

COMPOSITION AND CONDITION OF NATURALLY AGED PAPERS

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ABSTRACT—The properties of forty naturally aged papers taken from books dating from 1477 to 1793 were assessed using two indicators of paper condition: degree of polymerization and yellowness index. These data were interrelated with three variables that may impact long-term paper stability: pH, gelatin content, and residual metals content. More stable specimens (high degree of polymerization and low yellowness index values) were strongly associated with high pH. High pH specimens were found to contain lower amounts of aluminum, potassium, and sulfur, as well as higher amounts of calcium and magnesium. Papers with more than 5.5% w/w gelatin content exhibited high pH, while those containing less than 5.5% w/w gelatin content showed both a range in pH and a broad range of aluminum, potassium, and sulfur content. Consequently, high gelatin content specimens were in good condition while low gelatin content specimens ranged in condition from poor to good. Results suggest that pH is the controlling factor in long-term stability and that gelatin needs to be present above some content level to provide long-term stability. The origin of high pH may lie in the alkaline calcium and magnesium residues.

TITRE—Composition et état des papiers naturellement vieillis. **RÉSUMÉ**—Les propriétés de quarante échantillons de papier naturellement vieillis, prélevés dans des livres et datant de 1477 à 1793, ont été déterminées en utilisant deux indicateurs de l'état du papier: le degré de polymérisation (DP) et l'index de jaunissement (IJ). Ces données ont été mises en corrélation avec trois variables qui peuvent affecter la stabilité du papier à long terme: le pH, le taux de gélatine et le taux de résidus métalliques. Les échantillons plus stables (DP élevé et valeurs basses d'IJ) ont été généralement associés à un pH élevé. Les échantillons ayant un pH élevé se sont avérés contenir de petites quantités d'aluminium (Al), de potassium (K), et de soufre (S), ainsi que des quantités plus élevées de calcium (Ca) et de magnésium (Mg). Les papiers ayant un taux de gélatine supérieur à 5,5% g/g avaient en général un pH plus élevé, alors que

ceux contenant un taux de gélatine inférieur à 5,5% g/g exhibaient une gamme de pH et une grande variété de taux d'Al, K et S. En conséquence, les échantillons ayant un taux élevé de gélatine étaient en bon état tandis que ceux avec un taux de gélatine plus bas étaient dans un état allant de bon à pauvre. Les résultats suggèrent que le pH est le facteur qui contrôle la stabilité à long terme des papiers et que la gélatine doit être présente au-dessus d'un certain niveau pour assurer une stabilité à long terme. L'origine d'un pH élevé peut possiblement être liée aux résidus alcalins de calcium et de magnésium.

TITULO—Composición y condición de papeles envejecidos naturalmente. **RESUMEN**—Las propiedades de cuarenta papeles envejecidos naturalmente, tomados de libros que datan entre 1477 y 1793, fueron analizados usando dos indicadores de las condiciones del papel: el grado de polimerización (GP) y el índice de amarillamiento (IA). Estos datos fueron interrelacionados con tres variables que pueden impactar en la estabilidad a largo plazo del papel: pH, contenido de gelatina, y contenido de metales residuales. Las muestras más estables (con valores de GP alto y de IA bajo) resultaron fuertemente asociadas a un pH alto. Se determinó que las muestras con un pH alto contenían bajas cantidades de aluminio (Al), potasio (K), y azufre (S), así como también altos contenidos de calcio (Ca) y magnesio (Mg). Los papeles con un contenido de gelatina mayor a 5,5 % p/p mostraron un pH alto, mientras que aquellos con un contenido de gelatina menor a 5,5 % p/p mostraron tanto una variedad de valores de pH, así como un amplio rango de contenido de Al, K y S. Por consiguiente, las muestras con un alto contenido de gelatina estaban en buenas condiciones mientras que las condiciones de las de contenido bajo de gelatina variaban de pobres a buenas. Los resultados sugirieron que el pH es un factor determinante en la estabilidad a largo plazo y que el contenido de la gelatina tiene que estar por encima de cierto nivel para proveer una estabilidad a largo plazo. El origen de un pH alto puede deberse a los residuos alcalinos de Ca y Mg.

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TÍTULO—Composição e condição de papéis envelhecidos naturalmente. **RESUMO**—As propriedades de quarenta papéis envelhecidos naturalmente, retirados de livros e datados de 1447 a 1793 foram avaliadas utilizando dois indicadores da condição do papel: grau de polimerização (GP) e índice de amarelecimento (IA). Estes dados foram inter-relacionados com três variáveis que podem ter impacto na estabilidade do papel a longo prazo: pH, conteúdo de gelatina e conteúdo de metais residuais. Os espécimens mais estáveis (valores altos de GP e de baixo IA) estavam fortemente associados a altos valores de pH. Especimens com alto valor de pH demonstraram que continham quantidades baixas de alumínio (Al), potássio (K) e enxofre (S) como, também, valores altos de cálcio (Ca) e de magnésio (Mg). Papéis com quantidades superiores a 5,5 w/w% de gelatina exibiam valores altos de pH, enquanto que aqueles com quantidade inferior a 5,5 w/w% de gelatina demonstravam, simultaneamente, variedade nos valores de pH e uma ampla variedade de conteúdo de Al, K e S. Consequentemente, espécimens com alto conteúdo de gelatina estavam em boa condição enquanto espécimens com baixo valor de gelatina variavam entre a má e a boa condição. Os resultados sugerem que o pH é um factor controlador na estabilidade a longo prazo e que o conteúdo de gelatina precisa estar acima de determinado nível para promover a estabilidade a longo prazo. A origem de um pH pode depender de resíduos alcalinos de Ca e de Mg.

1. INTRODUCTION

For decades, conservators have been interested in understanding how changes in paper production have affected the aging of paper. Some aged papers have been known to yellow, embrittle (Couch 1985), and exhibit foxing (Tang 1978). On the other hand, some aged papers are stable, remaining relatively white and strong over time (WJBRL 1974; Barrett and Mosier 1995). The reason for this stability is not fully understood, but there is a belief that certain factors—such as gelatin content, pH, trace metal content, and cellulose purity—play important roles.

