

Investigations of Nondestructive Methods for the Estimation of Gelatin Content in Paper

ABSTRACT

A large portion of printing and writing paper produced in Europe between the fourteenth and the eighteenth centuries is believed to contain gelatin sizing. Some of these papers have survived in exceptional condition after centuries of long-term natural aging. However, no survey of the gelatin content of a large representative sample of these papers has ever been accomplished. To undertake such a survey, or to evaluate the gelatin content in important artifacts on paper during conservation treatment, new non-destructive analysis techniques must be developed. We are engaged in experiments employing near infrared (NIR) and ultrasonic (US) instrumentation for this purpose. In general we have found that NIR spectra and US values correlate with gelatin content in laboratory-made samples and in historical paper specimens. As a result of this work, we believe both techniques deserve further research attention.

INTRODUCTION

Recent research provides increasing evidence that gelatin plays a positive role in the permanence of paper. Dupont (2003) demonstrated that gelatin likely behaves as a sacrificial component in paper due to preferential hydrolysis of the protein molecules over those of the cellulose. Gelatin can also bind transition-metal ions such as iron (II) and copper found in iron-gall inks (Kolar et al. 2003; Kolbe 2004). Bowden and Brimblecombe found the same effect when they used gelatin to model the impact of copper on leather and collagen artifacts (2003). This is important because transition metals can enter the paper via contamination (such as in the water supply used to make the paper) as well as from iron-gall inks. Very recent-

ly, Baty and Barrett have confirmed the anticipated role of gelatin as a pH buffer in paper (2005).

Yet little is known about the actual quantity of gelatin present in historical papers and its relationship to the permanence of those papers. In 1972 Barrow analyzed ten seventeenth- and eighteenth-century writing papers, and found they contained 2.6–5.8 weight percent glue. To the best of our knowledge, Barrett and Mosier's "The Role of Gelatin in Paper Permanence" (1995) was the first article to relate the present condition of historical paper specimens to the quantity of gelatin present. Specifically, using a small-sample destructive test, they established a possibly significant correlation between higher gelatin content and better permanence (as indicated by lighter color). But they tested only forty specimens. To obtain a clear picture of gelatin's role in the stability of paper subjected to long term natural aging, a survey of many hundreds of specimens is necessary. Since the sample pool must include some of the most rare, best-performing papers extant, the development of new non-destructive analysis techniques is essential.

This article summarizes our recent investigations of near infrared (NIR) and ultrasonic (US) testing methods for the estimation of gelatin content in paper.

NIR spectroscopy utilizes infrared radiation with wavelengths in the range 700 to 2500 nm as opposed to the mid-infrared (mid-IR) range (2500 to 200,000 nm) that is more frequently used in conservation (Derrick et al. 1999). Because of advances with detectors and personal computers, NIR is becoming more commonplace, and it is employed by pulp and paper manufacturers specifically in the areas of troubleshooting, diagnostics, condition monitoring, and moisture detection (Hojjatie et al. 2001), as well as in many other industries. The peaks in NIR spectra are combinations of overtones and overlapping bands, so, unlike the mid-IR range, it is usually not possible to associate specific chemical functional groups with certain peaks in a NIR spectrum. While mid-IR is better suited to qualitative analysis of an unknown for comparison with a database, NIR has advantages for quantitative analysis of

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Specimen	Date	Assayed % Gel	Standard Deviation	Used for Figure 8 NIR	Used for Figure 11 US
1 W35	1685	0.01	0.01		X
2 W75	1793	0.48	0.05	X	X
3 W153	1607	0.33	0.08		X
4 W157	1627	0.52	0.07	X	X
5 W90	1712	0.73	0.06	X	X
6 W71	1789	0.78	0.10	X	X
7 W70	1798	1.10	0.20		X
8 W107	1761	0.97	0.06	X	X
9 W100	1750	1.00	0.10	X	X
10 W93	1736	1.40	0.02	X	X
11 T16	1499	7.60	0.82		X
12 T165	1660	4.30	0.50	X	X
13 T117	1775	3.80	0.27	X	X
14 T3	1704	3.00	0.68		X
15 T139	1716	3.00	0.25	X	X
16 T99	1757	2.30	0.17	X	X
17 T114	1794	2.00	0.26	X	X
18 T137	1757	1.30	0.10	X	X
19 T150	1679	0.80	0.15		X
20 T101	1754	0.46	0.04	X	X
21 T2	1701	3.20	0.35	X	
22 W33	1685	0.03	0.00	X	
23 W74	1795	0.30	0.03	X	
24 T83	1711	2.10	0.24	X	
25 T96	1727	1.30	0.13	X	
26 W145	1779	1.30	0.14	X	X
27 W155	1635	0.02	0.00	X	
28 T91	1778	1.30	0.10	X	X

