Forensic Chemical Detection and Identification Using Raman and Infrared Spectroscopy

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I. Introduction

WITH the current state of the opioid crisis[1] and terrorist threats[2] around the world, law enforcement officers and soldiers in the field require a reliable method of detecting and identifying drugs of abuse and explosives. Spectroscopy is a popular analytical tool used in forensic science that studies the interaction between electromagnetic radiation and matter. Researchers classify spectroscopy based on the type of radiation used, nature of the interaction, and type of matter analyzed (atoms, molecules, nuclei). Regardless of the method, each chemical produces a unique spectrum which can be used for detection and identification[3].

Raman spectroscopy is a technique that has grown in popularity in recent years due to its unique advantages. There is little to no sample preparation needed, the technique is non-destructive to the sample and a Raman spectrum can be acquired within seconds. To acquire the spectra, a sample is illuminated with a monochromatic light source, the incident light is scattered and collected by a lens where it is sent through a filter that only passes the inelastic scattered light. This light is then spectrally separated with a grating before it is sent to a detector. The Raman spectrum collected represents the minuscule fraction that undergoes inelastic scattered light that has different energy, resulting in a different frequency and wavelength than the incident light. The spectrometer detector measures the shift in frequency caused by vibrations occurring within a molecular structure and plots the frequency shift (Raman shift) on a spectrum with intensity of light. Because the Raman effect is so weak, the resulting spectrum can be masked by any fluorescence that may result from the absorption of incident light, causing complications when dealing with certain analytes.

Infrared spectroscopy measures the interaction between light and a material in a slightly different way. A spectrum is produced by measuring the amount of incident radiation absorbed or scattered at each IR frequency[4]. Unlike Raman spectroscopy, the radiation used is invisible, making it a suitable stealthy method for standoff detection of illicit materials[4-5]. Both methods are based on molecular vibrations; IR spectroscopy detects changes in dipole moment whereas Raman spectroscopy detects changes in polarizability. Because of this, molecules can be Raman-active, IR-active, or both. Therefore, researchers use both methods in a complementary manner for purposes of chemical detection and identification.

The objective of this project was to use the IR and Raman microscope spectrometers to measure and analyze forensic materials of interest. In doing so, the project would provide valuable reference information for some of NRL Code 6365's projects involving the standoff detection of illicit materials[5] and would verify the composition of Code 6365s chemical coupons provided to other research institutions.

II. Materials

A Renishaw inVia Raman microscope (Figure 1a) was used to make all Raman measurements. It was equipped with two different excitation wavelengths (532nm and 633nm), two different gratings (1800 l/mm and 600 l/mm) and four different microscope objectives (5x, 20x, 50x, 100x). With these features, the spectrometer was able to avoid fluorescent signal, change the spectral resolution, and change magnification of sample images by adjusting settings, respectively. Renishaws WiRE software was used to operate the microscope and conduct analysis on the Raman spectral data. Origin was used for additional spectral analysis.

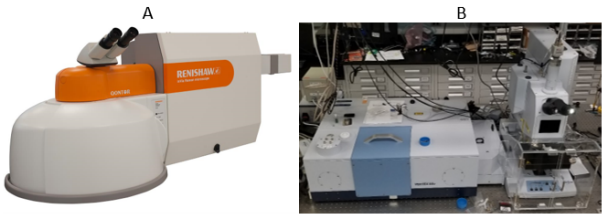

Fig. 1. (a) Renishaw inVia Qontor Raman microscope used for acquiring Raman spectra. (b) Bruker Vertex 80v IR spectrometer used for acquiring IR spectra.

A Bruker Vertex 80v infrared spectrometer (Figure 1b) was used to make measurements of infrared spectra. It had a Hyperion 3000 microscope attachment, along with multiple different MCT and DTGS interchangeable detectors for measuring transmittance, reflectance, and diffuse reflectance.

Trace analytes of interest such as PETN (Pentaerythritol tetranitrate), RDX (1,3,5-trinitro-1,3,5-triazine), and caffeine were obtained and used to make two specialized types of samples clutter samples and fingerprint samples. An assortment of eight different chemical substances (Appendix Table 1) were used to make each clutter sample. The fingerprint samples

were made using a fingerprint press and crambe oil to model human sebum oil.

