

Raman Spectroscopy: The Science Behind the Technology

This paper discusses the different portable analytical technologies available for identifying seized explosives, narcotics, and other unknown substances.



Introduction

First responders, often police, firefighters and hazmat teams, encounter unknown substances in a wide range of scenarios, including train derailments, overturned semi-tractor trailers on major freeways, fires and explosions at chemical plants, illicit drug manufacturing laboratories (clandestine labs), and those associated with terrorist activities. Historically, first responders have been ill prepared to handle the multitude of unknown chemicals and materials found during such events, relying only on their training, intuition, and common sense to respond to the situation at hand. Typically, first responders would collect and send samples of suspect materials to a forensic crime laboratory for subsequent identification, a time consuming and costly undertaking. More recently, however, several analytical tools have become available that can allow identification of suspect materials in the field.

Chemical analysis technologies provide the ability to identify small amounts of unknown substances. The majority of chemical substances are white solid materials, indistinguishable by color, texture, odor, and other basic properties. These sophisticated chemical analytical tools are used to identify materials based on their unique chemical properties.

This paper explains the different chemical analysis technologies used to identify unknown solid and liquid substances, focusing on technologies that can be deployed by first responders in the field, and, more specifically, the advantages of one of these technologies, Raman spectroscopy.

Chemical Analysis Technologies

The three most prevalent analytical technologies available for chemical identification in field situations are colorimetric tests [1], Fourier transform infrared spectroscopy (FTIR) [2], and Raman spectroscopy [3,4]. Other effective tools used for the analysis of unknown materials include capillary electrophoresis (CE) [5], gas chromatography/mass spectrometry (GC/MS) [6], and high performance liquid chromatography (HPLC) [7]; but these methods are only used in laboratory settings.

Infrared (IR) spectroscopy probes the molecular structure of chemicals using infrared radiation, which interacts with molecular bonds to produce a unique spectral fingerprint of the analyzed compound. Low energy infrared light, emitted from a low temperature black body source, impinges on a sample. Most FTIR instruments measure absorption based on the loss in transmission of the infrared light. The light is separated in wavelength, transmitted through the sample, and each wavelength is detected in sequence.

Among the many types of IR instruments available are dispersive and filter-based systems, but by far the most common form utilizes the interaction between a fixed and a changing light path to produce optical interference. The 'interferogram' is recorded as a function of time and can be converted from temporal to wavelength coordinates using a Fourier transform. This process is the basis of the Fourier transform infrared (FTIR) spectrometer.

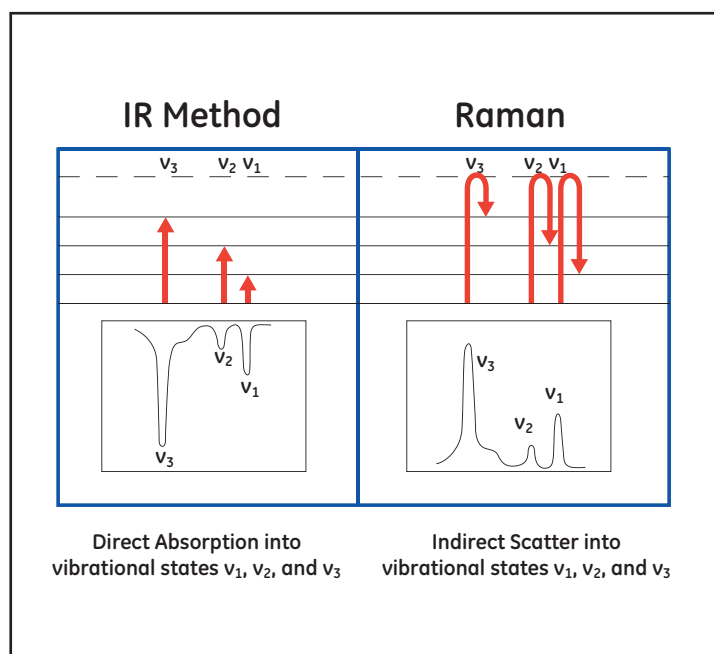


Figure 1:

Infrared spectroscopy involves the absorption of low energy radiation into the vibrational levels of the molecules being analyzed. Molecular bonds with permanent dipoles, such as carbonyl bonds, are IR active and result in strong absorption peaks. Raman spectroscopy results from the inelastic scatter of higher energy radiation into vibrational states of the molecules being analyzed. Molecular bonds with easily polarizable electrons, such as double bonds, triple bonds, and aromatic structures, produce strong Raman signals.

