Forensic Applications Of Vibrational Spectroscopy Techniques To Identify Prescription Drugs And Mixtures

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Abstract

One major issue faced by law enforcement is drug related crimes. In the past, drug related crimes included drugs such as cocaine, methamphetamines etc. Today, prescription drugs, specifically pain medications are almost as prevalent due to rampant drug abuse. Officials responding to crime scenes (e.g. firefighters, police and hazmat teams) are often ill equipped to handle the ever growing magnitude of drugs that are encountered at crime scenes. These samples generally are collected, sent to crime labs for extensive analysis which can be time-consuming and impede swift justices. However, recently several analytical techniques have been developed which can be used in the portable mode. These techniques can be used to identify white powders which are otherwise indistinguishable based on color, texture and odor. In the present study we have utilized two analytical techniques: Fourier Transform Infrared spectroscopy (FT-IR), and Raman Spectroscopy to identify various prescription drugs.

INTRODUCTION

According to the Federal Bureau of Investigation (FBI), drugs are becoming more and more prominent as motivations for crimes. The most recent annual data from the Federal Bureau of Investigation (FBI) show that 12.2 percent of more than 14 million arrests in 2008 were for drug violations, the most common arrest crime category (1). Additionally, the abuse of common over-the-counter (OTC) pain medication drugs has also escalated in the past decade. In 2008, it was estimated that 7 million individuals aged 12 and older were dependent on or had abused illicit drugs in the past year, compared with 6.9 million in 2007. The drugs with the highest dependence or abuse levels were marijuana, prescription pain relievers and cocaine. Many of these drugs are considered “controlled substances” that have a legally recognized potential for abuse. Detecting and identifying controlled substances is a critical step in law enforcement's fight against drug-related crime and violence. In addition, newer synthetic designed drugs are being introduced on a frequent basis into the general population.

The present study examines two analytical techniques (Fourier transform infrared spectroscopy and Raman Spectroscopy) that can be used to identify unknown compounds frequently encountered by first responders in the field. These two analytical techniques have the additional advantage that they can also be used in the portable mode. Other techniques used for drug identification (gas chromatography, mass spectrometry and capillary electrophoresis) are primarily used in a laboratory setting (2, 3).

Infrared (IR) spectroscopy utilizes infrared radiation to probe the chemical structure of the drug/compound. The radiation interacts with the bonds of the compound producing a unique spectral fingerprint of the drug. The identity of the compound is determined by comparing spectra against a database of FT-IR of known spectra present in a library. Infrared spectroscopy has been used extensively in forensics (4-6). In comparison, the Raman spectroscopic technique utilizes a monochromatic light source (e.g. a laser) focusing onto a sample and analyzing the resulting scattered light (7). Raman spectroscopy is therefore a rapid and convenient method of identifying unknown samples and has been used in forensics including in the portable mode (8-11). Raman spectroscopy is sometime preferred over Infrared spectroscopy because aqueous solutions can be analyzed without the strong interfering water absorption bands. Additionally, spectra from Raman spectroscopy can be obtained through glass bottles and various forms of packaging (12). One major problem that Raman spectroscopy that is observed is the signal may be weak and obscured by fluorescence. This issue can be circumvented by using surface-enhanced Raman Scattering (SERS). The use

of SERS requires the presence of a roughened surface made of metals or colloids (13, 14). The advantage of SERS is the minute quantity of sample required, often seen at crime scenes. This also results in minimal damage to the original sample.

In the present study we compare data obtained from various OTC and presciption medications using the two techniques. We also evaluate the ability of the two techniques to identify individual components of a drug mixture (Excedrin® and its individual components: Caffeine, Acetaminophen and Aspirin).

METHODS

Drug Test Samples: The OTC drugs and prescription medications: Acetaminophen, Excedrin, Caffeine, Aspirin, Ibuprofen, Naproxen, Gabapentin, Alprazolam (anti-anxiety) Promethazine (antihistamine), Cephalexin (antibiotic) and Synthroid (Hypothyroid) were obtained from a local drug store.

