In a comparative evaluation of seven procedures for determination of pH of paper, 55 different paper and pulp samples were used. Six procedures were based on cold extraction and subsequent determination of extract pH, either using a variety of combined pH electrodes or using a mixture of coloured acid/base indicators. One procedure involved impregnation of the sample with a solution of indicators and subsequent spectrophotometric determination of pH of air-dry samples.

The correlation of determinations showed that most extraction methods give comparable data for acidic samples, with the exception of gelatine surface-sized samples. For samples with alkaline aqueous extracts, the effect of atmospheric CO$_2$ and slow dissolution of earth-alkali metal carbonates should be taken into account, which is not the case with any of the standardised methods for determination of paper pH. Since CO$_2$ enters into equilibria as a weak acid, it will decrease the equilibrium pH of solutions of CaCO$_3$ and MgCO$_3$, the difference amounting to more than 1.5 pH units. A new procedure is therefore proposed for determination of pH of alkaline papers basing on rapid equilibration with CO$_2$ and dissolution of carbonates. The repeatability of determinations is satisfactory, providing data with standard deviation less than 0.15 pH units.

A discussion of the concept of paper pH follows, in view of the role of water content in air-dry paper and implications on stability of paper. The different procedures are compared in view of sample consumption, measurement repeatability and systematic error.

1 Introduction

Of all paper properties, acidity/alkalinity is probably the crucial one for stability of its most important structural element, the cellulose. It is well known that in an acidic environment, the dominant degradation mechanism of cellulose is acid hydrolysis, and in an alkaline environment, two reaction pathways, oxidation and alkaline degrada-
Paper acidity/alkalinity could be estimated using some arbitrary procedure, e.g. by extraction and subsequent titration. Such methods were proposed quite early. However, the term paper pH was also early to emerge and methods of its estimation compared almost at the same time as, coincidentally, the term pH was finally consistently defined. The content of acidic or alkaline salts in the material may seem to be closely related with pH, yet pH is intended to be a measure of the activity of hydrogen ions in solution:

\[
pH = -\log a_H = -\log \left( \frac{m_H \gamma_H}{m^0} \right)
\]

where \(a_H\) is the relative activity, \(\gamma_H\) is the molal activity coefficient of the hydrogen ion \(H^+\) at the molality \(m_H\), and \(m^0\) is the standard molality. It also depends on the standard state activity. In aqueous solutions the standard state of hydrogen ion is at infinite dilution.

Thus, pH is defined in terms of a quantity that cannot be measured by any method. In practice, measurements depend on calibration of the electrode system. According to the operational definition of pH, the pH of a test solution \(pH_s\) is obtained from the difference of the electromotive forces \(E_s\) and \(E_t\) of two equal potentiometric cells, of which one contains a standard reference solution \(S\) of known pH:

\[
\text{pH}_s = \text{pH}_t + \left( E_s - E_t \right) / k,
\]

where \(k\) is the practical Nernst slope of the electrode system, ignoring the difference in the residual junction potential \(E_{\text{j}}\). To ensure a reliable pH measurement in practice, a potentiometric cell consisting of a glass and a reference electrode is standardised with pH buffers in accordance with IUPAC rules and using NIST primary standard buffer substances. This procedure can be applied also for mixtures of water/organic solvent, where the standard state for \(a_H\) is conditioned by buffers prepared in an adequate solvent mixture.

Since Browning, several comparative evaluations of methods for determination of paper pH were published and comparable values were obtained for acidic papers using most methods.

All comparisons, however, were performed with too small sample sets (usually 5-15) with too small variabiliy of parameters, e.g. type of sizing, raw material, additives etc., an exception being the paper stability study by Bansa and Hofer with 22 samples described, including measurements of pH using three methodologies. The effect of non-homogeneity of aged samples on repeatability should be evaluated as most standard methods, e.g. cold extraction (TAPPI T 509 om-02, ASTM D778-97(2002)), hot extraction (TAPPI T 435 om-02, ASTM D778-97(2002)) or surface (TAPPI T 529 om-99) pH determination specify that repeatability is from 0.1 (acidic papers) to 0.3 (alkaline papers) pH units. Furthermore, in order to provide an estimation of pH of alkaline papers, the effect of atmospheric CO₂ on the pH measurement and on the actual pH in alkaline papers should be evaluated.

2 Experimental

2.1 Paper samples

A description of papers and pulps used in the study are given in Table 1, together with the type of raw material used in paper production, determined according to SCAN-G3:90 and SCAN-G4:90 standards. From books, only paper parts without print were used.

Deacidified samples were prepared by immersion in aqueous solutions of 0.04 mol L⁻¹ Mg(HCO₃)₂ or 0.01 mol L⁻¹ Ca(HCO₃)₂ for 30 min. Samples were equilibrated at room conditions prior to use.

