



# Impact of accumulation of organic acids on the degradation of cellulose in historic paper

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## ABSTRACT

The acidity of historic paper, a property crucial for its preservation, is thought to mainly depend on the type of sizing. However, this research shows that during its degradation, paper acidity increases mainly due to the formation of non-volatile carboxylic acids, which accelerate acid-catalysed hydrolysis. Whether and how this accumulation depends on paper composition has not been studied systematically so far. A collection of 89 European paper samples, dated between 1844 and 1990 was analysed for organic acids content and other conservation-relevant properties. Oxalic acid was the acid determined in the highest concentrations and with the strongest influence on paper pH. Multivariate data analysis revealed correlations between lignin content and oxalic and formic acid contents, highlighting the dominant influence of lignin on acid production. The results also indicate that the content of oxalic acid in paper increases by approximately 0.01 mmol/g per year, resulting in a decrease of pH at 0.008 per year (assuming other variables remain constant). To assist in paper conservation, a portable, non-invasive Raman spectroscopic method was developed to determine the lignin content of historic paper, using partial least squares regression. The research results are significant as they demonstrate the dominant impact of oxalic acid on acidic paper conservation.

## 1. Introduction

Paper has been an important information carrier for centuries, and as such is a large part of many historical collections, as well as the main material in archives and libraries. The main component of paper is cellulose, but the residual substances from plant-based crude material (e.g., lignin, hemicelluloses, mineral particles, colorants (Area & Cheradame, 2011)) and added auxiliary chemical agents (e.g., filling material, such as clay, TiO<sub>2</sub>, CaCO<sub>3</sub>, and sizing material, such as alum and rosin (Jablonský & Šima, 2021)) from papermaking procedures can affect the chemical stability of the main cellulose polymer. The main degradation processes affecting the stability of cellulose are acid hydrolysis of glycosidic bonds and oxidation at the ends of the polymer chains (Jablonský & Šima, 2020; Małachowska, Dubowik, et al., 2021). Both processes are influenced by factors such as light, temperature, humidity, and acidity (Havermans & Dufour, 1997; Bukovský, 2000; Menart et al., 2014; Małachowska, Pawcenis, et al., 2021), and are regarded as autocatalytic (Calvini et al., 2007; Jablonský et al., 2020).

It is well known that the pH of paper is strongly correlated with its stability, with papers with lower pH degrading faster due to increased rates of hydrolysis (Calvini et al., 2007; Vibert et al., 2023), leading to significant conservation challenges (Zervos & Alexopoulou, 2015). There are several known parameters contributing to paper acidity and consequently cellulose depolymerisation: alum-rosin sizing, presence of lignin, migration of acids from ink or other nearby materials and intake of acidic gasses from the environment (Area & Cheradame, 2011; Jablonský et al., 2020; Pedersoli et al., 2011). Additionally, the pH of paper has been known to decrease during aging (Shahani & Harrison, 2002; Vibert et al., 2023), which points to the formation of acidic degradation products (Carter et al., 2000; Strlič et al., 2009).

Alum-rosin sizing was used between ca. 1850 and ca. 1980 to reduce wetting of the cellulose fibres and improve writability (Jablonský et al., 2020). It has been known since the 19<sup>th</sup> century that alum-rosin sizing negatively affects the stability of paper (Shahani & Harrison, 2002), it has been traditionally regarded as the main culprit for the low pH of paper produced in the 20<sup>th</sup> century. It is assumed that the hydrolysis of

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alum (aluminum sulfate) releases oxonium cations that contribute to paper acidification (Jablonský et al., 2020). However, only a poor correlation between Al content and paper pH for European papers from this period with pH between 4.3 and 9 was found (Strlič et al., 2020). Abietic acid, a weak resin acid, is sometimes also assumed to contribute to paper acidity with its deprotonation (Jablonský et al., 2020) which was not confirmed for the dataset under study (Strlič et al., 2020).

In the same era, the prevalent raw material for paper production became groundwood, which lead to the inclusion of lignin into the paper matrix (Jablonský et al., 2020). It was observed that groundwood papers become yellow and acidic quicker than pure cellulosic paper (Bégin et al., 1998), and it was also presumed that lignin could catalyse cellulose degradation (Derkacheva & Tsytkin, 2018) and thereby shorten paper lifetime (Menart et al., 2014). It was also observed that acidic lignin-containing papers emit high amounts of acidic VOCs, which can cause damage to other paper items in a collection due to “cross-infection” (Carter et al., 2000; Strlič et al., 2011). However, discoloration does not necessarily lead to the loss of paper strength (Bégin et al., 1998; Carter, 2007; Havermans & Dufour, 1997) and the pH value of paper cannot be used as an indirect indicator of lignin content (Burge et al., 2002). Other findings cast doubt on the negative influence of lignin, for example it was reported that high lignin content was found within already acidic papers (Bégin et al., 1998), which may have led to erroneous interpretations of the effects of lignin content (Bukovský, 2000; Burge et al., 2002; Strlič et al., 2009). It was also reported that lignin can protect the cellulose from degradation in papers with neutral pH and suppress its oxidation (Małachowska, Dubowik, et al., 2021).

Lignin content in historic paper is traditionally determined using destructive methods, such as gravimetry after acid hydrolysis (Klason's lignin, TAPPI method T222) (Bukovský, 2000), acetyl bromide method with UV-VIS detection (Iiyama & Wallis, 1988; Strlič et al., 2020) or phloroglucinol spot test (TAPPI method T401) (Burge et al., 2002). FT-Raman spectroscopy methods have been developed to determine lignin content in wood (Gao et al., 2024) and pulps (Agarwal et al., 2003; Ibrahim et al., 1997; Sun et al., 1997) non-destructively and an IR reflectance method has been developed for non-destructive determination of lignin content in paper (Derkacheva & Tsytkin, 2018). Raman methods have not been used for historical paper samples until now, although a portable, non-invasive method would be useful in the context of paper conservation.