FT-IR

FT-IR spectra were obtained using a JASCO FT/IR-4200 spectrometer with the Ge Attenuated Total Reflectance (ATR) accessory with a resolution of 0.5 cm^{-1}. The detector is a deuterated L-Alanine Triglycine Sulfate (TGS) which is temperature (peltier) stabilized. The powdered drug sample was placed onto the ATR crystal and pressure of 75psi was evenly applied and the sample spectrum was collected. The sample was then cleaned from the crystal surface and an additional spectrum was collected for the next sample. A spectral range of 700–4000 cm^{-1} was employed. Spectra obtained were compared to databases (JASCO KnowItAll ®) to verify the identity of the drugs.

RAMAN SPECTROSCOPY

A small amount of sample (approx 1 microgram) was placed onto a glass slide on a removable stage on a Perkin Elmer® Raman station 400™ instrument. The excitation source was a near-infrared 785-nm laser (100 mW at the sample), with a spot size of 100 µm. A spectral range of 220–3200 cm^{-1} was employed. The detector was a temperature controlled charged coupled device (CCD) detector (−50 °C) incorporating a 1024 × 256 pixel sensor. Spectra were acquired using Spectrum software and images were acquired using SpectrumIMAGE software, both supplied by PerkinElmer. The video camera was focused onto the slide and the laser was focused and applied twice for ten second intervals.

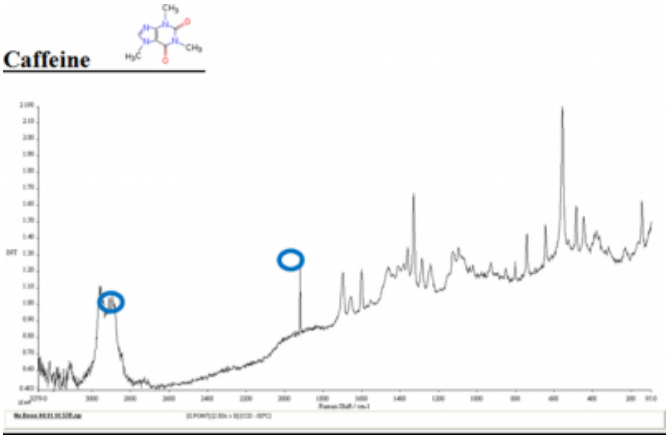
RESULTS AND DISCUSSION

FT-IR AND RAMAN SPECTRA FOR INDIVIDUAL OTC DRUGS

The FT-IR and Raman spectra for the three compounds (Caffeine, Acetaminophen and Aspirin) contained peaks (some overlapping) corresponding to the functional groups present in their structures (Fig 1, 2, 3). The FT-IR and Raman data for Caffeine showed characteristic peaks for C-H stretching (2850-3000 cm^{-1}) corresponding to the presence of 3 methyl groups (Fig. 1a, b).