Fig. 1. Table of historical specimens used in the experiments. Some specimens were excluded from the NIR model calculations because of their large standard deviation relative to the gelatin concentration or because further analysis showed that they were being given too much weight in the calculations.

certain materials. For example, cellulose absorbs so strongly in the mid-IR that peaks from a paper sample may be distorted, and the signal from weaker-absorbing compounds and minor components may be overwhelmed. In the NIR range cellulose does not absorb as strongly, so quantitative analysis may be more feasible.

In previous work, historic paper specimens with known gelatin content were analyzed quantitatively and non-destructively using mid-IR (Ormsby and Barrett 2002). Preliminary work during that project using laboratory-made controls indicated that NIR might be better suited to this application. In the present research, a portable UV-VIS-NIR spectrometer was used to analyze the controls and historical specimens.

Ultrasonic (US) techniques offer an alternative non-destructive technique for estimating gelatin content. In the

paper industry US measurements are used to determine paper strength non-destructively both in the laboratory and online—on a rapidly moving web of new paper. Research has shown that increasing amounts of gelatin content in laboratory samples or historical papers correlate with increasing z-direction (through the thickness of the sheet) US properties (Barrett 1989; Waterhouse and Barrett 1991; Barrett et al. 2000). Based on this earlier work we have continued testing on the US properties of both paper types using new instrumentation (SoniSys 3D-UTI) developed by SoniSys, Inc. of Atlanta, GA.

PROCEDURES

Laboratory-prepared Whatman and flax handmade paper samples used in our experiments were sized in 0.5%,

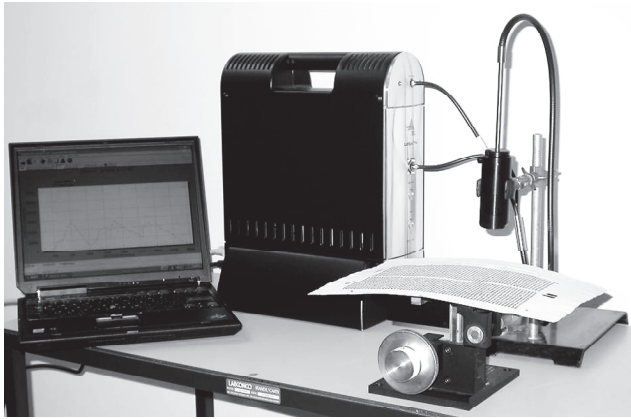


Fig. 2. Reflectance spectra were collected with a portable UV-VIS-NIR spectrometer. The historic paper specimen was placed on an adjustable stage for focusing.

1%, 2%, 4%, 6%, and 8% gelatin solutions (wt/wt) prepared using a photographic-grade gelatin and hard water as documented by Barrett and Mosier (1992). Percent of final-weight gelatin pick-up values shown in the figures were obtained by preconditioning and conditioning all specimens and then using the first bare sheet as the zero gelatin content baseline.

Figure 1 lists all historical paper specimens used in our experiments. Hydroxyproline determinations were undertaken as described by Barrett and Mosier (1995).

NIR

Reflectance NIR spectra were gathered with a LabSpec Pro spectrometer (Analytical Spectral Devices, Inc.) and a wide-angle, non-contact probe as shown in figure 2. The probe illuminated an area approximately one square centimeter on each paper specimen (fig. 3). Samples were placed on top of a sheet of Tyvek (DuPont), which provided a uniform background. For each specimen spectra were taken at random locations that did not have ink or obvious signs of staining or other damage. A total of six spectra were taken from each specimen, three each from the front and back. Each spectrum was acquired in approximately five seconds. The spectra were averaged to help compensate for variation across the surface of the page due to possible non-uniform gelatin coating. The data were analyzed using GRAMS/PLSplus IQ software (ThermoElectron).

