

Applications of Vibrational Spectroscopy in Criminal Forensic Analysis

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1 INTRODUCTION TO FORENSIC ANALYSIS

Sir Arthur Conan Doyle is believed by many to have first popularized the application of forensic analysis through his fictional character Sherlock Holmes, originally published in 1887. This work is thought to have inspired many of the early forensic scientists. One of these was Frenchman Edmond Locard, who proposed that when two objects come into contact with one another, a cross-transfer of evidence occurs.^{1,2} This statement is known as Locard's Exchange Principle and is the foundation for use of physical evidence to link or at least associate a suspect to a crime scene or a victim. Depending on the nature of the evidence, a wide range of analytical methods are used in forensic casework. This article illustrates how vibrational spectroscopy is used to identify or compare physical evidence in criminal forensic analysis.

A broad definition of the term "forensic", according to 'Webster's New World Dictionary,' is "suitable for a law court or public debate". With the application of forensic science, one must demonstrate in court that the evidence analyzed has relevance to the case in question. The significance of evidence related to a case is often determined by whether the physical evidence has individual or class characteristic properties.

Individual characteristics are properties of evidence that can be attributed to a common source with an extremely high degree of certainty. Class characteristics are properties of evidence that can only be associated with a group and never with a single source.³

Fingerprint and DNA evidence are accepted as having individual characteristics. However, fibers or copy toners are identified by their class characteristics and, because of the large production of these materials, they cannot be individualized. The strength of fiber evidence depends on the likelihood of those same type of fibers being randomly located on the suspect. Common fibers such as blue or white cotton from jeans or shirts, respectively, have little evidential value. But blue nylon-6,6 fibers with an unusual cross-section would have more significant value, because there are fewer in existence. Forensic scientists have thoroughly developed statistical values for DNA and fingerprint data to demonstrate individual characteristics. Statistics are more difficult to apply to class evidence, but approaches to apply them are being investigated. The information obtained by vibrational spectroscopy is usually characteristic of classes of materials, but in some instances the identification of specific components demonstrates an uncommon characteristic. If a contaminant on an evidential material is identified as a rare substance specific to the crime scene, the evidence would demonstrate a high likelihood of originating from the crime scene. Therefore, vibrational spectroscopy is used to identify chemical properties that contribute in varying degrees to the evidential value in criminal forensic analysis.

2 GENERAL USE OF VIBRATIONAL SPECTROSCOPY IN FORENSIC ANALYSIS

2.1 Infrared spectroscopy

Several authors have provided general overviews for the use of infrared (IR) spectroscopy in forensic analysis.^{4–6} The applications vary to cover a wide range of physical evidence in the form of bulk materials and micro-sized particles. Historically, dispersive IR spectrometers were generally found useful for bulk samples such as drugs. Micro-sized samples were analyzed with skilled patience in beam condenser accessories. For example, the Royal Canadian Mounted Police (RCMP) Forensic Service Laboratories (FSL) used high-pressure diamond-anvil cells in beam condensers for the analysis of automotive paint chips transferred from hit-and-run vehicles.^{7–9}

With the development of Fourier transform infrared (FT-IR) spectroscopy, the application of IR to forensic analysis became more prevalent because of the increased speed and sensitivity of FT-IR. The development of diffuse reflection (DR) accessories provided ease of sample introduction for several forensic applications. Samples with matte-finished surfaces could be analyzed with no sample preparation. Samples such as illicit drugs that previously required extensive grinding to make KBr pellets required less preparation. Suzuki was the first to apply the DR method to forensics with the analysis of drugs, polymers, wood and solvents.¹⁰ He continued with additional work on drugs,¹¹ polymer foams¹² and paints.^{13,14} Document analysis by DR has been reported for copy toners^{15,16} and inks.¹⁷

It was not until the 1990s that the use of FT-IR became more regularly applied in forensic laboratories. The introduction of lower cost spectrometers and microscopes paved the way for FT-IR use in forensic analysis. FT-IR microscope development is considered a milestone achievement for forensic analysis and is considered the most significant recent advancement for microsample analysis.⁵ Sample preparation to introduce specimens into microscopes is frequently easier, because only a small portion of the sample is required for placement in the IR beam for transmission spectroscopy. For example, to analyze paint from a surface, all that is required is a sliver sliced from the surface with a scalpel. Therefore, standard sized samples are often reduced in size and analyzed in microscopes because of convenient sample preparation.¹⁸ The reflection techniques, reflection-absorption (R-A), specular reflection, diffuse reflection (DR), and internal reflection spectroscopy (IRS), frequently referred to as attenuated total reflection (ATR),¹⁹ provide additional ease of sampling in IR microscopes. Because reflection methods require little or no

sample preparation, they are used at least as frequently as traditional transmission methods.

Gas chromatography (GC) with IR detection (GC/IR) for analysis of mixtures has not found much application in forensic analysis. GC combined with mass spectrometry (MS), or GC/MS, superseded GC/IR, and the ultimate sensitivity benefits of MS for trace components have overshadowed the use of GC/IR in forensic analysis. However, GC/IR used as a separation and identification tool for large samples has proven successful in drug analysis. Because IR analysis can be used to identify isomers, it can sometimes be used to identify isomeric forms that render a drug active and subsequently controlled.

The recent developments of single or multiple reflection, horizontal ATR accessories for use in sample compartments have been very useful for forensic analysis. Small liquid or solid samples, less than a millimeter in diameter, can be measured. Typically, diamond internal reflection elements (IREs) are used for durability. Some IREs consist of thin diamonds backed with other materials to reduce cost. These ATR accessories offer the option of extended frequency ranges to near 200 cm^{-1} in spectrometers with cesium iodide optics. The extended range can be used to nondestructively acquire information regarding paint pigments and inorganic fillers in polymeric materials.

2.2 Raman spectroscopy

Recent technological advancement in Raman spectrometers has provided a reason for exploring this method in forensic applications. While the applications have been slow to find their way into forensic laboratories, the advantages are being recognized and Raman spectrometers are starting to find use in forensic analysis.²⁰ Fourier transform (FT) Raman received early attention in the redevelopment of Raman technology. The 1064 nm near-infrared (NIR) excitation laser that is used with FT systems causes fewer samples to fluoresce than the visible wavelength lasers previously used. However, with the lower energy, longer wavelength laser, signal averaging and rapid scans provided by FT systems are required to attain the quality of spectra desired. Unfortunately, the lower scattering power of the longer wavelength excitation impedes application to microsamples that are commonly required with forensic analysis, thus limiting the use of microscopes with FT Raman. Dispersive Raman systems that use NIR lasers ranging from 780 to 840 nm have greater scattering efficiency. Combined with sensitive charge coupled device (CCD) detectors and improved monochromators, these systems have more general use compared to FT Raman systems and have thus taken the forefront for a wide range of sample analysis. Additionally, fiber optic probes are used

on dispersive systems to sample through glass bottles and plastic bags, making noninvasive sampling possible. These probes contribute to the application of small, rugged Raman spectrometers designed specifically for field use. Portability and ease of sampling are attractive features that are included in these Raman systems that can be used along with an array of other analytical instruments to be carried to crime scenes where the analysis of potentially hazardous materials is conducted without risk of transporting them back to the laboratory.

