

Studies on the determination of pH value and difference figure of leather

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SUMMARY

The precise data of the pH and difference figure determination procedure of aqueous extracts from leather according to ISO 4045 were determined by means of an interlaboratory test. At the same time, single procedural steps were examined closely in order to detect their impact on the result.

1 INTRODUCTION

Leather manufacture is a multi-stage, complex process. The resulting product is not poor in ions. The pH value is an important parameter for assessing different leather types. At first glance, the determination procedure seems to be very simple and practicable for everyone. A precise description of the procedure is essential for the reproducibility of results obtained in different laboratories. Only in this way, influencing factors such as leather type, sample preparation, temperature during extraction and measurement, the quality of the water used, the quality of the utilised electrodes and the calibration of the measuring device can be designed comparably. The listed parameters should be analysed in the interlaboratory test in order to allow an assessment of their influence on the result.

2 INTERLABORATORY TEST

2.1 Experimental approach

Eleven laboratories from the leather industry, the chemical industry and the testing service sector participated in the interlaboratory test on the determination of the pH value and difference figure according to ISO 4045.

Four different samples were examined in the interlaboratory test, namely:

- Leather 1: wet blue, air-dried,
- Leather 2: crust, chromium-free,
- Leather 3: finished leather, chromium-free, based on Leather 2,
- Leather 4: lining leather, chrome-tanned.

All leather samples were centrally ground and homogenised, and afterwards shipped to the participants. Before the test, the ground samples were conditioned in a standard climate. Three parallel determinations of the pH value and every time of the difference figure for each sample were performed in the laboratories.

The type of devices (shaker, pH meter) used and the testing conditions (e.g. shaking frequency, temperature during extraction and pH measurement, filtration yes/no,

Table 1: Precise parameters of the pH determination.

Parameter	Abbr.	Leather 1	Leather 2	Leather 3	Leather 4
Overall average	X	3.80	3.86	3.56	3.59
Number of data	n	33	33	33	33
Repeatability standard deviation	S _r	0.025	0.037	0.026	0.025
Repeatability coefficient (%)	V _r	0.6	1.0	0.7	0.7
Repeatability (P=95 %)	r	0.07	0.10	0.07	0.07
Reproducibility standard deviation	S _R	0.080	0.152	0.090	0.088
Reproducibility coefficient (%)	V _R	2.1	3.9	2.5	2.5
Reproducibility (P=95 %)	R	0.22	0.43	0.25	0.25

**Table 2: Precise parameters of the determination of difference figure.**

Parameter	Abbr.	Leather 1	Leather 2	Leather 3	Leather 4
Overall average	X	0.42	0.54	0.50	0.59
Number of data	n	33	33	33	33
Repeatability standard deviation	S _r	0.027	0.034	0.035	0.023
Repeatability coefficient (%)	V _r	6.5	6.3	6.9	3.9
Repeatability (P=95 %)	r	0.08	0.10	0.10	0.07
Reproducibility standard deviation	S _R	0.066	0.095	0.058	0.062
Reproducibility coefficient (%)	V _R	15.6	17.5	11.5	10.4
Reproducibility (P=95 %)	R	0.18	0.27	0.16	0.17

time to a steady reading of pH value) were documented exactly every single time.

2.2 Precise data of the test procedure

Within the scope of the interlaboratory test, precise data for the determination of the pH value and difference figure of the aqueous extract from leather were calculated. The statistical analysis of pH data sets did not identify any outlier. The existing data were rounded up to 0.05 (if not already done) and used for the calculation of precise parameters. These performance figures of the procedure are summarised in *Table 1* for the determination of pH value. *Figure 1* illustrates typical values of pH and difference figure of a chrome-tanned leather (leather 4).

In case of the determination of difference figure, data sets of leathers 1, 2 and 4 did not contain outliers. A statistical straggler (standard deviation, Cochran test) was identified for the data set of leather 3, but this value was not eliminated in further calculations. The precise parameters obtained are shown in *Table 2*.

The precise data determined provide indications on the

performance of the procedure and are at the same time a valuable guide for the self-assessment of a laboratory using this procedure.

3 INFLUENCE OF SINGLE PROCEDURAL STEPS

In addition, the interlaboratory test offered the possibility to consider the effect of single procedural steps on the result, namely:

- influence of reduction degree (cutting),
- influence of shaker type,
- influence of shaking rate,
- influence of solid matter separation,
- influence of the calibration buffer,
- influence of electrode age.