III. Methods

The Raman instrument was used to measure samples of RDX , PETN , and caffeine. The spectra produced are displayed in Figure 2.

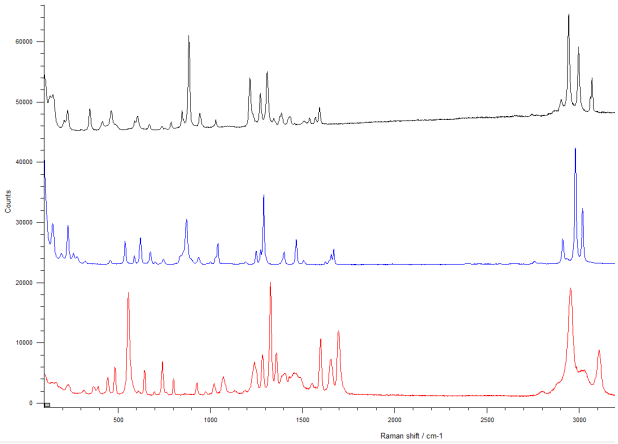

Fig. 2. Raman spectra of RDX (black), PETN (blue) and caffeine (red).

To verify, the measured spectra were compared with Raman spectra from literature and the internal forensic spectra library. However, this process was inefficient as both literature and built-in library spectra were not able to provide the necessary information. Literature spectra were acquired under different conditions (pressure, temperature, excitation wavelength, etc.) than our instrument and the built-in library did not include spectra of interest. Because of these limitations, we decided to create our own Raman spectral database.

To construct the library, bulk samples of analyte were obtained and sprinkled onto a small glass slide. For safety reason, only trace amounts of explosives such as RDX and PETN were handled in this process. Because the Raman instrument can measure individual particles, no additional sample preparation was needed. For each chemical, the glass slide was placed in the microscope holder and a series of particles were measured with the 50x objective. Measurement parameters such as laser power and exposure time were adjusted to optimize spectrum intensity and avoid damaging of particles. Three measurements on different particles were made for each analyte but the spectrum with the highest intensity and clearest features (qualitatively determined) was loaded into a library database in the Renishaw WiRE software (Figure 3). This process was repeated using both 532nm and 633nm excitation wavelengths.

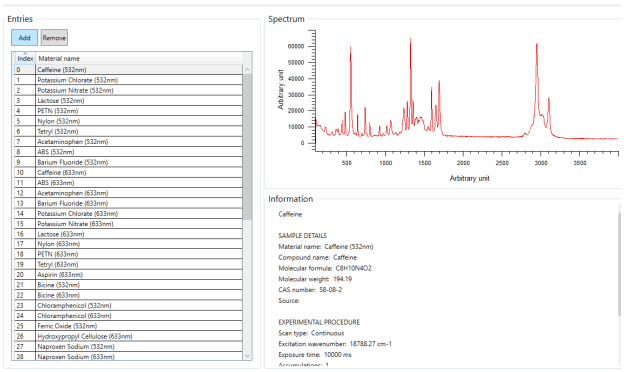

Fig. 3. Library database created inside the Renishaw WiRE software. A library entry of caffeine is shown with spectra, sample details, and experimental procedure stored in the database.

With a suitable reference database to use, chemical image maps of samples were able to be created, where a spectrum was measured at every point in a defined area on the sample. The first mapping experiment we conducted was one with a clutter sample. To create a clutter sample, a clutter mix was sprinkled onto a glass slide, consisting of eight different chemicals (Appendix Table 1). In addition to these eight, a main target component of interest is added to a slide resulting in eleven total chemicals. The goal for the instrument is to detect the component of interest, analogous to finding a needle in a haystack. This mapping experiment tests the effectiveness of the instrument and simulates a real-life situation in which the component of interest is masked by other materials. To conduct the experiment more efficiently, the Raman instrument was set to a Streamline focus laser (532nm) which allowed simultaneous collection of spectra at many points along a line. The spectra were collected over a defined area of the clutter sample. This experiment was run overnight for about 18 hours, collecting over 600,000 spectra, and was repeated three times.

