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REVIEW

SHORT COMMUNICATION

WHAT IS THE pH OF ALKALINE PAPER?

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Abstract

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-

tion are predominant[1]. The amount of literature published on the stability of paper-based materials in the recent years[2] demonstrates a need to understand the degradation phenomena better, therefore an estimation of paper acidity/alkalinity is a pre-requisite. In addition, the decision for any chemical treatment with the aim to prolong paper lifetime is based on such estimation. Considering the role of this parameter also in the permanent paper standards (ANSI/NISO Z39.48, ISO 9706, ISO 11108), its proper determination is of primary importance.

Paper acidity/alkalinity could be estimated using some arbitrary procedure, *e.g.* by extraction and subsequent titration. Such methods were proposed quite early[3]. However, the term *paper* pH was also early to emerge and methods of its estimation compared[4] almost at the same time as, coincidentally, the term pH was finally consistently defined[5]. 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*[6]:

$$pH = -\log a_H = -\log\left(\frac{m_H \cdot \gamma_H}{m^o}\right),$$

where a_H is the relative activity, γ_H is the molal activity coefficient of the hydrogen ion H^+ at the molality m_H, and m^o 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_t 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_S:

$$pH_t = pH_S + (E_s - E_t) / k,$$

where k is the practical Nernst slope of the electrode system, ignoring the difference in the residual junction potential (E_{jt}-E_{jS}). 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[7].

Since Browning[8], several comparative evaluations of methods for determination of paper pH were published[9-11] 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 variability of parameters, *e.g.* type of sizing, raw material, additives *etc.*, an exception being the paper stability study by Bansa and Hofer[12] 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 CO_2 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} $Mg(HCO_3)_2$ or 0.01 mol L^{-1} $Ca(HCO_3)_2$ 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,

No.	Description
1	Book, 1938, 100% sulphite softwood pulp
2	Book, 1902, 50% groundwood, 50% sulphite softwood pulp
3	Book, 1874, 50% groundwood, 50% sulphite softwood pulp
4	Book, 1957, 60% groundwood, 40% sulphite softwood pulp
5	Book, 1940, 70% groundwood, 30% sulphite softwood pulp
6	Book, 1984, 50% bleached hardwood kraft pulp, 50% bleached sulphite softwood pulp
7	Book, 1962, 20% bleached hardwood kraft pulp, 80% bleached sulphite softwood pulp
8	Book, 1870, 70% cotton pulp, 30% annuals (alkaline wheat straw)
9	Book, 1922, 70% groundwood, 30% sulphite pulp
10	Book, 2002, 70% bleached hardwood kraft pulp, 30% bleached sulphate softwood pulp.
11	Book, 1951, 50% groundwood, 50% sulphite pulp
12	Book, 1951, 60% groundwood, 40% sulphite pulp
13	Book, 1930, 60% groundwood, 40% sulphite pulp
14	Book, 1960, 50% groundwood, 50% sulphite softwood pulp
15	Book, 1990, 75% groundwood, 25% bleached sulphite softwood pulp
16	Book, 1986, 50% groundwood, 50% kraft pulp (softwood/hardwood = 1/1)
17	Newspaper, 2003, 60% groundwood , 40% recycled fibres
18	Filter paper Whatman No. 1 (Maidstone, UK), 2001, 100% cotton
19	Bleached softwood sulphate pulp (Pöls, Austria), 2001
20	Cotton pulp (Radeče, Slovenia), 2001, 100% cotton
21	sample 18, deacidified with $Ca(HCO_3)_2$
22	sample 19, deacidified with $Ca(HCO_3)_2$
23	sample 20, deacidified with $Ca(HCO_3)_2$
24	sample 18, deacidified with $Mg(HCO_3)_2$
25	sample 19, deacidified with $Mg(HCO_3)_2$
26	sample 20, deacidified with $Mg(HCO_3)_2$
27	sample 18, immersed in phosphate buffer, pH = 11
28	sample 18, immersed in phosphate buffer, pH = 9
29	sample 18, immersed in phosphate buffer, pH = 7
30	sample 18, immersed in phosphate buffer, pH = 5
31	sample 18, immersed in phosphate buffer, pH = 3
32	sample 18, immersed in phosphate buffer, pH = 10.5
33	sample 18, immersed in phosphate buffer, pH = 9.5
34	rag paper (surface sized), 1600, 100 % cotton
35	rag paper (surface sized), 2001, 100 % cotton
36	rag paper (surface sized), 2001, 100 % cotton
37	rag paper (surface sized), 2001, 100 % cotton
38	rag paper (surface sized), 2001, 100 % cotton
39	rag paper (surface sized), 2001, 100 % cotton
40	paper, 19th century*, 100 % cotton
41	paper, 19th century*, 100 % cotton
42	paper, 19th century*, 100 % cotton
43	paper, 19th century*, 100 % bleached sulphite soft wood pulp
44	paper, 19th century*, 100 % cotton
45	paper, 19th century*, 50 % cotton, 50 % alkaline straw pulp
46	rag paper (surface sized)*, 100 % cotton
47	rag paper (surface sized)*, 100 % cotton
48	rag paper (surface sized)*, 100 % cotton
49	rag paper (surface sized)*, 100 % cotton
50	rag paper (surface sized)*, 100 % cotton
51	rag paper (surface sized)*, 100 % cotton
52	rag paper (surface sized)*, 100 % cotton
53	rag paper (surface sized)*, 100 % cotton
54	rag paper (surface sized)*, 100 % cotton
55	rag paper (surface sized)*, 100 % cotton

