In *A Study in Scarlet* (1887)—the first appearance of Sherlock Holmes—the great detective declares: “I never guess. It is a shocking habit” (1). Not guessing, but knowing, is at the heart of forensic science. To the degree that the guesswork is taken out, evidence comes ever closer to the judicial ideal of innocence or guilt that is “beyond a reasonable doubt”. And since seeing is believing—and generally the preferred way of knowing to human beings (which includes judges, police, and juries)—it is not unexpected that illuminating adjuncts—instruments that use probing light beyond or supplemental to what human eyes can see—have proven among the most effective ways to achieve that loss of doubt required in the analysis of modern crimes.

Because these techniques conserve samples and minimize or eliminate the potential for contamination, they are popular and have earned a reputation for reliability among criminal investigators. Their ability to “eye” the evidence represents an advance nearly unmatched by any other form of scientific instrumentation since the classic magnifying glass of Sherlock Holmes.

The techniques are ideal for analyzing hair and fibers, paints and inks, tapes, greases, powders, and almost any other evidential debris left at a crime scene—from forged social security checks to condom lubricant on a murder–rape victim (2).

Two of these “visual” techniques, IR and Raman spectroscopy, provide both the power and understandability of “fingerprint-matching” to the most esoteric chemical comparisons. According to Bruker Optics, “Infrared and Raman spectroscopy are among the most widely used techniques for criminal investigation” (3). In fact, so popular are the methods that Thermo Nicolet’s Avatar Fourier transform (FT) IR spectrometer was featured in the first episode of the CBS forensic police drama *CSI: Miami* (4).

**Waste Not, Want Not**

The most important benefit of the various spectroscopic analyses, whether UV, IR, near-IR (NIR), or even X-ray, is the ability to do nondestructive analysis. With forensic evidence, this is critical for two reasons. First, much of the evidence obtained, especially for crimes that are difficult to solve, is found in minute quantities—whether a single strand of hair or a particle of paint or powder. The legal ramifications of destroying all or most of the evidence to identify it are too numerous to discuss, all of them bad. Consider, for example, the problems arising from a request by the defense to perform its own analysis being met by a demur from the prosecution that it had already “used up” the entire sample!

Second, with the adversarial legal system in place in the United States, having an analytical instrument “interact” with a sample, however benignly, only leads to potential for claims that evidence was altered by the instrument itself or by whatever sample preparations were required to make the evidence amenable to testing.

**The IR Finger**

The IR spectrum is apt for the analysis of a wide variety of forensic samples. FTIR spectroscopy is particularly suited to identifying the organic compounds in biological samples. The technique relies on identifying the unique absorption patterns of laser-produced IR radiation.

Although IR for forensic analysis uses light spectra as its means...
of identification, it is structured more like those Russian psychics of the Cold War era who could purportedly “read” normally printed text with their fingertips, as if they were eyes. In forensic IR, a diamond lens “fingers” the samples, providing the necessary contact. Laser light passes through the diamond lens and is reflected back from the sample and the absorption pattern recorded.

Among the many applications of FTIR in forensic analysis is the identification of illicit drugs and precursor chemicals found in the host of clandestine drug labs proliferating in major—and not so major—cities throughout the United States. These criminal operations produce everything from refined heroin to the latest designer drugs for an increasingly demanding market. Typically, samples are removed as evidence for laboratory analysis, and common street drugs such as cocaine, heroin, and LSD are easily and rapidly identifiable using IR.

But rapid on-site testing is also possible using a portable FTIR instrument, such as the TravelIR developed by SensIR Technologies (www.sensir.com). In this device, the external surface of the diamond wafer lens is placed against the sample, and the internal surface is in optical contact with a ZnSe focusing lens that introduces the IR beam at the appropriate angle. Because the system allows entry of visible light, a video microscope attached to a monitor can be used to view the sample as it sits on the diamond face. Law enforcement investigators can generate IR spectra to identify any number of drug-manufacturing chemicals (such as stereoisomers of ephedrine, a precursor to methamphetamine, also known as crystal meth) or the final drugs themselves (such as stereoisomers of ephedrine, a precursor to methamphetamine, also known as crystal meth) or the final drugs themselves (5). On-site analysis provides the benefit of identifying the compounds immediately and helping to narrow the evidentiary chain from crime scene to laboratory identification.