3 POLYMER ANALYSIS

3.1 General polymers

Vibrational spectroscopy is applicable to a wide range of physical evidence. Because polymers are so common, they frequently play an evidentiary role in criminal cases. Polymeric materials such as fibers, paints and adhesive tapes are frequently analyzed to identify characteristic information regarding their composition. Physical and chemical information on these materials is stored in computer databases to help determine the manufacturer or, supplier, or simply to discriminate between many similar samples of material. Some of the available databases will be described as part of the analyses mentioned in the forthcoming pages. Other general polymeric materials found as evidence do not fall into a particular category and must be studied on a case-by-case basis without the aid of comparison with similar material in a database.

The following is a case example where a polymeric material became important evidence. Early one morning, on a luxury cruise ship off the coast of California, a man reported to the captain that his wife had been blown overboard. Considering the minimal wind conditions, the captain became suspicious and alerted the law enforcement authorities. Several hours after the overboard report, the woman's body was recovered by the US Coast Guard. The clothing that both the man and woman were wearing at the time of the incident was forwarded to the FBI Laboratory. The woman's running pants appeared soiled with an orange substance on both legs. Careful examination of her pants with a stereo microscope revealed orange-colored, rubbery particles. Examination of the man's running pants also revealed rubbery particles that appeared identical. On the ship's deck, at the location of the overboard incident, there was an orange-colored, rubberized running track. A portion of the track material was removed from the ship and forwarded to the laboratory for analysis. The particles were removed from both pairs of running pants and flattened in a compression cell to make them sufficiently thin to perform transmission analysis using an FT-IR microscope system.

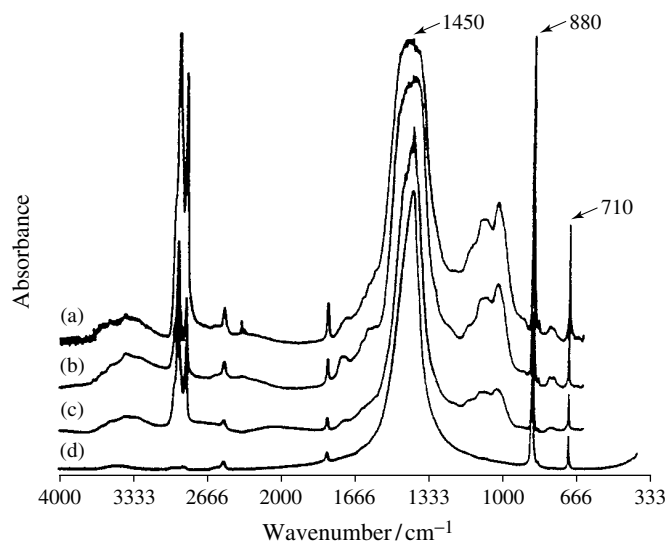


Figure 1. Cruise ship homicide case. Spectra of rubber particle evidence from sweat pants from both (a) the victim and (b) the suspect, (c) running track and (d) calcite reference.

Particles from the track material were prepared in the same way, and the spectra of all three samples were compared as shown in Figure 1. The three spectra of the rubberized material matched closely. The material was heavily filled with calcite (CaCO_3), identified by the intense, broad C–O antisymmetric stretch near 1450 cm^{-1} , and narrow out-of-plane and in-plane bends near 880 and 710 cm^{-1} , respectively.²¹ To determine the force required to embed the particles in the pants, a fabric similar to that of the pants was rubbed across the removed track piece at different degrees of pressure. The investigators found that it was necessary to rub the fabric with significant pressure, such as in the case of dragging a person, to cause the transfer and embed the material in the fabric. They determined that the transfer of particles suggested an altercation between the individuals, and, therefore, this evidence weighed heavily and resulted in a homicide conviction. The combined comparison of evidential materials by microscopic examination, IR analysis, and physical testing played a significant role in this case without witnesses.

3.2 Copy toners

Questioned documents involving fraud and threatening letters are often produced on printers, copy machines and facsimile machines. The machine model identification of this common office equipment has been achieved through comparison of the resins of the toners used as ink. These “copy toners” have been studied for forensic analysis as a class of polymeric material. An example where copy toner analysis was used to produce an investigative lead was in a case involving a copied address label. A packaged

bomb, mailed to a corporate executive, had an address label that appeared to be an enlarged copy of the company's return address logo typically used on company envelopes. Investigators suspected that the bomb had been mailed by an employee with access to internal supplies and that the person had copied an envelope using equipment within the company. There were over 200 copy machines, involving 62 different copier models, located throughout the facility. It was important for the investigators to know the copier model used to narrow the area of the investigation to employees with convenient access to a copier model of the type used to print the label. Sample pages were prepared from each of the 62 models and forwarded to the FBI Laboratory for analysis. In the laboratory, the samples were prepared for IR analysis using a heat transfer technique to remove the toner from the documents. The preparation technique involves heating the back of the paper with a soldering iron at a specified temperature and smearing the toner onto aluminum foil attached to a glass microscope slide. Spectra were obtained with an FT-IR microscope by R-A. With this method, the IR beam passes through the sample and is reflected from the aluminum foil to the detector via the microscope optics.²² Figure 2(a) shows the original spectrum of the toner from the bomb package label. This spectrum is sloped due to scattering from the carbon black particles used for the copy image. The

baseline flattened spectrum in Figure 2(b) is typical of a styrene/acrylate copolymer. Significant variations in the IR spectra are produced by the polymeric resins which contain numerous additives that vary in type and quantity. A visual comparison of the case sample spectrum was made with the 62 spectra of the model types in the building. One Kodak model type matched closely with the case sample spectrum. The spectrum was also searched in an IR database of copy toner resins categorized based on over 800 copier and printer models.²³ The search software narrowed the toner type to a group containing 24 models of machines. By careful scrutiny of the peaks, it was possible to narrow the spectra to six Kodak models in the database. The Kodak copier model from the corporate building was included in the computer search. Therefore, the results of the visual inspection and the computer search of the spectra corroborated. Two-thirds of the binders contained in the spectral database consist of the styrene resins plus additives to provide desired properties in particular copy machines. Other types of binders used are phenolic and polyethylene resins. The regions boxed off in Figure 2(b) contain small bands from the additives that provide the differentiating spectral features of this toner resin. Because the building contained only eight examples of that particular Kodak model, the results of this analysis permitted the investigators to narrow their search to personnel working in limited locations of the