Table 1: Samples of paper and pulps. 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.
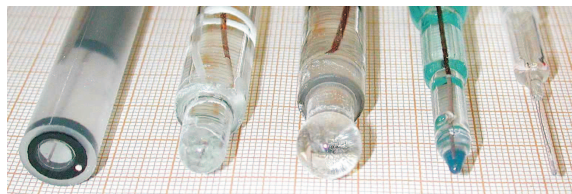

Fig. 1: Electrodes used in the study: from left to right: flat combined pH electrode, macro combined pH electrode, "aqua-trode", pointed semi-micro combined pH electrode, micro combined pH electrode.

Germany) at 25,000 r.p.m.. An appropriate stainless steel mixing rod was hand-crafted at the University of Ljubljana.

For the determination of VIS diffuse reflectance spectra, Minolta CM-3610 d spectrophotometer with Spectra Magic software (Langenhagen, Germany) was used. Minolta polymeric standards were used for calibration.

The following procedures for determination of pH were used.

2.2.1 "Standard"

According to the Tappi 509 om-02 standard method, sample of 1.00 ± 0.01 g is extracted in 70 mL cold MilliQ water for 1 h at 25 ± 5 °C. It was ensured that there was no contact between electrode surface and paper bits in the extraction medium. The results are an average of 7 determinations.

2.2.2 "Surface"

According to the Tappi 529 om-88 standard method, a drop of MilliQ water was placed on a sample, the flat-surface combined pH electrode pressed against it, and the pH value read after being constant for 30 s. The results are an average of 7 determinations.

2.2.3 "Pen"

The sample was wetted with a drop of MilliQ water, and with the coloured acid/base indicator-containing pen (pHydrion, Talas, New York, USA), a stroke was made. After 15 s, the colour of the trace was compared with the pH scale provided by the producer. The results are an average of 7 determinations.

2.2.4 "Equilibrium"

In a 100-mL beaker, 1.00 ± 0.01 g sample was weighed, 70 mL MilliQ water was added (same as "Standard"). The sample was mixed at 250 r.p.m. and pH was followed continuously until a constant pH reading was obtained. The pH-meter Iskra MA 5740 (Kranj, Slovenia) was used with a combined pH glass electrode of the same producer. One determination was usually performed, for selected samples triplicate determinations were done.

2.2.5 "Proposed"

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.

2.2.6 "Micro"

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).

2.2.7 "Colourimetric"

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_2CO_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[13] 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

$$y_{method1} = k \cdot x_{method1} + n$$

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,
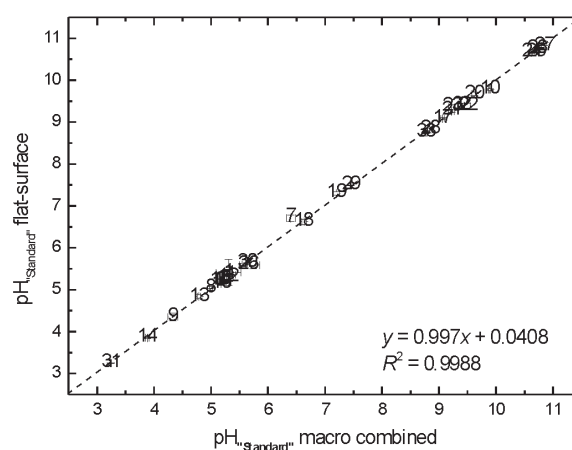

