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Detecting Forgeries Through Ink Analysis Using FTIR Microscopy

A key element in proper forgery analysis or document verification is the ability to differentiate ink sources. Due to their ability to elucidate structural information without degrading the sample, both FTIR and Raman spectroscopy have become important workhorses in the field of ink and document analysis. They have even been used to identify the order in which inks are applied to a document and to determine the age of a document. Unfortunately, Raman characterization of inks is often impeded by the highly efficient process of luminescence. As such, the use of the longer wavelength provided by FTIR can be more insightful to differentiate inks that exhibit significant luminescence.

The most straightforward method to attenuate Raman-induced fluorescence is to change the laser excitation wavelength. Unfortunately, the intensity of Raman scattering (I_{RS}) varies inversely with the excitation source wavelength. Increasing the excitation wavelength by 2 fold would decrease the I_{RS} by 16 fold. Nevertheless, it is not uncommon to see lasers of either 785 or 1064 nm being used to perform ink characterization even considering the substantial signal loss. Additionally, increasing the laser wavelength changes the diffraction-limited laser spot diameter, effectively decreasing the resolution of the analysis.



Figure 1. Three colored Sharpies were characterized using Raman (left) and FTIR (right) microscopy. Raman and FTIR spectra were collected using an excitation source of 532 nm and a ceramic filament, respectively. Perhaps the easiest way to bypass luminescence is to avoid Raman spectroscopy altogether for some types of ink analysis. FTIR is a strong alternative to Raman, and by virtue of its infrared excitation source. spectra are not convoluted by luminescence. To illustrate the advantage of FTIR. а comparison of three Sharpie® inks on a substrate is shown in Figure 1. While the Raman spectra (Figure 1, left) give no structural information regarding the constituents of the ink, the FTIR spectra are much more informative (Figure 1, right).

To test the ability of the FTIR to differentiate unknown ink samples, three promotional black ballpoint pens were obtained



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from three different companies: Company A, B, and C. Because the pens were promotional (handed out at conferences or other events), it was unknown if the generic inks they contained were similar or not. As such, small pen strokes were generated on white printer paper and then were imaged using FTIR. The results are shown in Figure 2. Small shifts in peak locations and the development of new peaks are all used to differentiate one brand of ink from another. Important peaks for comparison are indicated with lines in Figure 2. No spectral shifts were applied prior to analysis.

As can be seen from Figure 2, the peak at 871 cm⁻¹ is constant among all samples except that it is absent for Company B. The spectral bands at 1160 cm⁻¹ shift for Companies B and C, the bands at 1360 cm⁻¹ and 1581 cm⁻¹ shift for Company A, and a new peak at 1656 cm⁻¹ is present for Company C. It should be noted that all pen strokes were characterized within one hour of being written. Thus, spectral differences are not resulting from time-dependent behaviors of carrier solvents, aromatic additives, or adhesives in the inks.

When analyzing inks or documents, nondestructive techniques are generally preferable to destructive techniques. Raman and FTIR spectroscopy are very well-suited to this end, and both exhibit the required sensitivity for accurate characterizations. When analyzing colored compounds, however, Raman scattering can easily become quenched by the overpowering and far more efficient process of fluorescence. As such, FTIR becomes a powerful alternative to characterize such samples as its IR excitation renders fluorescence contributions negligible. Furthermore, both Raman and IR signals are extremely sensitive to the surrounding environment of the atoms involved in the absorption or scattering of the excitation photons, and signal shifts down to 1 cm⁻¹ resolution can be observed.



Figure 2. Three pens from three companies (Company A, B, and C) were characterized by ATR-FTIR spectroscopy. Subtle differences in peak locations were used to differentiate one ink from another. Peaks originating solely from substrate remained constant from sample to sample, while the contributions from the ink induced unique signal shifts in the corresponding spectrum. Scan details: 128 scans/spectrum, spectral resolution = 4 cm⁻¹.