FT-IR Microspectroscopy in Forensic and Crime Lab Analysis

Key Words
Counterfeit, FT-IR Micro-spectroscopy, Hair, Ink, Paint, Tablet

Introduction

Forensic and crime lab samples can range from drugs to fibers. Some of these samples can be quite small and light microscopes are often used to help examine evidence collected from the crime scene. The visual aid of an optical microscope can provide investigators with a clearer picture of the evidence, especially at the microscopic level. However, sometimes more information is necessary in order to prove beyond a reasonable doubt that a suspect is guilty or innocent. Therefore, a reliable and flexible analytical technique is necessary to provide both visual and chemical information.

Fourier transform infrared spectroscopy (FT-IR) has proven to be a valuable tool for the forensic scientist on the macroscopic level. FT-IR microspectroscopy extends the use of traditional FT-IR by allowing for quick, non-destructive analysis of samples approaching 10 microns. The new Thermo Scientific™ Nicolet™ iN™10 infrared microscope is a powerful combination of an optical microscope with an integrated FT-IR. The Nicolet iN10 provides the forensic scientist with an analytical tool to visually and chemically analyze illicit tablets, hair, fibers, inks, and paints. The integrated design does not require an external spectrometer, making the Nicolet iN10 a powerful, compact FT-IR microscope.

Evidence is an essential part of any court case. For the first time, the unique ability to verify microscope performance through software provides the investigator, and the jury, with confidence that the data is reliable. The Nicolet iN10 can be operated without the need for liquid nitrogen, allowing the lab to quickly examine evidence in any location. The Thermo Scientific™ OMNIC™ Picta™ software makes operation simple and quick for even the untrained microscopist. Powerful wizards help guide the user through reflection, transmission, and ATR analysis.

Ink on Paper

Counterfeiting money is one of the oldest criminal activities known. Criminals no longer have to rely on highly skilled offset printing techniques to produce counterfeit notes. Technological advances allow for the unskilled person, with access to a photographic copier or scanner, to produce high quality counterfeit currency. However, there are distinct characteristics present in the paper and ink used in the printing process, which can identify counterfeit bills and even trace their origin.

Typically, ink is analyzed by elemental analysis, X-ray and mass spectroscopy. These methods allow for complete characterization but are destructive and time-consuming. Infrared spectroscopy has not been

Thermo SCIENTIFIC

fully utilized in the identification of ink and contaminants found on paper due to the strong infrared absorbance from cellulose between 1200-950 cm^{-1}. However, the quick and non-destructive nature of infrared imaging and Attenuate Total Reflectance (ATR) FT-IR microscopy and has emerged as a key benefit when analyzing criminal evidence. The Thermo Scientific Nicolet iN10 microscope can now play an important role in fraudulent document analysis.

Analysis of suspect inks can help reveal the type of ink and how it was applied to the paper. Ink applied by photostatic or inkjet methods can often be distinguished from offset printing techniques by visual inspection. However, with advanced printing technology this is becoming more difficult. FT-IR microscopy allows for quick chemical imaging of both the ink and paper material. This provides unambiguous information that can be directly compared to genuine documents.

Figure 1 shows a chemical image of a U.S. twenty dollar bill. The black ink can be chemically distinguished from the paper and the surrounding background ink. The chemical and visual images can be compared, showing the high resolution of the infrared microscopic information. Once the desired information is located by rapid chemical imaging, ATR analysis can provide detailed spectral information with little interference from the cellulose contribution.

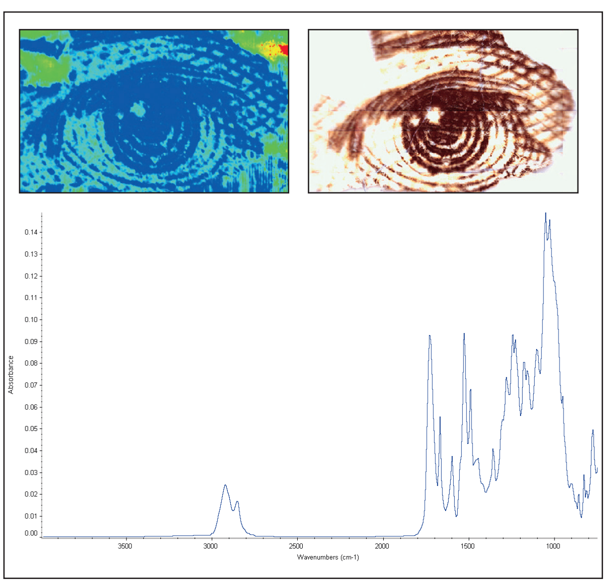

Figure 1: (Upper left) Chemical image of Andrew Jackson's eye on $20 U.S. currency (Upper right) Video mosaic of Jackson's eye (Lower) Black ink spectrum collected by Tip ATR. Chemical imaging highlights the distribution, while ATR analysis provides detailed spectral information of the ink.