Fig. 2: A comparison of pH values of paper extracts obtained by the "Standard" method using the flat combined pH electrode and the macro combined pH electrode. Error bars represent standard deviations obtained from 7 determinations. Each sample is represented by its respective number. Samples used: 1-34.
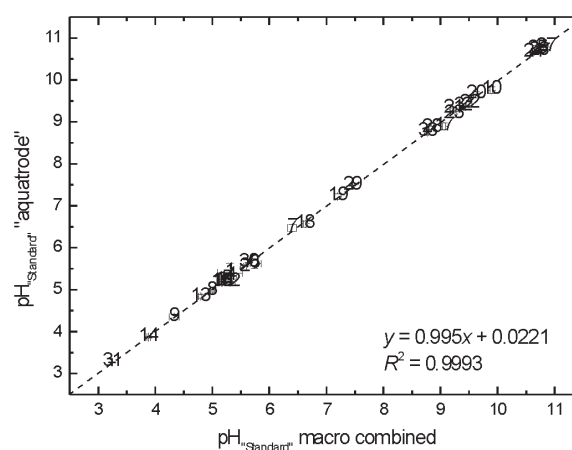

Fig. 3: A comparison of pH values of paper extracts obtained by "Standard" method using the low-ionic strength combined pH electrode - "aquatrode" and the macro combined pH electrode. Error bars represent standard deviations obtained from 7 determinations. Each sample is represented by its respective number. Samples used: 1-34.

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.

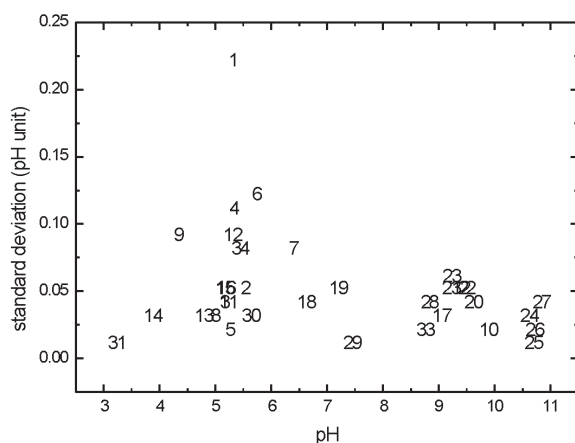It is advisable to round up determinations by the "Standard" method to the nearest 0.1 pH unit,

Fig. 4: A comparison of standard deviations (*N* = 7) for pH values of paper extracts obtained by "Standard" method using the macro combined pH electrode. Each sample is represented by its respective number. Samples used: 1-34.
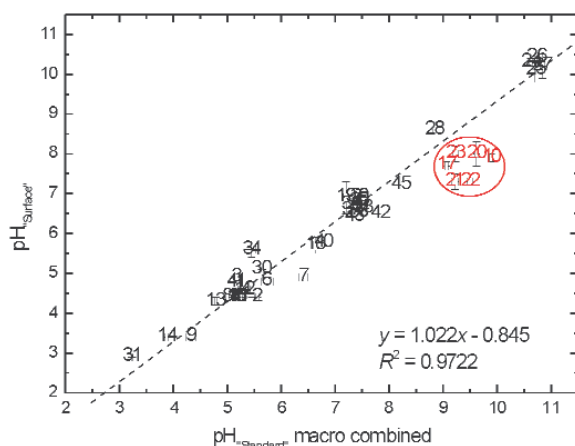

$$y = 1.022x - 0.845$$
$$R^2 = 0.9722$$

Fig. 5: A comparison of pH values of paper extracts obtained by the "Surface" and the "Standard" method. Error bars represent standard deviations obtained from 7 determinations. Each sample is represented by its respective number. Samples used: 1-34, samples 10, 17, 20-23 are excluded from correlation.