Low-molecular weight carboxylic acids are among the most commonly found acidic organic species in paper (Area & Cheradame, 2011; Jablonský, Hrobonová, et al., 2012). Acetic, formic, oxalic, lactic, glycolic, succinic, malic, tartaric, maleic, and some aromatic acids have been reported in the literature (Dupont et al., 2007; Souguir et al., 2008; Bogolitsyna et al., 2011; Jablonský et al., 2011; Pedersoli et al., 2011; Jablonský, Botkova, & Hrobonová, 2012; Jablonský, Hrobonová, et al., 2012; Becker et al., 2016; Čabalová et al., 2017). These are formed as degradation products from both cellulose and lignin (Area & Cheradame, 2011; Bogolitsyna et al., 2011; Dupont et al., 2007; Jablonský, Botkova, & Hrobonová, 2012; Novotný et al., 2008; Potthast et al., 2022; Shahani & Harrison, 2002; Zervos, 2010), via oxidation of monosaccharides (detailed reactions in (Marcq et al., 2009; Novotný et al., 2008)) as well as via lignin degradation products, such as aromatic acids, aliphatic aldehydes, benzaldehydes and other phenols (Lee & Inaba, 2013; Shahani & Harrison, 2002). Oxidation of carbonyl groups on carbohydrates leads to formation of peroxides and carboxylic functional groups (Kolar, 1997; Małachowska, Pawcenis, et al., 2021; Małachowska, Dubowik, et al., 2021). Oxidative processes and formation of low-molecular weight acids from cellulose are also influenced by Fenton-like catalytic mechanisms in the presence of metal species, originating from ink or impurities in paper (Jablonský & Sima, 2021). Lignin can be oxidatively depolymerized into phenolic monomers, cyclic organic species and also dicarboxylic acids (Chio et al., 2019; Costa et al., 2021; Gillet et al., 2017; Li et al., 2015). Oxalic acid is known to be naturally present in wood, especially in bark, as an end product of plant

metabolism (Krasowski & Marton, 1983), but is also formed during bleaching of paper pulp (Sjöde et al., 2008). It is thought to be primarily produced as an end-product of the oxidation of the lignineous components of pulp and less from cellulose (Krasowski & Marton, 1983). Interestingly, oxalic acid has been also shown to act as a deterrent for further cellulose oxidation during ozone bleaching (Roncero et al., 2003).

The decrease of paper pH during natural aging is a significant conservation concern, attracting much research. While it has been attributed to formation of weak organic acids in high concentrations (Shahani & Harrison, 2002) already in the early 2000s, there has been much speculation as to the sources and the acids mainly responsible for the observed accumulation of acidity (Becker et al., 2016; Bogolitsyna et al., 2011; Dupont et al., 2007; Jablonský et al., 2011; Jablonský, Botkova, & Hrobonová, 2012; Jablonský, Hrobonová, et al., 2012; Souguir et al., 2008). The focus was the formation of acetic and formic acid (Jablonský et al., 2011; Jablonský, Hrobonová, et al., 2012) determined in measurable concentrations in most damaged book samples (Dupont et al., 2007) and thus even assumed to represent a significant air quality concern in libraries and archives (Becker et al., 2016; Dupont & Tetreault, 2000; Mašková et al., 2017). However, it has been argued that weak acids such as acetic acid cannot influence cellulose degradation (Ligterink & Di Pietro, 2018; Menart et al., 2014; Pedersoli et al., 2011). While oxalic acid has been found to form during accelerated degradation of model paper samples (Lee & Inaba, 2013), it remains unresolved how much it contributes to paper degradation or acidity.

The determination of low molecular weight organic acids can be challenging due to their high polarity, high ionization potential, low molecular weight and volatility, resulting in high limits of detection. Common methods for their determination include capillary zone electrophoresis with UV or mass spectrometric detection (Bogolitsyna et al., 2011; Dupont et al., 2007; Lee & Inaba, 2013; Shahani & Harrison, 2002), ion-exclusion chromatography with UV detection (Čabalová et al., 2017; Jablonský et al., 2011; Jablonský, Botkova, & Hrobonová, 2012; Jablonský, Hrobonová, et al., 2012) and ion-exchange chromatography with conductivity detection (Gibson & Watt, 2010; Kraševc et al., 2021). Volatile acids such as acetic and formic acid can also be determined by SPME-GC-MS (Clark et al., 2011; Dupont & Tetreault, 2000; Pedersoli et al., 2011; Strlič et al., 2011).

To resolve the open questions of acidity accumulation during natural aging of historic paper and source attribution, low molecular weight organic acids were extracted from a substantial set of historical paper samples. Their possible origins and the effect on pH were investigated using statistical methods.

## 2. Hypotheses

1. Oxalic acid accumulates during aging of paper.
2. Lignin is the dominant source of oxalic acid in paper.
3. Oxalic acid is the main source of increased acidity of paper during natural degradation.

## 3. Materials and methods

### 3.1. Paper samples and database

Sacrificial historic paper samples from the collection of the Heritage Science Laboratory Ljubljana were used, together with the database of their properties published in 2020 by Strlič et al. (Strlič et al., 2020). From the original collection of European paper, a subset of 89 samples was selected for analysis, based on age, pH, and lignin content (Fig. 1) (see SI S1 for dataset details). The papers were produced between 1844 and 1990, with the majority produced before 1950 and evenly distributed by production years. 31 samples contained <50 mg/g of lignin and were arbitrarily categorized as ‘bleached paper’. 58 samples, categorized as ‘groundwood paper’, contained between 50 and 291 mg/g of

lignin. Reference lignin content values for the investigated samples were collected from the database of the paper (Strlič et al., 2020). Therein, lignin content was determined with UV spectrometry at 280 nm after dissolution of 1–1.5 mg of paper sample in acetyl bromide, glacial acetic acid and perchloric acid, and alkali lignin was used for the construction of a calibration curve. The majority of selected samples were acidic (with only 11 samples with pH >6.5, of which 5 with pH >7), and can be considered representative of the types of paper in the selected time interval, given their equal distribution relative to their age and lignin content. The time period presents materials that are of the most significant concern to paper conservation.

Paper pH and molecular weight (MW) were re-measured at locations close to where sampling for other analyses was performed. The cellulose degree of polymerisation (DP) was determined again for the samples with a high lignin content. The standard viscometry method using a glass capillary viscometer (ISO 5351, 2004) was used after delignification as described in (Malesič et al., 2021). The sample thickness was measured using a digital calliper.

### 3.2. Extraction and analysis of organic acids

35–40 mg of ink-free paper sample was accurately ( $\pm 0.0001$  mg) weighed into a vial. 1 ( $\pm 0.001$ ) mL of ultrapure water (MQ) was added to the vial, which was then ultrasonicated for 1 h. The extract was separated from the paper sample and a fresh solvent added for another hour of ultrasonication. The two extracts were combined and filtered through a 0.45  $\mu\text{m}$  Nylon filter (Chrom4, Germany) before injection. Each sample was injected in duplicate.

Anion-exchange chromatography (IC) was carried out using a Dionex ICS-5000 (Thermo, USA) ion chromatograph, consisting of an isocratic pump, eluent generator (Dionex EGC KOH III, Thermo, USA), an electrochemical suppressor (Dionex AERS 500, 4 mm, set to 40 mA; Thermo, USA) and a conductivity detector. A Dionex IonPac AS11-HC analytical

column (250  $\times$  4 mm; Thermo, USA) was used, with a 1 mL/min mobile phase flow and 25  $\mu\text{L}$  sample injection volume.

