J7 Characterizing Inks on Intact Documents Using Attenuated Total Reflection Infrared Spectroscopy

John F. McClelland, PhD, Jeffrey S. Sweterlitsch, PhD, and Roger W. Jones, PhD, Iowa State University, Ames Laboratory, Ames, IA*

The attendee will learn details of an infrared spectroscopy approach to characterizing and identifying inks on intact documents.

Inks are complex mixtures of dyes, resins, and other proprietary additives in a volatile vehicle. When ink is written on paper, the presence of the pulp, pigments, binders and other components of the paper substantially increase the chemical complexity of the complete sample. Often, visual inspection or thin-layer chromatography provides sufficient information to answer the questions arising in a particular case, but both of these approaches make use of only a small portion of the potential information available from such chemically complex mate- rials. Infrared spectroscopy has long been used for the analysis of complex materials because the infrared portion of the spectrum is par- ticularly information rich. However, the physical nature of ink written on paper has usually led scientists either to remove the ink from the paper or to perform microspectroscopy using an infrared microscope. The application of attenuated total reflection (ATR) spectroscopy to *in situ* ink characterization without the complexity and expense of an infrared microscope is presently under study. This approach should require less examiner time and document damage compared to other techniques. In ATR, the spectrometer beam passes through an infrared- transmitting crystal so that it reflects off the surface of the crystal. The sample is pressed against the crystal at the point where the beam reflects. The resulting spectrum is akin to that from conventional transmission spectroscopy. ATR accessories are available commercially that have sensing areas as small as 250 μm wide, so an intact document can be positioned on the ATR sensing crystal such that only the region within an ink line is analyzed. The probe depth of ATR generally does not exceed 3 μm, so the spectral contributions of the ink are emphasized in an ATR spectrum from an intact document, although the paper spectrum is still present. Proper subtraction of the spectrum of blank paper from that of the document produces a spectrum sufficiently characteristic of the ink that it can be used for identification purposes.

Methods are under development for reliably acquiring analytically useful spectra from ink on intact documents using a commercial ATR accessory with a silicon crystal. The details of this method will be discussed. Sample alignment has proven critical to attaining high-quality, reproducible spectra. In addition, many papers are spectroscopically highly variable across their surface on the scale of the ATR sampling area, so a consistent method of sampling, as well as a consistent method of subtracting the blank-paper spectrum are necessary for the difference spectra to be analytically characteristic of the ink. Simple “by eye” subtractions are not sufficient. Techniques for searching spectral libraries are being explored to determine the best approaches for using collections of reference ATR ink spectra to identify inks *in situ*. Small libraries of ATR-based ink spectra have been built up and successfully used to identify ink on intact documents. Libraries based both on the ink-on-paper spectra directly and on the difference spectra after subtracting off the paper contributions are being examined.

Ink, Documents, ATR Spectroscopy

** Presenting Author*