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. Saverwyns *et al.*[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[14-16] in which the correlations were less satisfactory, anyway. In a more recent study[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[12], the error is -2.1 pH units (*N* = 22, R^2 = 0.7586). In the work by Brandis[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[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"[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 reexamination 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-
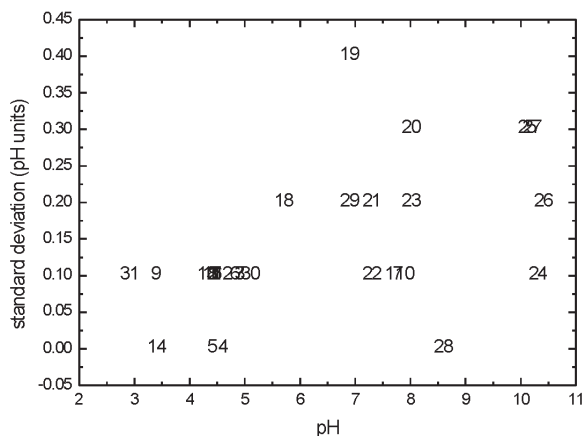
Fig. 6: A comparison of standard deviations ($N = 7$) for pH values of paper extracts obtained by "Surface" method. Each sample is represented by its respective number. Samples used: 1-34.
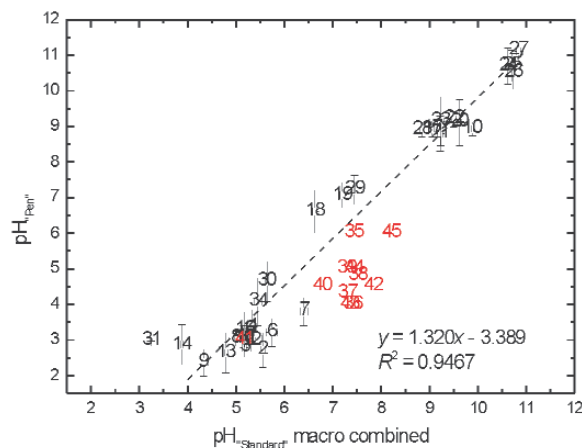

Fig. 7: A comparison of pH values of paper extracts obtained by the "Pen" and the "Standard" method. Error bars represent standard deviations obtained from 7 determinations. Each sample is represented by its respective number. Samples used: 1-45, samples 35-45 are excluded from the correlation.

ing that not only sample heterogeneity is a problem, but also other properties, some of which are more typical for alkaline samples than for acidic samples (*e.g.* surface charge). The very low solubility of alkali-earth metal carbonates, which is additionally also a very slow process, may be another such characteristic.

It is advisable to round up determinations by the "Surface" method to the nearest 0.1 pH unit, bearing in mind the repeatability being in the range of 0.2, and in the alkaline region 0.35 pH units. For determinations to be comparable with the "Standard" method, the flat-surface combined pH electrode must be validated against it in order to determine the systematic error (suspension effect).

Another often used procedure for determination of paper pH, *i.e.* by using pens containing coloured acid/base indicators, was compared with the "Standard" method (Fig. 7). From the less satisfactory correlation, several conclusions can be made. Since the correlation coefficient is still satisfactory ($R^2 = 0.9459$), pH pens may be useful, yet the readings, performed according to the producer's instructions are particularly uncertain (if compared with the "Standard" method) in the acidic region - and may be too low by more than 2 pH units. Undoubtedly, one of the reasons for this phenomenon is the yellow colour of the aged paper material itself, rendering the estimation of the very similar colour hue of the indicator difficult in certain cases. For alkaline papers, the results of the "Pen" method are in good correlation with the "Standard" method, and the errors in determination smaller.

The typical standard deviation for pH determinations using the "Pen" method are particularly high, and range from 0.1 to 0.7 pH units ($N = 7$). Given the unsatisfactory correlation, the method cannot be advised for determination of pH (espe-

cially not for acidic samples), but rather for its approximate estimation.

A further 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:

$$CO_2(g) \rightleftharpoons CO_2(aq),$$
$$CO_2(aq) + H_2O \rightleftharpoons HCO_3^- + H^+,$$
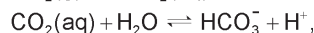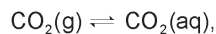
act as a weak acid in aqueous solutions, and due to the high solubility of $Ca(HCO_3)_2$ and $Mg(HCO_3)_2$, as compared to $CaCO_3$ and $MgCO_3$, more of the respective carbonates will dissolve if atmospheric CO_2 is given free access.