3.1 Influence of the reduction degree (cutting)

Two participants were provided with non-ground samples in order to examine the effect of sample preparation (reduction degree). The following three variants were compared:

Figure 1: Variation of laboratory averages of the pH value (left) and difference figure (right) for the chrome-tanned leather 4. The continuous red line corresponds to the overall average of all participating laboratories; the dashed lines correspond to the standard deviation ($\pm s$).

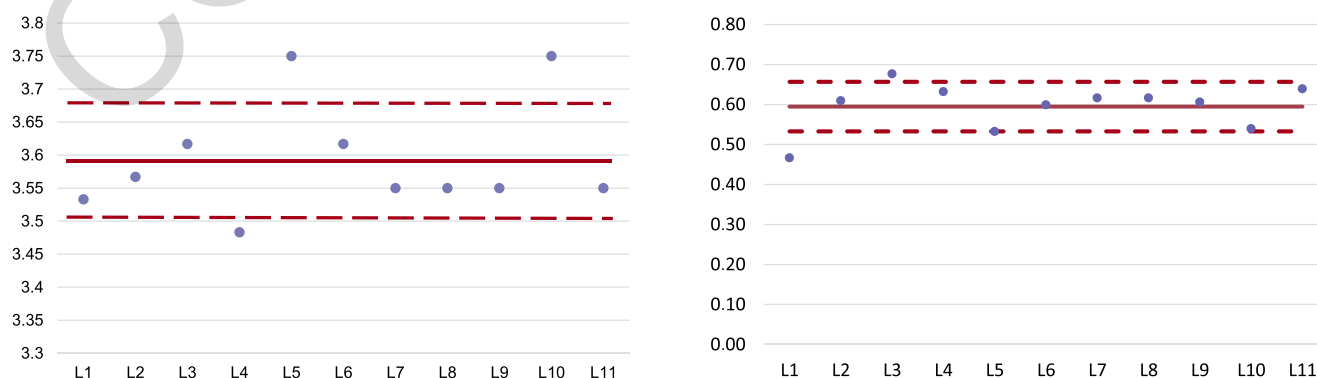




Table 3: pH-measurements of aqueous extracts of differently disintegrated leather samples (lab 9), results not rounded to 0.05.

Sample	Reduction Ratio		
	Ground	Cut	
		fine	coarse
Leather 1	3.78	3.79	3.79
	3.76	3.77	3.78
	3.76	3.77	3.78
Leather 2	3.80	3.77	3.74
	3.78	3.76	3.74
	3.78	3.76	3.74
Leather 3	3.56	3.58	3.58
	3.56	3.57	3.58
	3.56	3.58	3.58
Leather 4	3.57	3.57	3.56
	3.57	3.57	3.56
	3.56	3.57	3.56

- ground, according to ISO 4044, perforated strainer (4+0.5mm),
- coarsely cut, (5x5mm), average mass per piece (26–38mg),
- finely cut, (2x3mm, with 4–6mg and 3x3mm, with 13–16mg mass per piece).

The experiments referring to the influence of the reduction degree on the test result did not show significant differences (t-test for independent random samples, homogeneity of variance) of the results of the three different reduction variants. *Table 3* presents the results of one participant.

3.2 Influence of the shaker type

The impact of the shaker type utilised was investigated by comparing a device shaking overhead with one shaking horizontally. One of the two labs involved in the experiment used a shaking frequency equivalent to 21 revolutions per minute for an overhead shaker and 50 to-and-fro movements per minute for a horizontal shaker. In the second lab, an overhead shaker with a revolution speed of 50 revolutions per minute and a horizontal shaker with 250 to-and-fro motions were applied.

Generally, three different overhead shaking devices of different frequencies (21, 30, 50/min) were used in the interlaboratory test. Most of the horizontal shakers in use (5) had shaking frequencies of 50/min, but two laboratories applied shakers with 60 and even 250 to-and-fro movements per minute.

Under the employed conditions (see above), the shaker type had no effect on the final result. However, it is necessary to coordinate frequencies, because the contact intensity of the extraction medium in the overhead shaker differs from that in the horizontal shaker (*Table 4*).

Table 4: Influence of the shaker type by means of decanted leather extracts.

