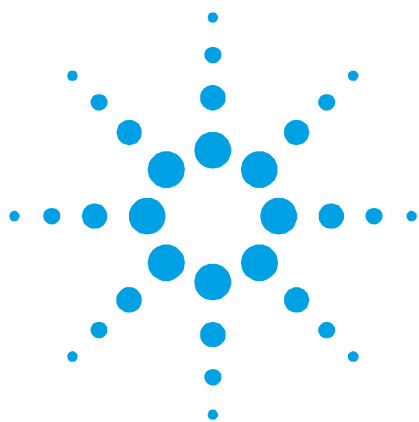




ATR FTIR imaging in forensic science

Application Note

Author

Sergei G. Kazarian*, Camilla Ricci*, Simon Boyd**, Mustafa Kansiz**

* Imperial College UK

** Agilent Technologies, Inc.

Introduction

Conventional Fourier transform infrared (FTIR) spectroscopy and microscopy have been widely used in forensic laboratories for a number of years. This instrumentation has many potential applications for the analysis of forensic samples, including the identification of illicit drugs, fingerprints, gunshot residues, explosives, pharmaceuticals, and so on. Recent advances have allowed this technology to be extended further by using attenuated total reflection (ATR) FTIR spectroscopy/microspectroscopy. This has permitted the non-destructive measurement of different portions of a sample or even spectral mapping of its entire surface with little or no sample preparation. Most samples can simply be presented to the ATR surface in their present state.

A recent approach to acquiring infrared spectra of forensic samples involves the use of imaging array detectors. Imaging detectors allow for an examination of a sample's chemical distribution, making it possible to examine the heterogeneity of a sample. By using an $n \times n$ focal plane array (FPA[†]) detector (where $n = 16, 32, 64$ or 128), a grid of spectra is obtained in approximately the same amount of time that is required to acquire one spectrum with a single-element detector. For example, a 64×64 FPA[†] will simultaneously collect 4096 spectra from an image area of up to 2.5×3.5 mm² using a (ZnSe) imaging accessory. By simultaneously acquiring thousands of spectra within minutes, FPA[†] detectors provide information about the identification and concentration of specific compounds and their distribution in the measured field of view. An FPA[†] detector is superior to single-element detector technology (such as single point mapping), as it dramatically reduces the collection time required to obtain multiple spectra, and provides improved spatial resolution and signal-to-noise performance of obtained images¹.



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The same argument can be used for linear array mapping. Infrared ATR chemical imaging (both micro and macro) have increased the use of mid-IR spectroscopy in forensics, as they simplify sample preparation, are rapid and accurate, and provide reliable 2D chemical images that can be thought of as *chemical photography*².

We have recently demonstrated how ATR FTIR imaging can be used to identify or compare physical evidence in forensic analysis³⁻⁵. In this study, the use of ATR FTIR imaging in forensic science is demonstrated through the measurement of fingerprint residues, both directly, and using a lifting medium. The detection of an exogenous substance (the drug paracetamol) on a suspect's fingertips is also demonstrated.

Instrumentation

All spectral images were recorded using a Cary FTIR spectrometer coupled to a large sample (LS) accessory and a Pike Vee-Max imaging ATR accessory. Direct fingerprint imaging was performed using a Specac ATR accessory. Both of these accessories incorporated a ZnSe internal reflective element (IRE). Infrared images were collected with a 64 x 64 pixel liquid nitrogen cooled mercury cadmium telluride (MCT) FPA⁺ detector in rapid scan mode.

NOTE: It is also possible to perform the above measurements with the Specac Imaging Golden Gate ATR Accessory, exclusive to Agilent. This accessory provides a preserved aspect ratio of 1:1, while providing increased spatial resolution of 10 µm for more sample detail with a field of view of up to 640 x 640 µm.

Table 1. Instrument parameters used in the collection of all images in this study

	Instrument Parameters	Settings
Detector	MCT 64 x 64 FPA	
Source	Mid-IR	Medium
ATR	Pike Vee-Max Specac ATR	
IRE	ZnSe	
Collection	Sample scans	16
	Background scans	16
	Resolution (cm ⁻¹)	8
	Aperture	open
	Symmetry	asym
Computation	Apodization type	BH4
	Zero filling factor	auto

Materials and reagents

Tape-lifted fingerprints were lifted from metal surfaces using a commercial gel (BVDA Gelatine Lifter), provided by the Home Office Scientific Development Branch (HOSDB). Paracetamol was obtained from capsules of commercially available Panadol.

Sample preparation

Fingermarks were laid directly on to the IRE of the ATR. In a second experiment, images containing trace amounts of paracetamol were obtained in the same way after transferring a small number of particles of the substance to the fingertip. Tape-lifted samples were obtained from fingerprints made on a metal door handle. The fingerprints were collected by placing a gel lift over the defined area of the door handle, smoothing the gel in place and then peeling it off. The tape was then firmly applied to the ATR surface to ensure homogenous contact.