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-
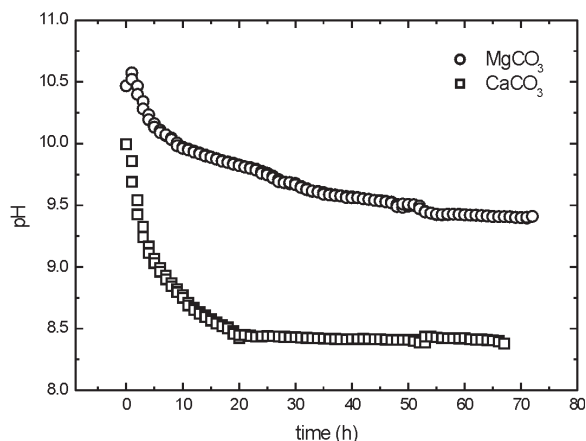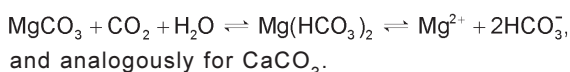
Fig. 8: Change of pH of suspensions of $CaCO_3$ and $MgCO_3$ with time. The suspensions were constantly stirred at 250 r.p.m..
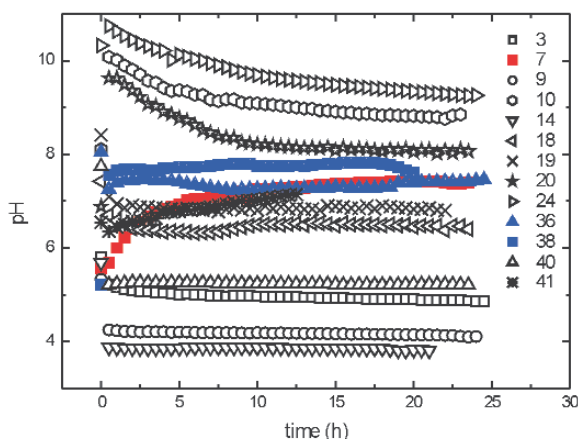

Fig. 9: Stationary pH values of paper extracts measured continuously according to the "Equilibrium" method. Each sample is represented by its respective number. Only a few samples are represented for the reason of clarity. Blue symbols represent gelatine surface-sized paper, the red one represents sample 7.

lowed 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:

$$MgCO_3 + CO_2 + H_2O \rightleftharpoons Mg(HCO_3)_2 \rightleftharpoons Mg^{2+} + 2HCO_3^-,$$

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_2CO_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 sys-

tem, 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
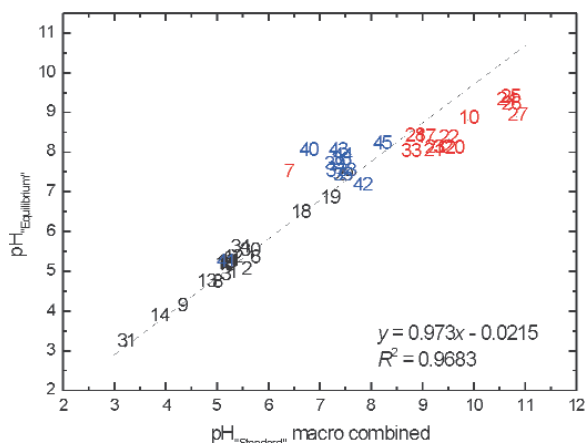
Fig. 10: A comparison of pH values of paper extracts obtained by the "Equilibrium" and the "Standard" method. Each sample is represented by its respective number. Samples used: 1-45, alkaline samples (in red, 7, 10, 17, 20-28, 32, 33) and gelatine surface sized samples (in blue, 35-45) are excluded from correlation.

Fig. 11: Determination of extract pH at various ratios of m_{sample}/V_{H2O} in the defibrillated sample pulp suspension. Electrode used: pointed combined pH electrode. Each sample is represented by its respective number.

considerably increases during the experiment. Regarding the fibre analysis (Table 1), the sample does not differ from the rest in any aspect.

The standard deviations for most of the samples (Table 2) is below 0.15 pH units, for alkaline samples up to 0.3 pH units.

Sample	pH	S.D.
5	5.11	0.13
7	7.46	0.08
14	3.82	0.08
17	8.34	0.06
19	6.83	0.04
26	9.17	0.33

Table 2: Stationary pH of certain samples and the corresponding standard deviations using the "Equilibrium" method ($N = 3$).

The pH values obtained using the "Equilibrium" method were compared with those obtained with the "Standard" method (Fig. 10). Data for acidic papers correlate fairly well; however, alkaline samples typically give equilibrium pH determinations of one to several pH units lower than according to the "Standard" method - the effect of taking in account the role of atmospheric CO_2. Gelatine sized papers typically give data 0.5 to 1 pH unit higher according to the "Equilibrium" method - the surface, which is extracted first during the "Standard" method, must obviously be more acidic than the bulk.