Because the IR light interacts strongly with the sample, the test material must be diluted, typically using potassium bromide (KBr), and pressed to make a pellet, or Nujol, which is used to make a mull. Both of these methods produce thin samples that are diluted in the target analyte, allowing the transmission of sufficient IR energy, to allow for a measurement. The pattern of absorption as a function of wavelength (usually represented in energy units of wavenumbers [cm^{-1}]) is the FTIR spectrum or "spectral fingerprint" of the sample. To identify the unknown substance, its FTIR spectrum is correlated against a database of FTIR spectra of known materials, often referred to as a library.

Under appropriate conditions, light passing through a medium with a high refractive index into a medium with a lower refractive index results in total internal reflection. Looking up at the surface of a pool from underwater represents a good example of this phenomenon. If the angle between the viewer and the surface is sufficiently small, the water/air interface exhibits total internal reflection and becomes a perfect mirror. When a material is placed in contact with the totally reflecting surface, a small amount of the incident light penetrates the interface as an evanescent wave and can interact with and be absorbed by the sample. This phenomenon, referred to as Attenuated Total Reflection (ATR), forms the basis of a new sampling accessory for FTIR instruments, and has recently become the most common sampling interface for routine FTIR analysis. In the late 1990's, FTIR microscopy was combined with an ATR coupled to a diamond window to produce an abrasion- and corrosion-resistant sampling device. Field FTIR devices employ the ATR technique as their primary sampling interface because it greatly simplifies sample preparation and eliminates the need for KBr or Nujol.

Colorimetric assays rely on the reaction of specific chemicals with an unknown compound to create a color change indicative of the sample material. In preparing a colorimetric assay, the operator places a small amount (1-10 milligrams) of the unknown onto a special white plate or into a tube or small plastic bag. Chemicals and solvents are then added and

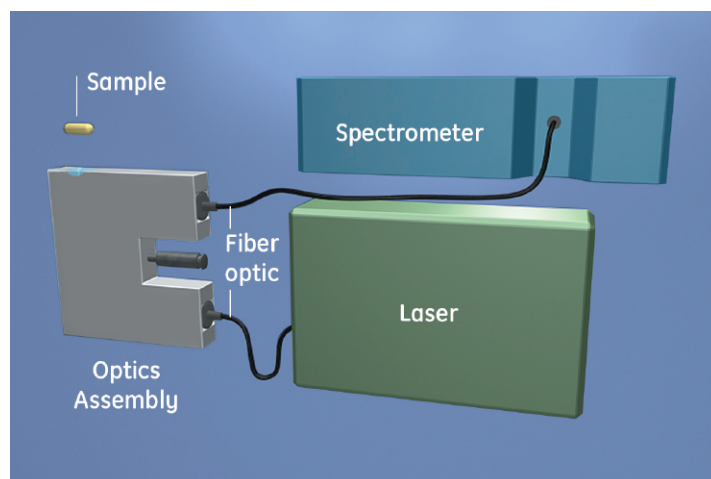


Figure 2:

Components of a Raman Spectrometer

allowed to react for a specific amount of time. If the unknown contains the substance targeted by the specific test, a color change results, which can then be compared to a standard chart to identify the substance.

Though the process may be simple and fast (≤ 2 minutes), positive identification of the specific color requires operator interpretation, often a challenge in poor lighting conditions. Also, these tests are only used to eliminate the presence of a particular material. If a substance fails to turn the target color, the operator can safely assume the sample does not contain the contraband substance being tested for, or the amount present is below the sensitivity of the particular test. If the sample does produce the target color for a particular test, at best the operator can assume the sample may contain the contraband material. Thus, these tests are referred to as presumptive, and always require a second confirmatory test. Color tests are non-specific and subject to cross reactions with many other materials [8]. Several tests may be required to classify an unknown narcotic sample, while as many as ten tests may be needed simply to classify an unknown sample in a Hazmat situation [9]. Color test kits must be kept away from direct sunlight and excessive heat to prevent the chemicals contained in them from becoming degraded and useless. Chemical test kits have a finite shelf life, typically six to twelve months under ideal storage conditions. Another major drawback to colorimetric assays is that, as new designer drugs are created [10], the time lag between the development of a color test kit and its commercial availability may be months or years.