2.2 Determination of pH

The electrodes were calibrated with citrate/HCl (pH 4.00) and boric acid/KCl/NaOH (pH 10.00, Sigma-Aldrich, Germany) buffers. The latter buffer was used up to one month. The pH-meter Metrohm 691 (Metrohm, Herisau, Switzerland) was used with the following electrodes:

- flat combined pH electrode (Metrohm 6,0227.100, pH 0-14, 0-80 °C),
- macro combined pH electrode (Metrohm 6,0233.100, pH 0-14, 0-80 °C),
- combined pH electrode "aquatrode" (Metrohm 6,0253.100, pH 0-13, 0-60 °C),
- pointed semi-micro combined pH electrode (Metrohm 6,0236.100, pH 0-14, 0-80 °C),
- micro combined pH electrode (MI-415-2cm, Microelectrodes Inc., Bedford, USA).

The electrodes used are presented on Fig. 1.

Additionally purified deionised MilliQ water (Millipore, Molsheim, France) was used for the preparation of all solutions and extractions. Samples were defibrillated in a reaction tube (16x100 mm) using a Proxxon precision hand drill with a stand (Minimot 100/P, Niersbach).
Table 1: Samples of paper and pulp. Where available, the source and date are provided. Where indicated, the concentration of phosphate buffer was 0.1 mol L\(^{-1}\). Asterisk denotes a historical sample, no additional data available.

<table>
<thead>
<tr>
<th>No.</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Book, 1938, 100% sulphite softwood pulp</td>
</tr>
<tr>
<td>2</td>
<td>Book, 1992, 50% groundwood, 50% sulphite softwood pulp</td>
</tr>
<tr>
<td>3</td>
<td>Book, 1874, 50% groundwood, 50% sulphite softwood pulp</td>
</tr>
<tr>
<td>4</td>
<td>Book, 1957, 60% groundwood, 40% sulphite softwood pulp</td>
</tr>
<tr>
<td>5</td>
<td>Book, 1940, 70% groundwood, 30% sulphite softwood pulp</td>
</tr>
<tr>
<td>6</td>
<td>Book, 1984, 50% bleached hardwood kraft pulp, 50% bleached sulphite softwood pulp</td>
</tr>
<tr>
<td>7</td>
<td>Book, 1982, 20% bleached hardwood kraft pulp, 80% bleached sulphite softwood pulp</td>
</tr>
<tr>
<td>8</td>
<td>Book, 1870, 70% cotton pulp, 30% annuals (alkaline wheat straw)</td>
</tr>
<tr>
<td>9</td>
<td>Book, 1922, 70% groundwood, 30% sulphite pulp</td>
</tr>
<tr>
<td>10</td>
<td>Book, 2002, 70% bleached hardwood kraft pulp, 30% bleached sulphate softwood pulp</td>
</tr>
<tr>
<td>11</td>
<td>Book, 1951, 50% groundwood, 50% sulphite pulp</td>
</tr>
<tr>
<td>12</td>
<td>Book, 1951, 60% groundwood, 40% sulphite pulp</td>
</tr>
<tr>
<td>13</td>
<td>Book, 1930, 60% groundwood, 40% sulphite pulp</td>
</tr>
<tr>
<td>14</td>
<td>Book, 1960, 50% groundwood, 50% sulphite softwood pulp</td>
</tr>
<tr>
<td>15</td>
<td>Book, 1990, 75% groundwood, 25% bleached sulphite softwood pulp</td>
</tr>
<tr>
<td>16</td>
<td>Book, 1986, 50% groundwood, 50% kraft pulp (softwood/hardwood = 1/1)</td>
</tr>
<tr>
<td>17</td>
<td>Newspaper, 2003, 60% groundwood, 40% recycled fibres</td>
</tr>
<tr>
<td>18</td>
<td>Filter paper Whatman No. 1 (Maidstone, UK), 2001, 100% cotton</td>
</tr>
<tr>
<td>19</td>
<td>Bleached softwood sulphate pulp (Pols, Austria), 2001</td>
</tr>
<tr>
<td>20</td>
<td>Cotton pulp (Radzice, Slovenia), 2001, 100% cotton</td>
</tr>
<tr>
<td>21</td>
<td>Sample 18, decacidified with Ca(HCO(_3))(_2)</td>
</tr>
<tr>
<td>22</td>
<td>Sample 19, decacidified with Ca(HCO(_3))(_2)</td>
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<tr>
<td>23</td>
<td>Sample 20, decacidified with Ca(HCO(_3))(_2)</td>
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<tr>
<td>24</td>
<td>Sample 18, decacidified with Mg(HCO(_3))(_2)</td>
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<tr>
<td>25</td>
<td>Sample 19, decacidified with Mg(HCO(_3))(_2)</td>
</tr>
<tr>
<td>26</td>
<td>Sample 20, decacidified with Mg(HCO(_3))(_2)</td>
</tr>
<tr>
<td>27</td>
<td>Sample 18, immersed in phosphate buffer, pH = 11</td>
</tr>
<tr>
<td>28</td>
<td>Sample 18, immersed in phosphate buffer, pH = 9</td>
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<td>29</td>
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<td>32</td>
<td>Sample 18, immersed in phosphate buffer, pH = 10.5</td>
</tr>
<tr>
<td>33</td>
<td>Sample 18, immersed in phosphate buffer, pH = 9.5</td>
</tr>
<tr>
<td>34</td>
<td>Rag paper (surface sized), 1800, 100% cotton</td>
</tr>
<tr>
<td>35</td>
<td>Rag paper (surface sized), 2001, 100% cotton</td>
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<tr>
<td>36</td>
<td>Rag paper (surface sized), 2001, 100% cotton</td>
</tr>
<tr>
<td>37</td>
<td>Rag paper (surface sized), 2001, 100% cotton</td>
</tr>
<tr>
<td>38</td>
<td>Rag paper (surface sized), 2001, 100% cotton</td>
</tr>
<tr>
<td>39</td>
<td>Paper, 19th century(\ast), 100% cotton</td>
</tr>
<tr>
<td>40</td>
<td>Paper, 19th century(\ast), 100% cotton</td>
</tr>
<tr>
<td>41</td>
<td>Paper, 19th century(\ast), 100% cotton</td>
</tr>
<tr>
<td>42</td>
<td>Paper, 19th century(\ast), 100% cotton</td>
</tr>
<tr>
<td>43</td>
<td>Paper, 19th century(\ast), 100% bleached sulphite soft wood pulp</td>
</tr>
<tr>
<td>44</td>
<td>Paper, 19th century(\ast), 100% cotton</td>
</tr>
<tr>
<td>45</td>
<td>Paper, 19th century(\ast), 50% cotton, 50% alkaline straw pulp</td>
</tr>
<tr>
<td>46</td>
<td>Rag paper (surface sized)(\ast), 100% cotton</td>
</tr>
<tr>
<td>47</td>
<td>Rag paper (surface sized)(\ast), 100% cotton</td>
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<tr>
<td>48</td>
<td>Rag paper (surface sized)(\ast), 100% cotton</td>
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<tr>
<td>49</td>
<td>Rag paper (surface sized)(\ast), 100% cotton</td>
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<td>50</td>
<td>Rag paper (surface sized)(\ast), 100% cotton</td>
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<td>51</td>
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<td>52</td>
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<td>53</td>
<td>Rag paper (surface sized)(\ast), 100% cotton</td>
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<tr>
<td>54</td>
<td>Rag paper (surface sized)(\ast), 100% cotton</td>
</tr>
<tr>
<td>55</td>
<td>Rag paper (surface sized)(\ast), 100% cotton</td>
</tr>
</tbody>
</table>