One relatively recent adaptation of IR spectroscopy has become supremely valuable in modern forensic analysis. In 2000, science writer William Atkinson reported that IR microspectroscopy was the wave of the future (6). By coupling the IR spectrometer to a standard light microscope, the ability to achieve spectra of defined sample areas coupled to observations of their microscopic fine structure has enabled the analysis of ever-smaller shreds of evidence, as well as more sophisticated analysis of larger pieces.

FIGURE 1: Raman spectra of common drugs of abuse. (Image provided by Kaiser Optical Systems based on data from the Mesa, AZ, Police Department.)

With little or no sample preparation, analysis of hair (with and without hair care products), clothing, and furniture or carpet fibers can be performed to yield images for morphological differentiation coupled to the chemical analysis that the IR can provide. For example, FTIR is capable of differentiating between the highly similar nylon-6 and nylon-6,6, which differ only by the presence of alternating methylene groups. FTIR microspectroscopy is also used as one of the most common methods of examining and differentiating inks—providing identifying evidence using several parameters, including color, texture, and composition.

Researchers at the Advanced Light Source facility at the Lawrence Berkeley National Laboratory (www.lbl.gov) reported that they are implementing a powerful new laser system a “couple of hundred times brighter than conventional IR spectromicroscopy,” allowing IR analysis of samples as small as a few micrometers, significantly improving the sensitivity of the technique.

The Raman Eye

Raman spectroscopy relies on the subtle observation of the very small proportion of scattered radiation that is altered in wavelength as a result of collision with any solid, liquid, or gas molecule. This inelastic scattering is caused by specific shifts in the vibrational and/or rotational states of the impacted molecules. Unfortunately for the early days of Raman analysis, the comparatively weak nature of the scattering and the high background of elastic light scattering against which it must be observed made it an unpopular technique until powerful and directed lasers could be used to eliminate these difficulties.

With these improvements in Raman technology, including the introduction of FT-Raman, the level of sensitivity became comparable to that obtainable with standard IR, and the technique became useful for almost any kind of sample and took off in the forensic arena. Especially valuable is Raman’s ability to analyze samples without physical contact, unlike the diamond probes of typical FTIR, where contact between analyzer and sampler is required. Furthermore, portable Raman spectrometers and microscopes are becoming common, with units available from several manufacturers (7).

One of the greatest advantages of Raman is its ability to analyze substances in sealed, transparent containers, whether plastic or glass. It is easy to see how this would be a valuable property for noncontact analysis of potential drugs of abuse or hazardous

---

**Some Commercial Sources of IR and Raman Equipment and Adjuncts for Forensic Analysis**

- Bio-Rad Laboratories, Informatics Division www.knowitall.com
- B&W Tek Inc. www.bwtek.com
- Bruker Optics www.brukeroptics.com
- Digilab, LLC www.digilabglobal.com
- Jasco www.jasoinc.com
- Jobin Yvon Horiba, Ltd. www.jobinyvon.com
- Kaiser Optical Systems, Inc. www.kosi.com
- Ocean Optics www.oceanoptics.com
- PerkinElmer, Inc. www.perkinelmer.com
- Photonics Industries International, Inc. www.photonix.com
- SensIR Technologies www.sensir.com
- Shimadzu Scientific Instruments www.ssi.shimadzu.com
- Thermo Nicolet www.thermo.com/ramanma
compounds found in plastic bags or in glass or plastic vials. For example, Raman, using NIR laser light sources, has proved capable of matching FTIR in the “fingerprinting” of drugs of abuse and their precursors such as cocaine, lidocaine, methadone, and crystal meth (Figure 1) (8).