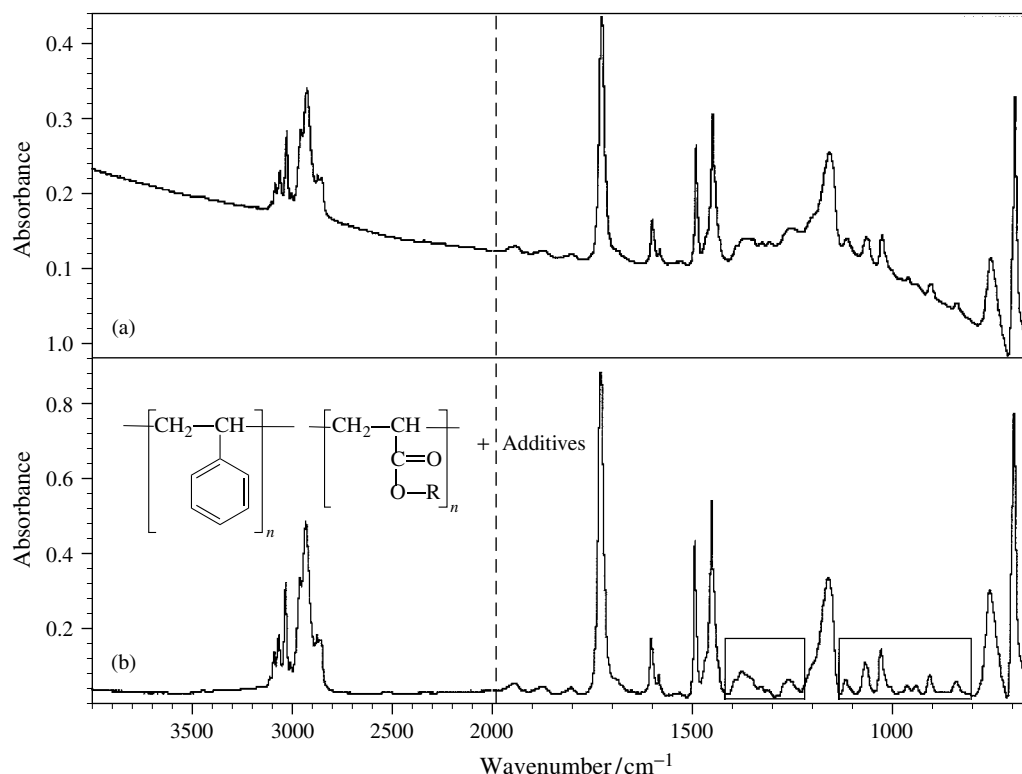


Figure 2. Poly(styrene:acrylate) resin copy toner spectrum from an address label on a bomb package: (a) original uncorrected spectrum; (b) flattened spectrum showing boxed regions where additive absorptions can be observed.

building. Thus, a suspect was determined in considerably less time than if the company's entire personnel required investigation.

3.3 Fibers

Textile fibers are often transferred between clothing during personal contact in violent crimes such as rape and homicide. The foremost method of analysis for this type of evidence is visual light microscopy, though IR is very useful to further specify fiber type. Fibers from the clothing of the victim and suspect are screened microscopically for similarity, closely comparing physical and optical properties of the fibers. These properties may vary significantly due to the color, shape, texture, and chemistry of textiles. Polarized light microscopy is used to determine the generic classification of the polymer type, and IR microscopic analysis plays an important role by identifying subclasses of synthetic fibers.^{24,25} A spectral library of 83 polymeric fiber types, obtained by transmission spectroscopy on flattened single fibers, was developed to aid forensic examiners in the identification of fiber composition.²⁶⁻²⁹ IR is particularly useful for subclassifying acrylic fibers that are seen frequently as a wool alternative in sweaters and readily transfer between individuals during contact. These fibers consist of at least 85% polyacrylonitrile²⁸ plus copolymers and ionic end-groups to enhance dyeing properties. Figure 3 shows spectra of the three most common acrylic copolymers. The band shape of the C–O stretch in the region between 1300 and 1000 cm^{-1} varies depending on its

position or environment within the comonomer structure as a methacrylate, methyl methacrylate or vinyl acetate. Over 20 variations of acrylics can be identified by IR.³⁰ Thus, IR is a very useful tool in providing information that further discriminates fiber types to enhance the evidential value of a sample.

Raman spectrometry promises to complement IR analysis of textile fibers due to the ease of sampling and the additional information it provides. Light microscopy analysis requires fiber samples to be mounted in a liquid medium, under coverslips, on a glass slide. Because glass absorbs strongly in the IR, the fibers must be removed and cleaned prior to IR analysis. Raman analysis, on the other hand, has been successfully performed on single fibers mounted on glass microscope slides,^{31,32} thus avoiding the need to remove the fibers from the slide mount. The additional sample preparation time is not required and, once mounted, the chance of fiber loss is minimal. Figure 4 illustrates the process of obtaining a nylon-6 fiber spectrum using microscopic Raman analysis. Figure 4(a) includes spectral contributions from the fiber, Permunt mounting medium and glass from the coverslip. Figure 4(b) shows the result of Permunt subtracted from the original spectrum. The nylon-6 spectrum remains in Figure 4(c) after the glass contributions are subtracted. The baseline is flattened for the final spectrum shown in Figure 4(d). The signal-to-noise ratio is less than obtaining a spectrum without being mounted under a coverslip, but it is sufficient to identify the fiber by the prominent characteristic bands as labeled. The band assignments of the major peaks are labeled in

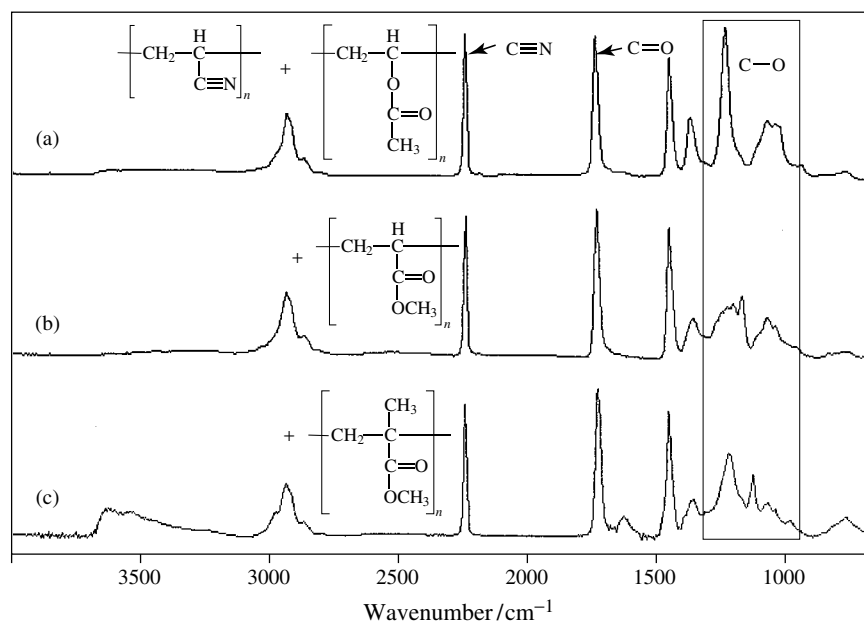


Figure 3. IR spectra of acrylic copolymer fibers: (a) poly(acrylonitrile:vinyl acetate); (b) poly(acrylonitrile:methyl acrylate); (c) poly(acrylonitrile:methyl methacrylate).