Beginning in 1963, the W. J. Barrow Research Laboratory (1963, 1964, 1974) undertook a major project to determine which properties of a piece of paper influence its long-term stability. During the course of that study, roughly 1500 book papers were

examined. Using physical strength measurements (which reflect the strength of and bonding between fibers), pH values, as well as the retention of properties following thermal aging, the laboratory concluded that papers with high pH showed the best long-term stability. Further, the lab used results from spot testing analysis to argue that for paper to be considered archival, it should be free from alum (WJBRL 1969), a sizing component added to gelatin baths to prolong shelf life and to help gelatin harden after coating it on paper. However, an exploration of the effect of gelatin coatings, common to Western paper up until around 1800 (when alum-rosin internal size was introduced), was lacking in that study.

Barrett and others addressed the issue of the effect of gelatin coatings on long-term stability by looking at a select group of naturally aged papers (Barrett 1989; Barrett and Mosier 1995). Results from those studies suggested that, in addition to pH, gelatin contributes to paper stability. However, both studies also concluded that more research was needed to clarify the relationship between gelatin and long-term stability. Dupont (2003a) concluded that gelatin may retard the aging of cellulose if certain quantities of gelatin size are used. Kolbe (2004) showed that a gelatin coating can retard the negative impact of iron gall ink on paper. More recently, Baty and Barrett (2007) offered possible mechanisms by which gelatin may act to slow degradation.

This study examined in more depth which properties promote long-term stability in naturally aged book papers. Special attention was given to the effects of pH, residual metals, and gelatin content. Fiber type was determined using light microscopy. The pH of the specimens was assessed using the cold water extraction technique. Gelatin content was probed using gas chromatography-mass spectroscopy (GC-MS). The new GC-MS method was based upon the recovery of seven “stable” amino acids: alanine, glycine, L-valine, L-leucine, L-isoleucine, L-proline, and L-hydroxyproline (Schilling and Khanjian 1996). The yellowness index (YI) of each specimen was analyzed using a reflectance spectrophotometer. The degree of polymerization (DP) of cellulose in each specimen was measured using gel permeation chromatography (GPC). The concentration of metals in each specimen was studied using inductively coupled plasma-optical emission spectrometry (ICP-OES). Elements analyzed included: calcium (Ca) and magnesium (Mg), alkaline earth metals associated with alkaline reserve; aluminum (Al), potassium (K),

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and sulfur (S), components associated with alum; and copper (Cu) and iron (Fe), metals associated with oxidative degradation and discoloration. Details for specimens analyzed and analytical methods employed are presented in the Appendix.

2. RESULTS

The 40 specimens were divided into two categories, Dark and Light, based on visual assessment. The 20 Dark and 20 Light specimens are identified in table 1. Dark and Light specimens were given the prefixes D and L, respectively. Specimens in this data set that were from the Barrow Collection, now held at the Library of Congress, are identified by Barrow specimen number, in parentheses. Country of origin and/or publication date of a specimen, where known, are identified in table 1.

Optical microscopy showed that fibers taken from every specimen in the data set were fibrillated; Dark

specimens on the whole had fibers that were more fibrillated than those from Light specimens. Though fibrillation made fiber identification difficult, polarized light microscopy of disintegrated fibers indicated that all 40 specimens in the data set were primarily made from flax bast fiber. As it is still unclear whether or not all fiber types age in the same way, this finding was fortuitous, permitting the properties of all specimens in this data set to be directly compared to one another. Dark specimens D5, D7, and D20 as well as Light specimens L2 and L18 showed the presence of small amounts of cotton fiber. Dark specimen D7 also had a small amount of shive in it.

The pH of the specimens showed that, in general, Dark specimens were more acidic than Light specimens. Dark specimens were acidic, with a pH 4.0–6.6, with the exception of D2, D8 and D20, which had pHs of 7.6, 7.9 and 7.6, respectively. Light specimens were alkaline, with a pH range of 7.3–9.9; 12 showed pH values of 9.0 or greater (L2, L3, L4, L5, L6, L7, L10, L11, L13, L15, L16, and L19).

The gelatin content measured for the specimens showed that the average Dark specimen contained less gelatin than the average Light specimen. For Dark specimens, the gelatin content ranged from 0.13 to 4.68% w/w. For Light specimens, it ranged from 2.02 to 11.36% w/w, 8 specimens having a gelatin content above 5.5% w/w (L2, L3, L8, L12, L13, L15, L18, L20).

The measured YI of specimen sheets showed that in general, Dark specimens were more yellow than Light specimens. However, while the original classifications were based on visual assessment, analysis showed that the two categories overlap slightly. The YI range for Dark specimens was 16.7–38.6, while for Light specimens, the range was 9.2–18.1.

Molecular weight measurements showed that cellulose in Light specimens tended to have higher DPs than in Dark specimens. Light specimen DPs ranged from 2030–3840, while Dark specimen DPs ranged from 680–3290.

Table 2 shows the results of the analysis for residual metals. In general, Dark specimens contained less Ca and Mg and more Al, K, and S than Light specimens. The Ca content in the specimens varied most, ranging from 680–24000 ppm. Mg content also ranged broadly, from 160–4600 ppm. Al, K, and S were present in smaller quantities, 80–1500 ppm, 70–1670 ppm, and 180–3970 ppm, respectively. Cu and Fe contents were relatively low, 0–40 ppm and 110–750 ppm, respectively.

Table 1. Summary of country of origin, publication year, gelatin content, pH, yellowness index, and degree of polymerization for all the specimens in the data set