Figure 4 shows the spectra from a group of historic specimens dating from 1483–1798. The variation in the peak heights, particularly near 1400–2400 nm, is presumably related to differences in the concentration of gelatin sizing, which were known to range from 0–7% by weight based on Barrett and Mosier's work. To evaluate this relationship, statistical analysis was performed to calculate a model relating the NIR data to the gelatin content.

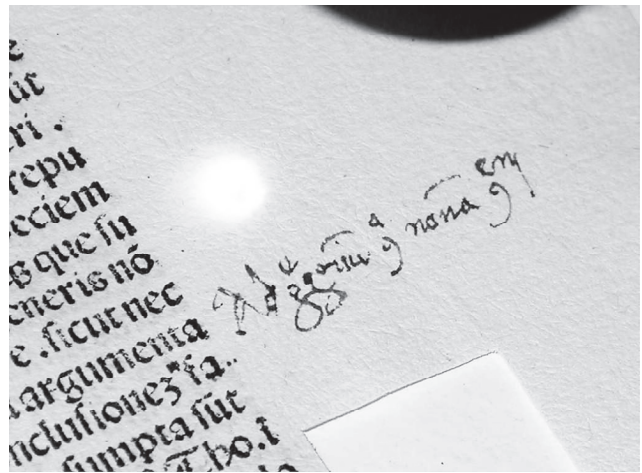


Fig. 3. Spectra were taken from an area of approximately one square centimeter. The missing rectangular area was previously removed to make destructive hydroxyproline measurements.

Although spectra were collected in the UV and visible ranges, as shown, these points were not included in calculating the model. Previous work using a fluorescence microscope had indicated that the UV range might be useful because of gelatin's fluorescence (Ormsby 2001), but with the UV-VIS-NIR spectrometer the UV signal-to-noise ratio was too low to supplement the NIR data. The visible range was also not used in the model, but the data are available for possible future analysis such as calculating colorimetric values.

The statistical analysis software offers several methods for developing the model, and each option has a number of variables that must be selected. Once the calculations are completed, a variety of techniques is used to evaluate the quality and robustness of the model. For example, by plotting various statistics it may become apparent that a particular spectrum skews the results or that the model fits

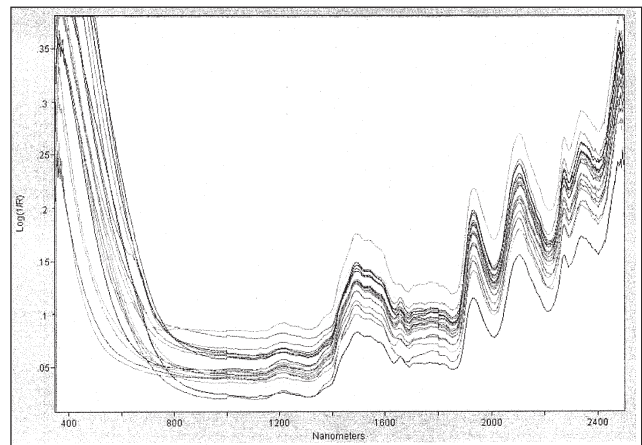


Fig. 4. UV-VIS-NIR spectra collected from papers produced between 1483 and 1798 are shown. The UV range is at the left and the NIR range is at the right.