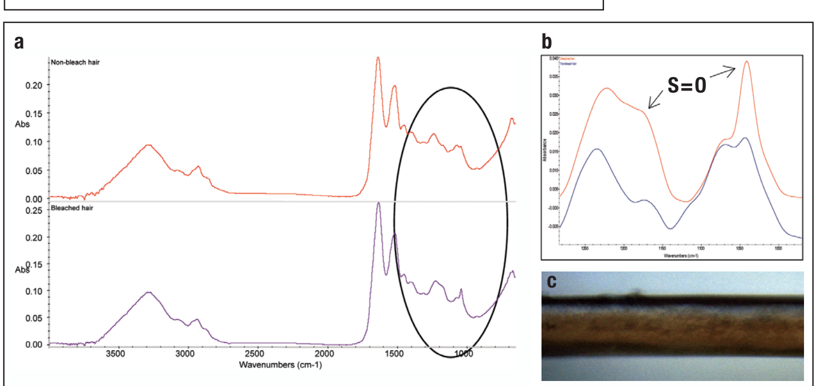

Figure 2: (a) Spectra of non-bleached (red) and bleached (purple) hair. (b) Expanded region showing S=O stretching regions (c) Video image of un-bleached hair fiber.

Fiber and Hair Analysis

Many kinds of fibers are often found at crime scenes and can provide valuable or even crucial information. For instance, forensic scientists are trained to identify and correlate physical hair features and appearances to a particular ethnic group. This information may be useful in identifying potential suspects but may not isolate one suspect from another. FT-IR microscopy can combine visual microscopic hair fiber analysis with valuable and discriminating infrared chemical information. Hair fiber chemical information can reveal residual hair styling products (such as hairspray and conditioners) and protein structure changes due to chemical treatments (such as bleaching). This additional information may prove essential in identifying a suspect.

Oxidation of hair can occur chemically or by natural sunlight. Chemical oxidizers such as hydrogen peroxide and persulfates are often found in bleaching products. Oxidation of the amino acid cystine to cysteic acid can occur in hair, resulting in an increase of the S=O stretching absorbance. Hair fiber analyzed by reflection absorption and Ge Tip ATR clearly show the difference between untreated and chemically treated hair. Figure 2b shows the region between 1400 and 900 cm^{-1} revealing the spectral differences due to the oxidation of cystine to cysteic acid. The top spectrum shows the increase of the S=O symmetric cysteic acid stretch located at ~1040 cm^{-1} and the asymmetric S=O stretch at 1175cm^{-1} due to the bleaching process.

Visual microscopy is also used to identify and compare natural and synthetic fiber evidence. A highly skilled forensic scientist can identify the physical characteristics that distinguish between different generic fiber classes. However, further analysis, including chemical analysis, is needed to determine the chemical subclass.[1] FT-IR microscopy has emerged as a powerful analytical tool that can quickly determine a fiber's subclass in a non-destructive manner and little sample preparation. All of which is important in the forensic community where preserving the evidence is critical.

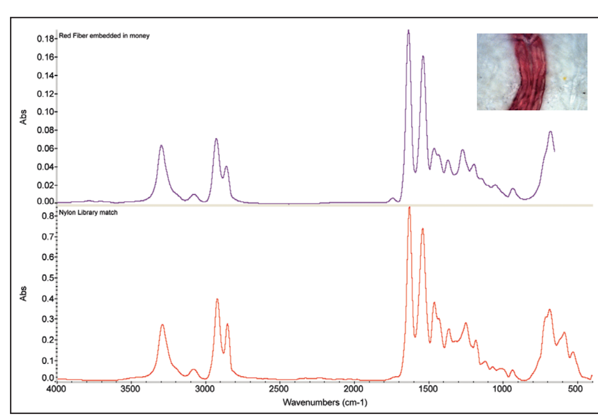

Figure 3: (Upper spectrum) Spectrum of Nylon fiber embedded in currency. (Lower spectrum) Nylon Spectral library match. (Right) Visual image captured by OMNIC Picta software.