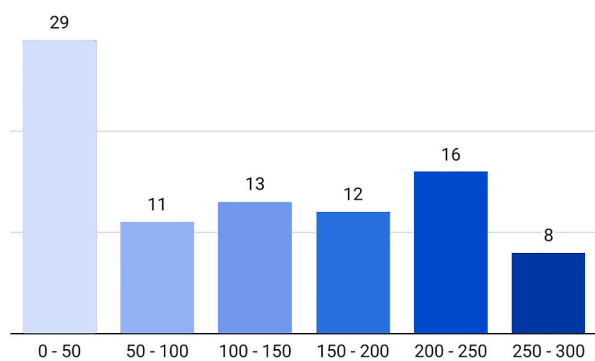
The gradient of the mobile phase was set as follows: equilibration at 0.5 mM of KOH for 10 min; a slow increase in KOH concentration until 1.5 mM at 30 min; ramp up until 16.5 mM at 35 min; final concentration of 18.3 mM at 50 min; return to 0.5 mM at 53 min; followed by run end.

The following organic acids were determined in the form of anions: lactate (LA, retention time 13.9 min), acetate (AC, 14.1 min), propionate (PR, 15.9 min), formate (FO, 17.5 min), succinate (SC, 39.5 min), maleate (ML, 41.4 min), and oxalate (OX, 43.4 min). Quantification using calibration curves ( $R^2 > 0.99$ ) was performed in the concentration range 0.05–10 mg/L.

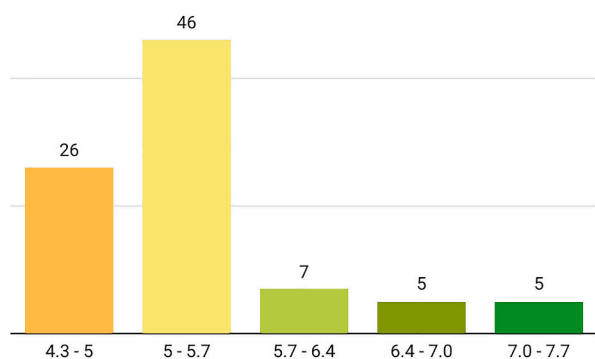
To confirm their identification, a cross-check with an ion-exclusion chromatographic method (IEX) was performed. A Supelco C-610H, 30 cm  $\times$  7.8 mm, 9  $\mu\text{m}$  chromatographic column was used on a System 1100 Series HPLC-DAD (Agilent Technologies, USA), with detection at 210 nm and injection volume of 25  $\mu\text{L}$ . 18 mM  $\text{H}_3\text{PO}_4$  in aqueous solution was used as the mobile phase, with flow rates 0.5 mL/min (0–25 min) and 0.8 mL/min (26–30 min). Oxalate (retention time 8.2 min), maleate (10.6), tartrate (TA, 11.5), pyruvate (PY, 12.1), glyoxylate (GX, 12.4), malate (MA, 12.9), glycolate (GL, 15.8), succinate (16.1), lactate (16.3), formate (17.8), acetate (19.4), fumarate (FU, 20.6), and propionate (23.2) were determined. LOQs were estimated to 5 mg/L (LA, AC, PR, GL, GX, FO, MA), 2.5 mg/L (SC, TA), 0.5 mg/L (PY, OX), and 0.1 mg/L (FU, ML).

Standard solutions were prepared from: sodium acetate (GramMol, Croatia, *p.a.*), sodium propionate (Fluka, Switzerland,  $\geq 99\%$ ), maleic acid (Fluka, USA,  $\geq 99\%$ ), oxalic acid (Fluka, USA,  $\geq 99\%$ ), ammonium formate (Sigma Aldrich, Germany,  $\geq 99.0\%$ ), succinic acid (Sigma Aldrich, USA,  $\geq 99.0\%$ ), L-malic acid (Sigma Aldrich, USA,  $\geq 99\%$ ), fumaric acid (Sigma Aldrich, USA,  $\geq 99.0\%$ ), tartaric acid (Honeywell, Germany, analytical reagent), glyoxylic acid monohydrate (Sigma Aldrich, USA, 98%), glycolic acid (Sigma Aldrich, USA, 99%), sodium

### Lignin Content



### pH



### Year of production

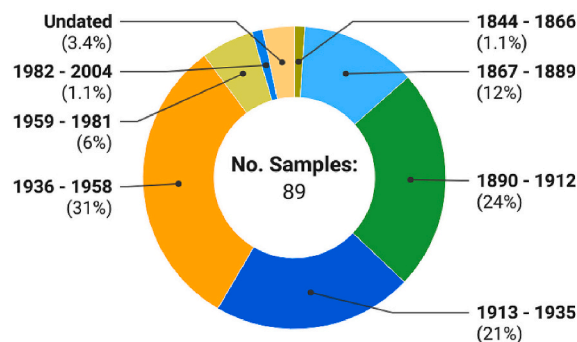


Fig. 1. The selected set of paper samples, categorized by lignin content, year of production and pH.

pyruvate (TCI, Japan,  $\geq 97\%$ ), DL-lactic acid (Sigma Aldrich, USA,  $\sim 90\%$ ). MQ water (MilliQ system, Millipore, USA) was used for all dilutions.

### 3.3. Raman and XRF spectroscopy

A BRAVO handheld Raman spectrometer (Bruker Optics GmbH, Germany) equipped with Duo LASERTM excitation (785 and 852 nm) and SSETM (Sequentially Shifted Excitation) patented fluorescence mitigation was used. The experimental parameters and the calibration were automatically optimized by the software, including an automatic baseline correction step. Raman spectra were obtained at 4–5 locations on samples, averaged and smoothed (over 9 points) using Bruker OPUS 8.1 software (see SI S2 for Raman dataset details).

A handheld XRF spectrometer (Vanta C-series, Evident/Olympus, Japan), equipped with a silicon drift detector and a 4-watt X-ray tube with application-optimized anode materials (Rh and W, 8–40 kV), was used as an exploratory tool to investigate iron content. For each sample, the average of three replicate measurements was calculated. Since the measurements were not calibrated to reference standards, quantification was not performed. Instead, iron content is reported as intensity in counts, based on the 6.4 keV peak, which is proportional to the concentration (González et al., 2024). The data are reported in SI S1.

### 3.4. Data analysis

To investigate the relationships between the samples based on their properties, Spearman's rank correlation (Spearman, 1904) and principal component analysis (PCA) (Jolliffe, 2002; Miller & Miller, 2005; Wold et al., 1987) were utilized to provide valuable insights into how different properties are related and to assess the strength of the relationships between variables. For Spearman's analysis, pairwise sets of variables were prepared using different numbers of samples for each pairwise comparison due to missing measurements. PCA was applied to combinations of selected variables for all the samples after data standardization and removal of any records with missing data. Multiple linear regression (MLR) (Jobson, 1991) was used to model the dependency of the properties on each other, offering an understanding of the variables influencing the dataset.

Partial least squares (PLS) regression (Breton & Lloyd, 2014; Miller & Miller, 2005) was used to build a regression model for the estimation of lignin content in paper samples based on Raman measurements and the reference values (as determined by (Strlič et al., 2020) for the same samples).

All analyses were conducted using both OriginPro (Version 2024 SR1; OriginLab Corporation, USA) and R (Version 4.2.2; R Foundation for Statistical Computing, Austria) software. The dataset and results are provided in the supplementary materials.

