Nondestructive Measurement of the Gelatin Content of Historic Papers Using Near Infrared Spectroscopy

Abstract

Development of methodology and preliminary results for measuring the gelatin content of historic papers using near infrared (NIR) technology is reported. An examination of 159 papers from 1460–1791 showed the mean gelatin content dropped by 20% every 50 years over this time period. These findings will be tested in a larger examination of fifteen-hundred historical papers.

The William Barrow Laboratory’s pioneering 1974 research on fifteen-hundred historical papers resulted in a new understanding of papermaking history and paper stability. However, the study did not include data on gelatin, despite the fact gelatin was a common ingredient in sixteenth- through eighteenth-century papers. Furthermore, fifteenth-century papers were not studied even though such paper often remains in exceptional condition.

Previous work by members of this group demonstrated the potential of near infrared (NIR) spectroscopy to nondestructively measure the gelatin content of historic papers. NIR spectra are gathered from specimens with known gelatin content determined by destructive methods. A model is calculated and then used to make nondestructive measurements of historic specimens.

In earlier work the model was calibrated using an industrial method to measure hydroxyproline, an amino acid specific to gelatin. The limited precision of this procedure and lack of data at higher concentrations restricted the application of this model. In the current project, calibration data were determined using a gas chromatographic method originally developed to analyze proteinaceous binding media in paintings. Samples were taken from 10 locations on 40 historic specimens. Reflectance spectra were collected near each sampling site on both sides of the sheet using an Analytical Spectral Devices LabSpec Pro UV/VIS/NIR spectrometer. To evaluate the repeatability of the spectral measurements the data were collected in three separate sessions. The system was completely shut down and the probe was disassembled between sessions. Experiments were also conducted to attempt to reduce the influence of humidity variations. Historic specimens were placed in desiccators at 20–25% RH for at least one day. They were then removed and immediately placed under the probe, and spectra were collected over the next 10–15 minutes as the specimens adjusted to the ambient RH of 50–55%.

The spectra and amino acid data were analyzed with GRAMS/PLSPlusIQ software. For each specimen the 60 spectra collected over the three sessions were averaged. A model was developed using the first derivative of the spectra over two ranges in the NIR. To reduce the response to humidity variations a region near 1900 nm was excluded. Although the instrument also gathers data in the ultraviolet and visible wavelengths, these ranges did not prove useful for the modeling because of low signal-to-noise ratios and high variability among the specimens.

The gelatin amino acid measurements and the gelatin concentrations predicted by the NIR model are plotted in figure 1. Compared to the previous work, the new model covers a broader range and predicts the gelatin content more precisely. The regression line fit to the data has an R-squared value of 0.92. The outer lines are the 95% prediction intervals. Based on these results there is a 95% probability that the nondestructive NIR predictions match the destructive amino acid measurements within ±1.3 and -1.6 over the range of 0 to 6 percent gelatin by weight. In the range of 6 to 8 percent gelatin the 95% prediction interval is ±1.5 to -2.0, and from 8 to 12 percent the interval is ±2.0 to -3.0.
A total of 159 papers made from 1460–1791 were examined using the new model. A statistically significant drop in the gelatin concentration over time was observed, as plotted in figure 2. The mean gelatin concentration fell by 20% every 50 years with a 95% confidence interval of 16.6% to 23.4%.

To be more confident that the results shown in figure 2 are representative of general trends in papermaking a larger number of specimens will be examined. A new survey of fifteen-hundred papers made between the fifteenth and the nineteenth centuries is underway. In addition, two other nondestructive methods are under investigation for research on historical papers: x-ray fluorescence for determination of calcium (Ca), magnesium (Mg), potassium (K), aluminum (Al), sulfur (S), iron (Fe) and copper (Cu) levels, and ultrasonic techniques for the estimation of strength properties.

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