Recently, federal currency mints have embedded special fibers into the paper as an added defense against counterfeiting. Utilizing attenuated total reflection (ATR) on the Nicolet iN10, the small security fibers in a circulating bill can be examined as shown in Figure 3. The visual image through the Nicolet iN10 clearly shows the red fiber, and the ATR data identifies it as nylon. ATR microspectroscopy provides high spectral quality with little surrounding cellulose contribution. This allows for exceptional library identification.

Tablets

Rapid analytical techniques that provide chemical composition and distribution of active ingredients for illicit drug tablet analysis are very important in forensic investigations. Sentencing guidelines can be based on both possession and quantity, so both qualitative and quantitative information are needed. Imaging with the Nicolet iN10 MX infrared imaging microscope provides a quick and non-destructive analysis technique well suited for homogenous and heterogeneous tablets. Unlike other macroscopic analytical techniques, FT-IR microspectroscopy does not require sample dissolution, which can destroy evidence and cause insoluble or re-crystallized products. The Nicolet iN10 MX, OMNIC Picta software and Thermo Scientific™ OMNIC™ Specta™ analysis tools provide drug composition information and insight to the criminal manufacturing process. Coupled with the system verification tools, this can give the investigator powerful information for use in court.

The Nicolet iN10 MX imaging infrared microscope is the first system engineered specifically for chemical imaging analysis, while providing the speed, sensitivity, and resolution of traditional infrared microscopy. Figure 4 shows a chemical image of prescription drug tablet collected using rapid imaging mapping on a Nicolet iN10 MX.

A 5 × 5 mm area was selected and the infrared data collected in approximately five minutes. The chemical image indicates the active ingredient in blue; clearly, this is the bulk of the material. However, the green and red contours indicate another component is present. Simply clicking inside one of the green/red contours reveals the spectrum of the other tablet component – in this case, an unregulated excipient.

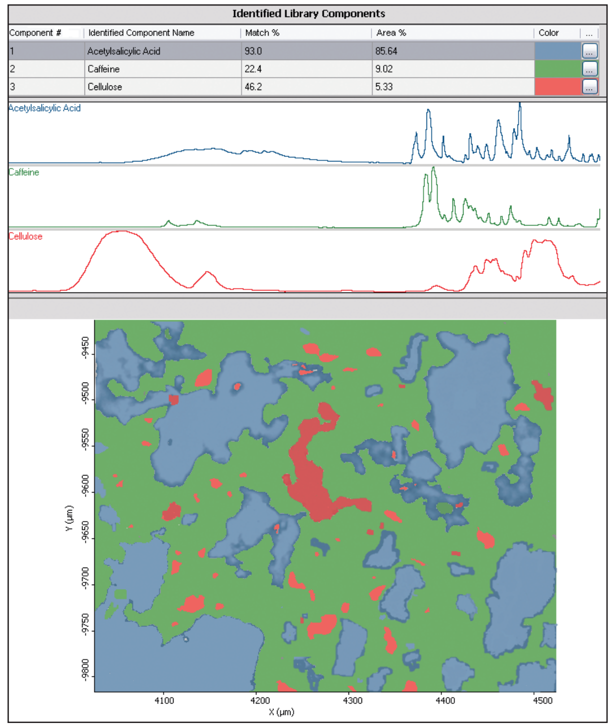

Figure 5: Tablet analysis of over-the-counter tablet by Picta Multicomponent Wizard

The OMNIC Picta software also features automatic collection and analysis wizards. For example, the random mixture wizard can automatically analyze and identify multiple components with a single click. Figure 5 shows the multicomponent wizard screenshot for an over the counter tablet. The wizard automatically creates a list of the main components by cross-correlating the collected map spectra. The wizard calculates the individual component area contribution and provides semi-quantitative distribution information. Each component can then be identified by spectral library information to provide further chemical information.