A second experiment was conducted on a fingerprint sample. The fingerprint sample was created using a model artificial finger on an automated fingerprint press. To model the deposition of explosive onto a surface, the artificial fingerprint was loaded with crambe oil to simulate human sebum oil and then loaded with traces of RDX explosive particles. Afterwards, the material on the artificial finger was deposited onto a glass slide. At the time of publication, only one sample was analyzed but an intriguing experiment would be to examine the deposition of fingerprint residue over successive contacts. Only a small section of the overall larger fingerprint sample was able to be analyzed due to time considerations. The experiments discussed took over 3 days to measure.

With the infrared instrument, spectral data for different chemicals were acquired using the different detectors for transmittance, reflectance, and diffuse reflectance. Because the infrared beam is much larger than the Raman laser beam, the IR instrument is not able to take spectra at close adjacent points like the Raman instrument. Additionally, it is often hard to distinguish between the spectra of the background material and sample material. It was difficult to obtain sufficient spectral signal for analytes on a glass substrate, so we decided to make a clutter sample on gold using the same process.

To create a map, we selected points of measurement at large particles.

IV. Results and Analysis

A. Methodology

Map analysis was conducted using two chemometric methods: Principal Components Analysis (PCA) and a direct classical least-squares (DCLS) component analysis. The PCA method is mathematically based and finds a defined maximum number of different spectral components. By going through each generated component, we were able to ascertain the component spectrum and compare it to our library, giving us a list of potential chemicals. However, the generated spectral components were mathematically defined so there were several repeat candidates. Therefore, using the PCA method exclusively was not reliable for an accurate analysis and was only useful for a preliminary examination.

Following running the PCA to get a potential list of candidate chemicals, the candidates were put into the direct classical least squares (DCLS) components analysis. This method searches through each of the measured spectra and conducts a correlation test to see if they match with the reference spectra. Each component is assigned a color lookup table (LUT) that displays intensity of signal based on similarity to the library spectra. Adjusting the LUT was important to ensure that only true particles were shown on the map.

B. Specificity Sample Analysis

The analysis process was done on a sample with three components RDX, potassium chlorate, and caffeine. This experiment was done to test the capability of the library in an environment with more than one analyte. The Raman instrument was able to identify all three components on all of the particles in the field of view (Figure 4).

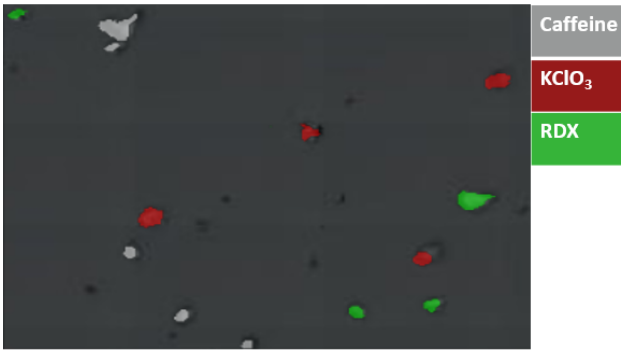

Fig. 4. Generated map of Specificity Sample with color coded legend. Black (unshaded) spots on the image were determined to be scratches on the glass background or materials that were not Raman active.

C. Clutter Sample Analysis

The map for the caffeine clutter sample is shown in Figure 5. By assigning a color to each chemical substance, a map for 6 of 8 of the chemicals on the clutter sample was generated. Particles that did not produce a spectrally distinct signal from glass were not colored. The instrument was successful in detecting traces of caffeine, the component of interest.

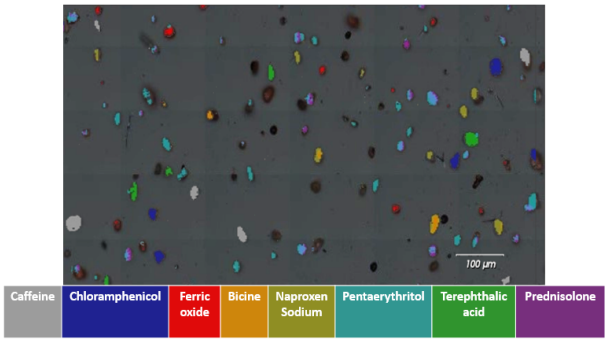

Fig. 5. Generated post-analysis map of caffeine clutter sample with color-coded legend. Unshaded particles did not produce a Raman signal distinct from glass. Dark grey background is glass.