Raman spectroscopy, like FTIR, probes the molecular structure of unknown materials by analyzing the interactions of light with the sample's chemical bonds. However, unlike FTIR, which relies on the direct absorption of low energy, broadband light into vibrational states of the molecule, Raman spectroscopy involves the inelastic (loss of energy) scatter of high-energy, monochromatic (single wavelength) light, typically from a laser, off the molecules of the sample. As the laser light's electromagnetic field interacts with the molecular bonds, a small fraction of the scattered photons lose some of their energy to a vibrational mode of the molecule, and are lower in energy (or longer in wavelength) than the original laser light. This is referred to as Stokes-shifted light. If the particular vibrational mode is already in an excited state (a common condition at higher temperatures), the scattered photon may gain some energy and have a shorter wavelength (more energy) than the incident laser light. Such scatter is known as AntiStokes-shifted light. Each Raman active bond in the molecule causes the emission of a different wavelength of light. Thus, while the light incident on the sample has one wavelength, the light scattered off the sample has many, which carry the information about the identity of the sample.

The scattered light is collected and sent to a detection system. There are two major detection methods for Raman spectroscopy: FT Raman, based on the Fourier transform process described for FTIR spectroscopy; and another based on a diffraction grating spectrometer, which spatially separates the light, similar to how a prism spreads sunlight into a rainbow of color. The latter often uses a charge-coupled device (CCD) — a one- or two-dimensional array of small

detectors, similar to those used in digital cameras and video recorders — to detect the light. Each detector element collects light of a different color, which is digitized to produce the Raman spectrum, which consists of a sequence of peaks at the wavelengths where Raman-shifted light is emitted. Each peak is associated with a different bond in the molecule. This pattern, unique to each substance, is searched against a library, similar to FTIR spectroscopy, and the best correlated sample is considered the most likely match.

Performance Requirements for Controlled Substance Identification

When comparing technologies, several important performance requirements can be used to evaluate their utility for identifying unknown bulk substances at clandestine drug labs, border crossings, ports of entry and other locations. Those requirements include selectivity, range of compounds detected, operator safety and logistics, and sample preparation.

Selectivity refers to the ability to distinguish between compounds. Many legal or safe materials have chemical structures similar to illicit or hazardous substances. The majority of solid chemicals occur as white powders, indistinguishable by color, smell, or texture. Colorimetric tests are useful for chemical classification, because of their sensitivity to functional groups on the chemicals. However, these tests do not provide unique results for each compound and are prone to false positive reactions with many common materials. Both the Raman and FTIR spectroscopic methods provide a highly unique spectral fingerprint of the unknown substance's chemical structure, which allows for, in the great majority of cases, unequivocal identification of the suspect material.

Range of compounds detected relates to the number and type of materials that a method can uniquely identify. First responders encounter many different types of materials, including drugs, explosives, solvents, precursors, diluents, and a wide range of hazardous substances. Color tests are available for fewer than two-dozen drugs and a handful of explosives. Hazmat kits require that a series of physical (burn, dissolution, etc.) and chemical tests be performed before an unknown material can be put into a specific class. Even then, most chemical tests do not provide the exact identity of an unknown. Both Raman and FTIR methods can analyze compounds ranging from plastics to poisons. Typical responses to these materials are placed into a database or "library" and the response from the unknown substance is compared with hundreds or even thousands of library entries, resulting in a reliable, positive identification of the substance.

Operator Safety and Logistics cover potential hazards that operators may face during routine use and other practical considerations, such as regulatory issues for hazardous chemical disposal, safety, etc. Raman instruments contain powerful lasers. However, proper system design should mitigate any laser safety issues. FTIR systems contain a heated element that produces the infrared radiation. Again, an instrument design that prevents physical contact with hot sources eliminates the possibility of burns.

