APPLICATION NOTE

UV/VIS Spectroscopy

Authors:

Dipl.-Chem. Anke Drewitz, GMBU e.V.

Photonik und Sensorik
Jena, Germany

Dr. Ivo Stemmler

PerkinElmer, Inc.
Rodgau, Germany

Characterization of Iron Gall Ink on Paper in Artificial Aging Processes

Introduction

Historical manuscripts are subject to deterioration due to aging processes under different storage and handling conditions. There can be physical, chemical and biological factors with different impact on papers and parchments or inks and dyes. Optical methods are preferred for the evaluation of historic manuscripts because of its non-destructive character. Optical methods can be applied in situ and are considered to be non-invasive if care is taken on the dosage of illumination.[1] Changes in color and material composition can be correlated to optical parameters.[2,3] Iron gall inks are known to cause damage to cellulose, the main component in papers.[4] Light-induced fading or color change of a material, a form of photochemical damage caused by the absorption of optical radiation, can be monitored by absorption and reflection measurements. For the development of characterization methods and accompanying to hyperspectral imaging characterization of iron gall ink on papers and parchments artificial aging processes of modern materials were used to simulate the aging processes in historic manuscripts. Figure 1 shows two sheets of modern hand-made paper with iron gall ink writings at different ink concentrations. After an irradiation with black light lamps and storing at 90 °C (rel. humidity 40-80%) a fading and color change of the ink as well as a yellowing of the paper can be monitored. Some results of the diffuse reflectance measurements and the calculation of color values according to the CIE 1976 L*a*b* system of such unaltered and aged papers with and without ink are presented.

PerkinElmer®
For the Better

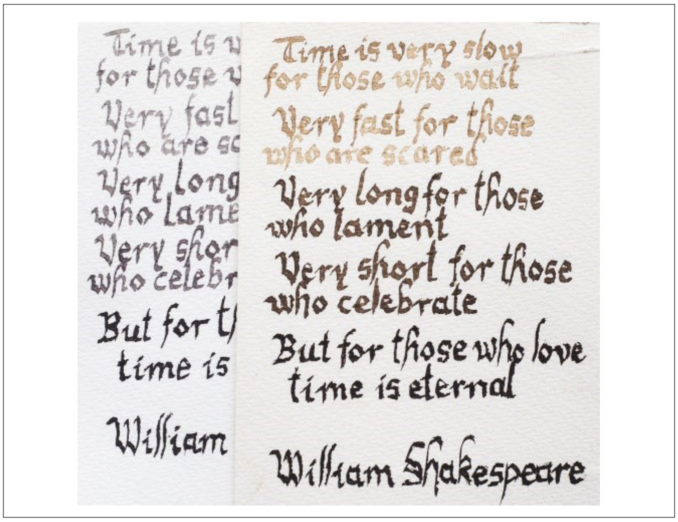

Figure 1. Manuscript with iron gall ink on hand-made paper unaltered (left) and aged (right).

Diffuse Reflectance Measurements

Reflectance measurements are the best method for characterizing inks on papers because of the non-transparent character of the paper base. For the measurements a PerkinElmer LAMBDA® 1050+ WideBand UV/Vis/NIR spectrophotometer with a 150 mm WideBand InGaAs integrating sphere (L6020322) was used (Figure 2). The paper samples were adjusted at the reflectance port of the sphere. The correction files at 100% and 0% (blocked sample beam) were taken with Spectralon™ standards at the reference and measuring ports. The spectra were recorded in the complete solar wavelength range from 250 nm to 2500 nm.

The parameters of the measurement method are shown in Figure 3. In some measurements the gain of the InGaAs detector was varied from 14 to 16 to optimize the SBW in the range where the detector and monochromator are changed. Table 1 shows a summary of the instrumental parameters.