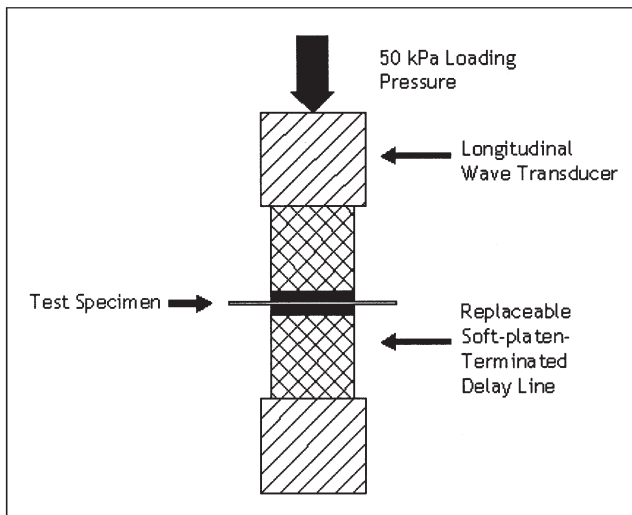


Fig. 5. Schematic diagram of the SoniSys out-of-plane (through the thickness of the sheet) stiffness tester showing principles of ultrasonic measurement. In this dry-contact technique a paper specimen is sandwiched between two piezoelectric ceramic transducers and the speed of ultrasonic waves traveling through the sample is measured. A 50 kPa loading pressure and Neoprene-terminated plastic delay lines are used to enhance acoustic coupling.

the data poorly in a certain range. Through a process of trial and error the model's variables are adjusted to optimize it. In this project, a partial least squares method was applied to the first derivative of the spectra. Further details are available upon request.

US

Using the Whatman laboratory-prepared samples and historical specimens assayed for gelatin content by Barrett and Mosier (1995), a number of tests were run. The apparatus employed in all tests was a SoniSys 3D-UTI ultrasonic testing instrument set up for paper stiffness measurement through the out-of-plane ("through the thickness of the sheet") or z-direction. The instrument was used with a transducer at an excitation frequency of 1 MHz and a loading pressure of 50 kPa. A neoprene platen 19 mm in diameter was used for all tests. Unless noted otherwise, paper was tested at 50% relative humidity (RH) after conditioning for 24 hours at 50% RH. In all experiments ultrasonic data were collected at a total of ten randomly selected points along the surface of each specimen away from printed areas whenever possible. Mean and standard deviations of the measured data were stored in a spreadsheet file. Figure 5 is a schematic diagram of the SoniSys out-of-plane stiffness tester. Figures 6a–d shows different views of the SoniSys 3D-UTI ultrasonic testing instrument in its out-of-plane configuration including a photo of a paper sample in place during testing.



Fig. 6a.

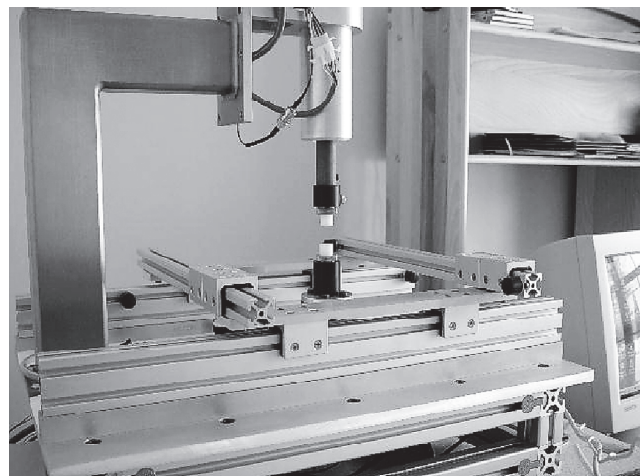


Fig. 6b.

RESULTS AND DISCUSSION

NIR

Preliminary work focused on samples of gelatin-sized flax paper controls. The gelatin content was determined by weighing the paper before and after the sizing bath and calculating the percent weight gain. These data were used by the analysis software to calculate a model relating the gelatin content to the NIR spectra. The results are plotted in figure 7. If the model were perfect then all the points would fall along the straight line and the R^2 value would equal 1. If there were no relationship between the gelatin content and the NIR spectra then the points would be scattered randomly around the graph and the R^2 value would be close to 0.