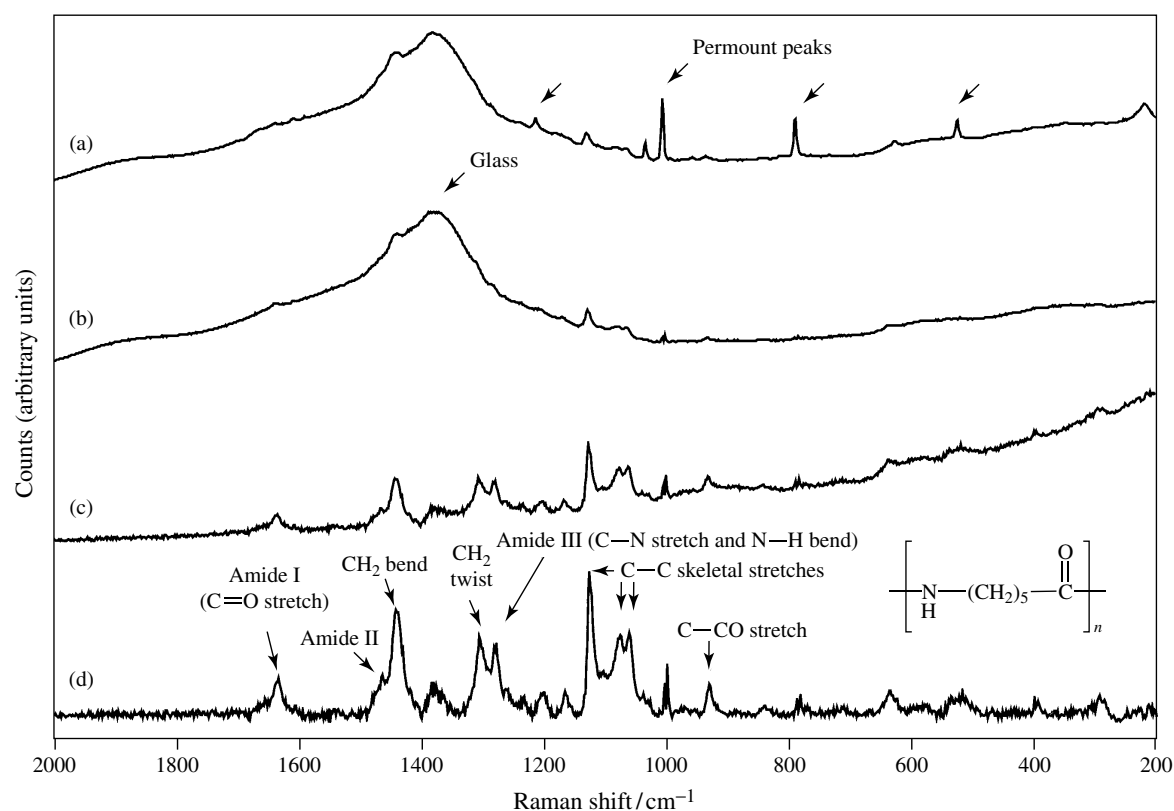


Figure 4. Raman spectra of a nylon-6 fiber mounted under a coverslip on a glass microscope slide: (a) original spectrum, (b) Permout mounting medium subtracted; (c) glass subtracted; (d) baseline flattened with the major characteristic bands labeled.

accordance with Hendra *et al.*³³ Raman spectra differ from IR spectra because the selection rules for Raman vary from IR, thereby producing complementary information. The information obtained by Raman is at times more definitive in determining the polymeric structure. Since Raman spectroscopy demonstrates spectral response from dyes, the dye information can be useful. However, the dye spectral features can interfere with identification of the polymeric composition of fibers. A protocol to determine whether to use Raman or IR when analyzing dyed and undyed fibers, grouped by generic class, is currently being established in the FBI Laboratory. To further characterize the fibers, dye spectral features could provide information regarding the dye type. Studies have been conducted using surface enhanced Raman spectroscopy (SERS) to study dye composition using silver colloid substrates.^{34,35} While the spectral features are significantly enhanced by SERS, this method requires that the fibers are removed from the glass slides, resulting in an additional step and a chance of fiber loss. Raman analysis has demonstrated certain advantages over IR, but the strengths and limitations of both are still under study to determine where each of the methods can be used to obtain the greatest information with the most convenient analysis procedure.

3.4 Paints

IR spectroscopy of paints has been useful in forensic analysis since the 1960s. Automotive, architectural, art, marine, aircraft, tool, and other types of paints may become evidence in a variety of crime scene scenarios.³⁶ After visual light microscopy, IR analysis offers the most information in forensic paint examination. The organic binders are frequently identified with IR, and both organic and inorganic pigments can often be identified. Scientists from the RCMP have been classifying automotive paints based on chemical composition since the 1970s.⁷⁻⁹ The original analysis was performed with the use of high-pressure diamond-anvil cells in beam condensers on dispersive IR spectrometers. Since then, the RCMP and other analysts have changed to using the less cumbersome low-pressure compression diamond cells with beam condensers in FT-IR systems. Inorganic pigment components in paints have revealing spectral features at the lower wavenumbers. Beam condensers are used rather than FT-IR microscopes to overcome the limited frequency range of mercury cadmium telluride (MCT) detectors used in IR microscopes. For paint analysis, the extended range to near 200 cm^{-1} is obtained with CsI optics and a standard deuterated triglycine sulfate (DTGS) detector in the spectrometer bench.

Physical and chemical information obtained by light microscopy and IR analysis on automotive paint, used to potentially identify make, model and year of vehicles, is readily searched in a database. The computerized library, developed by the RCMP, is widely used by forensic laboratories throughout North America.³⁷ Necessitated by the international nature of the automotive industry, European, Japanese and Australian forensic laboratories will soon be contributing to this database in order to provide a more comprehensive collection. Scientists from forensic working groups of the listed countries are contributing automotive paint samples and data from their respective nations and plan to continue collaboration.

Paint types other than automotive do not usually display as much diversity in chemistry, color and layer structure. Therefore, a wider variety of analytical instruments are often used to characterize these paints. Along with microscopy and IR spectroscopy, other methods frequently used are pyrolysis GC/MS and inorganic analysis by scanning electron microscopy with energy dispersive X-ray spectroscopy (SEM/EDX) or X-ray diffraction (XRD) analysis.

Researchers are beginning to demonstrate the usefulness of Raman analysis for organic and inorganic pigment identification in paint.^{38,39} Figure 5 compares IR and Raman paint spectra of a yellow acrylic melamine enamel automotive paint. The IR spectrum in Figure 5(a) clearly shows the resin binder features. The N–H stretch near 3350 cm^{-1} , the C–H stretches near 3000 cm^{-1} , the C=O stretch near 1730 cm^{-1} , the C–N stretch near 1540 cm^{-1} , and the typical C–O envelope from 1300 to 1000 cm^{-1} are observed in the IR. Of particular interest to paint analysis are any contributions by pigments. The weak, broad band at 868 cm^{-1} appears to be contributed by chrome yellow, as shown in the reference spectrum (Figure 5(b)). However, because of the band's comparatively low intensity and lack of detail in the paint spectrum, it would be difficult to positively identify chrome yellow by this method alone. The peaks labeled at 659 , 425 and 357 cm^{-1} are rutile, a crystal form of titanium dioxide. Figure 5(d) is the Raman spectrum of the yellow auto paint. The major peaks at 843 and 365 cm^{-1} match up with the Raman spectrum of chrome yellow shown in Figure 5(c). Peaks at 611 and 446 cm^{-1} are contributed by rutile, as shown in