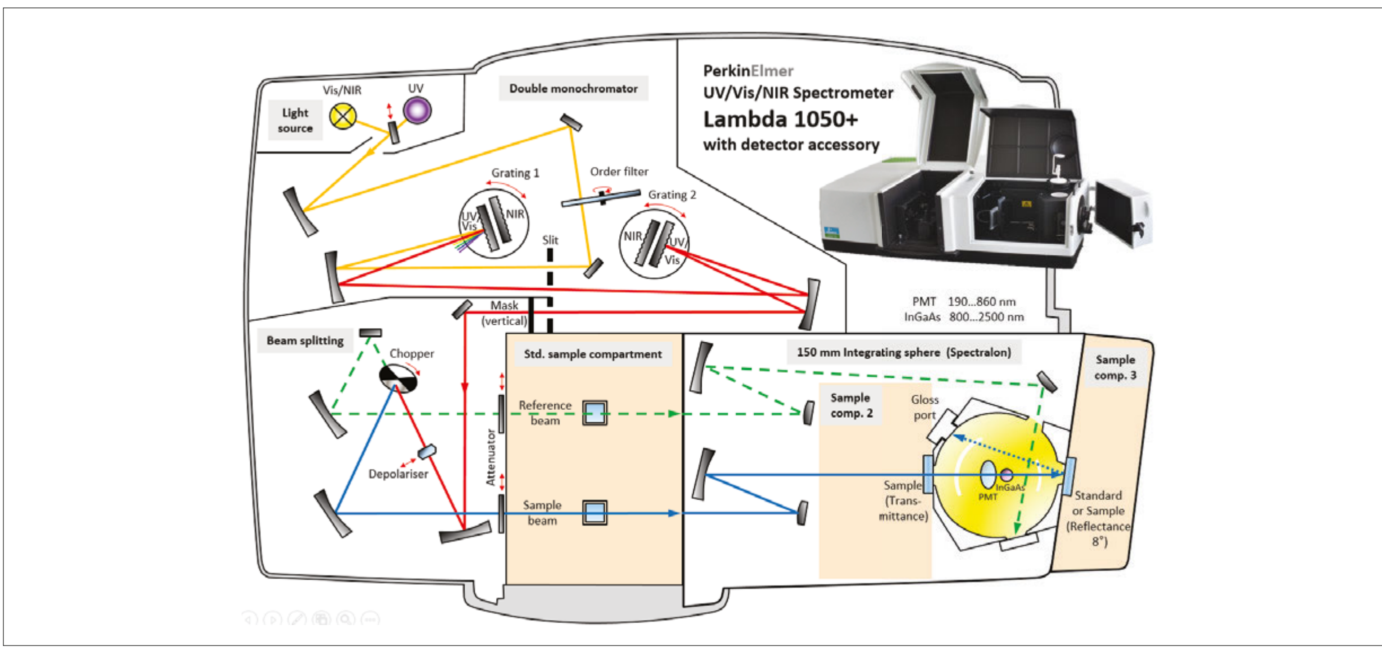

Figure 2. Optical scheme PerkinElmer LAMBDA 1050+ with 150 mm Integrating Sphere.