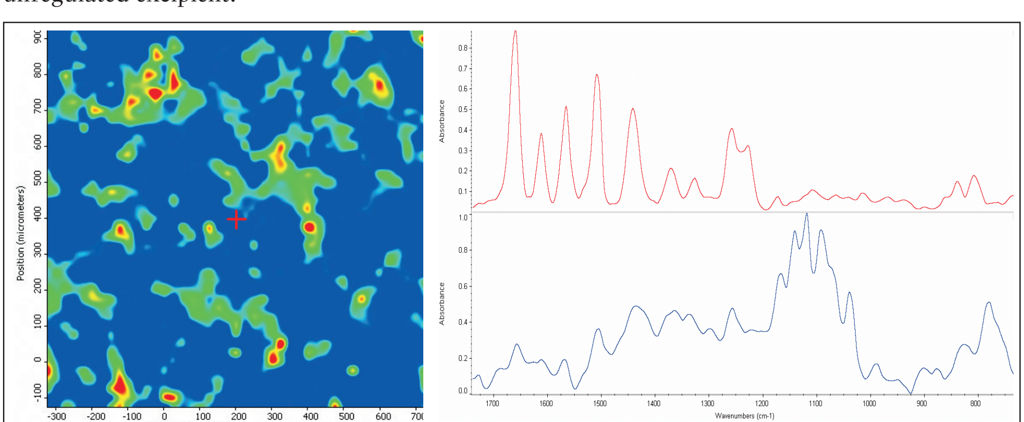

Figure 4: (Left) Chemical image of prescription drug. (Right) Red spectrum is the active ingredient and the blue spectrum is the excipient.

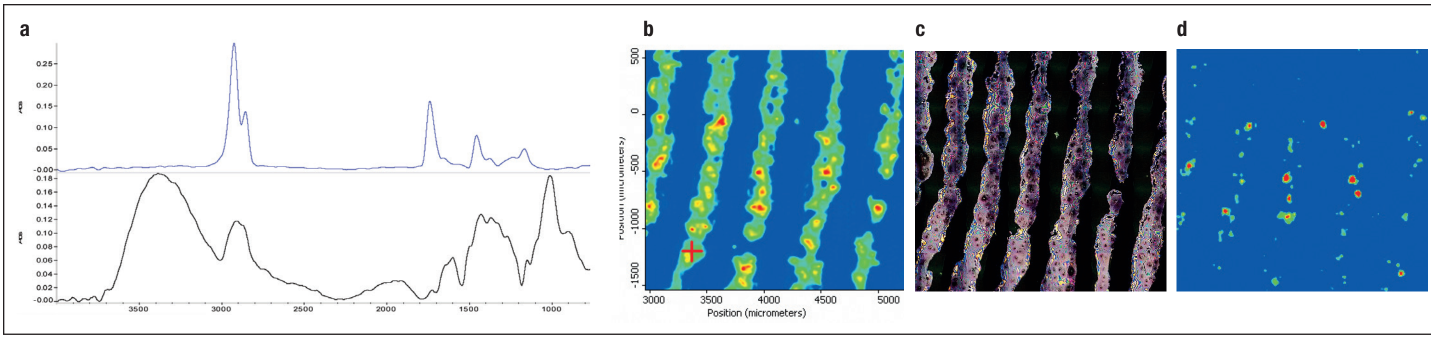

Figure 6: (a) Spectrum of natural triglyceride esters; (b) chemical image of fingerprint; (c) video image of fingerprint; (d) chemical image highlighting the fibrous wood contaminate.

Trace Analysis

Fingerprint information can be useful in identifying or confirming a suspect's involvement in a crime. While fingerprints are unique to an individual, there is more information present than just the fingerprint pattern. FT-IR microspectroscopic analysis can elicit chemical information left behind with the fingerprint. This chemical information can help trace a suspects last step before a crime.

Figure 6 shows the chemical image and corresponding video image of a 2 × 2 mm fingerprint impression made on a reflective microscope slide. The main component of the fingerprint is natural sebum oil from the skin (triglyceride esters). However, several small contours outside the fingerprint indicate another component. The lower right chemical image in Figure 6 shows a region of the fingerprint revealing a small amount of fibrous wood material. Chemical imaging quickly provides the unique fingerprint pattern while revealing important and unexpected trace chemical information.

Paint Analysis

Paint chip evidence can be found at a crime scene involving an automobile. In most cases, the paint or paint chip is transferred to a victim or object involved in the accident. Automotive paint consists of multiple layers of chemically different materials, including binders, primers, pigments and protective resins, which are applied individually to a car's plastic or metal surface. A chip of paint will usually preserve information about the individual paint layers and can be visually examined through an optical microscope. Normally, the chemical identification of the paint layers requires dissolution and chemical extraction. Using fast mapping FT-IR microscopy provides quick chemical identification of each layer. The images in Figure 7 show the analysis of a multi-layer paint sample. Layer 1 is the outer protective polyurethane coating, layer 2 shows the base coat and polypropylene polymer (main component of the bumper), layer 3 is the paint binder layer.

