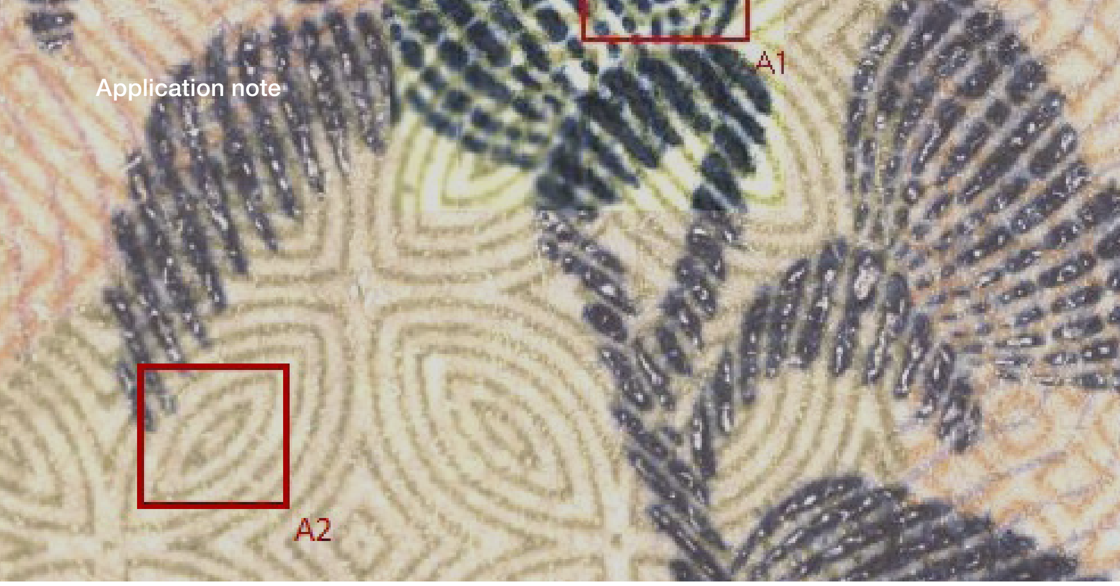
Application note



Analyzing inks and toners with FTIR microscopy

Forensic document analysis

The examination and authentication of documents is a typical focus of forensic science, and investigators are routinely asked to determine the origin and make up of a variety of written and printed materials, including letters, wills, contracts, checks, bank notes, seals, stamps, etc. This analysis looks at both the inks/toners as well as the paper onto which they are applied.

While most paper is primarily composed of cellulose, it can be processed in different ways and can contain a variety of additives and coatings. Ink analysis can require the differentiation of ink types, identification of ink sources, determining the sequence that inks were applied, or even ascertaining the age of the ink.

Figure 1. Nicolet RaptIR FTIR Microscope with ATR accessory.

FTIR microscopy

While a variety of analytical techniques are used for forensic document analysis, Fourier-transform infrared (FTIR) spectroscopy is typically utilized as an initial screening tool because it is non-destructive, and samples are conserved for any subsequent analyses. FTIR microscopy combines infrared spectroscopy and visible microscopy for joint visualization and chemical analysis of microscopic samples. FTIR microscopy can be used for single spot analysis, or it can create infrared images that use molecular information to show the spatial distributions of components across a sample area.

In this application note, a Thermo Scientific™ Nicolet™ RaptIR™ FTIR Microscope (Figure 1) was used to collect visual images and infrared data from a variety of ink and toner samples. The Nicolet RaptIR FTIR Microscope utilizes a motorized nosepiece to smoothly switch between a 10x visual objective and a proprietary 15x infrared objective. This allows you to quickly collect high-quality visual mosaic images and efficiently locate small samples or areas of interest. Switching to the 15x infrared objective provides you with higher-magnification visual images as well as optimized infrared spectra.

The infrared spectra in this application note were collected using a slide-on germanium-tip attenuated total reflectance (ATR) accessory on the 15x infrared objective. No additional sample preparation is needed for ATR data collection; the only requirement is contact between the ATR crystal and the sample. A pressure sensor in the microscope can automate sample contact using a customized contact pressure.

Complete forensic analysis of documents is an extensive topic beyond the scope of this application note. Instead, we will focus on obtaining spectra from a few types of inks/toners and discuss the factors that impact their analysis. An example where FTIR is used to differentiate between two overlapping types of blue ballpoint pen ink will also be presented.