Specimen	Country	Pub. Year	Gelatin Content (wt. %)	pH	YI	DP
D1	England	1764	1.36	4.2	18.6	1010
D2 (1484)	Monguntiae	1608	0.14	7.6	16.7	2090
D3	Holland	1695	3.10	4.4	26.8	1010
D4	England	1769	3.25	4.2	28.0	810
D5	England	1772	3.02	4.0	22.5	990
D6	France	1749	3.73	5.6	20.1	1640
D7 (1170)	England	1734	2.31	4.7	24.3	1330
D8 (1382)	Switzerland	1645	0.13	7.9	17.2	3290
D9 (1269)	France	1695	0.13	6.1	17.9	1320
D10 (1052)	USA	1778	1.84	4.4	35.6	990
D11 (1214)	Savoy	1711	1.54	5.4	30.2	990
D12		1757	3.44	5.2	25.6	1460
D13	England	1739	4.68	4.8	21.5	1680
D14 (1452)	Holland	1611	4.22	4.8	31.0	1060
D15 (1158)	Scotland	1733	1.89	4.8	23.7	1550
D16 (1019)	England	1793	1.01	4.3	25.9	680
D17 (1523)	Switzerland	1584	3.37	6.6	20.6	1890
D18 (1187)	Savoy	1727	1.22	4.3	38.6	680
D19 (1101)	Holland	1757	2.98	5.0	29.1	1020
D20 (1512)	Germany	1599	0.86	7.6	23.8	1930
L1	Italy	1479	4.54	8.9	12.2	2670
L2		1503	6.66	9.2	17.3	2880
L3	Spain	1770	8.94	9.0	9.2	3140
L4	England	1723	3.24	9.4	11.4	2100
L5	England	1737	2.02	9.4	10.6	2900
L6	Italy	1498	4.55	9.1	12.0	3130
L7	Italy	1495	4.98	9.1	12.9	2030
L8	France	1488	8.44	7.3	16.5	3080
L9	Italy	1483	4.90	8.4	18.1	2490
L10 (1208)		1711	2.18	9.6	10.0	2680
L11	Germany	1477	5.07	9.4	15.6	2620
L12	Italy	1482	7.78	8.9	11.8	2270
L13		1400s	11.36	9.0	12.7	2870
L14 (1379)	Italy	1641	3.71	8.8	11.7	3490
L15 (1239)	England	1701	6.76	9.1	9.4	3210
L16 (1340)	England	1660	4.38	9.3	17.1	3840
L17		1700s	4.76	6.8	12.4	2090
L18	Italy	1499	10.84	8.7	13.1	2670
L19 (1245)	England	1704	3.43	9.9	11.6	3180
L20	Italy	1483	6.42	8.7	14.6	2740

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Table 2. Summary of the calcium, magnesium, aluminum, potassium, sulfur, copper, and iron contents for all the specimens in the data set

Specimen	Element (ppm)						
	Ca	Mg	Al	K	S	Cu	Fe
D1	2450	600	1500	1730	3520	20	150
D2	3790	470	140	200	620	10	390
D3	3810	340	1200	1370	3970	10	230
D4	1610	390	1100	1370	2370	20	150
D5	1140	160	1200	1260	3220	30	110
D6	2590	390	510	1210	1450	20	430
D7	1650	240	1000	950	2120	40	210
D8	4560	740	200	70	180	10	460
D9	1310	300	100	140	390	10	310
D10	1000	160	610	940	1660	20	240
D11	2480	820	480	760	1500	10	280
D12	680	720	500	710	1020	30	560
D13	2120	380	1500	910	2510	30	260
D14	1430	610	600	1220	2040	10	250
D15	1230	160	640	760	1270	30	750
D16	760	480	1300	1670	2620	20	190
D17	3020	640	260	290	300	40	440
D18	980	510	850	510	1780	10	210
D19	770	240	390	1170	1080	10	230
D20	4820	840	230	210	340	10	290
L1	24000	1750	770	790	490	20	290
L2	19900	3700	240	440	660	30	300
L3	11200	1900	610	480	1020	10	160
L4	6690	2950	270	140	570	10	250
L5	6110	3480	530	120	870	10	290
L6	10000	3490	510	700	830	30	260
L7	18100	1450	540	300	440	20	230
L8	4740	1350	280	490	520	10	210
L9	6100	1730	80	440	350	10	270
L10	6170	4270	330	230	350	10	310
L11	6900	3080	370	810	300	20	400
L12	12700	1500	500	390	400	20	240
L13	11600	1390	550	260	580	20	280
L14	2660	980	300	150	220	10	190
L15	4370	1930	280	270	730	10	130
L16	12600	1260	200	300	420	10	380
L17	2350	850	450	510	710	10	210
L18	7390	2590	400	330	680	20	230
L19	5280	4600	160	280	360	10	290
L20	3500	2210	250	490	380	10	280

3. DISCUSSION

3.1 pH VS. PAPER CONDITION INDICATORS

The first goal of this work was to see if, similar to Barrow, this data set would show high pH associated with the attributes of long-term stability, namely high DP and low YI. In figure 1, a plot of DP versus pH,

a positive correlation between the two properties was observed: when the pH was alkaline, specimens had a high DP, and conversely, when the pH was acidic, specimens had a low DP. The DP was probably lower in low pH specimens because the acid present would catalyze hydrolysis of the cellulose (Whitmore and Bogaard 1994).

Hydrolysis also leads to aldehyde group formation (Whitmore and Bogaard 1994). Lewin suggested that the presence of aldehyde groups on the C₁ carbon

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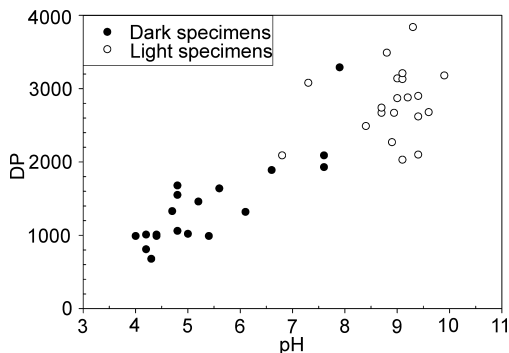


Fig. 1. Relationship between pH and degree of polymerization (DP)

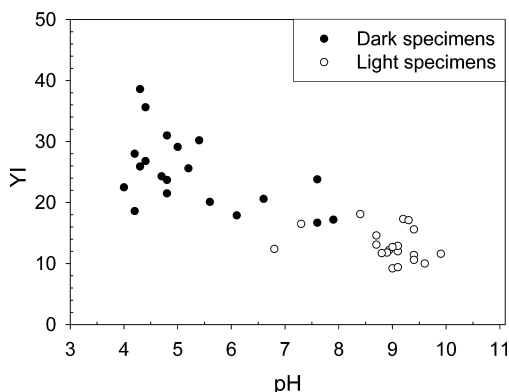


Fig. 2. Relationship between pH and yellowness index (YI)

of cellulose causes yellowness (1965). While the color of paper is not always an accurate indication of paper condition (Lee et al. 1994), it is often a manifestation of the chemical breakdown of cellulose or gelatin molecules. Therefore, the effect of pH on yellowness was probed. Figure 2, a plot of YI versus pH, showed an inverse correlation between yellowness and pH. When the pH was alkaline, specimens showed a low YI; conversely, when the pH was acidic, specimens showed a high YI. The relationship between pH and long-term stability properties found here was in good agreement with Barrow.