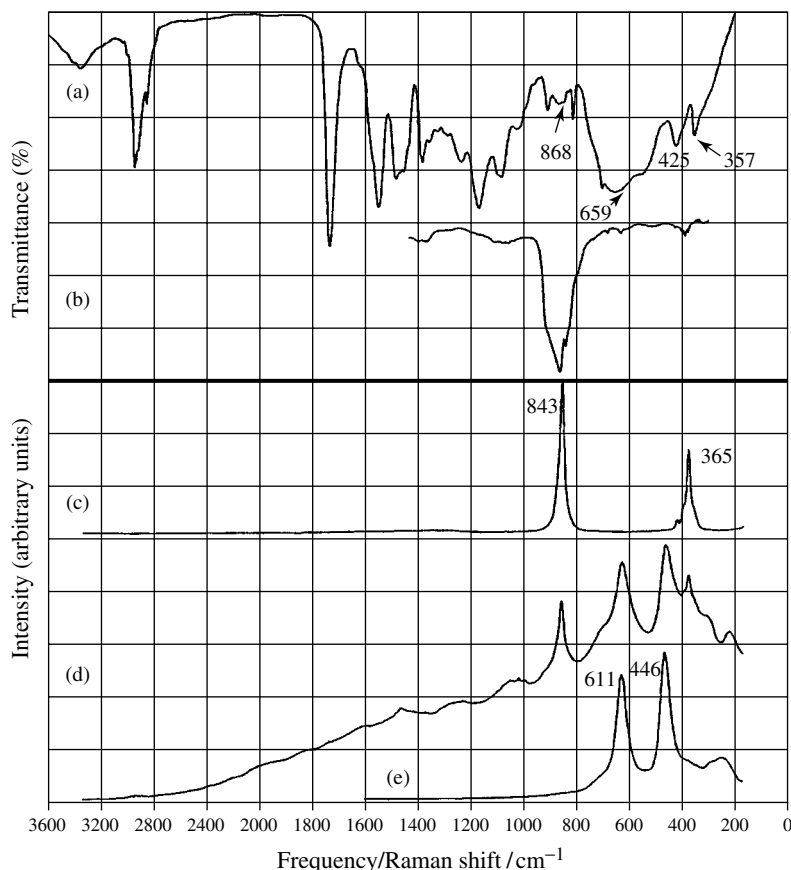


Figure 5. IR and Raman spectra of yellow acrylic melamine enamel auto paint with pigments: (a) IR spectrum of the auto paint; (b) IR spectrum of chrome yellow pigment; (c) Raman spectrum of chrome yellow pigment; (d) Raman spectrum of the yellow auto paint; (e) Raman spectrum of rutile. (Spectra provided by E. Suzuki, Washington State Patrol, Forensic Laboratory, Seattle, WA.)

Figure 5(e). With Raman, the high scattering efficiency of some pigments, relative to those of binders, helps to easily determine the pigment components, as interfering binder peaks are not a problem.

3.5 Tapes

Pressure-sensitive adhesive tapes play an important role in forensic analysis as evidenced by their diverse uses. Electrical tapes can be used in wiring electronic devices to bombs, duct tapes in binding victims of violent crimes, and other tapes in wrapping packages containing drugs, bombs or other threatening material. By carefully characterizing tapes submitted as evidence, they can be compared with known tapes in a suspect's possession or they can be studied to develop investigative leads when the brand can be established. IR spectroscopy can be useful with ATR accessories in determining the major organic components of both the adhesives and backings. In the past multiple reflection accessories were used, but more recently single reflection ATR accessories for the IR microscopes have been used to acquire spectra of small, uncontaminated areas on the tapes. While this is convenient, the frequency range is limited by the MCT detectors used on the microscopes which cut off near $700\text{--}650\text{ cm}^{-1}$. A study has demonstrated the usefulness of a single-reflection, horizontal sample compartment accessory using a diamond interface backed with KRS-5.⁴⁰ This accessory provides a spectral range from 4000 to 260 cm^{-1} when used with cesium iodide optics in the spectrometer. The extended range below 400 cm^{-1}

permits acquisition of spectral features of the inorganic fillers commonly found in duct tape adhesives and less frequently found in the film backing. Figure 6(a) shows an atypical duct tape backing spectrum containing calcium carbonate (calcite). The calcite filler has a lattice band²¹ near 315 cm^{-1} that would not have been observed without the extended frequency range capabilities. The C–O asymmetric stretching band²¹ near 1450 cm^{-1} underlies the C–H bending band near 1460 cm^{-1} . The C–O out-of-plane bend can be observed near 880 cm^{-1} . The spectrum in Figure 6(b) is more typical of polyethylene backing showing only the C–H bands without the filler features. Because fillers are not typically used in the backings, analysis of this unusual duct tape evidence could provide increased discriminating value.

To more fully characterize tapes, other analytical methods are used. The physical characteristics are observed and measured with the unaided eye and microscopically, and inorganic composition is determined by SEM/EDX and XRD analysis. Physical characteristics, such as the yarn counts and weave type on the fabric reinforcement within duct tapes, may quickly narrow down the brand possibilities. XRD can provide further information about the inorganic components like distinguishing between anatase and rutile crystalline forms of titanium dioxide extenders. TiO_2 is frequently used in duct tape adhesives and some manufacturers prefer a specific crystalline structure, thus identification of the mineral type can assist with identifying the manufacturer. All of the information obtained by the various analyses has recently been placed in a searchable database for quick comparison of tape properties.⁴¹

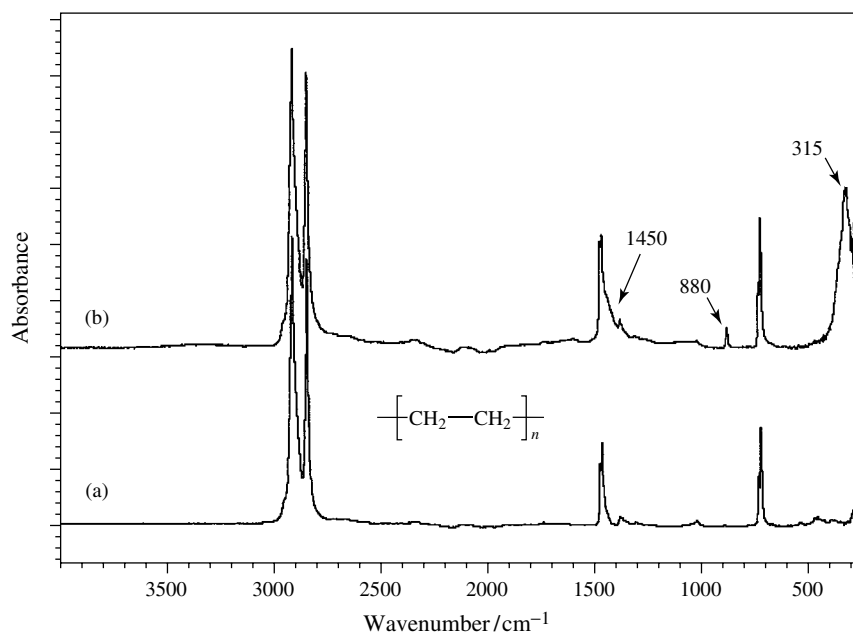


Figure 6. IR spectra of duct tape backing film by ATR: (a) typical polyethylene backing; (b) backing containing calcite.