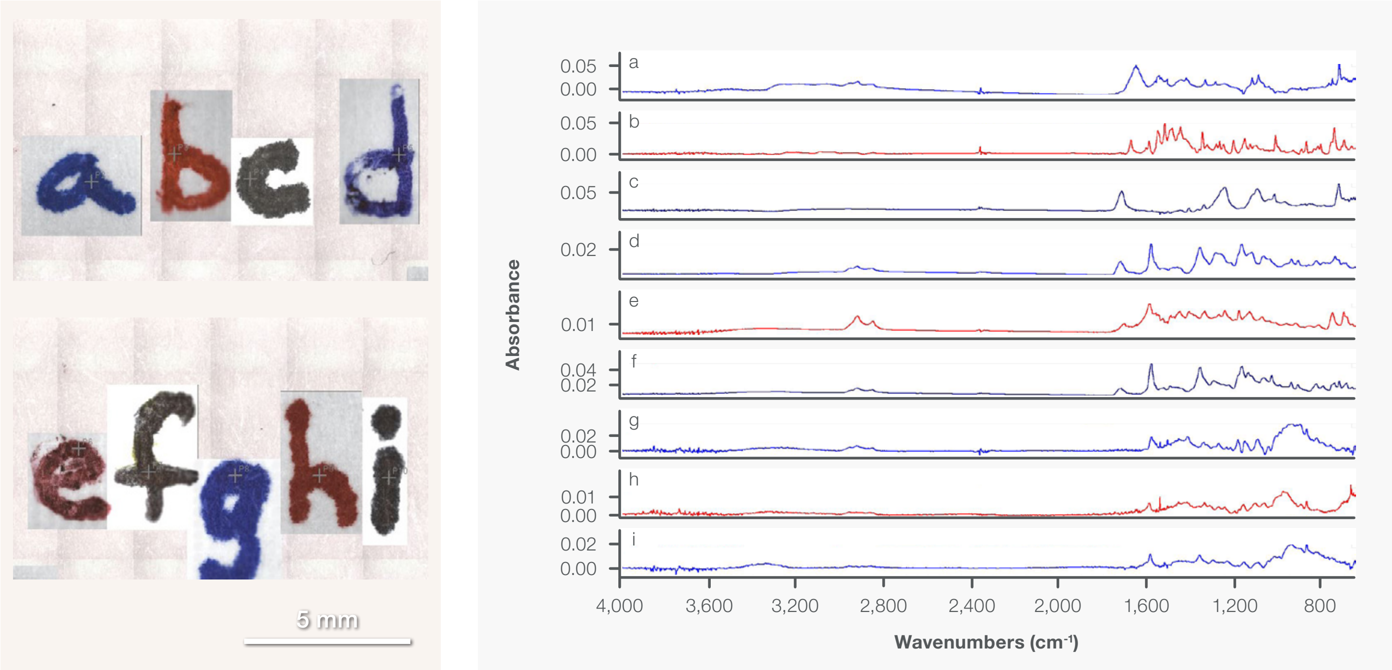


Figure 2. ATR infrared spectra from letters (a–i) handwritten on white paper with pens of assorted colors from various manufacturers. The paper spectrum has been subtracted to remove its contributions from the signal.

Ink analysis with ATR and FTIR

Spectra from various pens are shown in Figure 2. Initial measured spectra represent a mixture of contributions from the paper as well as the ink. Since each can consist of multiple components, it is usually advisable to sample from several points to evaluate potential variations in the spectral contributions of both the paper and the ink. The infrared contributions of the paper have been subtracted from each of the spectra shown in Figure 2.

Visual inspection of the spectra reveals clear differences between inks of different colors, and even between inks of the same color. There are also some cases where the inks are very similar, and differences are hard to evaluate just from visual inspection.

Ink analysis is not limited to handwritten samples. Figure 3 shows infrared images from two areas of a printed banknote. Data collected at the flower is based on a peak of calcium carbonate that is present in the ink. While paper can also contain calcium carbonate, the spatial evidence seems to indicate that this signal is primarily associated with the ink and not the paper. The second imaged area shows some of the background pattern; the infrared image is based on a carbonyl peak of an ink component. While it was possible to differentiate the ink from the paper, the ink signal was much weaker for the background pattern than the flower. This is likely because the ink used in the flower is raised and sits on the paper surface, whereas the background pattern appears to penetrate the paper more significantly. This illustrates a critical consideration for this kind of analysis: ATR is a surface technique, and the less ink that is present at the surface, the weaker the signal will be. This makes it much more complicated to deconvolute the contributions of the ink from the paper.

