	
2184		-----		-----	
2213		-----		-----	
2221		-----		-----	
2229		-----		-----	
2232		-----		-----	
2246		-----		-----	
2247		-----		-----	
2256		-----		-----	
2290		-----		-----	
2293		-----		-----	
2295		4.75	ex	-----	ASTM D2810 does not mention dilution & pH “undiluted” >4.00
2296		-----		-----	
2301		4.04	ex	-----	ASTM D2810 does not mention dilution & pH “undiluted” >4.00
2310		-----		-----	
2311		-----		-----	
2330		-----		-----	
2351		-----		-----	
2358		-----		-----	
2360		-----		-----	
2364		-----		-----	
2367		-----		-----	
2368		-----		-----	
2370		-----		-----	
2373		-----		-----	
2375		-----		-----	
2379		-----		-----	
2380		-----		-----	
2381		-----		-----	
2383		-----		-----	
2386		-----		-----	
2389		-----		-----	
2390		-----		-----	
2446		-----		-----	
2449		6.58	ex	-----	ASTM D2810 does not mention dilution & pH “undiluted” >4.00
2453		-----		-----	
2460		-----		-----	
2477		-----		-----	
2481		4.65		-----	
2489		-----		-----	
2495		-----		-----	
2497		-----		-----	
2504		-----		-----	
2511		-----		-----	
2519		-----		-----	
2532		-----		-----	
2540		-----		-----	
2561		-----		-----	
2563		-----		-----	
2569		-----		-----	
2572		-----		-----	
2590		-----		-----	
2592		-----		-----	
2597		-----		-----	
2612		-----		-----	
2619		-----		-----	
2643		-----		-----	
2649		4.60	ex	-----	ASTM D2810 does not mention dilution & pH “undiluted” >4.00
2656		-----		-----	
2668		-----		-----	
2674		-----		-----	
2695		-----		-----	
2701		4.7	ex	-----	pH “undiluted” >4.00, not necessary to dilute 10x

2702	-----		-----	
2711	4.98	ex	-----	pH “undiluted” >4.00, not necessary to dilute 10x
2712	-----		-----	
2727	-----		-----	
2730	-----		-----	
2741	-----		-----	
2743	5.08	ex	-----	pH “undiluted” >4.00, not necessary to dilute 10x
2749	4.805	ex	-----	pH “undiluted” >4.00, not necessary to dilute 10x
2752	-----		-----	
2756	3.8	ex	-----	pH “undiluted” was statistical outlier
2765	-----		-----	
2766	4.44		-----	
3100	-----		-----	
3117	-----		-----	
3146	4.55		-----	
3150	-----		-----	
3154	-----		-----	
3160	-----		-----	
3172	-----		-----	
3176	4.84	ex	-----	pH “undiluted” >4.00, not necessary to dilute 10x
3197	-----		-----	
3200	4.15	ex	-----	
3210	4.546	ex	-----	pH “undiluted” >4.00, not necessary to dilute 10x
3214	-----		-----	
3220	3.2	ex	-----	Result excluded, because pH diluted < pH undiluted
3225	-----		-----	
3228	-----		-----	
3237	-----		-----	
3238	4.18	ex	-----	pH “undiluted” >4.00, not necessary to dilute 10x
3243	-----		-----	
3248	4.14	ex	-----	pH “undiluted” >4.00, not necessary to dilute 10x

normality	not OK
n	3
outliers	0 (+17 excl)
mean (n)	(4.547)
st.dev. (n)	(0.1050)
R(calc.)	(0.294)
R(D2810:13)	(0.127)





APPENDIX 2
Analytical Details ISO17226-2

labnrs	Reagents checked for absence of formaldehyde	If yes, please give absorbance of reagents	Tested for other compounds which cause a coloring with acetylacetone?	If yes, please give absorbance	Was the absorbance of the solution corrected?	If yes, please give absorbance of the sample solution before and after correction	Remarks on Additional Questions:
110	Yes	0.0003	No		Yes	before= 0.3840, after= 0.3210	
213	No		No		No		
348	---		---		---		
362	Yes		No		No		There was not enough sample for additional testing for other substances that may cause coloring.
551	---		---		---		
622	Yes	0.053	Yes	16635/a:0.114, 16635/b:0.116	Yes	before correction : 16635/a:0.536, 16635/b:0.541, after correction 16635/a:0.389, 16635/b:0.392	
623	Yes	0	Yes	0	No		
840	Yes	0	Yes	0.053	Yes	0.353	
2108	---		---		---		
2115	No		No		No		
2129	Yes		Yes		Yes		
2132	Yes	0.017 abs	Yes	0.002 abs	No		
2138	Yes	0.0018	No		No		
2165	---		---		---		
2172	No		---		---		
2184	---		---		---		
2213	No		No		No		
2221	---		---		---		
2229	---		---		---		
2232	Yes	0.0186	Yes	0.0868	Yes	before : 0.542 after :0.505	
2246	Yes	0.016	Yes	0.002	No		
2247	---		---		---		
2256	Yes	0.0003	Yes	0.0615	Yes	0.2623/0.2005	The aqueous extract, which contains color, was further analyzed by HPLC
2290	---		---		---		
2293	Yes	0.000	Yes	0.065	---	before correction 0.419, after correction 0.354	