4 DRUGS

IR has been used for the analysis of both licit and illicit drugs for many years.^{4,42} The computerized drug library produced at the Georgia State Crime Laboratory (GSCL) is a standard in forensic analysis. Currently, it contains over 2000 spectra of drugs and related chemicals. Samples prepared in standard 13-mm KBr pellets have been used for inclusion of drug spectra in the library. However, recently the GSCL successfully applied ATR to drug analysis.⁴³ Horizontal ATR sample compartment accessories with three reflections provide sufficient sensitivity to acquire spectra of approximately 400 ng of lysergic acid diethylamide (LSD) as a film cast from chloroform (Figure 7). The region between 2400 and 1800 cm^{-1} was blanked to remove the uncompensated diamond absorption produced by the IRE. The ATR spectra of drugs can be successfully searched in the original transmission spectral library in spite of the intensity differences in the peaks. This method is beginning to gain acceptance in laboratories around the USA. The FBI Laboratory has started an ATR database of drugs for computer spectral searching. Recently, a drug library of 455 spectra by ATR was produced at the Illinois State Police Laboratory.⁴⁴

GC combined with IR (GC/IR) simplifies the analysis of drug mixture samples typical of those associated with clandestine laboratories and is a standard procedure of the Drug Enforcement Administration (DEA) laboratories. For the analysis of methamphetamine and related compounds, the DEA is required to identify the optical

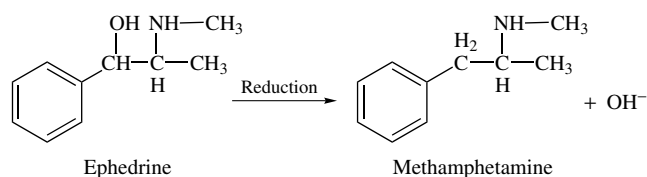


Figure 8. Reduction reaction of ephedrine to methamphetamine.

stereoisomers (d and l forms). IR is more effective than MS in differentiating diastereoisomers. Thus, the diastereoisomers ephedrine and pseudoephedrine, which are precursors for methamphetamine, are identifiable compounds by this method. Figure 8 shows the reduction reaction of the ephedrine to methamphetamine. Figure 9 illustrates the comparison of the gas phase spectra of these compounds. In Figure 9(a) and (b), the region between 1300 and 1000 cm^{-1} shows subtle but consistently different spectral features of the diastereoisomers ephedrine and pseudoephedrine. The spectra of amphetamine and methamphetamine, shown in Figure 9(c) and (d), respectively, do not have the OH stretching band near 3600 cm^{-1} , because the reduction reaction removes the OH attached to the carbon next to the phenyl group. The spectra of amphetamine and methamphetamine differ in the entire region below 1700 cm^{-1} . The most pronounced difference lies with the NH deformation band near 1600 cm^{-1} , which is significantly greater in intensity for the primary amine, amphetamine. Once these components are identified, capillary electrophoresis (CE) is required to determine the optical stereoisomer (d or l enantiomer) present. Since the

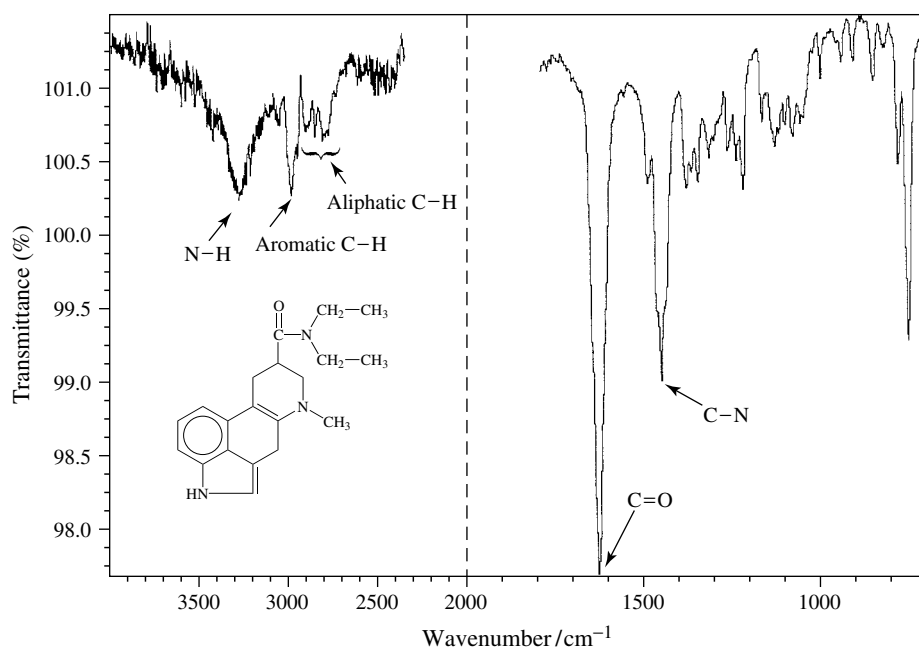


Figure 7. Spectrum of 400 ng of LSD by ATR. (Spectrum provided by Robert Ollis, Georgia Bureau of Investigation Crime Laboratory, Decatur, GA.)

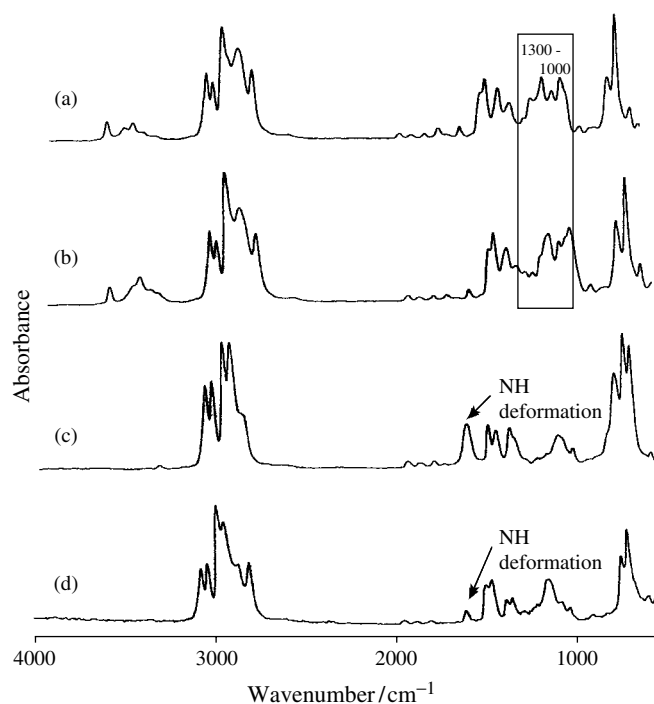


Figure 9. Clandestine laboratory mix separated by GC/IR. Spectra of: (a) ephedrine; (b) pseudoephedrine; (c) amphetamine; (d) methamphetamine. (Spectra provided by Henry Blum, DEA Laboratory, Washington, DC.)

most potent and sought-after methamphetamine is the d enantiomer, the DEA analyzes the mixtures to confirm the presence of d-methamphetamine. Either the l-ephedrine or the d-pseudoephedrine enantiomer may be used to produce d-methamphetamine. CE separates all eight structures of ephedrine, pseudoephedrine and methamphetamine for the final identification of the existing d or l enantiomer versions.