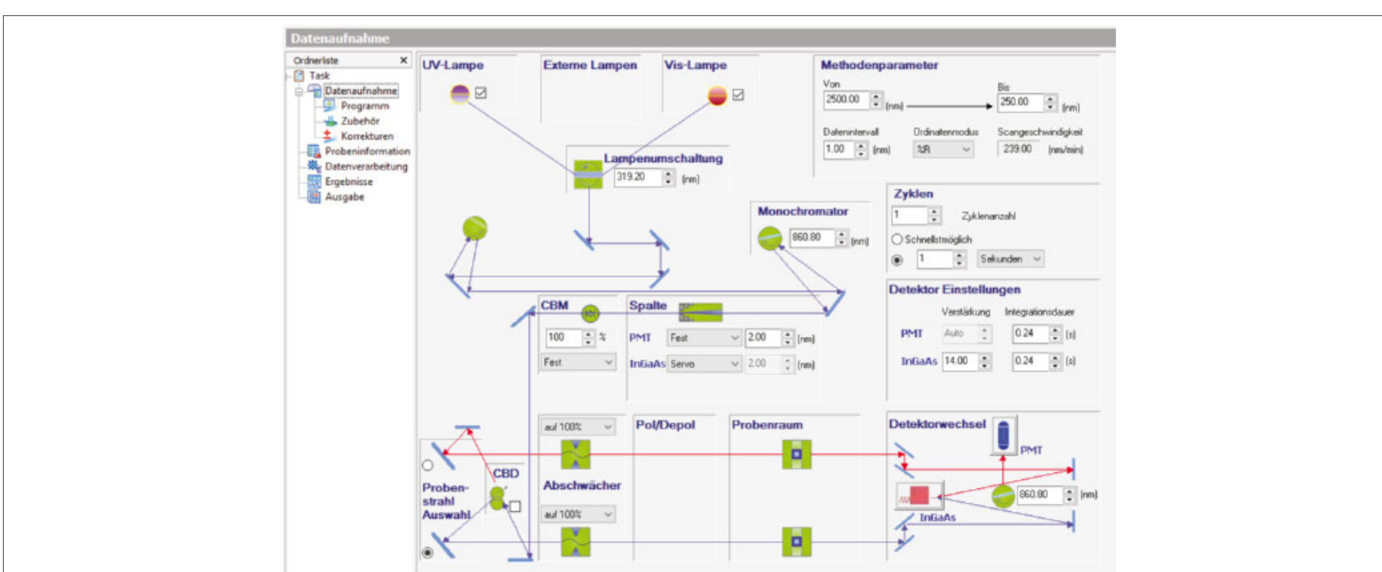

Figure 3. UVWinLab™ Method parameters (German version).

Table 1. Measurement Parameters.

Wavelength Range	250 - 2500 nm
Data Interval	1 nm
Slit (Spectral Band Width)	UV/Vis: 2 nm; NIR: Servo /Gain 14
Integration Time	0.24 s
Common Beam Mask	100%
Common Beam Depolarizer	Off
Detector And Monochromator Change	860.8 nm
Additional 0%T-Baseline	Yes

Results

Spectral changes resulting from different ink concentrations on a hand-made paper are shown in Figure 4. The pigmented blue-black ink shows a broad absorption band from the UV over visible to the NIR around 1000 nm. The absorption bands in the NIR over 1000 nm are mainly affected by the paper itself, only small changes are caused by the ink.

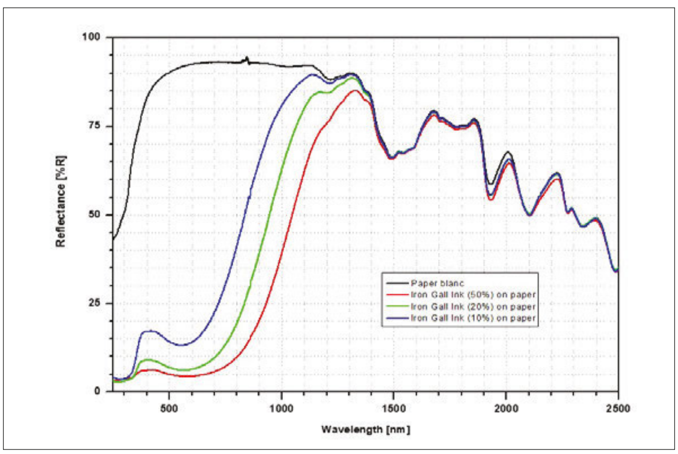

Figure 4. UV/Vis/NIR spectra of paper samples with iron gall ink (different concentrations, v/v).

The ink on paper samples were aged by heat only (Figure 5) and in combination with UV irradiation (Figure 1). Spectral changes of the paper base due to different processes are shown in Figure 6. The aged papers show a yellowing and darkening which can be observed by a reduced reflectance around 500 nm. Changes of common concentrated iron gall ink on paper during aging processes are not visible to the naked eye because of the high ink concentrations but can be recorded by the spectrometer (Figure 7).

Figure 5. Aged test sheet with iron gall ink, untreated paper in the background.

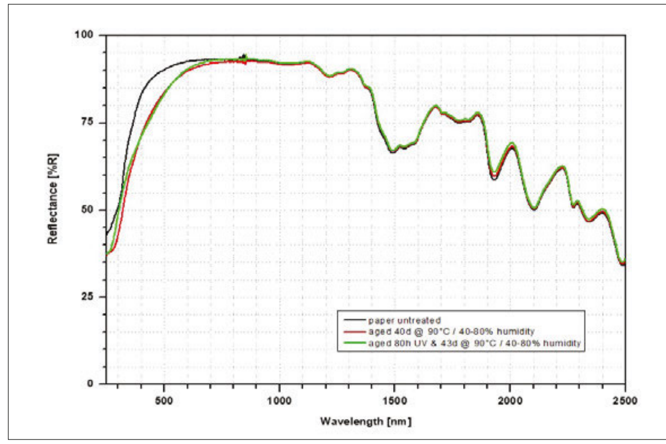

Figure 6. Comparison of spectral signatures from untreated and artificially aged papers.