What is the pH of alkaline paper?, e-PS, 2004, 1, 35-47
Samples are weighed (0.0700 ± 0.005 g) into reaction tubes and 5 mL MilliQ water is added, previously aerated for 30 min in order to obtain a CO$_2$-saturated solution (for samples with pH > 7). Defibrillation and mixing (25,000 r.p.m.) should last 15 min for samples with alkaline pH, and only until a homogeneous pulp is obtained for acidic samples. The pointed semi-micro combined pH electrode was used. The results are an average of 5 determinations.

Samples were cut out with a perpendicularly cut and sharpened surgical needle of inner diameter 0.8 mm. The average weight of such samples depended on the grammage of a particular paper, and was approximately 30-50 µg. Aerated water was added (2 µL) and the pH was determined once the reading stabilised (after max. 5 min).

To samples of size approximately 2×4 cm, 5 µL of a neutralised equimolar mixture of coloured acid/base indicators (phenolphthalein, bromothymol blue, bromocresol green, bromophenol red) prepared in methanol (2 mmol L$^{-1}$) was added. For the neutralisation of 4 mL of the indicator solution in methanol, 70 µL of Na$_2$CO$_3$ solution in water ($c = 20$ mmol L$^{-1}$) was needed. The samples were dried and equilibrated at room conditions prior to use. From the VIS reflectance spectra of sample areas, background spectra were subtracted, and the ratio of absorbances at 440 and 590 nm was used to obtain a calibration line. The results are an average of 7 determinations.

3 Results and Discussion

3.1 Evaluation of the existing procedures

In order to evaluate the statistical parameters of the “Standard” method, several different combined pH electrodes were used. Deming regression analysis was used in order to take into account the statistical errors of both methods under comparison, as expressed with standard deviation (S.D.). The regression lines

\[ y_{\text{method}} = k \cdot x_{\text{method}} + n \]

should, in the optimal case, have the following properties $k = 1$, $n = 0$, correlation coefficient $R = 1$. In the comparisons to follow, the determinations using a common macro combined pH glass electrode according to the “Standard” method were used as reference.