labnrs	Reagents checked for absence of formaldehyde	If yes, please give absorbance of reagents	Tested for other compounds which cause a coloring with acetylacetone?	If yes, please give absorbance	Was the absorbance of the solution corrected?	If yes, please give absorbance of the sample solution before and after correction	Remarks on Additional Questions:
2295	---		---		---		
2296	---		---		---		
2301	Yes	0	Yes	0.247	Yes	Before : 0.540 After : 0.293	
2310	Yes	0.007 abs	No		Yes	before - 0.2148 abs, after - 0.2078 abs.	
2311	Yes	0.005	Yes	0.0672	Yes	Before correction:0.3690 and after correction:0.3018	
2330	Yes	0.0060	No		No		
2351	---		---		---		
2358	Yes	0.002	No		No		
2360	Yes		---		---		
2364	Yes	0.0009	No		No		
2367	---		---		---		
2368	---		---		---		
2370	Yes	0.003 Abs	No		No		
2373	---		---		---		
2375	Yes	0.0002	---		---		
2379	Yes	0.019	Yes	0.027	No		
2380	No		No		No		
2381	---		---		---		
2383	Yes		Yes		Yes		
2386	---		---		---		
2389	No		No		No		
2390	Yes	Absorbance of Reagent : 0.0	Yes	Absorbance : 0.105	Yes	Absorbance of sample solution: 0.334-0.105= 0.229	
2446	Yes	-0,001	---		Yes		
2449	Yes		---		---		
2453	Yes	0.000	---		---		
2460	Yes	0.017	Yes	0.139	No		
2477	---		---		---		
2481	---		---		---		
2489	No		---		---		

labnrs	Reagents checked for absence of formaldehyde	If yes, please give absorbance of reagents	Tested for other compounds which cause a coloring with acetylacetone?	If yes, please give absorbance	Was the absorbance of the solution corrected?	If yes, please give absorbance of the sample solution before and after correction	Remarks on Additional Questions:
2495	No		No		No		
2497	---		---		---		
2504	Yes	ND	Yes	ND	Yes	0.1504	-
2511	Yes		Yes		Yes		
2519	Yes	0.001	No		No		
2532	No		---		---		
2540	No		No		No		
2561	---		---		---		
2563	Yes	0,001	---		---		
2569	No		No		No		
2572	Yes	0.0	---		---		
2590	No		No		No		
2592	---		---		---		
2597	No		No		No		
2612	---		---		---		
2619	No		No		No		
2643	Yes	0.0229	Yes	0.0473	Yes	before : 0.3268, after : 0.2653	
2649	Yes	0.0095 abs	Yes	0.1821 abs	Yes	Before Correction : 0.2440abs & After Correction: 0.1068abs	
2656	---		---		---		
2668	---		---		---		
2674	---		---		---		
2695	No		No		No		
2701	No		No		No		
2702	Yes	0.003	No		No		
2711	---		---		---		
2712	---		---		---		
2727	Yes	0,012	Yes	0,069	Yes	before - 0,883; after - 0,688	
2730	---		---		---		
2741	Yes	0.0011	Yes	0.1201 abs	Yes	before : 0.4306 abs, after : 0.3105 abs	
2743	No		No		No		

labnrs	Reagents checked for absence of formaldehyde	If yes, please give absorbance of reagents	Tested for other compounds which cause a coloring with acetylacetone?	If yes, please give absorbance	Was the absorbance of the solution corrected?	If yes, please give absorbance of the sample solution before and after correction	Remarks on Additional Questions:
2749	Yes	0.049	Yes	0.110/0.115	Yes	before: 0.296/0.285 and after: 0.186/0.170	
2752	Yes	0.0	No		Yes	0.048	
2756	No		No		No		
2765	---		---		---		
2766	No		No		No		
3100	Yes	0.0020	Yes	0.0064	Yes	0.389/0.325	
3117	---		---		---		
3146	No		---		---		
3150	No		No		No		
3154	No		No		No		
3160	Yes	0.040	Yes	0.138	Yes		Absorbance of the sample solution is corrected as it is measured against a blank with acetylacetone.
3172	---		---		---		
3176	Yes	0	No		No		
3197	Yes		No		No		
3200	No		No		No		
3210	---		---		---		
3214	---		---		---		
3220	Yes	0.008	No		No		
3225	No		No		No		N/A
3228	---		---		---		
3237	Yes	0	No		No		
3238	No		No		No		
3243	No		No		No		
3248	No		No		No		

APPENDIX 3

Number of participants per country

3 labs in BANGLADESH
1 lab in BRAZIL
2 labs in BULGARIA
1 lab in CAMBODIA
1 lab in ETHIOPIA
5 labs in FRANCE
10 labs in GERMANY
1 lab in GUATEMALA
7 labs in HONG KONG
11 labs in INDIA
3 labs in INDONESIA
10 labs in ITALY
4 labs in KOREA
2 labs in MEXICO
1 lab in MOROCCO
19 labs in P.R. of CHINA
3 labs in PAKISTAN
2 labs in PORTUGAL
1 lab in SINGAPORE
2 labs in SPAIN
2 labs in SWITZERLAND
3 labs in TAIWAN R.O.C.
2 labs in THAILAND
1 lab in TUNISIA
5 labs in TURKEY
1 lab in U.S.A.
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
W = test result withdrawn on request of participant
ex = test result excluded from calculations
n.a. = not applicable
n.e. = not evaluated
n.d. = not detected
fr. = first reported

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