Results and discussion

Macro ATR FTIR imaging and fingerprint analysis

The oldest method of personal identification for forensic purposes is fingerprint analysis. The ability to identify suspects from fingerprints left at a crime scene is possible due to the unique nature of the arrangement of ridges on each person's finger pads. ATR FTIR spectroscopic imaging with a ZnSe accessory offers a new and complementary means of studying the chemistry of fingerprints. A major feature of ATR FTIR imaging is its ability to provide spatially resolved chemical information.

As shown in Figure 1, direct imaging of a fingerprint can be quickly and simply obtained by monitoring the distribution of proteins. This chemical image was generated by integration of the area between 1700 and 1600 cm^{-1} , a region representative of the amide I band of proteins. The chemical image was collected with 16 co-added scans representing a collection time of just 13 seconds at a spatial resolution of $\sim 50\ \mu\text{m}$.

The Resolutions Pro software can display chemical images of any wavenumber range with just one mouse click, thereby simplifying chemical analysis and data interpretation. Alternatively, a complete IR spectrum of any pixel can be displayed by clicking anywhere on the chemical image.

Current non-invasive methods of latent fingermark collection typically involve lifting fingermark residues from a surface using a lifting medium. The use of tape-lifting techniques is of paramount importance. They allow latent fingermarks to be collected from surfaces (such as door or mug handles, curved glass surfaces or computer screens) that are difficult to access when using powdering or other detection methods. The method also maintains the integrity of samples, allowing for further analysis or archiving purposes. Latent fingerprint analysis involves monitoring the distribution of sebaceous material captured within the fingerprint. Fingertip pads may

accumulate sebaceous gland secretions due to frequent contact with regions rich in this gland, such as the face.

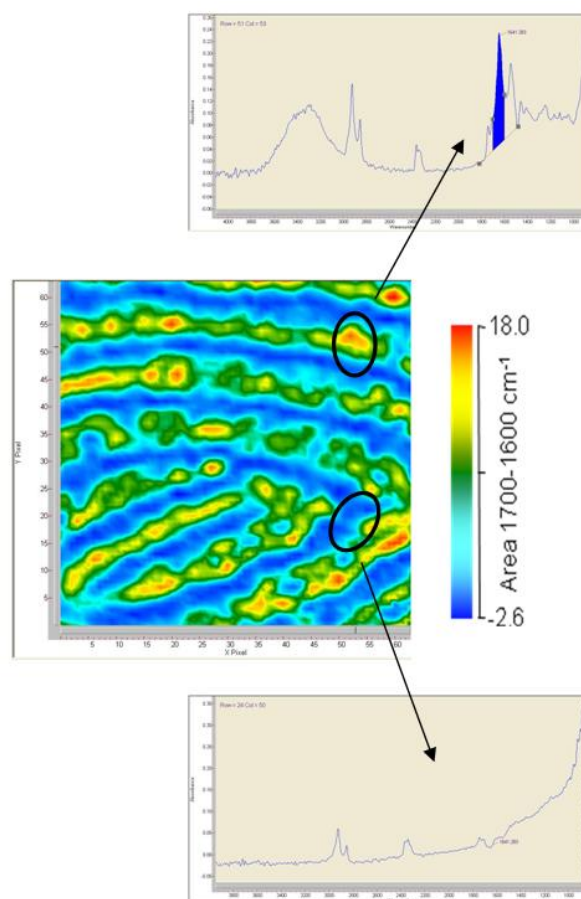


Figure 1. ATR FTIR chemical image and corresponding spectra of the protein distribution within a fingerprint surface. The size of the imaged area is approximately $3.2 \times 4.5\ \text{mm}^2$. The image was collected with 16 co-added scans representing a collection time of 13 s at a spatial resolution of $\sim 50\ \mu\text{m}$.

In this study we explored the use of a commercial gel (BVDA Gelatine Lifter) to collect fingermarks from the surface of a metal door handle^{5,6}. Figure 2 illustrates the chemical image of one of these fingermarks based on the distribution of lipids. This image is based on the integrated area between 2855 and 2840 cm^{-1} , which correlates to the $\nu\text{C-H}$ stretch of the sebaceous material captured within the fingerprint. This spectral region is typically used for chemical imaging of fingerprints because interference from the overlapping

absorbance of the substrate can reduce the quality of images at other wavelength ranges. Depth profiling using a variable angle ATR can aid to enhance the images even further by reducing interference from the lifting medium⁶.