The data show that there is no difference in the determinations if different types of electrodes are used (flat combined pH electrode - Fig. 2, “aquatrode” - Fig. 3), as the correlation parameters $k$, $n$, and $R$ are not significantly different from the ideal. It is especially interesting that using the electrode, designed for determination of pH in solutions of low ionic strength, pH determinations are identical, leading to the conclusion that ionic strength in aqueous paper (and pulp, in the case of samples 18, 19, 20) extracts is not critically low.

The samples, as can be judged using the “Standard” method, are homogeneous - however, it should be taken into account that the sample mass used is 1 g. For 7 determinations, the standard deviation is lower than 0.10 pH unit for most samples (Fig. 4), the repeatability is therefore excellent, even in the region of alkaline pH extracts.

It is advisable to round up determinations by the “Standard” method to the nearest 0.1 pH unit,
bearing in mind the repeatability being in the same range.

The "Standard" procedure, despite the excellent reproducibility of measurements, should be re-evaluated due to the following concerns. According to different standards, mixing is either prescribed or not - given the low solubility of alkaline fillers (e.g., carbonates), the mode and time of extraction does not seem to be adequate. This may not be of concern for acidic samples. Indeed, the mode of sample preparation turns out to be critical as soon as two essentially different procedures of pH determination are compared. Extraction of well soluble compounds in a small amount of water and subsequent determination of pH using a flat combined pH electrode is referred to as "Surface" method. Saveryns et al.\textsuperscript{11} found out that the amount of added water may be critical - in our case, we followed closely the standard procedure (Tappi 529 om-88).

In Fig. 5, a comparison of pH determinations obtained with the "Surface" and the "Standard" method is presented. A satisfactory correlation is obtained ($R^2 = 0.9722$), with the slope close to ideal. However, the results of the "Surface" method are systematically too low for 0.84 pH units. This was not noticed in earlier comparisons\textsuperscript{4-16} in which the correlations were less satisfactory, anyway. In a more recent study\textsuperscript{11}, a fairly good correlation was obtained, however, the bias (calculated here), is -0.14 pH units ($N = 12$, $R^2 = 0.9604$). In the work by Bansa and Hofer\textsuperscript{12}, the error is -2.1 pH units ($N = 22$, $R^2 = 0.7586$). In the work by Brandis\textsuperscript{10}, a negative systematic error for flat-electrode surface pH estimations ("Surface" method) is also present if compared to cold extraction methods ("Standard" method), yet due to unavailability of original data, it cannot be calculated here. This indicates that by pressing the electrode against paper surface, the possibly charged fibres and particles influence the electric field at the electrode surface (suspension effect\textsuperscript{17}), causing the readings to be too low. Both charged functional groups on macromolecules and particles, and an unattained equilibrium with the added aqueous phase may account for the systematic error.

Despite the error, surface measurements give a good estimation of paper pH, which can be validated using the standard cold extraction methods (TAPPI T 509 om-02, ASTM D778-97(2002)). For use on historical paper samples, it is more recommendable than the "Standard" method, for which a large sample is needed, and which is destructive. Although not perceived as such, the "Surface" method is also destructive, as in order to perform the measurement, a spot of diameter at least 2 cm must be wetted, which will unavoidably lead to migration of soluble compounds to the edges of the spot, leaving non-aesthetic marks, and possibly leading to a more rapid degradation along the so-called "tide-lines"\textsuperscript{18}.

From the correlation shown in Fig. 5, samples 10, 17, 20-23 were excluded. For these samples, a higher content of CaCO$_3$ was determined or even added, indicating that at least for a large group of paper samples (represented by contemporary paper and historical rag paper), the "Surface" method will give data about 2 pH units too low. Sample 20, although cotton pulp, is unusually alkaline which might reflect the alkaline production process. This indicates that determination of pH of alkaline papers requires a thorough re-examination of the methods available.

Another property of the "Surface" method can be outlined (Fig. 6). The standard deviations ($N = 7$) are much bigger than with the "Standard" method, and also seem to depend on sample pH, indicat-
cially not for acidic samples), but rather for its approximate estimation. Afurther property of the "Pen" method is that for gelatine surface-sized papers, it will give estimations 1.5-3.5 pH units too low (samples 35-45). This should be taken into account when historical rag papers of approximately neutral bulk pH are analysed - the estimations may be severely underestimated.