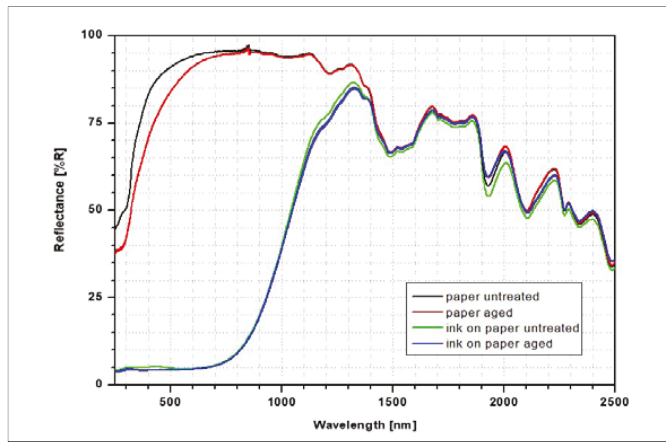

Figure 7. Comparison of spectral signatures from unaltered and artificially aged iron gall ink on paper.

Colorimetric Evaluation

Changes in color can be valued through the CIE L*a*b* system. From above illustrated, already measured, spectra colorimetric coordinates according to the CIE L*a*b* system were calculated using the UVWinLab™ implemented templates (Whiteness/Yellowness). For this work the CIE L*a*b* 1976 method with 10 degree observer angle and illuminant D65 was chosen. The calculated values for selected samples are presented in Figure 8. The darkening and yellowing of the paper through artificial ageing are shown by decreasing L* and increasing b* respective. The ink-on-paper samples provide similar effects. The red to green component a* is only slightly affected by the ageing processes.

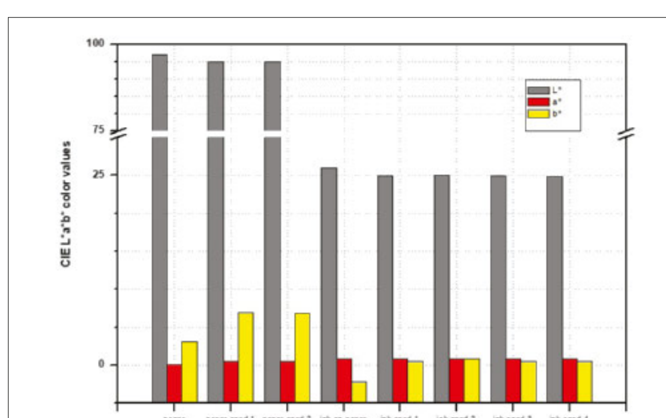

Figure 8. CIE 1976 (L*a*b*) color values for untreated and aged papers, parts with and without iron gall ink

The CIE 1976 (L*a*b*) color differences of some probes of paper with and without iron gall ink as a result of the ageing process (Figure 9) were calculated from equation[5].

$$\Delta E^*_{ab} = \sqrt{[(\Delta L^*)^2 + (\Delta a^*)^2 + (\Delta b^*)^2]}$$

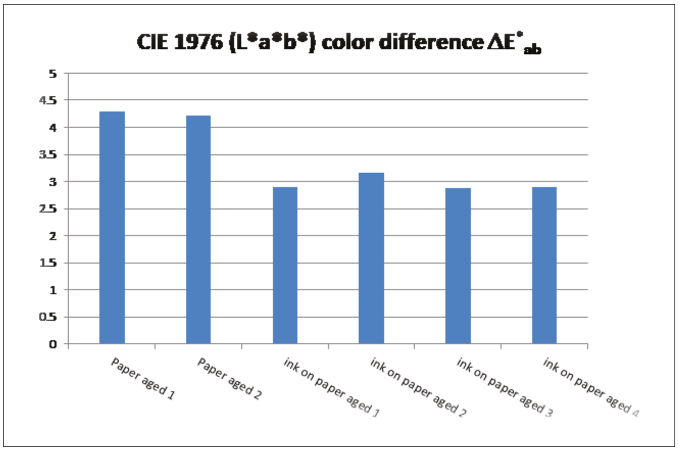

Figure 9. CIE1976 (L*a*b*) color differences between untreated and artificially aged samples.