It is obvious that neither the "Standard" nor the "Surface" method provide data that would take into account the effect of CO_2 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.
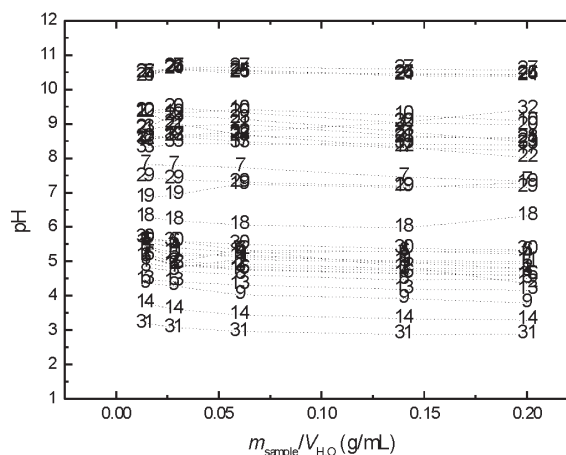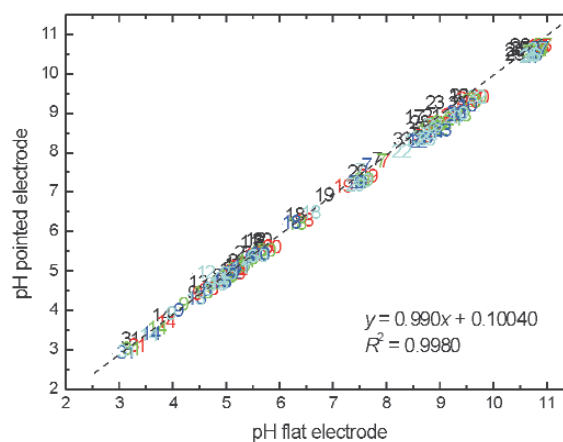

Fig. 12: A correlation of pH determinations in sample extracts prepared by defibrillation at various ratios of m_{sample}/V_{H2O} (represented by different colours of series of determinations) using the pointed semi-micro combined pH electrode in the sample pulp *vs.* determinations using the flat combined pH electrode in the supernatant extract after centrifugation. Each sample is represented by its respective number ($N = 165$).

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 m/V 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;
- using a flat-surface combined pH electrode in the extract above the pulp, after separation by centrifugation (to avoid suspension effects).
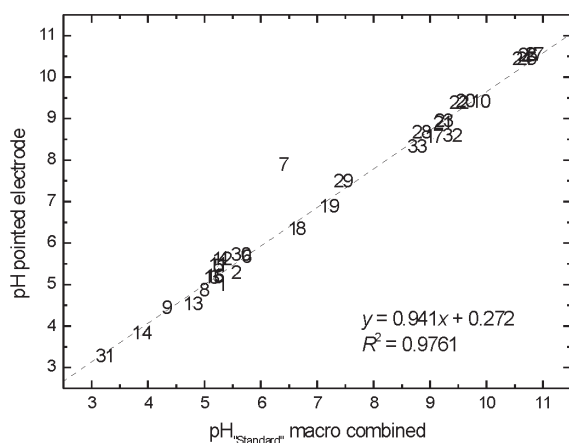
Fig. 13: A comparison of pH values of paper extracts obtained by defibrillation of samples at m_{sample}/V_{H2O} ratio 0.0140 g/mL using the pointed semi-micro combined pH electrode with pH determinations obtained using the "Standard" method. Each sample is represented by its respective number.
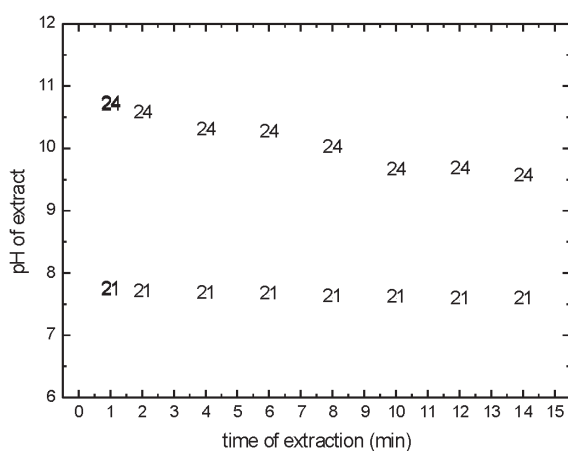

Fig. 14: Changes in determinations of pH in extracts during a prolonged extraction using mixing at 25,000 r.p.m. and m_{sample}/V_{H2O} = 0.0140 g/mL.