Pigment analysis is an increasingly important use of Raman spectroscopy for criminal forensic purposes—traces of paint and fragments of colored materials are common pieces of evidence in crimes such as hit-and-runs, for example; and art pigments and inks in forgeries.

In addition, Raman has proved useful for the precise identification of explosives as well as their postdetonation residues—an application that is unfortunately becoming ever more pertinent in a world of Homeland Security and increasing troop incursions on foreign soils (Figure 2) (8).

### Going "Postal" with IR

As detailed by SensIR Technologies, its portable IR device was critical in dealing with a potential terrorist incident—one that “brought an entire city block to a standstill”—at a Washington, DC, post office on February 15, 2002. A package spilled an unidentified white powder into the receiving area, raising alarm because of the anthrax contamination and scares that the city had faced after the 9/11 tragedies. A fire department response team brought the SensIR portable IR HazMat system they use to identify unknown materials. After “preliminary tests directly at the spill site were negative for the presence of anthrax and other biological warfare agents,” a sample of a few grains of the powder was tested with the diamond interface of the portable IR unit. Upon comparison of the spectrum obtained with a large library of spectra maintained by the unit, the potential threat was identified within 30 s as baby formula—“an innocent gift for a new mother, not a biological weapon.”

If one is hard-pressed to choose between Raman and FTIR microspectrometry, combination units are becoming available from companies such as Jobin Yvon Horiba (www.jobinyvon.com). Most commercial suppliers of both IR and Raman systems have instructive online applications notes for each of their instruments detailing the possibilities of each technology (see box, “Some Commercial Sources of IR and Raman Equipment”).

### Libraries of Crime

Few things are less useful than a fingerprint found at the scene of the crime for which there is no collection of suspect prints for comparison. So too, all of the spectral information obtained by IR and Raman analysis of crime scene materials is moot without applicable databases of spectral patterns to which to compare it. Thus, one of the most important facets of using these technologies is the informatics-based analysis that provides a positive identification for samples being examined.

Almost all suppliers of these instruments provide searchable libraries of pertinent forensic compounds and samples for cross-comparison. These include FTIRSearch (https://ftisearch.com) by Thermo Nicolet and Thermo Galactic, which requires paid membership, and Thermo Galactic’s Spectra Online (http://spectra.galactic.com/SpectraOnline), which requires user registration.

Commercial informatics suppliers also provide access to extensive IR and Raman databases. For example, BioRad’s KnowItAll group provides access to multiple libraries of IR and Raman spectra for forensic analysis, including spectra of automobile paint chips, dyes and pigments, drugs, and fibers (www.knowitall.com).

Several public-access libraries are also available. For example, the U.S. Geological Survey maintains a UV-NIR spectral data set for a wide variety of minerals (http://speclab.cr.usgs.gov/spectral.lib04/spectral-lib.desc+plots.html). The Raman Spectroscopic Library of Natural and Synthetic Pigments (pre-~1850 A.D.) (www.chem.ucl.ac.uk/resources/raman/speclib.html) is particularly useful for those interested in the analysis of antiques involving the crime of forgery.

### The Evidentiary Eye

With scientific instruments such as Raman and IR augmenting the limited senses of the modern descendants of Sherlock Holmes, there is a much greater chance not only of solving crimes, but also of getting convictions based on the quality of the evidence. And in the new world of terrorist threats (real or imagined), rapid deployment and analysis using these techniques are critical to maintaining public safety and continuity of public services. In both these areas of crime and security, “guesses” can be more than just a shocking habit—they can be disastrous. It is inevitable that there will continue to be a growing role for analytical techniques, from IR to X-rays, from Raman to MS, in helping modern law enforcement prevent the tragedies that guesswork can involve.

### References

(1) The complete Sherlock Holmes stories online; www.citsoft.com/holmes3.html.
(3) Bruker Optics; www.brukeroptics.com/applications/forensics.html.
(7) Harris, C. M. Anal. Chem. 2003, 75, 75A–78A.

Mark S. Lesney is a senior associate editor of Today’s Chemist at Work. Send your comments or questions about this article to tcw@acs.org or to the Editorial Office address on page 3.