Chemical test kits, containing strong acids and bases, as well as other toxic chemicals, have a finite shelf life and must be stored and disposed of properly. With EPA guidelines for waste disposal becoming more stringent, the cost of waste disposal may be significant. Also, chemical test kits often contain reactant chemicals in glass ampoules. While breaking open ampoules, broken glass can breach the test kit, releasing reagents, the unknown, and shards of glass, which can provide a means for hazardous materials to enter the blood stream.

Sample preparation involves the steps required to get the sample of unknown substance ready for analysis. Obviously, minimizing the handling of unlabelled, potentially hazardous compounds reduces exposure and risks. However with some sampling methods, such as color tests, the opening of sealed vials, ampoules or plastic bags cannot be avoided, exposing operators to potential hazards.

The FTIR/ATR method requires the operator to place a small amount of the unknown substance directly onto the diamond surface of the ATR element. Such sampling methods increase the operator's risk of exposure. Depending on the nature of the substance, the ATR crystal, or even the entire instrument, may require decontamination after an analysis. In addition, as with color tests, substances sealed in ampoules, bottles or bags must be opened, exposing the operator to hazardous materials for which they may not be properly equipped. This is especially true of potential biological agents (BWA) or chemical warfare agents (CWA). Raman spectroscopy, in contrast, uses visible light, which can penetrate most plastic bags and glass or plastic ampoules. In many cases, the sample can be analyzed in its original, sealed package, reducing or eliminating potential exposure to unknown hazards.

	Color Tests	FTIR	Raman
Selectivity	••	•••	••••
Range of Compounds Detected	•	••••	•••
Operator Safety and Logistics	••	••	••••
Sample Preparation	••	•••	••••

•••• Excellent ••• Good •• Fair • Poor

Raman versus FTIR Technology

Advances in component technologies have allowed for the development of excellent portable Raman and FTIR systems, comparable in performance to their bench top counterparts. Portable FTIR systems have become quite compact, with volumes less than 0.2 ft³, and weighing only 22-30 pounds (10-13.6 kg). Recent improvements in key components for Raman systems have allowed for the development of instruments approaching handheld size, with volumes less than 0.2 ft³,

and weighing less than seven pounds (3.18 kg). And, while FTIR systems typically allow for lower detection limits than their Raman counterparts, most instruments for laboratory and field use employ the ATR accessory to greatly simplify sample handling. This results in a much smaller sample interaction volume, reducing the signal strength from samples when compared to transmission measurements. As a result, FTIR/ATR and Raman instruments both achieve sensitivities of around 10% by weight for binary mixtures of solids. In addition, since the Raman signal is not limited to a small interaction volume, the sensitivity for analyses of dissolved substances can be less than one part per thousand, or 0.1% by weight. This is especially true for aqueous samples, since water has a very low Raman signal, whereas the strong IR absorption of water limits the method to a sensitivity of greater than 10%.

Limitations imposed by the ATR approach give Raman spectroscopy another key advantage over FTIR/ATR. The ATR method, which relies on evanescent waves produced during the total internal reflection at the diamond surface, has a limited penetration depth of 1-2 microns—not enough to penetrate the coatings found on many over-the-counter and prescription tablets. Analysis of such samples by FTIR/ATR will result in the identification of the coating material (if it is in the database) and not the target substance(s). In order to analyze the active ingredient(s), FTIR/ATR requires removal of the coating.

By contrast, the near-infrared laser wavelengths employed by most portable Raman instruments, coupled with the weak Raman cross-section of most coating and inactive ingredients, result in penetration depths of hundreds of microns (powders) to millimeters (liquids). Raman analysis penetrates most tablet coatings to provide data about the active ingredient(s) of the pill. Instances where the coating is particularly thick or opaque may require removal of some coating to assure optimum analysis of the contents.

The limited penetration depth of the FTIR/ATR technique also has significant implications for unknown samples found inside bags or bottles. Such samples can range from the innocuous, like baby powder or baking soda, to potential biohazards, such as anthrax. Since the IR radiation of the FTIR/ATR method cannot readily penetrate the container wall, the container must be opened for sample collection. This exposes the operator to the potential hazard and can lead to the contamination of evidence or the suspicion of tampering. Raman analysis penetrates the walls of glass vials and clear plastic, eliminating the need to open containers and greatly reducing the risk of exposure. In addition, the non-destructive Raman method preserves the sample for subsequent laboratory tests or for use as evidentiary material, a critical consideration when only a small amount of sample is available.