The results from the flax controls are promising since most points are near the line and the R^2 value is close to 1. With the historical specimens there is much more variation not only in age but also in fiber type, production methods, additives, contaminants, etc. The model for these

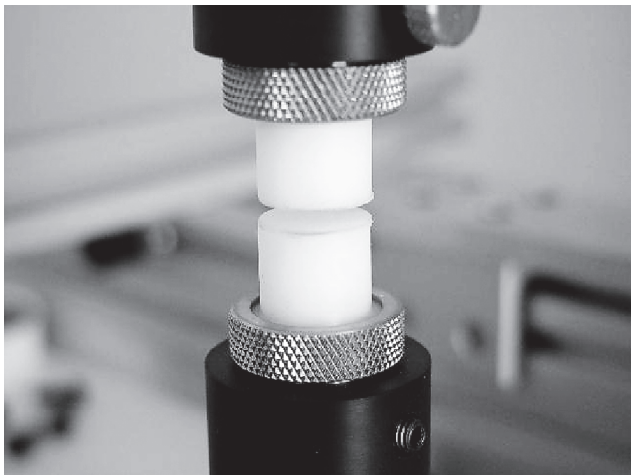


Fig. 6c.

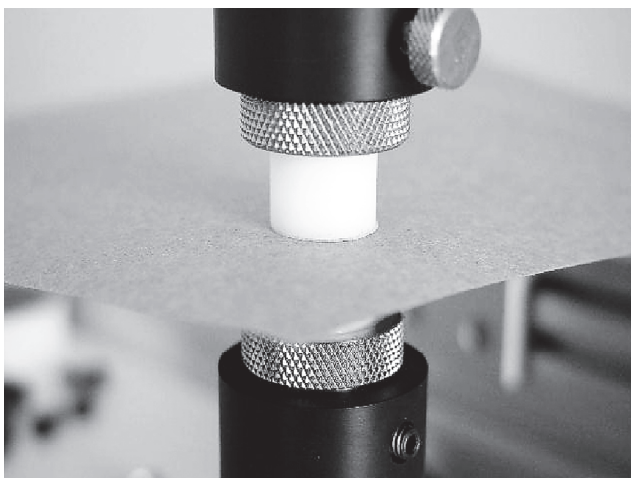


Fig. 6d.

Fig. 6. Photographs of the SoniSys 3D-UTI ultrasonic instrument with (a) a metallic shield and computer used for data acquisition and monitoring, (b) a close-up view of the base support, and also close-up views of the transducer-delay line assemblies (c) without and (d) with a test specimen. By measuring the sample thickness according to a TAPPI standard and also measuring the time of flight of ultrasound through the paper specimen, the ultrasonic velocity is determined. From that the paper specific stiffness along the thickness direction is calculated.

specimens is likely to be less successful than with the controls, and figure 7 shows the results. The points are spread further from the line, and the R^2 value is 0.70 compared to 0.94 with the controls.

With the control samples in figure 7 the gelatin content was determined by the weight gain. For the historical specimens the gelatin data plotted on the horizontal axis in figure 8 are from Barrett and Mosier's 1995 destructive measurements of hydroxyproline, an amino acid component of gelatin. The hydroxyproline procedure is difficult

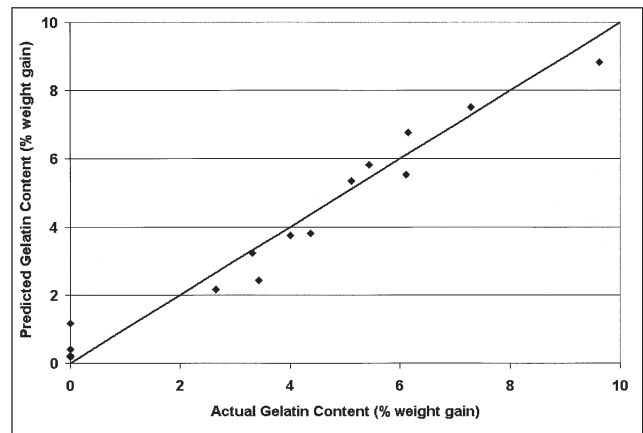


Fig. 7. The horizontal axis shows the gelatin concentration of flax control samples as determined by the weight gain from sizing. The vertical axis is the gelatin concentration as predicted by the model based on the NIR spectra. If the model were perfect then all the points would fall on the line.