3.2 The role of atmospheric CO$_2$

From the results, especially those presented in Fig. 5, it seems that the slow dissolution and low solubility of alkali-earth metal carbonates should be taken into account if a more realistic determination of alkaline paper pH is attempted. Since atmospheric CO$_2$ enters the dissolution and, consequentially, the equilibrium affects pH (also in paper in real situations), it cannot be disregarded. In both most frequently used and standardised methods, the time to achieve equilibrium seems to be too short (i.e. 1 h or a few minutes in the "Standard" or the "Surface" method, respectively). CO$_2$ will, due to the acid-base equilibrium:

$$\text{CO}_2 + \text{H}_2\text{O} \rightarrow \text{H}_2\text{CO}_3 \rightarrow \text{H}^+ + \text{HCO}_3^-$$

act as a weak acid in aqueous solutions, and due to the high solubility of Ca(HCO$_3$)$_2$ and Mg(HCO$_3$)$_2$, as compared to CaCO$_3$ and MgCO$_3$, more of the respective carbonates will dissolve if atmospheric CO$_2$ is given free access.

While the equilibrium solubility is a parameter depending on temperature and atmospheric pressure, the rate with which carbonates will dissolve depends on a variety of other less controllable parameters, e.g. size and shape of carbonate particles, rate and type of mixing, etc. In Fig. 8, pH of suspensions of CaCO$_3$ and MgCO$_3$ was fol-
allowed continuously. Both dry samples were powders and in a large excess to saturation.

The initial pH of of CaCO$_3$ and MgCO$_3$ solutions (10 and 10.5, respectively) corresponds to the theoretical pH of saturated aqueous solutions in the absence of CO$_2$, i.e. 9.95 and 10.45, respectively. Since MgCO$_3$ is more soluble the initial pH is approximately 0.5 pH unit higher. With the absorption of atmospheric CO$_2$ pH decreases due to the neutralisation reaction:

$$\text{MgCO}_3 + \text{CO}_2 + \text{H}_2\text{O} \rightleftharpoons \text{Mg(HCO}_3)_2 \rightleftharpoons \text{Mg}^{2+} + 2\text{HCO}_3^{-},$$

and analogously for CaCO$_3$.

The final pH of saturated solutions with access of CO$_2$ was in the case of CaCO$_3$ 8.35 (S.D. = 0.09, N = 3, time to reach the equilibrium: 1 day), and in the case of MgCO$_3$ 9.35 (S.D. = 0.08, N = 3, time to reach the equilibrium: 3 days). For a saturated CaCO$_3$ solution the actual pH corresponds to the pH of a solution of HCO$_3^-$ with a negligible concentration of CO$_3^{2-}$, which can be calculated from $pK_a$ values for H$_2$CO$_3$ ($pK_{a1} = 6.4, pK_{a2} = 10.2$). In the case of MgCO$_3$, the pH of its saturated solution is higher and indicates a mixture of CO$_3^{2-}$ and HCO$_3^-$. Taking into account the pH and the $pK_a$ values, it can be estimated that only a small amount of CO$_3^{2-}$ is present in both solutions, and HCO$_3^-$ can be titrated using the usual neutralisation titration. The titrations show that in a saturated solution of Ca(HCO$_3$)$_2$ the concentration of hydrogen carbonate is 1.34 mM (S.D. = 0.04, N = 3) and of Mg(HCO$_3$)$_2$ the concentration of hydrogen carbonate is 9.9 mM (S.D. = 0.1, N = 3). The solubility of MgCO$_3$ is higher, which is well-known, but the process of dissolution proceeds more slowly.

This result explains why CaCO$_3$-containing papers in Fig. 5 give apparently low readings with the "Surface" method. Given that CaCO$_3$ dissolves more quickly if CO$_2$ has access to the system, the equilibrium is achieved more easily if the "Surface" method is applied than if "Standard" method is applied. The transport of CO$_2$ through the water surface is apparently much too small if no mixing is applied.

### 3.3 Equilibrium pH

Since the dissolution of CaCO$_3$ and MgCO$_3$ is slow and is certainly not finished within one hour, as required by the "Standard" method, the question appears, what is the overestimation of pH of alkaline papers using methods, which do not take into account the role of atmospheric CO$_2$. The pH of samples, prepared according to the "Standard" method was therefore continuously followed for a prolonged period of time of several days (Fig. 9). Constant mixing was assured to enable a better access and transport of CO$_2$ through the phase boundary.

In Fig. 9, the trends of achieving equilibrium are evident. Extracts of acidic samples barely change their pH throughout the experiment, while alkaline samples achieve the equilibrium fairly slowly, most only after 24 h, in several cases even after longer periods. Gelatine surface-sized samples are another interesting group of samples, with a changing pH of the aqueous extract - in most cases an equilibrium is obtained only after 24 h, and may differ considerably from the initial reading. Regarding the "Equilibrium" method, gelatine sizing may be problematic from two points of view: silver ions, leaching from the reference electrode, may precipitate with proteins on the frit, and the resulting clogging may render the readings inaccurate. Furthermore, microbial degradation of samples, starting after sample wetting may result in the same effect.