## 4. Results and discussion

### 4.1. Determination of organic acids and their influence on pH

The organic acid extraction procedure was optimized with regards to the solvent (MQ water, 10 mM NaOH (pH  $\sim 10$ ), phosphate buffer (pH 6.8) or 18 mM phosphoric acid (pH 2.2); mixing mode of extraction (shaker or ultrasonication); sample mass (40 or 100 mg); and extraction time (1–4 h, number of consecutive extractions). Extraction into NaOH solutions was efficient; however, systematic concentration increases in the second consecutive extraction of the same sample indicated that the samples were being degraded during the extraction, leading to an overestimation of acid content. Among the other solvents, MQ extraction showed the highest efficiency. Ultrasonication led to higher extraction efficiency than shaking, while the opposite was true for the increase in sample mass. Longer extraction times resulted in higher concentrations, but multiple consecutive extractions of the same sample

were more efficient (Fig. 2), resulting in the method as specified in the Methods section.

While the developed method does not lead to a complete extraction of the organic acids from the paper, two sequential extractions contribute to approx. 90 % of the total extractable acids. Also, since the extraction solvent is the same as in the standard method for pH determination (Strlič et al., 2020), the measured organic acid content is consistent with the pH determination of paper. Water insoluble salts, e. g. calcium oxalate are not a concern, as they influence neither the extracted acid content nor the paper pH determined.

The IC quantification limits, ranging from 0.11 mg/L for SC to 0.69 mg/L for PR (calculated as 10-times the standard deviation of the intercept divided by the calibration curve slope (Kruve et al., 2015); LA 0.20 mg/L, AC 0.57 mg/L, FO 0.18 mg/L, ML 0.57 mg/L, OX 0.22 mg/L) enabled us to analyse much lower amounts of paper samples compared to the literature (quantification limits of 42.8 mg/L for FO and 92.2 mg/L for AC reported in e.g. (Jablonský, Hrobonová, et al., 2012; Čabalová et al., 2017)) where 2 g of paper was extracted in 15 mL of water. The quantification limits for the IEX technique applied in this work were also too high for all the investigated acids except for PY, OX, ML and FU. This provided an independent confirmation of the identity for OX in all samples.

The uncertainty of the acid quantification was determined with a triplicate analysis of six diverse paper samples (SUR509, 617, 622, 884, 885 and 963). The average relative standard deviation values were 15.5 % for LA, 12.4 % for AC, 5.3 % for FO, 7.3 % for SC, 3.3 % for ML and 5.0 % for OX which apply also to the rest of the sample set.

The organic acids in paper were determined in the following ranges: LA 0.04–0.44 mg/g of paper, AC 0.03–0.42 mg/g, FO up to 0.1 mg/g, SC up to 1.55 mg/g and OX 0.02–1.83 mg/g (see also Fig. 3). These values correspond to molar contributions of the total determined acid content of LA 4–37 %, AC 6–48 %, FO up to 38 %, SC up to 46 % and OX 7–79 %, confirming that OX is the prevalent acid.

In the literature, 0.4–3.7 mg/g of FO and 0.8–5.8 mg/g of AC were reported in 12 book paper samples from 18<sup>th</sup> to 20<sup>th</sup> century (lignin content  $< 2.68\%$ ) (Čabalová et al., 2017), while up to 4.8 mg/g of AC and 0.8 mg/g of FO were determined in artificially degraded newsprint papers (Jablonský, Hrobonová, et al., 2012). In paper samples from 1878 to 1923, GL and OX were determined in the largest amounts, corresponding to up to 2.7 mg/g of OX and 0.76 mg/g of GL (Lee & Inaba, 2013). The values, determined in our sample set, are lower compared to the literature, which could be a result of differences in the

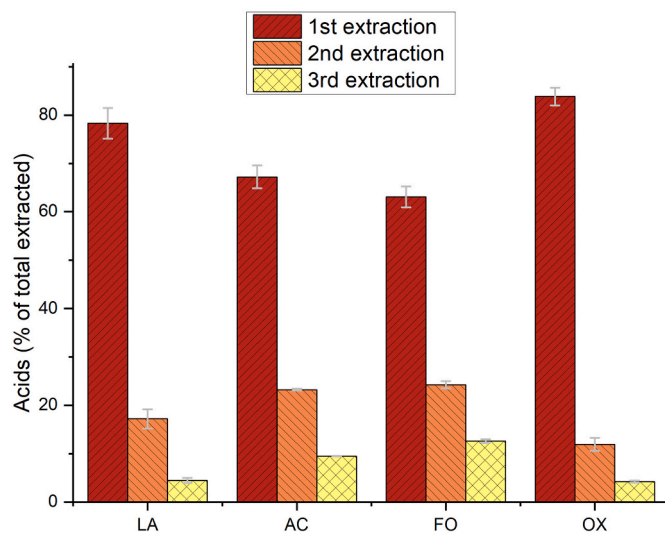
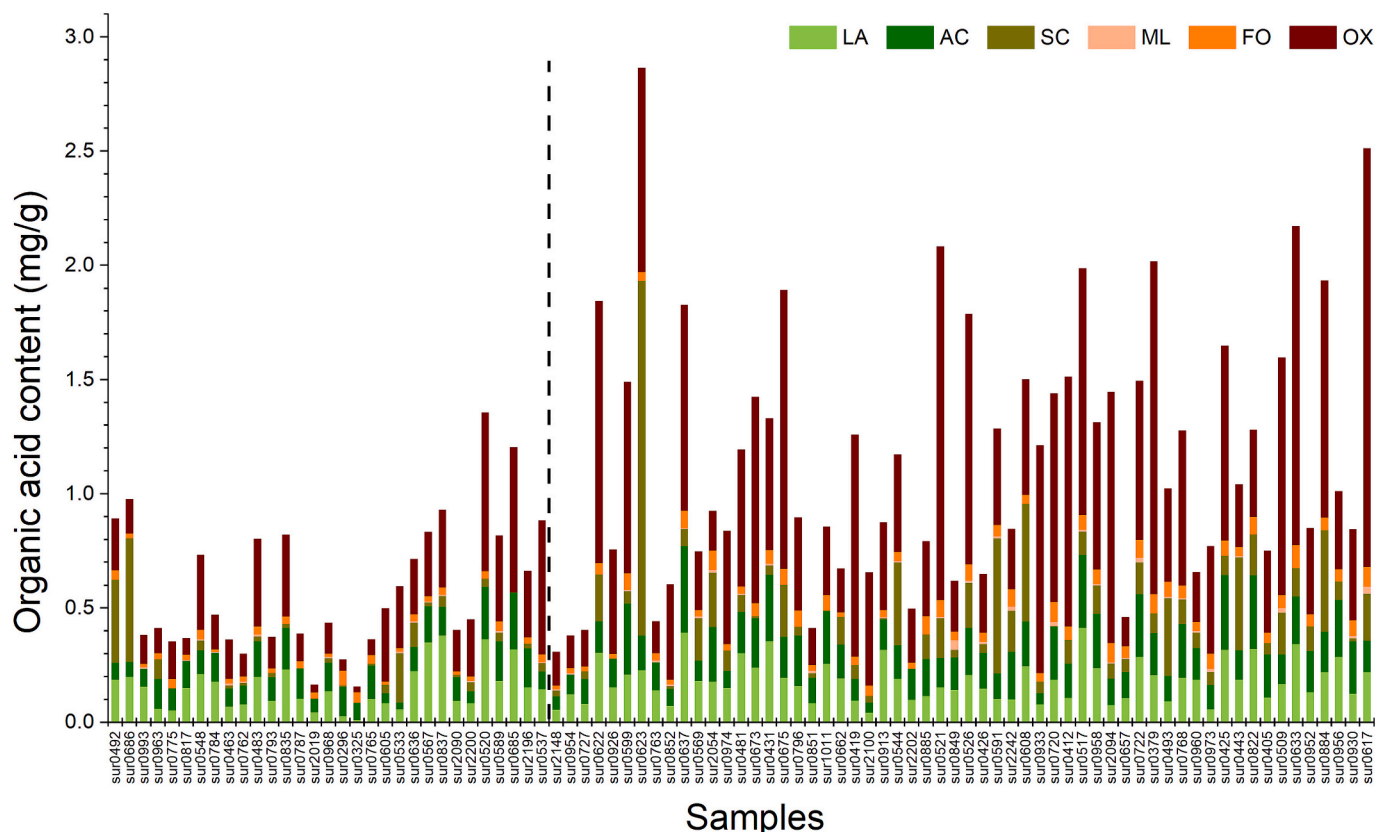