3.2 pH VS. RESIDUAL ELEMENTS

The second goal of this work was to carefully examine the relationship between long-term stability and residual element contents. Previously, Barrow

looked for the presence of Ca by testing papers for carbonates (WJBRL 1974); he also looked for the presence of Al using spot tests (WJBRL 1969). These tests were indirect measurements of both metals. In 1989, Barrett reported using proton-induced X-ray emission analysis (PIXE) to test for the presence of Ca, Mg, Fe, Cu, Al, K, and S, as well as silicon (Si), chlorine (Cl), zinc (Zn), lead (Pb), and manganese (Mn), and stated qualitatively that specimens in good condition contained higher levels of Ca, Mg and Zn. While the concentrations of common residual elements studied in that project and in this one are in general agreement, results reported here are based on more quantitative assessments of residual elements.

It was originally thought that the Dark specimens would contain significant quantities of Cu and Fe because copper pigments (Banik 1989) and iron (Shahani and Hengemihle 1986) are known to discolor paper. Tang reported that in several badly foxed books, Cu in amounts over 90 ppm and Fe in amounts over 500 ppm were associated with foxed spots and degraded areas (Tang 1978). From an analysis of 100 historical documents, Budnar et al. (2004) reported the mean Cu and Fe contents in areas written in iron gall ink to be 4100 and 31900 ppm, respectively; in areas surrounding the ink, Cu and Fe contents were 80 and 580 ppm, respectively.

The concentration of Cu found in the specimens in this study was, in all cases, lower than those found in foxed spots or iron gall ink deposits in other studies. Only two specimens, D12 and D15, had Fe levels exceeding 500 ppm. Comparison of Cu and Fe contents to the other variables—pH, YI, DP, and gelatin content—showed no strong correlations. Therefore, from this data set, no relationships were indicated between Cu and Fe and long-term stability.

The effect of metal content on pH was examined, since pH was found to affect long-term stability. Figure 3a plots the amounts of Ca and Mg, alkaline earth metals associated with alkaline constituents, versus pH. Specimens were always alkaline (pH > 7.0) when the amount of Ca was at or above 5000 ppm or the Mg concentration was above 840 ppm. Below those quantities it was not possible to predict pH. All of the Light specimens met the Mg criterion for alkalinity, while all but 4 contained the Ca concentration necessary to exhibit alkaline behavior. In contrast, none of the Dark specimens had Ca or Mg contents exceeding either of these concentrations. It was concluded that certain quantities of Ca or Mg may be

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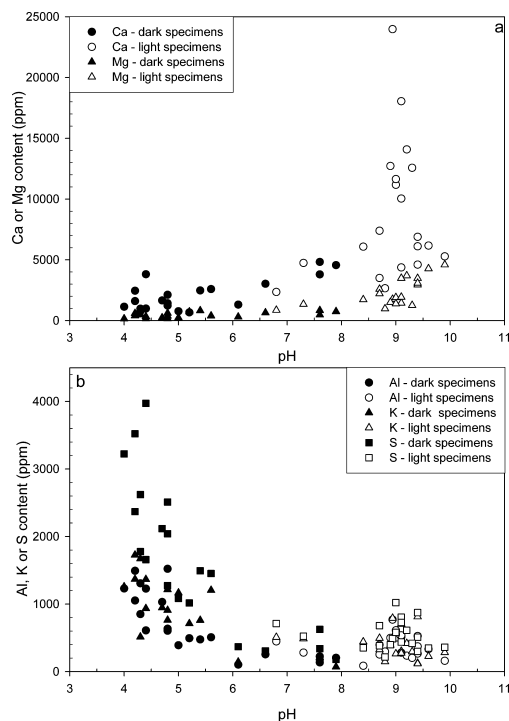


Fig. 3. (a) Relationship between pH and calcium (Ca) and magnesium (Mg) content (b) relationship between pH and aluminum (Al), potassium (K), and sulfur (S) content

necessary in a sheet of paper to ensure an alkaline pH over long periods of time.

Figure 3b shows a plot of the elements associated with alum, Al, K, and S, versus pH. When the Al content was above 610 ppm, the K content was greater than 810 ppm, or the S content was greater than 1020 ppm, a correlation with low pH (<5.5) was found. When the Al, K, or S values were below those levels, it was not possible to predict the pH. Dark specimens showed a broad range of Al, K, and S contents, while for Light specimens, the range was much more narrow. Results illustrated in Figure 3b compare well with previous conclusions that the use of alum made paper acidic (Shahani and Wilson 1987; Green 1992), and further suggest that levels exceeding specific amounts of Al, K, or S are necessary to produce detrimental, acidic properties.

Some of the presence of sulfur in paper may be influenced by a book's exposure to air pollution, and this, in turn, may help explain why most of the concentrations of Al, K, and S in this data set were not observed to exhibit alum's 1:1:2 Al:K:S stoichiomet-

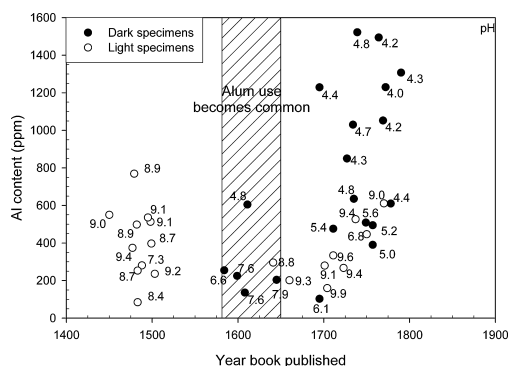


Fig. 4. Relationship between year a book was published and aluminum content; shaded area indicates the time frame alum use became predominant in Europe; numbers indicate the pH of the specimen

ric ratios. However, these elements did show strong correlations with one another, and their occurrence in larger quantities coincided with the approximate period when alum came into common use in paper manufacture.

There is no precise date for the introduction of alum into European papermaking. Estimates of its introduction range from ca. 1579 or earlier (Brückle 1992) to 1634 (WJBRL 1974) to 1650 (Clapp 1972; Erhardt and Tumosa 2005); however, it is generally accepted that by the late 1600s, alum was in common use. Barrow noted that there was an overall decline in the pH values of paper made after his proposed date of 1634 for the introduction of alum (WJBRL 1974). While it is likely that these elements are associated with alum, more analysis would be necessary to definitively draw that conclusion.