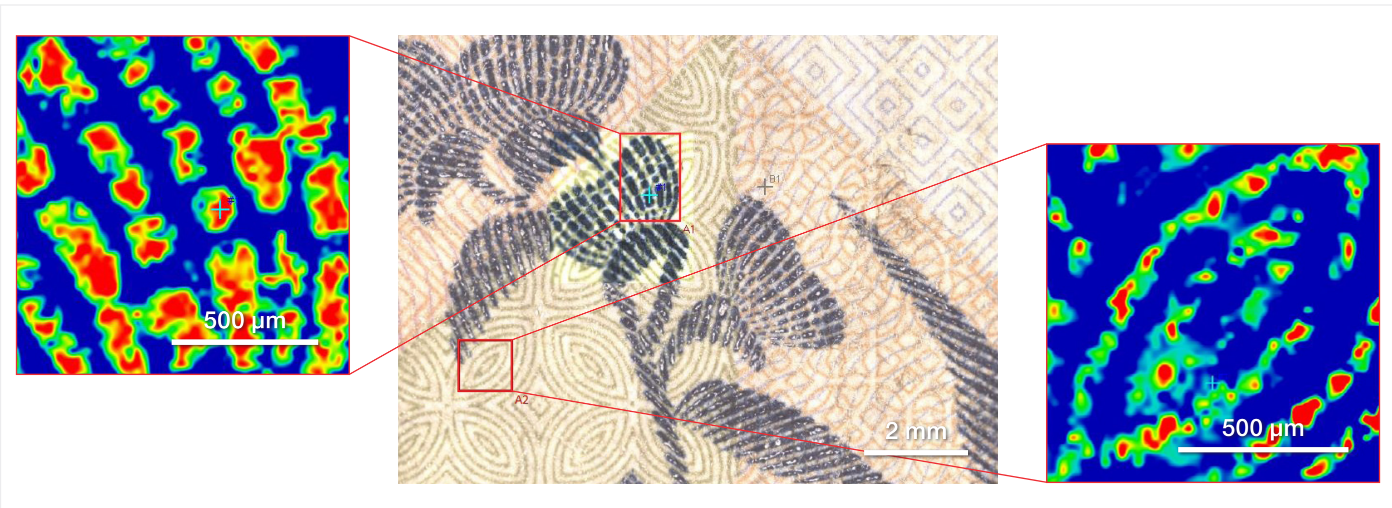


Figure 3. Infrared images generated from the printed designs on a banknote. Peak area images were generated for the flower, using a calcium carbonate peak at 871 cm-1 (left), and the background pattern, using a carbonyl peak at 1735 cm-1 (right).

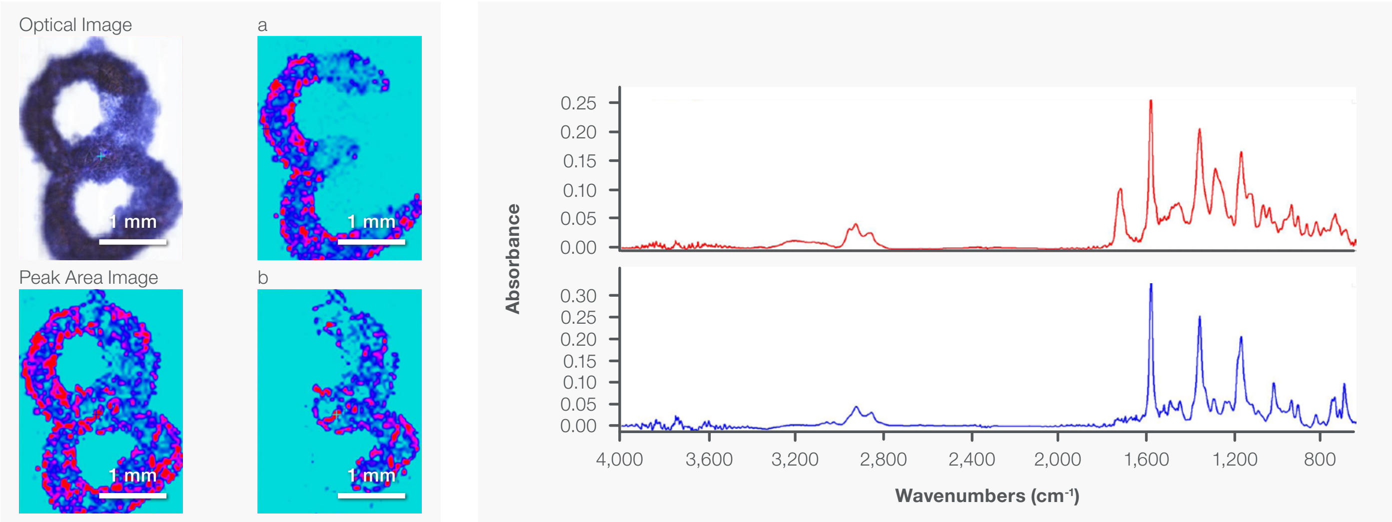


Figure 4. Infrared ATR images of two different inks used to write the number "8". a) The original "3" can be seen in the infrared image based on the peak at 1722 cm^{-1}. b) Infrared image of the second ink that was used to change the "3" into an "8," based on the peak at 701 cm^{-1}. The paper spectrum has been subtracted to remove its contributions from the signal.