Fig. 2. The effect of consecutive extractions on the total determined content of selected acids (LA – lactic acid, AC – acetic acid, FO – formic acid, OX – oxalic acid).



**Fig. 3.** Content of organic acids in paper samples, sorted by lignin content. The dashed line separates 'bleached papers' on the left from 'groundwood papers' on the right.

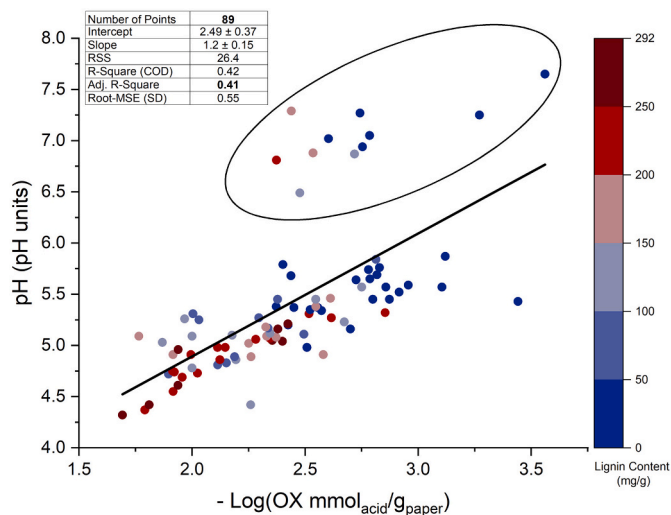
paper composition, aging history, and/or extraction procedures.

A strong linear correlation between OX content [expressed  $-\log(\text{mmol}_{\text{acid}}/\text{g}_{\text{paper}})]$  and paper pH was found (Fig. 4), confirming that this acid has the dominant influence on paper pH (see SI Table S3). There are two clearly distinguishable sample groups, separated based on their pH (acidic or approx. neutral), but not influenced by other parameters such as lignin content, ash content, or MW (see section SI S3.1 for details). The difference could be caused by a poorer extraction efficiency for the

neutral samples, given that OX is likely found in less soluble forms, such as calcium oxalate. Another reason could be a difference in the mechanism of acid production, given that at higher pH values, the rate of cellulose oxidation increases while the hydrolysis rate decreases.

FO has also shown a correlation with pH, though weaker than OX, while AC showed a fair correlation (SI Fig. S9 and S10). However, all the acids exhibited a correlation with each other. Due to that and the strong intercorrelation of acid contents, already observed for FO and AC (Čabalová et al., 2017), MLR analysis between all the acids and pH degenerates into a linear regression equation between pH and  $-\log(\text{OX})$ . For acidic samples  $\text{pH} = 3.34 + 0.77 (-\log(\text{OX}))$  ( $R^2 = 0.61$ ) (SI Fig. S1) and for neutral samples  $\text{pH} = 5.36 + 0.61 (-\log(\text{OX}))$  ( $R^2 = 0.46$ ) (SI Fig. S2).

The strong contribution of OX to paper acidity originates in its physicochemical properties. OX is one of the strongest naturally occurring organic acids. It is a dicarboxylic acid with a low  $\text{pKa}_1$  value ( $\text{pKa}_1 = 1.25$ ,  $\text{pKa}_2 = 4.28$ ), while its vapour pressure is 0.001 mmHg (PubChem, 2024) (see also SI Table S1), meaning that it is a strong acid and contributes double its molar concentration of oxonium ions compared to monocarboxylic acids in the pH range characteristic for acidic paper ( $\text{pH} < 6.5$  (Strlič & Kolar, 2005)). In contrast to AC ( $\text{pKa} = 4.76$ ; vapour pressure 15.7 mmHg (PubChem, 2024)) and FO ( $\text{pKa} = 3.75$ ; vapour pressure 42.59 mmHg (PubChem, 2024)) it is also much less volatile, leading to lower emissions of OX from paper and thus a greater rate of accumulation. It also means that this acid is less prone to migration between paper sheets in the usual range of water contents in paper (Tétreault et al., 2013).



**Fig. 4.** Effect of oxalic acid concentration on paper pH. Linear regression was applied to 89 sample data sets. Dots represent the samples, colored according to lignin content (explained later). The ellipse delineates the group of samples with a pH over 6.5.

#### 4.2. Sources of oxalic acid

Given the defining importance of acidity for the rate of paper degradation, and the observed clustering of samples into acidic and

neutral (Fig. 4), the following investigation focused on the acidic group of samples. To explore the correlations between various paper properties, degradation markers and papermaking practices, PCA and Spearman rank correlation analysis were applied to the 78 acidic samples. The analysis includes seven individually measured variables (pH, MW, lig, Ash, Al, ros, and car) along with the age and four of the extracted acids (OX, FO, AC and LA) (Figs. 5 and 6) (see also SI Table S2). These four acids were emphasized due to their consistent extraction in all the samples and their significance as reported in the literature. Age is defined as the period from the reported year of production (dat) to the year when the paper properties were measured (2007–2008), as the samples have been refrigerated since then to slow degradation down.

The results confirm the negative correlation between pH and oxalic acid (OX, mmol/g), highlighting their strong association with lignin content (lig, mg/g) and formic acid (FO, mmol/g). While this supports the hypothesis that lignin significantly contributes to paper acidity (Strlič et al., 2009), it also underscores lignin's important role as a source of OX and FO, which could be the underlying reason for the observed contribution.