Finally, a significant advantage that Raman spectroscopy has over FTIR spectroscopy is in the analysis of mixtures that may contain narcotic or explosive materials. The infrared cross-sections of most materials are quite similar, so that a mixture of equal amounts of two substances will generate a spectrum in which the peaks of each compound have approximately equal intensity. However Raman cross-sections can vary by more than three orders of magnitude. In addition, the prevalence of double

bonds and aromatic structures in narcotics and explosives result in very strong Raman bands when compared to cutting agents and diluents often found in street samples and prescribed medications. Thus, it is often the case that, in a mixture, Raman peaks from the substance of interest dominate the spectrum, allowing for increased sensitivity. Even when two or more strongly Raman active substances are in the same sample, the fact that Raman spectra of a material typically contain fewer peaks than IR spectra, and that the Raman peaks are narrower than their IR counterparts, makes it much easier to resolve mixture spectra. In addition, to produce a useable signal for solid materials, the FTIR/ATR method requires that the sample be pressed onto the diamond ATR crystal with significant force. In some cases, peaks of the substances in the sample can shift; and the sample can be altered in crystalline structure, or even liquefied, all of which have significant impact on the identification of unknown pure materials, and even more so on complex mixtures.

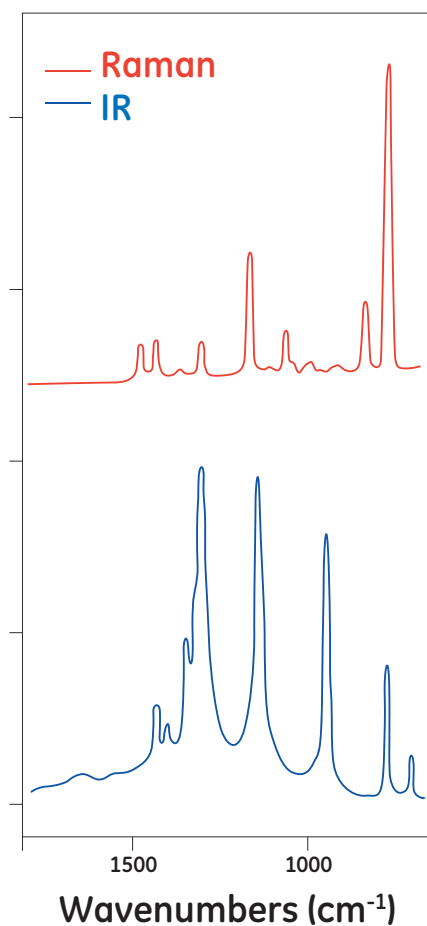


Figure 3:

Comparison of the Raman and IR spectra of dimethylsulfone, a common cutting agent for methamphetamine. The IR spectrum was collected with an instrument resolution of 2 cm⁻¹, while the Raman spectrum was acquired with an instrument resolution of 15 cm⁻¹. Despite this, most of the peaks in the Raman spectrum are narrower than the peaks in the IR spectrum. The Raman peak widths in this example are instrument bandwidth limited, whereas the IR peaks are inherently broad. The narrower Raman line widths are a benefit to mixture analysis, as it reduces spectral overlap between the peaks of the components.

Summary

As we look to help first responders and federal agents identify a total solution, bulk identification technologies become an integral part of that solution. Spectroscopic techniques can offer significant improvements over today's standard narcotic and hazardous material chemical test kits in their simplicity and ability to provide unequivocal identification of an unknown substance, instead of just the broad material classification provided by the chemical tests. Such systems can complement X-ray scanners and trace detection equipment by providing confirmation once a suspected illicit substance is found.

Because of their ability to identify thousands of unique substances, from narcotics to explosives to common household substances, spectroscopic techniques are extremely useful when facing a truly unknown material, especially substances available in only limited amounts that need to be retained for court evidence. Raman spectroscopy offers the advantage of identifying potentially hazardous substances by a unique fingerprint, based on the chemical structure of the unknown, and can do so through the walls of sealed plastic bags and transparent bottles, vials, and ampoules without opening the container. Therefore, Raman spectroscopy can be an ideal tool to aid in substance analysis during arrests for possession, seizures of clandestine manufacturing laboratories, large seizures at borders and ports of entry, and in first responder situations.

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