Pitfalls to Watch For

Ink structures on paper should have minimum dimensions and had to be carefully adjusted within the incident light beam. With an SWB of 2 nm the illuminated spot is 3 x 8 mm^2 (width/height) and with 5 nm the width changes to 8 mm. With proper adjustment it can be avoided to get artifacts from gratings, detector, lamp, and filter changes. The use of the common beam depolarizer doesn't prevent the appeared artifacts. An illustration of the impacts of improper adjustments and suboptimal parameters on the reflectance measurements of an 8 mm wide coat of iron gall ink on paper (Figure 5) are shown in Figure 10. The artifact around 860 nm (detector and grating change point) is avoidable by increasing NIR gain and so reducing slit and spot size. As an alternative with same effect spot size limitation can also be reduced by using an aperture which is placed at the cuvette position. This has the advantage that with the white light alignment the maximum spot size can be seen for the complete UV/Vis/NIR spectrum. Second advantage is to work with lower NIR gain and therefore with less noise in NIR part of the spectrum.

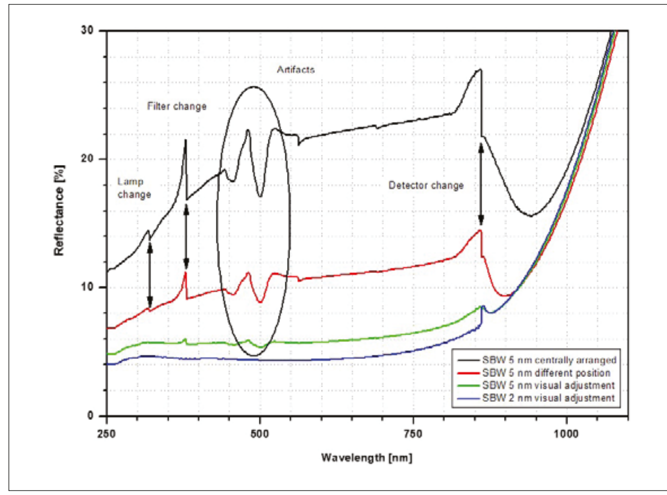

Figure 10. Impact on spectral signatures from unadjusted probes and suboptimal parameters (8 mm wide coat of iron gall ink on paper).

Conclusion

Ageing processes with heat and irradiation result in chemical and photochemical damages to the characterized materials. These changes can be detected by optical spectroscopy and valued through color differences according to the CIE L*a*b* systems. The LAMBDA 1050+ Wide Band spectrometer in combination with the 150 mm integrating sphere combination provides an excellent platform for the spectral characterization of manuscript materials in ageing processes.

References

1. Liang, H., 2011. Advanced optical imaging methods for investigating manuscripts. In: S. Neate, D. Howell, R. Ovenden and A.M. Pollard, eds., *The technological study of books and manuscripts as artefacts: research questions and analytical solutions.* Oxford: Archaeopress, pp. 55-66. ISBN 9781407307671.
2. Dolgin, B., Bulatov, V., Schechter, I., Anal. Bioanal. Chem. (2007), http://dx.doi.org/10.1007/s00216-007-1410-0.
3. M. Ciglanská, et al., The influence of pollutants on accelerated ageing of parchment with iron gall inks, Journal of Cultural Heritage (2013), http://dx.doi.org/10.1016/j.culher.2013.09.004.
4. Potthast, A., Henniges, U. & Banik, G. Iron gall ink-induced corrosion of cellulose: aging, degradation and stabilization. Part 1: model paper studies. *Cellulose* 15, 849–859 (2008). https://doi.org/10.1007/s10570-008-9237-1.
5. Hunt, R.W.G., Pointer, M.R., Measuring colour, 4th ed., 2011, John Wiley & Sons, Ltd, p. 59.

PerkinElmer, Inc.
940 Winter Street
Waltham, MA 02451 USA
P: (800) 762-4000 or
(+1) 203-925-4602
www.perkinelmer.com

PerkinElmer®

183670 PKI