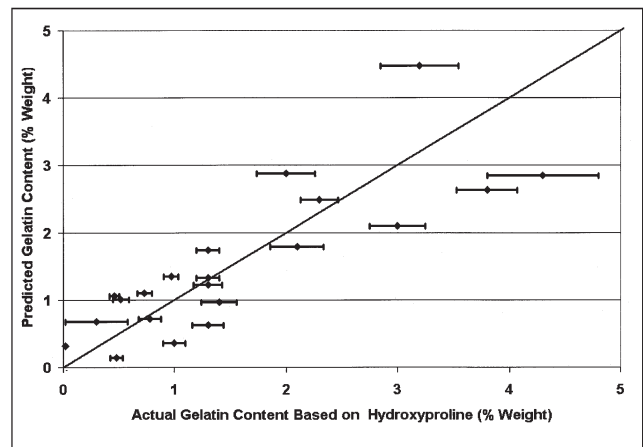


Fig. 8. The horizontal axis shows the gelatin concentration determined by destructive hydroxyproline measurements of the historic specimens. The vertical axis is the prediction from the NIR model. Compared to figure 7 the points are farther from the line. Note the different scale for this graph as well as the wide error bars on some hydroxyproline measurements.

and time-consuming. In addition, the precision of some measurements was poor, as indicated by the error bars shown in figure 8. These bars represent the standard deviation of nine measurements from each specimen (fewer measurements were made on some specimens because of the limited sampling area available). As illustrated in figure 8, the error bars tend to become larger at the higher gelatin content. Unfortunately, in this range there were also fewer historical specimens to work with. Therefore, the model has difficulty in fitting the data at higher concentrations.

It might be possible to fine-tune the model by experimenting with different variables or algorithms, but the model can only be as good as the data used to calibrate it.

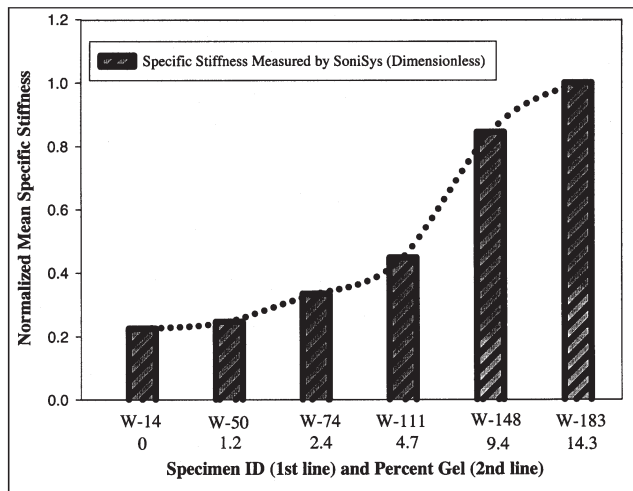


Fig. 9. The horizontal axis shows the weight percent gelatin concentration in the Whatman laboratory prepared samples. The vertical axis shows z-direction out-of-plane specific stiffness as dimensionless quantities.

Given the limitations of the hydroxyproline measurements, it is unlikely that the model's performance can be improved substantially. An alternative is to find a more accurate method to measure hydroxyproline. One promising candidate is gas chromatographic analysis of amino acids (Schilling et al. 1996). Designed for working with microgram-sized samples from paintings, the sensitive method was evaluated by studying the effect of pigments and accelerated aging on the analysis of gelatin (Schilling and Khanjian 1996). Future work will explore using this technique to analyze the historic paper specimens.

US

Figure 9 shows normalized mean ultrasonic specific stiffness values obtained on the laboratory-prepared Whatman papers. Measurements were repeated three times during a three-week period and comparison of the three measurements resulted in a maximum coefficient of variation of 6.1% for all specimens. Figure 10 confirms the trend of increasing US value with increasing gelatin concentration reported in earlier publications (Waterhouse and Barrett 1991; Barrett, et al. 2000). In the paper industry, increasing US value is generally associated with increasing degree of refining or beating. This is because increased beating produces more bonding, a denser sheet, and an increased capacity to transmit sound waves. The increased beating and bonding also produce generally higher strength characteristics. It has therefore been possible to obtain US estimates of strength properties with no destructive testing. Increased beating might be considered as one source of higher US values in historical papers as well; however, high-quality book and writing papers were made from very well-worn and carefully sorted old rags. In the stamper or