Raman spectroscopy is beginning to attract interest both in the laboratory and for field drug analysis. Many drugs are excellent Raman scatterers, and therefore lend themselves to rapid analysis with direct laser beams, fiber optic probes and microscopes. The application of fiber optic probes provides the ability to obtain spectra for drug samples contained in plastic bags or bottles, thereby making field analysis simple. Several field portable Raman spectrographs have become available on the market. These instruments have been compared for such features as frequency range, resolution, laser excitation and portability in terms of power requirements, size and weight.⁴⁵ While still in an early stage, this field approach appears to have great promise.

5 EXPLOSIVES

As with many types of forensic evidence, explosives produce unique IR spectra, thus making IR useful for identification of the major components in bulk explosives.⁴⁶ Separation

methods are often required with mixtures of components, prior to spectroscopic methods to identify the components. Due to the sensitivity often required, particularly for post-blast residues, GC/MS is frequently applied to explosives analysis. Liquid chromatographic methods, ion chromatography and CE are also frequently applied because of the separation capabilities of these methods.

ATR has been successfully applied to plastic explosives in bulk form and after extraction. Keto⁴⁷ demonstrated an extraction method for the determination of C-4 military explosive. In his method, the explosive hexahydro-1,3,5-trinitro-1,3,5-triazine (RDX), the plasticizer and the rubber binder from C-4 are separated selectively by solvent extraction and filtration. The extracts are cast as a film on an ATR crystal for IR analysis. Bartick and Merrill⁴⁸ have shown how the development of a database of bulk plastic explosives can be used to successfully identify the general plastic explosive type and even the manufacturer. A library of pure explosives components can be searched to potentially identify the explosive material. Figure 10 shows the explosive component RDX, identified from a questioned plastic explosive mixture. A library search of the plastic explosive library identified the questioned explosive as C-4.

Often, unknown materials are found at crime scenes and, for safety considerations, it is important to determine the chemical composition prior to handling and bringing the material to the laboratory for analysis. Early studies with Raman spectroscopy of trace explosives were done by Lewis *et al.*^{49–52} to determine the basic requirements of a field portable system. Successful results were obtained for all samples with a 1064-nm laser FT system, and most samples were successfully analyzed on a dispersive system using 632.8 nm excitation. Lewis *et al.* considered the best potential for field systems to be a compromise that would

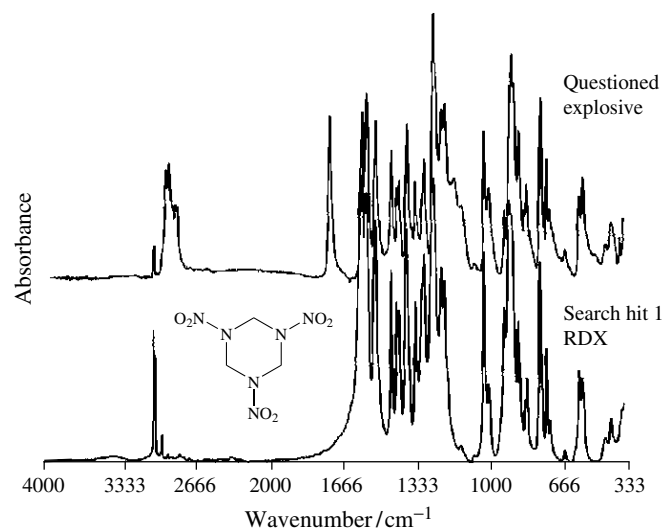


Figure 10. ATR spectrum of a C-4 plastic explosive mix and RDX library pick for the explosive component.

use a NIR 785-nm laser on a dispersive spectrometer. Cheng *et al.*⁵³ have done additional studies that include imaging Semtex plastic explosive deposited in fingerprints on aluminum foil. RDX and pentaerythritol tetranitrate, the explosive Semtex components, were isolated in the prints, and spectra were obtained with a microscope system. Currently, the FBI Laboratory uses an echelle dispersive Raman spectrograph that operates with a 785-nm laser and a fiber optic probe that has become successful for field analysis.⁵⁴ An explosives library has been developed for use with this instrument.⁵⁵

Current developments in portable FT-IR instrumentation also show promise for field analysis of explosives. Recently, SensIR Technologies (Danbury, CT) introduced a portable instrument referred to as the TravellIR[®], that uses a single reflection ATR arrangement for sample analysis.⁵⁶ Liquid and solid sample analysis is easily conducted in the field. A preliminary study of explosive samples has been conducted at the FBI Laboratory's FSRU. IR and Raman field methods are expected to complement one another.

6 SUMMARY AND FUTURE DIRECTION

Vibrational spectroscopy is used throughout forensic laboratories for many applications. IR analysis with FT-IR instrumentation has many applications in the areas such as polymers, drugs and explosives. With the exception of field analysis, where methods have just started to develop, IR has reached a level of maturity in forensic applications. Raman, on the other hand, is just beginning to develop. Both laboratory and field methods are anticipated to flourish in the next few years. The greatest developments are expected for field analysis using portable Raman spectrometers. The instruments will require small size designs providing the performance needed by specific sample types, and cost will be a major factor. The greatest challenge, with both Raman and IR field analysis, lies with the development of the software so that nontechnical law enforcement officials can quickly, conveniently, and accurately use the instruments to get the pertinent investigative information. Of great importance is that instrument operators do not obtain false information. A false positive identification of critical chemicals could result in unjust arrests. A false negative could place examiners in danger by contact with hazardous materials. If research continues at the same level, these challenges are expected to be met within the next few years.

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ABBREVIATIONS AND ACRONYMS

DEA	Drug Enforcement Administration
FSL	Forensic Service Laboratories
GSCL	Georgia State Crime Laboratory
IRE	Internal Reflection Element
LSD	Lysergic Acid Diethylamide
RCMP	Royal Canadian Mounted Police
RDX	Hexahydro-1,3,5-trinitro-1,3,5-triazine
SEM/EDX	Scanning Electron Microscopy with Energy Dispersive X-ray Spectroscopy

REFERENCES

1. E. Locard, *Police J.*, **1**, 177 (1928).
2. E. Locard, *Am. J. Police Sci.*, **1**, 276 (1930).
3. R. Saferstein, 'Criminalistics, An Introduction to Forensic Science', 7th edition, Prentice Hall, Upper Saddle River, NJ (2001).
4. E.M. Suzuki, 'Forensic Applications of Infrared Spectroscopy', in "Forensic Science Handbook", ed. R. Saferstein, Prentice-Hall, New York, 71-195, Vol. III (1993).
5. E.G. Bartick and M.W. Tungol, 'Infrared Microscopy and its Forensic Applications', in "Forensic Science Handbook", ed. R. Saferstein, Prentice-Hall, New York, 196-252, Vol. III (1993).
6. C. Roux, P. Maynard and M. Dawson, *Chem. Aust.*, 11 (1999).
7. P.G. Rogers, R. Cameron, N.S. Cartwright, W.H. Clark, J.S. Deak and E.W.W. Norman, *Can. Soc. Forensic Sci. J.*, **9**, 1 (1976).
8. P.G. Rogers, R. Cameron, N.S. Cartwright, W.H. Clark, J.S. Deak and E.W.W. Norman, *Can. Soc. Forensic Sci. J.*, **9**, 49 (1976).
9. P.G. Rogers, R. Cameron, N.S. Cartwright, W.H. Clark, J.S. Deak and E.W.W. Norman, *Can. Soc. Forensic Sci. J.*, **9**, 103 (1976).
10. E.M. Suzuki and W.R. Gresham, *J. Forensic Sci.*, **31**, 931 (1986).
11. E.M. Suzuki and W.R. Gresham, *J. Forensic Sci.*, **31**, 1292 (1986).
12. E.M. Suzuki and W.R. Gresham, *J. Forensic Sci.*, **32**, 377 (1987).
13. E.M. Suzuki and W.R. Gresham, *J. Forensic Sci.*, **34**, 164 (1989).