Figure 4 considers the effect of the introduction of alum by plotting publication date versus Al content. Next to each data point is the pH determined for that specimen. The gray area in the figure indicates the time period when alum came into common use in Europe. Every specimen in this data set made before alum became widely used showed a high pH. Specimens made after that period fell into three categories. Category I comprised specimens whose Al content was higher than 610 ppm. These specimens were acidic regardless of their alkaline earth metal content. Category II consisted of specimens whose Al content was lower than 610 ppm, and had Ca or Mg contents exceeding 5000 and 840 ppm, respectively. These specimens were alkaline. Category III specimens had an Al content lower than 610 ppm and

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Ca or Mg contents below 5,000 and 840 ppm, respectively. These specimens were acidic. These results may provide insight into which elements, and at what concentrations, control long-term pH.

3.3 GELATIN VS. PAPER CONDITION INDICATORS

The third goal of this project was to understand how gelatin content affected the properties associated with long-term stability. Figure 5, a plot of cellulose DP versus gelatin content, showed there was no overall correlation between gelatin content and DP. However, when a specimen had more than 5.5% w/w gelatin content, a high DP was observed. When the gelatin content was less than 5.5% w/w, it was not possible to predict DP.

Figure 6, a plot of YI versus gelatin content, also showed no overall correlation between gelatin content and yellowness. Similar to the DP results however, when the gelatin content was greater than 5.5% w/w, specimens had low YI values. When the gelatin content was less than 5.5% w/w, it was not possible to predict YI.

While high gelatin content samples (greater than 5.5%) showed good long-term stability properties—high DP and low YI—low gelatin content specimens did not have any predictable relationship with the two of the indicators of long-term stability. It was noted though that some specimens with low gelatin content still showed low YI and high DP. In order to better understand the results from the gelatin analysis, figure 7, a plot of pH versus gelatin content, showed that specimens containing more than 5.5% w/w

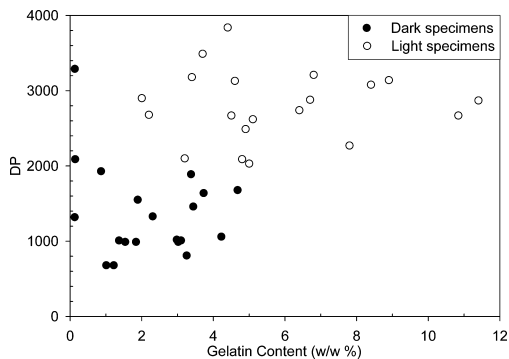


Fig. 5. Relationship between weight percent (w/w%) gelatin content and degree of polymerization (DP)

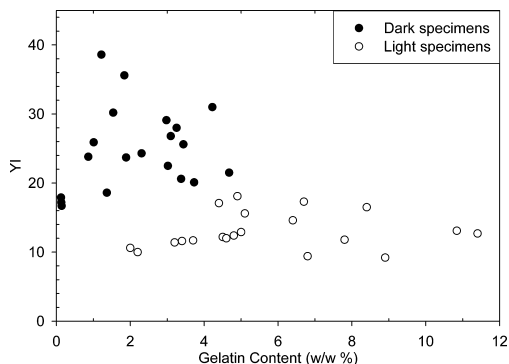


Fig. 6. Relationship between weight percent (w/w%) gelatin content and yellowness index (YI)

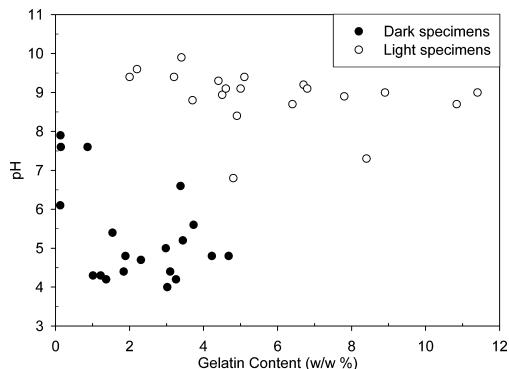


Fig. 7. Relationship between weight percent (w/w%) gelatin content and pH

gelatin content also exhibited high pH. Specimens containing less than 5.5% w/w gelatin did not show a predictable relationship with pH.

Since it was concluded previously that DP and YI values were strongly associated with pH, and all high gelatin content specimens were alkaline, it was impossible to verify that high gelatin content alone contributes to high DP and low YI values. Had there been specimens in the data set with high gelatin content and low pH, it may have been possible to uniquely assess the effect of gelatin content on DP and YI; however, there were no such specimens in this data set. Further research on the properties of specimens with high gelatin content and low pH will be required to understand the role that gelatin plays in long-term stability. From the work reported here and the work of Dupont (2003a) though, it appears that specific quantities of gelatin may be necessary to provide beneficial long-term stability.

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3.4 GELATIN VS. RESIDUAL ELEMENTS

In contrast to DP and YI results, a relationship between gelatin content and some residual metals was found. Figure 8a shows a plot of the elements associated with alum versus gelatin content. Low amounts of Al, K, and S were found in specimens with gelatin content greater than 5.5% w/w. When the gelatin content was less than 5.5% w/w, Al, K, and S contents varied widely. The Dark specimens showed a wider range of the Al, K, and S contents than the Light specimens. The connection between low gelatin content and higher alum content may be due to the discovery of the gelatin-hardening effect of alum (which allowed the papermaker to use less total gelatin on a sheet of paper to achieve a given level of stiffness).

Figure 8b shows a plot of Ca and Mg versus gelatin content. Here, it was a challenge to identify a clear relationship between gelatin content and Ca or Mg.

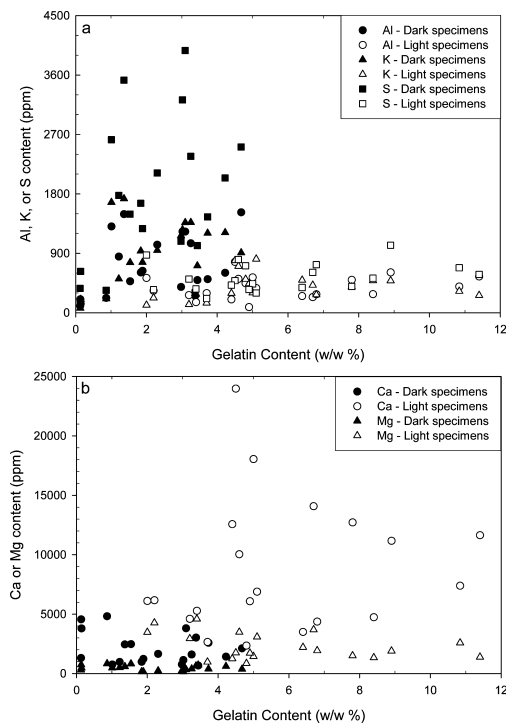


Fig. 8. (a) Relationship between gelatin content and aluminum (Al), potassium (K), and sulfur (S); (b) relationship between gelatin content and calcium (Ca) and magnesium (Mg)

It may be that some Ca or Mg was included separately from the gelatin during papermaking, for instance, as a step in rag pulping (Barrow 1978).