D. Fingerprint Sample Analysis

The same analysis method was run for the mapped cross section of the fingerprint sample we created. The instrument was able to successfully detect and identify particles of RDX, the component of interest (Figure 6). However, for future study, it would be helpful to see if we could detect smaller RDX particles hidden in the crambe oil. This measurement has been performed but the analysis is forthcoming.

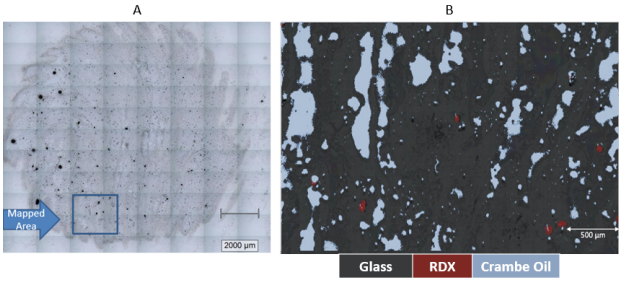

Fig. 6. (a) Microscope image of entire fingerprint sample taken with the 5x Raman microscope objective. Mapped cross section of fingerprint is labeled in blue. (b) Generated post-analysis map for cross section of fingerprint sample with color-coded key.

E. Infrared Clutter Sample Analysis

The same analysis method used with the Raman instrument was not able to be used for the IR Clutter Sample as the mapping method was different. Due to time considerations, the spectral data was not able to be analyzed completely. However, we were able to detect and identify our component of interest, RDX (Figure 7a). By qualitatively comparing the peaks and dips of the measured spectrum with a reference spectrum, a spectral match was able to be determined (Figure 7b). This process is inefficient and work is needed to replicate our Raman mapping analysis process.

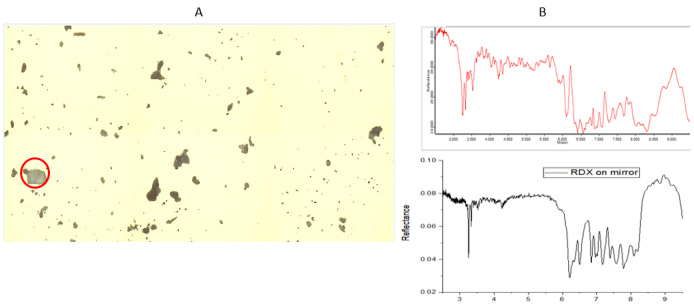

Fig. 7. (a) Microscope image of IR clutter sample, consisting of clutter mix on a gold background. RDX, the component of interest, was detected and identified. (b) Comparison of measured spectrum (top) to reference spectrum (bottom) to find a spectral match.

V. Discussion and Summary

Vibrational spectroscopy has demonstrated itself to be a viable alternative to conventional forensic detection tools. This study was able to successfully utilize both Raman and infrared micro-spectroscopy methods to identify and detect chemicals of interest. Used in conjunction with one another, infrared and Raman spectroscopy can provide a complementary and complete chemical identification system.

As seen with the infrared instrument, it is sometimes difficult to distinguish a chemicals identity from the background that it resides on. This is an important consideration for future studies, as real world conditions are often different from laboratory conditions. It is also important to note that traces of materials of interest may be harder to detect and identify in real-world situations and methods for detection must be adjusted to account for that.

Appendix

Hydroxypropyl Cellulose
Bicine
Naproxen Sodium Salt
Prednisolone
Terephthalic Acid
Pentaerythritol
Sucralose
Ferric Oxide

TABLE I
Chemicals used in clutter mix.