Sample 7 is an interesting outlier - the only initially fairly acidic sample, whose pH of extract...
3.4 The "Proposed" method

Although for acidic samples the mass/sample/volume liquid ratio was already optimised as the standard procedures were agreed upon, the same might not apply to alkaline paper samples. An optimisation of the mass/sample/volume liquid ratio was therefore performed. To 5 mL MilliQ water in a sample tube, 0.0140 (same ratio as in the "Standard" method), 0.0280, 0.0600, 0.1400 or 0.2000 g of sample were added.

The samples were defibrillated using a mixing rod at 25,000 r.p.m. After a homogeneous pulp was obtained, the pH was determined using two procedures:
- using a pointed semi-micro combined pH electrode in the sample pulp
- using a flat-surface combined pH electrode in the supernatant extract after centrifugation

It is obvious that neither the "Standard" nor the "Surface" method provide data that would take into account the effect of CO₂ and thus mirror the situation in alkaline paper samples more realistically. Since the "Equilibrium" method is far too time-consuming, a new and simple procedure for determination of pH is needed for routine analysis.
From the data presented in Fig. 11 it is obvious that the variations in determinations are fairly small, smaller than the repeatability of pH determination according to the "Equilibrium" method (Table 2). The difference between pH determinations using the smallest and the biggest \(m/V\) ratio is not significant. This is important, as working with a very big \(m/V\) ratio is difficult due to the very high amount of sample added. At a smaller \(m/V\) ratio, sample consumption may be fairly small, and even less is needed if an amount of water less than 5 mL is taken.

A further comparison of determinations of pH for both types of electrode (Fig. 12) indicates that the pointed electrode is not prone to a suspension error, as it gives readings equal to those obtained using the flat-surface electrode in the supernatant extract. For further optimisation, it was therefore decided that the pointed semi-micro combined pH electrode would be used at the \(m_{\text{sample}}/V_{\text{H2O}}\) ratio 0.0140 g/mL.

The pH determinations obtained at \(m_{\text{sample}}/V_{\text{H2O}}\) ratio 0.0140 g/mL can now be compared with the determinations using the "Standard" method. As evident from the correlation presented in Fig. 13, nothing was yet achieved regarding equilibration with atmospheric CO\(_2\), as the determinations are still equal and the determined pH of alkaline samples is still too high. Only sample no. 7 obviously equilibrates even after a very short period of mixing (cf. Fig. 10).

Since mixing (25,000 r.p.m.) accelerates the absorption of atmospheric CO\(_2\), its duration needs to be optimised. Additionally, MilliQ water used for the preparation of extracts was aerated for 15 min to obtain a saturated CO\(_2\) solution. Two typical samples were used, purified cotton pulp, deacidified using Ca(HCO\(_3\)\(_2\)) - sample 21, and the one deacidified using Mg(HCO\(_3\)\(_2\)) - sample 24. From the results presented in Fig. 14, it can be concluded that equilibration is rapid with samples containing CaCO\(_3\), while longer mixing is needed to dissolve an equilibrium quantity of MgCO\(_3\).

With the optimised "Proposed" procedure, a remarkable correlation is evident with the determinations using the "Equilibrium" method (Fig. 15). In the correlation, all samples are included, even the gelatine surface-sized samples, although these samples are not homogeneous. With the optimised extraction procedure, a rapid equilibration with atmospheric CO\(_2\) can be achieved to enable routine determination of sample pH using the "Proposed" method.

Repeatability of determinations with the "Proposed" method is remarkably high - S.D. for most samples is below 0.1 pH unit (Fig. 16). It is therefore advisable to round up determinations by the "Proposed" method to the nearest 0.1 pH unit.
3.6 The "Colourimetric" method

Due to the acid-base equilibria, in which they take part, changes of spectroscopic properties of pH-sensitive molecular probes ("indicators") indicate the pH of their environment. As they may be able to penetrate the regions of lower crystallinity, a more realistic estimation of pH may thus be tolerable.

For calibration, a series of pure cellulose sheets was prepared, immersed in a series of phosphate

3.5 The "Micro" method

Using hollow needles, "micro"-sampling has become a popular method of obtaining small samples of paper in conservation science\textsuperscript{11}. The samples can be fairly small, down to 100 µm or even less in diameter, and the damage conferred to an object of historical values due to sampling may thus be tolerable.

Downsizing of pH determination using "micro"-sampling was already attempted by Saverwyns et al.\textsuperscript{11}. A correlation of his data with a standard extraction procedure shows a very convincing correlation factor ($R^2 = 0.9600$, $N = 16$).

In our study, we added 2 µL of water, saturated with atmospheric CO$_2$, to a sample of diameter 0.8 mm, and determined the pH once the reading stabilised. At least 3-5 determinations were performed per sample. In our study of 55 samples (Fig. 17), the correlation is less satisfactory ($R^2 = 0.8336$), but it should be noted that the repeatability was in our case extremely low and standard deviations of up to 1.5 pH unit are not exceptional (Fig. 18), most being up to 0.5 pH units. Such low repeatabilities are not surprising, given the heterogeneity of real samples, as demonstrated by Saverwyns et al.\textsuperscript{11}

In any case, the "Micro" method of pH determination is a welcome addition to the collection of possible procedures. However, if an average value of pH of a larger sample is needed, it is inevitable that several samples are taken until an acceptable standard deviation is obtained. It is advisable to round up determinations by the "Micro" method to the nearest 0.5 pH unit, bearing in mind the repeatability being in the range of 0.5 pH units (Fig. 18).