4. STATISTICAL ANALYSIS

In addition to relating assessed properties of naturally aged papers to long-term stability, a statistical analysis was completed in an attempt to quantify relationships between properties. A Pearson's correlation coefficient, ρ , was calculated to determine whether a linear relationship existed between any of the two measured properties from this study. By definition, ρ values range from -1 to 1 . Values of ρ between 0.7 and 1.0 or -0.7 and -1.0 mean the two properties are strongly associated with one another. Values of ρ between 0.3 and 0.7 or -0.3 and -0.7 are weakly associated with one another. Values of ρ between -0.3 and 0.3 have little or no association with one another. Positive ρ values indicate a positive relationship exists between the two properties (as pH increases, DP increases, for example). Negative ρ values indicate an inverse relationship exists between the two properties (as pH increases, YI decreases, for example).

For every ρ calculation made, a concomitant p-value calculation was also made. A p-value is used to test the probability that a null hypothesis, which is a third evaluation made during a statistical analysis, is true. In the analysis undertaken here, the null hypothesis assumes that no relationship exists between two properties (between Cu and YI, for example). When the p-value is greater than 0.05 , the null hypothesis is probably true, meaning that no relationship exists between the two measured properties. As the p-value increases, up to 1 , the probability that the hypothesis is significant increases.

Conversely, when the p-value is small, less than 0.05 , the null hypothesis is not significant and therefore should be rejected. For this data set, a p-value less than 0.05 means a relationship does exist between the two properties. Using p-values, it was possible to filter out relationships based upon the probability the null hypothesis was significant, and then rank the remaining relationships in terms of the strength of the associations from Pearson's correlation coefficient calculations.

Table 3 shows the Pearson's correlation coefficient values (ρ) and the p-values in parentheses calculated from data in this study. Results lightly grayed out had p-values greater than 0.05 , meaning

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Table 3. Pearson's Correlation coefficient ρ , and corresponding p-values in parentheses below. Shaded data indicate the two properties probably do not have a relationship with one another ($p > 0.05$)

	YI	pH	Gelatin content (GC) (wt. %)	DP	Ca	Mg	K	Elements (ppm)			Fe
	ρ	ρ	ρ	ρ	ρ	ρ	ρ	Al	S	Cu	
	(p-value)	(p-value)	(p-value)	(p-value)	(p-value)	(p-value)	(p-value)	(p-value)	(p-value)	(p-value)	(p-value)
YI											
pH	-0.837 (<0.001)										
GC (wt %)	-0.462 (-0.002)	0.458 (0.003)									
DP	-0.800 (<0.001)	0.891 (<0.001)	0.485 (0.001)								
Ca (ppm)	-0.528 (<0.001)	0.660 (<0.001)	0.467 (0.002)	0.538 (<0.001)							
Mg (ppm)	-0.640 (<0.001)	0.794 (<0.001)	0.329 (0.038)	0.641 (<0.001)	0.482 (0.001)						
K (ppm)	0.552 (<0.001)	-0.748 (<0.001)	-0.191 (0.240)	-0.690 (<0.001)	-0.318 (0.045)	-0.446 (0.004)					
Al (ppm)	0.383 (0.014)	-0.660 (<0.001)	-0.137 (0.401)	-0.592 (<0.001)	-0.204 (0.208)	-0.409 (0.008)	0.780 (<0.001)				
S (ppm)	0.554 (<0.001)	-0.788 (<0.001)	-0.259 (0.108)	-0.708 (<0.001)	-0.404 (0.009)	-0.481 (0.001)	0.842 (<0.001)	0.889 (<0.001)			
Cu (ppm)	0.167 (0.306)	-0.311 (0.051)	0.160 (0.326)	-0.229 (0.156)	-0.012 (0.942)	-0.171 (0.293)	0.311 (0.050)	0.364 (0.020)	0.267 (0.096)		
Fe (ppm)	0.058 (0.725)	0.027 (0.869)	-0.232 (0.150)	0.087 (0.596)	-0.036 (0.825)	-0.044 (0.788)	-0.212 (0.190)	-0.329 (0.038)	-0.321 (0.043)	0.198 (0.223)	

it was probable that no relationship existed between those two properties.

Two plots were created to illustrate extreme outcomes of the statistical analyses. In figure 9a, the ρ for Al and gelatin content was -0.137 , meaning little or no association existed between aluminum and gelatin. The p-value, which was 0.401, showed there was probably no relationship between the two properties. In figure 9b, the ρ for Al and S was 0.889, meaning there was a strong and positive association between the two properties (as Al increases, S increases). The p-value, which was <0.001 , meant the probability that there was no relationship between Al and S was very small.

The Pearson's correlation coefficients and related p-values offered numerical support for the assessments made using analytical techniques. The strongest association was between pH and DP ($\rho = 0.891$), indicating DP is strongly affected by pH. The second and third strongest relationships were between S and Al ($\rho = 0.889$) and S and K ($\rho = 0.842$), indicating that these three elements were connected to one another. Ca and Mg were negatively correlated with YI and positively correlated with pH and DP, indicating that these alkaline earth metals may have a positive impact on long-term paper stability. Correlations between gelatin content and pH, YI, and DP were weak, indicating that gelatin content may not have the consistent beneficial impact as was previously thought.

Finally, although it was thought that Cu and Fe might contribute to the dark appearance of the Dark specimens, no correlation was found between YI and Cu or Fe. This may have been due to the low content of these metals in these specimens. Al was found to have a probable relationship with both Cu and Fe, however the ρ values for both fell into the little or no association category.