There is a clear and strong association between all the acids, likely because they are formed through related reactions, as suggested in (Novotný et al., 2008). The strongest observed correlation is between OX and FO, and the total sum of organic acids, which could indicate that OX and FO are formed from other, more complex organic acids (Lee & Inaba, 2013). Although FO is strongly correlated with lignin, it was measured in low concentrations and is the most volatile of all the investigated acids. Additionally, there is a moderate correlation between reducing carbonyl groups (car) and OX, which shows that oxidative processes contribute to the formation of both cellulose carbonyl groups and free carboxylic acids. This correlation is confirmed by PCA as well as MLR analysis.

The data also confirm the strong correlation between the degree of polymerisation (DP) and molecular weight (MW) with the age of the paper, consistent with the well-known Ekenstam equation, which correlates DP with the degradation rate over time (Sato & Dobson, 1973), and the linear relationship between DP and MW (Agarwal, 2019) as well as their correlation to paper strength. These variables are also linked to other properties influenced by papermaking practices, such as ash content (%), aluminum (Al, mg/g), and rosin content (mg/g). The

correlation between acids and MW further confirms the contribution of these factors to the condition of the paper, as reported in (Jablonský et al., 2011; Jablonský, Botkova and Hrobonová, 2012).

The loadings plot of PC2 versus PC1 shows a separation along PC1 between degradation markers (such as pH and MW) and factors either introduced during production (such as lig, Al and ros) or accumulated through the degradation process (such as acids and car). The contribution of ash content in the selected samples is unclear, as it shows poor or no correlation with the measured variables. Al, ros, and car are all positively associated with the age of the paper, consistent with the history of papermaking: alum-rosin sizing was dominant between 1850 and 1990, leading to accumulation of carboxyl groups as the paper degraded (Cabalová et al., 2017; Strlič et al., 2020). The acids also correlate with the age of the samples, with older samples containing more acids, particularly OX and LA. This accumulation could be related to the less volatile nature of these acids as well as the amount of handling through the lifetime of the sample (LA being present in human sweat (Sato & Dobson, 1973)).

The lack of correlation between lignin content and age suggests that there was no significant shift in production processes over the period during which the paper was produced. The observed accumulation of OX over time, being related to lignin content, could explain the decrease in pH as the paper ages, assuming consistent production processes across the investigated period.

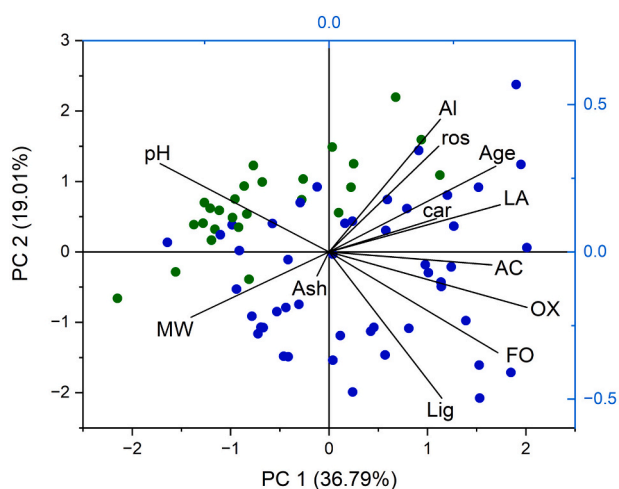
To verify the correlation between lignin and OX and to test the hypothesis that lignin or its constituents in paper play a significant role in the production of OX, multiple linear regression (MLR) was performed. Lig and age were included as predictors of OX concentration to explore their potential contributions to OX production. Table 1 presents the MLR summary, with all the parameters expressed in their logarithmic forms:  $\log(\text{OX})$  and  $\log(\text{lig})$ . The correlation observed between OX and lig underscores the significant impact of lignin content on OX concentrations, meaning that higher lignin content in paper leads to more OX accumulation.

The MLR results also indicate a good contribution of age to the accumulation of OX, with an increase of approximately 0.01 mmol/g per year, assuming other variables remain constant. This would lead to a decrease of paper pH at 0.0077 per year. An increase in OX content in the range 20–60 % has been noted before, in loose-leaf paper that underwent two weeks of accelerated degradation at 80 °C and 65 % RH, along with a decrease in GL content, but the authors noted that since the organic acid ratios changed in comparison to those in naturally degraded paper, a similarity between accelerated and natural degradation cannot be assumed (Lee & Inaba, 2013). By focussing on naturally aged samples, our research alleviates this concern.

Since it is well known that transition metals play an important role in cellulose degradation via Fenton-like reactions (Williams et al., 1977; Tang, 1978; Fellers et al., 1989; Strlič & Kolar, 2005; Jablonský & Šima, 2021), visual markers such as foxing, inks or other contamination were avoided during measurements for all dataset properties. However, almost all paper matrices contain small amounts of iron, introduced during the papermaking process (McCraedy, 1996; Tang, 1978). Since the variance in sample thickness is  $<0.03$  mm, a handheld XRF spectrometer was used as an exploratory tool to investigate iron content and its potential correlation with organic acids and pH. Spearman correlation and linear regression analyses (see section SI S3.5 for details) revealed no correlation between iron content and either OX or pH. It is still possible that transition metals have a significant impact on OX accumulation and reduced pH, if contained in higher concentrations, e.g. in inks. However, this was not the subject of our research.

#### 4.3. Non-destructive determination of lignin content in paper

Given that lignin constituents in paper have been identified to strongly correlate to OX content and thus acidity in paper during natural aging, it is crucial to propose a non-destructive method for the



**Fig. 5.** PCA biplot showing the loading plots for PC2 versus PC1 for acidic samples ( $N = 78$ ), including the measured variables: pH, molecular weight (MW), tensile strength (TS), reducing carbonyl groups (car), lignin content (lig), ash content (Ash), aluminum (Al), and rosin (ros), along with their age and acid contents: oxalic acid (OX), lactic acid (LA), formic acid (FO), and acetic acid (AC). Dots represent 78 samples grouped into two classes: green circles for 'groundwood' and blue circles for 'bleached'.