Figure 1

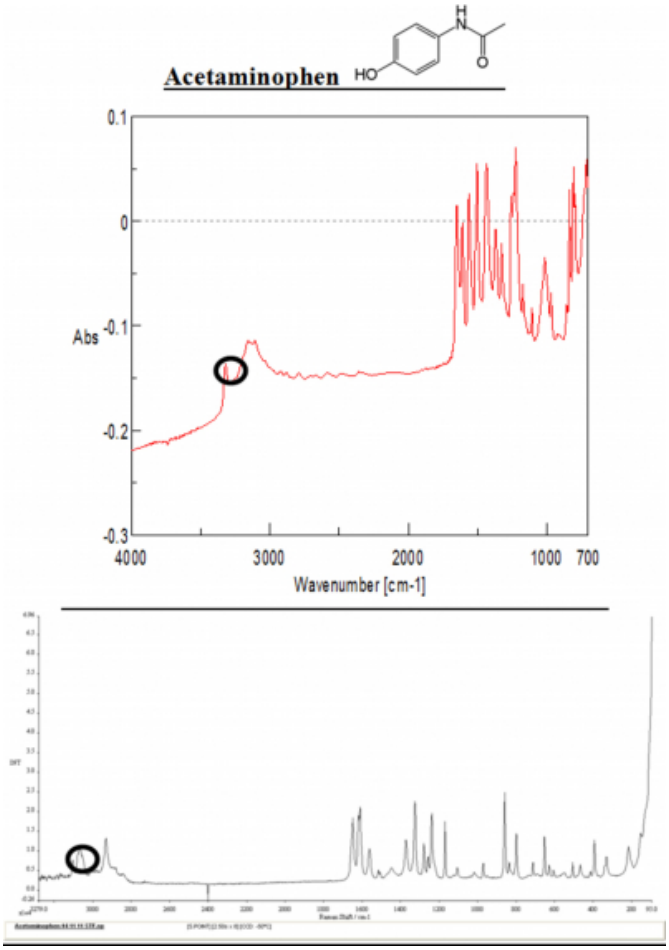
Fig. 1. Comparison of a) FT-IR and b) Raman spectra for Caffeine



Similarly data for Acetaminophen showed distinguishing peaks for N-H stretching at 3300-3500 cm^{-1} along with peaks corresponding to the presence of OH group (3400-3650 cm^{-1}) and C-O stretching at 1670-1780 cm^{-1} (Fig 2a,b).

Figure 2

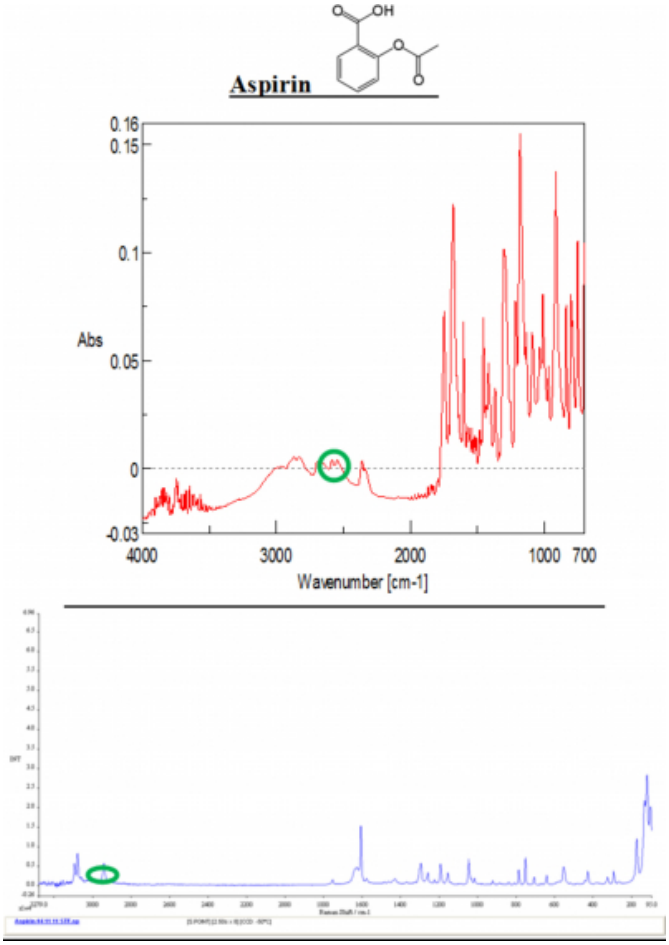
Fig. 2. Comparison of a) FT-IR and b) Raman spectra for Acetaminophen



Finally for Aspirin, the presence of a broad peak at 2500-3100 cm^{-1} indicated the presence of a carboxylic group (Fig. 3a).