5. CONCLUSIONS

Since the landmark work of William Barrow, surveys of naturally aged papers have been undertaken to explore the variables in composition that influence the stability of paper, and to provide validation for accelerated aging tests designed to probe paper stability. Results from earlier surveys indicated that pH is probably the most important factor in the stability of both the strength and color of paper. There is a growing belief that other paper ingredients, such as gelatin, alum, or trace elements, may also play a role in stability; perhaps directly, by affecting the pH, or indirectly, through chemical mechanisms not yet fully understood. Understanding the mechanisms by which the ingredients of a paper affect its long-term aging is critically important in identifying papers that may be at risk of rapid deterioration. Such insight will provide a key to designing conservation treatments

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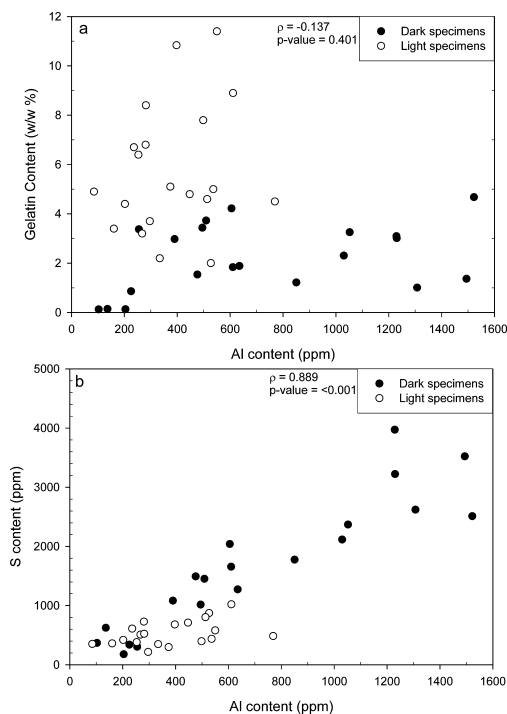


Fig. 9. Two data sets used to calculate the Pearson's Correlation Coefficient (ρ) and p-values of: (a) Aluminum (Al) content and weight percent (% w/w) gelatin content; $\rho = -0.137$ and p-value = 0.401; the two properties had little or no association with one another and a relationship between the two probably did not exist. (b) Aluminum content (Al) and sulfur (S) content; $\rho = 0.889$ and p-value = < 0.001 ; the two properties were strongly associated with one another and a relationship between the two was highly probable.

meant to increase stability or to treat ancillary problems without decreasing overall stability. As understanding of the importance of these variables has evolved, even the simplest of conservation treatments, such as aqueous washing to reduce discoloration, has become more sophisticated. Now, control over pH and trace elements during a conservation procedure is commonplace. Questions remain about the influence on stability of other ingredients, such as gelatin or alum, and conservation treatments will continue to be developed as new information is gained.

In the survey reported in this paper, assessments were made of the current condition of forty linen papers ranging in age from 215 to 531 years. While the initial properties and aging conditions of these papers are unknown, the role of pH, gelatin content,

and residual metals on their long-term stability could be inferred. High pH specimens were associated with positive chemical (high DP, high Ca and Mg contents) and appearance (low YI) measures of stability. Low pH specimens showed signs of appearance loss via discoloration, chemical signs of degradation via low cellulose DP, and larger quantities of Al, K, and S, the elements associated with alum. These results led to the conclusion that pH was the predominant property affecting the long-term stability of these specimens.

While a direct relationship between gelatin content and DP or YI was not observed, it was discovered that when the gelatin content was above 5.5% w/w, specimens were in generally good condition. These high gelatin content samples showed low YI, high DP, and lower amounts of Al, K, or S. Specimens with a gelatin content below 5.5% w/w tended to have broad distributions of YI, DP, Al, K, and S, and therefore demonstrated a range of condition. More work will be necessary to clarify the role of gelatin in the long-term stability of paper. It appears that a specific quantity of gelatin may be necessary to provide long-term stability.

The results of research reported here support the view that pH is the most important factor in the strength and color stability of paper. The current study begins to illuminate which ingredients, and in what quantity, have an effect on pH. While there was some evidence that gelatin levels above 5.5% w/w are beneficial, more work is needed to clarify the relationship between gelatin concentration and pH. These results show that alum plays a more important role in pH during long term natural aging than was previously thought. While all the papers contained some quantities of Al, K, and S, the elements present in alum, it was not until certain levels were present that a detrimental effect on the specimens was observed. A deeper investigation into the impact of alum concentration on long-term paper stability may be in order. Finally, it appeared that Ca and Mg, like alum, impacted paper stability when present in certain quantities. Further study into the effect of the varying amounts of these two elements on pH would be useful.

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APPENDIX

Paper Specimens

The 40 specimen sample set was selected to span a range in gelatin content (0% to 11.4%), condition (dark to light in color), apparent strength (weak to strong), and overall quality (poor to good). Provenance and previous storage conditions for all the specimens are unknown but care was taken to avoid specimens where there was evidence of exposure of the entire leaf to water, conservation treatment, signs of binder resizing such as an overly flat sheet lacking in type impression, or any discoloration from handling. An additional priority was to select sheets with the largest available homogeneous non-print area to permit the largest number of small sample destructive and non-destructive tests.

In general, the specimens identified as Dark in this study showed evidence of insufficient beating, unskilled sheet forming or couching, and other signs of rough workmanship. This contrasted with the other half of the specimens, identified as Light in this study, where most showed evidence of uniform high quality rag selection, carefully executed beating, good formation quality, skilled couching, and overall superior attention on the part of the papermaker to producing a quality finished sheet.

The date cited for each specimen was the original publication date of the book from which the specimen was taken, or was an estimate of the date of production provided by the editor of the McBey Watermark Collection (Cohen 1981). The 40 sheets in the final set were selected from a pool that included: 500+ Barrett and Barrow book leaves printed between 1479 and the late 1700s (McBey unprinted leaves included); 35+ early printed leaves specially purchased by University of Iowa (UI) Special Collections in November 2005; 13 specimens supplied by Terry Belanger at University of Virginia (UVA) Rare Book School in December 2005; 15 18th century broken books from

the UI Libraries discard/rebinding training collection acquired in November 2005; 12 specimens supplied by Bill Cotter in December 2005; and 32 duplicate or new specimens specially pulled from Barrow's broken books at the Library of Congress in December 2005.

Fiber identification

Specimens were pulped using a micro-disintegrator and analyzed to determine the type of fiber and the average fiber length. The TAPPI standard test method TAPPI T-401 and polarized light microscopy were used to determine the fiber type of each sample.

Gelatin analysis

For each specimen, 3 samples were analyzed to determine the gelatin content. A 1.2 mm Whatman Harris micropunch was used to punch disks from 10 different locations in the same historical leaf. Those disks were then amassed to make one sample that weighed 4–7 mg air dry (AD). For the thinnest sheets weighing approximately 50 g/m² this required the equivalent of 1 cm² or about 88 disks. For the heavier papers weighing closer to 100 g/m², about 44 disks were needed.