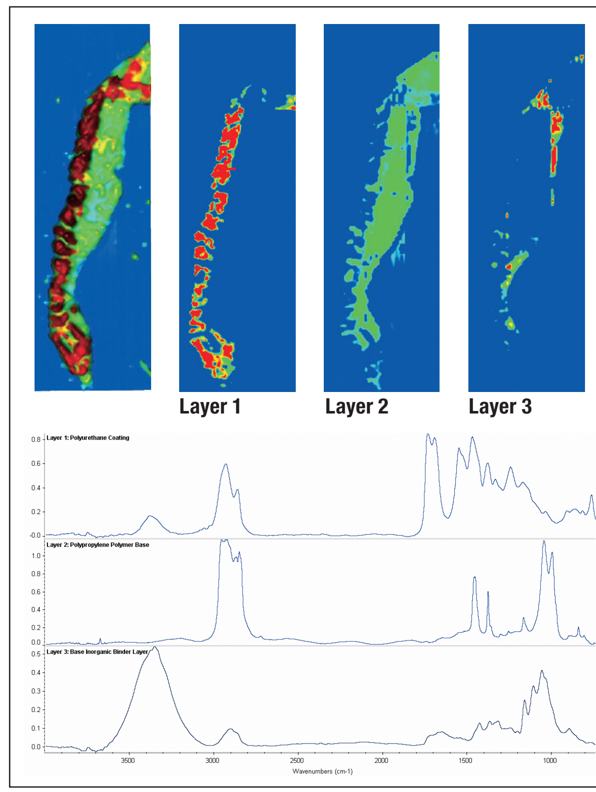

Figure 7: (Upper) Chemical image of a car bumper paint chip layers. (Lower) Spectra of identified layers: Layer 1: protective coating. Layer 2: base coat and polypropylene polymer, Layer 3: binder layer.

Residues

Chemical residues obtained from a crime scene can provide valuable information and additional clues. Residues are often sensitive to evidence handling and ideally analyzed with little interaction. FT-IR microscopy can locate and analyze trace residues without sample preparation or removal. Figure 8 demonstrates the sensitivity of infrared microscopy for this application. A portion of a 10-cent Euro coin was analyzed using the Nicolet iN10 MX imaging microscope. The detailed chemical image (upper left) reveals a thin pink outline around the stamped coin markings. The residue spectrum indicates the material is protein based and is most likely attributed to human skin and oil residue. However, this demonstrates how quickly evidence can be analyzed for trace materials.

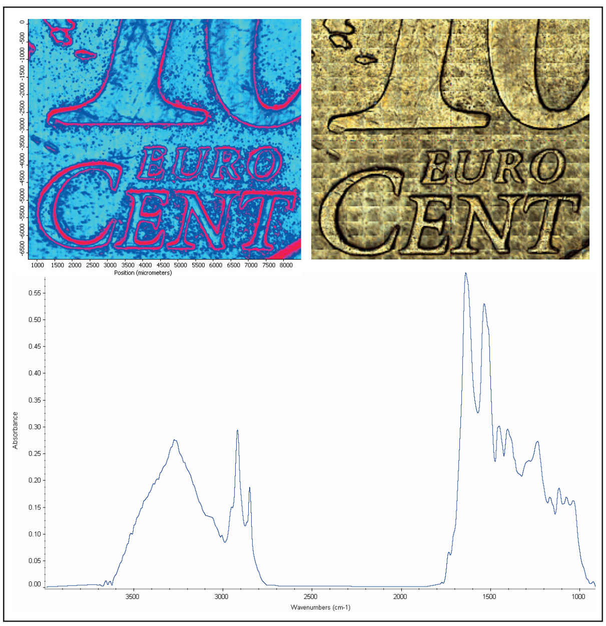

Figure 8: (Upper Left) Chemical image of 10-cent Euro coin (Upper Right) Mosaic video capture of coin sample area (Lower) Spectrum of amide residue.

Summary

The Nicolet iN10 infrared microscope and the Nicolet iN10 MX imaging microscope provide the forensic scientist with rapid visual and chemical information for many types of samples. The sensitivity and non-destructive nature of infrared ensures accurate interpretation while preserving evidence. The spatial resolution and sensitivity of linear array imaging can quickly reveal the presence of trace materials. OMNIC Picta's performance verification and available validation package provides confidence in the results, which is important when presenting data in court. In addition, we offer innovative OMNIC Specta software. OMNIC Specta has the most advanced peak and multi-component search feature.

References

1. *The Development of a Spectral Data Base for the Identification of Fibers by Infrared Microscopy;* Mary W. Tungol, Edward G. Bartick and Akbar Montaser. Applied Spectroscopy, 44, 4 page 543-549

AN51517_E 10/13M