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_{sample}/V_{H2O} ratio 0.0140 g/mL.
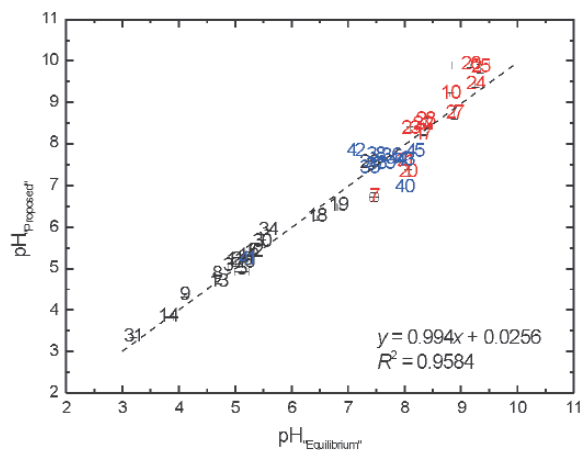

Fig. 15: A comparison of pH values of paper extracts obtained by the "Proposed" ($N = 5$) and the "Equilibrium" procedures. Each sample is represented by its respective number. All samples (in red: alkaline samples; in blue: gelatine surface sized samples) are included in the correlation.

The pH determinations obtained at m_{sample}/V_{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, 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 thereforee advisable to round up determinations by the "Proposed" method to the nearest 0.1 pH unit.
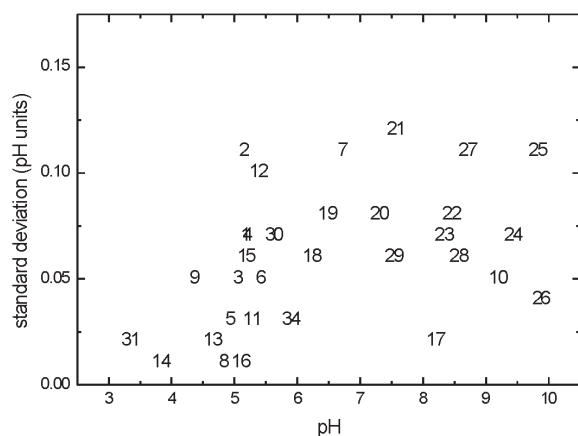
Fig. 16: A comparison of standard deviations ($N = 3$) for pH values of paper extracts obtained by the "Proposed" method. Each sample is represented by its respective number. Samples used: 1-34.

Fig. 17: A comparison of pH values of paper extracts obtained by the "Micro" and the "Proposed" method. Error bars repre- sent standard deviations obtained from 3 and 5 determina- tions, respectively. Each sample is represented by its respective number.

3.5 The "Micro" method

Using hollow needles, "micro"-sampling has become a popular method of obtaining small sam- ples of paper in conservation science[11]. The sam- ples 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.*[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 per- formed 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.*[11]

In any case, the "Micro" method of pH determina- tion 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, bear- ing 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.
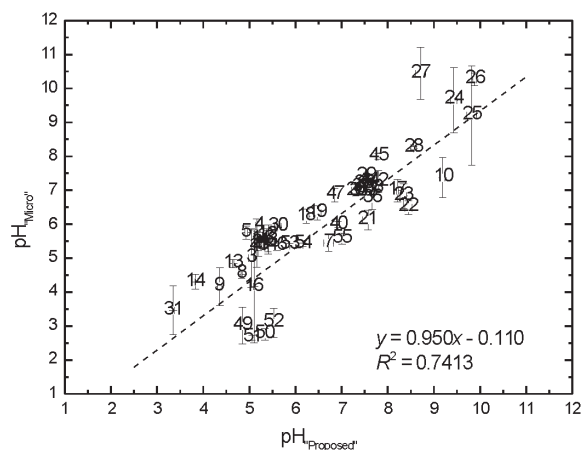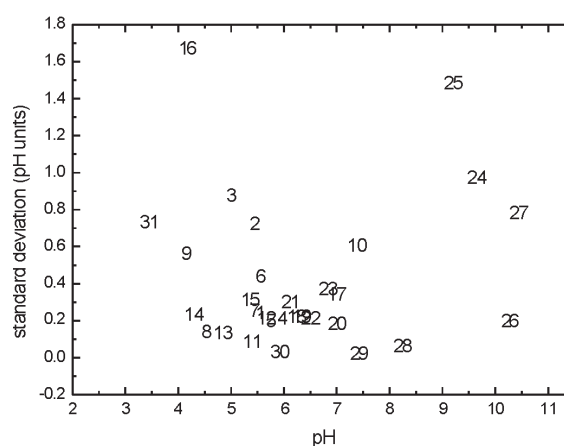

Fig. 18: A comparison of standard deviations ($N = 5$) for pH values of paper extracts obtained by "Micro" method. Each sample is represented by its respective number. Samples used: 1-55.