All of the Light specimens were punched out using the same side of a Whatman supplied self-healing pad followed by a brief burst of Norazza Duster canned air to clear the punch tip between specimens. The Dark specimens were sampled in the same way using the opposite side of the pad during punching. After punching, disks were transferred to a tared, 2 ml screw-topped autosampler vial. The vial had previously been uncapped, dried for 30 minutes at 105°C, then recapped and cooled in a desiccator. Each sample was transferred to one of these cooled vials and the AD weight recorded.

Gelatin was extracted from each sample for gas chromatography–mass spectrometer (GC-MS) analysis following an established protocol that uses dilute aqueous hydrochloric acid (HCl) (Halpine 1995): to each sample vial, 1000 μ L of 0.1 N HCl was added. After capping, the vials were heated for 1 hour at 105°C. Once cooled, a 100 μ L aliquot of each extract solution was transferred to a Reacti-Vial and evaporated to dryness with a stream of nitrogen on a Reacti-Therm heating block at 55°C. To each Reacti-Vial, 5 μ L of a 200 ppm norleucine internal standard solution (in 0.1 N HCl) and 100 μ L of 6 N aqueous HCl

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were added. The vials were heated in an oven for 24 hours at 105°C, and then cooled to room temperature. Derivatization and quantitative GC/MS analysis were carried out using a silylating reagent (Schilling 2005).

Gelatin content, reported as a percentage, is the ratio of the weight of the gelatin in the paper sample to the weight of the whole paper sample. Gelatin content was calculated from the concentrations of 7 of the most stable amino acids (alanine, glycine, L-valine, L-leucine, L-isoleucine, L-proline, and L-hydroxyproline) present in each paper sample extract. The total weight % (% w/w) of the stable amino acids in each paper sample was converted to % w/w gelatin in the paper by a conversion factor (modern parchment contains 56.5% w/w of stable amino acids). Reported gelatin content values were the average of 3 unique measurements.

Yellowness index (YI)

The YI was measured according to the ASTM standard test method E313-00. A GretagMacbeth Color-Eye 7000 colorimeter controlled by Propalette Optiview Gold version 5.2 software was used to collect the data. Data were collected using a single thickness of sample; no backing material was placed behind the specimen. Values reported are the average of 4 separate tests.

pH

The TAPPI standard test method T-509 was used to measure the pH with several exceptions. The paper to water ratio was 0.0357g paper in 2.5 mL water. All pH measurements were made in a sealed glove bag that was purged of carbon dioxide by using nitrogen gas. Water used for each sample was brought to a pH of 7.3 by distilling it according to Appendix A.3 of the TAPPI method. An Orion ROSS pH microprobe electrode attached to a Thermo-Orion model 720A benchtop pH meter was used to measure the pH. Due to the small quantity of sample, only one pH measurement was made per specimen.

Degree of polymerization (DP)

After pH analysis, a modification of the solvent exchange protocol developed by others (McCormick et al. 1985; Dupont 2003b; Strlic and Kolar 2003) was used to prepare the specimen for DP analysis. Each specimen was first soaked in 2.5 mL of water for

24 hours. The specimen, while constantly stirring, was soaked twice in methanol for 1 hour followed by filtration. This procedure was then repeated twice using dimethylacetamide (DMAc). Finally, the specimen was dissolved in 5 mL of an 8% (w/v) solution of lithium chloride (LiCl)/DMAc, stirred continuously for 24 hours at room temperature, then stored at 4°C for 7 days. On the day of analysis, solutions were diluted to 0.0625% (w/v) cellulose in a 0.5% (w/v) LiCl/DMAc solution.

Molecular weight distributions (MWD) of the dissolved specimens were collected using a Waters 2695 Separations Module coupled to a Waters 2414 refractive index detector and Empower software, database version 5.0. Separations were carried out using 3 Waters HR Ultrastaygel columns in series, HR5, HR4 and HR3, held at 70°C. The refractive index detector was set to its highest temperature, 50°C. The mobile phase was a 0.5% (w/v) solution of LiCl/DMAc and was flowed at a rate of 1 mL/minute. An autosampler was used to inject 125 μ L aliquots of sample solution into the GPC. Eight pullulan standards covering the range of molecular weights were dissolved in the LiCl/DMAc solvent and analyzed to generate a calibration curve. Averages of three injections of each specimen solution were used to determine the MWD and weight-average molecular weight (M_w). The degree of polymerization (DP) was calculated by taking the M_w and dividing by the monomer molecular weight of cellulose, 162 g/mol.

Residual metals analysis

Using a diamond blade, samples from 10 unique locations in each specimen, adjacent to the same locations where material was removed for other analyses, were cut and assembled to make one sample for analysis. The total weight of each sample was 0.1 g AD. Samples were digested in Teflon screw-top vials at ~105°C for 24–26 hours using a 1:10 23 N hydrofluoric acid (HF):8 N nitric acid (HNO₃) solution. Resulting solutions were diluted to 400 times the original paper weight with Milli-Q deionized water. A Thermo iCAP 6500 inductively coupled plasma-optical emission spectrometer (ICP-OES) was used to measure parts per million (ppm) quantities of calcium (Ca), magnesium (Mg), potassium (K), aluminum (Al), sulfur (S), copper (Cu), and iron (Fe); the wavelength used to measure the presence of each element was 370.6, 285.2, 769.8, 237.3, 180.7, 324.7,

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and 259.9 nm, respectively. Raw ICP-OES counts were blank-subtracted and corrected for the dilution volume. Synthetic Library of Congress Preservation Research and Testing Division (LC PR&TD) solution standards were used as calibration standards. Precision for each element except Al is better than 1%; for Al, it is better than 2%. Accuracy (based on replicate analysis of standard solution) is better than 2%, except for Fe, which is better than 4%.

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SOURCES OF MATERIALS

Methanol
Fisher Scientific code A452SK
<http://www.fishersci.com>

Dimethylacetamide
Spectrum chemicals code HP562
<http://www.spectrumchemical.com>

Lithium chloride
Sigma-Aldrich code 310468
<http://www.sigmaaldrich.com>

hydrofluoric acid
Sigma-Aldrich code 339261
<http://www.sigmaaldrich.com>

Nitric acid
Sigma-Aldrich code 225711
<http://www.sigmaaldrich.com>

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