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References

(1)U.S. DEPARTMENT OF HEALTH AND HUMAN SERVICES. (n.d.). What is the U.S. Opioid Epidemic? Retrieved from https://www.hhs.gov/opioids/about-the-epidemic/index.html

(2) Roser, M., Nagdy, M., Ritchie, H. (2013, July 28). Terrorism. Retrieved from https://ourworldindata.org/terrorism

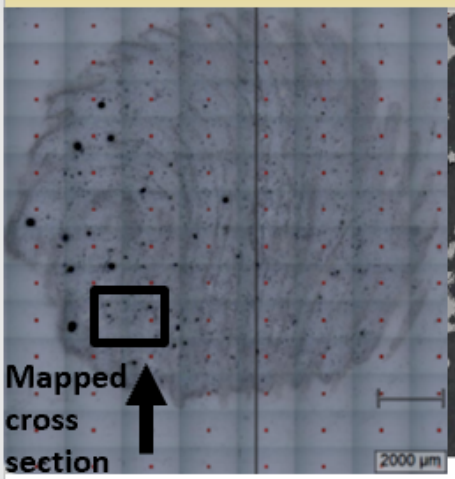
(3) van der Meer, F. (2018). Near-infrared laboratory spectroscopy of mineral chemistry: A review. International Journal of Applied Earth Observation and Geoinformation, 65, 71-78. https://doi.org/10.1016/j.jag.2017.10.004

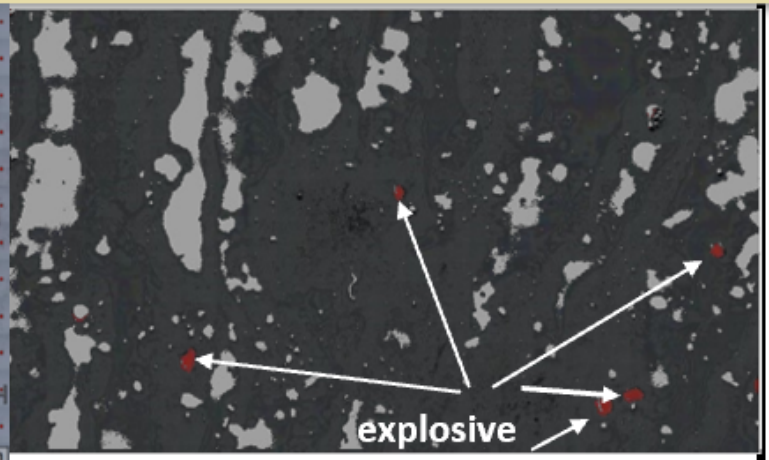
(4) Khandasammy, S. R., Fikiet, M. A., Mistek, E., Ahmed, Y., Halamkova, L., Bueno, J., Lednev, I. K. (2018). Bloodstains, paintings, and drugs: Raman spectroscopy applications in forensic science. Forensic Chemistry, 8, 111-133. https://doi.org/10.1016/j.forc.2018.02.002

(5) Breshike, C. J., Kendziora, C. A., Yoon, Y., Furstenberg, R., Nguyen, V., McGill, R. A. (2019). Infrared backscatter imaging spectroscopy for standoff detection of trace explosives. Proc. SPIE 11010, Chemical, Biological, Radiological, Nuclear, and Explosives (CBRNE) Sensing XX, 1101004. https://doi.org/10.1117/12.2518951

(6) Harper, L., Powell, J., Pijl, E. M. (2017). An overview of forensic drug testing methods and their suitability for harm reduction point-of-care services. Harm Reduction Journal,14(1). doi:10.1186/s12954-017-0179-5

Chemical Detection and Identification Using Raman & Infrared Spectroscopy





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Project Dates: June 24 – August 16

Project Objective and Research Approach:

- Use Raman and IR Spectroscopy to:
  - Measure and analyze forensic materials of interest (chemicals relating to the synthesis and composition of drugs/explosives)
  - Provide valuable reference data for other branch projects
  - Verify composition of chemical coupons provided to other research institutions
- Explore advantages and disadvantages in using both techniques for forensic detection and identification

Results / Accomplishments

- Created a library database of over 50 Raman/Infrared spectra of materials of forensic interest
- Able to use library database to create "maps" of samples
- Created model trace fingerprint sample and used library for detection and mapping

Next Steps:

- Use library in a real-world setting
- Analyze chemical mixtures in which multiple spectra are mixed