Again, a large underestimation of pH of heavily gelatine surface-sized papers (samples 49-52 in Fig. 17) is possible, up to a few pH units.

4.3 The "Colourimetric" method

Due to the acid-base equilibria, in which they take part, changes of spectroscopic properties of pH-sensitive molecular probes ("indicators") indicate the pH of their environment. As they may be able to penetrate the regions of lower crystallinity, a more realistic estimation of pH may be obtained, especially if no additional water needs to be added (as in the "Pen" method).

For calibration, a series of pure cellulose sheets was prepared, immersed in a series of phosphate
buffers (0.1 mol L\(^{-1}\), samples 27-31) of nominal pH 3, 5, 7, 9, 11, and dried. The pH of these samples was then determined according to the "Standard" method and according to the "Proposed" method, which are illustrated in Fig. 19. Although the solubility of phosphates is high, the slow equilibration with atmospheric CO\(_2\) leads to no curvature of the calibration curve for the "Standard" method, while the role of CO\(_2\) is well expressed in determinations according to the "Proposed" method, where there is no significant difference between samples 27 (immersed in buffer of pH 11) and 28 (immersed in buffer of pH 9).

It becomes immediately evident that determinations obtained by any spectroscopic method will ultimately depend on the type of calibration, i.e. validation against a chosen potentiometric method (Fig. 19).

As the most appropriate way to quantify changes in reflectance spectra, once the background spectra are subtracted, a ratio of absorbances at two wavelengths was chosen instead of a single absorbance at some selected wavelength. In this way, small variations in the amount of indicator applied cancel out. The ratio of absorbances at 590 and 440 nm turned out to provide the best sensitivity (i.e. \(\Delta(A_{590}/A_{440})/\Delta \text{pH}\)). The calibration curve (with the "Proposed" method used to obtain pH values) can be described with the following equation:

\[
pH = 8.0194 \left( \frac{A_{590}/A_{440} - 0.01568}{3.72361 - A_{590}/A_{440}} \right)^{0.11007},
\]

and is presented in Fig. 20.

Fig. 20: Calibration curve for determination of pH according to the "Colourimetric" method.

Fig. 19: Correlation of determinations of pH of phosphate buffer-containing samples (nos. 27-31) with the "Standard" and the "Proposed" method with the nominal buffer pH. The correlation was calculated for data obtained by the "Standard" method.

Taking into account the nature of the calibration curve, data scatter should be highest in the regions pH > 10 and pH < 5. However, since coloured substances, contained in the matrix of degraded papers, may be washed away from the measured spot using the methanol solution of indicators, the background may not be representative, so some further data scatter is expected due to this reason.

The correlation between the "Colourimetric" and the "Proposed" method is, however, still not satisfactory (Fig. 21). The data scatter is high and parameters \(k\) and \(n\) are far from ideal. This mirrors the fact that a comparatively high amount of indicator has to be introduced in the cellulosic matrix in order to obtain a measurable signal. Since the indicator influences the acid-base equilibrium by consuming hydrogen ions in acidic samples and hydroxyl ions in alkaline samples, the slope of the regression line is less than 1.

3.7 Further considerations

As briefly outlined in the Introduction, pH is intended to be a measure of the activity of hydrogen ions in solution. With paper being a heterogeneous system, we see little chance for a consistent definition of paper pH. Tentatively, paper pH may be defined in terms of activity of hydro-
gen ions in the paper matrix; however, it is inevitable that the content of water must be sufficient, so that dissociation, hydration and mobility of ionic compounds is possible. In amorphous cellulose, the content of water may be up to 18%1, whereas in crystalline regions it is considerably less. According to recent NMR studies, if the content of water in paper is <3%, the molecules are practically immobile. However, if the content is >9%, there is evidence of a condensed water phase, which means that it becomes available to all potential chemical reactions19. Since the content of water in a cellulose fibre is a distributed property, paper pH will be a distributed (or localised) property, as well.

Paper additives and functional groups bound to a cellulose macromolecule may also lead to pH distribution. It was demonstrated that pH inside a fibre may be considerably lower (4 pH units) than in its vicinity due to non-extractable macromolecular acids. However, if the authors used 0.1 mol L⁻¹ NaCl as the extraction medium, the electrolyte caused redistribution of hydrogen ions leading to an overall equal pH in the fibre and in the extraction medium20. Additives in paper might therefore have a similar effect.