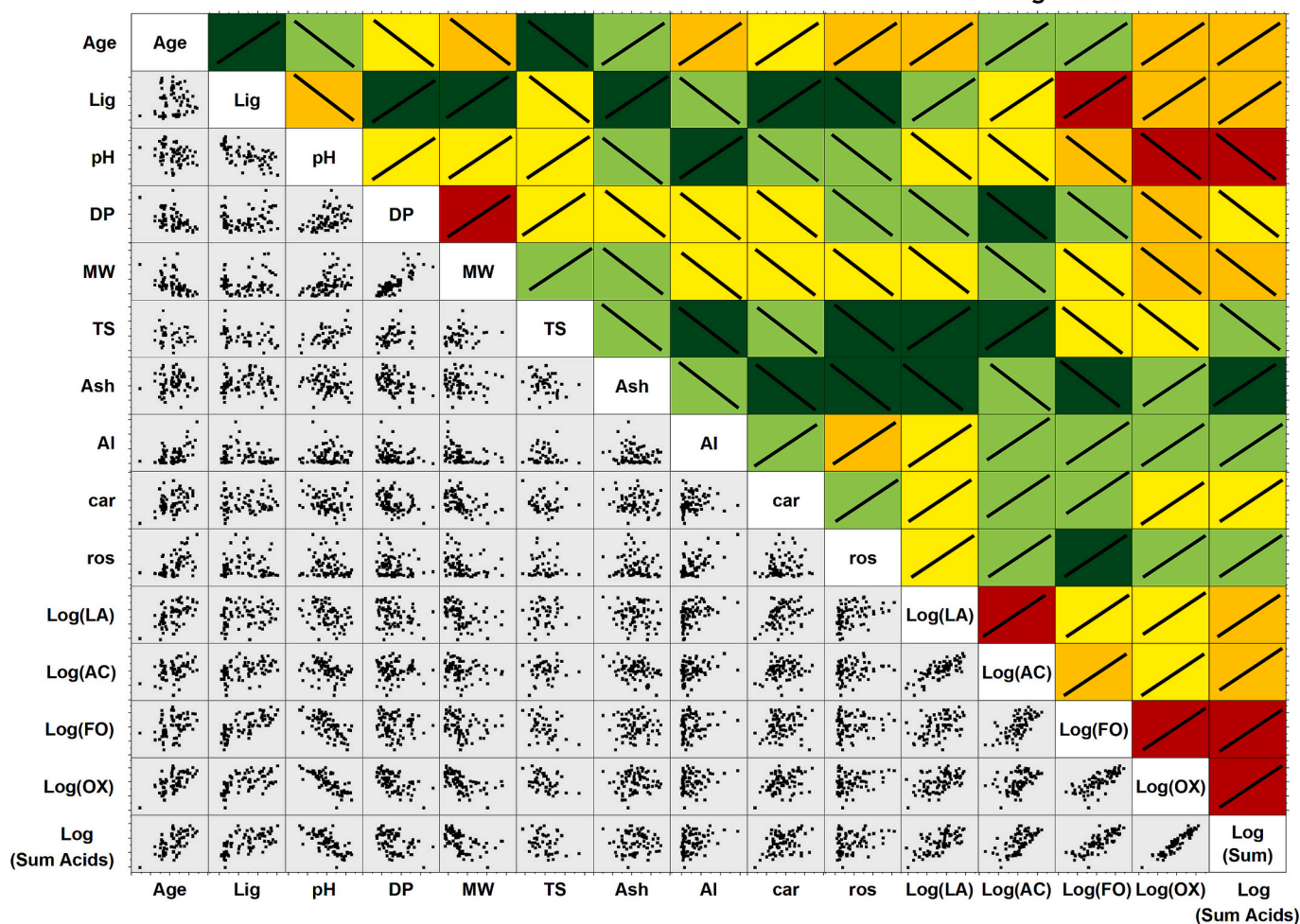


Fig. 6. Correlation matrix and Spearman's rank correlations for 15 selected variables in 78 acidic paper samples. The strength of the correlation between pairs is indicated by colour, with red representing strong correlations ( $R^2 > 0.7$ ). The direction of the correlation is shown as black lines in a positive (/) or negative (\) direction (see SI Table S2).

Table 1

Multiple linear regression (MLR) summary for the correlation between age, lignin content (lig) and oxalic acid content (OX).

Log(OX)	Parameter	Estimated Coefficient	Standard Error	t-Value	Prob>  t	Observations (N)	73
	Intercept	-4.08	0.16	-26.17	7.1194E-38	Adj. R-Square	0.64
	Age	0.01	0.001	7.02	1.1498E-09	SSR	3.6
	Log(lig)	0.5	0.07	7.36	2.7221E-10	Root-MSE (SD)	0.23
						F Value	62.27
						Prob>F	<0.0001

determination of lignin content in paper that could be of use in paper conservation. Raman spectroscopy can differentiate between paper samples with high and low lignin content as shown in Fig. 7. The spectrum of SUR956 reveals a prominent lignin band at  $1598\text{ cm}^{-1}$ , along with additional bands at  $1662$ ,  $1268$ , and  $1032\text{ cm}^{-1}$ , and cellulose bands, whereas SUR784 shows only cellulose bands at  $1476$ ,  $1380$ ,  $1338$ ,  $1152$ ,  $1120$ ,  $1096$ ,  $994$ ,  $968$ ,  $896$ ,  $520$ ,  $492$ ,  $458$ ,  $436$ , and  $380\text{ cm}^{-1}$  (Agarwal, 2019; Agarwal & Ralph, 1997).

Based on these spectral features, a PLS regression model was developed to determine the lignin content in paper using the Raman spectra of 89 paper samples with known lignin content values, in the spectral range  $3200\text{--}170\text{ cm}^{-1}$  (see also SI Fig. S19 for details). The model was trained with a calibration dataset of 70 samples and validated with an

independent dataset of 19 samples. No additional pre-treatments were applied to the spectral dataset for the modelling.

The model performance is satisfactory (Fig. 8), with a root mean square error of calibration (RMSEC) of  $23.5\text{ mg/g}$ ,  $R^2 = 0.92$  using 3 factors, and a root mean square of prediction (RMSEP) of  $\sim 40\text{ mg/g}$ ,  $R^2 = 0.81$ , about three times that of the analytical method ( $SD = 13.56\text{ mg/g}$ ) (Strlič et al., 2020). These results are useful for collection surveys and classification; however, incorporating more samples could enhance prediction accuracy. For classification, paper samples with lignin content below  $80\text{ mg/g}$  were categorized as 'bleached'. For comparison, the delignification pre-treatment has to be performed before DP determination for samples with lignin content above  $50\text{ mg/g}$  (Malešič et al., 2021; Strlič et al., 2020). This confirms that Raman spectroscopy with