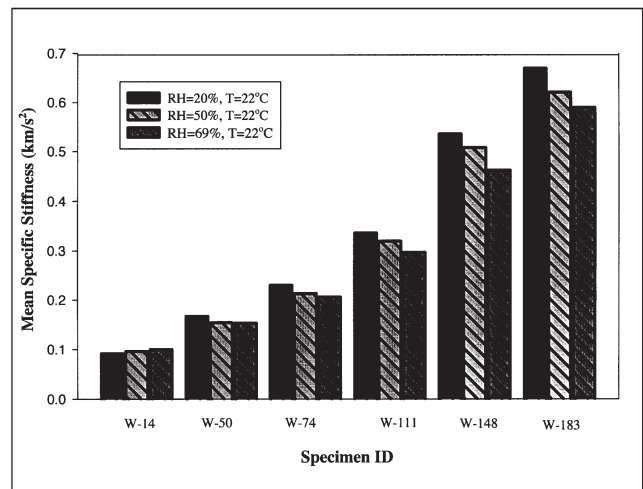


Fig. 10. The horizontal axis shows the Whatman samples with gelatin content increasing from left to right. The vertical axis shows z-direction out-of-plane specific stiffness values in $(\text{km/s})^2$ units.

beater they responded to beating rather quickly (compared to new fiber), shortening to the point where a pulp for making well-formed sheets was possible in a short period of time. With such brief beating times, the finished sheets after drying were not especially strong. We believe the majority of their strength and high US values came from the addition of gelatin.

US analyses are normally done on papers that have been conditioned in a controlled atmosphere prior to the test, whereas any regime for analyzing large numbers of books in special collections libraries will require testing under varying RH conditions. The impact of defacto condition-

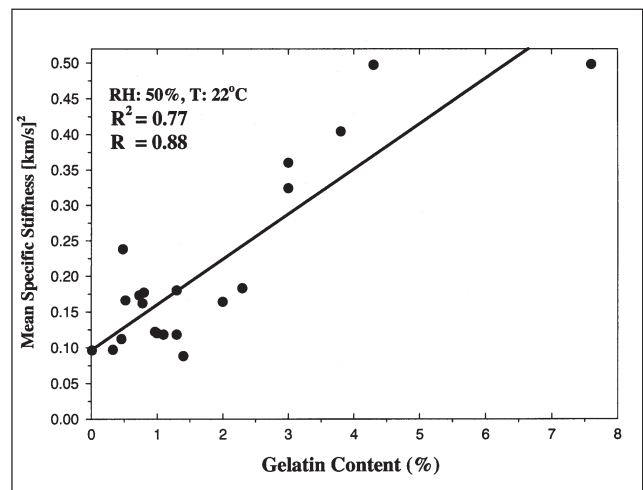


Fig. 11. The horizontal axis shows the gelatin content for the historical specimens increasing from left to right. The vertical axis shows z-direction out-of-plane specific stiffness values in $(\text{km/s})^2$ units.

ing “in the stacks” immediately prior to testing has yet to be investigated. In the paper industry, changes in RH produce a predictable variance in US data output for papers not sized with gelatin. The very preliminary results shown in figure 10 suggest the effect is the same for gelatin-sized papers, and we expect to be able to devise a formula to compensate for tests on historical papers executed in ambient conditions at RH values above or below the normal 50% RH. The ideal correction factor may eventually be based on the moisture content of the paper itself—a property which can be measured non-destructively.

Figure 11 shows relatively good agreement between US values and the known hydroxyproline assayed gelatin content of twenty-one historical specimens.

As indicated in the NIR discussion, our future efforts will focus on new amino acid analyses of a larger pool of historical specimens in order to arrive at “standards” with more precisely known gelatin content. This will permit the development of more refined US as well as NIR methods.

CONCLUSIONS AND FUTURE WORK

NIR and US methods deserve additional research attention for use in the non-destructive analysis of historical papers. US data combined with NIR data may be able to eventually give a composite picture of gelatin quantity and quality. In addition, NIR is used in several industries for moisture content determination, and a model might be developed for historical paper specimens. Likewise, because US methods are used to accurately predict the strength properties of modern-day papers, with research they may eventually be used to estimate the strength of historical papers.

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