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") indi- cate 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 the "Colourimetric" method, a fairly high amount of indicator has to be added due to the low extinction coefficient. It turns out that the spectroscopic properties (colour) change drasti- cally with rapid changes in humidity of alkaline samples - an indication of the correctness of the above conclusion that the slow dissolution of alkali-earth metal carbonates cannot follow rapid changes in ambient RH.

For calibration, a series of pure cellulose sheets was prepared, immersed in a series of phosphate
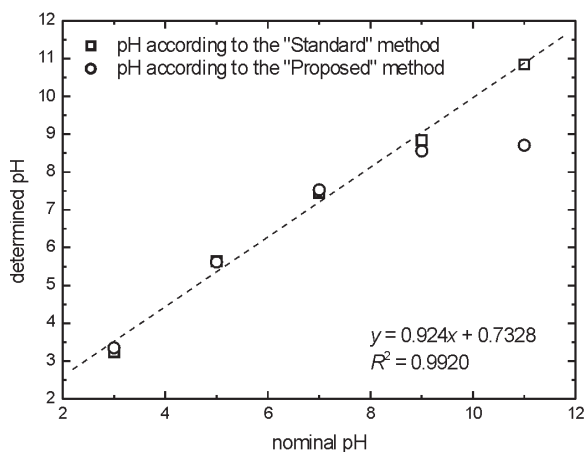
Fig. 19: Correlation of determinations of pH of phosphate buffer-containing samples (nos. 27-31) with the "Standard" and the "Proposed" method with the nominal buffer pH. The correlation was calculated for data obtained by the "Standard" method.
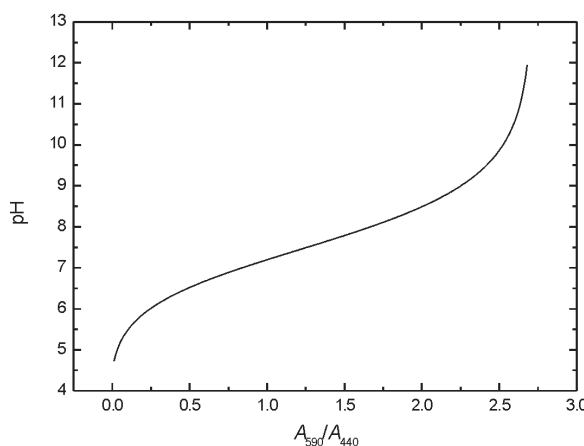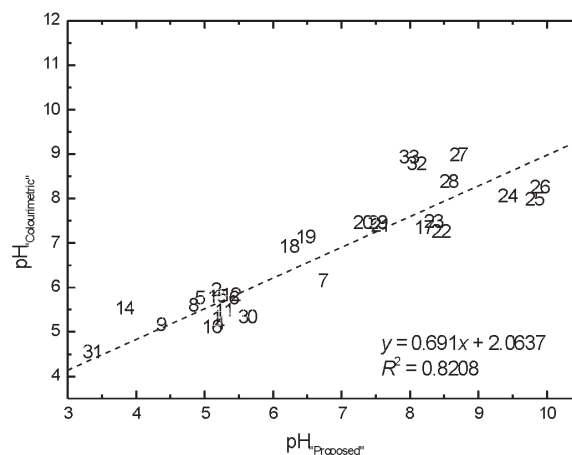

Fig. 21: A comparison of pH values of paper obtained by the "Colourimetric" ($N = 7$) and the "Proposed" procedures for samples 1-33. Each sample is represented by its respective number.

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

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" and according to the "Proposed" method. 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.* $\Delta(A_{590}/A_{440})/\Delta pH$). The calibration curve (with the "Proposed" method used to obtain pH values) can be described with the following equation:

$$pH = 8.0194 \cdot \left(\frac{A_{590}/A_{440} + 0.01568}{3.72361 - A_{590}/A_{440}} \right)^{0.11807} ,$$

and is presented in Fig. 20.

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 reactions[19]. Since the content of water in a cellulosic fibre is a distributed property, paper pH will be a distributed (or localised) property, as well.

Paper additives and functional groups bound to a cellulosic 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 medium[20]. 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 molal activity coefficient γ_{H+} = 0.9, the pH will be higher by 0.05 pH units, and values higher by 1.5 (γ_{H+} = 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 CO_2 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 CO_2 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 $CaCO_3$, 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 $MgCO_3$-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 $CaCO_3$-containing pulps was determined to be approx. 8.5, and the pH of $MgCO_3$-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 microcombined 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.

Acknowledgements

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