14. E.M. Suzuki and W.R. Gresham, *J. Forensic Sci.*, **34**, 180 (1989).
15. W.D. Mazzella, C.J. Lenard and P.A. Margot, *J. Forensic Sci.*, **36**, 449 (1991).
16. W.D. Mazzella, C.J. Lenard and P.A. Margot, *J. Forensic Sci.*, **36**, 820 (1991).
17. R.A. Merrill and E.G. Bartick, *J. Forensic Sci.*, **37**, 528 (1992).
18. E.G. Bartick, *Appl. Spectrosc.*, **39**, 885 (1985).
19. E.G. Bartick, M.W. Tungol and J.A. Reffner, *Anal. Chim. Acta*, **288**, 35 (1994).
20. A.H. Kuptsov, *J. Forensic Sci.*, **39**, 305 (1994).
21. R.A. Nyquist, C.L. Putzig and M.A. Leugers, 'Handbook of Infrared and Raman Spectra of Inorganic Compounds and Organic Salts, Volume 1, Infrared and Raman Spectral Atlas of Inorganic Compounds and Organic Salts', Academic Press, New York (1997).
22. R.A. Merrill, E.G. Bartick and W.D. Mazzella, *J. Forensic Sci.*, **41**, 264 (1996).
23. E.G. Bartick and R.A. Merrill, 'The Development and Evaluation of a Photocopy Toner Spectral Database Obtained by Microscopical IR Analysis', Presented at the AAFS Annual Meeting, New York (1997).
24. M.W. Tungol, E.G. Bartick and A. Montaser, 'Forensic Examination of Synthetic Textile Fibers', in "Practical Guide to Infrared Microspectroscopy", ed. H. Humecki, Marcel Decker, New York, 245–286 (1995).
25. K.P. Kirkbride and M.W. Tungol, 'Infrared Microscopy of Fibres', in "Forensic Examination of Fibres", eds J. Robertson and M. Grieve, Taylor and Francis, Philadelphia, 179–222 (1999).
26. M.W. Tungol, E.G. Bartick and A. Montaser, *Appl. Spectrosc.*, **44**, 543 (1990).
27. M.W. Tungol, E.G. Bartick and A. Montaser, *Spectrochim. Acta Electron.*, **46B**, 1535E (1991).
28. M.W. Tungol, E.G. Bartick and A. Montaser, *J. Forensic Sci.*, **36**, 1027 (1991).
29. Federal Trade Commission Rules and Regulations under the Textile Products Identification Act, Title 15, US Code Section 70, 16 CFR 303.7.
30. M.C. Grieve, *Sci. Just.*, **35**, 179 (1995).
31. J.V. Miller and E.G. Bartick, 'Forensic Analysis of Synthetic Fibers Using Raman Spectroscopy', Presented at the AAFS Annual Meeting, Orlando, FL (1999).
32. J.V. Miller, 'Introduction of Raman Spectroscopy to the Forensic Analysis of Fiber', MS Dissertation, The George Washington University, Washington, DC (1999).
33. P.J. Hendra, W.F. Maddams, I.A.M. Royaud, H.A. Willis and V. Zichy, *Spectrochim. Acta*, **46A**, 747 (1990).
34. P.C. White, C.H. Munro and W.E. Smith, *Analyst*, **121**, 835 (1996).
35. P.C. White, C. Rodger, V. Rutherford, Y. Finnon, W.E. Smith and M. Fitzgerald, *SPIE*, **3576**, 77 (1998).
36. S.G. Ryland, 'Infrared Microscopy of Forensic Paint Evidence', in "Practical Guide to Infrared Microspectroscopy", ed. H. Humecki, Marcel Decker, Inc., New York, 163–244 (1995).
37. J.L. Buckle, D.A. Macdougall and R.R. Grant, *Can. Soc. Forensic Sci. J.*, **30**, 199 (1997).
38. G. Massonnet and W. Stoecklein, *Sci. Just.*, **39**, 181 (1999).
39. E.M. Suzuki, *J. Forensic Sci.* (in press).
40. R.A. Merrill and E.G. Bartick, *J. Forensic Sci.*, **45**, 93 (2000).
41. E.G. Bartick and R.A. Merrill, 'The Development of an Information Database for Duct Tapes', Presented at the AAFS Annual Meeting, Reno, NV (2000).
42. J.A. Seagal, 'Forensic Identification of Controlled Substances', in "Forensic Science Handbook", ed. R. Saferstein, Prentice-Hall, New York, 68–160, Vol. II (1988).
43. R.J. Ollis, Jr, J. Fitzpatrick and S. Ellis, 'Illicit Drug Identification Using a Multiple IRE in FTIR Spectroscopy', Presented at The Pittsburgh Conference, New Orleans, LA (2000).
44. C.V. Koulis, K.J. Hymes and J.L. Rawlins, *J. Forensic Sci.*, **45**, 876 (2000).
45. B. Eckenrode, E.G. Bartick, S.D. Harvey, M. Vucelick, R.W. Wright, R.A. Huff and D.M. Hickey, *Forensic Sci. Commun.* (in press).
46. S. Zitrin, 'Analysis of Explosives by Infrared Spectrometry and Mass Spectrometry', in "Forensic Investigation of Explosions", ed. A. Beverage, Taylor & Francis, Bristol, PA, 267–314 (1998).
47. R.O. Keto, *J. Forensic Sci.*, **31**, 241 (1986).
48. E.G. Bartick and R.A. Merrill, 'Proceedings of the International Symposium on the Forensic Aspects of Trace Evidence', US Government Printing Office, Washington, DC, 277–279 (1991).
49. I.R. Lewis, N.W. Daniel, Jr, N.C. Chaffin, P.R. Griffiths and M.W. Tungol, *Spectrochim. Acta, Part A*, **51**, 1985 (1995).
50. I.R. Lewis, N.W. Daniel, Jr and P.R. Griffiths, *Appl. Spectrosc.*, **51**, 1854 (1997).
51. I.R. Lewis, N.W. Daniel, Jr and P.R. Griffiths, *Appl. Spectrosc.*, **51**, 1868 (1997).
52. N.W. Daniel, Jr, I.R. Lewis and P.R. Griffiths, *Mikrochim. Acta*, (Suppl.), **14**, 281 (1997).
53. C. Cheng, T.E. Kirkbride, D.N. Bachelder, R.J. Lacey and T.G. Sheldon, *J. Forensic Sci.*, **40**, 31 (1995).
54. R.A. Huff and D.M. Hickey, 'A Portable Raman System for the Detection of Explosive Materials', 15th Triennial Meeting IAFS, Los Angeles, CA (1999).
55. N.T. Kawai and J.A. Janni, *Spectroscopy*, **15**(10), 32 (2000).
56. J. Coates and J. Reffner, *Spectroscopy*, **15**(4), 19 (2000).