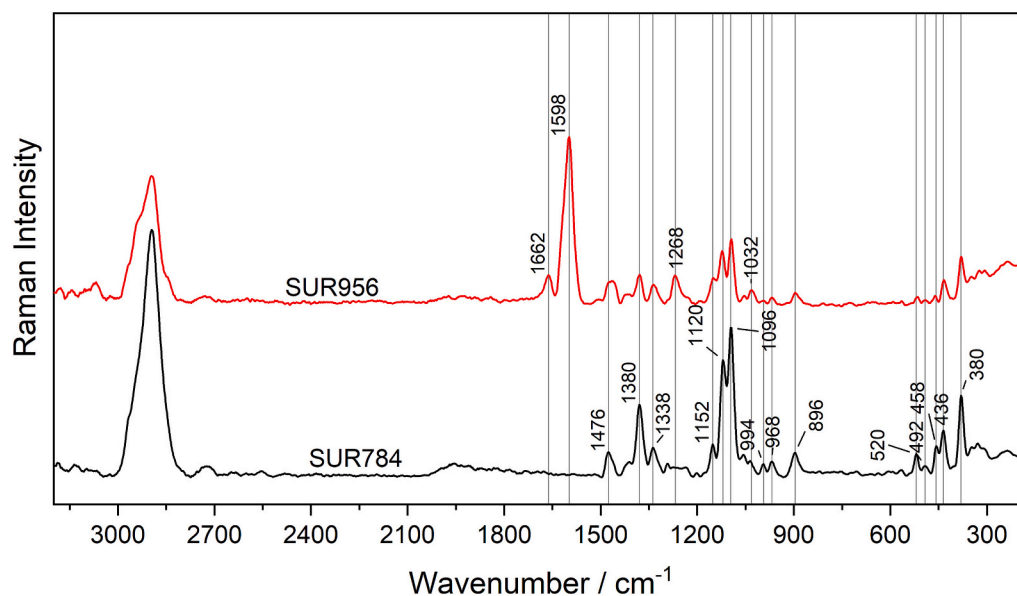


Fig. 7. Raman spectra of samples SUR784 (lignin content 23.4 mg/g) and SUR956 (lignin content 267.7 mg/g), recorded with a portable Raman spectrometer (785 and 852 nm excitations). Spectra are shifted on the y-axis for clarity.

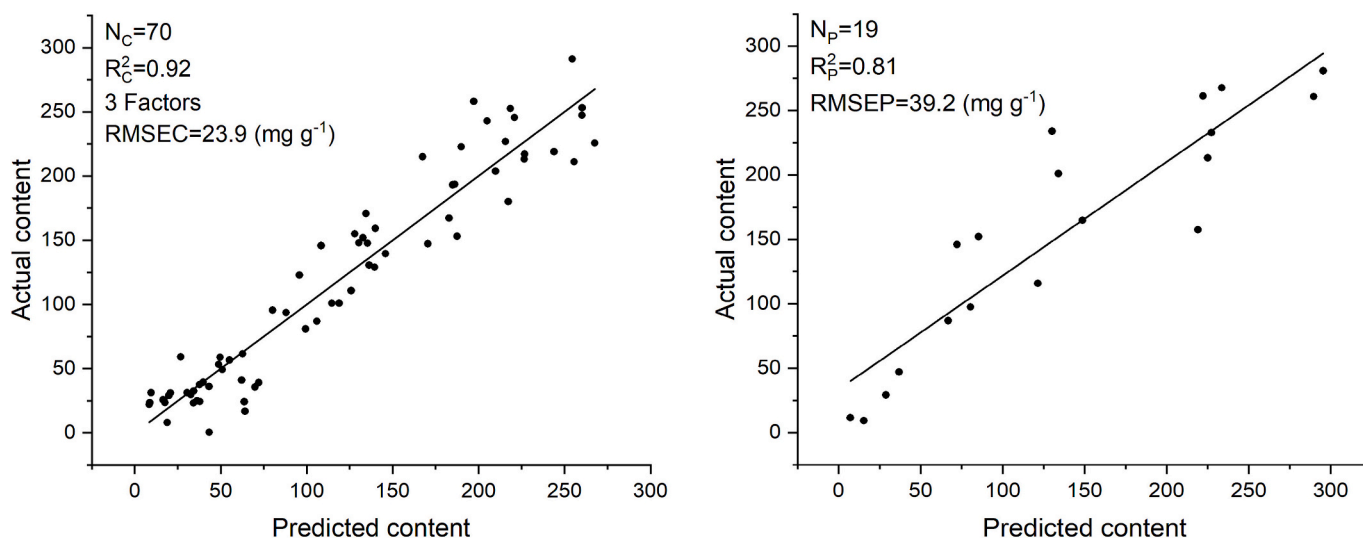


Fig. 8. PLS regression model for the determination of lignin content in paper. Comparisons of predicted vs. actual content for the two sets, for Calibration (left) and Validation (right).

PLS calibration is a robust and non-invasive approach for the determination of lignin content in historic paper.

## 5. Conclusions

The results of this work show, for the first time, that oxalic acid is the most important contributor to the decrease of paper pH during natural aging. This is likely due to its low pKa values and low volatility, and it therefore strongly affects the rate of cellulose degradation of importance in library and archival preservation.

The correlation between oxalic acid and lignin content indicates that the presence of lignin in paper strongly contributes to the production of oxalic acid, either as a direct precursor or as a promotor of cellulose degradation pathways leading to oxalic acid and additional research is needed to confirm the exact processes. The low volatility of this acid subsequently leads to its accumulation in paper. The non-invasive method for the determination of lignin with Raman spectroscopy

developed in this work can help with identifying papers at risk for high oxalic acid content.

The low volatility of oxalic acid means that it cannot be found as a pollutant in archival air. It also likely contributes to protonation of acetic and formic acids, and thus their much-studied emission from historical paper. Importantly, the effect of this acid on paper degradation can be strongly reduced by deacidification conservation processes that include  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$  ions leading to the formation of less soluble oxalates. The contribution of acetic and formic acid to historic paper degradation, which has been a major concern in paper conservation literature during the past two decades, can thus be considered of lesser importance.

Until now, oxalic acid production in paper was not well researched, but the results of this work show its defining importance for the future of paper conservation. Additional research would be needed to elucidate its mechanisms in lignin-containing paper.



## Abbreviations

AC	acetic acid
DP	degree of polymerisation
FO	formic acid
FU	fumaric acid
GL	glycolic acid
GX	glyoxylic acid
IC	anion-exchange chromatography
IEEX	ion-exclusion chromatography
LA	lactic acid
MA	malic acid
ML	maleic acid
MLR	multiple linear regression
MW	molecular weight
OX	oxalic acid
PCA	principal components analysis
PLS	partial least squares regression
PR	propanoic acid
PY	pyruvic acid
RMSEC	root mean square error of calibration
RMSEP	root mean square of prediction
SC	succinic acid
TA	tartaric acid
VOC	volatile organic compounds

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## CRediT authorship contribution statement

**Ida Kraševc:** Writing – review & editing, Writing – original draft, Methodology, Investigation, Formal analysis. **Aleksander Kravos:** Writing – review & editing, Writing – original draft, Methodology. **Klara Retko:** Writing – review & editing, Writing – original draft, Methodology, Investigation, Funding acquisition, Conceptualization. **Irena Kralj Cigić:** Writing – review & editing, Funding acquisition, Conceptualization. **Matija Strlič:** Writing – review & editing, Funding acquisition, Conceptualization. **Hend Mahgoub:** Writing – review & editing, Writing – original draft, Visualization, Formal analysis.

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## Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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## Data availability

The dataset and Raman measurements are provided as supplementary files (.xlsx). Additional details, figures, and tables from the analysis are included in a separate Supplementary Material file (.docx).

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