Considering that in cellulose the content of water with sufficient mobility and activity is low, it is likely that it is saturated with soluble solids surrounding the fibres. If their amount is sufficient to keep the ionic balance in solution stable, an addition of water to enable a potentiometric determination of pH is possible. All extraction methods of paper pH estimation are actually based on this assumption, although the amount of water, its temperature, and the type of electrode may vary. With extraction methods, activity of hydrogen ions is determined in solutions in which the ionic balance is imposed by equilibration with the composite material (paper), so that in effect, averaging is done. Such values may be defined as operational pH.

On the other hand, the activity of solvated hydrogen ions in the cellulosic matrix is strongly influenced by local water and electrolyte concentrations, forming liquid junctions and possibly bridging cooperating active sites. With increased water content, reaction channels open up with increased water content, that were unavailable with additives in quiescent solid form due to their lower mobility and insufficient amount of water for proper solvation. Taking into account the equation given in Introduction, it is therefore likely that the topical pH in cellulosic fibres will be higher than values determined in paper extracts. With a molar activity coefficient γ₄H⁺ = 0.9, the pH will be higher by 0.05 pH units, and values higher by 1.5 (γ₄H⁺ = 0.05) pH units can easily be expected in the case of low humidity and consequentially low water content in the paper under observation. It is therefore clear that topical pH of paper depends on the water content of the material. This conclusion is of immense importance in studies of stability of paper.

In line with the above considerations, any methodology, unable to provide a picture of hydrogen ion activity distribution along the whole structure of fibres and additives at laboratory environmental conditions, will give an averaged value of paper pH. Such a value (operational value of pH) may be sufficient for a number of applications. Additionally, since paper pH will depend on its water content and this in turn depends on the humidity of the surrounding atmosphere, it is difficult, if not impossible, to determine the true value and estimate the accuracy of any paper pH measurement. Determination of paper pH therefore remains, until proper nano-size pH-sensitive probes are available, a matter of an arbitrary procedure.

4 Conclusions

Determination of operational pH is relatively straightforward if paper samples are acidic. For such samples, all extraction procedures will give data in good agreement with the standard cold extraction procedure. Irrespective of the fact that the true pH of paper is difficult to determine, we believe that CO₂ should be taken into account when determining pH of alkaline paper. As with the present standard methods, this is not the case, a new method is proposed.

If samples are alkaline, the following can be concluded:

- If the duration of extraction is too short or if the mixing is not adequate, the slow dissolution of alkali-earth metal carbonates and the slow absorption of atmospheric CO₂ will not allow for proper equilibrium to be achieved. Determinations of pH of such alkaline extracts according to the standard extraction methods will lead to pH values which may be up to 1.5 pH units too high. The repeatability is still below 0.15 pH units, yet sample consumption is high: 1 g is needed.
- With the surface method, the repeatability is lower, up to 0.30 pH units, yet this may also reflect sample inhomogeneity. The time of dissolution and the amount of water are sufficient for rapid dissolution of the equilibrium amount of CaCO₃, the pH of such samples determined by the surface method will therefore not correlate with the measurements obtained by the cold extraction procedure. Determination of surface pH cannot be considered as a non-destructive method, due to marks left at the edge of the wetted part of paper, along which paper degradation proceeds faster. Gelatine used as surface sizing
leads to low values of surface pH of otherwise neutral to moderately alkaline papers.

- If using the standard cold extraction procedure, the time to achieve equilibrium is excessively long especially in the case of MgCO₃-containing papers yet it can be shortened to 15 min if intensive mixing is used. Having optimised the type of mixing and the sample to water ratio, we propose a new procedure. Using this new procedure, pH of CaCO₃-containing pulps was determined to be approx. 8.5, and the pH of MgCO₃-containing pulps approx. 9.5. In paper, the type and amount of additives may influence these values considerably. Repeatability of determinations using the proposed procedure is lower than 0.12 pH units, the amount of sample needed is 0.07 g.

- Miniaturisation of the procedure using micro-combined pH electrodes leads to a satisfactory correlation with the proposed method, yet with lower repeatability: values of 1.0 pH unit are acceptable. The amount of sample needed for such determination is low (circular cut of diameter <1 mm), yet several samples are needed to obtain a satisfactory average value.

- Determination of pH using pH pens may provide rough estimations, with errors up to several pH units. Caution should be taken especially if degraded, intensively yellow papers are under observation, as colour evaluation of the indicator is then difficult.

- If a solution of appropriate coloured acid/base pH indicators is added to paper, dried, and the reflectance spectrum of the spot is determined, the resulting spectra correlate with sample pH. The correlation depends on the choice of calibration standards. Furthermore, washing out the coloured degradation products may lead to erroneous results.

- Due to the slow dissolution of alkali-earth metal carbonates, rapid changes in relative atmospheric humidity and the resulting changes of water content in paper lead to fluctuations in local pH. This should be taken into account in paper stability studies.

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