Figure 3

Fig. 3. Comparison of a) FT-IR and b) Raman spectra for Aspirin



When comparing the FT-IR and Raman spectroscopy data for the compounds, as expected, many of the peaks observed on the FT-IR were also found in the Raman spectra (Fig 1, 2, 3). One difference between the spectra was the sharpness of the Raman peaks as compared to the FT-IR spectra. Raman peaks tended to be narrower than their IR counterparts. Additionally, hydroxyl (OH) and carbonyl groups (asymmetric, dipolar bonds) showed stronger infrared (IR) peaks (3400-3650 cm^{-1} and 1670-1780 cm^{-1}). In comparison, the symmetric bonds in aromatic rings and C=C bonds gave sharper Raman peaks. Similar results were obtained with Ibuprofen, Naproxen, Gabapentin, Alprazolam, Promethazine, Cephalexin and Synthroid (data not shown).

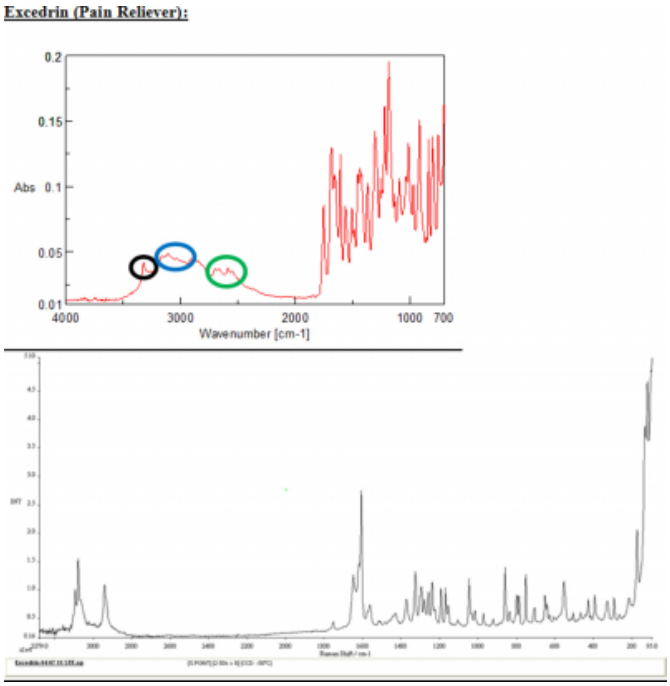
COMPARISON OF FT-IR AND RAMAN SPECTRA FOR DRUG MIXTURES

To compare the effectiveness of the two techniques in distinguishing mixtures of drugs, a commercially available OTC drug Excedrin® was utilized. An examination of

Excedrin® indicated that the peaks were a composite of Caffeine, Aspirin and Acetaminophen in both the FT-IR and Raman spectra (Fig 4).

Figure 4

Fig. 4. Comparison of a) FT-IR and b) Raman spectra for Excedrin



Specifically, the N-H stretch at 3300-3500 cm^{-1}can is seen in both the FT-IR and the Raman spectra corresponding to the presence of Acetaminophen as well as in Excedrin®. Similarly the C-H stretch of the methyl groups at 2850-3000 cm^{-1} and the OH stretch of the carboxyl group at 2500-3100 cm^{-1} could be attributed to similar peaks in Caffeine and Aspirin respectively. When comparing the data obtained from both the techniques, the Raman spectra exhibited fewer peaks than the IR spectra (Fig 4a and b). Additionally, since double bonds and aromatic structures are frequently present in narcotics as compared to the diluents and cutting agents, Raman spectra may provide more information in these mixtures. The Raman peaks also appear to be sharper and narrower than the IR peaks making it easier to resolve peaks in mixtures.

CONCLUSIONS

The advantages of using FT-IR and Raman spectrosopy for detection of prescription drugs are that they give rapid data, are easy to use and are easily adaptable to the portable mode. Even though both methods probe vibrations in molecules and showed similar profiles, striking differences were observed when comparing the spectra. The Raman spectra had the advantage of providing sharper peaks for symmetric bonds in aromatic compounds and those that contain double bonds (often present in narcotics), while FT-IR showed stronger peaks for asymmetric hydroxyl and carbonyl groups. In addition fewer peaks of interest in Raman spectra may facilitate mixture analysis.

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