Sample	Shaker	
	Overhead 21/min	Horizontal 50/min
Leather 1	3.78	3.80
	3.76	3.80
	3.76	3.80
Leather 2	3.80	3.83
	3.78	3.78
	3.78	3.78
Leather 3	3.56	3.58
	3.56	3.56
	3.56	3.57
Leather 4	3.57	3.62
	3.57	3.62
	3.56	3.60

3.3 Influence of the shaking rate

The influence of the shaking frequency could not be examined for one laboratory due to lab equipment reasons. The evaluation of measuring data of different labs (L9, L5, and L10), using overhead shakers, gave a hint on frequency related differences: The pH value slightly increased with rising frequency. However, this result has to be viewed critically and should be verified by experiments performed under replicable conditions.

3.4 Influence of solid matter separation

Two participants of the interlaboratory test determined the pH value and difference figure after decanting as well as after filtration (folded filter, medium filtration speed) of the aqueous extract.

The comparison of measurements of filtrated and decanted aqueous leather extracts also showed no statistically significant differences between the two approaches.

3.5 Influence of the calibration buffer

Additionally, the buffer solutions used routinely by several participants (L1, L4, L9, L10) as well as the aqueous extract of leather 3 prepared by lab 9 were measured mutually using lab specific measuring devices and lab specific procedures (L1, L4 and L9) for the electrode adjustment. All participating labs adjusted the measuring system standard-compliant with at least two buffer solutions with pH values suited to include the expected pH of the sample.

The measurements performed by laboratories L1, L4 and L9 on diverse buffer solutions and on the aqueous leather 3 extract concurred well (*Table 5*). Certainly, these participants considered the standard (interval pH 3 – pH 7) rigorously.

However, the evaluation of the testing conditions indicated that the majority of the participants (6 out of 11) did not respect the specifications of the standard ISO 4045

**Table 5: Counter measurements of buffer solutions and of leather 3 extract, results not rounded to 0.05.**

Solution	L1		L4	L9
	Device 1	Device 2		
Calibrated interval	pH (3 - 7)	pH (3 - 7)	pH (3 - 7)	pH (3 - 9)
L1				
Buffer pH 3.0	2.96	2.96	2.97	2.96
Buffer pH 4.0	4.01	4.00	4.01	4.00
Buffer pH 7.0	6.99	7.02	7.00	6.99
L4				
Buffer pH 4.0	4.00	3.96	4.00	4.01
Buffer pH 7.0	7.00	7.06	7.01	7.04
L9				
Buffer pH 3.0	3.01	2.96	3.00	2.98
Buffer pH 7.0	7.00	7.03	7.00	7.02
Buffer pH 9.0	8.99	9.00	8.98	9.00
L10				
Buffer pH 4.0	4.01	3.98	4.00	4.01
Buffer pH 7.0	7.00	7.05	7.02	7.02
Extract of leather 3	3.77	3.77	3.83	3.85

and used the buffer solution of pH 4 as the lowest one.

3.6 Influence of electrode age

Another laboratory performed experiments on the influence of electrode aging and the procedure for the adjustment of the electrode system. The aqueous extracts of the four leather samples were measured in original state and after filtration (folded filter, medium filtration speed) always with a new and an old glass electrode. These were adjusted previously in two ways: one experimental variant used buffer solutions of pH values 3 and 7, the second buffer solutions of 4 and 7.

The performed tests did not indicate any statistically authoritative conclusion on the influence of the electrode age on the measurements.

4 CONCLUSIONS

The studies performed in the interlaboratory test on the determination of pH value and difference figure of the aqueous extract from leather facilitated the calculation of the precise parameters of the procedure, data not available presently in the standard. As a result an important orientation guide for self-assessment becomes available for the user of the procedure. Simultaneously, the obtained parameters display the performance of the procedure described in ISO 4045. It is advisable to include the precise parameters in the standard in the course of a revision.

At the same time, it was revealed that the reduction rate has no effect on the result under the conditions used. The filtration did not affect the results.

The standard defines a shaking rate of 50/min for a horizontal shaker. Other devices can be used if their shaking frequency is adjusted to the nominally specified shaker.

Water shall be used that is as poor in ions as possible, with a conductivity of $< 0.055 \mu\text{S/m}$ (resistance of $18.2 \text{ M}\Omega\text{cm}$). It is important to use the same water quality for the extraction, the subsequent measurement, including the determination of the difference figure, and that it is also at the same temperature.

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