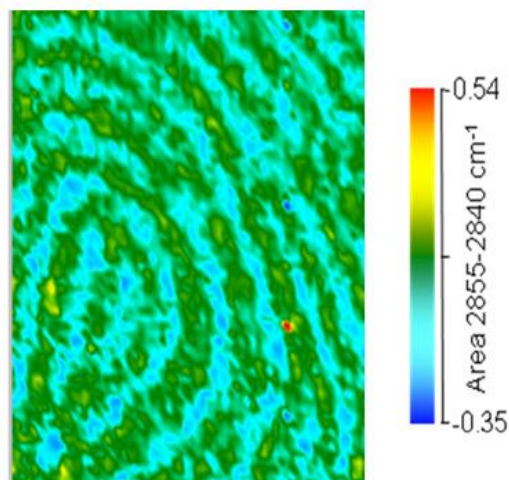


Figure 2. ATR FTIR image of a latent fingerprint lifted from a door handle using BVDA Gelatine Lifter⁷. The scale bar on the right shows the integrated value of C-H stretch of sebaceous material between 2855—2840 cm^{-1} . The imaged area was collected with a Pike Vee-Max accessory at an angle of incidence of 44.6° and is approximately $4.3 \times 5.9 \text{ mm}^2$.

Tape-lifted samples provide a means of obtaining fingerprints from inaccessible regions of a specimen and permit archiving of the samples.

Macro ATR FTIR imaging and homeland security

The applicability of ATR FTIR imaging to fingerprint analysis can be extended beyond its ability to provide fingerprint identification. The technique can also be used for homeland security applications such as linking a specific individual to a specific act through the detection of exogenous substances found on that person's hands^{3,5}. One example involves the detection of trace drug materials that remain on a suspect's hands after drug handling. To model this scenario, the drug paracetamol (also known as acetaminophen) was intentionally handled, and the infrared spectra of contaminated fingerprints were acquired. The chemical image displayed in Figure 3

has been generated based on the absorbance at 1228 cm^{-1} (which is characteristic of a strong $\nu_{\text{Ph-N}}$ absorbance band of paracetamol). The imaged area is $\sim 4.3 \times 5.9 \text{ mm}^2$ with a spatial resolution of $\sim 50 \mu\text{m}$. The highlighted paracetamol particle is of the order of $100 \mu\text{m}$ in size. Finer pixel configurations (for example, 128×128) or other internal reflective elements (for example, germanium) can be used to resolve particles down to $20 \mu\text{m}$ in size. The chemical image in Figure 3 demonstrates that ATR FTIR spectroscopy can locate and positively identify microscopic particles from a mixture of common materials found on an individual's finger.

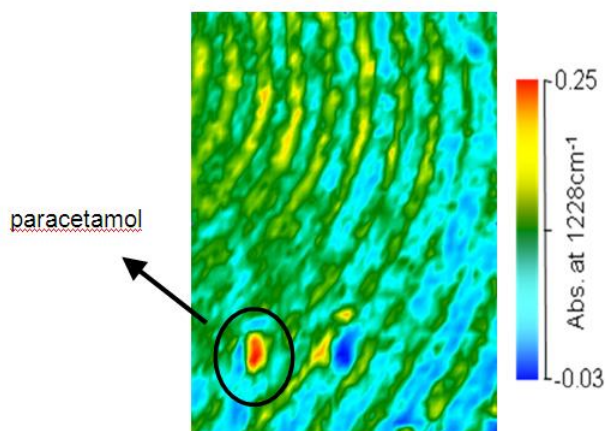


Figure 3. ATR FTIR image of the distribution of the $\nu_{\text{Ph-N}}$ band (at 1228 cm^{-1}) on a fingerprint that is contaminated with paracetamol. The imaged area was collected with a Pike Vee-Max accessory at an angle of incidence of 44.6° and is approximately $4.3 \times 5.9 \text{ mm}^2$.

Even trace amounts of exogenous substances (down to $20 \mu\text{m}$ particle size) can be easily located within a fingerprint using macro ATR FTIR imaging. Substances can be identified by comparison of extracted spectra with a library of known standards.

Conclusion

The use of macro ATR FTIR imaging spectroscopy in forensic science has been demonstrated through the measurement of fingerprint residues, both directly, and through the use of a lifting medium. Macro ATR FTIR imaging spectroscopy permits fast and easy

analysis of fingerprints, even from regions of a specimen that are difficult to sample.

The technique is particularly useful as it is non-destructive and allows for archiving of tape-lifted samples. It also enables the detection of trace quantities (>20 µm particle size) of exogenous substances (such as drugs, pharmaceuticals, or explosives) on a suspect's fingertips or from tape-lifted samples recovered at a crime scene³. Agilent Cary FTIR spectrometers provide excellent infrared energy throughput when coupled to a macro ATR imaging accessory, translating to excellent signal-to-noise performance⁷. When coupled with an FPA[†] detector, this also allows for fast image acquisition at high spatial resolution.

The powerful Resolutions Pro software permits a wide range of analyses to be performed and allows for easy identification and spatial mapping of materials of interest.

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