Deconvoluting mixtures of inks

Figure 4 shows the differentiation of two blue inks used in a handwritten number. Microscopic visual inspection of the "8" shows some inconsistencies in the ink, but additional confirmation would be critical for any enforcement action. Infrared analysis of the ink shows that the "8" is clearly made up of two distinct types of blue ink, and that the "3" was modified to make it look like an "8." Both ink spectra have peaks that are consistent with a blue pigment (Victoria blue/methyl blue), but the ink of the "3" appears to contain an additional alkyd resin not found in the other ink. This demonstrates how FTIR can be used to differentiate between two inks without the need for a full database and discriminate methods.

Toner analysis with FTIR

Rather than printing with ink, laser printers utilize toner, which is a powder-based medium. Figure 5 shows infrared spectra from several colored lines generated on a laser printer, which uses a microscopic mixture of 4 toners (black, cyan, magenta, and yellow) to generate printed colors. Toners typically have a polymer base with added pigments; this polymer resin base generally dominates the infrared spectra due to its high proportion relative to the pigment.

In Figure 5, the infrared spectra for all toners appear to be largely the same, save for some minor differences. For example, the spectra from the red, green, and yellow lines appear to be discreet from the black and blue lines; this is likely the result of all three colors utilizing yellow toner. Some of the smaller peaks can therefore be attributed to the yellow pigment. Overall, it appears that differences in the resin base would be easier to distinguish due to the minor signal contribution from the pigments. This means that documents from different laser printers will likely be more difficult to tell apart unless there are distinguishing features in their respective resin bases.

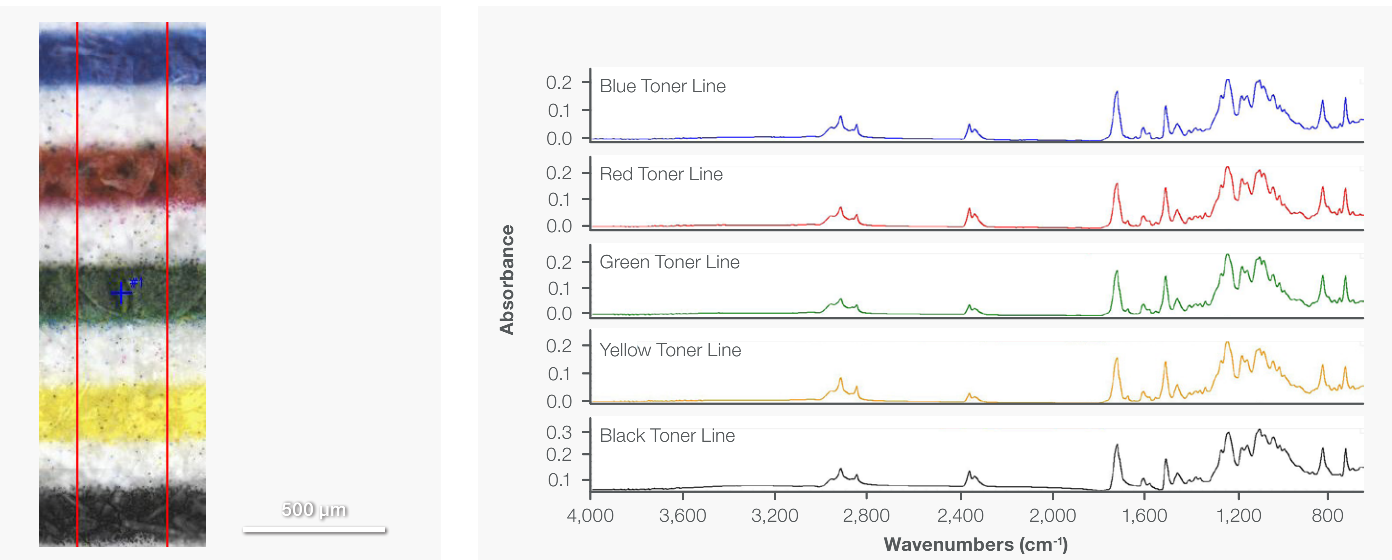


Figure 5. ATR infrared spectra from lines printed using a laser printer. The colored lines are made up from a mixture of up to four toners (black, yellow, cyan, and magenta).

Conclusions

The Nicolet RaptIR FTIR Microscope provides exceptional visual and spectroscopic insights into ink and toner samples. The non-destructive FTIR analysis preserves evidence for further testing, or presentation in court, while providing specific and detailed information about the sample. As shown, even in cases where a document was altered, the spectral data can be used to differentiate between inks. The speed and specificity combine to make the Nicolet RaptIR FTIR Microscope an ideal tool for any forensics laboratory.

Learn more at **thermofisher.com/forensics**